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PARTICLE FORMATION AND GROWTH IN SEMIBATCH EMULSION POLYMERISATION REACTORS

by

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A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

April 1998

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Dedication

TO MY MOTHER AND FATHER
ACKNOWLEDGEMENTS

I wish to thank my supervisor, professor B. W. Brooks, for his assistance and advice during the course of this research. My special thanks to Mr A. Milne for his assistance during the experimental work. My gratitude to Messieurs John Bates and Graham Moody for their collaboration in using electron microscope and photon correlation spectroscopy. It is pleasing to acknowledge the help of the following members of staff: David Smith, Steve Gravy, Martin Kerry, and Terry Neale.

Finally, I wish to acknowledge the help and friendship of technical and laboratory staff of the chemical engineering department and all those who made my study at the department fruitful and memorable.
SUMMARY

An investigation of emulsion polymerisation of butyl acrylate in batch and semibatch reactors has been carried out. The important phenomena of particle formation and kinetics in semibatch emulsion reactors with neat monomer feed and monomer emulsion feed have been studied. An investigation of batch emulsion polymerisation of butyl acrylate was also undertaken in order to provide the supporting evidence to elucidate particle formation in the semibatch emulsion process.

Different start-up procedures were studied to determine their effect on the particle formation and kinetics of the polymerisation reaction. The effects of monomer distribution, emulsifier distribution, initiator distribution, feed rate, temperature and pre-period time on the particle formation and steady-state rate of polymerisation were investigated. Experimental studies reveal that particle formation in semibatch emulsion polymerisation is influenced by partitioning of ingredients, such as emulsifier and monomer, between the charge and the feed rate and controlling the growth rate of particles at monomer-starved conditions. The latter is applied by adjusting the monomer or monomer emulsion feed rate at a desired level.

Changes in start-up procedure were found to have a significant effect not only on the transients before a steady-state, but also on the ultimate steady-state rate of polymerisation reaction achieved and final number of particles obtained. All variables affecting primary and secondary particle formation, and especially emulsifier concentration, could equally influence the steady-state rate of polymerisation reaction.

Evidence was obtained indicating that secondary nucleation can occur through homogenous nucleation. The particle size distribution (PSD) development in the course of reaction for the semibatch emulsion process was investigated. Partitioning of ingredients between the charge and the feed and monomer starved nucleation were found to be the main two factors that control the PSD and number of particles formed.
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Fig. G.7: Micrographs for the final latexes from the runs BK, BBD, and BBC; a) KPS = 0.54 g/litre, (R/F)\textsubscript{H} = 20 %; b) KPS = 0.54 g/litre, (R/F)\textsubscript{H} = 40 %; c) KPS = 1.08 g/litre, (R/F)\textsubscript{H} = 20 %.
LIST OF SYMBOLS

\( A_m \)  
total surface area of micelles

\( A_p \)  
total surface area of all particles

\( a \)  
dimensionless parameter \( (8\alpha)^{1/2} \)

\( a \)  
distribution ratio of radicals between the inner and the outer surface of particles

\( a_s \)  
particle surface area per unit molecule of emulsifier

\( c \)  
pseudo first order coefficient for termination, \( (k_n/v_p) \)

\( D \)  
diffusion constant, \( \text{cm}^2/\text{sec} \)

\( d_p \)  
diameter of particle

\( D_p \)  
diameter of particle

\( D_{ps} \)  
diameter of swollen particle

\( D_p \)  
self-diffusion constant of a monomer radical in the particle

\( D_n \)  
number average diameter of particles

\( D_s \)  
surface average diameter of particles

\( D_v \)  
volume average diameter of particles

\( D_w \)  
weight average diameter of particles

\( D_w \)  
diffusion coefficient of monomer in the aqueous phase

\( D_1 \)  
intensity average diameter of particles

\( D_z \)  
z-average diameter of particles

\( E \)  
emulsifier concentration

\( E_0 \)  
initial emulsifier concentration

\( E_w \)  
emulsifier concentration in the water phase

\( E_a \)  
emulsifier concentration adsorbed on the particles

\( f \)  
initiator efficiency

\( F \)  
efficiency factor for radical entry into particles

\( F_f \)  
efficiency factor of entry for radical with the chain length of \( j \)

\( f_r \)  
Response factor

\( g(t) \)  
correlation function

\( G_i \)  
constant defined by Eq.2.5

\( I \)  
initiator concentration, \( \text{mol/litre} \)

\( I \)  
transmitted intensity

\( I_0 \)  
initial initiator concentration

\( I' \)  
concentration of initiator or primary radicals, \( \text{mol/litre}^{-1} \)

\( I_m \)  
\( I_{m-1} \)  
Bessel functions of the first kind

\( J_{\text{crit}} \)  
critical degree of polymerisation for homogenous nucleation

\( K \)  
constant defined by Eq. 2.1

\( k_{1s}, k_2 \)  
rate constants for radical capture by micelles and particles, respectively

\( k_r \)  
second-order rate coefficient for radical entry into particles

\( k_{aj} \)  
second-order rate coefficient for entry of a radical with a length of \( j \) into particles

\( < k_{aj} > \)  
average second-order rate coefficient for radical entry into particles

\( k_{ar} \)  
second-order rate coefficient for radical entry into seed particles

\( k_d \)  
first-order rate coefficient for initiator decomposition, \( \text{min}^{-1} \)

\( k_{de} \)  
rate coefficient for the radical desorption from the particles = \( k_r \)

\( k_{DM} \)  
first-order rate coefficient for desorption of monomeric free radical from the particles

\( k_f \)  
rate coefficient for the radical desorption from the particles

\( k_{m} \)  
rate constant for transfer to monomer

\( k_{p} \)  
rate constant for transfer to polymer

\( k_{RT} \)  
rate constant for transfer to transfer agent
$k_d$ radical desorption rate constant, cm/sec
$k_p$ propagation rate constant
$k_{pl}$ propagation rate constant for initiator radicals
$k_{tp}$ second-order rate coefficient for termination within latex particles
$k_{tw}$ second-order rate coefficient for termination in the aqueous phase
$k_{w}$ termination constant for termination between an initiator radical and a growing radical
$L$ distance a radical will diffuse before precipitating
$M$ concentration of monomer, mol/litre
$M_0$ initial monomer concentration, mol/litre
$m$ dimensionless parameter $k_{tp}/k_p$
$m_d$ partition coefficient for monomeric radicals at the particle-water interface
$m_s$ concentration of micelles in the water phase
$M/E$ monomer/emulsifier ratio
$M_r$ monomer concentration required for monomer-saturated nucleation
$M_m$ aggregation number of micelles
$M_p$ concentration of monomer in polymer particles
$M_p^{sat}$ saturation concentration of monomer in the polymer particles
$M_w$ molecular weight of monomer
$M/W$ monomer/water ratio
$M_w$ concentration of monomer in the aqueous phase
$M_w^{sat}$ saturation concentration of monomer in the aqueous phase
$n$ number of radicals in a particle
$n$ average number of free radicals per latex particle
$n_i$ number of particles with diameter $D_i$
$N_a$ Avagadro's number
$N_n$ number of particles containing $n$ radicals
$N_p$ number of polymer particles
$N_{p1}$ number of primary polymer particles
$N_{p2}$ number of secondary polymer particles
$N_s$ number of seed particles
$P_{tr}$ weight of polymer formed at the end interval $I$
$P_n$ concentration of polymer molecules with the chain length $n$
$P_m$ probability of absorption of radicals in the micelles
$r_m$ radius of micelle
$r_p$ radius of particle
$r_{up}$ radius of unswollen particle
$R$ gas constant
$[R]$ concentration of radicals
$R_a$ rate of monomer addition
$R_{ai}$ rate of addition of comonomer $i$
$R_{ae}$ rate of aqueous phase addition
$R_d$ rate of initiator decomposition
$(R/R_f)_b$ buffer in the initial reactor charge to buffer in the overall feed
$(R/R_f)_e$ emulsifier in the initial reactor charge to emulsifier in the overall feed
$(R/R_f)_i$ initiator in the initial reactor charge to initiator in the overall feed
$(R/R_f)_m$ monomer in the initial reactor charge to monomer in the overall feed
$(R/R_f)_w$ water in the initial reactor charge to water in the overall feed
$R_{tm}$ rate of transfer to monomer
$R_{tp}$ rate of transfer to polymer
$R_{rt}$ rate of transfer to chain transfer agent
$R_i$ rate of initiation, mol sec$^{-1}$ litre$^{-1}$
\( R_i \) (j = 1, i, j-1, j-1, j) concentration of a radical with a length of j in the water phase
\( R_i \) concentration of initiator radicals
\( R_{ni} \) concentration of radicals with the chain length n
\( R_p \) overall rate of polymerisation, mol sec\(^{-1}\) litre\(^{-1}\)
\( R_{pi} \) rate of polymerisation for comonomer i
\( R_{tc} \) rate of termination by combination
\( R_{td} \) rate of termination by disproportionation
\( R_{w} \) overall oligoradical concentration in the aqueous phase
\( R_{w0} \) initial emulsifier concentration
\( S \) surface coverage ratio
\( T \) temperature
\( t \) time
\( t_{end} \) time at the end of interval I
\( t_{pp} \) pre-period time, sec
\( V_p \) volume of polymer phase
\( v_p \) volume of polymer particle
\( V_{am} \) partial molal volume of monomer
\( W \) amount of water
\( W' \) Electrostatic repulsion between the charged oligomeric radical and the charged particle surface
\( W_0 \) overall monomer concentration
\( x \) fractional monomer conversion
\( x_{end} \) monomer conversion at the end of interval I
\( x_{end} \) monomer conversion at the end of interval II
\( x_i \) instantaneous conversion
\( x_f \) final conversion
\( x_{end} \) overall conversion
\( Y \) dimensionless parameter defined by Eq. 1.7
\( \alpha \) dimensionless parameter \( \rho v_p N_{p} k_{pp} \)
\( \alpha' \) dimensionless parameter \( \rho v_p N_{p} k_{pp} \)
\( \beta \) numerical constant given by Eq.5.6
\( \beta \) probability of propagation and termination for a radical in the aqueous phase
\( \varepsilon \) radical capture efficiency
\( \phi_p \) volume fraction of polymer in polymer particles
\( \phi_{am} \) volume fraction of monomer in polymer particles
\( \rho \) rate of radical entry into a particle
\( \rho_e \) rate of radical entry into polymer particles
\( \rho_f \) rate of coagulation of primary particles with themselves
\( \rho_i \) rate of radical initiation in the water phase
\( \rho_m \) density of monomer, g/cc
\( \rho_p \) density of polymer, g/cc
\( \theta \) scattering angle
\( \eta \) viscosity
\( \mu \) volumetric growth rate of a particle, cm\(^3\) sec\(^{-1}\)
\( v_p \) specific volume of polymer, cm\(^3\)/g
\( v_m \) specific volume of monomer, cm\(^3\)/g
\( \Gamma \) interfacial tension between latex particles and the aqueous phase
\( \chi \) Flory-Huggins interaction parameter
\( \delta \) mass transfer resistance
\( \delta \) capture efficiency for radicals in a micelle relative to a particle of the same size
Interest in emulsion polymerization is strong because it offers the possibility of producing products with special properties not easily produced by other types of polymerization processes. Because the main reaction medium is water, not an organic solvent, its importance is steadily increasing with efforts to design environmentally benign processes. Emulsion polymerization is widely used in industry to produce latexes for a variety of applications such as latex paints, adhesives, coatings, binders in paper and textile products, synthetic rubber, etc. Apart from these commodity products, there are “high value added” products, such as for drug carrier and diagnostic kits in biomedical applications. There are thus considerable incentives for understanding emulsion polymerisation processes.

Although emulsion polymerization has been studied and used for several decades, progress has been slow. Industrial practice relies heavily on experience while several controversial issues are still being studied. The literature related to the emulsion polymerization is vast but universally accepted conclusions are scarce.

Emulsion polymerization can be carried out using batch, semibatch or continuous processes. While the general trend in chemical industry is to approach from conventional batch process to continuous process, semibatch processes are being developed for many latexes, due to greater flexibility of semibatch processes in product design. An important feature of the semibatch emulsion polymerization is that it offers a greater degree of operational flexibility than either batch or continuous processes.
The control of polymer latexes properties is becoming of great industrial importance, as the production of an increasing number of products involves emulsion polymerization processes. A major property of the latex resulting from an emulsion polymerisation is the size of particles. Control of the latex particle size is the key to guarantee the quality of latex products. Many end-use properties, such as adhesive strength, viscosity, film forming, opacity, penetration, and stability are critically influenced by the particle size distribution (PSD) of the polymer latex. Particle size control may be achieved by using a semibatch processes. The qualitative understanding of the quantities which control both the average particle size and the PSD is quite important. It is possible to design the recipes and the feed policies of monomer, emulsifier, and initiator components to yield a desired PSD in the semibatch emulsion polymerisation. The objective of this research work is to investigate the effect of various reaction parameters on the particle formation and growth for emulsion homopolymerisation of butyl acrylate in semibatch reactors.
Chapter One

Fundamentals Of Emulsion Polymerisation

1.1 INTRODUCTION

Of the three major techniques used in free radical polymerisation (bulk, suspension, and emulsion), emulsion polymerisation is the most complex one. The complexity of the reaction is however offset by its flexibility, since emulsion polymerisation provides the advantage of high reaction rates, high molecular weight polymer and easy to handle low viscosity latex. In this chapter a fundamental review on particle formation and kinetic events in emulsion polymerisation is presented.

1.2 FREE RADICAL POLYMERISATION AND KINETICS

The important chemical reactions in free radical polymerisation and the rate expressions for these reaction steps are as follow:

- **Initiation**
  
  \[ I \rightarrow 2I^* \]
  \[ I^* + M \rightarrow R_I \]

  \[ R_I = k_I [I] \]

- **Propagation**
  
  \[ R_n + M \rightarrow R_{n+1} \]

  \[ R_P = k_P [M] [R] \]

- **Termination**
  
  \[ R_n + R_m \rightarrow P_{n+m} \]
  \[ R_{tc} = k_{tc} [R]^2 \]

  \[ R_{td} = k_{td} [R]^2 \]
Chapter One

1.3 EMULSION POLYMERISATION

Following the Harkins' original description (1945) of the mechanism of emulsion polymerisation and according to the quantitative theory developed by Smith and Ewart (1948), emulsion polymerisation behaviour (in batch reactors) in its three distinct time intervals may be simply explained as follows.

Interval I: In this interval, which is usually referred to as the "nucleation or particle formation stage", free radicals generated in the aqueous phase enter micelles and form new polymer particles. If a radical enters a polymer particle bearing a radical, termination reaction might happen and the particle becomes inactive. Upon receiving a particle from aqueous phase, a new chain propagation cycle starts in a dead particle. Growing particles absorb emulsifier from the aqueous phase to become stable. This diminishes the availability of uninitiated-micelles to the generated radicals. The end of interval I is marked by depletion of all uninitiated-micelles and a cessation in the particle formation cycle.

Interval II: In this interval particle growth occurs as they are continuously fed with monomer by monomer droplets. Due to fast rate of monomer diffusion from the droplets to the particles through aqueous phase, particles remains saturated with monomer. This interval is usually referred to as the "particle growth stage".

Interval III: It starts after monomer droplets have been completely consumed. Polymerisation proceeds in the particle with the remaining monomer within them. For water soluble monomers, the monomer concentration in the particles will decrease more slowly at the start of interval III. Also the particle volume may at first slightly increase with increasing conversion before it eventually starts to decrease slightly. The particle growth may happen at this interval by particle coagulation. For most
monomers more than half of the monomer polymerises in the interval III, which is indicative of the importance of this interval.

The decrease in concentration of monomer during interval III leads to a steady increase in the viscosity. Then the interval III kinetics of emulsion polymerisation reactions resembles that of mass polymerisation at the high conversion region where diffusion controlled termination and propagation reactions occur. Whereas in bulk polymerisation, the isothermal gel effect is almost dependent on polymer concentration, in emulsion polymerisation conditions such as number of particles, particle size, and initiator concentration must be taken into account. Numerous attempts have thus been made to study chain polymerisation to high conversions and a number of well-known models have been developed (Marten and Hamielec, 1972; Soh and Sundberg, 1982a, b; Chiu et al, 1983).

Assuming that the latex particles are the main sites of polymerisation in the emulsion polymerisation, the polymerisation rate is given by:

\[ R_p = k_p M_p N_p \bar{n} / N_a \]  

where \( k_p, M_p, N_p, \) and \( \bar{n} \) are propagation rate constant, monomer concentration in polymer phase, number of particles and average number of radicals per particle, respectively.

### 1.4 MONOMER CONCENTRATION IN POLYMER PARTICLES

In interval I and II, a common assumption is that \( \varphi_m \), the volume fraction of monomer within the polymer particles (\( \varphi_p = 1 - \varphi_m \)), is constant and determined by the equilibrium swelling of growing particles. Morton et al (1954) considered the saturation swelling of latex particles by monomers or solvents having limited solubility in the water phase. When the swollen latex particle is in equilibrium with the free monomer phase the partial molar free energy of the monomer, which is the sum of energy of mixing of polymer and monomer and particle/water interfacial energy, will be zero. Morton et al expressed the free energy of mixing in terms of the classical Flory-Huggins theory and interfacial free energy in terms of the Gibbs-
Thomson equation and by combining the above terms obtained the following expression:

$$\ln(1 - \varphi_p) + \varphi_p + \chi \varphi_p^2 + (2\Gamma V_{sm}/r_{up}RT) \varphi_p^{1/3} = 0$$ \hspace{1cm} 1.2

Here $\Gamma$ is the interfacial tension between latex particles and the aqueous phase, $\chi$ is the Flory-Huggins interaction parameter, $V_{sm}$ is the partial molar volume of monomer, and $r_{up}$ is the radius of unswollen particle. While the Morton equation is certainly correct, it cannot be easily used for prediction of $M_p$. There appears to be no means of directly measuring the interfacial tension between water and a latex particle. Moreover, the value of $\chi$ cannot be reliably assigned. Nevertheless, the values of $\chi$ and $\Gamma$ can be fitted to the equation by measuring $\varphi_m$.

Morton’s equation predicts that $M_p$ varies strongly with radius for particles with diameter smaller than 20 nm. Thereafter, $M_p$ is only weakly size-dependent and usually it is assumed to be size-independent above 30 nm. It is a standard practice to assume that $M_p^{sat}$ does not change during interval I and II. However, for the interval I where the particles are quite small, constant $M_p^{sat}$ cannot be easily justified.

During interval III, monomer concentration in polymer particles are not maintained at saturation conditions and decreases with time. When monomer droplets are no longer present, latex particles are unable to swell to their saturation equilibrium size and the aqueous phase will not be saturated with monomer. For sparingly water-soluble monomer, $M_p$ at the interval III is easily obtained since all monomer is located inside the particles. For more water-soluble monomers the value of $\varphi_p$ will depend on the partitioning of monomer between the polymer and water phase. An analogue for the Morton equation, that dealt with partial swelling of latex particles, has been derived (Vanzo et al, 1965).

$$\ln(1 - \varphi_p) + \varphi_p + \chi \varphi_p^2 + (2\Gamma V_{sm}/r_{up}RT) \varphi_p^{1/3} = \ln (M_w/M_w^{sat})$$ \hspace{1cm} 1.3
Where $M_w$ and $M_{w}^{\text{sat}}$ are the concentration and the saturation concentration of monomer in the aqueous phase, respectively. If $\chi$ and $\Gamma$ are known from saturation swelling by using the Morton equation, then the Vanzo equation can be used to predict the partial swelling of polymer particles.

The thermodynamic equilibrium approach has been extended by Guillot (1980) to emulsion copolymerisation systems and recently studied by many investigators for equilibrium swelling (Maxwell et al., 1992b; Tseng et al., 1982; Gugliotta et al., 1995) and partial swelling (Noel et al., 1993; Maxwell et al., 1992a). Although this approach is indeed fundamental and very promising, it involves many parameters, specially for multicomponent polymer systems, which are not easily obtainable. Many empirical correlations have been reported in the literature for the calculation of $M_p$ in different systems such as VA (Dunn and Taylor, 1965), and MMA (Nomura and Fujita, 1994). For the calculation of partial swelling a general empirical equation has been suggested (Gilbert, 1995) which found to be valid for VA, MMA, and St as the following:

$$M_w/M_{w}^{\text{sat}} = [M_p/M_p^{\text{sat}}]^{0.60}$$

### 1.5 AVERAGE NUMBER OF RADICALS PER PARTICLE

It is usually assumed that, during the interval $I$, particles are so small that they can not have more than one radical and instantaneous termination occurs upon the arrival of the second radical. This is called a “zero-one” system. When termination becomes rate-determining, a particle may contain more than one radical. Smith and Ewart derived the equation for the time evolution of the population of particles containing any number of radicals as follows:

$$\frac{dN_n}{dt} = \rho (N_{n-1} - N_n) + k_{de} [(n+1)N_{n+1} - nN_n] + c [(n +2)(n+1)N_{n+2} - n(n-1)N_n]$$

where $N_n$ is the number of particles having $n$ radical, $\rho$ the rate of radical entry into a particle ($\rho_a / N_p$), $k_{de}$ is the first order rate coefficient for the radical desorption from the particles, and $c$ is the pseudo-first order rate coefficient for termination ($k_p/\nu_p$).
Smith and Ewart could not solve the steady-state of the above equation. However, they considered three limiting cases:

- **Case I, \( \bar{n} \ll 0.50 \) :** This is the case that chain transfer of radicals to monomer and subsequent desorption from the particles and termination in the aqueous phase proceed quickly relative to propagation (\( \rho \ll k_{de} \)). Vinyl acetate and vinyl chloride exhibit case I kinetics.

- **Case II, \( \bar{n} = 0.50 \) :** This case, which is most generally known as the Smith-Ewart theory, involves instantaneous termination in the particles. Case II kinetics applies to low-conversion emulsion polymerisations of many monomers, such as styrene and acrylic monomers. This is the case that radical desorption rate is negligible compared with the radical entry rate into the particles (\( k_{de} = 0, \rho \ll c \)).

- **Case III, \( \bar{n} \gg 1.0 \) :** This is the case where radical number is much higher than one. Generally, case III kinetics applies to high-conversion polymerisation when termination reactions become diffusion controlled and transfer reactions and radical desorption are slow relative to propagation.

Stockmayer (1957) derived a general solution to the Smith-Ewart recurrence formula involving Bessel functions. O’Tool (1965) modified his treatment later. The solution of this equation, as given by O’Toole, for the average number of radicals per particle is

\[
\bar{n} = \left( \frac{a}{4} \right) \frac{I_m(a)}{I_{m-1}(a)}
\]

1.5b

where \( I_m \) and \( I_{m-1} \) denote modified Bessel functions,

\[
a = (8 \alpha)^{1/2} = \left(8 \rho_a \nu_p / N_p k_{tp} \right)^{1/2} \quad \text{and} \quad m = k_{de} \left( \nu_p / k_{tp} \right)
\]

\( \rho_a \) is the rate of radical entry into all polymer particles. An important further contribution to the analysis of recurrence equation was made by Ugelstad *et al.* (1967). Stockmayer and O’Toole treatment regards the desorption of radicals as involving the destruction of radical activity. Ugelstad *et al* accounted for the likely
possibility that radicals that exit from the reaction loci contribute to the stationary
concentration of free radicals in the aqueous phase which is available for entry into a
reaction loci. Then they distinguished the bimolecular mutual termination between
radicals in the particles from that which occurs in the aqueous phase and allowed the
different termination constant for both phases. The resultant balance of radicals for the
aqueous phase is

$$\rho_a = k_a R_w N_p = \rho_l + k_{de} \Sigma \bar{n} N_n - 2 k_{tw} R_w^2$$ \hspace{1cm} (1.6)

The above equation was rewritten in a dimensionless form by inserting $R_w = \rho_a / k_a N_p$
in the above equation and multiplying each term by $v_p / N_p k_p$ as:

$$\alpha = \alpha' + m \bar{n} - Y \alpha^2$$ \hspace{1cm} (1.7)

where

$$\alpha = \rho_a v_p / N_p k_p, \hspace{0.5cm} \alpha' = \rho_l v_p / N_p k_p, \hspace{0.5cm} m = k_{de} v_p / k_p, \hspace{0.5cm} Y = k_{tw} / k_a N_p v_p.$$

Now by means of equations 1.5b and 1.7, $\bar{n}$ may be evaluated as a function of $\alpha'$, $m$, and $Y$. Since it is inconvenient to use equations 1.5b and 1.7 directly, several
approximation equations for $\bar{n}$ have been derived for the case $Y = 0$. Ugelstad et al
(1969) derived an expression for case I when $\bar{n} < 0.2$ which accounts for the
possibility that two radicals can co-exist in a particle:

$$\bar{n}_I = R_l^{1/2} (v_p/2k_p + v_p^{2/3}/2k_{de}')^{1/2}$$ \hspace{1cm} (1.8)

where $k_{de}$ is related to $k_{de}'$ through the following expression:

$$k_{de} = k_{de}' (N_p/v_p)^{2/3}$$ \hspace{1cm} (1.9)

For the case II kinetics the number average radical is simply $\bar{n}_I = 0.50$. For the case
III the $\bar{n}$ can be approximated by:
\[
\bar{n}_{\text{III}} = \left( R_1 v_p / 2N_p k_{ip} \right)^{1/2}
\]

Multiplying this equation by the particle concentration gives an expression for radical concentration very similar to that derived for bulk polymerisation.

The necessary condition for quasi-steady-state approximation to be valid is that the change in equilibrium value of \( \bar{n} \) with increasing degree of conversion is a slow process compared to the rate of establishment of the equilibrium value. In the interval III the rate of change in \( \bar{n} \) is dependent on the extent of variation of \( k_{ip} \). This varies with different monomers.

1.6 PARTICLE NUCLEATION

Two different approaches have been used to explain particle nucleation in emulsion polymerisation reactions: micellar nucleation (sometimes called heterogeneous nucleation) and homogeneous nucleation.

1.6.1 Micellar nucleation

1.6.1.1 Smith and Ewart model

Smith and Ewart (1948) were the first who attempted to quantify particle nucleation in emulsion polymerisation by adopting the micellar theory of Harkins. The fundamental assumption of this theory is that the free radicals generated by initiator in the aqueous phase are absorbed in surfactant micelles at a rate proportional to the surface area of the micelles. The rate of absorption is either assumed constant (upper limit) or decreasing with time because of competition with new particles (lower limit). Nucleation stops when all surfactant molecules have been consumed by adsorption onto the new particles. This theory assumes that the volumetric growth rate of a particle is constant in the interval of particle formation and also ignores radical desorption from the particles. Generally the rate of micellar nucleation may be expressed by:
where $P_m$ is the probability of absorption of radicals in the micelles. The final Smith-Ewart expression is usually presented as:

$$N_p = K \left( \frac{\rho_1}{\mu} \right)^{0.4} (a_s S)^{0.6}$$

where $\rho_1$ is the rate of radical generation, $\mu = \text{d}v_p/\text{d}t$ the rate of particle volume growth, $a_s$ the specific area of the surfactant, and $S$ the surfactant concentration. The constant $K$ is 0.53 for upper limit where only micelles can absorb initiator radicals and $P_m = 1.0$, and 0.37 for the lower limit where particles can compete with micelles in absorption of initiator radicals and $P_m = \left[ A_m / (A_m + A_p) \right]$. This theory has been extensively discussed and it seemed to fit well for monomers of low water solubility, such as styrene.

1.6.1.2 Newer models

Further derivations based on the micellar theory have been advanced to create a more detailed picture than that of Smith and Ewart. Parts et al (1965) considered that, during nucleation, particles having one radical may receive the second radical and become inactive and hence the average radical number per particle in the lower case will decrease. They applied a numerical integration of the nucleation equations but ended up with almost the same conclusions as Smith and Ewart. They found that the average number of radicals per particle is almost one through the entire nucleation period due to the large number of micelles. Gardon (1971) presented a new treatment that predicts decay of $\tilde{n}$ from the initial value of 1 to the steady-state value of one half. However, it was shown that such a refinement does not change the predictions of $N_p$ and $R_p$ of SE theory.

Radical desorption in the Smith-Ewart theory for number of particles was ignored (see equation 1.12). If the radical desorption from the particles is important, it must be included in $\rho_a$ as:

$$\rho_a = \rho_1 + k_{de} N_p \tilde{n}$$
assuming negligible aqueous-phase termination. Nomura et al investigated micellar nucleation for vinyl acetate and styrene emulsion polymerisation using equation 1.11 and the following expression for \( P_m \)

\[
P_m = \frac{k_1 m_a}{(k_1 m_a + k_2 N_p)} = (1 + \epsilon N_p / S_m)^{-1} \tag{1.14}
\]

where

\[
\epsilon = (k_2 / k_1) M_m
\]

\( M_m \) is the aggregation number of a micelle. Here, \( \epsilon \) may be regarded as the radical capture efficiency of a particle to a micelle. Nomura et al (1976) and Harada et al (1972) analysed the particle formation in vinyl acetate (VAc) and styrene emulsion polymerisations, respectively, using the above scheme. They found out that the efficiency factor \( \epsilon \) favours particles and moreover the value of \( \epsilon \) was a few orders of magnitude greater than that predicted by diffusion theory, specially for VAc monomer.

It has been shown that (Ugelstad et al, 1969; Nomura et al, 1976; Hansen and Ugelstad, 1979d) if chain transfer to monomer and radical desorption is important, the general expression for the particle number based on micellar nucleation mechanism is

\[
N_p \propto S^0 T^{-a} \tag{1.15}
\]

where \( 0.60 < a < 1.0 \) depending on the chain transfer constant and water solubility of monomer.

The radical desorption decreases the particle growth rate and hence increases the number of particles, according to equation 1.12. Furthermore, the desorbed radicals may re-enter the micelle and enhance particle nucleation.

A general form of probability of radical absorption in micelles has been presented by Hansen and Ugelstad (1979d) as:

\[
P_m = \left[ 1 + \left( \frac{N_p}{\delta N_m} \right) (r_p / r_m)^x \right]^{-1} \tag{1.16}
\]
where $\delta$ is an efficiency factor for radical capture in a micelle relative to a particle of the same size and $x$ is the order of capture rate with respect to radius. The constant $x$ is $3 < x < 1$ depending on the regime of capture. The magnitude of $x$ and $\delta$ may change during particle formation period. They found that the apparent value of $\delta$ is considerably lower for vinyl acetate and vinyl chloride than styrene and other acrylates.

The introduction of desorption to an emulsion polymerisation system creates a new kind of radical "monomer radical" which could have a different efficiency factor with initiator radicals. The value of capture efficiency $\delta$ for the radicals formed by chain transfer are considerably lower than for the polymer radicals (Hansen and Ugelstad, 1979d). They used the following equation for the rate of particle formation in styrene system to incorporate the effect of different activity of monomer radicals, formed by chain transfer reactions, with the polymer radicals.

$$\frac{dN_p}{dt} = \rho_1 P_{lm} + k_{de} N_1 P_{mm}$$

where $P_{lm}$ and $P_{mm}$ absorption probabilities for radicals stemming from initiator and monomer radicals, respectively. Also a distinction was made between monomeric and initiator radicals. This concept was later adopted by Nomura and Fujita (1994) in modelling of particle formation in MMA system.

Gilbert and coworkers modified the micellar-nucleation model of Hansen and Uglestad with their new idea of the mechanism of entry as applied to homogenous nucleation.

1.6.2 Homogeneous nucleation

1.6.2.1 The Roe theory

Roe (1968) argued that the water soluble free radicals can not absorb into the hydrophobic interior of a micelle and they may start chain growth in the aqueous phase. The growing radicals will then adsorb surfactant and thus become new stable particles. In Roes' theory Smith and Ewarts' parameters and derivation are replaced
with exact copies based on homogeneous grounds. By no surprise, Roe ended up with the Smith-Ewart expression, proving that agreement with this expression does not have to imply micellar nucleation.

1.6.2.2 The Fitch-Tsai theory

The first attempt to formulate a homogeneous nucleation theory to predict the absolute number concentration of particles was made by Fitch and Tsai (1970a, b). This was supported by a large number of experiments on the polymerisation of MMA. Fitch and Tsai (1971a, b), based on the original idea of Priest (1952) in which propagation occurs in the water phase and self nucleation occurs when the chain reaches the critical degree of polymerisation, developed a quantitative model for homogeneous nucleation. The Fitch-Tsai theory, FT theory, considers that the final particle number is determined by competition between oligomer precipitation and adsorption, and coagulation in already formed particles:

\[
\frac{dN_p}{dt} = \rho_t - \rho_a - \rho_f
\]

1.18

Where \( \rho_a \) is the rate of radical entry into the particles. The mutual termination of radicals in the solution was neglected. The rate of radical adsorption was based on the idea of Gardon who suggested that the rate of capture of oligoradicals by pre-existing particles should be proportional to the collision cross-section. The rate of radical absorption is derived from geometrical consideration about the average length, \( L \), the radicals can travel before self-nucleation. The magnitude of \( L \) was estimated from the maximum degree of polymerisation of oligomers found in the aqueous phase. If the radical collides with an existing particle before it can travel this distance, it will not produce a new particle. \( \rho_a \) is expressed by

\[
\rho_a = \rho_t L N_p r_p^2
\]

1.19

Where \( r_p \) is the particle radius. By relating the particle surface area, \( N_p r_p^2 \), to the total growing polymer volume through the rate of polymerisation, they were able to obtain an explicit correlation for the rate of particle formation as follows:
\[ \frac{dN_p}{dt} = \rho_l [1 - \pi N_p]^{1/2} \left[ \left( \frac{3k_p M_w}{4k_{pp} \rho_p} \right) \ln \left( \cosh \left( \frac{\rho_l k_w}{t} \right) \right) \right] L \]

The final number of particles was predicted through the integration of above equation. This theory was tested on MMA systems and found a remarkable fit with experimental data, but called for a very low initiator efficiency, 11%.

According to the scheme of FT, during the early stage of polymerisation reaction no particles are present so that all radicals produce primary particles and \( \frac{dN_p}{dt} = \rho_l \). Later, when particles are present, they will capture oligomeric radicals in solution and \( \frac{dN_p}{dt} = \rho_l - \rho_a \). As more particles are formed, flocculation will occur if the particles are unstable. Flocculation, then, will occur until a critical surface potential is developed which effectively prevents further flocculation. The basic principles of Fitch theory is that formation of primary particles will take place up to a point where the rate of formation of radicals in the aqueous phase is equal to the rate of disappearance of radicals by capture of radicals by already formed particles: \( \rho_l - \rho_a \).

One of the important observation of Fitch and co-workers was that at submicellar surfactant concentrations, the particle number did not increase monotonically with time, but rather went through a maximum. This phenomena, which was called limited coagulation (limited because the coagulation stops when the surface charge and potential has reached a level where the particles are stable), is believed to be the common mechanism for stabilising the final particle number in low surfactant and surfactant free system.

According to the Fitch theory, the addition of emulsifier does not lead to any increase in the number of primary particles formed. It only leads to an increased stability of primary particles, preventing them from coagulation with a resulting decrease in the final number of particles formed. They explained that at low and intermediate concentration of surfactant it appears that limited flocculation regulates the final particle number. When no surfactant is used, this mechanism operates over such a short time interval that all particles ultimately will be about the same final size. At
intermediate surfactant concentrations, flocculation occurs over a longer period of time so that broader distributions are observed. Presumably, under these conditions the primary particles have insufficient electrostatic repulsion, and therefore they flocculate to form clusters whose total surface potential rises to a point where "stabilisation" occurs. When a sufficient amount of stabilising material is present, particle formation occurs over a short period of time and produces monodisperse colloids, indicating that no flocculation has subsequently taken place. The FT theory states that once sufficient surfactant is available to stabilise primary particles, $N_p$ should not therefore depend on the surfactant concentration (Fitch and Tsai, 1971a,b). This was partly confirmed in their experiments.

Although Fitch used a “collision theory” for radical absorption, he found later from seed experiments that the absorption rate is proportional to $N_p r_p$, which was also predicted by diffusion theory (Fitch and Shih, 1975). Based on the diffusion theory, they derived that $\rho_a = 4 D_w R_w N_p r_p$. The Fitch theory was hampered by the lack of a mathematical solution for the concentration of oligoradicals in the aqueous phase. This problem was finally resolved by Uglestad and Hansen.

1.6.2.3 The Hansen-Ugelstad theory

Hansen and Ugelstad (1978, 1979a) developed the initial treatment of Fitch by introducing three new assumptions: 1) The aqueous phase kinetics is fully developed to take into consideration propagation, termination and absorption of oligomeric radicals. 2) The capture of radicals in particles is a reversible diffusion process. 3) The primary particles are not stable until they are fully covered by emulsifier, and will undergo limited coagulation.

\[
\begin{align*}
\frac{dR_1}{dt} &= \rho_i - k_{pi} M_w R_i - k_{wi} R_i R_{tot} \\
\frac{dR_1}{dt} &= k_{pi} M_w R_i - k_{pi} M_w R_1 - k_{a1} N R_1 - k_{w1} R_1 R_1 - k_{w1} R_1 R_{tot} \\
\frac{dR_j}{dt} &= k_{pi} M_w R_{j-1} - k_{pi} M_w R_j - k_{a1} N R_j - k_{w1} R_j R_j - k_{w1} R_j R_{tot} \\
\frac{dN_p}{dt} &= k_p M_w R_{jcr-1} 
\end{align*}
\]

Addition of equations 1.21-23 up to $j_{cr-1}$ gives:
They defined an average adsorption constant as:

\[ <k_a> = \sum k_{aj}R_j / R_w \]  \hspace{1cm} (1.26)

\( R_w \) was obtained by assuming stationary state for all radicals and neglecting the term \( k_p M_w R_{jcr-1} \):

\[ R_w = \frac{\left[ (\langle k_a \rangle N_p)^2 + \rho_t k_{tw} \right]^{1/2} - \langle k_a \rangle N_p}{2k_{tw}} \]  \hspace{1cm} (1.27)

Assuming a steady state for all radicals \( R_j \) up to \( R_{jcr-1} \), including \( R_i \) radicals, they obtained from equations 1.21-24:

\[ \frac{dN_p}{dt} = \frac{\rho_t}{(1 + k_{tw} R_w / k_p M_w + \langle k_a \rangle N_p / k_p M_w)^{1-jcr}} \]  \hspace{1cm} (1.28)

Insertion of value of \( R_w \) in equation 1.28 gives the expression for the rate of formation of primary particles. In order to arrive at a analytical solution they assumed that \( R_w \) can be approximated by \((\rho_t / k_{tw})^{1/2}\). They ended up with the following expression:

\[ N_p(t) = \frac{1}{k_1} \left[ \left( k_1 \rho_t t + (k_2 + 1)^{1/jcr} \right)^{1/jcr} - k_2 - 1 \right] \]  \hspace{1cm} (1.29)

where

\[ k_1 = \frac{\langle k_a \rangle}{k_p M_w} \]

\[ k_2 = \frac{(k_{tw} \rho_t)^{1/2}}{k_p M_w} \]

The integration demands that all the “constants” must really be constant. This is not accurate for analytical solution since some variables, such as particle radius, increase with time due to propagation and by capture due interval I. The Hansen-Ugelstad model predicts that particles always will be formed at a steadily decreasing rate.
If seed particles are introduced into a homogeneous system they will capture radicals according to their number and size. Assuming that capture of radicals by newly formed particles is negligible at sufficiently high values of number of seeds, they arrived at the following expression for rate of primary particle formation:

\[
\frac{dN_p}{dt} = \frac{\rho_l}{[1 + \langle k_{ac} \rangle N_s/k_p M_w + \langle k_{as} \rangle N_s/2k_p M_w + [(k_{as} N_s)^2 + 4\rho_l k_{w} ]^{1/2}/2k_p M_w]}^\text{crit-1}
\]

\(<k_{ac}>> and N_s are the mean capture constant for seed particles and number of seed particles, respectively. The equation 1.30 similarly can be integrated (Hansen and Ugelstad, 1978). The second and third contributions of Hansen and Ugelstad will be discussed under "Entry". They also developed their model to include the desorption of monomer radicals, and its possible fates in the aqueous phase and different absorption rates (Hansen and Ugelstad, 1982). The combination of the ideas and derivations of Fitch and Tsai and Hansen and Ugelstad has eventually been adopted as the "HUFT" theory.

1.6.2.4 Coagulative nucleation

Traditionally the comparison between theory and experiment with respect to particle nucleation is done by comparing final particle numbers and/or the rate of polymerisation. The Australian group (Feeney et al, 1984, 1987; and Lichti et al, 1993) argued that several other parameters, such as particle size distribution (PSD), molecular weight distribution (MWD), provide additional and more sensitive information about the nucleation mechanism. They measured the particle size distribution as a function of time and from the observation that these distributions are positively skewed, they concluded that the particle formation rate must be an increasing (or at least not decreasing) function of time, and this may only be explained by a limited coagulation mechanism or so-called coagulative nucleation.

They modified the HUFT theory by incorporating the kinetics of entry into the homogeneous nucleation model. According to their theory, entry occurs only if the aqueous phase radical has achieved a critical degree of polymerisation z. In the beginning of a polymerisation, and absence of particles, z-mers must undergo fates other than entry and grow to critical size (j crit-1) to form precursor particles. As
particles gradually start to appear the entry fate competes with precipitation fate until eventually the latter fate may become kinetically insignificant. The rate of particle formation is similar to equation 1.24. However, three classes of aqueous phase radical can be distinguished in their model, compared with two in HUFT theory, $i = 1, i = 2, ..., z-1, i = z, ..., J_{crit} - 1$. The number of particles was obtained by the iterative solution of equation 1.24 and steady-state concentration of the three radical species similar to HUFT treatment.

1.7 RADICAL ENTRY

In emulsion polymerisation free radicals are created in the aqueous phase and subsequently migrate into the particles. This process is called “entry”. Considerable efforts have been devoted to investigate this process and as a results a few models have been proposed.

1.7.1 Collisional model

Gardon (1968a) based his calculations on a geometric derivation of the radical absorption rate which gave the result that rate should be proportional to the particle surface area. This derivation was also adopted by Fitch and Tsai (1971a, b) in the development of their homogenous nucleation model.

1.7.2 Diffusional model

Fitch and Shih (1975) were perhaps the first who applied the diffusion model for radical absorption. They showed that the capture rate is proportional to the product of the particle number and radius:

$$\rho_a = k_a R_w N_p \quad \text{where} \quad k_a = 4 \pi D_w r_p$$

1.31

The absorption rate as expressed by “diffusion theory” is too high and tends to predict too few particles (Hansen, 1992). Hansen and Ugelstad (1978) re-investigated the absorption rate constant in order to derive an expression for capture efficiency. The Hansen and Uglestad adsorption equation is based on steady-state diffusion, and
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describes the combined adsorption to the interphase as a process of diffusion against a potential energy barrier. The energy change at the interphase is represented simply by a ratio, \( \alpha \), between the solubility in oil and water, and further diffusion was calculated by Danckwerts’ steady state equation. A key issue of the combined process is that radicals are captured in the particles only if they react there, otherwise they diffuse out again and back to the bulk phase. Thus \( k_d \) could be expressed as:

\[
k_d = 4\pi r_p D_w F
\]

where the factor \( F \), the “efficiency factor”, represents the lumped effect of both reversible diffusion and electrostatic repulsion. The factor is given by the expression

\[
1/F = (D_w/a D_p) / (X \coth X - 1) + W'
\]

where \( X = r_p (k / D_p)^{1/2} \) and \( k = k_p M_p + \tilde{n} k_p v_p /v_p \), where \( \tilde{n} = 0 \) or 1. \( a \) is the distribution ratio of oligomeric radicals between the inner and the outer surface of the particles. The large \( a \) values mean the radicals are oil soluble.

They simplified the equation in order to arrive at some limiting cases where the true physical process can be easily understood. They are:

\( i \)-Diffusion control in the water phase when the water solubility of the radical is very low and/or the particle are large. This results in the proportionality of the absorption rate to the particle radius. This case corresponds to irreversible diffusion, and it is this that called “diffusion theory”. In this case there may be some effect of electrostatic repulsion, represented by \( W' > 1 \):

\[
F = 1 / W' \implies k_d = 4\pi D_w r_p / W'
\]

\( ii \)-Diffusion control in the oil phase when the diffusion constant in this phase is very low. For this case, absorption rate is proportional to the particles surface:

\[
F = a r_p (k D_p)^{1/2} / D_w \implies k_d = 4\pi r_p^2 (k D_p)^{1/2}
\]
iii- Reaction control in the oil phase when the particles are small and/or the water solubility of the radicals is medium to high. Absorption rate was found to be proportional to the particle volume.

\[ F = \frac{a r_p^2 k}{3D_w} \Rightarrow k_a = a \nu_p k \]  

1.7.3 Colloidal model

This model was suggested by Penboss et al (1986). It has been suggested that the entering species is a large oligomer, whose entry rate coefficient is governed by colloidal considerations. This would predict that \( k_a \) should depend on the surface charge density and size of entering species. This model later was discounted by its originators since no change in \( \rho_n \) was observed with large changes in the surfactant coverage and the ionic strength in a typical styrene system (Maxwell et al, 1991).

1.7.4 Aqueous-phase growth model

The foundation of this model bears some similarities to those previously set forth in the HUFT model where the aqueous-phase kinetics of free radicals deriving from initiator decomposition are fully developed. It was suggested that irreversible free-radical capture by seed latex particles is negligible if the aqueous phase free radical is below a critical degree of polymerisation \( z \) (Maxwell et al, 1991). The fundamental assumption was made that entry occurs only if a radical attains a critical degree of polymerisation \( z \), which might be that sufficient degree to attain surface-activity; moreover, it was assumed that a \( z \)-mer can have no other fate except entry. The entry rate coefficient is then found from the rate of formation of \( z \)-mers;

\[ \rho = N_o k_p M_w R_{z-1} / N_p \]  

Applyng the steady-state approximation for the concentration of radicals and some algebraic manipulation, similar to those in HUFT model, they obtained the following expression:

\[ \rho = (2k_d[I]N_o/N_p)((k_d[I]k_{rw})^{1/2}/k_p M_w + 1)^{1-z} \]
An equivalent relation was deduced for the initiator efficiency $f$ given by:

$$ f = \{(k_0[I]k_{tw})^{1/2}/k_pM_w + 1\}^{1-z} $$  \hspace{1cm} (1.39)

According to this model the growth of the aqueous phase free radicals to a particular degree of polymerisation is the rate-determining step for free radical capture by latex particles. The diffusitive step was assumed to be so fast as not to be the rate-determining. Therefore the capture constant predicted by this model is independent of particle size. This model is for entry in the absence of particle formation. The model implies that $p$ should show a strong dependence on $M_w$. This latter quantity can be varied by changing polymer/monomer ratio during interval III of an emulsion polymerisation.

1.8 EXIT

The process of desorption of free radicals from a particle is called “exit”. Exit reduces the average number of radicals per particle. A free radical of reasonable size will be insoluble in the aqueous phase and consequently will not desorb. The three step mechanism for the exit process has been described by Nomura et al. (1971) as the following; First a monomeric free radical is generated by transfer. It can not exit if it propagates since dimeric and higher species are much less water-soluble. Secondly the monomeric free radical must diffuse through the interior of the latex particle to the particle surface and thereupon undergo desorption before it could increase its size. Thirdly, the exited free radical must diffuse away from the particle and into the aqueous phase. A quantitative derivation of desorption constant has been presented by Nomura et al (1971) and Nomura (1982) as:

$$ k_{de} = k_{f_m} [M_p] K_s/(K_s \bar{n} + k_p[M_p]) $$  \hspace{1cm} (1.40)

where $K_s = (12 D_w mt_d)/(1+2(D_w/m_t D_p) d_p^2)$  \hspace{1cm} (1.41)

$K_s$ = is the first order rate coefficient for desorption of a monomeric radical (or the rate of diffusion of a monomeric radical out of the particle), and $D_w$ and $D_p$ = diffusion coefficient of monomer radicals in the water phase and polymer phase respectively,
and $m_d$ = partition coefficient of monomeric radicals between water and particle phases.

In the absence of transfer agent, when the radical desorption from the particles and the reactivity of monomer are very high, as with vinyl acetate, the condition $k_p M_p \gg K_r n$ is fulfilled and the above equation can be simplified as

$$k_{de} = (12 \, D_w \, \delta/m_d \, d_p^2) \, (k_{fm}/k_p)$$  \hspace{1cm} (1.42)

where $\delta$ is the ratio of water side resistance to overall mass transfer resistance for monomer radicals and equals to $(1+D_w/D_p \, m_d)^{-1}$. Ugelstad and Hansen (1976) derived a similar expression for the diffusional escape rate by using a different approach as

$$K_e = 12D_pD_w/(m_d \, D_p + D_w) \, d_p^2$$  \hspace{1cm} (1.43)

Fris and Nyhagan (1973) derived a semiemprical correlation for desorption constant assuming that the diffusions of radical inside the polymer particles is rate-determining. Asua et al (1989) argued the instantaneous termination of re-adsorbed radicals in Nomura's model and considered the possibility of re-desorption of radicals and obtained the following expression for the exit constant:

$$k_{de} = k_{fm} [M_p] \, K_e / (\beta \, K_e + k_p [M_p])$$  \hspace{1cm} (1.44)

where $\beta$ is the probability that a monomeric radical reacts in the aqueous phase by either propagation or termination and is given by:

$$\beta = (k_p M_w + k_{tw} R_w)/(k_p M_w + k_{tw} R_w + k_0 N_p/N_A)$$  \hspace{1cm} (1.45)

When the propagation rate is much higher than the mass transfer rate, both models approach the same value. However an appreciable difference was reported for the case when the mass transfer coefficient has a value comparable to the propagation term.
Chapter Two

A Review Of Semibatch Emulsion Polymerisation Process

2.1 INTRODUCTION

Although the general trend in chemical industry is to proceed from batch and semibatch processes to continuous processes, semibatch emulsion polymerisation (sometimes called semicontinuous) processes are being developed for many latexes. This is due to greater flexibility of semibatch processes in product design and process operation and control compared with the other processes. Many of high-value added polymer latexes with special particle morphology and composition are being produced world wide by semibatch processes. These particular advantages of semibatch emulsion polymerisation are aside from those generally attributed to semibatch reactors (better control of heat release). Reaction control at steady state conditions, where the overall heat generation is rather constant, may be easily attained. In semibatch process, application of cold feed provides a supplementary way to cope with the heat generation.

Semibatch emulsion polymerisation process is a general term applied to a process with inflow. Theoretically, any kind of input may be added to a semibatch process. Many processes in emulsion polymerisation such as two- or multi-stage, and multi-feed sequential addition processes may be classified as "semibatch emulsion polymerisation systems", if the feed is continuously added to the reactor.
Semibatch emulsion polymerisation is extremely versatile and can produce materials ranging from a highly heterogeneous (co)polymer structure, such as multi-layered or core-shell structure, to a very homogenous composition, and from a monodisperse latex to a latex with the multimodal particle size distribution.

The works on semibatch process are abundant and scattered. In many research works a semibatch process has been considered as one mode of the batch reactor operation and has not received any special attention. This review concentrates on the studies aimed at obtaining some insights into the semibatch process or on the comparative studies of a semibatch process versus a batch process. It is the aim of this chapter to give a critical review of recent works on the kinetic features of semibatch emulsion polymerisation process. Contributions are made to classify the basic kinetic principles and to clarify the most important kinetic features of semibatch process. In this chapter a new interpretative view of section of literature is presented by the present author.

2.2 FEEDING POLICY

The most important advantage of a semibatch process is its flexibility to produce a wide variety of latexes. This is due to availability of more variables in semibatch processes compared with batch and continuous processes. The key variables are as follows:

2.2.1 Feed type

Any ingredients of an emulsion recipe, or combination of them, may be present in the feed of a semibatch emulsion polymerisation reactor as shown in figure 2.1. These are as follows:

- Monomer(s)
- Emulsifier or stabiliser
- Water
- Initiator
- Buffer (or electrolytes)
- chain transfer agent, etc.
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Review On Semibatch Process

On Semibatch Process

Monomer(s)
Emulsifier
Initiator
Buffer
Transfer agent, etc
Water

Mixing tank

ME feed

Reactor

Fig 2.1: Semibatch emulsion polymerisation process with feed components.

The quantity and the order in which these ingredients are added may be varied from batch to batch, depending on the desired properties and intended use of the latex. Two main types of feed have received much more attention than the others (Naidus, 1953); monomer feed (monomer addition technique, "M add") and monomer emulsion feed (monomer emulsion addition technique, "ME add"). In the M add the monomer(s) is added continuously to the other components in the reactor during the course of reaction. While in ME add technique the emulsified monomer, or the part of the initial emulsion recipe, is added continuously to the reactor. It should be noted that different definitions have been used for ME feed in the literature. ME feed may vary from emulsified monomer solution (Krackeler and Naidus, 1969) to a part of the emulsion recipe (Gerrens, 1969). While the major components of ME feed is monomer(s), emulsifier and water, it may contain other ingredients such as initiator, buffer, etc. This gives a wide variety of properties to the ME feed which strongly affect the overall polymerisation features. No clear distinction has been made in the literature on the composition of ME feed and its subsequent effects on the overall polymerisation features. ME feed may be also added to the reactor by two separate lines of monomer feed (M) and emulsifier feed (E) (Masa et al, 1993), or emulsified monomer feed and initiator solution feed (Vanderzande and Rudin, 1992).
Any of the ingredients may be added separately to the reaction mixture. Initiator addition policy (I feed) is usually used to maintain the same initiation rate in the course of polymerisation (Gilmore et al, 1993). If the duration of an M add semibatch process is very long, the aqueous solution of initiator may also be added continuously in a separate line to maintain the constant initiation rate (El-Aasser et al, 1983). In the ME add process, initiator may be contained in the feed for the same purpose. A few studies have been carried out on the optimal initiator addition policy to minimise the reaction time. E & I feed and E feed addition policies were also reported to be good tools in control of average particle size and distribution (Min and Gostin, 1979; Gordon and Weidner, 1981; Moritz, 1983). The addition of chain transfer agent has also been reported (Kukulj et al, 1997; Barudio et al, 1998). The addition of inhibitor solution to study the control strategies for semibatch emulsion polymerisation reactors has been also studied (deBuruaga et al, 1997).

2.2.2 Feeding method

The addition of M feed, ME feed or other ingredients to the reaction mixture may be carried out by a batch (shot or intermittent) or continuous addition method. However, even in the continuous addition method, the feed may not be supplied over the whole reaction. Semibatch process generally contains three successive operations as depicted in figure 2.2 (Omi et al, 1985): seeding batch (or preliminary batch), feed addition semibatch and finishing batch. The first stage has a profound effect on the course of polymerisation and will be further discussed under the topic of pre-period. This stage may be avoided by using a seed latex or by feeding monomer into the reactor from time zero. In the such a case the seeding stage proceeds during feed addition time. The finishing batch is carried out to assure that the least amount of unreacted monomer is left in the reaction mixture. The length of this stage depends on the degree of conversion at the end of monomer feeding period.

Continuous addition policies may have a time-varying or constant feed rate. Both techniques are widely used for the control of copolymer composition, while the first technique gives much more homogeneous structure. One way of varying the properties of latex particles is to change the monomer feed composition during semibatch
emulsion polymerisation. An ingenious method, called the “power method”, to alter the comonomer feed composition, hence copolymer composition, has been suggested by Basset and Hoy (1981). A series of tanks, say 3, with desired monomer contents are placed before the reactor. The content of the far tank is continuously fed to the middle tank, and from that to the near tank and is finally fed to the reactor. The feed rate from the tanks are kept constant at desired levels, respectively. The flow rates are adjusted so that all monomer mix tanks to empty simultaneously. In such a configuration, the composition of the near and middle tank outflows are continuously changing, the latter is the feed to the reactor. They indicated that while other monomer tank arrangements can be devised, the two and three-tank configurations can generate most of the monomer feed profiles likely to be of interest. Obviously the same approach, but more complicated, may be devised for time-varying feed flow rates. Today, with astonishing development in computer technology, it is easily possible to devise a desired profile of feed with varying composition.

Continuous addition methods can be used sequentially for a multifeed polymerisation process. This is a common practice to produce composite latexes with multi-layered or core-shell structure.

Fig.2.2: Schematic diagram of operations in semibatch emulsion polymerisation process.
2.2.3 Feeding time or rate

M feed or ME feed may be added to the reactor at any desired time or feeding rate. However, there is a critical flow rate below which the rate of polymerisation is controlled by the rate of monomer addition (Wesseling, 1968). At this condition, the monomer droplets have disappeared and the monomer concentration in the polymer particles is lower than the saturated concentration. This is referred to as a "starved" system. In a starved system, the polymerisation proceeds in the interval III. If the feeding rate is higher than the polymerisation rate, the monomer accumulates in the reactor and number of monomer droplets increase. This is usually called as "flooded" system. In a flooded process the particles are completely saturated with monomer(s) and reaction kinetics resembles those of a batch emulsion polymerisation reactor in the interval II. In interval II of batch polymerisation systems, the monomer droplets do not directly take part in the polymerisation reaction, but they only feed polymer particles through the aqueous phase to keep them saturated with monomer. It should be noted that this definition can not be applied for addition of any non-monomer containing feed. For these cases the feeding rate may have little effect on the polymerisation rate, hence the feeding time may be limited and must be adjusted with respect to the reaction time.

2.2.4 Distribution of feed

The distribution of recipe ingredients between the initial charge and the feed, has a substantial effect on the polymerisation rate, particle size average and distribution, molecular weights, etc. The distribution variables are usually defined in terms of the amount in the reactor charge to the amount in the overall feed recipe. The most important of those are as follows: monomer distribution ratio, \((R/F)_M\), emulsifier distribution ratio, \((R/F)_E\), initiator distribution ratio, \((R/F)_I\), buffer distribution ratio, \((R/F)_B\), and finally water distribution ratio \((R/F)_W\). All of these variables may be applied to a semibatch emulsion polymerisation process. It should be noted that these variables might have side effects. For example, the water distribution between the seed charge and the feed may also play an important role in a semibatch process. Emulsifier (anionic), initiator, and electrolytes (buffer) all stay in the aqueous phase. Hence by changing the distribution of water, subsequent variations may occur in the
concentration of electrolytes in the aqueous phase which in turn affect the overall polymerisation features (Snuparek and Kleckova, 1984).

2.2.5 Pre-period or seeding time

In any semibatch process, there is a time interval between initiation and the start of feeding which is called pre-period or seeding time. During seeding time, polymer particles are nucleated. Further growth of polymer particles are attained by absorption of the monomer from the feed. After the pre-period, nucleation may be fully stopped or be continued, depending on the polymerisation conditions. A seeding stage may be achieved by polymerisation of a part of initial recipe in situ or by using a specific seeding recipe in a separate batch reactor. The latter is an academic approach to study kinetics of batch, semibatch, and continuous emulsion polymerisation processes. If no pre-period is allowed, the seeding stage proceeds during the feed addition stage.

2.3 GENERAL ASPECTS OF SEMIBATCH PROCESS

Any conventional batch emulsion polymerisation usually passes through the three intervals I, II, and III. It is generally accepted that in a batch emulsion polymerisation during the interval I and II, the monomer concentration in the particles is thermodynamically controlled at a constant level. Generally, in semibatch processes the polymerisation reaction proceeds in the interval III. Interval III of an emulsion polymerisation is marked by presence of large amount of polymer molecules in the latex particles. The high percentage of polymer in the particle produces a highly viscous medium which hinders macromolecule movement and eventually results in a gel effect and sharp increase in the molecular weight (only if the molecular weight is controlled by termination reactions). At higher polymer concentration the movements of small molecules such as monomers become restricted and the glass effect occurs, if the reaction temperature is lower than glass temperature \( T_g \) of the polymer being produced. Chain transfer to polymer increases with increasing polymer concentration but chain transfer to monomer decreases. The monomer concentration in polymer particles has a strong effect on molecular weight development, grafting, reaction rate, etc. By variation of the semibatch process parameters, it may be possible to control the
latex properties by transfer between the different stages of emulsion polymerisation. It should be noted that if the reactor feed contains no monomer, the reaction follows the general trend of a batch process and is not limited to interval III.

![Diagram](image)

**Fig. 2.3:** Some schematic features of monomer-starved semibatch process compared with conventional batch process.

In a batch process, particle nucleation and particle growth occur in a time sequence. Although this sequence does not have any clear-cut boundary and in some instance these two stages may overlap. In a semibatch process, as well as continuous process, particle nucleation and growth may occur simultaneously. Particle growth for a starved semibatch process, spreads all over the reaction. While in a batch process it is limited to the interval I and II. In a batch process, the maximum particle size occurs at the interval II and after that particles shrink. In a semibatch process the particle shrinkage is limited to finishing stage. The average particle size at any conversion is lower for the seeded semibatch process than the corresponding batch process. Some of the features of a semibatch process is schematically compared with batch process in the figure 2.3. By applying appropriate feed policies to a semibatch process, it may be possible to hinder particle nucleation or to intensify it during particle stage growth.
An emulsion batch process is inherently a semibatch process. The monomer droplets in the reaction mixture behave as monomer reservoirs which feed polymer particles at constant rate and keep them (aqueous phase as well) saturated with monomer. Most of the monomer molecules in the reaction mixture do not take part in the reaction. This is identical to a flooded semibatch process in which monomer is fed at a rate to maintain the polymer particles and aqueous phase saturated with monomer (figure 2.4).

Semibatch emulsion polymerisation is proceeded and followed by a batch operation. The extent of the batch operations has a strong effect on the final performance of semibatch process. Two different conversions are defined in a semibatch process, based either on the instantaneous or final monomer concentration. In a single stage batch operation these two coincide. The semibatch operation-time increases with decreasing feeding time, and monomer distribution ratio between the precharge and the feed (at constant monomer feed rate). In a semibatch process, seeding stage may be eliminated from the process by using performed seeds to control the particle size and also the properties of the latex. In ME add semibatch process, monomer precharge is occasionally avoided to study particle nucleation. The polymerisation reaction starts when monomer feed is added to the reactor. This eliminates pre-period or seeding
stage. In an extreme case, where the monomer is charged very slowly to the reactor, the finishing stage might be very short and negligible. In such a case the latex properties are fully dominated by the semibatch operation.

2.4 DYNAMICS OF SEMIBATCH PROCESS

The dynamics of semibatch emulsion polymerisation process are different from those of a batch process, due to continuous addition of monomer, emulsifier, and other ingredients. In a batch emulsion polymerisation, monomer is distributed among the monomer droplets, aqueous phase, and polymer particle phase. In a flooded semibatch process, the same pattern of monomer distribution exists, while for monomer-starved conditions monomer is partitioned between the aqueous phase and the polymer particle phase. The distribution of emulsifier between different phases will also follow the monomer distribution pattern. At monomer flooded conditions, emulsifier molecules are mainly adsorbed on the polymer particles and dissolved in the aqueous phase and to a less extent adsorbed on the monomer droplets. At monomer starved conditions, emulsifier can only adsorb on the particles or dissolved in the aqueous phase, similar to interval III of a batch process.

Monomer units in monomer droplets can only contribute to the polymerisation reaction within the polymer particles if they overcome interfacial resistance of droplets/water, diffuse through the aqueous phase, cross the water/particle interface and finally diffuse into the polymer particles. Therefore 3 possible physical steps which might limit the overall polymerisation rate in a polymer particle are as follows: the diffusion of monomer within the aqueous phase, diffusion of monomer within the particles, and interfacial resistances (Brooks, 1970). In the interval III of a batch process since there is no separate monomer phase in the system, such diffusion across monomer droplets/aqueous interface can not be the rate determining step. However, in monomer-starved semibatch emulsion polymerisation although thermodynamic equilibrium does not account for the presence of monomer droplets in the reaction mixture, monomer droplets can exist in the reaction mixture at monomer starved-conditions if they are stable, for example by containing cosurfactant such as
hexadecane (Tang et al, 1991), or the rate of monomer transfer to the polymer particles is diffusion controlled. The latter conditions might exist at highly-starved conditions where the rate of monomer diffusion to the particles is severely reduced. This specially can occur in the initial stage of seeded semibatch emulsion polymerisation where particles are not plasticised by monomer and monomer diffusion into the polymer particles is very slow.

If the rapid diffusion of monomer through the aqueous phase is assumed, the thermodynamic equilibrium is expected to be quickly reached. Two approaches have been proposed for predicting the monomer concentrations in the polymer particles: thermodynamical and empirical (see section 1.4). While prediction of saturation swelling is very important specially for batch reactors, partial swelling is important for semibatch reactors at starved conditions in which, most of the reaction occurs at the interval III. It has been shown that monomer concentration in the aqueous phase at interval III is close to its saturation value (Noel et al, 1993; Maxwell et al, 1992). However, at a low monomer concentration in the particles, monomer concentration in the aqueous phase exponentially reduces to a very low value. This suggest that in a semibatch emulsion polymerisation system at a highly starved condition, chain growth in the water phase, which may lead to final chain precipitation and particle nucleation, may be substantially reduced.

In batch emulsion polymerisation, as the polymer particles grow with increasing conversion, their surface coverage by emulsifier molecules diminish, and particles become less stable and more susceptible to coagulation with other particles. The free emulsifier concentration in the aqueous phase falls because of additional surfactant being adsorbed onto new polymer particles surface. In a semibatch process with ME feed or neat emulsifier feed, monomer containing micelles (or non-containing in the case of neat emulsifier feed) are entering the system continually. The emulsifier associated with the incoming monomer emulsion can either remain in micellar form or diffuse to the growing particles in order to stabilise them, depending on the emulsifier concentration and micelle life time. The rate of growth of particles, which is a strong function of kinetics of polymerisation, also affects the rate of emulsifier adsorption.
from the aqueous phase to the oil phase. Also the free radicals generated have a choice of either initiating a new particle by entering a micelle, or initiating a polymer particle. The net result of competition for the distribution of the initiator, emulsifier and monomer among different phases determines the particle nucleation trend (Krackler and Naidus, 1969). The surface area occupied by one emulsifier molecule, is strongly dependent on the polarity of the polymer located at the particle surface. The emulsifier adsorption on the particle surface may change with morphology development in the course of polymerisation, which in turn affects the emulsifier concentration in aqueous phase. Monomer and emulsifier partitioning in the emulsion polymerisation are inherently linked to the kinetics of reaction. Any change in the balance of emulsifier concentration in aqueous media will influence particle formation and growth in the polymerisation process.

2.5 ESSENTIAL FEATURES

Recently a few reviews have been appeared in the literature regarding emulsion polymerisation processes. Penlidis et al (1985) reviewed the dynamic of emulsion polymerisation reactors. Vanderhoff (1987) reviewed mostly his research works on the morphology of the particles produced by semibatch process. Li and Brooks (1992) presented a short review on some of the most important features of the semibatch process. A new review on the control (product and process) of emulsion polymerisation reactors was published by Dimitratos et al (1995) which dealt with batch, semibatch and continuous reactors. Despite the date of publication, it only covers the literature up to the year 1991.

Naidus (1953) pioneered semibatch emulsion polymerisation processes. He defined M and ME feeds and explained particle size development in a semibatch process. The advantages of semibatch process, such as better temperature control and less amount of coagulum, were also considered. Farm et al (1955) studied the properties of latex BA/AN from a semibatch process. Yeliseyeva et al (1965) studied semibatch production of carboxylated acrylic latex. Gerrens (1968), Krackeler and Naidus (1968) and Wessling (1968) pioneered in performing the more systematically research works on semibatch processes. Since then, many studies have been carried out on the
semibatch emulsion polymerisation. Tables 2.1-2 show some of the most relevant contributions to elucidate semibatch emulsion polymerisation process. The most important features of semibatch process are as follows.

<table>
<thead>
<tr>
<th>Monomers</th>
<th>Feed type</th>
<th>Feed method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA/MMA</td>
<td>ME feed</td>
<td>constant</td>
<td>Snuparek (1972)</td>
</tr>
<tr>
<td>S/BA</td>
<td>ME feed</td>
<td>constant</td>
<td>Snuparek and Krska (1976)</td>
</tr>
<tr>
<td>S/AN</td>
<td>ME feed</td>
<td>constant</td>
<td>Snuparek et al (1977)</td>
</tr>
<tr>
<td>BA/AN</td>
<td>ME feed</td>
<td>constant</td>
<td>Snuparek et al (1977)</td>
</tr>
<tr>
<td>S/BA/AN</td>
<td>ME feed</td>
<td>constant</td>
<td>Snuparek et al (1977)</td>
</tr>
<tr>
<td>EA/BA</td>
<td>ME feed</td>
<td>constant</td>
<td>Snuparek et al (1981)</td>
</tr>
<tr>
<td>VA/BA</td>
<td>M &amp; I feed</td>
<td>constant</td>
<td>El-Aasser et al (1983)</td>
</tr>
<tr>
<td>S/AN</td>
<td>ME feed</td>
<td>constant</td>
<td>Omi et al (1985)</td>
</tr>
<tr>
<td>EA/EGDMA</td>
<td>ME feed</td>
<td>constant</td>
<td>Snuparek and Kleckova (1984)</td>
</tr>
<tr>
<td>BA/EGDMA</td>
<td>ME feed</td>
<td>constant</td>
<td>Snuparek and Kleckova (1984)</td>
</tr>
<tr>
<td>VA/BA</td>
<td>M feed</td>
<td>constant and closed loop time-varying optimal feed</td>
<td>Kong et al (1987)</td>
</tr>
<tr>
<td>VDC/BMA</td>
<td>M feed</td>
<td>constant</td>
<td>Lee et al (1992)</td>
</tr>
<tr>
<td>MA/VA</td>
<td>M feed</td>
<td>open loop time-varying optimal feed</td>
<td>Arzamendi and Asua (1991)</td>
</tr>
<tr>
<td>EA/MMA</td>
<td>M feed</td>
<td>open loop time-varying optimal feed</td>
<td>Arzamendi et al (1991)</td>
</tr>
<tr>
<td>S/MA</td>
<td>M feed</td>
<td>open loop time-varying optimal feed</td>
<td>German et al (1992)</td>
</tr>
<tr>
<td>S/MA</td>
<td>M feed</td>
<td>open loop time-varying optimal feed</td>
<td>German et al (1992)</td>
</tr>
<tr>
<td>MMA/BA</td>
<td>ME feed</td>
<td>Constant</td>
<td>Unzueta and Forcada (1995a, b)</td>
</tr>
<tr>
<td>MMA/VA/BA</td>
<td>ME feed</td>
<td>Constant</td>
<td>Unzueta et al (1993)</td>
</tr>
<tr>
<td>MMA/BA</td>
<td>ME feed</td>
<td>constant</td>
<td>Chern and Hsu (1995)</td>
</tr>
</tbody>
</table>

Abbreviation: AA = Acrylic Acid; AN = Acrylonitrile; BA = Butyl Acrylate; BM = Butyl Methacrylate; B = Butadiene; EA = Ethyl Acrylate; MA = Methyl Acrylate; MMA = Methyl Methacrylate; S = Styrene; VA = Vinyl Acetate; VCM = Vinyl Chloride monomer; VDC = Vinylidene Chloride

2.5.1 Kinetics of polymerisation

2.5.1.1 Polymerisation rate

While batch emulsion polymerisation is used only for those systems that polymerise sluggishly, the semibatch process is frequently used for the systems that polymerise rapidly and the heat of reaction is too high to be removed by the cooling system of the reactor (Vanderhoff, 1987; Naidus, 1953). However, semibatch polymerisation
Table 2.2: Some selected experimental studies on semibatch emulsion homopolymerisation systems.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Feed Type</th>
<th>Feed Distribution</th>
<th>Preperiod</th>
<th>Variable</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>VA</td>
<td>ME feed</td>
<td>$(R/F)_M = 10%$</td>
<td>0</td>
<td>emulsifier type</td>
<td>Elgood et al (1964)</td>
</tr>
<tr>
<td>VT</td>
<td>ME feed</td>
<td>seeded</td>
<td>0</td>
<td>formulations</td>
<td>Vandegaer (1965)</td>
</tr>
<tr>
<td>S</td>
<td>ME feed</td>
<td>$(R/F)_M = 10%$</td>
<td>5 min</td>
<td>batch vs semibatch</td>
<td>Krackler and Naidus (1969)</td>
</tr>
<tr>
<td></td>
<td>M and</td>
<td>$(R/F)_M = 10%$</td>
<td>5 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ME feed</td>
<td>$(R/F)_M = 10%$</td>
<td>5 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(R/F)_E = 10%$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(R/F)_W = 100%$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(R/F)_W = 100%$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>M feed</td>
<td>$(R/F)_M = 7.1%$</td>
<td>30 min</td>
<td>$R_a$</td>
<td>Gerrens (1969)</td>
</tr>
<tr>
<td></td>
<td>ME feed</td>
<td>$(R/F)_M = 20.0%$</td>
<td>30 min</td>
<td>$R_a$</td>
<td></td>
</tr>
<tr>
<td>MA</td>
<td>M feed</td>
<td>$(R/F)_M = 10%$</td>
<td>10 min</td>
<td>$R_a$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ME feed</td>
<td>$(R/F)_M = 10%$</td>
<td>0 min</td>
<td>$R_a$, $(R/F)_M$</td>
<td></td>
</tr>
<tr>
<td>VDM</td>
<td>M feed</td>
<td>$(R/F)_M = 4.5%$</td>
<td>-</td>
<td>$R_a$</td>
<td>Wessling and Gibbs (1973)</td>
</tr>
<tr>
<td>VA</td>
<td>ME feed</td>
<td>$(R/F)_W = 10%$</td>
<td>-</td>
<td>$R_a$</td>
<td>Batille et al (1978)</td>
</tr>
<tr>
<td>VCM</td>
<td>E &amp; I feed</td>
<td>seeded</td>
<td>-</td>
<td>$R_{aat}$, $I_0$, seed contents</td>
<td>Min and Gostin (1979)</td>
</tr>
<tr>
<td>VCM</td>
<td>E feed</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Gordon and Weidner (1981)</td>
</tr>
<tr>
<td>VA</td>
<td>ME feed</td>
<td>-</td>
<td>-</td>
<td>stirring speed $(R/F)_E$</td>
<td>Donesco et al (1985a)</td>
</tr>
<tr>
<td>BA, EA</td>
<td>ME feed</td>
<td>-</td>
<td>-</td>
<td>$(R/F)_E$, $R_a$</td>
<td>Snuparek et al (1990)</td>
</tr>
<tr>
<td>EA, BA, EHA</td>
<td>ME Feed</td>
<td>-</td>
<td>-</td>
<td>$(R/F)_E$</td>
<td>Snuparek (1979 a, b)</td>
</tr>
</tbody>
</table>
processes may have a higher polymerisation rate than batch process, if operated at gel effect condition (Farm et al, 1955; Hamielec and MacGregory, 1982; Penlidis et al, 1985; Lichti et al, 1982). It may be possible to achieve a higher rate of polymerisation if the gel effect occurs in interval III so that the polymerisation rate becomes greater than that in the interval II. Generally the semibatch emulsion polymerisation rate at starved condition is less than that of the corresponding batch process (Krackeler and Naidus, 1969). At flooded condition, there is no considerable difference in polymerisation rate of batch and semibatch process (Gerrens, 1969).

2.5.1.2 Steady-state rate of reaction

It had been observed in the industrial practice that a steady-state occurs in semibatch emulsion polymerisation under M or ME feed. This is a state at which the rate of polymerisation is controlled and kept constant by the rate of monomer addition \( R_p > R_a \). However in the real term, due to transient nature of a semibatch process, the state at which a constant value of polymerisation rate is established while other parameters such as \( M_p \) and \( \bar{n} \) are varying, is not a real steady state and the term pseudo-steady state should be referred to such a case (Dimitratos et al, 1990). The general equation 1.1 obviously governs the reaction rate in semibatch emulsion polymerisation.

According to equation 1.1 the polymerisation rate is proportional to \( N_p \), \( M_p \), and \( \bar{n} \). For simplicity \( N_p \) may be considered as a fixed variable at steady state for the system with no particle nucleation and coalescence. \( M_p \) and \( \bar{n} \) are interdependent and their exact values depend on the state of the system. At steady state if the monomer reacts as soon as it is fed to the reactor, the monomer/polymer ratio in the polymerisation sites (polymer particles) decreases with time, as the polymer builds up in the reactor. The decreasing \( M_p \) diminishes the rate of polymerisation, if it is not compensated by an increase in \( \bar{n} \) due to more restriction on macroradical movements for termination reaction or radical desorption. In such a system where the exact equality of \( R_p = R_a \) holds, the decreasing \( M_p \) in the course of reaction is evident. It is possible that the steady state is established at some lower rate than feeding rate \( R_p < R_a \). This is the case where \( \bar{n} \) is constant or only slightly increases with conversion. This means that
part of the monomer fed to the reactor does not react instantly and builds up in the reactor.

Assuming a constant \( N_p \), for a seeded system, Wesseling (1968) showed that for the systems that follow the Smith-Ewart mechanism \((\tilde{n} = 0.5)\), the reaction will approach a steady-state condition if the rate of monomer addition \( R_a \) is constant in a starved condition. Wessling analysis predicted that the steady state behaviour of \( M \) feed process should take the following relationship:

\[
\frac{1}{R_p} = \frac{1}{K} + (1 + \delta)R_a
\]  \hspace{1cm} 2.1

Where \( K \) is given by

\[
K = k_p n p \tilde{n} / N_a V_m
\]

and \( \delta \), which is of order 0.1, is given by:

\[
\delta = R_p / K (1 - V_p / V_m)
\]  \hspace{1cm} 2.2

\( V_m \) and \( V_p \) are the molar volumes of monomer and polymer, respectively. The number of growing particles affects steady-state behaviour. As \( N_p \) increases, the range where \( R_p \) is controlled by \( R_a \) increases. The same effect is obtained by an increase in the rate of propagation. The range of control is broadened by increasing equilibrium swelling (Wesseling, 1968). For a seeded system, it was shown that the inequality equation 2.1 becomes an equality equation of the form:

\[
1/R_p = 1/K + 1/R_a
\]  \hspace{1cm} 2.3

His analysis showed that only if a fixed radical concentration in polymer particles is assumed, will the steady-state rate of polymerisation be equal to the rate of addition.

\[
R_p = R_a
\]  \hspace{1cm} 2.4

Gercens (1969) investigated the semicontinuous emulsion polymerisation of styrene (S) as a sparingly water-soluble monomer and methyl acrylate (MA) as a monomer
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with moderate water solubility. It was reported that for both monomers at starved condition, a steady state is reached with M feed, as well as ME feed, so that $R_p = R_a$. By calculation of $M_p$ from conversion data, he obtained a slight decrease in the $M_p$ over the time that $R_p$ is constant. It was explained that the decrease in $M_p$ is compensated by an increase in $\tilde{n}$ which was attributed to the gel effect. In all runs with high feed rate monomer droplets were formed, $R_p$ remained constant and independent of $R_a$. For both monomers the initial rate of polymerisation versus the initial charge resulted in straight lines through the origin. Li and Brooks (1993) modelled the semibatch emulsion polymerisation of styrene using the literature values for styrene and found that equation 2.3 can virtually predict the $R_p$ versus $R_a$ at steady state. Bataille et al (1978) applied the ME add technique to the VA emulsion polymerisation in the presence of non-ionic emulsifier (polyethylene oxide propylene oxide). A steady state was observed in the controlled region. However, the equation $R_p = R_a$ was not obtained and the reciprocal relation proposed by Wessling was confirmed. The equation $R_p = R_a$ was reported for M add semibatch process using PVAl as emulsifier (Moritz, 1983).

The steady-state rate of reaction for emulsion copolymerisation systems has been also studied by a few researchers. The comonomer reactivity ratio and comonomer distribution ratio between the polymer phase and water phase could play an important role in the kinetics of emulsion copolymerisation systems. Snuparek and Krkska (1976) studied semibatch emulsion copolymerisation of two sets of sparingly water-soluble monomers, namely S/BA and BA/BMA at low feeding rates with ME feed. By measuring unreacted monomers in the reaction mixture they showed that a stationary state is reached beyond which the copolymer composition is practically constant and equal to that of ME feed and that the rate of polymerisation of individual monomers equals to the corresponding feeding rate. A steady state for the terpolymerisation of two sparingly water-soluble monomers S and BA with the water-soluble monomer AN at starved condition and with ME feed was achieved at which $R_{pl} = R_{al}$ (Snuparek, 1977). As with the homopolymerisation case, many researchers reported that steady state rate of copolymerisation reactions were achieved so that $R_p < R_a$. Wessling and Gibbs (1973) investigated VDC and VDC/BA semibatch polymerisation systems. They
showed that for both cases the overall polymerisation rate is proportional to, but not equal to, the total feeding rate at starved conditions. A proportionality constant of 0.91 was found for both systems \( R_p = 0.91R_a \). The role of more water-soluble monomer in establishing steady state appears more questioning. Using a reactor component balance for monomers in a semibatch copolymerisation process, Dimitratos et al (1990) derived the following general expression for steady state condition:

\[
\frac{1}{R_{pi}} = G_i + \frac{1}{R_{ai}} \tag{2.5}
\]

They showed that a steady-state rate depends on the distribution of monomers between aqueous and oil phase, \( N_p, K_p \) and \( \bar{n} \). For the case of both sparingly water-soluble monomers and water-soluble monomers, they indicated that if radical concentration \( (N_p \bar{n}/V_p) \) remains fixed in the entire course of reaction, then the equality \( R_p = R_a \) is obtained. This is equal to \( M_p \bar{n} = \text{constant} \). In the case of seeded systems \( (N_p = \text{constant}) \) with a constant \( \bar{n} \), the relationship takes the form of equation 2.5. While in such a system for sparingly water-soluble monomer the constant or slowly varying \( \bar{n} \) is the only perquisite to reach to steady state, the constant or slowly varying partition coefficient is also required for water-soluble monomers. They showed that at extremely low monomer feeds, the term \( R_{ai}G_i \) becomes very small relative to unity and the equation 2.5 takes the unified form of \( R_{pi} = R_{ai} \). In the experimental part of their analysis on VA/BA emulsion copolymerisation with M feed, they showed that, at the steady state, the polymerisation rate for BA is equal to its feeding rate, while VA consumption rate was found to be less than its feeding rate (proportionality constant of 0.85), indicating that the level of unreacted VA in the reactor builds up during the feeding period. The steady state and constant copolymer composition, similar to that of feed, have been reported for many copolymerisation systems.

Obviously, the perquisite conditions for achieving steady-state for any system is a sufficient rate of polymerisation to maintain the polymer particles at monomer starved condition. For example, for any ME add semibatch process there might be a
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characteristic initial charge beyond that no steady state at monomer starved conditions is reached (Gerrens, 1968). However, according to one report, the steady state of reaction was not achieved even at highly starved conditions. Makgawinata et al (1984) reported that for 80/20 VA/BA semibatch emulsion copolymerisation with monomer feed, the steady-state rate of polymerisation was not achieved even at starved conditions and the reaction rate was not directly proportional to the feed rate.

The sensitivity of overall polymerisation rate to number of particles for semibatch emulsion processes can be inferred from the corresponding dependence for conventional batch process (see equations 1-8 and 1-10 in association with equation 1.1). Similarly, in a semibatch emulsion polymerisation the polymerisation rate is rather insensitive to \( N_p \) if polymerisation proceeds according to (a) case III kinetics, (b) case I kinetics, (c) or the polymerisation rate is highly controlled by the rate of monomer addition. It should be noted that according to equation 2.3, the steady state rate of reaction is influenced by the number of particles.

The rate of polymerisation for ME add semibatch emulsion polymerisation of VA was found substantially constant with variation of the surfactant concentration over a 10 fold range (Glubekian, 1968). Vinyl acetate is a good example of case I kinetics. For the seeded semicontinuous emulsion terpolymerisation of styrene, 2-ethylhexyl acrylate and methacrylic acid with ME feed using three different emulsifier types, Masa et al (1993) reported that the type and amount of surfactant had no effect on the overall polymerisation rate although they influenced the extent of secondary nucleation. They obtained a value of \( \bar{n} \) ranged from 0.075 to 0.42, indicating that the polymerisation proceeded according to case I kinetics. Similarly, for seeded semibatch emulsion and miniemulsion polymerisation of butyl acrylate, it was reported that despite a significant secondary nucleation for miniemulsion run, the overall rate of polymerisation remained constant for both runs. This was attributed to the case III kinetics of the polymerisation system with a radical number greater than 15.0 (Tang et al, 1991). The insensitivity of overall rate of polymerisation to the increase in the number of particles due to secondary nucleation has been reported for other case III kinetic systems (Urretabizkaia et al, 1994; Unzueta et al, 1995a).
2.5.1.3 Transition time

There is a time lag before the system reaches steady-state conditions. During this period the monomer/polymer ratio in polymer particles is not constant and changes with time. It was shown that the time required to reach the steady-state for a non-swollen seeded semibatch emulsion polymerisation system depends on the rate of monomer addition, number of particles and monomer reactivity (Wesseling, 1968). Increasing \( R_a \) extends the time it takes to reach steady state. The system with the largest number of particles reaches steady state the fastest. An increase in the monomer reactivity produces a similar effect. In copolymerisation systems, the more reactive comonomer reaches steady state the sooner (Dimitratos et al., 1990). For unseeded semibatch process, the analysis of transition time is not straightforward and depends on the many variables such as monomer charge, emulsifier charge, pre-period time, etc. For example, Moritz (1983) reported that for M add semibatch emulsion polymerisation of VA, when the initial monomer charge exceeded the solubility level (25 g/litre), the reaction rate at once increased to the stationary value. The transition time for unseeded semibatch emulsion polymerisation has not been studied so far.

2.5.2 Particle formation

Particle nucleation in semibatch emulsion polymerisation reactors are further complicated by the continuous addition of the emulsifier, monomer, and initiator to the reaction mixture. The mode of addition of emulsifier during polymerisation affects both particle formation and growth.

2.5.2.1 Surface tension variation

Surface tension is the prime variable for monitoring particle nucleation mechanism in emulsion polymerisation because it is directly related to the concentration of free emulsifier in the aqueous phase. At emulsifier concentrations well below the CMC, nucleation is dictated by a homogenous mechanism, while at the CMC, or above, a micellar nucleation is predominant. In the interval I of a conventional batch emulsion polymerisation, the newly nucleated growing particles adsorbs additional emulsifier from the aqueous phase to get stabilised. However, the molecular emulsifier
concentration in the water phase and also surface tension remain constant at CMC as a result of the breakage of uninitiated-micelles. When all micelles are depleted, the emulsifier adsorption by growing particles from the aqueous phase is partly compensated by emulsifier release from shrinking monomer droplets and consequently the concentration of free emulsifier decreases, which results in a sharp increase in surface tension of the latex (Gardon, 1968b). The surface tension levels off in the beginning of interval III at the value, well above the CMC, which is determined by equilibrium distribution of emulsifier between oil and water phase (Harada, 1972).

The variation of surface tension with time for semibatch emulsion polymerisation with ME feed is highly dependent on the emulsifier distribution ratio. In fact, the (R/F)E ratio affects mechanism of both particle formation and growth and the final particle size. Three different kinds of surface tension variations may be perceived in a semibatch process with a monomer emulsion feed (Snuparek, 1974). If a high amount of emulsifier is present in the initial reactor charge, the same trend as conventional batch polymerisation is observed which is characterised by a constant surface tension at nucleation stage, subsequent increase in surface tension during feeding and then a constant final value for it. In such a case the amount of emulsifier added to the polymerisation system is not enough to cover the surface of growing particles and an increase in the surface tension results. On the other hand if no emulsifier is placed into the reactor before the addition of ME feed, a lower amount of particles will be formed in the course of polymerisation and the amount of emulsifier continuously added to the reactor is enough to saturate the surface of particles. The surface tension decreases from that of water (or water saturated with monomer) to the CMC and remains constant at this value. Between the two limiting cases, there is a third case in which the emulsifier concentration ratio in the initial reactor charge is very low and around CMC. At such a distribution the surface tension sharply increases at the beginning due to rapid particle nucleation and then decreases again to the CMC value. On the contrary to the first case, a much lower number of particles is formed for the next two cases and particles are kept fully covered by a large amount of emulsifier fed into the reactor (Snuparek, 1974). In any of these conditions homogenous or heterogeneous nucleation may contribute to the particle formation.
Surface tension has been used as a major variable for particle formation monitoring in semibatch emulsion polymerisation processes. In order to prevent particle coagulation, particle surfaces should be kept covered with an adequate soap layer. While, to prevent particle formation, the soap concentration must be maintained at a low level not to generate new micelles which in turn would produce a second crop of latex particles (Vandegaer, 1965). This means that surface tension should be kept constant within a band for any particular system. The optimum region to work in during a growth-emulsion polymerisation to avoid secondary particle formation and particle coagulation, depends on the monomer(s) type and polymerisation conditions. It has been suggested that a surface tension between 30 and 50 dyne/cm represents the safe region where the particles are about completely covered and where no new micelles have yet been formed (Vandegaer, 1965).

Monomer-oligomer emulsifier may have a strong contribution to particle nucleation in a semibatch process. In a monomer starved process, while the particles are emulsifier starved, particle formation may happen by monomer-oligomer emulsifier molecules originated from persulphate end-group of initiator. This is a common difficulty in producing polymer particle composites, such as core-shell, by multi-stage semibatch process. Rudin and coworkers (Wang et al, 1995 and 1996; Paine et al, 1995) developed a method for prediction of secondary nucleation by taking into account the formation of “in situ” or oligomeric surfactant during polymerisation. They recommended that a safe band for surface tension to prevent particle formation and coagulation for 64/36 MMA/BA system is 51 ± 6 dynes/cm.

2.5.2.2 Secondary nucleation

The most important aspect of particle nucleation in semibatch emulsion polymerisation with monomer emulsion feed, is secondary nucleation. Both micellar and homogeneous nucleations can contribute to the secondary nucleation, depending on the conditions. The prediction of secondary nucleation for seeded batch emulsion polymerisation has been analysed by a few researchers (Hansen and Ugelstad, 1979a; Morrison and Gilbert, 1995). The same methodology can be used for the prediction of secondary nucleation in semibatch emulsion polymerisation.
The early literature on the semibatch emulsion polymerisation mostly dealt with secondary nucleation through micellar mechanism. The micelles can appear during the semibatch emulsion operation whenever the total amount of emulsifier in the reactor is in excess of the amount of emulsifier required to cover the surface of growing seed particles and to saturate the critical micelle concentration in the aqueous phase. By a simple calculation of the amount of emulsifier required to provide a monomolecular cover of all latex particles, Gerrens (1969) showed that for monomer flooded conditions, if the emulsifier is fed at some specific rate which is the same as or lower than the rate at which it is used by the adsorption on the increasing particle surface, no new particles are formed.

Min and Gostin (1979) provided an academic case study for secondary nucleation through micellar nucleation. They studied the evolution of bimodal particle size distribution in seeded semibatch emulsion polymerisation of vinyl chloride. The initiator and emulsifier were metered into the reactor during the polymerisation, while all the monomer was placed in the initial charge. By using different seed quantity and seed solid content, seed particle size, and initial initiator concentration, they showed that whenever the micelles appeared in the reactor, the second crop of particles formed. The application of larger amount of seed particles made micelles appear at a higher conversion, resulting in a bimodal particle size distribution at later stage of the reaction. This is simply because the larger surface area of particles requires more emulsifier coverage. This leaves less emulsifier at any time available to form micelles. The application of smaller size seed particles similarly resulted in a delay for appearance of secondary particles. The application of the larger initial initiator concentration resulted in a greater initial radical flux into the seed particles. This causes the seed particles grow to a larger size and subsequently, the second generation particles to appear later. The semibatch experiment reported by Min and Gostin is virtually a batch process in which polymerisation proceeded through monomer-saturated conditions. Chern et al (1997) conducted a research work similar to that reported by Min and Gostin (1979), but at monomer starved conditions. By injecting sodium dodecyl sulphate (SDS) into the reaction medium in semibatch seeded emulsion polymerisation, a second crop of tiny primary particles were induced and a
bimodal PSD was produced. The similar results to those reported by Min and Gostin were obtained. The concentration of seed particles was the most important variable for controlling the particle size distribution, followed by the time when the surfactant was injected into the reactor. An experiment with a smaller number of seed particles and earlier addition of surfactant favoured bimodal PSD, as expected. Secondary nucleation was more delayed when a larger number of seed particles was used or the emulsifier was injected later during the monomer feeding.

Secondary nucleation can occur through homogenous nucleation when the amount of free emulsifier is below the CMC. If the number of seed particles in the initial charge is not sufficient to capture all oligoradicals, secondary nucleation might occur through homogeneous nucleation. The effect of emulsifier concentration, below CMC, is to increase the surface charge density of primary particles and hence reduce the rate of particle coagulation. Unfortunately, there is not enough experimental data in this regard in the literature. A systematic study is required to elucidate the effect of emulsifier concentration in the feed on the rate of secondary nucleation through homogenous nucleation mechanism. One approach to quantify the effect of emulsifier concentration is to define a "critical surface coverage ratio" beyond that the particles are completely stabilised and their tendency to absorb emulsifier molecules diminish.

This provides a way for estimation of number of secondary particles at the conditions where the surface of existing particles are not fully saturated with emulsifier. Dimonie et al (1984) who studied batch emulsion copolymerisation of styrene and acrylonitrile on polystyrene seed particles, introduced the idea of critical surface coverage. They claimed that after particles reached a critical protection level called "critical surface area", all new aqueous-phase copolymer chains or new primary particles were captured almost totally by the pre-existing particles and no new particles was formed. This concept was verified by Urquiola et al (1991) in their study of seeded semibatch emulsion copolymerisation of vinyl acetate and methyl acrylate. New particles will be formed if the total amount of emulsifier present in the reactor exceeds the amount required to cover a critical fraction of the surface area of the existing polymer particles plus the amount needed to obtain an equilibrium emulsifier concentration in the aqueous phase. They also showed that the total number of particles was controlled by
the total amount of emulsifier and it was independent of the way in which the polymerisation was carried out.

It is well accepted that during micellar nucleation in conventional batch emulsion polymerisation, particle surfaces are saturated with emulsifier. In semibatch emulsion polymerisation, a second type of micellar nucleation may be involved where particles surface are emulsifier-starved. In semibatch emulsion polymerisation with monomer emulsion feed, the emulsifier associated with incoming monomer emulsion can either remain in the micellar form or diffuse to the growing particles in order to stabilise them. The break-up rate of micelles is expected to increase with the decreasing emulsifier concentration in the aqueous phase. Brooks (1973) stated that although the rate of micelles break-up is fast, is not instantaneous. It might be possible that incoming micelles capture radicals from the aqueous phase before they break up. He proposed that particles may not be saturated with emulsifier in continuous stirred tank emulsion reactors. The same mechanism may influence particle nucleation in semibatch reactors. In addition to the life-time of micelles, which is predominantly dictated by emulsifier concentration on particles surfaces, initiator concentration and polymer particle number (or surface area) may also contribute to particle formation. Even if such a mechanism exists, as the number of polymer particles increases, the competition for free radicals also increases and monomer containing micelles have a lower probability of acquiring a free radical before all of its monomer and/or emulsifier diffuse away. After a certain point, the probability of an incoming monomer-containing micelle forming a new particle becomes rather low. The incoming emulsifier can then be considered to become less and less efficient in its ability to form particles (Krackeler, 1968). Since the suggested mechanism can be operative at emulsifier concentration lower than CMC where homogenous nucleation dominates, its experimental verification can not be easily made.

Secondary nucleation can occur through monomer droplet nucleation if the size of incoming monomer droplets is sufficiently reduced so that they can compete with polymer particles for radicals. Generally in conventional emulsion polymerisation, monomer droplets are not considered as the locus of initiation, due to their big size
and hence low overall surface area compared with that for the micelles and polymer particles. To create an emulsion of very small droplets, the droplets must be stabilised against coalescence and diffusional instability by adding an appropriate cosurfactant, such as hexadecane. Tang et al (1991) showed that for BA semibatch emulsion polymerisation at starved conditions with a miniemulsion ME feed, a large number of new particles were formed compared with conventional ME semibatch and batch processes. They indicated that monomer droplet nucleation contributes to particle formation because the higher surface area of very small monomer drops can absorb radicals. Similarly, a continuous particle nucleation was also reported for the semibatch miniemulsion terpolymerisation of VA/BA/MMA, while both the initial charge and the feed were miniemulsions (Unzue et al, 1993).

Similar to CSTR systems, particle number oscillation has been also reported for semibatch emulsion polymerisation with ME feed. Snuparek et al (1990) showed that for BA emulsion polymerisation particle number may exhibit some oscillations during the feeding of the monomer emulsion. The particles grow rapidly, generating enough surface area to cause an emulsifier-starved system with a very small rate of particle formation, even with particle flocculation. Since emulsifier is continuously added, it is possible for the system to return to an emulsifier excess condition and new particles are formed (Snuparek et al, 1990). No analysis on the mechanism of secondary nucleation was presented. They were able to show that such an oscillation is associated with the corresponding oscillation in the surface tension. The oscillation in the amount of the unreacted monomer and particle diameter with time has been also reported by other research group (Denesco, 1985a, b).

2.5.3 Particle growth

The appearance of a distribution in particle sizes of polymer latexes is primarily due to the fact that nucleation occurs over a period of time during which existing particles grow. The PSD, therefore, is coupled interdependently to the kinetics of polymerisation reactions. Vanderhoff et al (1956) proposed that the volumetric growth rate of individual particle for a batch emulsion polymerisation is written in a power law form:
\[ \frac{dv_p}{dt} = -kD_p^c \]  

where \( k \) is a constant which may change with the nature of the environment. The above equation can be rearranged in terms of particle diameter as

\[ \left( \frac{\pi}{D_p} \right) \frac{dD_p}{dt} = 2kD_p^{c-3} \]

If \( c = 3 \), the relative rate of diameter growth, \( dD_p/D_p \), is independent of size and PSD will remain constant in terms of diameter. If \( c > 3.0 \) bigger particles grow very fast and PSD broaden relatively during growth stage and If \( c < 3 \), the smaller particles will grow faster than the large ones and PSD will be self-sharpening. The exponent \( c \) depends on the monomer type, polymerisation conditions and particle size. For polystyrene the exponents 2.5 and 0 - 1.0 were reported for the particle size of above and below 150 nm, respectively (Vanderhoff et al, 1956).

In a batch polymerisation the rate of particle growth for any monomer is constant at fixed conditions and particle size. In a semibatch emulsion polymerisation, the rate of particle growth can be controlled by the rate of monomer addition. Crackeler and Naidus (1969) suggested that surface polymerisation for semibatch process requires that the growth rate should be proportional to the surface of the particles; \( c \) equals 2.0. Recently it has been confirmed that by applying a semibatch process to a polystyrene bidisperse system, it is possible to achieve a low value for \( c \) and to carry out the polymerisation at the self-sharpening conditions (Liotta et al, 1997). The relative narrowing of the bidisperse system increases as the weight fraction of polymer inside the particles increases; lower monomer feed rate. However, the advantage is offset by a longer reaction of time required to reach the complete conversion. Semibatch emulsion polymerisation is a very attractive operation mode for particle size distribution narrowing of polydisperse system.
2.5.4 Particle size average and distribution

2.5.4.1 Maximum particle size

The size of the latex particles obtained by conventional emulsion polymerisation using an ionic emulsifier is in the 30-200 nm range. Bigger particles with size up to 500 nm may be obtained by using emulsifier-free emulsion polymerisation. This size is unreachable for a conventional batch emulsion polymerisation. Latexes with particle size exceeding 1000 nm could be obtained by the application of a semibatch multistage emulsion polymerisation process (Cook et al 1992; O'callaghan et al, 1995a, and 1995b). A semibatch process provides an excellent control over the particle size average and distribution of final latex particles.

2.5.4.2 Comparative study of batch and semibatch processes

The polymerisation technique has a profound effect upon the particle size. The comparative study of Batch (B), M add ME add semibatch emulsion polymerisation has not been clearly done in the literature and some vague and contradictory issues still exist. In the early literature it was reported that the average particle size for an identical emulsion recipe decreases in the following order: Batch, M add and ME add semibatch process (Naidus, 1953). The batch and ME add semibatch process is claimed to give more uniform particle size distribution than the M add semibatch process. The ME add semibatch process was found to leads to the most stable emulsions with the least amount of coagulum (Naidus, 1953; Snuparek, 1974). According to Gerrens (1969), latexes made by M add semibatch processes show the same particle size distribution as those made by the batch process. The comparative study of particle formation in batch and semibatch process have not been reported for a wide range of polymerisation conditions. The effects of different polymerisation conditions such as varying overall emulsifier concentration, M/W ratio, and monomer feed rate need to be investigated.

2.5.4.2.1 Monomer feed

The initial loading in semibatch process has a major effect on the particle nucleation. The elimination of monomer droplets from initial charge increases the
emulsifier/monomer ratio and makes more emulsifier molecules available to contribute to particle formation (Naidus, 1953). The effect is not large, because the surface area of monomer droplets is negligible compared with micelles.

M/W ratio in the seeding batch operation of semibatch process may have a great impact on the particle nucleation stage, specially when a long pre-period is allowed. Recently M/W ratio in the batch emulsion polymerisation, which once was believed not to be a critical factor, has been received more attention. In a batch process, final particle diameter is mainly determined by M/W ratio, while particle number is expected to remain constant and independent of M/W ratio, provided that no particle coagulation happens due to polymer phase concentration. Chaterjee et al (1979) and Nomura and Harada (1981) have found that a larger number of latex particles is formed at low M/W ratio than that at high M/W ratio at constant emulsifier concentration. The same explanation as Krackeler's was given by them to account for this. Dunn (1992) explained that when the amount of monomer is reduced below the amount required to saturate the emulsifier micelles with solubilised monomer it is likely that the rate of polymerisation in the latex particles will ultimately become diffusion controlled reducing the rate of dilatation so that the surface of growing particles can be kept continually saturated with adsorbed emulsifier precluding all particle coalescence. Dunn's hypothesis is based on the assumption that in the conventional emulsion polymerisation (high M/W) the rate at which the emulsifier is adsorbed on the polymer particles in the presence of emulsifier micelles may be insufficient to saturate the surface layer of latex particles. This explanation is different from that given by Krackeler which considered the long nucleation period. A monomer-starved technique at very low M/W ratio has been recently adopted to study the nucleation mechanism in emulsifier-free emulsion polymerisation (Hergeth et al, 1991 and 1992).

No significant difference in average particle size and distribution was observed with increasing feed rate for styrene, methyl acrylate and vinyl acetate monomers (Crackeler and Naidus, 1969, Gerrens, 1969, Moritz, 1983). However, such a conclusion should not be generalised and must be verified for different polymerisation
conditions. For emulsifier-free emulsion polymerisation of BA, the latex particle size increased with an increase in the monomer feed rate. A large amount of scrap was formed for the run with highest monomer feed rate (Chern and Lin, 1995). However, later it was reported that at a low buffer concentration, the reverse was true and a large amount of scrap was formed for the run with highest monomer feed rate.

The partitioning of non-ionic emulsifier between water phase and monomer phase affects the particle formation. Consequences of this partitioning were seen in a semibatch copolymerisation of S/BA using TRITON X-405 as emulsifier where all the surfactant was initially present in the aqueous phase; in this case, too many particle were nucleated leading to massive coagulation due to insufficient surfactant being available to stabilise the particles (Ozdeger et al, 1997).

For copolymerisation systems, the variation of particle size with comonomer feed should be also taken into consideration. For vinylidene chloride/butyl methacrylate (VDC/BMA) copolymerisation system, the particle size of semibatch latexes was found smaller than that of batch process for a high BMA content, while the reverse was true for a low BMA content in the feed. The final particle size increased with BMA content in the feed for both batch and M add semibatch process (Lee et al, 1992). For VA/BA system, the average particle diameters for semibatch copolymer latexes were found to be smaller than those of batch latexes (El-Aasser et al, 1983). The same trend was observed for BA homopolymer, while for PVA the reverse was true. The average particle size of batch copolymer latex was reported to be independent of the copolymer composition, whereas for semibatch copolymer latexes the average diameter was reported to decrease with increasing BA content. Polydispersity was also found to increase with increasing BA content. The difference in latex particle size was explained in terms of locus of initiation, the copolymer composition, the effect of particle morphology on the adsorption of emulsifier and colloidal stability during the course of polymerisation. Since the monomer starved condition was employed, the copolymer composition within the particles was expected to be homogeneous. Particle surfaces richer in more hydrophobic BA monomer, adsorb more emulsifier which in turn results in a high level of colloidal
stability of latex particles. Thus, the particles with small average size and distribution were obtained. Particles with surfaces rich in more hydrophilic VA monomer, become less stable due to poor emulsifier packing and coalescence with other particles. Hence the average particle size increases and particle size distribution narrows.

Kong et al. (1987) studied the influence of copolymerisation pathway on the particle size, surface and morphology in VA/BA emulsion copolymerisation. Four different processes: conventional batch, composition controlled (semi)batch, core-shell and emulsifier free semibatch were investigated. In the batch process, average particle size was found to increase with BA content, except at 100% BA where size decreases. This result is in conflict with what has been published by this research group before and the results reported by EI-Aasser et al. (1983). For the composition-controlled semibatch process, the average particle size was found to increase with BA content in the feed which is again in contrary to what has been reported by EI-Aasser et al. (1983). In core-shell procedures, the average particle size was reported to increase with VA content. Discrepancies of results obtained do not permit the drawing of any precise conclusion for VA/BA system. For semibatch emulsifier-free copolymerisation of VA/BA, the particle size diameter decreased with increasing BA content in the feed, going through a minimum around 20 % mole ratio of BA, and then increased with BA content afterwards (Kong et al., 1987).

2.5.4.2.2 Monomer emulsion feed

It is expected that the higher the quantity of emulsifier present in the initial formulation, the greater is the number of micelles formed and more micelles are probably initiated by free radicals. This leads to a greater number of polymer particles formed which in turn leads to a smaller particle size of the final product for a particular quantity of monomer available in the initial recipe (Snuparek, 1974).

The start-up procedure for semibatch process with ME feed can vigorously change the number of particles and its PSD. The simplest case for study is obtained when the whole recipe containing all ingredients is divided into two parts: initial charge and monomer emulsion feed. If polymerisation is started with a specified portion of the
whole recipe, $r$, polymerisation will proceed only with $r$ percent of the particles formed with the same recipe using a batch process, provided that no new latex particles are generated during the ME feed (Gerrens, 1969). He showed that for such a system, at a constant $r$, the narrowest PSD is obtained for the lowest monomer emulsion feed rate. It was mentioned that the pre-period and the feed rate $R_a$ determine whether or not new latex particles are formed during ME feed. There is a critical feeding time for each system beyond that no new particles are formed during the feed and that the number of particles is independent of $R_p$. Similarly, for any system there might be a critical preperiod time, above which secondary particle formation is completely suppressed (Gerrens, 1969).

If different distribution of ingredients between the initial charge and the feed are used, then the particle formation rate is affected correspondingly. Emulsifier distribution ratio, $(R/F)_{E}$, is thought to be the most important variable. If the emulsifier is added in the course of polymerisation in amounts below the CMC in order to avoid further micelle formation, the initial emulsifier will determine the number of particles to be formed during the polymerisation reaction (Naidus, 1953). Crackeler and Naidus (1969) studied the effect of emulsifier distribution ratio and feed rate on the kinetic features. However, their findings have not received specific attention as deserved, perhaps due to difficult terminology they have used to explain their results. For ME feed, the number of particles increased with feed rate and the PSD narrowed. Snuparek (1974) claimed that except for the low $(R/F)_{E}$ ratio (lower than 15/85) and with various feeding time (60-132 min) particles with constant size were obtained. This indicated that a large number of primary particles underwent extensive limited flocculation. This claim that the number of particles is determined by the emulsifier concentration in the whole recipe and is independent of the way it is added to the reactor, has been reported by Uroquila et al (1991) for the seeded semibatch emulsion copolymerisation of vinyl acetate and methyl methacrylate. Vanderhoff (1985) summarised reported works on the effect of emulsifier concentration in batch emulsion polymerisation reactors and suggested that a plot of number of particles versus emulsifier concentration should take the S-shaped curve. The near horizontal curve at emulsifier concentrations well above the CMC was suggested to be due to a
controlling effect of radical generation in the aqueous phase. A S-shaped plot of Np versus emulsifier concentration has been reported by other investigators (Dunn and Hassan, 1986). Poehlein et al (1988) simulated the variation of particle number at the steady state and transient state with micelle concentration and obtained the S-shaped curve for all monomer types. Similarly, it can be concluded that for any semibatch emulsion polymerisation using a high emulsifier concentration, the number of particles formed might be independent of the way emulsifier is added to the reactor.

Bataille et al (1978) investigated VA semibatch polymerisation with no initial charge of emulsifier which is identical to the case defined by Snuparek as a non-coagulation system. They found out that the numbers of particles per ml diminished as the polymerisation proceeded. They attributed it to the extensive limited flocculation. However, a decreasing concentration of polymer particles in ME add semibatch process, when number of particles remains virtually constant, is the consequence of water addition to the reaction mixture. Similar results were also reported by Elgood et al (1964) for semibatch emulsion polymerisation of vinyl acetate with monomer emulsion feed.

Recently, a few studies on semibatch emulsion polymerisation with non-ionic emulsifier or mixed emulsifier systems have appeared in the literature. The concentration of anionic surfactant in the initial reactor charge, was reported to be the most important parameter in determining the particle size of semibatch emulsion polymerisations using mixed anionic and non-anionic surfactant systems (Chern and Hsu, 1995; Chern and Lin, 1996). For the unseeded semibatch emulsion polymerisation of BA/MMA, narrower PSDs with larger average particle sizes were obtained when mixed anionic and non-anionic surfactant systems were used, compared with those obtained with single anionic systems (Unzueta et al, 1995b). Urretabizkaia (1994) reported that for the seeded semibatch emulsion polymerisation of VA/BA/MMA with monomer emulsion feed and using Alipal Co-436 as non-ionic emulsifier, no clear effect of the emulsion feed rate on the evolution of the number of polymer particles was observed. Higher amount of emulsifier increased the secondary nucleation of polymer particles, which had no significant effect on the polymerisation
rate. They reported that secondary nucleation augmented when more emulsifier was charged into the initial charge, at a constant overall emulsifier concentration. More secondary nucleation was observed for the higher overall initiator concentration.

2.5.4.2.3 Other feeds

Emulsifier addition may be used to control the formation of new particles and the overall size distribution. Min and Gostin (1979) investigated the effect of emulsifier and initiator additions on the particle formation in semibatch emulsion polymerisation of VCM. Micelle formation would result in the birth of a second crop of particles. By measuring of the rate of heat evolution from a total heat balance on reactor and a pre-knowledge of the relation between polymerisation rate and average particle size, Gordon and Weidner (1981) showed the dependence of particle size on the heat evolution rate. Emulsifier feed was then regulated to give a desired temperature profile and hence particle size. Moritz (1983) reported that when polyvinyl alcohol (PVAL) was added later during the course of semibatch emulsion polymerisation of VA, the probability of being grafted to the surface of particles was reduced and the number of particles formed decreased. Obviously, the rate of reaction was reduced but the inhibition period was largely reduced as well. It was suggested that the semibatch wise PVAL addition can be used as a technique to control grafting reactions. The application of other feeds to semibatch emulsion polymerisation is mentioned in section 2.2.2.

2.5.5 Particle stability and coagulation

In a semibatch process with low initial loading, the initial surface to volume ratio of the reaction mixture is very low, compared to an identical batch polymerisation. Although the effect of surface coagulation is negligible for stable emulsion systems, it may be important for unstable systems. The initial mixture in a semibatch process for seeding, receives more energy per unit volume by stirrer (power/volume) compared with the batch process at full reactor capacity. This may be a critical factor in semibatch emulsion polymerisation reactors which operate at a higher stirring speed. It is possible to employ double or triple impellers to distribute the mixing energy more homogeneously in the increasing volume of reaction mixture.
The formation of coagulum can often be correlated with agitation rate and mode of addition of ingredients. Generally, the rate of coagulum formation increases with agitation rate. Some exceptions have been also reported. For semibatch emulsion polymerisation of VA the coagulum content and particle size did not increase with stirring speed and showed minima at a particular stirring speed (Donescu et al., 1985a, b). The same result was reported for EA semibatch emulsion polymerisation (Eliseeva, 1981). Continuous addition of monomer often reduces the amount of coagulum, compared to that formed in batch process. The coagulum deposited on the reactor surfaces may be the result of polymerisation of the monomer in the vapour space above the latex. Polymerisation in the vapour space of the reactor will form solid polymer in the form of particles which may stick to the reactor surfaces or fall into the latex. A semibatch process is marked by a large overhead space area due to gradual increase in the reaction mixture volume. However, when the semibatch process is operated at the starved condition (no monomer droplet), the vapour pressure of monomer is rather low due to its dissolution within polymer particles. Hence, the monomer concentration and then overhead polymerisation is supposed to be less important, compared to batch polymerisation process (Vanderhoff, 1981).

In a semibatch process, the feed is usually added to the reactor by dropping it through the vapour space to the upper surface of the latex. In such circumstances, mixing must be sufficient to disperse monomer into the reaction mixture instantly. If the mixing is not vigorous enough, a stagnant film of monomer is formed on the surface of the latex which will undergo surface polymerisation. Surface polymerisation causes more coagulum formation and also composition drift in the case of semibatch copolymerisation systems (Vanderhoff, 1981). Under-baffled reactors may be used in order to form a limited vortex on the surface and disperse the surface layer into the reaction mixture, instantly.

Due to continuous addition of emulsifier, semibatch emulsion polymerisation processes with monomer emulsion feed are expected to give the highest stability for the latexes. The formation of coagulum in semibatch emulsion polymerisation have been studied by some researchers (Snuparek, 1979a, b) and has been modelled as well.
(Chern et al, 1996). Similarly, the tendency of the polymerisation system to form coagulum is greatly impeded by the emulsifier distribution between the initial reactor charge and the emulsion feed. The amount of coagulum can be reduced significantly with an increase in the amount of the surfactant in the feed (Snuparek, 1979a). If the polymerisation is started with a high content of emulsifier concentration in the initial charge, a large number of small particles appear, which might undergo extensive flocculation during the growth stage of the polymerisation. The flocculation of particles stops, where the surface area of particles become so small that the amount of emulsifier present just provided the required stability. With a very low content of emulsifier in the initial reactor charge no flocculation occurs and even a nucleation of new particles took place toward the end of the monomer emulsion feeding (Snuparek, 1979a). The use of a non-ionic emulsifier, with or without anionic one, to stabilise the growing seed in semibatch emulsion polymerisation of MMA/BA caused a colloidal destabilisation of the system and led to a broad PSD (Unzueta and Forcada, 1995a).

Particle stability increases with increasing particle diameter but decreases exponentially with increasing ionic strength of the aqueous phase (Ottewil, 1982). Low initiator levels, produce low ionic strength and therefore high particle stability. For such a case the number of particles is determined by the rate of particle formation. As the initiator level increases, the number of particles is dictated by the rate of coagulation. In the presence of electrolytes, the increase in ionic strength and subsequent effect in de-stabilising the particles by compressing their double-layer becomes more severe. Chern and Lin (1996) grew PBA seed particles by adding neat monomer feed and studied the particle stability during the growth. They found out that the variation of particle stability with monomer feed rate depends on the buffer concentration in the reactor. At low buffer concentration, particle stability increased with decreasing monomer feed rate, while at higher buffer concentration the reverse was found; particle stability decreased with increasing monomer feed rate. They attempted to explain it by the trade-off between two parameters: A longer intensive mixing for the lower feed rate which cause particles experience more coagulation and the formation of a larger number of carboxyl groups on the surface of particles which stabilise particles against coagulation (Chern et al., 1997a). The reagent buffer, was
claimed to promote ionisation of carboxyl groups on the BA particle surface. Vandenzade and Rudin (1992) investigated the effect of ionic strength on particle size average and distribution of VA/BA seeded semibatch emulsion copolymerisation within ME feed. As the buffer concentration was increased, the particle size increased until gross coagulation occurred. The particle size was greatly reduced as a result of decreasing the initiator and buffer pre-charge. This was attributed to a decrease in ionic strength at the beginning of the reaction. It was mentioned that the decrease in the initiator concentration decreases the rate of production of radicals for initiation. The decrease in radical generation rate should result in a decrease in surface charge density since fewer oligomers are being generated and the size of particles will increase. They suggested that the initiator concentration had a significant effect on the ionic strength of the medium but less effect on the surface charge density, since the net effect is to increase the particle size. Water distribution ratio can also indirectly affect particle coagulation. Snuparek and Klekova (1984) studied water distribution between the initial charge and the feed. They added all of the reducing agent into initial reactor charge and investigated a few water distribution ratios. They reported particle flocculation to a greater extent at low \((R/F)_w\) ratio, which referred to higher electrolytes concentration in the initial charge.

In batch polymerisation, the tendency of particles to flocculate increases with the increasing monomer solubility. Surprisingly, the tendency to coagulum formation was found to increase with increasing alkyl length in acrylic monomers. This was attributed to the greater concentration of carboxyl groups on the surface of particles for the lower acrylates compared with higher acrylates (Snuparek, 1979a). The concentration of chemically bound functional groups located on the particle surface was found to have a strong effect on the particle stability and on particle coagulation. This functional groups includes mainly carboxyl groups which is formed from acid hydrolysis of ester groups. A minor amount of acrylic acid can stabilise particles and decrease the particle size. This has been verified for semibatch processes by some researchers (Snuparek, 1979b; Chern and Lin, 1996). However, Huo et al (1988) reported a higher rate of particle coagulation for carboxylated VA/2-EHA latex produced by semibatch process with increasing acrylic acid concentration.
2.5.6 Average molecular weight and distribution

Molecular weight development in emulsion polymerisation reactions is a very complex phenomenon which depends on many important events such as radical desorption, absorption, termination, etc. The instantaneous number average molecular weight is given by:

\[ M_n = \frac{R_p}{R_i} \]  

According to equation 2.8, \( M_n \) is directly proportional to \( M_p \) and \( N_p \) (see equation 1.1 for the definition of \( R_p \)) and inversely proportional to \( R_i \). At a starved condition in a M add process, \( M_p \) is lower than that in the interval I and II of a conventional batch process. Supposing that \( N_p \) is identical for both batch and semibatch processes, \( M_n \) would be lower in a semibatch process. In ME add process, \( N_p \) and \( M_p \) are both lower than those in batch process, then \( M_n \) would inevitably be lower in semibatch process compared with B process.

Gerrens (1969) showed that for both M and ME feed, the degree of polymerisation increases with increasing \( R_a \). With constant \( \bar{n} \) and \( N_p \), \( M_n \) ought to be proportional to \( M_p \). However, for both S and MA, \( M_n/M_p \) was found to increase with decreasing \( M_p \) (lower \( R_a \)). This was attributed to branching. For a flooded condition, \( M_n \) was shown to be constant and independent of \( R_a \). Krackeler and Naidus (1969) found that the \( M_n \) for ME add and M add semibatch process is lower than that in batch process. This was explained by lower effective \( M_p \) in semibatch process. However, the \( M_n/M_o \) ratio obtained in their experiments indicated that the uniform monomer distribution was unlikely. In order to explain the results, they suggested that concentration gradients exists throughout the particle with the greater \( M_p \) in the outer zone of particles. Hence the reaction would be localised primarily in the outer zone which has a thickness that depends on the amount of monomer present. The \( M_p \) at the reaction sites would tend to have a more uniform value throughout the reaction. Therefore, the MWD breadth for batch, ME add and M add semibatch process may be expected to show no great difference. Bataille et al (1978) obtained the bimodal molecular weight distribution for semibatch emulsion polymerisation of VA. The main peak appeared in the low
molecular weight region, followed by a very sharp peak in the high molecular weight region. The second peak was attributed to the solution polymerisation of VA in the aqueous phase. An increase in the polydispersity with conversion was observed in all runs which were attributed to an increase in density of chain-branching.

Lee et al (1992) reported the same trend in the molecular weight development of seeded semibatch emulsion copolymerisation of vinylidene chloride (VDC) and butyl methacrylate (BMA) with reactivity ratios of 0.22 and 2.41, respectively. Such a comonomer pair gives an initial copolymer richer in the more active monomer, BMA, and later copolymer richer in the less reactive monomer, VDC. In general, both the number-average and weight average molecular weights of the copolymers prepared by semibatch process were lower than those of their batch process. The narrower MWD was also found for the semibatch process, compared with the batch process. It was explained that batch process produces BMA-rich copolymer of high molecular weight at the beginning and VDC-rich copolymers of low molecular weight at the end of polymerisation, due to composition drift. Hence, the semibatch process gives a copolymer with a constant composition and molecular weight.

VA/BA emulsion copolymerisation in a semibatch reactor has been studied by many research groups. These two monomers possess widely desperate reactivity ratios. El-Aasser et al (1983) found bimodal molecular weight distributions (MWD) in most semibatch latexes with a substantial amount of low molecular weight fraction, while unimodal distribution was found for batch process. The first peak was found to have a lower molecular weight average than the corresponding batch copolymers, for all copolymer composition. The second peak in the high molecular weight region, which was attributed to the transfer reactions, was found to be strongly affected by the copolymer composition. The MWD for batch latexes was narrower and less dependent on composition than that of semibatch latexes. For the semibatch process, molecular weights decreased with increasing BA content in the copolymer feed up to 37 wt %, followed by an increase with further increase in BA content. The similar results were reported by Kong et al (1987) for VA/BA semibatch emulsion copolymerisation system. From the literature it is understood the molecular weight development in
Semibatch emulsion copolymerisation processes is highly dependent on the type of comonomers and process conditions and general conclusions can not be easily made.

2.5.7 Copolymer microstructure and composition

Batch reactors, which are widely used for homopolymerisation, are not ideal reactors for copolymerisation of monomers with large difference in reactivity ratio because composition drift occurs. The extent of compositional drift depends on the ratio of reactivity ratio \( r_1/r_2 \), the initial monomer feed composition and the monomer conversion. One of the main advantages of a semibatch emulsion polymerisation process compared with a batch process is the possibility of controlling chemical composition of co- or ter-polymers. Homogeneity of copolymers has a great influence on various properties such as: hardness, film formation, etc. The first report on the effect of various monomer addition methods on the emulsion copolymerisation has been given by Chujo et al (1969). They studied a VA/BA emulsion copolymerisation system which, normally in a batch process, gives a very heterogeneous copolymer structure, due to the wide difference in the reactivity ratios of VA and BA. They showed that homogenous copolymers were obtained by continuous M addition methods, while heterogeneous copolymers were obtained by initial addition of total monomers or stepwise monomer addition method. The effects of comonomer composition and method of monomer addition on bulk and surface properties of VA/BA copolymer latex were examined by several investigators (El-Aasser et al, 1983; Kong et al, 1987; Misra et al, 1983). Pichot et al (1981) studied the compositions and sequence distributions of VA/BA copolymers obtained with batch and semibatch emulsion polymerisation by H and C-NMR. It was emphasised that a semibatch process gives more homogenous copolymers, compared to a batch process.

Guyot et al (1981) used online GC to control copolymer composition in the emulsion copolymerisation of S/AN by applying a feedback control system. They found that the copolymer composition drifted toward higher styrene levels than where expected. They showed that this was due to a favourable distribution of AN in the aqueous phase which was not accounted for in their initial model. The same policy was adopted by the Guyot et al (1984) to obtain uniform composition in the AN/Butadiene...
copolymers, while the monomer partitioning among different phases was included in their model. The uniform composition was verified by a single glass transition temperature for the product.

Hamielec and Macgregor (1983) elaborated some feed policies which can be used to maintain constant copolymer composition in the course of reaction with S/AN solution copolymerisation. According to Hamielec and Macgregor two basic monomer feed policies may be used in semibatch reactors to minimise composition drift. In policy 1 all of the slower monomer and a sufficient amount of the faster monomer to give the desired composition are placed in the reactor. Then the faster monomer is fed to the reactor with a time-varying rate to maintain the mole ratio of comonomers constant. In policy 2 a part of comonomer feed with predetermined mixture to give the desired composition is added to the reactor. Thereafter, comonomer feed is continuously added to the reactor in a time-varying rate in order to maintain a constant comonomer concentration in the polymer particles. It is also possible to run policy 2 without any initial loading of comonomers feed. In practice these feed policies are widely used with constant feed rate, due to the practical advantage of working with a constant flow rate pump. The methodology was extended to emulsion copolymerisation (Broadhead et al, 1985; Hamielec et al, 1987). However, the strict application of these policies is not possible in the flooded region where monomer droplets are also feeding the polymer particles. The extent of deviation depends on the amount of monomers accumulated in the system. The policies may be safely applied to a semibatch reactor at starved condition.

Arzamendi and Asua (1989) made the comparative study of the different feed policies, as illustrated by Hamielec et al, by mathematical simulation of seeded semibatch emulsion copolymerisation of VA/MA. The terms "semistarved process" and "starved process" were applied to the feed policies 1 and 2, respectively. It was shown that the semistarved process with variable feed rate is the only M add policy that ensures the production of a copolymer of a constant composition during the copolymerisation reaction. A nearly constant copolymer composition was obtained under starved condition at long feeding time. At shorter feeding time, a heterogeneous copolymer
was obtained due to predominant composition drift at the initial (seeding) and final (finishing) stages of polymerisation. Furthermore, it was shown that the semistarved process requires much less reaction time for completion than the starved process. It is apparent that from the practical point of view the application of a constant feed flow rate is much more advantageous than usage of a time-dependent flow rate. It was reported that applying constant semistarved feed policy may give a less homogenous composition, while making the process time shorter and feeding more practical. The verification of their mathematical simulation model to the seeded semibatch copolymerisation of VA/MA and MMA/EA was carried out in their subsequent papers (Arzamendi and Asua, 1990; Arzamendi et al, 1991). The iterative approach developed by Arzamendi and Asua was extended to control the composition of copolymers obtained from technical grade monomers including inhibitors (Arzamendi and Asua, 1993). The optimal monomer addition strategy to control the copolymer composition in reactors with limited capacity for heat removal was also described by this research group (Arzamendi and Asua, 1991). The similar approach was adopted by German and coworkers (Van Doremaelle et al, 1992; Schoonbrood et al, 1993) to calculate the optimal feed policy to control the copolymer composition in the seeded semibatch copolymerisation of S/MA. It was emphasised that the feeding policy 1 or semistarved strategy provides the shortest way to reach the latex with desired composition.

As stated before, semibatch operations are usually preceded and followed by a batch operation, seeding batch and finishing batch, respectively. It has been observed that at the very beginning of the multicomponent emulsion polymerisation of monomers with desperate water solubility, such as S/AN and S/MA, the copolymers are richer in the more water soluble monomer than is expected from copolymer composition equation. On the other hand, the duration of finishing batch depends on the monomer concentration in the polymer particles at the end of feeding time. The lower the feeding rate, the lower monomer concentration in the particles and the less composition drift in the finishing batch. The composition distribution involved in these two batch operations may influence the final copolymer composition in the semibatch process (Arzamendi et al, 1987).
2.5.8 Particle morphology

The development of the morphology of the latex polymer particles involves two stages. First, formation of new polymer chains in some location within the polymer particles and second, if these new polymer chains are incompatible with the polymer previously formed, migration of polymer chains. Phase separation causes the surface composition of particles have a large deviation from the cumulative copolymer composition. Batch process can be used for the production of composite latexes only if two (or more) monomers with wide differences in reactivity ratio and/or in polarity reacts (Daniel, 1985). The VA/BA copolymerisation system is a good example for this case. In a VA/BA batch emulsion copolymerisation, a heterogeneous structure with a rich VA outlayer (core-shell structure) is formed. Semibatch processes with a continuous or discontinuous variation of composition of the monomer feed may be used to produce a wide variety of latex composites. The versatility of semibatch emulsion polymerisation processes to adjust the morphology of particles and related properties has been discussed by many researchers (Vanderhoff, 1987; Rudin, 1995). Because of the enormity of literature on particle morphology, we shall not attempt an exhaustive bibliography, instead we shall attempt to outline the distinctive effects and advantages of semibatch emulsion polymerisation compared with batch process for production of composite latexes.

Krackler and Naidus (1969), who carried out the comparative study of batch versus semibatch emulsion polymerisation of styrene, noticed that the $M_w / M_n$ ratio obtained for the semibatch process was close to that of batch process. In order to explain this, they suggested that a concentration gradient exists throughout the particle with the greater $M_p$ in the outer zone of particles. Hence, the reaction would be localised primarily in the outer zone with a thickness which depends on the amount of monomer presents. Since the $M_p$ at reaction sites would tend to have a more uniform value throughout the reaction, the MWD breadth for batch and semibatch process may be expected to show no difference. The original scheme of Krackler and Naidus was adopted by Grancio and Williams (1970) to construct their theoretical model of "core-shell" morphology with new experimental foundlings and insights. Williams' initial arguments were based on conversion-time data which showed a constant
polymerisation rate up to the conversion 60%. He explained these results by considering a constant $M_p$ and $\tilde{n}$ at the shell around the particles which was considered as the main site of the reaction. Based on the simple diffusion law, Napper argued that a large difference in $M_p$ in the particles is not expected. Gardon (1973) indicated that the constant reaction rate may be attributed to a compensating effect of increasing $\tilde{n}$ because of a gel effect. Vanderhoff supported this hypothesis by the possibility of anchoring of ionic end groups of macroradicals on the particle surface. By the characterisation of polystyrene latexes using persulphate ion initiator, he demonstrated that more than half of the polymer end groups remained on the particle surface (Vanderhoff and Van den hul, 1970). Kao et al (1984) studied seeded semibatch emulsion polymerisation of styrene with M feed. They added that under styrene-rich conditions uniform styrene distribution inside the polymer matrix may be assumed. However, under styrene lean conditions, which are formed during slow monomer feeding, significant monomer gradients develops inside the particles due to slow monomer diffusion rate through the polystyrene matrix. A monomer rich shell was proposed (for $M_p < 0.4\text{mol/lit}$) in order to explain experimental results.

Only a few homopolymers are compatible, hence a complication occurs when two monomers with different structure take part in a copolymerisation reaction. It may be expected that the particle morphology is dictated by the compatibility of polymer chains. However, the polymerisation kinetics makes a strong contribution to particle morphology. The thermodynamic factors determine the stability of the ultimate particle morphology, while the kinetic factors determine the ease with which such a thermodynamically preferred morphology can be achieved (Chen et al, 1993). The thermodynamic property which determines particle morphology, is probably the interfacial energy associated with the various surfaces between phases. The most important kinetic factors are particle viscosity, molecular weight, crosslink density, and degree of grafting between phases. Phase separation occurs more quickly with small molecules and low viscosity polymers than with high molecular weight polymers. All of these factors may be affected by employing a semibatch process.
Many polymer latexes with a wide variety of properties are being produced as core-shell latexes or in a more complicated morphological shapes by co- or multi-component polymerisation. Okubo (1990) has reported a number of morphologies other than core-shell for two-stage latex particles such as "raspberry like", "mushroom-like", "half-moon like", etc. Composite latexes are being produced by two or multi-stage emulsion polymerisation system. The mode of addition of second or later stages of monomer feed could be batch (shot) or continuous. If all the monomer is added to the reactor in one shot, a high level of second-stage monomer accumulates in the first-stage particles. In contrast when the second stage-monomer is gradually added to the first-stage particles in such a low amount that starved condition pertains, the lower monomer concentration prevails in the particles. Hence the second stage monomer will be present primarily in the form of polymer molecules which are relatively hindered in mobility compared with monomer molecules.

The application of semibatch processes is more useful when final latex morphology is not thermodynamically favourable. This is the case when the desired core polymer is more hydrophilic than the shell polymer. In order for the particles to achieve inverted morphology, the phases must overcome the kinetic barrier. The first-stage polymer must diffuse to the outside and the second phase must diffuse to the inside of the particles. Lee and Rudin (1992) studied the effects of both thermodynamic forces and kinetic considerations on morphology of particles with a more hydrophilic polymer core. They concluded that batch polymerisation conditions decreases the kinetic barrier to inversion; whereas, semibatch polymerisation imposes a higher kinetic barrier.

Okubo (1990) investigated the variation of the number of PS-rich domains within the PBA/PS composite particle as a function of conversion using a semibatch process. He showed that at highly starved conditions, using the so-called drop-wise method, the number PS-rich domain increased with an increase in the conversion, because the viscosity within the particles is kept at high levels throughout the polymerisation, whereas the number of PS-rich domain was almost constant in the flooded system.
Surface morphology of the latex particles is another critical factor when improved colloidal stability or enhanced adhesivity to a given substrate is required. Functionalised latexes are prepared by using monomer bearing a chemical reactive group, such as carboxylic monomers (mainly acrylic and methacrylic acids), ionic and non-ionic monomers (acrylamide, methacrylamide, etc). Emulsion polymerisation in the presence of functional monomers comprises water-phase and oil-phase polymerisation, which cause the reaction mechanism to be more complex. pH and ionic strength of the reaction mixture drastically affect the functional monomer solubility and reactivities in radical copolymerisation. Hence the distribution of the ingredients between the seed charge and the feed is more critical in semibatch polymerisation of functional monomers. El-Aasser et al (1985) studied batch and semibatch emulsion polymerisation of different carboxylated latexes, such as S and MMA, by investigating the alkali-swelling behaviour of carboxylated latexes which strongly depends on the loci of carboxyl groups and the hydrophobicity of the base monomer in the copolymer latex. They showed that semibatch processes gave a more uniform distribution throughout the particle than the batch process, which gave less surface localisation of functional groups. Huo et al (1988) investigated batch and semibatch operation of carboxylated VA/EHA latex in order to produce a pressure-sensitive adhesive with desired mechanical properties. They showed that with semibatch operation with ME feed, a latex with larger particles and less surface swelling was obtained. They found the semibatch process more useful in producing a latex with desired larger particle size, less surface swelling, as well as highly branched structure. Generally, a semibatch process with constant feed composition permits a better control of homogeneity within the particles and is not well adapted to the surface localisation of functional monomers. However, a semibatch process with a time-varying composition feed, such as power feed method, is well suited to produce particles with desired surface morphology.
2.6 CONCLUSIONS FROM THE LITERATURE STUDY

It is understood from the literature review that kinetics of polymerisation and monomer and emulsifier distribution between oil and water phase, kinetics of emulsifier adsorption and particle stability and kinetics of morphology development play important roles in particle formation in semibatch emulsion polymerisation systems. Despite many relevant publications, the particle formation mechanism in semibatch emulsion polymerisation, specially with ME feed, is not well elucidated. Several controversial issues are still unsolved. The following general conclusions may be drawn from the literature review regarding particle formation and growth:

1. The comparative study of particle formation in batch and semibatch process have not been reported for a wide range of polymerisation conditions. The effects of different polymerisation conditions such as varying overall emulsifier concentration, M/W ratio, and monomer feed rate need to be investigated. There are controversial issues about the similarity between particle formation in batch and semibatch reactors which need to be resolved.

2. Particle formation under monomer starved conditions with M feed needs more investigation.

3. The role of homogenous nucleation in semibatch emulsion polymerisation with ME feed needs more investigation.

4. The role of process variables, such as pre-period time, in unseeded semibatch process has not been reported in the literature.

5. The particle size development in semibatch emulsion polymerisation with ME feed has not been fully investigated. The effect of monomer emulsion feed composition on the particle formation has not been reported.

6. The effect of monomer distribution ratio in a semibatch process has not been investigated in details.

7. The effect of water phase kinetics on the rate of particle formation has not been studied.
Chapter Three

Experimental Procedure

3.1 INTRODUCTION TO PARTICLE SIZE MEASUREMENT

For the latex particles with diameters in the range of $< 0.50 \mu m$, different techniques such as dynamic light scattering or photon correlation spectroscopy (PCS), transmission electron microscope (TEM), intensity or transmission light scattering, size exclusion chromatography (SEC), hydrodynamic chromatography, disc centrifuge or ultracentrifugation, and soap titration can be used (Fitch, 1997).

SEC or hydrodynamic chromatography (HDC) works by passing the latex through a packed column whose flow patterns are such that larger particles elute more quickly than smaller ones. By using a suitable detector (one based on light scattering) and calibration with monodisperse particles, a full particle size distribution (PSD) can be obtained. Disc centrifugation, theoretically can provide a simple technique for measurement of particle size and its distribution. In disc centrifuge particles are separated radially by their sedimentation velocities, according to their size and relative densities. A light source on one side and a photodetector on the other view the passage of particles at a fixed point, thereby producing a curve of turbidity as a function of time at a given radial distance from which may be calculated the PSD. The particle size analysis by ultracentrifugation for particles smaller than 100 nm becomes too long
and hence impractical. Disk centrifugation with a photo-sediment detector (DCP) can
gives results comparable with TEM for both the average size and the total distribution,
although it is not that much accurate. DCP requires calibration with standard PS
latexes. Soap titration, which is based on the emulsifier adsorption, is the simplest
method to determine particle size average. However, the precision of the results is not
high, due to uncertainty in pinpointing the CMC value.

In this research work, particle size measurements of polymer latexes have been made
by using TEM and PCS. Therefore these techniques are explained in more details in
Appendix F.

3.2 POLYMERISATION APPARATUS AND PROCEDURE

3.2.1 Apparatus

Butyl acrylate emulsion polymerisation, at the conditions studied, shows a very high
rate of polymerisation. For most of the experiments and specially those using high
emulsifier or initiator concentrations and a high temperature, the reactions are highly
exothermic. The application of constant-temperature water bath was not practical
since a large amount of reaction heat was released within a first few minutes of
reaction, leading to a temperature rise as high as 20 °C. In order to carry out the
experiments isothermally, a jacketed reactor with adjustable cooling temperature was
used. The temperature of cooling water was adjusted by using the mixture of a stream
of cold water (tap water) and a stream of hot water coming from a constant-
temperature water bath. The required cooling water temperature was manually
obtained by mixing different ratio of cold and hot streams through a valve.
All experiments were carried out in a jacketed one-litre glass reactor equipped with a
four-bladed flat turbine type impeller with a width of 1/3 of vessel diameter, a
standard four baffle plates with the width of 1/10 of vessel diameter located at 90°
interval, an overhead reflux condenser, a thermocouple, a sampling device, sampling
port for nitrogen purge, and an inlet for feeding ingredients. The stirrer rate was kept
constant at 325 rpm. For batch runs the stirrer blades was held 3 cm below to free
surface. For semibatch runs the position of the stirrer blades was lifted from time to
time to 3 cm from surface to avoid the formation of free monomer layer. This assured that the incoming monomer got mixed with the reaction mixture as soon as it entered the reactor. The temperature of the reactor contents was controlled at the desired temperature within ±1.0 °C by pumping water with appropriate temperature through the jacket. Sampling was carried out at the desired time interval by removing an aliquot of 2-3 g latex by a hypodermic syringe. The schematic of the semibatch process is shown in figure 3.1.

A reciprocal pump with three different heads was used for feeding the monomer and the aqueous solution to the reactor. The flow rates of the pump heads were adjusted at the desired level before the feeding. Then the flow rates were measured at the end of each experiment and compared with the set values to assure the constant rate during feeding. The precision of the pump was quite satisfactory and generally was in the range of 0.1- 2.0 % of the set values. For a very few experiments the variation in the flow rates up to ± 5.0 % was observed. For all experiments, the average flow rate measured in the beginning and at the end of feeding was used.

3.2.2 Latex Preparation

For the batch operation the reactor was initially charged with most of the deionised water and all of other ingredients except initiator. Initiator was dissolved in 20 cc of distilled deionised water (DDI) from the overall recipe. All of the ingredients were separately purged with nitrogen for 30 minutes and then transferred to the reactor. Then the reactor was heated to the desired temperature while being purged with overhead nitrogen for 30 minutes and then the initiator was added to the reactor. The rate of nitrogen bubbling was decreased in order to minimise evaporation.

In the semibatch experiments with monomer feed only part of the monomer together with all of emulsifier, initiator, buffer, and water was placed in the initial charge and the rest was fed to the reactor using the pump at a constant rate. The monomer was purged with nitrogen for 30 minutes and then was kept in a blanket of nitrogen during feeding.
Figure 3.1: Schematic presentation of semibatch emulsion polymerisation process used for experimental work.
In the semibatch experiments with monomer emulsion feed only part of the monomer together with parts of emulsifier, initiator, buffer, and water was placed in the initial charge and the rest was fed to the reactor using two different streams. Monomer was fed through the first stream and the aqueous solution of emulsifier, initiator and buffer was fed through the second stream. The monomer feed and the aqueous solution were kept in a blanket of nitrogen during feeding. The feeding time of two streams was set so that they finished at the same time. It should be noted that for all graphs and tables, the rate of addition given is based on the monomer feed.

3.2.3 Reagents

The butyl acrylate (BA), was obtained from Aldrich (99+%, inhibited with 10-15 PPM MEHQ). The monomer was initially washed with 10.0% sodium hydroxide solution and distilled water several times and then distilled under vacuum at 52.5 °C. The monomer were stored at -18 °C. In the recent experiments, the monomer was only distilled under vacuum once. The initiator, potassium persulphate (KPS), and the emulsifier, sodium lauryl sulphate (SLS), were obtained from different sources and were used as received. Sodium bicarbonate (SbC) was used as a buffer to adjust the pH of the emulsions. The chemicals used and their specification and suppliers are given in Appendix B.

3.3 POLYMERISATION MONITORING

3.3.1 Conversion

3.3.1.1 Gravimetry

Method one: Withdrawing aliquots of about 1-2 g by a syringe at appropriate intervals and pouring it to a small aluminium foil dish. Methanol containing small amount of hydroquinone, to prevent further polymerisation, is added to samples to reduce mixture viscosity and hinder skin formation. Monomer, methanol and water were driven off by drying to constant weight in a vacuum oven at 60 °C. The dried polymer was weighed to calculate monomer instantaneous conversion, based on a simple mass
balance equation. The conversion at the time $t$ was calculated using the following formula:

$$x_i = \frac{\text{weight residue / aliquot weight} - \text{solid fraction}}{\text{monomer fraction}}$$

The solid fraction accounts for the weight percentage of initiator, emulsifier, and buffer in the reactor and monomer fraction for the monomer percentage in the reactor at the time $t$ (see \textit{equations 3.3 - 3.8} for calculation of the concentration of each component in the reactor at the time $t$ for the semibatch process).

\textit{Method two:} The polymers were precipitated with mixture of methanol and acetone containing a small amount of hydroquinone to prevent further polymerisation and then filtered off with a glass crucible (no. 4). The precipitated polymer may be dried in a vacuum oven to obtain total monomer conversion, as stated above. The instantaneous conversion was calculated using the following formula:

$$x_i = \frac{\text{precipitated polymer weight / aliquot weight}}{\text{monomer fraction}}$$

\textbf{3.3.1.2 Chromatography}

Conversion can be either measured by direct weighing of the polymer formed or indirectly by measuring the amount of unreacted monomers left in the filtrate. The instantaneous conversion was determined by measuring the content of the monomer in the filtrate obtained as above using a Pye Unicam 304-FID GLC. A general purpose column, wall coated-fused silica-CP-SIL5, was used. The GC measurements were carried out at the following conditions: column temperature of $80 \, ^\circ\text{C}$, injector and detector temperature of $140 \, ^\circ\text{C}$; the flame fuel gases H$_2$ and air at 15.0, and 10.0 kg/cm$^2$, respectively, and the carrier gas He at the flow rate of 20 ml/min. The samples of 1 $\mu$l were injected to the column. Dioxane was used as the internal standard to avoid the effect of variation in sample volume to the injection port. Conversion was calculated by measuring the content of the monomer in the filtrate, as obtained in the precipitation method of the conversion measurement (gravimetry method 2) routine mentioned before, with a minor difference that the methanol used...
for polymer precipitation contained a small proportion of Dioxane as the internal standard.

\[
\frac{A_{BA}}{A_{DO}}
\]

\[
\frac{W_{BA}}{W_{DO}} = F_r \frac{A_{BA}}{A_{DO}}
\]

where \( W_{BA} \) and \( W_{DO} \) are the weight of BA and Dioxane in the sample, and \( A_{BA} \) and \( A_{DO} \) are surface areas of the BA and Dioxane in the chromatographs, respectively. \( F_r \) is the response factor of BA compared to the internal standard Dioxane. Several standard solutions and emulsions containing BA, water, acetone, methanol, and dioxane with known volume were prepared and injected to the GC. From the chromatographs obtained and the weight ratios of BA and DO in the samples, the calibration curve shown in figure 3.2 was drawn, according to the above equation. The slope of this graph shows the value of response factor, \( F_r = 0.585 \), which remains constant with concentration ratio of BA and DO, and also the concentrations of other ingredients such as water, methanol, and acetone. Using the response factor, and the known values of BA and DO peak areas and weight of DO in the sample, it is possible
to calculate the BA weight in the sample from which instantaneous conversion can be calculated.

![Conversion versus time for a typical BA batch emulsion polymerisation](image)

Fig.3.3: Conversion versus time for a typical BA batch emulsion polymerisation using gravimetric and gas chromatography methods.

The results obtained for a typical sample by gravimetric methods show 99.6% agreement. The difference between the result of gravimetric methods and chromatography method was $2 \pm 0.50\%$. Despite this difference, all methods were proved to be successful in measuring conversions. *Figure 3.3* shows the conversion obtained for a BA batch emulsion polymerisation using the three methods. The gravimetry method one was used for conversion calculations for most of the experiments.

### 3.3.2 Particle size measurement

#### 3.3.2.1 Photon correlation spectroscopy

#### 3.3.2.1.1 Sample preparation

Photon correlation spectroscopy (PCS or Quasi-light scattering, QLLS) technique was used for particle size measurement (Malvern new model "Zetamaster"). The laser light scattering measurements were carried out at 90 degree angle. The Cumulant method
was used for data analysis (see Appendix F). Ten runs were carried out and the average was assigned as the mean average size of particles. Sample preparation was carried out according to the following procedure. Samples withdrawn from the reactor was diluted with filtered and distilled water and then was placed in the instrument. Although PCS is a very fast method for the measurements of particle size average, precautions should be taken for sample preparation and data analysis. The following points were considered for sample preparation and interpreting results.

3.3.2.1.2 Concentration dependence

Although PCS theoretically is concentration-independent, it is very important that for any particular samples the regime where this holds is found. If the particle concentration is too high multiple scattering will occur and an incorrect result will be obtained, with the mean size too low and the polydispersity too high. The answer to this uncertainty simply is to dilute the sample by two and measuring the particle size again. Plotting size versus concentration easily determines the maximum concentration that can be used by observing the point above which the z-average ceases to be constant. This was found to be below 0.1 wt %, as shown in figure 3.4. If the sample is too diluted, long experiments are required to obtain good statistics.

![Graph showing the sensitivity of PCS measurements to sample concentrations (dilution ratio).](image-url)

**Fig. 3.4:** The sensitivity of PCS measurements to the sample concentrations (dilution ratio).
3.3.2.1.4 Ionic strength effect

The application of deionised water could lead to small error in the size measurement, since the low ionic strength gives a very thick electrical double layer, which increases the apparent size. No appreciable decrease in the size of particles was observed with addition of low amount of electrolyte, sodium chloride, to the dilution water. However, the dilution with a rather high concentration of sodium chloride, \( > 10^{-3} \) mol/litre, led to an increase in the particle size due to particle coagulation. This is shown in figure 3.5. Distilled water was used for sample preparation.

![Graph showing the sensitivity of PCS measurements to the electrolyte concentration of dilution water.](image)

Fig.3.5: The sensitivity of PCS measurements to the electrolyte concentration of dilution water.

3.3.2.1.5 Particle shrinkage

Particle sizing required the latex to be highly diluted in water whereupon the unreacted monomer inside the particles may diffuse out of the particles, depending on the water solubility of the monomer. Water-solubility of BA at 25 °C is around 0.90 g/litre. A simple mass balance shows that a dilution by water even up to \( 10^3 \) times
would be enough to drain almost all BA monomer out of particles. This indicates that particle sizing by PCS would determine the unswollen particle size. Using the saturation value of monomer concentration in the particles, together with conversion in the reactor, it was possible to calculate the swollen or actual particle size (equation 3.14). For all PCS measurements a few hours were allowed prior to any measurement to assure that monomer had enough time to diffuse out of the polymer particles.

In the first few minutes of polymerisation reactions, the polymer particles are very small and their concentration is very low. In order to have enough particles in the sample to have a reasonable measuring time by PCS, the dilution should be carried out with less than $10^3$ water ratio and usually in the order of $10^2$ fold water. In addition, more free monomer is available early in the reaction. This indicates that particle sizing for the initial period of reaction might give a partial-swelling value for particles. For these samples, the diluted sample with water containing 0.20 g/litre SLS and hydroquinone as inhibitor, were placed in the 50 °C oven for several hours prior to measurements, to drive off the excess monomer. Generally the average size obtained by this method was $1.0 \pm 2.0$ % lower than that obtained by direct examination of early samples from the reaction mixture. It should be noted that this effect was negligible for semibatch reactions since the nucleation started with a small proportion of monomer in the initial charge.

*Figure 3.6* shows the variation in particle size with monomer concentration in the aqueous phase. The particle size reaches a plateau at monomer concentration above 0.60 g/litre. However, it seem that the increase in particle size is not in accord with its monomer saturation value obtained by kinetic analysis and GC method. Considering a monomer saturation value equal to 4.0 g/litre (based on $x_{cr} = 0.45$), a final particle size of around 100.0 nm was expected for the seed particles of diameter size 80 nm. But, the maximum diameter size of the seed particles was obtained as 90.0 nm at the higher concentration of BA. It seems that PCS method is not precise enough for measurements of monomer saturation value of particles. However, it should be added that no correction has been made for the refractive index of the medium due to addition of BA. This might partly explain the reason for such a difference.
3.3.2.1.6 Particle size adjustment

For calculation of $N_p$, as given in equation 3.9, volume average diameter should be known. TEM provides the complete distribution data from which $D_v$ can be calculated. However, PCS method gives $z$-average diameter which is larger than volume average. The application of $z$-average to the equation 3.9 (see page 89) causes an underestimation of $N_p$.

In order to obtain the better estimation of volume-average diameter, the distribution curves from TEM measurements were analysed. The values for $D_n$, $D_v$, $D_w$, $D_h$, and PDI obtained using the distribution data for the latexes made by semibatch polymerisation with monomer and monomer emulsion feed are given in chapter 5 and 6. Here, only the values for PDI, and the ratio of intensity average over volume average, $D_I/D_v$, for final latexes are listed in table 3.1. The intensity weighted average, $D_h$, was calculated using equation F.15 from appendix F. The equation F.14 also predicted very close values to the $D_I$ obtained by the other formula (results are not given here). An important conclusion can be made from this table. The ratio of intensity average over volume average, $D_I/D_v$, takes on a range from 1.05 to 1.20 for M add process and from 1.09 to 1.43 for ME add process, depending on the PDI of the sample. $D_I/D_v$ ratios were found in satisfactory agreement with PDI values, despite the
preparation method of latexes. At high PDI values, the agreement between PDI and $D_d/D_v$ decreases.

Table 3.1: PDI and $D_d/D_v$ obtained for final latexes from M and ME processes by TEM.

<table>
<thead>
<tr>
<th>Run</th>
<th>PDI</th>
<th>$D_d/D_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M Feed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BU</td>
<td>1.03</td>
<td>1.05</td>
</tr>
<tr>
<td>BX</td>
<td>1.03</td>
<td>1.06</td>
</tr>
<tr>
<td>BY</td>
<td>1.04</td>
<td>1.07</td>
</tr>
<tr>
<td>BV</td>
<td>1.05</td>
<td>1.07</td>
</tr>
<tr>
<td>BB</td>
<td>1.08</td>
<td>1.10</td>
</tr>
<tr>
<td>BG</td>
<td>1.09</td>
<td>1.10</td>
</tr>
<tr>
<td>BF</td>
<td>1.15</td>
<td>1.18</td>
</tr>
<tr>
<td>BC</td>
<td>1.17</td>
<td>1.17</td>
</tr>
<tr>
<td>BD</td>
<td>1.22</td>
<td>1.20</td>
</tr>
<tr>
<td>ME feed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BBC</td>
<td>1.07</td>
<td>1.07</td>
</tr>
<tr>
<td>BQ</td>
<td>1.10</td>
<td>1.09</td>
</tr>
<tr>
<td>BR</td>
<td>1.12</td>
<td>1.10</td>
</tr>
<tr>
<td>BN</td>
<td>1.13</td>
<td>1.14</td>
</tr>
<tr>
<td>BP</td>
<td>1.14</td>
<td>1.12</td>
</tr>
<tr>
<td>BI</td>
<td>1.14</td>
<td>1.14</td>
</tr>
<tr>
<td>BBD</td>
<td>1.16</td>
<td>1.13</td>
</tr>
<tr>
<td>BO</td>
<td>1.23</td>
<td>1.24</td>
</tr>
<tr>
<td>BG</td>
<td>1.25</td>
<td>1.23</td>
</tr>
<tr>
<td>BH</td>
<td>1.36</td>
<td>1.27</td>
</tr>
<tr>
<td>BBF</td>
<td>1.39</td>
<td>1.33</td>
</tr>
<tr>
<td>BW</td>
<td>1.48</td>
<td>1.29</td>
</tr>
<tr>
<td>BT</td>
<td>1.67</td>
<td>1.43</td>
</tr>
</tbody>
</table>

One way to convert the z-average data obtained by PCS to the volume-average usable for calculation of $N_p$ is to multiply the z-averages by their corresponding $D_d/D_v$ ratio, afterward called conversion factor $C_f$, measured by TEM. However, this is not a convenient method and furthermore the conversion factor $C_f$ is not constant and varies in the course of reaction as the PDI of the latexes changes. Therefore, for each series of experiment only a constant $C_f$ was used to convert the z-average obtained by PCS to the volume-average needed for calculation of $N_p$. This seems to provide a better estimation for the number of particles compared with direct application of the z-average. Similarly, Alducin et al (1994) reported a comparison between the z-average diameters measured by PCS and the volume-average diameters measured by TEM for polydisperse latexes so that $D_d/D_v = 1.25$. 

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The $C_r$ value of 1.10 was used for all M add experiments and those having a PDI smaller than 1.15. For all other experiments (having a PDI greater than 1.25), a $C_r$ value equal to 1.25 was used. It should be noted that since primary particles are mostly monomodal (see chapter 6 for the definition of primary particles), then application of such a correction factor to whole data overestimates the number of particles during early stage of the reaction. This might lead to a confusing conclusion if the results of the two categories of PDI, as classified above, are compared for the early stage of the polymerisation reactions.

3.3.2.2 Transmission electron microscopy (TEM)

3.3.2.2.1 Particle hardening

This technique, which is very tedious, was adopted as the main method to measure the particle size distribution. The latexes were diluted with $10^3 - 10^4$ distilled water. The most difficult problem in using TEM was particle coalescence and film formation, specially for the soft polymer of BA, under the beam of the electron microscope. Several techniques were examined to overcome this problem. Using staining agents such as silver nitrate, and osmium trioxide did not lead to satisfactory results. Phosphotungestic acid was found to be good staining agent for the system. No improvement was found by spraying the latexes on the carbon grid. Very good results were obtained by crosslinking of the polymer latex by UV light. The proper intensity, exposure time and the cell size were found by trial. This technique proved to be very successful. As a result, UV crosslinking was adopted as the main method for polymer hardening. However, it was found that under some conditions very big particles appeared in the samples. This may be due to particle coalescence during radiation which must be avoided during sample preparation.

The latex was diluted to 10-100 PPM, depending on the particle concentration, and placed in a quartz cell of 2 mm radius. Then the sample cells were exposed to UV radiation using a mercury lamp. High-energy irradiation initiates simultaneous crosslinking and degradation in polymers (Bradford and Vanderhoff, 1959). For polybutyl acrylate the crosslinking was predominant, since exposing these latexes to high-energy irradiation transformed each particle into a rigid particle. The latexes
were highly diluted before irradiation; hence, the primary absorption of energy is in the aqueous phase. If the free radicals initiating cross-linking reaction emigrate from the aqueous phase to the particles, then it is expected that the presence of an initiator in the aqueous phase would lead to a higher rate of crosslinking. The experiments performed using aqueous solution of $1 \times 10^{-3}$ mol/litre KPS did not show any reduction in exposure time required to obtain hard particles, at a constant irradiation intensity. Then it can be assumed that free radicals are mainly formed inside the particles by abstraction of hydrogen atoms on the polymer backbones.

Then, the two main variables in particle hardening by irradiation are recognised as the intensity of radiation and duration of exposure. The intensity of radiation was indirectly varied by adjusting the distance of the sample cells from the UV lamp. The duration of exposure was varied from few hours to two days. The best configurations for the particles hardening were obtained at the radiation intensity of 6.0-12.0 mW/cm$^2$ and for the exposure time of 20-24 hours.

### 3.3.2.2.2 Particle measurement

Particle sizes were determined using a JEOL 1000X TEM operated at 60 kv accelerating voltage. A small drop from the cross-linked latex was transferred onto a carbon grid. The grid was allowed to dry under reduced pressure in the microscope. One of the main problems of the electron microscope is the difficulty in obtaining a representative sample. At least a 1000 particles have to be counted to give a statistical satisfactory result and this number should be larger the wider is the size distribution. From different parts of the grid various photographic shots were taken. Only those samples were taken into account which did not show any sign of coagulation in the sample. From each sample several micrographs were prepared to allow reliable PSD measurements. Usually between 1000 to 1500 particles were counted, depending on the broadening of sample. It should be noted that for the same reasons as those presented in section 3.3.2.1.5 for PCS, and also because the high vacuum applied to TEM quickly evaporates all remaining monomer, the particle size obtained by TEM is the unswollen size of particles.
3.3.2.2.3 Particle sizing

Given a set of micrographs, an accurate PSD is obtained by particle sizing of micrographs. This particle sizing can be carried out either manually using an optical particle-size analyser or using computer-scanning techniques (image analyser). The use of TEM to obtain a reliable PSD is laborious, even with the availability of software and hardware for image recognition, which can take the scanned TEM image and recognise overlapping particles. Overlapping particles are common in any micrograph containing a sufficient number of particles for the result to be statistically meaningful. In a micrograph, particles are not sharply defined but have fuzzy boundaries and it seems that current software is less skilled at determining the particle size distribution than the human eye.

An attempt was made to measure the particle size by a PC-image analysis software (Foster Findly). The first attempts showed that a satisfactory result may be obtained, if the contrast is sufficiently high and particles are not overlapping. A complete agreement between the results of two methods was obtained (not shown). However, for the micrographs of overlapping particles the image analysis software was proved to be inefficient, since the time allocated for particle recognition and sizing by using the software far exceeded that for manual measuring of the particles. The optical sizing method was used for most of the micrographs.

3.3.2.2.4 Particle size calibration

The magnification of TEM was calibrated with a series of diffraction grating replicas which have 2160 line/mm. In order to correct the size data for particle shrinkage under the electron microscope beam, a monodisperse PBA particles was prepared using an emulsifier-free batch emulsion polymerisation of BA. TEM measurements approved that the PSD of the standard was quite sharp (PDI = 1.02). The particle size obtained by the PCS instrument, Zetamaster, was equal to 110 ± 3 nm. However, the particle size average measured by TEM compared with that by PCS showed 29.0 % difference, which can be attributed to the particle shrinkage. Such a shrinkage for already cross-linked PBA particles might seem to be more than expected. However, the shrinkage of particles was so obvious that it could be visually observed as soon as
the sample grid was placed under the electron beam in the TEM. The shrinkage of BA homo- and co-polymer particles, and then the underestimation of particle size by TEM compared with PCS, has been reported before (Rivera et al., 1989). The comparison made for the commercial PS particles measured by PCS and TEM, showed a 2-10 % shrinkage in radius for particles if they are measured with TEM. A satisfactory agreement within ± 2.0 was obtained between the sizes obtained by PCS methods and the nominal size of PS standard particles.

For calibration of PBA particle size, the diffraction grating replicas at the same conditions were used. Then the TEM correction factor, hereafter called $C_{TEM}$, was used to correct the size data as

$$D_{corr} = C_{TEM} D_i$$

Where $D_{corr}$ is the corrected size of PBA particles used for construction of PSD curves and calculations of averages. $C_{TEM}$ was considered 1.29, as discussed above. Then, it can be concluded that PBA particles showed a shrinkage of 22 % (1-$C_{TEM}^{-1}$) during TEM measurements. Similarly, Hansen (1979a) used an expression of the kind $D_{corr} = C_1 D_i + C_2$ to correct the particle size for shrinkage and focus adjustment.

3.3.3 Surface tension measurements

All surface tension measurements were made using a Du nouty ring tensiometer at room temperature. No correction was made on the reading. Surface tension monitoring of semibatch experiments was followed by taking samples of about 2-3 ml from polymerisation reactor at desired time intervals and placing them on watch glasses, covered by plastic lids to prohibit the gradual evaporation of the latex. Samples were allowed to cool to room temperature. Generally 15-20 minutes was allowed for samples to reach thermodynamic equilibrium before any surface tension recorded.
Critical Micellar Concentration of SLS was measured using both tensiometer and conductometer and is given in the Appendix C. A value of $1.70 \pm 0.05$ g/litre was obtained for SLS in the water which is in good agreement with the literature data. The CMC of SLS in the water in the presence of electrolytes and monomer was also measured by the same methods which is given in Appendix C.

3.3.4 Monomer concentration in the polymer particles and aqueous phase

The distribution of monomers between polymer particles and water phase was measured for a PBA seed using the following procedure. The performed seed was initially mixed with the monomer for a long period of time to assure that particles are swollen to their equilibrium size. The monomer droplets in the samples were separated as a monomer layer with a high speed centrifuge. A fraction of the aqueous phase under the monomer layer which contains only the monomer-swollen particles is taken out with a syringe and poured to excess acetone and then methanol containing a small amount of dioxane as internal standard. The precipitated polymers were filtered off and filtrate was subjected to GC measurement. The same procedure as that outlined in the section 3.3.1.2 was followed. From the separate measurements the saturated concentration of BA in the water was found to be $0.90 \pm 1.0$ g/litre. From this figure and the data obtained by GC, the monomer concentration in polymer particles was found to be $4.20 \pm 0.20$ mol/litre which is in accord with kinetics value obtained.

3.3.5 Viscosity measurements

Viscosity measurements were carried out for a few latexes using a HAAKE viscometer. The experimental procedure is explained in the Appendix D.

3.4 CALCULATIONS

For the kinetic and particle formation analysis of batch and semibacth emulsion polymerisation of BA, the following calculations have been carried out. The kinetics and physical properties data required for calculations are given in Appendix A.
3.4.1 Conversions

**Instantaneous conversion:** For the semibatch experiments the instantaneous conversion at a given time is defined as the weight ratio of the polymer in the reactor to the total monomer in the reactor. The instantaneous conversion, $x_i$, is the real specification of the system and defines the status and properties of the reaction mixture. The calculation of $x_i$ has been shown in the section 3.3.1.

**Overall conversion:** It is defined as the weight ratio of polymer in the reactor to the total polymer and monomer in the recipe. Overall conversion is only the measure of overall polymerisation rate and is not physically related to the status of the system. It should be noted that for batch polymerisation both these conversion are the same. Both conversions are related through the following definition:

$$X_0 = \frac{(R_a (t-t_{pp}) + M_0) x_i}{W_0}$$  \[3.1\]

where $X_0$ is the overall conversion, $x_i$ the instantaneous conversion, $t$ the time, $t_{pp}$ the pre-period time, $W_0$ overall monomer concentration, and $M_0$ initial monomer concentration.

By differentiation from the above equation, the appropriate equation for the rate of reaction is obtained.

$$R_p = \frac{(R_a (t-t_{pp}) + M_0) \frac{dx_i}{dt} + R_a x_i}{3.2}$$

The above equation allows the calculation of the overall rate of polymerisation from the instantaneous conversion-time experimental data. In order to avoid experimental errors in $\frac{dx_i}{dt}$ at each time interval, it is more convenient to fit the whole data on $x_i$-t curve with a polynomial and then replace the term $\frac{dx_i}{dt}$ value by that predicted by differentiating from the polynomial. Since the current study mostly dealt with steady-state rate of reaction, this approach was not used. The steady state $R_p$ was directly calculated from the slope of the linear parts of overall conversion versus time curves.
3.4.2 Mass balance

The balance of the ingredients in the reactor at the time \( t \geq t_{pp} \) are given as follows:

\[
\begin{align*}
P &= [M_0 + (t - t_{pp}) R_a] x_i \\
M &= M_0 + (t - t_{pp}) R_a \\
I &= I_0 + (t - t_{pp}) F_I R_{aa} \\
E &= E_0 + (t - t_{pp}) F_E R_{aa} \\
W &= W_0 + (t - t_{pp}) F_W R_a \\
B &= B_0 + (t - t_{pp}) F_B R_a
\end{align*}
\]

Where \( P, M, I, E, W, \) and \( B \) are the amount of polymer, monomer, initiator, emulsifier, water, and buffer in the reactor at the time \( t \). The same characters with the index \( 0 \) means the corresponding value at the time \( t = 0 \), or initial charge of corresponding components. \( F \) factors are the corresponding weight ratio of the ingredients in the feed. \( R_a \) and \( R_{aa} \) are the rates of monomer and aqueous phase addition, respectively. \( t_{pp} \) is the pre-period time.

3.4.3 Number of particles

The number of particles at any conversion was determined using:

\[
N_p = (6 M x_i / \pi \rho_p D_v^3)
\]

where \( M \) is the monomer concentration in the reactor, \( \rho_p \) polymer density and \( D_v \) volume average particle diameter.

3.4.4 Particle Size averages and distribution

The number-, weight-, volume-, and intensity averages and PDI were calculated using the following equations (see Appendix F, equations F.9 - 18):

\[
D_n = \sum n_i D_i / \sum n_i
\]
\[ D_w = \frac{\sum n_i D_i^4}{\sum n_i D_i^3} \]
\[ D_v = \left( \frac{\sum n_i D_i^3}{\sum n_i} \right)^{1/3} \]
\[ D_z = \left( \frac{\sum n_i D_i^6}{\sum n_i D_i^3} \right)^{1/2} \]
\[ \text{PDI} = \frac{D_w}{D_v} \]

In this research work PDI was used as the measure of breadth of distribution. For constructing the PSD, curves with radius increment of 5-10 \( nm \) has been considered. For example; all particles with unswollen diameter between 50 and 60 \( nm \) were put in one bin, those with unswollen diameter 60-70 \( nm \) were put into another, and so on. It is implicit in the definition of PSD that an infinitely small radius increment has been taken. While theoretically the bin size can be reduced to a much lower size, practically it is limited to measurement increments. In our experiments the measurement precision for particle diameters was almost 4-5 \( nm \). So a diameter increment above twice of that, 10 - 20 \( nm \), was considered for construction of PSD curves. This indicates that PSD curves are not expected to approach to true PSD by decreasing the bin size below 10 \( nm \) in the current experiments.

For calculations of different averages the above equations were used. It should be noted that while the bin sizes were used for presentation of PSD curves, for calculation of averages all data were considered. In other words, the data were not divided into bins having 10 \( nm \) width corresponding to the method used for construction of PSD curves.

### 3.4.5 Monomer concentration in polymer particles

Monomer concentration in the polymer particles can be calculated using the following expressions:

\[ M_p = (1-x_{cr}) \rho_m / (1-x_{cr} + x_{cr} \rho_m / \rho_p ) \, \text{MW} \quad x_i \leq x_{cr} \quad 3.10 \]
\[ M_p = (1-x_i) \rho_m / (1-x_i + x_i \rho_m / \rho_p ) \, \text{MW} \quad x_i > x_{cr} \quad 3.11 \]

Where MW is molecular weight of the monomer and \( x_{cr} \) the conversion at which for a BA batch emulsion polymerisation the transition from interval II to interval III occurs. The \( x_{cr} \) is found from the kinetic studies (presented in the chapter 4) and saturation studies (presented in the section 3.3.4) to be \( 0.475 \pm 0.025 \). BA solubility in the water
phase is rather low and around 1.0 g/litre. Then in the calculation of $M_p$ it was safely assumed that no monomer is in the aqueous phase. It should be noted that more complicated equations have been suggested for calculation of $M_p$ in terms of monomer feed rate and other variables of semibatch processes with exactly the same precision (Makgawinta et al, 1984). In fact, the same equations as those for batch process were used in this research work, but with the difference that instantaneous conversion of semibatch process replaced the conversion in batch process.

### 3.4.6 Swollen particle size

The unswollen particle sizes are directly obtained from PCS and TEM measurements. The swollen particle size was obtained first by calculation of polymer phase volume as follows:

$$V_p = M x_i MW [1 + (1-x_{cr}) / x_{cr} \rho_m)] / \rho_p \quad x_i \leq x_{cr} \quad 3.12$$

$$V_p = M x_i MW [1 + (1-x_i) / x_i \rho_m)] / \rho_p \quad x_i > x_{cr} \quad 3.13$$

Then the swollen diameter of particles is obtained as:

$$D_{ps} = (6 V_p / N_p \pi)^{1/3} \quad 3.14$$

### 3.4.7 Particle surface coverage ratio

The average particle surface coverage is calculated as follows:

$$SC = N_a E_a a_s / \pi D_{ps}^2 N_p \quad 3.15$$

Where $a_s$ is the area occupied by a emulsifier molecule on the surface of polymer particles. The value obtained for $a_s$ together with literature values are given in Appendix A and C. It should be noted that the swollen particle size calculated from equation 3.14 was used for the calculation of surface coverage ratio. $E_a$ is the amount of emulsifier adsorbed on the particles given by:
\[ E_a = E - E_w \] \hspace{1cm} 3.16

\( E_w \) is the amount of emulsifier dissolved in the aqueous phase. At the interval I of the systems containing emulsifier concentration greater than the CMC value, emulsifier saturated conditions \( E > E_{CMC} \); \( E_w \) is initially equal to the emulsifier critical micellar concentration \( E_{CMC} \). At the emulsifier-starved conditions, such as interval II and III of a batch process or even interval I when \( E < E_{CMC} \), \( E_w \) is less than \( E_{CMC} \) depending on the emulsifier distribution between the aqueous phase and polymer particles. At the conditions studied, the CMC of SLS in the water in the presence of initiator and buffer is depressed to a low value, 0.80 - 1.0 g/litre (see Appendix C). Hence, for simplicity and since the equilibrium distribution of SLS between the water phase and the polymer PBA particles is not known, \( E_w \) was assumed zero for the estimation of surface coverage ratio. SC greater than 100 \% means that particles are fully covered by emulsifier molecules and excess emulsifier molecules exist in the aqueous phase.

3.4.8 Radical number

The average radical number is simply obtained from the overall rate of reaction as:

\[ \bar{n} = \frac{R_p N_a}{k_p M_p N_p} \] \hspace{1cm} 3.17

where

\( R_p \) is the rate of polymerisation
\( M_p \) is the monomer concentration in the polymer particles
\( N_p \) is the number of particles
\( k_p \) is the propagation rate constant
\( N_a \) is Avagadro’s number
4.1 INTRODUCTION

A series of batch experiments were carried out to obtain a fundamental understanding of particle formation and kinetics in butyl acrylate (BA) emulsion polymerisation. The kinetic behaviour of the BA system at low monomer and emulsifier concentrations was of main concern, since most of semibatch emulsion polymerisation processes start up with such conditions. In addition, the results obtained facilitate the comparative study of batch and semibatch emulsion polymerisation systems. The following variables were investigated:

*Emulsifier concentration:* A wide range of SLS concentration, 0.25 - 20 g/litre (8.7×10⁻⁴ - 7×10⁻² mol/litre), was used.

*Initiator concentration:* A concentration ranging from 0.135 to 1.08 g/litre (0.5×10⁻³ - 4×10⁻³ mol/litre) was considered.

*Monomer/Water ratio:* 0.50, 0.20, 0.10, 0.05, and 0.025 were used.

*Buffer concentration:* 0.0, 0.54, and 1.61 g/litre concentrations of Sodium bicarbonate (SBc) were used as buffers.

*Reaction volume:* 0.250, 0.500, and 0.750 litre reaction volumes were used.
Chapter Four

Batch Emulsion Polymerisation

4.1 RECIPE OR PREPARATION

The standard recipe considered to study the kinetic features of BA batch emulsion polymerisation process is listed in table 4.1. Other formulations have been mentioned where appropriate. All figures given on the graphs are based on one litre of aqueous phase.

4.2 BACKGROUND

Compared with other commercial monomers only a few studies have been reported on butyl acrylate (BA) emulsion polymerisation. Most of these works have been devoted to the application of mixed initiator or emulsifier systems.

Capek et al (1984) studied emulsion polymerisation of butyl acrylate at 70 °C, using water soluble initiator ammonium persulphate (AP) and anionic emulsifier sodium dodecylbenzene sulphonate. They observed rapid rates of reaction in their experiments specially at high initiator concentrations which was attributed to the gel effect.

Maxwell et al (1987) investigated the seeded emulsion polymerisation of butyl acrylate, using both persulphate and γ-radiolysis for initiation. They found that the termination mechanism is ‘residual’ due the high chain entanglement within the particles. The free-radical capture efficiency was reported to be high, but significantly <100% at high initiator concentration. Capek et al (1994a) investigated the emulsion polymerisation of BA with ammonium persulphate as initiator and a mixture of sodium dodecylbenzene sulfonate and twin emulsifiers at 60 °C. The range of AP was 0.5×10⁻³ - 20×10⁻³ mol/litre. They reported a continuous particle nucleation in the course of reaction. They found that above AP concentration 5×10⁻³ mol/litre the rate of polymerisation per particle, or radical number per particle, decreased while the
overall rate of polymerisation showed a slight increase. They suggested that chain termination occurs by primary radical termination and/or by the residual termination. Equilibrium monomer concentration in the particles in interval II was found to be constant and independent of surfactant concentration in the feed. In a subsequent paper Capek (1994b) reinvestigated the effect of initiator concentration and type on the kinetic features of BA polymerisation. His findings will be discussed later.

4.3 RESULTS AND DISCUSSION

4.3.1 Effect of emulsifier concentration

For the calculation of number of polymer particles, \( N_p \), rate of polymerisation, \( R_p \), surface coverage ratio by emulsifier, \( SC \), and number of radicals per particle, \( \tilde{n} \), readers are referred to chapter 3. Figure 4.1 shows the effect of initial emulsifier concentration on the number of polymer particles produced in the course of reaction. Generally the nucleation period increases with emulsifier concentration. When the initial emulsifier concentration is low (\(< 2.50 \text{ g/litre})\), the number of polymer particles seems to be constant from the start of polymerisation. If the initial emulsifier concentration is high (\(> 5.0 \text{ g/litre})\), polymer particles appear to be generated up to the high conversions. By measuring the particle size and conversion throughout the polymerisation and calculating the corresponding particle numbers, it is possible to estimate the end of interval I. Obviously, a longer nucleation period is observed for polymerisation runs using a higher concentration of emulsifier.

According to the SE theory, the particle number concentration is proportional to the surfactant concentration to the 0.60 power. It has been shown that if chain transfer to monomer and radical desorption is important, the general expression for the particle number based on micellar nucleation mechanism is \( N_p \propto S^a T^{1-a} \) where \( 0.60 < a < 1.0 \) depending on the chain transfer constant and water solubility of monomer (Nomura et al, 1976, Hansen and Ugelstad, 1979d). The radical desorption decreases the particle growth rate and hence increases the number of particles. Furthermore, the desorbed radicals may re-enter the micelle and enhance particle nucleation. For BA, the desorption rate coefficient has been reported to be in accord with the prediction of a
Effect of SLS Concentration

Fig. 4.1: The variation in final number of polymer particles with conversion for different emulsifier concentrations.

Effect of SLS Concentration

Fig. 4.2: The variation in final number of polymer particles versus SLS concentration.
transfer/diffusion mechanism and the dominant fate of desorbed free radicals is to re-enter latex particles. This means that the rate of reaction is not affected by rate of radical desorption (Maxwell et al, 1987).

Figure 4.2 shows the effect of initial emulsifier concentration on the number of polymer particles produced. The line shown on the graph is a linear least square fit to the whole data on the log-log scale. The whole data point on the graph can be approximated by a single line with the slope of 0.54 which falls within the range of prediction of SE theory. Sutterlin (1980) performed experiments at 80 °C using ammonium persulphate as initiator and SLS as emulsifier within a high range of initiator concentration. He predicted a single exponent relationship as \( N_p = [S]^{0.70} \) for a wide range of SLS concentration, \( 2 \times 10^{-5} - 2 \times 10^{-1} \text{ mol/litre} \), both below and above CMC. The \( N_p \)-SLS curve suggests that homogenous nucleation is important in butyl acrylate emulsion polymerisation, since the slope of \( N_p \) - SLS curve does not change at low SLS concentrations.

Figure 4.3 shows the time evolution of conversion at different emulsifier concentrations with other parameters fixed. Three separate regions can be distinguished in the conversion-time curves for the lower SLS concentrations (< 1.25 g/litre). The first interval is located within the conversion range 0-10%, interval II within 10 - 50 % and interval III above 50 % conversion. For the higher SLS concentrations ( > 1.25 g/litre) almost a constant rate of reaction was observed from the beginning to 45 - 50 % of monomer conversion which is indicative of interval II. The interval I is suppressed for these runs possibly due to a very high rate of particle formation in the beginning of the reactions. For the calculation of steady-state rate of polymerisation, conversions between 10 and 50 % were used for all runs since they account for the interval II kinetics. The slope of a linear portion of conversion-time curve varies in proportion to the 0.50 power of emulsifier concentration, as depicted in figure 4.4.

The rate of polymerisation is drawn versus the number of particles in figure 4.5. The rate of polymerisation is found to be proportional to \( N_p^{0.95} \) at a constant initiator concentration. This clearly indicates that in the system under study, \( R_p \) is highly
Effect of SLS Concentration

![Graph showing the effect of SLS concentration on conversion over time.]

Fig. 4.3: The time evolution of conversion for different emulsifier concentrations.

Effect of SLS Concentration

![Graph showing the steady-state rate of polymerisation versus emulsifier concentration.]

Fig. 4.4: The steady-state rate of polymerisation versus emulsifier concentrations.
influenced by emulsifier concentration and hence by $N_p$. Such a dependence is very close to the case II kinetics of SE theory which predicts $R_p \propto N_p^{1.0}$. However, as we will discuss later the system under study is a high-\textit{n} system and is expected to behave similar to case III kinetics where particles have a large number of radicals and the rate of polymerisation is independent of particle concentration.

The average number of radicals per particle, $\bar{n}$, can be calculated using the following equation:

$$R_p = k_p M_p N_p \bar{n} / N_a$$

where, $k_p$, $M_p$, $N_p$, and $R_p$ are propagation rate constant, monomer concentration in polymer phase, number of particles and, rate of polymerisation, respectively.

The application of this equation requires that $M_p$ and $k_p$ should be known. $M_p$ can be obtained by number of methods. For BA emulsion polymerisation with a significant steady-state region, the kinetic approach seems to be quite satisfactory; from the value of conversion at which the rate of polymerisation falls below its steady-state value. This conversion is expected to correspond to the transition from stage II to III.

From the data depicted in figure 4.3 the fractional conversion, or the polymer weight fraction, at the end of stage II ($x_{cr}$) was obtained as 45.0%, which is corresponding to monomer concentration equal to 4.0 mol/litre. This is in good agreement with literature data (Maxwell et al, 1987; Capek, 1984). The $M_p$ obtained by using other
methods are also in satisfactory agreement with the results obtained by kinetic approach and is discussed in chapter 3. The propagation constant, \( k_p \), has been obtained from the literature. Literature values for \( k_p \) are widely spread and their application might introduce some uncertainty to the number of radicals calculated (see appendix A for the literature values for \( k_p \)). In fact, radical number is a model-based quantity whose magnitude highly depends on \( k_p \). In this research work \( k_p \) was taken as \( 450 \text{ lit/mol.sec} \) (Maxwell et al, 1987).

Table 4.2: Variation of kinetic parameters with SLS concentration.

<table>
<thead>
<tr>
<th>SLS conc. g(Mole/Lit)</th>
<th>( N_p \times 10^{-17} \text{ Litre}^1 )</th>
<th>( R_p \times 10^3 \text{ Mole.Litre}^{-1}.\text{Sec}^{-1} )</th>
<th>( \bar{n} )</th>
<th>Coagulum wt% of M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25(8.7\times10^{-4})</td>
<td>0.60</td>
<td>39.8</td>
<td>3.7</td>
<td>13.3</td>
</tr>
<tr>
<td>0.50(1.7\times10^{-3})</td>
<td>0.74</td>
<td>47.3</td>
<td>3.6</td>
<td>6.8</td>
</tr>
<tr>
<td>1.25(4.3\times10^{-3})</td>
<td>1.17</td>
<td>69.4</td>
<td>3.3</td>
<td>1.8</td>
</tr>
<tr>
<td>2.50(8.7\times10^{-3})</td>
<td>1.85</td>
<td>106.9</td>
<td>3.2</td>
<td>1.1</td>
</tr>
<tr>
<td>5.0(1.7\times10^{-2})</td>
<td>2.51</td>
<td>143.2</td>
<td>3.2</td>
<td>0.6</td>
</tr>
<tr>
<td>10.0(3.4\times10^{-2})</td>
<td>3.55</td>
<td>203.3</td>
<td>3.2</td>
<td>nil</td>
</tr>
<tr>
<td>20.0(6.9\times10^{-2})</td>
<td>6.38</td>
<td>408.8</td>
<td>3.2</td>
<td>nil</td>
</tr>
</tbody>
</table>

From the relation between \( N_p \) and \( R_p \) with emulsifier concentration, the variation of radical number, which according to equation 4.1 is proportional to \( R_p/N_p \), with emulsifier concentration was found to be proportional to \( [S]^{0.04} \). Such a dependence predicts a very slight decrease in \( \bar{n} \) with emulsifier concentration. Generally in emulsion polymerisation as the number of particles increases at a fixed initiator concentration, the rate of radical capture per particle decreases and a smaller number of radicals per particle is obtained. For BA emulsion polymerisation a more rapidly decreasing number of radicals per particle with increasing emulsifier concentration (SDBS) has been reported elsewhere (Capek et al, 1984). One possibility which can explain this is the acceleration in the rate of initiator decomposition in the presence of SLS and BA. The results presented in the chapter 5-6 also confirm such an acceleration in the rate of initiation. The acceleration in the decomposition rate of
initiator in the presence of emulsifier (SDBS) has been observed for BA emulsion polymerisation by other researchers (Capek et al., 1984).

All polymerisation runs carried out at low emulsifier concentrations suffered coagulation. The amount of coagulation has been tabulated in *table 4.2*. The extent of coagulation increased with conversion and decreasing emulsifier concentration. For instance, the run carried out with \([S] = 0.25\) g/litre suffered a massive coagulation during particle growth, due to high rate of particle growth and insufficient emulsifier molecules to stabilise the particles. The decrease in the number of particles with conversion for the experiment using 0.25 g/litre SLS is shown in *figure 4.1*. For this particular case, the number of particles at its maximum (20% conversion) was considered as the final number of particles and used for *figure 4.2*.

### 4.3.2 Effect of initiator concentration

*Figure 4.6* shows the variation in number of particles with the progress of the reaction for different initiator concentrations. For lower initiator concentrations a continuous particle nucleation in the course of reaction was obtained. A higher initial rate of particle nucleation was obtained with increasing initiator concentration and the number of polymer particles reached a constant value at a lower conversion.

The SE theory predicts a proportionality value of 0.40 between particle number and initiator concentration. This proportionality is another distinguishing feature between sparingly water-soluble monomers and water soluble monomers. The exponent is expected to be greatly influenced by the radical desorption. The literature values for different monomers are very wide and could be as low as zero (for vinyl acetate). *Figure 4.7* shows the variation of number of polymer particles with initiator concentration. The number of particles increases with KPS concentration. The initiator dependence exponent for particle number was found to be 0.39 from this graph. Capek (1994b) showed that for BA emulsion polymerisation the \(N_p\) order with respect to initiator concentration might increase with increasing initiator concentration. The exponents 0.40 and 0.30 were reported for the high and low range
Effect of KPS Concentration

Fig. 4.6: The variation in number of polymer particles with conversion for different emulsifier concentrations.

Effect of KPS Concentration

Fig. 4.7: The variation in final number of polymer particles versus KPS concentration.
concentration of ammonium persulphate (AP), \([\text{AP}] < 1 \times 10^{-4}\) and \([\text{AP}] > 5 \times 10^{-3}\), respectively. The exponent obtained for this series of experiments, which almost corresponds to the high AP region of Capek's data, is in accord with literature and SE theory prediction.

The conversion-time curves for different initiator concentrations are shown in figure 4.8. For almost all runs, no interval I was observed on the conversion-time curves which again can be attributed to the high rate of particle formation in the initial stage of the reaction. Interval I can be observed if a very low concentration of initiator is used (Capek, 1984, 1994a). The polymerisation rate, number of polymer particles and radicals per particle are given in table 4.3. It is clear from the graph that stationary rate of polymerisation increases with KPS concentration. For KPS concentration greater than 1.08 g/litre, a distinctive suppression in the rate of polymerisation and radical number was observed (not shown). A similar effect has been reported for BA emulsion polymerisation with ammonium persulphate as initiator (Capek, 1994a). The suppression of the rate for high initiator concentration can be attributed to the primary radical termination.

Capture efficiency decreases with increasing initiator concentration and decreasing monomer concentration in the aqueous phase, due to enhancement of radical termination in the aqueous phase (see. equation 1.39). Maxwell et al applied a qualitative criterion for the capture efficiency. They reported that for butyl acrylate system free-radical capture efficiency is high, but significantly < 100 % at high initiator concentration. They used potassium persulphate (KPS) as initiator within the

### Table 4.3: Variation of kinetic parameters with KPS concentration.

<table>
<thead>
<tr>
<th>KPS conc. g(Mole/Lit)</th>
<th>(N_p \times 10^{-17})</th>
<th>(R_p \times 10^{-3})</th>
<th>(\bar{n})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.135(0.5 \times 10^{-3})</td>
<td>2.2</td>
<td>11.4</td>
<td>3.0</td>
</tr>
<tr>
<td>0.270(1 \times 10^{-3})</td>
<td>2.6</td>
<td>15.1</td>
<td>3.2</td>
</tr>
<tr>
<td>0.540(2 \times 10^{-3})</td>
<td>3.6</td>
<td>20.3</td>
<td>3.2</td>
</tr>
<tr>
<td>1.080(4 \times 10^{-3})</td>
<td>4.8</td>
<td>26.0</td>
<td>3.1</td>
</tr>
</tbody>
</table>
concentration range of $0.2 \times 10^{-4} - 1.5 \times 10^{-3}$ mol/litre. The corresponding radical capture efficiency was found to be within 32-246% which almost shows an order of magnitude variation in the radical capture efficiency with the concentration range of KPS studied. Our experiments were carried out above their region $5 \times 10^{-4} - 4 \times 10^{-3}$ mol/litre and obviously very low capture efficiencies should be expected for such a high initiator concentration. It can be easily calculated that by applying the same data, as those used by them, the radical capture efficiency for our experiments within the KPS concentration used is very low. The results obtained is in accord with the literature.

Figure 4.9 shows the log-log plots of polymerisation rate for interval II versus initiator concentration. The order of polymerisation reaction with respect to the initiator concentration in the range of $0.5 \times 10^{-3} - 4.0 \times 10^{-3}$ mol/litre was found to be 0.40 from figure 4.9 which is in accord with exponent 0.33 - 0.46 found elsewhere for the high - low AP concentration range. At high initiator concentration, the radical capture efficiency becomes very low which will lead to a lower dependence of $R_p$ and radical number on the initiator concentration.

Butyl acrylate polymerisation was found to be a high-$\tilde{n}$ system. A radical number between 3-4 was obtained for most of the reactions. A higher average number of free radicals per particle ranging from 3 to 9 has been also reported for this system based on a much smaller number of seed particles compared with the present study (Maxwell et al, 1987). A large number of radicals in particles can only be accounted for by a very low rate of termination. The termination rate constant for BA emulsion polymerisation has been found to be a few orders of magnitude less than typical values for bulk polymerisation at zero polymer weight fraction (Maxwell et al, 1987; Capek et al, 1984). In emulsion polymerisation the viscosity in the particles is very high and polymerisation may be treated in the range of “high conversion polymerisation” where diffusion controlled termination is dominant. The equilibrium monomer concentration of 4.0 g/litre and the low $T_g$ (-58 °C) of the polymer would not account for such a low value of termination constant. In order to explain this low termination rate constant, it has been suggested that the termination mechanism is ‘residual’ due the high chain entanglement within the particles (Maxwell et al, 1987,
Effect of KPS Concentration

Fig. 4.8: The time evolution of conversion for different KPS concentrations.

Effect of KPS Concentration

Fig. 4.9: The variation in stationary rate of polymerisation versus KPS concentration.
Capek et al., 1984). The residual termination mechanism for BA polymerisation system even at such a high monomer/polymer ratio is supported by the high degree of polymer branching (Lovel et al., 1991). However, the residual termination model at its present stage can not predict such a low value of termination rate constant (Maxwell et al., 1984).

The radical number per particle stayed constant with initiator concentration. The exponential relationship was found to be $[I]^{0.01}$. This can be attributed to the low capture efficiency which systematically decreases with increasing $[I]$ as discussed by other researchers. Again this is in accord with the finding of Capek who reported that the rate per particle exponent can vary from 0.18 to -0.06 for a wide range of ammonium persulphate concentration as discussed above. The variation of number of radicals per particle for BA emulsion polymerisation was reported to increase three fold, 3 to 9, as the result of almost two orders of magnitude increase in KPS concentration (Maxwell et al., 1987).

Particle nucleation is usually modelled by applying a 1 - 0 system in which it is assumed that primary particles of small size can at most have one radical. This assumption seems not to be valid in butyl acrylate emulsion polymerisation. The examination of the rate of reaction by using number of particles in the initial stage of reaction (based on equation 4.1) clearly shows that primary particles must have appreciably more than one radical. Due to entanglements of growing radical in the particle, chain termination is hindered and each entry may lead to increase in the number of radicals in the primary particles.

### 4.3.3 Effect of monomer concentration

The evolution of number of polymer particles with the progress of reaction have been shown in figures 4.10 -11 for different monomer/water ratios at two emulsifier concentrations; 10, and 2.50 g/litre, respectively. Generally, a longer nucleation period was obtained for lower M/W ratios in terms of both conversion and time, if nucleation continues to the interval III. A continuous nucleation up to the end of reaction is observed for low M/W ratios with $S_0 = 10.0$ g/lit. For the medium
Effect of M/W Ratio

**SLS=10.0 g/Litre**

![Graph showing the variation in number of polymer particles with conversion for different monomer concentrations at SLS=10 g/Litre.](image)

**Fig. 4.10**: The variation in number of polymer particles with conversion for different monomer concentrations at SLS=10 g/Litre.

**SLS=2.50 g/Litre**

![Graph showing the variation in number of polymer particles with conversion for different monomer concentrations at SLS=2.50 g/Litre.](image)

**Fig. 4.11**: The variation in number of polymer particles with conversion for different monomer concentrations at SLS=2.50 g/Litre.

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emulsifier concentration $S_0 = 2.50 \text{ g/litre}$, particle nucleation ceased at earlier conversion compared with that at $S_0 = 10.0 \text{ g/litre}$ for the same M/W ratio. Particle nucleation for the lowest SLS concentration quickly terminated, and particles suffered coagulation afterwards in the course of reaction.

Figure 4.12 shows the log-log plots of final number of polymer particles versus initial monomer concentration for the three emulsifier concentrations studied. For the SLS concentration 10 g/litre, a practically straight line was obtained which showed a sudden decrease at low values of M/W. This was not expected and in the opposite a greater number of particles was expected to form at low M/W ratios. Table 4.4 reveals some important points about experiments carried out at the high emulsifier concentration and low M/W ratios. The surface coverage of polymer particles by emulsifier at the end of reaction for the runs using 10 g/litre emulsifier with M/W = 0.025, 0.05 and 0.10 exceeds 100%, indicating that the amount of monomer phase in the above experiments was not sufficient to expand the surface of particles to such an extent that all emulsifier molecules are adsorbed, leaving free micelles in the reaction mixture. Therefore for the three runs with the lowest M/W ratios and SLS concentration of 10 g/litre, the number of particles are based on the contribution of lower amount of emulsifier in the particle nucleation. For these runs particle nucleation continued to the interval III where monomer droplets are already depleted. Particle formation in the interval III of batch process will be discussed in the succeeding part. For the run using M/W=0.20, a full surface coverage of particles (99.8%) is obtained as shown in the table 4.4. However, it should be noted that for the calculation of surface coverage ratio no allowance was made for emulsifier molecules dissolved in the aqueous phase. Considering the aqueous phase is close to CMC, a surface coverage of less than 100 percent is obtained for this run. No variation of $N_p$ was observed for SLS concentration of 2.50 g/litre for the range of M/W > 0.025. For this SLS concentration, particle formation lasted very shortly and virtually occurred in the interval I (monomer saturated nucleation).
The effect of M/W ratio should not be neglected at a low emulsifier concentration, where the amount of adsorbed emulsifier on the surface of monomer droplets might be significant compared with the amount available in the reaction mixture. At the low emulsifier concentration of 0.25 g/litre, monomer concentration showed a great impact on the number of polymer particles and polymerisation rate. In the classical theory of emulsion polymerisation, monomer droplets do not exert a significant effect on the polymerisation features because the emulsifier molecules adsorbed on the monomer droplets are outweighed by the huge number of emulsifier molecules in the aqueous phase. However, at a low emulsifier concentration (<<CMC), most of the emulsifier molecules are adsorbed on the monomer droplets and do not contribute to the particle formation. In addition, since newly formed particles are not sufficiently stabilised by emulsifier molecules, their collision with themselves and monomer droplets might lead to an extensive particle coagulation. This was practically observed in all polymerisation runs carried out using low emulsifier concentrations. It can be concluded that at the low emulsifier concentration the variation of number of particles and rate of polymerisation with M/W ratios are more pronounced. Due to massive coagulation at the low emulsifier concentration, the conversion measurements were not precise enough to perform a comparative study of the rate of polymerisation at different M/W ratios. However, the final number of
particles are shown in figure 4.12. The number of particles decreases with increasing M/W ratio due to coagulation.

Table 4.4: Effect of M/W ratio on the colloidal properties of the emulsion.

<table>
<thead>
<tr>
<th>M/W</th>
<th>Particle diam.</th>
<th>N_p×10^{-17} Litre^{-1}</th>
<th>Surface coverage, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLS=10.0 g/litre:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>137.8</td>
<td>3.55</td>
<td>62.0</td>
</tr>
<tr>
<td>0.20</td>
<td>97.7</td>
<td>3.82</td>
<td>99.8</td>
</tr>
<tr>
<td>0.10</td>
<td>77.8</td>
<td>3.85</td>
<td>176.0</td>
</tr>
<tr>
<td>0.05</td>
<td>61.3</td>
<td>4.01</td>
<td>276.3</td>
</tr>
<tr>
<td>0.025</td>
<td>55.0</td>
<td>2.79</td>
<td>495.0</td>
</tr>
<tr>
<td>SLS=2.50 g/litre:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>170.2</td>
<td>1.62</td>
<td>19.5</td>
</tr>
<tr>
<td>0.20</td>
<td>131.5</td>
<td>1.61</td>
<td>37.3</td>
</tr>
<tr>
<td>0.10</td>
<td>102.9</td>
<td>1.64</td>
<td>58.4</td>
</tr>
<tr>
<td>0.025</td>
<td>65.7</td>
<td>1.60</td>
<td>148.4</td>
</tr>
</tbody>
</table>

α-Surface coverage ratios have been calculated assuming that no emulsifier is present in the aqueous phase. Surface coverage greater than 100 means that particles are fully covered by emulsifier and excess exists in the emulsion (see chapter 3).

Figures 4.13-14 give the monomer conversion and the monomer converted versus reaction time for different monomer concentrations at SLS of 10 and 2.50 g/litre. The variation in the amount of monomer phase produced a family of curves which branch off from a single stem, i.e., the initial rate of polymerisation was independent of the amount of monomer phase. For both SLS concentrations, practically no effect of monomer concentration on the polymerisation rate was observed. For the experiment using 10 g/litre SLS with M/W ratio 0.025, a slightly lower rate of polymerisation was observed which can partially explained by a smaller number of particles produced due to depletion of monomer before all micelles are consumed. Other possible reasons could be the high rate of radical desorption from very small polymer particles generated at low M/W ratios and lower monomer concentration of small polymer particles according to Morton's equation. It may be concluded that for
Effect of M/W Ratio
SLS = 10.0 g/Litre

![Graph showing the effect of M/W ratio on conversion with SLS = 10.0 g/Litre.](image)

**Fig. 4.13:** The time evolution of conversion for different monomer concentrations at SLS = 10 g/litre (Small graph shows the time evolution of polymer formed for different monomer concentrations).

Effect of M/W Ratio
SLS = 2.50 g/litre

![Graph showing the effect of M/W ratio on conversion with SLS = 2.50 g/litre.](image)

**Fig. 4.14:** The time evolution of conversion for different monomer concentrations at SLS = 2.50 g/litre (Small graph shows the time evolution of polymer formed for different monomer concentrations).
medium and high emulsifier concentrations, the number of particles and rate of polymerisation are practically independent of monomer concentration. At low emulsifier concentration, $M/W$ influences both number of particles and the rate of polymerisation reaction.

4.3.4 Particle Nucleation in the interval III

In the classical SE theory, it is assumed that particle nucleation ceases in the interval I where particles are still saturated with monomer and hence the rate of particle growth is almost constant and independent of conversion. It might be possible that at a high emulsifier concentration and/or low $M/W$ ratio, particle formation extends to the interval III where particle growth ceases and monomer concentration in the polymer particles decreases with time. The two consequences of these events are as follows:

- Micelles in the interval III are not saturated with the monomer and hence they are smaller in size.
- Monomer concentration in the aqueous phase drops from the saturation value according to the monomer concentration in the particles.

Lean-swollen micelles are expected to have a lower radical capture efficiency since they expose a smaller outer surface to incoming radicals and produce a higher possibility for radical desorption. The lower concentration of monomer in the aqueous phase would reduce the rate of radical propagation in the aqueous phase and hence decrease the rate of radical capture by lean monomer-swollen micelles. Both effects will result in a lower rate of particle formation in the interval III. However, since particles do not grow in the interval III of a batch process, micelles are not depleted and micelle concentration stays almost constant. This might give rise to the possibility of particle formation in the interval III of a batch process. In fact particle formation in the interval III of a batch process involves monomer diffusion from the mature particles to the newly-borne ones. This will lead to a slight shrinkage of existing polymer particles at the cost of the growth for the newly formed particles. The net effect would be a reduction in the average particle size.
Chapter Four

Batch Emulsion Polymerisation

Table 4.4 shows that for the experiments using 10 g/litre emulsifier, all emulsifier molecules are consumed by growing particles if M/W ratio is greater than 0.10. For experiments carried out with M/W ratio equal or lower than 0.10, free micelles would be present up to the end of reaction. A larger number of polymer particles, compared with those obtained by using M/W ratio greater than 0.10, is expected if particle nucleation could have occurred equally in lean-monomer swollen micelles in the interval III. This was partially fulfilled for the experiment using M/W = 0.05 as shown in figure 4.12.

An experiment was performed in order to study particle nucleation in the interval III of a batch process. For this study a two-stage batch polymerisation with the overall M/W = 0.50 was carried out. In the first stage five percent of monomer (M/W = 0.025) was initially placed in the reactor and the reaction started by addition of initiator solution. After fifteen minutes when the initial monomer concentration was almost depleted, the remaining 95% monomer, heated to the reaction temperature, was added in one-shot to the reactor. Some induction period was observed after addition of second stage monomer. This induction time assures that particles are swollen with monomer at the start of the second stage reaction. The reaction time was considered after the induction period finished. The results were compared with those from a single stage batch with the same overall M/W = 0.50 in figures 4.15-16.

A larger number of polymer particles was obtained for the two-stage batch polymerisation process, compared with that for a single-stage batch process. In the first stage of the two stage run particle nucleation partly occurs in the interval III at the monomer-starved conditions where the rate of particle formation and growth is limited due to short supply of monomer. The number of polymer particles at the end of first stage is still lower than that for the single stage run. However, it should be borne in mind that the amount of monomer loading in the first stage was not enough to consume all emulsifier molecules and free micelles were present till the end of stage one. By addition of the second stage monomer, particle growth occurred for all those particles initially formed during the first stage polymerisation. In addition, new particles were produced since excess emulsifier micelles were available in the
Effect of Number of Stage

Fig. 4.15: The variation in number of polymer particles with time for single and two stage polymerisations.

Effect of Number of Stage

Fig. 4.16: The time evolution of conversion for single and two stage polymerisations.
reaction medium. Both of these effects led to a high rate of polymerisation in the beginning of second stage polymerisation. A larger number of polymer particles was obtained at the end of second stage, compared with that from single stage batch polymerisation process. Had the particle nucleation not proceeded in the interval III, the same number of particles would have been obtained for both runs. This clearly confirms that despite low radical capture efficiency presumed for lean-swollen micelles, particle nucleation at the interval III of a batch process (monomer-starved condition) will occur and might lead to the formation of a large number of particles.

Interval III for BA monomer is within 45-100% conversion. The monomer concentration in the beginning of the interval III is 4.0 mol/litre which is continuously decreasing with conversion. Accordingly the monomer concentration in the water phase, and in the monomer-swollen micelles decrease so that particle formation becomes more difficult as the reaction proceeds in the interval III. It is expected that particle nucleation rate decreases with conversion in the interval III of batch emulsion polymerisation.

4.3.5 Effect of buffer concentration

The effect of buffer concentration on the polymerisation features has been studied. Figure 4.17 shows that at the condition studied, the buffer concentration did not practically affect number of polymer particles. Figure 4.18 shows the conversion-time curves for different buffer concentrations. A slightly larger rate of polymerisation was obtained if 0.54 g/litre buffer was used in the polymerisation. It is well accepted that the presence of electrolytes in the water phase reduces the emulsifier solubility and decreases the CMC value of the emulsifier which in turn increases the number of polymer particles (see appendix C). However, addition of too much electrolyte reduces the particle stability by compressing their double layers and enhances particle coagulation. As it is clear from figure 4.18 the initial rate of particle nucleation increases with buffer concentration, while at higher conversion the rate of particle formation slightly drops due to coagulation.
Effect of Buffer Concentration

Fig. 4.17: The time evolution of conversion for different buffer concentrations.

Effect of Buffer Concentration

Fig. 4.18: The variation in number of polymer particles with conversion for different buffer concentrations.
4.3.6 Effect of reaction volume

The variation of reaction volume with time particularly occurs in semibatch emulsion polymerisation reactors where part of the monomer and other ingredients are added to the reactor at later stages. Reaction volume may affect the particle formation rate in emulsion polymerisation reactors. At a constant stirring speed, the time frequency of particles passing through the high shear impeller zone increases as the reaction volume decreases. This might influence the rate of particle coagulation by increasing the rate of particle collisions, specially for large reactors. This study was performed to investigate the effect of varying reaction volume on the batch polymerisation features. The same recipe using a high SLS concentration 10 g/litre has been used for three reaction volumes equivalent to 0.750, 0.500, and 0.250 litre. The conversion-time and \( N_p\)-conversion curves shown in figures 4.19-20 clearly demonstrate that all polymerisation runs are practically identical and no effect of reaction volume on the polymerisation features are observed for the conditions studied. However, it is expected that reaction volume plays a more critical part for non-stabilised latexes.
Fig. 4.19: The time evolution of conversion for different reaction volumes.

Fig. 4.20: The variation in number of polymer particles with conversion for different reaction volumes.
CHAPTER FIVE

Semibatch Emulsion Homopolymerisation of Butyl Acrylate with Monomer Feed

5.1 INTRODUCTION

In order to study the particle formation and growth in the semibatch emulsion polymerisation of butyl acrylate (BA) with monomer feed (M add process), experiments detailed in tables 5.1-2 were carried out. The following variables were investigated for the neat monomer addition mode:

- **Feed rate**: Four different feed rates were chosen for all experiments as 42.5, 85.0, 185.0, and 385.0 g/h. These correspond to the feeding times of 354.0, 177.0, 81.0, and 39.0 minutes, respectively, when no monomer is initially present in the reactor charge.
- **Overall concentration of emulsifier**: Three amounts of emulsifier sodium lauryl sulphate (SLS) were used in all experiments as 0.125, 2.50, and 10.0 g/litre. These correspond to 0.05, 0.50, and 2.0 wt % of the total amount of monomer in the charge and the feed, respectively.
- **Overall concentration of initiator**: Two amounts of initiator were used as 0.5406 and 1.6218 g/litre (2×10⁻³ and 6×10⁻³ mol/litre aq.).
- **Monomer Distribution ratio**: 0, 5, 10, 20, 40 wt % of total amount of monomer were placed in the initial charge.
- **Pre-period time**: 2.50, 5.0, and 10.0 minutes were considered.

In the semibatch process with a neat monomer feed all emulsifier, initiator, water and a part of monomer are charged into the reactor. The remaining monomer is fed to the reaction vessel at a constant rate. The formulations of all experiments are detailed in
table 5.1. The final solid content of all polymerisations was 33.3 wt %. The experimental sets designed to study the kinetic features of BA semibatch emulsion polymerisation process are given in table 5.2.

5.2 BACKGROUND

Semibatch emulsion polymerisation reactors with neat monomer feed have been studied by a few researchers. A comprehensive review on their works is given in the chapter 2 and it is not repeated here (see especially sections 2.5.1 and 2.5.4.2.1).

<table>
<thead>
<tr>
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<th>Variables</th>
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</tr>
<tr>
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<td>50</td>
<td>185°c</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
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</tr>
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<tr>
<td>20</td>
<td>50</td>
<td>185</td>
<td>2.5</td>
</tr>
</tbody>
</table>

a: The feed rate for this run deviated +5% from the set value.
5.3 RESULTS

5.3.1 Effect of feed rate

The effect of feed rate on the kinetics of semibatch emulsion polymerisation of BA has been examined by using two emulsifier concentrations, 1.25 and 5.0 g. These are labelled as sets 1 and 2, respectively. For both series, 20 wt % (50 g) of monomer was initially charged into the reactor. A pre-period time, $t_{pp}$, of 2.50 minutes was allowed before monomer was fed to the reactor.

<table>
<thead>
<tr>
<th>Table 5.3: Specifications for different experimental sets.</th>
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<tr>
<td>Sets</td>
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</tr>
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<tr>
<td>11</td>
</tr>
<tr>
<td>12</td>
</tr>
</tbody>
</table>

Rate of polymerisation: A simple mass balance shows that in the steady state period the monomer does not instantly polymerise and accumulates in the reactor. Figure 5.1 depicts a typical graph of the amount of PBA formed, BA fed and reacted in the course of reaction for the set 1. The two lines of polymer and monomer feed diverge from each other, indicating that unreacted butyl acrylate accumulates in the reactor. The monomer accumulation in the reactor increases with feed rate. In the beginning of the reaction, the initial monomer in the reactor polymerises quickly and its concentration starts decreasing, in spite of simultaneous addition of monomer to the reactor. At one point the level of unreacted monomer in the reactor reaches the minimum level and starts increasing afterwards. The minimum decreases with feed rate. The BA accumulation in the reactor was greater at the higher feed rates, leading to a higher monomer concentration in the polymer particles. At the end of monomer feeding, the amount of free BA levelled off.
Figures 5.2-3 show the monomer concentration in the polymer particles, $M_p$, versus overall conversion. The appropriate equations for calculation of $M_p$, $N_p$, $R_p$, $\bar{n}$, and PSD size data are given in chapter 3. As it is clear from the graphs, by applying semibatch feeding policy, the level of particle swelling with monomer can be kept at a low level during monomer starved conditions. During the initial period of the reaction, the polymerisations were almost carried out at flooded conditions for both emulsifier concentrations and all monomer feed rates used. However, the period of flooded conditions decreased with increasing SLS concentration and decreasing feed rate.

Figures 5.4-5 present the effect of feed rate on the time evolution of the overall and instantaneous conversions during BA emulsion polymerisation at two SLS concentrations. The higher the feed rate, the faster the rate of polymerisation. Alternatively, a higher rate of polymerisation was obtained for the higher initial SLS concentration. At the lower feed rate the polymerisation rate approached the rate of monomer addition, specially for the higher SLS concentration (see figure 5.1). The end of feeding can be inferred from the conversion-time graphs as the point where both overall and instantaneous conversions converge.
Effect of Monomer Feed Rate

SLS = 5.0 g

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Charge, g</th>
<th>Feed, g</th>
<th>Conversion Rate, g/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA</td>
<td>50</td>
<td>200</td>
<td>Ra = 375 g/h</td>
</tr>
<tr>
<td>DDI</td>
<td>500</td>
<td>-</td>
<td>Ra = 185 g/h</td>
</tr>
<tr>
<td>SLS</td>
<td>5.0</td>
<td>-</td>
<td>Ra = 85 g/h</td>
</tr>
<tr>
<td>KPS</td>
<td>0.27</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>SBr</td>
<td>0.27</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Pre-period time = 2.5 min.

Fig. 5.2: Monomer concentration in the polymer particles versus overall conversion for different feed rates using 5.0 g of SLS in the initial charge.

Effect of Monomer Feed Rate

SLS = 1.25 g

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Charge, g</th>
<th>Feed, g</th>
<th>Conversion Rate, g/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA</td>
<td>50</td>
<td>200</td>
<td>Ra = 185 g/h</td>
</tr>
<tr>
<td>DDI</td>
<td>500</td>
<td>-</td>
<td>Ra = 85 g/h</td>
</tr>
<tr>
<td>SLS</td>
<td>1.25</td>
<td>-</td>
<td>Ra = 42.5 g/h</td>
</tr>
<tr>
<td>KPS</td>
<td>0.27</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>SBr</td>
<td>0.27</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Pre-period time = 2.5 min.

Fig. 5.3: Monomer concentration in the polymer particles versus overall conversion for different feed rates using 1.25 g of SLS in the initial charge.
Effect of Monomer Feed Rate

SLS = 5.0 g

Fig. 5.4: Time evolution of overall (filled symbols) and instantaneous conversions (empty symbols) for different monomer feed rates using 5.0 g of SLS in the initial charge.

Effect of Monomer Feed Rate

SLS = 1.25 g

Fig. 5.5: Time evolution of overall (filled symbols) and instantaneous conversions (empty symbols) for different monomer feed rates using 1.25 g of SLS in the initial charge.
**Particle formation:** The effect of feed rate on the particle formation and growth for both concentrations of SLS are shown in figure 5.6-9. It was concluded in the chapter 4 that for a BA batch polymerisation using 10.0 g/lit of SLS at the conditions studied, the number of particles is dependent on the initial monomer charge if \((R/F)_{M}\) is less than 0.40 (This is equivalent to M/W ratio less than 0.20 for the corresponding batch process). Since \((R/F)_{M}\) ratio used for this series of experiments is 0.20, then it is expected that particle nucleation to be continued during feeding for all three feed rates. The same trend of particle formation was observed for all three feed rates up to the conversion 60 %. For the feed rates 375 and 185 g/h, \(N_p\) remained constant afterwards, while a small increase in \(N_p\) was obtained for the feed rate 85 g/h. Figure 5.7 reveals the evolution of particle size versus overall conversion for the same series. Interestingly, the average particle size showed a decrease in the initial period of reaction. This may be explained by the enhanced rate of particle formation shortly after pre-period time due to the reduced particle growth rate. This will be discussed later. At the lower initial emulsifier concentration, 2.50 g/lit, all micelles are depleted early within the pre-period time; leading to nucleation-free feeding stage. Figure 5.8 shows that for such a low SLS concentration the number of polymer particles is independent of feed rates. A steep increase in the size of particles was obtained for 2.50 g/lit emulsifier concentration, as depicted in figure 5.9. Unlike higher SLS concentration, no decrease in the average particle diameter was observed in the initial period of reaction. Figure 5.9 shows that at a constant conversion the size of swollen particles is largest for the highest feed rate, since particles contains more monomer at the higher monomer feed rates. Obviously at the end of reaction the size of particles converged. Figure 5.9 also shows that the size of unswollen particles are almost the same for all three runs in terms of conversion.

Figures 5.10-11 show the PSD of final latexes for some of the experiments using 5, and 1.25 g of SLS, respectively. In corroboration with what stated above, almost the same PSD is obtained for the experiments using SLS concentration of 1.25 g, while for the experiments using 5.0 g of SLS the PSD curve broadened with decreasing feed rate. The particle size averages measured by PCS and TEM and polydispersity indexes (PDI) of the final latexes are given in table 5.3.
Effect of Monomer Feed Rate

SLS = 5.0 g

**Fig. 5.6:** The particle number versus overall conversion for different feed rates using 5.0 g of SLS in the initial charge.

**Effect of Monomer Feed Rate**

SLS = 5.0 g

**Fig. 5.7:** Average diameter of swollen polymer particles versus overall conversion for different feed rates using 5.0 g of SLS in the initial charge.
Effect of Monomer Feed Rate

SLS = 1.25 g

Fig.5.8: Particle number versus overall conversion for different feed rates using 1.25 g of SLS in the initial charge.

Fig.5.9: Average diameter of swollen polymer particles versus overall conversion for different feed rates using 1.25 g SLS in the initial charge. The small figure on the corner shows the diameter of unswollen particles versus overall conversion.
Effect of Monomer Feed Rate

**SLS = 5.0 g**

![Graph](image)

**Fig.5.10:** Variation in PSD of final polymer particles with monomer feed rate using 5.0 g of SLS in the initial charge.

---

Effect of Monomer Feed Rate

**SLS = 1.25 g**

![Graph](image)

**Fig.5.11:** Variation in PSD of final polymer particles with monomer feed rate using 1.25 g SLS in the initial charge.
5.3.2 Effect of monomer distribution

Four sets of experiments were designed to investigate the effect of monomer distribution between the initial charge and the feed, \((R/F)_M\), on the kinetics of BA polymerisation reaction. These are labelled as sets 3-6. Monomer distribution ratio varied between 0-0.40. The series 4-6 have been carried out using monomer feed rate of 185 g/h and SLS concentration of 0.50, 2.50, and 5.0 g in the initial charge, respectively. The set 3 was performed using 5.0 g of SLS, but at a higher feed rate, 385 g/h.

**Steady state rate of polymerisation:** Figure 5.12 shows a typical variation in \(M_p\) with conversion for the experiments using SLS concentration of 5.0 g and feed rate of 385 g/h (set 3). The \(M_p\) showed some oscillations for the lower \((R/F)_M\) ratios before approaching to the steady-state value. The highest steady-state value for \(M_p\) was established for \((R/F)_M = 40\) wt %. The \(M_p\) for the lower \((R/F)_M\) ratios almost stabilised at the same levels. Figure 5.13 demonstrates overall and instantaneous conversions versus time for the same series of experiments. A slight difference between steady-state rates of polymerisation was observed. However, particle size measurement indicated a large increase in the number of polymer particles formed with decreasing \((R/F)_M\) ratio.

Figures 5.14-15 compare the conversion time curves for different \((R/F)_M\) ratios using monomer feed rate of 185 g/h and SLS concentration of 5.0, and 1.25 g, respectively. For both series a small increase in the steady-state rate of reaction was observed with decreasing \((R/F)_M\) (please note that Figure 5.14 might be misleading since the run using \((R/F)_M = 0.20\) has been carried out with monomer feed rate of 195 g/h). Figure 5.15 shows that slightly a higher rate of polymerisation was obtained for \((R/F)_M = 5\) compared with those for \((R/F)_M =20\) and 40 wt %. This implies that the steady-state rate of polymerisation is more sensitive to variation in monomer distribution ratio at the lower overall emulsifier concentration, *i.e.* less number of polymer particles.

The polymerisation reactions start by the monomer present in the initial charge. The accumulation of unreacted BA during the steady-state rate of polymerisation increases
with \((R/F)_M\) ratio. The same trend for free monomer as those in figure 5.1 is observed for all \((R/F)_M\) ratios except for \((R/F)_M = 0\). For this case since there is no monomer in the initial charge, polymerisation can only occur when some monomer is fed to the reactor. At the start of feeding monomer accumulates in the reactor. When enough monomer was fed to the reactor to initiate particle nucleation, the level of monomer in the system quickly decreases and then increases again, due to subsequent monomer addition. Figure 5.14 shows free monomer versus time for various \((R/F)_M\) ratios used for set 5. The inhibition period could practically influence the kinetic features of semibatch emulsion polymerisation if \((R/F)_M = 0\). This will be discussed in the next chapter.

**Particle nucleation**: The number of particles versus overall conversion and monomer distribution ratios for the experiments using 5.0 g of SLS and feed rate of 385 g/h are shown in Figure 5.16. A larger number of polymer particles is obtained for the lower \((R/F)_M\) ratios. As it is clear from figure 5.16, particle nucleation stops at the earlier conversion for \((R/F)_M = 40\%\) and 20\%, while it continues to the higher conversion for \((R/F)_M = 5\%\); indicating a longer nucleation period. Figure 5.17 shows a small decrease in the average particle size in the initial stage of reaction for almost all \((R/F)_M\) ratios studied.

Figures 5.18-19 show the variation in number of particles with overall conversion for the experiments using 185.0 g/h feed rate and 5.0, and 1.25 g SLS, respectively. The rate of particle formation is highly enhanced for the reactions using high SLS concentration of 5.0 g, specially if no monomer is initially present in the reactor. For SLS concentration of 1.25 g, the number of particles only slightly increased within four fold increase in the \((R/F)_M\) ratio. It was shown before that in the batch emulsion polymerisation of BA with overall SLS concentration of 5 and 1.25 g, the number of particles is influenced by monomer concentration if \((M/W) \leq 0.20\) and \(\leq 0.025\), respectively.

Figure 5.20 shows the PSD of the final latexes for the individual runs of set 3. Figures 5.21-22 show the particle size distribution of final latexes for the sets 3 and 5,
collectively. The particle size averages obtained by calibrated TEM was in agreement with those obtained from PCS. The particle size data are given in table 5.3. The PSD of final latexes became broader as \((R/F)_M\) decreased. The PSD curves present a negative skewness which increased with decreasing \((R/F)_M\) ratio. The long tail of the lower end of PSD curves is the results of long nucleation period obtained at low \((R/F)_M\) ratios. For \((R/F)_M = 0.40\) a sharper PSD was expected, compared with corresponding batch process, since particle nucleation ceased very early in this reaction. However, a rather broad PSD was obtained which can be attributed to the particle formation or experimental error. Similarly, a broader distribution was obtained for the lower \((R/F)_M\) ratios from set 5, as shown in figure 5.22.

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<th>Run Number</th>
<th>Variable</th>
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<th>TEM (D_n) nm</th>
<th>(D_{vol})</th>
<th>(D_w)</th>
<th>(D_l)</th>
<th>PDI</th>
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<tbody>
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<td>118.6</td>
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<td>100.6</td>
<td>106.7</td>
<td>111.2</td>
</tr>
<tr>
<td></td>
<td>BF(1)</td>
<td>(R_a = 85) g/h</td>
<td>99.5</td>
<td>108.9</td>
<td>82.0</td>
<td>86.1</td>
<td>94.3</td>
<td>101.2</td>
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<td><strong>Set 3</strong></td>
<td>BG(10)</td>
<td>((R/F)_M = 40)%</td>
<td>96.5</td>
<td>138.3</td>
<td>128.0</td>
<td>130.9</td>
<td>136.2</td>
<td>139.8</td>
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<td></td>
<td>BB(3)</td>
<td>((R/F)_M = 20)%</td>
<td>98.8</td>
<td>118.6</td>
<td>99.0</td>
<td>100.6</td>
<td>106.6</td>
<td>111.2</td>
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<tr>
<td></td>
<td>BC(9)</td>
<td>((R/F)_M = 10)%</td>
<td>97.7</td>
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<td></td>
<td>BD(8)</td>
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<td>98.3</td>
<td>77.2</td>
<td>83.3</td>
<td>94.1</td>
<td>100.1</td>
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<tr>
<td><strong>Set 5</strong></td>
<td>BU(5)</td>
<td>((R/F)_M = 20)%</td>
<td>87.6</td>
<td>186.8</td>
<td>171.0</td>
<td>173.1</td>
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<td>BV(11)</td>
<td>((R/F)_M = 5)%</td>
<td>86.4</td>
<td>163.6</td>
<td>155.1</td>
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<td>170.0</td>
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<td><strong>Set 9</strong></td>
<td>BX(4)</td>
<td>(I_0 = 0.27 ) g</td>
<td>88.9</td>
<td>193.6</td>
<td>169.7</td>
<td>171.2</td>
<td>174.9</td>
<td>182.6</td>
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<tr>
<td></td>
<td>BY(7)</td>
<td>(I_0 = 0.81 ) g</td>
<td>93.0</td>
<td>161.1</td>
<td>144.3</td>
<td>146.7</td>
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**Effect of Monomer Distribution Ratio**

**SLS = 5.0 g**

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<tr>
<td>SLS</td>
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</tr>
<tr>
<td>KPS</td>
<td>0.27</td>
</tr>
<tr>
<td>SBr</td>
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</tbody>
</table>

---

**Fig. 5.12**: Monomer concentration in polymer particles versus overall conversion for different (R/F)m ratios using 5.0 g SLS in the initial charge (set 3).

---

**Effect of Monomer Distribution Ratio**

**SLS = 5.0 g**

---

**Fig. 5.13**: Time evolution of overall conversion for different monomer distribution ratios using 5.0 g SLS in the initial charge. Instantaneous conversions are shown on the small graph (set 3).
Effect of Monomer Distribution Ratio

Fig. 5.14: Time evolution of overall conversion (filled symbols) and instantaneous conversion (empty symbols) for different (R/F)m ratios using 5.0 g SLS in the initial charge (The small figure shows the variation of free monomer with time).

Effect of Monomer Distribution Ratio

Fig. 5.15: Time evolution of overall conversion (filled symbols) and instantaneous conversion (empty symbols) for different (R/F)m ratios using 1.25 g SLS in the initial charge.
Effect of Monomer Distribution Ratio

**SLS = 5.0 g**

**Fig.5.16:** Particle number versus overall conversion for different (R/F)m ratios using 5.0 g SLS in the initial charge.

**Fig.5.17:** Average unswollen particle diameter versus overall conversion for different monomer distribution ratios using 5.0 g SLS in the initial charge.
Effect of Monomer Distribution Ratio

**SLS = 5.0 g**

<table>
<thead>
<tr>
<th>Charge, g</th>
<th>M feed rate=185g/h</th>
<th>Pre-period=2.5min.</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>SLS</td>
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<td></td>
</tr>
<tr>
<td>KPS</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>SB</td>
<td>0.27</td>
<td></td>
</tr>
</tbody>
</table>

Fig.5.18: Particle number versus overall conversion for different (R/F)m ratios using 5.0 g of SLS and 185.0 g/h monomer feed rate (set 4).

Effect of Monomer Distribution Ratio

**SLS = 1.25 g**

<table>
<thead>
<tr>
<th>Charge, g</th>
<th>M feed rate=185g/h</th>
<th>Pre-period=2.5min.</th>
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<tr>
<td>SLS</td>
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<td>KPS</td>
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<tr>
<td>SB</td>
<td>0.27</td>
<td></td>
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</tbody>
</table>

Fig.5.19: Particle number versus overall conversion for different (R/F)m ratios using 1.25 g of SLS and 185.0 g/h monomer feed rate (set 5).
Fig. 5.20: The variation in PSD of final latexes with monomer distribution ratio using 5.0 g of SLS in the initial charge; (R/F)m = a) 40%, b) 20%, c) 10%, d) 5%.
Effect of Monomer Distribution Ratio

SLS = 5.0 g

Fig. 5.21: Variation in PSD of final polymer particles with monomer distribution ratio using 5.0 g of SLS in the initial charge.

Effect of Monomer Distribution Ratio

SLS = 1.25 g

Fig. 5.22: Variation in PSD of final polymer particles with monomer distribution ratio using 1.25 g of SLS in the initial charge.
5.3.3 Effect of emulsifier concentration

The effect of emulsifier concentration on the BA polymerisation features was investigated using two feed rates of 185 and 85 g/h. These are labelled as series 7 and 8, respectively. Both series were carried out using 20 wt % of monomer in the initial charge. The emulsifier concentration varied from 1.25 to 5.0 g.

**Steady state rate of polymerisation:** Any increase in the initial emulsifier concentrations would lead to a higher rate of particle nucleation and polymerisation rate. The level of monomer concentrations in the polymer particles and reactor showed a decrease with increasing SLS concentration.

*Figures 5.23-24* show the time evolution of overall and instantaneous conversions for the two feed rates of 185 and 85 g/h, respectively. For both sets, an increase in the steady-state rate of polymerisation was obtained by increasing SLS concentration. However, a smaller difference was observed for the lower feed rate, indicating that this dependence is minor at a lower feed rate where the rate of polymerisation is highly controlled by the rate of monomer addition. This will be discussed later.

**Particle nucleation:** *Figures 5.25-26* compare the number of polymer particles formed versus overall conversion for emulsifier concentrations of 1.25 and 5.0 g at two different feed rates 185, and 85 g/h, respectively. A larger number of particles formed at the highest SLS concentration for both feed rates. The particle formation stops at a lower conversion for the reaction with the low SLS concentration (1.25 g). A rather long particle formation period was obtained for the polymerisation reaction using 5.0 g of SLS specially at the lower feed rate of 85 g/h.
Effect of Emulsifier Concentration

Monomer feed rate = 185 g/h

![Graph showing the effect of emulsifier concentration on conversion over time for different SLS concentrations with a monomer feed rate of 185 g/h.]

Fig. 5.23: Time evolution of overall conversion (filled symbols) and instantaneous conversion (empty symbols) for different SLS concentrations with monomer feed rate of 185 g/h.

Effect of Emulsifier Concentration

Monomer feed rate = 85.0 g/h

![Graph showing the effect of emulsifier concentration on conversion over time for different SLS concentrations with a monomer feed rate of 85 g/h.]

Fig. 5.24: Time evolution of overall conversion (filled symbols) and instantaneous conversion (empty symbols) for different SLS concentrations with monomer feed rate of 85 g/h.
Effect of Emulsifier Concentration

Monomer feed rate = 185.0 g/h

Fig.5.25: Particle number versus overall conversion for different SLS concentrations with monomer feed rate of 185.0 g/h.

Effect of Emulsifier Concentration

Monomer feed rate = 85.0 g/h

Fig.5.26: Particle number versus overall conversion for different SLS concentrations with monomer feed rate of 85.0 g/h.
5.3.4 Effect of initiator concentration

The effect of KPS was studied by using two KPS concentrations of 0.27, and 0.81 g. The SLS concentration of 1.25 g and \((R/F)_M = 0.20\) were used in both experiments.

*Steady state rate of polymerisation:* Figure 5.27 shows conversions versus time for the two different initiator concentrations. Slightly a higher rate of reaction was observed for the polymerisation run using the higher concentration of initiator.

*Particle nucleation:* The effect of initiator concentration on the \(N_p\) has been depicted in figure 5.28. A larger number of polymer particles was obtained for the higher concentration of initiator in the initial charge, as it was expected. The particle size data are given in table 5.3.

5.3.5 Effect of temperature

A couple of experiments (set 12) were carried out at standard conditions using different temperatures to study the effect of reaction temperature on the kinetic features. The SLS concentration of 1.25 g and \((R/F)_M = 0.20\) were used in both experiments.

*Steady state rate of polymerisation:* Figure 5.29 shows the conversions versus time for the two different reaction temperatures. As it was expected, a higher initial rate of polymerisation was obtained for the higher temperature 70 °C. However, a very little increase in the steady-state rate of polymerisation was obtained. The instantaneous conversion established at a higher value for the reaction temperature of 70 °C.

*Particle nucleation:* A larger number of polymer particles was formed at the higher temperature, as it is depicted in figure 5.30. Furthermore, particle formation ceased at a lower conversion for the higher temperature.
Effect of Initiator Concentration

Fig. 5.27: Time evolution of overall conversion (filled symbols) and instantaneous conversion (empty symbols) for different KPS concentrations.

Effect of Initiator Concentration

Fig. 5.28: Particle number versus overall conversion for different KPS concentrations.
Effect of Temperature

Fig. 5.29: Time evolution of overall conversion (filled symbols) and instantaneous conversion (empty symbols) for different temperatures.

Effect of Temperature

Fig. 5.30: Particle number versus overall conversion for different reaction temperatures.
5.3.6 Effect of pre-period time

Two sets of experiments were considered for studying the effect of pre-period time on the kinetic features of BA semibatch emulsion polymerisation reaction. In the first series (set 10) SLS concentration of 1.25 g and (R/F)\textsubscript{M} = 20 wt % were considered. The monomer feed rate was kept constant at 385 g/h. The pre-period time was varied in a short range within 2.5 to 5.0 minutes. In the next series, set 11, polymerisation was carried out using SLS concentration of 5.0 g, (R/F)\textsubscript{M} = 10 wt %, and feed rate of 185 g/h. The Pre-period time was varied in a longer range within 2.5 to 10 minutes. The sets 10 and 11 are examples of the systems with medium and low (M/E) ratios.

**Steady state rate of polymerisation:** Figures 5.31-32 depict the time evolution of conversions for both series. No variation in the steady state rate of polymerisation with pre-period time was observed for both series. The slight differences in the polymerisation rate in the first few minutes of reactions originate from different pre-period times and do not affect the rate of reaction afterwards. This was expected for the set 10 since the initial monomer charge was enough to deplete all micelles by the growing particles. For the set 11 (the one with low (M/E) ratio), particle nucleation continued into the feeding stage. However again no variation in the polymerisation rate with pre-period time was observed, as it was shown on the small graph of figure 5.31.

**Particle nucleation:** Figures 5.33-34 show the effect of pre-period times on the number of polymer particles formed for the sets 10 and 11, respectively. No variation in the final number of particles was observed within the pre-period times studied. This can explain the constant rate of reaction obtained for experiments using different pre-period times, as discussed above. For BA semibatch process with high (M/E) ratio, particle formation occurred only within the first few minutes of the reactions and was independent of the feed rate. For the low (M/E) ratio, particle nucleation continued into the feeding stage and lasted for the longer period of times, as shown in figure 5.34. For both runs of this set particle formation mainly and equally occurred during feeding stage. No indication of particle nucleation enhancement was observed for the experiment with pre-period time of 10.0 minutes.
Effect of Pre-period Time
SLS = 1.25 g : (R/F)m = 0.20

Fig. 5.31: Time evolution of overall conversion (filled symbols) and instantaneous conversion (empty symbols) for different pre-period times.

Effect of Pre-period Time
SLS = 5.0 g : (R/F)m = 0.10

Fig. 5.32: Time evolution of overall conversion (filled symbols) and instantaneous conversion (empty symbols) for different pre-period times (the small graphs show the variation in conversions versus corrected time, i.e., reaction time-preperiod time).
Effect of Pre-period Time

SLS = 1.25 g : (R/F)m = 0.20

Fig. 5.33: Particle number versus overall conversion for different pre-period times.

Effect of Pre-period Time

SLS = 5.0 g : (R/F)n = 0.10

Fig. 5.34: Particle number versus time for different pre-period times. The small graph shows the number of particles versus overall conversion.
5.4 DISCUSSION

5.4.1 Particle nucleation

In the interval I and II of a batch process, the monomer droplets act as reservoirs of monomer. The monomer diffuses from the droplets to the locus of polymerisation with the rate controlled by the free radical propagation in the particles. Hence, a batch emulsion polymerisation in the interval II may be inherently considered as a semibatch process in which the monomer is fed to the polymer particles by droplets. This is similar to the pumping of monomer from an external reservoir to the reaction mixture with a rate that keeps particles saturated with monomer. However, this process, which is called monomer-flooded semibatch, could have the following advantages over a conventional batch process when the feed contains monomer only:

- The importance of initiation in monomer droplets is further reduced, compared to a batch process.
- Less amount of emulsifier molecules are adsorbed on the monomer droplets and more is available for particle formation for the same total amount of monomer.
- Particle coagulation is expected to be less operative compared with a batch process where monomer droplets might accelerate particle coagulation.

These three factors are not believed to bear a major importance for a system with low M/E ratio where sufficient emulsifier molecules are available to outweigh emulsifier adsorption on the monomer droplets, and to protect particles against coagulation. However for a system with high M/E ratio, they must be taken into consideration, as it will be discussed later.

Particle nucleation in a batch process before interval III and monomer-flooded semibatch process are expected to be similar. Semibatch emulsion polymerisation reactors might enhance the rate of particle nucleation, compared with batch process, if operated at monomer-starved conditions. According to Smith and Ewart theory for
particle formation, the number of polymer particles generated in a conventional batch process is shown by the following expression:

\[ N_p = K \left( \frac{I_o}{\mu} \right)^{0.40} (\alpha_s S_0)^{0.60} \]  

where \( K \) is a numerical constant, \( \mu \) the volumetric growth rate per particle in interval \( I \), \( \alpha_s \) the adsorption area occupied by a molecule of emulsifier on the surface of polymer particles and \( S_0 \) the amount of emulsifier forming micelles per unit volume of water. It is clear from the above equation that the number of polymer particles is proportional to the volume growth rate of polymer particles during nucleation. Any variation in parameters which might reduce the volume growth rate \( \mu \), increases the number of polymer particles. The equation 5.1 has been obtained assuming that \( \mu \) is constant. The volumetric growth rate of a particle in a monomer-starved semibatch process at the steady-state is given by the following expressions:

\[ \mu = \frac{R_a}{N_p \rho_p} \]  

\[ \mu = \frac{R_a (1 + G R_a)}{N_p \rho_p \varphi_{ps}} \]  

where \( \varphi_{ps} \) is the volume fraction of polymer in the polymer particles at the steady-state. Equation 5.2 holds when the equation \( R_p = R_a \) governs the steady-state rate of reaction, while equation 5.3 is valid when the inverse relation \( 1/R_p = G + 1/R_a \) holds. Assuming that the steady-state rate of polymerisation can be reached early in the reaction and it is not much dependent on the number of polymer particles, \( \mu \) is related to the rate of monomer addition using Wesseling’s expressions, as shown above. Equation 5.2 predicts a linear relation between the rate of particle growth and monomer addition. According to equation 5.3, as factor \( G \) approaches zero the volumetric growth rate will be equal to the rate of monomer addition per particle \( (\varphi_{ps} \) approaches one). By applying a low monomer feed rate to a semibatch emulsion polymerisation reactor, it is possible to reduce the particle growth rate in favour of particle formation rate and to produce a larger number of polymer particles. Although the above equations can qualitatively predict the increase in the number of particles with decreasing monomer feed rate for semibatch process at monomer-starved
conditions, they can not be used quantitatively where particle formation occurs extensively since $\mu$ in such a case is not constant and decreases as more particles are being formed. Therefore the expression for $N_p$ should be modified to incorporate the effect of varying volume growth rate with increasing number of particles.

The seeding batch (see figure 2.2) is the most important stage of a semibatch process, because it controls particle formation in the whole course of reaction. For a semibatch process with a fixed recipe, the monomer distribution ratio is the key variable. In fact in a semibatch process with neat monomer feed the initial monomer charge in the reactor determines the initial M/E ratio and hence particle formation rate. For any monomer-fed semibatch process there is a threshold $(M/W)$ ratio, $(M/W)_{cr}$, above which the monomer present in the reactor charge is sufficient to consume all emulsifier micelles through nucleation. If emulsifier concentration varies, then a criteria which takes into account the variation of emulsifier concentration should be used. In this research work the $(M/E)$ ratio has been selected as a criterion to identify different regimes of particle formation in semibatch emulsion polymerisation processes.

In subsequent part expressions are derived for calculation of $(M/W)_{cr}$ and $(M/E)_{cr}$ in a batch emulsion polymerisation process which can be equally used for seeding batch of semibatch processes. Assuming that initiator radicals generated in the aqueous phase are preferentially captured by monomer swollen micelles rather than polymer particles, the rate of particle formation can be given as:

$$\frac{dN_p}{dt} = N_a R_i$$

The final number of particles is obtained as

$$N_p = N_a R_i t$$

The critical time $t_{cr}$ when particle nucleation ceases in a batch emulsion polymerisation is given by (Smith and Ewart, 1948):
where \( \beta = [(4\pi)^{1/2} (3 \mu)]^{2/3} \) and \( \mu = k_p \rho_m \varphi_m / N_a \rho_p \varphi_p \).

Incorporating the equation 5.5 in the general rate equation of emulsion polymerisation (equation 4.1) gives

\[
\frac{dx}{dt} = (k_p M_p R_i / M_0 N_a) t \quad 5.7
\]

The corresponding critical conversion is

\[
x_{ct} = (k_p M_p R_i / 2 M_0) t_{ct}^2 \quad 5.8
\]

The weight of polymer produced at the end of the particle nucleation period is simply obtained from equation 5.8 as

\[
P_{ct} = (k_p M_p R_i / 2) t_{ct}^2 \quad 5.9
\]

Combining equations 5.6 and 5.9 gives the following expression for \( P_{ct} \):

\[
P_{ct} = C_1 (E_0^{6/5} / I_0^{1/5}) \quad 5.10
\]

Since \( M_{ct} = P_{ct} / x_{ct} \), then the following expression is readily obtained for \( (M/E)_{ct} \) as

\[
M_{ct} = (M/W)_{ct} = C_2 E_0^{6/5} / I_0^{1/5}
\]

If the overall monomer and emulsifier concentrations in the charge are considered as the main variables, then an expression can be obtained for \( (M/E)_{ct} \). Dividing the above equation by \( E_0 \), the expression for \( (M/E)_{ct} \) is obtained as

\[
(M/E)_{ct} = C_3 (E_0 / I_0)^{1/5} \quad 5.11
\]
C₁, C₂, and C₃ are constants. According to the above expression, \((M/E)_{cr}\) is independent of \(M₀\) and increases with \(E₀\) and \(I₀\) to the power \(1/5\) and \(-1/5\), respectively. This means that the variation of \((M/E)_{cr}\) with polymerisation formulation is rather small. For an example, 10 fold increase in \(E₀\) will increase \((M/E)_{cr}\) only for 50%.

Two scenarios exist:

- \((M/E) \geq (M/E)_{cr}\): If a semibatch process is managed so that particle nucleation is limited to the seeding batch, particle formation occurs under monomer-flooded conditions and particles undergo growth in the subsequent stage and number of particles becomes independent of the feed rate. This condition can be achieved if a high initial \(M/E\) is used, as for those in the set 5 (with one exception) where no particle was formed during feeding, and a subsequent growth was observed for all particles, as shown in figures 5.9 and 5.19. The particle number obtained for the set 5 was around \(1.60 \times 10^{17}\) litre\(^{-1}\) which is almost equal to that obtained from the corresponding batch process.

- \((M/E) < (M/E)_{cr}\): For such a system the initial monomer charge is not enough to consume all emulsifier molecules and particle nucleation proceeds both during seeding batch and feeding stage. The particle formation rate is influenced by the rate of monomer addition and seeding batch conditions. This condition can be exemplified by the sets 3 (again with one exception) and specially 4 of the current experiments. For these sets, particle size measurements indicated an increase in the number of polymer particles with decreasing \((R/F)_{M}\) and monomer feed rates. For an extreme case that no monomer or a very low amount of monomer is placed initially in the reactor charge, a very low \(M/E\), the monomer is instantly consumed and particle nucleation mostly occurs during feeding. In such a case, the rate of particle formation will be dictated by the rate of monomer addition.
Depending on the conditions, particle nucleation in semibatch polymerisation can approach a batch process or becomes distinct from that. We may conclude that in a semibatch process with monomer feed, particle nucleation could be independent of monomer feed rate and similar to a batch process if, and only if, \((M/E) > (M/E)_{cr}\). This could explain why there are some contradictory results in the literature concerning similarities between particle nucleation in batch and semibatch processes (Gerrens, 1969; Krackeler, 1969). It should be noted that the qualitative classification presented above may be applicable to any \(M\) add semibatch process. However, its quantitative treatment depends on monomer type, reaction temperature, overall emulsifier and initiator concentrations.

Semibatch polymerisation reactors can produce more particles, compared with batch process, if particle nucleation is not limited to the seeding batch and at least partly occurs during the feeding stage. This can be caused by variation in a number of parameters such as monomer distribution ratio, emulsifier concentration, initiator concentration, monomer feed rate and pre-period time.

In this part, \((M/E)_{cr}\) is calculated by using the experimental results obtained for the batch process with different monomer distribution ratios and overall emulsifier concentrations. The results obtained in chapter 4 indicate that number of particles is constant and independent of \(M_0\) for a wide range of monomer charge at SLS concentration of 2.50 g/litre and for a narrower range at SLS concentration of 10.0 g/litre. For the SLS concentration of 2.50 g/litre, \(N_p\) becomes dependent on \(M_0\) for \((M/W) = 0.025\), while it is independent of \(M_0\) for \((M/W) = 0.10\). No experiments was performed for the range \(0.025 < M/W < 0.10\). However it can be safely assumed that \(N_p\) is independent of \(M_0\) for \(M/W \geq 0.05\) (see table 4.4), which is equivalent to \((R/F)_M = 0.10\) for the current semibatch study, so that \((M/E)_{cr} = 50/2.5 = 20\) (for simplicity, the weight basis has been used for calculation of M/E ratio). For the SLS concentration of 10 g/litre \(N_p\) was found to be independent of \(M_0\) for \(M/W \geq 0.20\). Similarly, this gives \((M/E)_{cr} = 200/10 = 20\). So for both series \((M/E)_{cr}\) was obtained equal to 20. According to equation 5.11 we might expect that four fold increases in emulsifier concentration, will increase \((M/E)_{cr}\) by 25%. However, it should be noted
that \((M/E)_{cr}\) for both emulsifier concentrations are approximated within the discrete intervals studied.

The \((M/E)\) ratios for the experiments using 2.5 and 10.0 g/litre SLS for the conditions of series 2 and 1 \([(R/F)_{M} = 20 \, \% \), \(M_0 = 100 \, \text{g/litre}\)], are calculated as 40 and 10, respectively. This indicates that particle formation for the former is limited to the seeding stage and hence independent of feed rate, \((M/E) > (M/E)_{cr}\), while for the latter it continues to the feeding stage and is influenced by the rate of monomer addition, \((M/E) < (M/E)_{cr}\). The results depicted in figures 5.6-9 agree with such a conclusion. In fact, the second series of experiments (set 2) is virtually a seeded semibatch polymerisation where particles grow during feeding stage. In the first series, secondary particle nucleation occurred during the monomer feeding resulting in a decrease in the average size of particles in the early stages of reaction.

Figure 5.35 depicts final number of polymer particles versus \((R/F)_{M}\) ratios. According to the discussion above, we might expect to find a range of \((R/F)_{M}\) ratios above which \(N_p\) is constant. This is clearly observed for the experiments using medium concentration of SLS, 2.50 g/litre, in figure 5.35. The number of polymer particles is almost constant and only shows some variations for \((R/F)_{M} < 0.10\). For the high SLS
concentration in the initial charge, 10.0 g/litre, a continuous increase in the number of particles with decreasing (R/F)_M was observed. The slope of the \( N_p-(R/F)_M \) curve increases with monomer feed rate, since particle nucleation continues to the feeding stage for this series of experiments. The results of batch experiments for 10 g/litre SLS indicate that \( N_p \) is expected to be constant above \( M/W = 0.20 \) which is corresponding to \( (R/F)_M=0.40 \).

For the lowest SLS concentration studied, 0.25 g/litre, \( N_p \) increases with decreasing \( (R/F)_M \) ratio. This trend cannot be explained in terms of \( (M/E)_{cr} \). In the chapter 4 it was shown that in the batch BA emulsion polymerisation at low SLS concentration, particle coagulation occurred in the course of reaction. As it was discussed before (page 148), in a semibatch process with a low emulsifier concentration, particle coagulation is enhanced with increasing monomer concentrations. The comparison of results obtained for very high \( (M/E) \) ratios with those from corresponding batch process shows that \( N_p \) is larger for semibatch process (see figures 5.35 and 4.12).

Variation in \( N_p \) with SLS concentration for different semibatch processes are given in table 5.4. It shows 7.2 and 4.4 fold increase in the final number of polymer particles with 4 fold increase in the initial emulsifier concentration for the reactions using feed rates of 85 and 185 g/h, respectively. The Smith-Ewart theory predicts that in a batch emulsion \( N_p \) is proportional to \( [S]^{0.6} \). In the chapter 4 it was shown that for BA batch emulsion polymerisation \( N_p \) is proportional to \( [S]^{0.54} \). This predicts a 2.1 fold increase in \( N_p \) for a 4 fold increase in the emulsifier concentration, which is far below those obtained for the semibatch process. However, it should be noted that the above comparison is not completely sound because of different conditions considered for experiments using low and high emulsifier concentrations. In the experiments using low emulsifier concentration particle nucleation was confined to the seeding batch and was almost similar to a batch process, while for the experiments using the high SLS concentration particle nucleation continued into the feeding stage and was highly affected by the monomer feed rate. This will widen the difference between the number of particles formed. A more sound comparison should be made when experiments
using different SLS concentrations are carried out at monomer-starved nucleation conditions.

Table 5.4: Variation of \(N_p\) and \(R_p/R_d\) with SLS concentration at different feed rates.

<table>
<thead>
<tr>
<th>Sets</th>
<th>Feed rate g/h</th>
<th>SLS=1.25 g</th>
<th>SLS=5.0 g</th>
<th>increase %</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>185</td>
<td>0.73</td>
<td>0.87</td>
<td>19.4</td>
</tr>
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<td>8</td>
<td>85</td>
<td>0.86</td>
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<td></td>
<td></td>
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<tr>
<td>7</td>
<td>185</td>
<td>8.0E+16</td>
<td>3.5E+17</td>
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<tr>
<td>8</td>
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<td>7.9E+16</td>
<td>5.7E+17</td>
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Semibatch emulsion processes with M feed provide a unique way to produce latexes with very fine particles. This can only be accomplished through suppressing particle growth rate by applying a very low monomer feed rate to a semibatch process with no or low initial monomer charge. The run BJ has been carried out at such conditions. Figure 5.18 shows that a massive number of polymer particles, \(2.60\times10^{18}\) Litre\(^{-1}\), is formed when polymerisation is carried out at highly monomer starved conditions; high emulsifier concentration and low initial monomer charge. The final particle size was almost 60 nm which is much smaller than particles of ordinary emulsion latexes. Due to continuous particle formation and relatively small particle sizes, the viscosity of the latex increased with conversion so that mixing became very difficult as the reaction proceeded.

Initiator concentration has a considerable effect on the course of particle formation in a semibatch process. If particle nucleation is limited to the seeding batch, \((M/E) > (M/E)_c\), the variation of number of particles with initiator concentration is expected to be similar to that in corresponding batch process. The experiments carried out to investigate the effect of KPS concentration are confined to this category. In the chapter 4 it was found out that for BA batch process \(N_p\) varies with \([KPS]^{0.39}\) within the KPS concentration range studied. Application of 3 fold increase in initiator concentration is expected to increase the number of particles by 53%. The results
shown in figure 5.27 indicates that for such an increase in the KPS concentration, 25% increase in the number of particles is obtained which is lower than what was expected.

According to equation 5.11, \((M/E)_c\) is proportional to the inverse if initiator concentration to the power 0.20. It is possible that the particle nucleation regime changes with KPS concentration. For example, a decrease in the initiator concentration could assure that particle nucleation is not confined to the seeding batch anymore and continues to the feeding stage. For a semibatch process with monomer-starved nucleation, the proportionality between \(N_p\) and \(I_0\) could be higher than that predicted by SE theory for a batch process.

The thermodynamic equilibrium distribution of monomer among polymer particles, water, and micelles could play an important role in the monomer-starved particle nucleation. The radical capture efficiency for the lean-monomer swollen micelles has not been studied in the literature. The main characteristics of particle nucleation in the interval III of a batch process has been discussed in the chapter 4. In the semibatch process the picture could be different from that of batch process, due to addition of monomer to the system. The incoming monomer is added to the aqueous phase and more easily diffuses into the micelles, if the polymerisation in polymer particles is diffusion controlled which is the case at highly starved conditions (although micelles might show more resistance towards monomer diffusion than polymer particles at normal conditions). This might improve the capture efficiency, compared with that in interval III of batch processes. It may also increase the monomer concentration in the aqueous phase and enhance particle formation through homogeneous nucleation mechanism.

In contrast with interval III of a batch process, in a semibatch process newly formed particles can grow to a larger size during the feeding stage and be easily detected. In a series of experiments the pre-period time was increased from 2.50 to 10.0 minutes expecting that that it would lead to the nucleation of more particles at the starved conditions. This is an example of the particle nucleation in the interval III of a batch process and subsequent particle growth by a semibatch process with M feed.
However, figure 5.34 shows no distinct difference for the number of particles. At the first glance, these results might be in contrast with the results obtained for BA batch emulsion polymerisation in the interval III where particle nucleation was reported (see chapter 4). However as it is evident from figure 5.32, the instantaneous conversion reaches 0.80 early in the reaction within 2.50 minutes. So by increasing the pre-period time from 2.50 to 10.0 minutes, the polymerisation proceeds from 0.80 to 0.95 conversion. This clearly indicates that at highly monomer-starved conditions (above 80% polymer) in a batch reactor, lean monomer-swollen micelles are not very competitive with polymer particles in capturing radicals. In the other words, particle formation is more pronounced at the early stage of interval III and decreases as the polymerisation reaction proceeds.

5.4.2 Particle size distribution

It is claimed that as the time span over which the particle nucleation occurred increases, the PSD of latexes would become broader (Krackeler and Naidus, 1969). Conventional batch emulsion polymerisation is a good example for PSD broadening with duration of nucleation period. This has also been verified in the current semibatch emulsion polymerisation experiments using high (M/E) ratios where particle nucleation started from monomer-flooded conditions. At monomer-flooded conditions, the rate of particle growth is independent of feed rate and is thermodynamically controlled at a constant level, similar to a batch process. At the monomer-starved conditions, the rate of particle growth is controlled by the rate of monomer addition and more particles might be produced. It was discussed before that in a semibatch emulsion polymerisation using \((M/E) > (M/E)_{cr}\), particle nucleation is limited to the seeding stage and independent of monomer feed rate. Figure 5.11 confirms that for such a condition almost the same PSD curves are obtained. In a semibatch emulsion polymerisation using \((M/E) < (M/E)_{cr}\), particle nucleation starts from the seeding batch and continues to the feeding stage where more particles are formed. The period of particle nucleation increased with decreasing monomer feed rate and \((R/F)_M\) ratio. Correspondingly, the larger PDI was obtained for the lower monomer feed rate and \((R/F)_M\) ratio as depicted in figures 5.21-22 and table 4.3. For the highest \((R/F)_M\) on the figure 5.20 a slightly larger PDI obtained, compared to the
corresponding batch process, than what was expected. This can be attributed either to experimental error or to a slight particle formation in the course of feeding, as shown in figure 5.12.

Small shoulders or peaks on the PSD curves from latexes using low \((R/F)_m\) ratios are observed in figure 5.20. While experimental error can not be ignored in constructions of PSD curves, the following hypothesis can be put forward to account for the occurrence of bimodal PSDs: According to classical theory of SE, the rate of particle nucleation is a decreasing function of time. This predicts a monomodal PSD for conventional batch emulsion polymerisations. In the semibatch emulsion polymerisation as the monomer concentration drops below its saturation value during the seeding batch, the rate of particle nucleation is expected to fall considerably (as outlined in the chapter 4). When the instantaneous monomer conversion exceeds 0.80 - 0.85, particle nucleation largely decreases; despite that, many lean monomer-swollen micelles are still in the reaction mixture. As soon as the monomer is fed to the reactor, monomer concentration in the polymer particles and micelles builds up and then the rate of particle nucleation increases. Such an increase in the rate of particle formation when it is associated with a low particle growth rate could result in the occurrence of bimodal particle size distribution. The results obtained for PSD curves are corroborated with data shown on figure 5.17 which indicate a decrease in the particle diameter in the first few minutes of monomer feeding due to enhanced particle formation.

5.4.3 Steady state rate of polymerisation

For a seeded semibatch process with case II kinetics, Wesseling obtained the following relation between the rate of monomer addition \((R_a)\) and the polymerisation rate \((R_p)\) at steady-state conditions:

\[
\frac{1}{R_p} = G + \frac{1}{R_a}
\]

where \(G\) is equal to \(1/K\) given by equation 2.1.
His analysis showed that only if a fixed radical concentration in the polymer particles is assumed, will the steady-state rate of polymerisation reaction (SSRR) be equal to the rate of addition.

$$R_p = R_a$$  \hspace{2cm} 5.13

The equality \textit{equation 5.13} has been suggested for semibatch emulsion polymerisation of styrene and methyl acrylate (Gerrens, 1969), and styrene/butyl acrylate (Snuparek and Krska, 1976). The reciprocal relation has been also reported for VA semibatch emulsion polymerisation (Bataille et al, 1978). The linear expression, $R_p = k R_a$, has also been suggested for VDC and VDC/BA semibatch emulsion polymerisation systems (Wesseling and Gips, 1973).

![Graph showing \( \frac{1}{R_p}, h/g \) versus \( \frac{1}{R_a}, h/g \) for different emulsifier concentrations.](image)

\textbf{Fig.5.36: The inverse of steady-state rate of polymerisation versus inverse of monomer addition rate for different emulsifier concentrations.}

The parameter $G$ in \textit{equation 5.12} is an indicator of process capability to consume monomer. Increasing the number of polymer particles, initiation rate and polymerisation temperature will decrease the parameter $G$. As $G$ decreases, the rate of polymerisation approaches the rate of monomer addition. Similarly at constant $G$, as the $R_a$ decreases, $R_p$ is less influenced by $G$. \textit{Figure 5.36} shows $1/R_p$ versus $1/R_a$ data for 2 sets of experiments at steady-state conditions, which all are confined to the
equation 5.12 drawn by Wesseling. According to equation 5.12 the slope and intercept of $1/R_p - 1/R_a$ curve should be one and $G$, respectively. Any increase in the SLS, and KPS concentrations, or temperature (Sajjadi and Brooks, 1997) could shift the corresponding line toward $R_p = R_a$ line. For example, a distinct line can be seen for experiments carried out with 2.5 g/lit of SLS. As the SLS concentration increased from 2.50 to 10.0 g/lit, the line shifted toward $R_p = R_a$ line, indicating higher steady-state rate of reaction at a fixed $R_a$. This may finally lead to an overlap with $R_p = R_a$ line so that one may think that the rate of polymerisation is confined to the equation $R_p = R_a$.

The results show that the SSRR is influenced by the number of polymer particles. In the chapter 4 it was found out that butyl acrylate emulsion polymerisation at the conditions studied is a high-$n$ system which is not confined to the CASE III kinetics. For the case III systems, polymerisation rate is independent of number of particles (see the combination of equations 1.1 and 1.10 for the overall rate of polymerisation). The experimental results obtained in this research work also show that for BA emulsion polymerisation the SSRR is influenced by the number of particles especially if the variations in number of particles are caused by SLS concentration in the feed.

Figure 5.37 shows the steady-state rate of polymerisation reaction over monomer addition feed rate ($R_p/R_a$) versus $(R/F)M$ ratio for different conditions. Obviously a higher $R_p/R_a$ would be expected for lower $R_a$, according to Wesseling's analysis. Generally, $R_p/R_a$ showed a slight increase with decreasing $(R/F)_M$ ratio, depending on the SLS concentration. The steady-state rates of polymerisation obtained for all three sets (3, 4, and 5) closely follow the particle nucleation trend in the course of reaction; a slight increasing $R_p/R_a$ with decreasing $(R/F)_M$ ratio occurs when it is associated with an increase in the number of particles but $R_p/R_a$ remains constant if the number of particles stays constant with variation in $(R/F)_M$ ratio. The decrease from $(R/F)_M = 0.40$ to 0.05 for SLS = 10 g/litre and $R_a = 385$ g/h, almost tripled the number of particles, as depicted in figure 5.35, while only slightly improved the rate of polymerisation, as shown in figure 5.37.
Fig. 5.37: The steady-state rate of polymerisation as a function of monomer distribution ratio for different SLS concentrations and monomer feed rates.

Overall emulsifier concentration showed a strong impact on the polymerisation rate. This can be easily deduced from figures 5.23-24. For experiments using constant feed rate 185 g/h, 19.4% increase in the $R_p$ was obtained by varying SLS concentration from 2.50 to 10 g/lit. However, when the same variation in SLS concentration was applied to the experiments using the lower feed rate of 85 g/h, an increase of 12.8% in the rate of polymerisation was obtained. Table 5.4 shows $R_p$/$R_a$ and $N_p$ for the two sets of experiments performed to study the effect of emulsifier concentration. It can be concluded that the steady-state rate of polymerisation is less sensitive to variations in emulsifier concentration at low monomer feed rate, where the rate of polymerisation is mostly controlled by the rate of monomer addition.

A very important point can be inferred from the data reported in table 5.4 and figure 5.35: Three fold increase in $N_p$ brought about by varying monomer initial charge did not affect $R_p$, but four fold increase in $N_p$ by varying SLS concentration improved $R_p$ for 20%. This clearly indicates that the rate of polymerisation is enhanced by SLS in the charge, and not only by the number of particles.

Similarly, any increase in the initiator concentration is associated with an increase in the number of polymer particles and the radical concentration which leads to a higher
rate of polymerisation, as depicted in figure 5.27. It should be noted that the effect of KPS on the kinetic features was only studied for the run with high initial M/E ratio; no particle nucleation during feeding.

The results obtained clearly show that although monomer feed rate controls the rate of polymerisation in monomer-starved semibatch emulsion polymerisation of BA, initial initiator and emulsifier concentrations and temperature are also important. The rate of polymerisation follows the expression originally derived by Wesseling. At high concentrations of initiator and emulsifier, and high temperature, along with a low $R_a$, the rate of polymerisation will approach the rate of monomer addition.

5.4.4 Monomer concentration in polymer particles

Since at the conditions studied the rate of BA polymerisation was rather high, the instantaneous conversion could reach to a high conversion, leading to a low monomer concentration in the polymer particles. This may be easily deduced from figures 5.2, 5.3, 5.12 and 5.14. When the monomer is fed to the reactor after pre-period time, $M_p$ may either a) initially decrease and then increase or b) only decrease with time until it reaches to a steady-state position. The variation in $M_p$ with time during the transition time depends on $(R/F)_M$, pre-period time and monomer feed rate (other formulation variables constant).

The change of monomer concentration in polymer particles during feeding stage in semibatch emulsion polymerisation reactors has a determining effect on the particle formation and coagulation. It is thought that particle coagulation is more severe during the sticky stage when particles contain more monomer (Hamielec and Macgregor, 1982). Although such a stage has not been precisely defined for BA emulsion polymerisation, it is expected that particle coagulation decreases with increasing monomer conversion in the interval III. This will be discussed in the forthcoming publications (unpublished results). The monomer concentration in the polymer particles is a strong function of monomer feed rate. For sparingly water-soluble monomers, such as butyl acrylate, $M_p$ is virtually dependent on instantaneous monomer conversion. At a constant monomer feed rate, $M_p$ is influenced by initial
initiator and emulsifier concentrations, and monomer distribution between initial charge and the feed. If polymerisation is carried out at a higher SLS or KPS concentration, a higher rate of polymerisation is obtained and the steady-state rate of reaction would be established at a lower value for $M_p$. Monomer distribution between the initial charge and the feed could affect $M_p$ in the same way as emulsifier concentration by increasing the number of polymer particles. A simple mass balance equation relates the overall and instantaneous conversions as follows:

$$X_o = \left( R_o \left( t-t_{pp}\right) + M_0 \right) x_i / W_0$$  \hspace{1cm} 5.14

Where $X_o$ is the overall conversion, $x_i$ the instantaneous conversion, $t$ the time, $t_{pp}$ the pre-period time, $W_0$ overall monomer concentration, and $M_0$ initial monomer concentration. By differentiation from the above equation, we obtain:

$$\frac{dX_o}{dt} = \left( (R_o \left( t-t_{pp}\right) + M_0 \right) \frac{dx_i}{dt} + R_o x_i) / W_0$$  \hspace{1cm} 5.15

or

$$R_p = \left( R_o \left( t-t_{pp}\right) + M_0 \right) \frac{dx_i}{dt} + R_o x_i$$

The establishment of steady state requires that the status of the system remains constant and does not change with time. Theoretically such a condition is acquired if $dx_i / dt = 0$, then:

$$x_i = \frac{R_p}{R_o}$$  \hspace{1cm} 5.16

So we might assume that at a real steady state, the instantaneous conversion of the monomer in the reactor is constant and equal to $R_p/R_o$.

For an emulsion polymerisation system confined to the equation 5.12, this ratio is equal to:

$$x_i = \frac{R_p}{R_o} = \frac{1}{(R_o G + 1)}$$
As the parameter G or the monomer feed rate $R_a$ decreases, the instantaneous conversion approaches unity. The parameter G can be obtained from the intercept of $1/R_p - 1/R_a$ curves for each set of experiments from figure 5.36. Table 5.5 compares the experimental $x_i$ and calculated $x_i$ by the above equation. A very good agreement was obtained.

<table>
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<th>Sets</th>
<th>M feed rate $g/h$</th>
<th>Instantaneous conversion $x_i, %$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>Experimental.</td>
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<tr>
<td>Set 2 (SLS=1.25 g)</td>
<td></td>
<td></td>
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<tr>
<td>BU</td>
<td>185</td>
<td>68.5</td>
</tr>
<tr>
<td>BX</td>
<td>85</td>
<td>81.5</td>
</tr>
<tr>
<td>BU1</td>
<td>42.5</td>
<td>90.0</td>
</tr>
<tr>
<td>Set 1 (SLS=5.0 g)</td>
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<td></td>
</tr>
<tr>
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<td>375</td>
<td>77.9</td>
</tr>
<tr>
<td>BA</td>
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<td>84.0</td>
</tr>
<tr>
<td>BF</td>
<td>85</td>
<td>92.1</td>
</tr>
</tbody>
</table>

A negligible increase in $x_i$, or decrease in $M_p$, with conversion within the steady-state was observed for almost all experiments. However, it should be mentioned that a very slight increase in $x_i$ is caused by the sampling from the reaction mixtures. In all experiments reported, 2-3 g of latexes was taken out at each time interval for gravimetry and PCS measurements. This introduces a very slight increase in the estimation of the rate of polymerisation which is manifested by the increase in $x_i$. Appendix E shows that if the correction is made for sampling, the increase in $x_i$ with conversion during steady states practically levels off. Apart from that, the slight increase in $x_i$ with time can be attributed to the increase in radical number with particle size. The variation of $M_p$ with conversion during steady-state period can be classified as follows:
• $M_p$ stays constant with conversion if $N_p$ and $\tilde{n}$ do not change. For such a case $x_i = R_p/R_a = 1/(R_aG + 1)$. Figure 5.3 depicts that for the set 2 the $M_p$ remained almost constant with conversion. This set is an example of a semibatch process with a short nucleation time (nucleation-free feeding stage).

• $M_p$ decreases with conversion if $\tilde{n}$ increases with conversion during the reaction. At steady state if the monomer reacts as soon as it is fed to the reactor ($R_p = R_a$), the monomer/polymer ratio in the polymerisation sites decreases considerably with time, as the polymer builds up in the reactor. This leads to a decreasing $M_p$ in the course of reaction so that $x_i < R_p/R_a$. This is the case where the radical concentration in the polymer particles remains constant with conversion, due to diffusion-controlled termination and radical desorption from the particles. Since in BA emulsion polymerisation the termination rate constant is very low, it is not further affected by the polymer concentration in the particles and it is expected to stay almost constant with conversion. If only a small increase in $\tilde{n}$ occurs in the course of reaction, it might be possible that $M_p$ shows a small decrease with conversion. Figure 5.2 shows that $M_p$ decreases slightly with conversion for the two lower feed rates. However, the decrease in $M_p$ with conversion is so low that the overall rate of polymerisations conform to equation 5.12 derived by Wesseling. The slight decrease in $M_p$ with conversion for the higher SLS concentration could be due to continuous particle formation with conversion.

• $M_p$ may increase with conversion at higher monomer feed rates if $x_i > R_p/R_a$. Any increase in $M_p$ during operation may eventually lead to a flooded state and can be expressed as a sign of deviation from the steady-state. When $M_p$ increases with time, the steady-state is unlikely to exist although the reactor still is in a monomer-starved state. The run 3 from the set 1, which was carried out at the high feed rate 385 g/h, showed a small increase with
conversion [see figure 5.2]. However, the overall rate of polymerisation could be approximated at steady-state conditions. Generally, $M_p$ is expected to remain constant or decrease with time if semibatch emulsion polymerisation reactors are to be operated at stable conditions.

It should be mentioned that an increase in the rate of polymerisation, and hence the decreasing trend of $M_p$, can be due to continuous particle nucleation in the course of reaction. For most of the experiments carried out, nucleation ceased early in the first half of the feeding time and $N_p$ remained constant afterwards.

In an attempt to present a unified view, Dimitratos et al. (1990) proposed that at a very low monomer feeding rate, the SSRR in semibatch emulsion polymerisation systems follows the relationship $R_p = R_a$. They argued that in all works reported in the literature on M add semibatch processes with $R_p = R_a$, the monomer feed rates were indeed extremely small to allow this equation to hold. However, as discussed above, for the system with constant $N_p$ and $n$, $R_p = R_a$ only if $x_i$ approaches one. The critical review of the works cited by them, shows that in no case steady-state was attained at the condition of $x_i \sim 1.0$. This suggests that the definition of "low feed rate" should be made in relation to the system under study. For polymerisation systems with a large number of particles and/or a high rate of propagation the equation $R_p = R_a$ holds for a higher range of $R_a$. It can be concluded that the variation of $x_i$ with overall conversion can be used for discrimination of different steady-state conditions in semibatch processes.

5.4.5 Pre-period time

During the pre-period time, a batch polymerisation reaction occurs in which all the initial ingredients in the reactor charge take part. The M/W ratio in the initial charge may be quite different from that in the recipe. This is a very common practice in semibatch emulsion polymerisation processes with M feed because all the recipe ingredients including emulsifier together with a small portion of monomer are placed in the initial reactor charge. In terms of particle formation, pre-period time does not
hold a major importance for the system under study. However, the importance of the pre-period time can be discussed in terms of \((M/E)\) ratio as follows:

- **\((M/E) \geq (M/E)_c\)**: Particle formation is independent of pre-period time and also feed rate. No new particle would be born during feeding since all the emulsifier micelles are fully depleted by particle formation within a short time. The set 2 which was carried out using SLS concentration of 1.25 g, clearly demonstrates this case [see figure 5.33].

- **\((M/E) < (M/E)_c\)**: For low \(M/E\), particle nucleation will mainly occur during feeding time. For this case pre-period time does not show significant effect on the number of polymer particles formed, and hence on the overall rate of polymerisation. The number of polymer particles is almost independent of pre-period time and only is dependent on the monomer feed rate. Set 11 is an example of this case. For a medium \(M/E\) ratio, but still lower than \((M/E)_c\), pre-period time might affect the polymerisation features. This is mainly dependent on the particle nucleation in the interval III of the seeding batch process. This is the case that particle nucleation strongly starts from the initial batch reaction under monomer-flooded conditions and then monomer-starved conditions (stage III of a batch process) and eventually continues to the feeding stage under monomer-starved condition. The number of polymer particles for this case is dictated by both pre-period-time and feeding rate, depending on their real values. By applying a longer pre-period time to a semibatch process with medium \(M/W\) ratio, it is possible to extend nucleation stage to the highly monomer-starved conditions and produce a larger number of polymer particles, if nucleation can occur during interval III of the seeding batch. The effect of pre-period time on the particle formation is expected to increase with monomer feed rates within the range of \((M/E) < (M/E)_c\).
The pre-period time bears a greater effect on the initial rate of polymerisation and transition time, rather than the rate of particle formation. Mathematical modelling can be easily used to quantify this classification at any particular conditions.

5.4.6 Transition time

Wesseling (1968) reported that for a seeded semibatch process \((N_p = \text{constant})\) with no initial monomer charge, the time required to reach steady state decreases with the rate of monomer addition. The transition time in a unseeded semibatch process might be quite complicated due to interaction of particle formation, monomer distribution ratio, pre-period time and monomer addition rate. Figure 5.5 shows that the transition time is shorter for the higher monomer feed rates, if pre-period time is kept short or the polymerisation rate in the seeding batch is low. This condition removes any possibility that the conversion at the end of pre-period time exceeds the steady-state value of instantaneous conversion. Since a lower steady state instantaneous conversion is established for the higher feed rates, the time required to reach the steady state is shorter. This is in contrast to the variation of transition time with feed rate in the seeded semibatch process, as originally discussed by Wesseling.

The prediction of transition time becomes complicated, if the pre-period time is rather long or the initial rate of polymerisation is high so that the steady state value of conversion can be exceeded during the seeding batch. Figure 5.4 shows such a case where the steady-state is reached sooner for the lowest monomer feed rate. This is clear because for the lower monomer initial charge a smaller amount of polymer is to be produced to reach the steady-state conversion (assuming that \(x_i\) is not much dependent on \(N_p\) at the steady-state). For any monomer addition semibatch process at a constant monomer feed rate and pre-period time, the transition time is a complex function of initial monomer charge, feed rate, pre-period time and polymerisation conditions. The steady-state can be reached earlier only if the monomer conversion at the end of pre-period time is closer to the steady-steady value. Obviously, the pre-period time which gives the appropriate conversion in the beginning of monomer feeding reduces the transition time. Any increase or decrease over this amount will produce a longer transition time compared with that of optimal one.
5.4.7 Average number of radicals per particle

The variation of $\bar{n}$ with relative time for different feed rates has been shown in figure 5.38. The data of set 2, which assimilates a seeded semibatch process where the nucleation ceases after seeding-batch and number of particles is constant, have been used for this graph. It may be concluded from the graphs that $\bar{n}$ remains almost constant during the feeding stage for all feed rates. A radical number bigger than one is obtained for all runs. The radical termination in BA emulsion polymerisation has been reported to be controlled by “diffusional termination” (Capek, 1984; Maxwell et al, 1987). This makes the termination process less sensitive to variation of polymer concentration in the polymer particles and hence $\bar{n}$ tends to remain constant for all feed rates. The horizontal line on figure 5.38 has been obtained by calculating $\bar{n}$ from the intercept of $1/R_p - 1/R_a$ curve, G, which is equal to 1.75. A very good agreement is obtained between $\bar{n}$ calculated by Wesseling’s correlation and experimental data, as shown in figure 5.38.

For the experiments using SLS concentration of 10.0 g/litre, figure 5.39 shows that $\bar{n}$ slightly varies with the feed rate. For this series of experiments, set 1, particle formation occurred during monomer feeding and hence more particles were formed for the lower feed rates. So this figure is based on a slightly different number of particles for each run, which deviates from the assumption for constant $N_p$ in Wesseling’s treatment. This causes a slight variation of $\bar{n}$ with feed rates. The line predicted by Wesseling correlation, which is based on a constant $N_p$, slightly underestimates $\bar{n}$.

Figure 5.40 shows the variation of radical numbers with overall conversion and KPS concentration for the set 9. Almost the same radical number obtained for the triple increase in the KPS concentration which is in accord to the results reported in chapter 4. The variation of radical numbers with emulsifier concentration and overall conversion is depicted in the figure 5.41 for the set 7. The radical number increased with decreasing SLS concentration. This might appear different from the results
Effect of Monomer Feed Rate

Fig. 5.38: Number average radical per particle for different monomer feed rates using 1.25 g SLS in the initial charge.

Effect of Monomer Feed Rate

Fig. 5.39: Number average radical per particle for different monomer feed rates using 5.0 g SLS in the initial charge.
Effect of Initiator Concentration

Charge, g  Feed, g

BA  50  200
DDI  500 -
Sbc - =KPS
SLS  1.25 -

M feed rate=65g/h
Pre-period=2.5 min.

Fig. 5.40: Variation in number average radical per particle with overall conversion and KPS concentration.

Effect of Emulsifier Concentration

Charge, g  Feed, g

BA  50  200
DDI  500 -
KPS  0.27 -
Sbc  0.27 -
SLS=10g/lit.aq.
SLS=2.5g/lit.aq.

M feed rate=185g/h
Pre-period=2.5 min.

Fig. 5.41: Variation in number average radical per particle with overall conversion and SLS concentration.
reported in the chapter 4 for a batch process where radical number did not vary significantly with SLS concentration. However, the larger number of particles formed for the high SLS concentration in the semibatch process, compared with that from the batch process, decreases radical capture rate appreciably so that a smaller radical number was obtained for the higher SLS concentration.

The variation of radical number with \((R/F)_M\) and relative time is shown in figure 5.42 for the set 4. This is the case that particle formation proceeds extensively during feeding stage. A larger radical number is obtained for higher \((R/F)_M\) ratio; a smaller number of polymer particles. The result obtained shows that the radical number decreases markedly with increasing the number of particles when the increase in \(N_p\) is not induced by increasing SLS or KPS concentrations (see chapter 4 for the variation of \(n\) with KPS and SLS concentrations).
CHAPTER SIX

Semibatch Emulsion Homopolymerisation of Butyl Acrylate With Monomer Emulsion Feed

6.1 INTRODUCTION

In a semibatch process with neat monomer feed, usually a primary nucleation could take place in the initial stage of reaction. The particle size distribution (PSD) of latexes from this process is usually monomodal which could be broad or sharp, depending on the polymerisation conditions. A number of emulsifier addition methods, such as shot-addition or varying feed rate addition, may be used to tailor make the latex with desired PSD. However, in a semibatch process with a standard monomer emulsion feed, constant feed rate and feed composition, the PSD of the final latexes is not very disperse and can be systematically studied. Unlike the semibatch process with monomer feed, it is possible to have secondary nucleations in semibatch processes with monomer emulsion feed if suitable conditions exist. The main aim of this series of experiments was to study particle nucleation at the conditions where secondary nucleation is probable. This was achieved by using no emulsifier in the initial charge for some experiments. Such a policy hereafter will be called “base conditions”. No monomer charge was also used for most of the experiments. The effects of variation in emulsifier, initiator, and monomer distribution ratios between the initial charge and the monomer emulsion feed on the kinetics features of polymerisation were investigated. The recipe used for semibatch reactions with monomer emulsion feed are listed in table 6.1. The following variables were investigated for monomer emulsion addition mode. All distribution ratios are based on the amount of the corresponding component in the initial charge to that in the whole recipe.
**Feed rate:** Three monomer feed rates were chosen for all experiments as 42.5, 85.0, and 185.0 g/h. These correspond to 354, 159, and 81 minutes feed times, respectively if no monomer is initially present in the reactor charge.

**Overall concentration of emulsifier:** Three amounts of emulsifier were used in all experiments as 2.50, 5.0, and 10 g/litre. These correspond to 2, 1, and 0.50 wt % based on the total amount of monomer in the charge and the feed.

**Overall concentration of initiator:** Two amounts of initiator were used as 0.5406 and 1.0812 g/litre (aq.) \([2 \times 10^{-3} \text{ and } 4 \times 10^{-3} \text{ mol/litre}].\)

**Monomer Distribution ratio:** Most of the experiments were carried out using no initial monomer charge. An experiment was carried out with 10 wt % of monomer in the initial charge.

**Emulsifier distribution ratio:** Four different emulsifier distribution ratios were used as 0, 20, 50, and 75 wt % (the amount in the initial charge to that in whole recipe).

**Initiator distribution ratio:** The 20, and 40 wt % distribution ratios were used.

### Table 6.1: Recipe used for semibatch emulsion polymerisation of BA with ME feed.

<table>
<thead>
<tr>
<th>Runs</th>
<th>Feed Charge, g</th>
<th>Feed , g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed rate</td>
<td>BA DDI SLS KPS SBe</td>
</tr>
<tr>
<td>1</td>
<td>BBF 42.5</td>
<td>250 400 5 0.216 0.216</td>
</tr>
<tr>
<td>2</td>
<td>BH 85</td>
<td>250 400 5 0.216 0.216</td>
</tr>
<tr>
<td>3</td>
<td>BK(1) 185</td>
<td>250 400 5 0.216 0.216</td>
</tr>
<tr>
<td>4</td>
<td>BF(2) 85</td>
<td>250 400 5 0.216 0.216</td>
</tr>
<tr>
<td>5</td>
<td>BBD 185</td>
<td>250 400 5 0.162 0.162</td>
</tr>
<tr>
<td>6</td>
<td>BBC 185</td>
<td>250 400 5 0.433 0.433</td>
</tr>
<tr>
<td>7</td>
<td>BM 185</td>
<td>250 400 4 0.216 0.216</td>
</tr>
<tr>
<td>8</td>
<td>BN 185</td>
<td>250 400 4 0.216 0.216</td>
</tr>
<tr>
<td>9</td>
<td>BO 185</td>
<td>250 400 1.25 0.216 0.216</td>
</tr>
<tr>
<td>10</td>
<td>BS(1) 185</td>
<td>250 400 1.25 0.216 0.216</td>
</tr>
<tr>
<td>11</td>
<td>BR 185</td>
<td>250 400 1.0 0.216 0.216</td>
</tr>
<tr>
<td>12</td>
<td>BP 185</td>
<td>250 400 0.625 0.216 0.216</td>
</tr>
<tr>
<td>13</td>
<td>BQ 185</td>
<td>250 400 0.325 0.216 0.216</td>
</tr>
<tr>
<td>14</td>
<td>BT 185</td>
<td>250 400 2.50 0.216 0.216</td>
</tr>
<tr>
<td>15</td>
<td>BW 185</td>
<td>250 400 4.0 0.216 0.216</td>
</tr>
</tbody>
</table>

(1): Experiments 3 and 10 repeated two and three times, respectively.
(2): All Experiments except experiment 4 were carried out at 50 °C. The experiment 4 was carried out at temperature 70 °C.
In the series with monomer emulsion feed some parts of monomer, as well as DDI, KPS, BSc, and SLS, were placed in the initial charge (see chapter 3). The remaining ingredients were fed to the reactor at the predetermined rates in two streamlines. In all experiments the first streamline only consisted monomer. The second streamline contained the aqueous solution of SLS, KPS, and SBe. The final solid content for all polymerisation was 33.3 wt %. All feed rates presented are based on the monomer content of the emulsion feeds. Particle size measurements by TEM have been carried out using micrographs of samples which some of them are given in Appendix G.

6.2 BACKGROUND

Semibatch emulsion polymerisation processes with monomer emulsion feed have been studied by a few researchers. A comprehensive review on their works is given in the chapter 2 and it is not repeated here (see sections 2.5.2, 2.5.4.2.2 and 2.5.5).

6.3 RESULTS

6.3.1 Effect of feed rate

In this series of experiments, 20% of all ingredients except monomer were initially charged to the reactor. The balance of components and all monomers and SLS were fed to the reactor using different feed rates. The initial KPS in the precharge was added to the reactor 10 minutes before feeding started.

Rate of polymerisation: Figure 6.1 presents the effect of feed rate on the time evolution of monomer fed, polymer formed and free monomer for BA semibatch process. In the early stage of reaction, monomer accumulates in the reactor. In a semibatch process with ME feed if no emulsifier and monomer are present in the initial reactor charge, polymerisation reaction might not start from the beginning of feeding and some delay occurs for the reactions to start. The initial rate of reaction is low and most of the monomer accumulates in the reactor. The rate of monomer accumulation in the reactor is highly dependent on the number of particles formed and might increase or decrease with feed rates. At the intermediate monomer feed rate
85.0 g/h (based on monomer), a rather constant rate of polymerisation was observed from the beginning. While for the lowest monomer feed rate 42.5 g/h, a gradual increase in the initial rate of polymerisation was obtained. *Figure 6.2* shows the variation in $M_p$ with relative time for the three different feed rates. The "relative time" is defined as the ratio of the time after beginning of the feeding over the overall feeding time. Then a relative time equal to "one" demonstrates the end of feeding and beginning of finishing batch. For the two lowest feed rates, $M_p$ falls below saturation level early in the reaction and shows a continuous decrease with time, while for the run with $R_a = 185.0$ g/h, monomer-flooded conditions were attained and $M_p$ remained at saturation value up to the later stage of feeding.

**Particle nucleation:** *Figure 6.3* shows the time evolution of the total number of polymer particles in the reactor during polymerisation reactions carried out using several feed rates. A larger number of polymer particles was obtained for the higher rate of monomer emulsion feed. As the monomer emulsion is fed into the reactor, the particle nucleation starts by depletion of emulsifier molecules in the reactor.

*Figure 6.4* shows the variation of surface tension with relative time for different feed rates. Initially surface tension of the reaction mixtures is high, since there is no emulsifier in the reactor charge. As the monomer emulsion is fed to the reactor, the surface tension rapidly decreases to CMC value and then increases as most of the emulsifier molecules are adsorbed on the growing particles. The relative time that surface tension of the reaction mixture remains at CMC value is longer for the higher feed rate, indicating a longer period of micellar nucleation. For all feed rates the surface tension in the later stage of reaction remained slightly above that at CMC value within 30-40 dyne/cm, depending on the monomer emulsion feed rate. The polymer particles appeared to be generated in some intervals of the reaction. *Figure 6.5* shows the variation of surface coverage ratio with relative time. The measurement of covering area of surfactant is explained in *appendix C*. The particle surface coverage ratio passes through a minima in the early stage of the reaction and then increases gradually afterwards as more emulsifier is added to the reactor.
**Effect of Monomer Emulsion Feed Rate**

![Graph showing the effect of monomer emulsion feed rate on various polymer properties](image)

Fig. 6.1: The time evolution of polymer formed (filled symbols), BA fed (dashed line), and unreacted BA (empty symbols) for three different emulsion feed rates.

**Effect of Monomer Emulsion Feed Rate**

![Graph showing the time variations in monomer concentration](image)

Fig. 6.2: The time variations in monomer concentration in the polymer particles for different monomer emulsion feed rates.
Effect of Monomer Emulsion Feed Rate

Fig. 6.3: Particle numbers versus relative time for different monomer emulsion feed rates.

Effect of Monomer Emulsion Feed Rate

Fig. 6.4: Surface tension versus relative time for different monomer emulsion feed rates.
The particle size distributions of final latexes are shown in figure 6.6. The corresponding micrographs are shown in figure G.1 of appendix G. Distinct bimodal distributions are observed for final particles from all feed rates. The second peaks at the higher size are indicative of particle nucleation in the beginning of feeding or primary nucleation. The first peak at the lower size represents secondary particle nucleation. The bimodal distributions can be represented as the sum of the two monomodal distributions if the diameters about which measured values are grouped are quite different. This could be done for some of the PSDs obtained in this research work. The particle size averages and polydispersities are given in table 6.2. The PDI for monomer-starved semibatch process with ME feed decreases with the increasing feeding rate. Figure 6.7 shows the evolution of a bimodal PSD for the latex from the experiment using the lowest feed rate. The corresponding micrographs are presented in figure G.2. The monomodal PSD of the latex at the initial stage of the reaction is gradually converted to a bimodal PSD in the course of reaction. Figures 6.8-9 compare the PSDs of the different latexes. The colloidal properties of latexes from all three feed rates are given in table 6.2. This table demonstrates the variation of PSD with monomer emulsion feed rates.
Fig. 6.6: PSD of final latexes for different monomer feed rates; a) 185 g/h, b) 85 g/h, c) 42.5 g/h (see also the corresponding micrographs in fig. G.2).
Fig. 6.7: PSD evolution for BA semibatch emulsion polymerisation using Rα = 42.5 g/h (For the PSD of the final latex see fig. 6.6.c, see also fig. 6.2 for the corresponding micrographs).
Effect of Monomer Emulsion Feed Rate

Fig. 6.8: The PSD curves for final latexes with different feed rates.

PSD Time Evolution

Fig. 6.9: The time evolution of PSD for the run using Ra = 42.5 g/h (Rt = relative time).
Table 6.2: Number (Dn), weight (Dw), volume (Dv), intensity (Dl) average diameters and PDI obtained by calibrated TEM and average diameter (D,) obtained by PCS of final latexes for different feed rates.

<table>
<thead>
<tr>
<th>Run</th>
<th>Feed rate g/h</th>
<th>PCS nm</th>
<th>Overall Peak</th>
<th>SEM, nm</th>
<th>Primary peak</th>
<th>Secondary peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Dn</td>
<td>Dv</td>
<td>Dw</td>
<td>Dl</td>
<td>Dn</td>
</tr>
<tr>
<td>BK</td>
<td>185.0</td>
<td>213</td>
<td>156 196 170 209 255 206 262 1.36</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BH</td>
<td>85.0</td>
<td>289</td>
<td>181 246 206 262 255 266 1.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BBF</td>
<td>42.50</td>
<td>255</td>
<td>183 254 208 276 296 300 1.01</td>
<td>153 180 1.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BBF17</td>
<td>42.50</td>
<td>220</td>
<td>173 246 201 260 255 265 1.04</td>
<td>119 151 1.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BBF13</td>
<td>42.50</td>
<td>206</td>
<td>173 207 214 213 206 212 1.03</td>
<td>99 116 1.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BBF9</td>
<td>42.50</td>
<td>163</td>
<td>168 178 173 179 1.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: Samples BBF9, BBF13, and BBF17 are those analysed from the run BBF at the different feeding time. The overall conversion for these samples are 13.5, 31.2 and 50.3 %. The final overall conversion for this run is 88.2 %.

6.3.2 Effect of emulsifier concentration

In this set of experiments, the effect of overall emulsifier concentration on the polymerisation features was investigated. All runs were essentially similar in that they did not use emulsifier and monomer in the initial reactor charge. These are runs BG, BT, and BS from table 6.1. The monomer feed rate was kept constant at 185 g/h for all runs.

Rate of polymerisation: Figure 6.10 shows the time evolution of overall conversion for polymerisations carried out using three different overall emulsifier concentrations. Inhibition periods were observed for almost all runs which increased with decreasing emulsifier concentration in the feed. A rather long inhibition period for the run BS with the lowest SLS concentration caused an accumulation of a large amount of emulsifier in the reactor which resulted in a nucleation of a large number of polymer particles. Hence, the results obtained for this experiment can not be taken into accounts for comparative study and is presented here only to highlight the effect of inhibition period on the kinetic features. This particular experiment which was repeated 3 times will be discussed later. The results obtained showed a higher rate of polymerisation for the larger SLS concentration in the feed. Figure 6.10 shows that for all three runs primary particle nucleation occurred at monomer-flooded conditions.
**Particle nucleation:** Figure 6.11 shows the variation of number of particles with relative time for the three different SLS concentrations in the feed. For SLS = 10 g/litre particle nucleation almost continuously occurs, while for SLS = 5.0 g/litre particle nucleation occurred at two time intervals which will be discussed later. For SLS = 2.5 g/litre, a greater number of polymer particles was formed than what was expected which stemmed from accumulation of emulsifier due to long inhibition period. Figure 6.12 compares the variation of surface tension with progress of reaction for different SLS concentrations in the feed. A higher steady-state surface tension was established in the course of reaction if lower SLS concentration was used in the feed. For the medium SLS concentration, 5.0 g/litre, after initial sharp drop, surface tension increases sharply and the number of polymer particles seems to increase afterwards. At high SLS concentration (SLS = 10 g/lit), the surface tension almost remains close to that of CMC value in the course of reaction, indicating that particle nucleation could continuously occur.

**Table 6.3:** Number ($D_n$), weight ($D_w$), volume ($D_v$), intensity ($D_l$) average diameters and PDI obtained by calibrated TEM and average diameter ($D_p$) obtained by PCS of final latexes for different overall SLS concentrations.

<table>
<thead>
<tr>
<th>Run</th>
<th>SLS Conc.</th>
<th>PCS nm</th>
<th>SEM, nm</th>
<th>Primary peak</th>
<th>Secondary peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/litre</td>
<td>D_u</td>
<td>D_v</td>
<td>D_l</td>
<td>D_u D_v D_l PDI</td>
</tr>
<tr>
<td>BK</td>
<td>10.0</td>
<td>213</td>
<td>156 196 170 209</td>
<td>1.25</td>
<td>- - - - - - - -</td>
</tr>
<tr>
<td>BT</td>
<td>5.0</td>
<td>253</td>
<td>151 251 188 268</td>
<td>1.67</td>
<td>263 272 1.03 103 134 135</td>
</tr>
<tr>
<td>BS</td>
<td>2.50</td>
<td>223</td>
<td>207 217 212 220</td>
<td>1.05</td>
<td>- - - - - - - -</td>
</tr>
<tr>
<td>BS2</td>
<td>2.50</td>
<td>268</td>
<td>288 311 297 318</td>
<td>1.08</td>
<td>- - - - - - - -</td>
</tr>
</tbody>
</table>

*Note:* The run BS2 is the re-run of BS with some difference. Due to a very small secondary peak for the run BS2, bimodal analysis was not carried out for this run. The final conversion for the run BS2 is 55.0%.

**Figure 6.13** shows that when a large concentration of SLS was used, the surface coverage ratio approached one again late in the reaction. For the two lower SLS concentrations particle surface coverage by emulsifier dropped early in the reaction from full coverage and then stayed at a constant level with the progress of reaction. **Figures 6.14-15** show the particle size distribution of final latexes. The corresponding micrographs are shown in figure G.3 of appendix G. The particle size averages and polydispersities are given in table 6.3. For the preparation of these graphs the PSD of the latex using 2.50 g/litre SLS was obtained from the re-run of experiment BS, BS2, which was conducted at specific conditions as will be explained later. Bimodal particle size distributions were found for almost all SLS concentrations. It should be
Effect of Overall SLS Concentration

Fig. 6.10: Time evolution of overall conversion (filled symbols) and instantaneous conversion (empty symbols) for different overall emulsifier concentrations.

Fig. 6.11: Number of particles versus relative time for different overall emulsifier concentrations.
Effect of Overall SLS Concentration

Fig. 6.12: Surface tension versus relative time for different overall emulsifier concentrations in the feed and no emulsifier in the charge.

Effect of Overall SLS concentration

Fig. 6.13: Surface coverage ratio versus relative time for different overall emulsifier concentrations and no emulsifier in the charge.
Effect of Overall SLS Concentration

Fig. 6.14: PSD of final latexes for different overall emulsifier concentrations; a) 10.0 g/litre, b) 5.0 g/litre, c) 2.50 g/litre. See also fig. G.3 for the corresponding micrographs.
noted that experiment BS using 2.50 g/litre SLS concentration produced a monomodal distribution, due to an inhibition effect. The PSD curve presented here in figures 6.14-15 is that from the re-run of experiment BS, BS2, which was carried out using a specific procedure as will be discussed later.

6.3.3 Effect of monomer distribution

An experiment, BW, was carried out to study the effect of \((R/F)_M\) on the kinetic features. For this run 20\% of monomer, SLS, KPS, SBc, and DD! were initially charged to the reactor. The balance of components were fed to the reactor at a constant rate of 185 g/h. The results from this run was compared with that with no initial monomer charge (run BM).

*Rate of polymerisation: Figure 6.16 compares the time evolution of conversions for the two monomer distribution ratios \((R/F)_M =10\) and 0.0 wt \%. A higher initial rate of polymerisation was obtained for \((R/F)_M = 10\) wt \% compared with that from \((R/F)_M = 0.0\) wt \%. The steady-state rate of polymerisation (SSRP) slightly increased with decreasing monomer charge.*
Chapter Six

**Particle nucleation**: Figure 6.17 depicts the variation of number of particles with overall conversion. The presence of monomer in the initial charge led to the formation of a smaller number of particles. Particle nucleation occurred at monomer-flooded conditions for the run with monomer charge. The variation of surface tension with conversion is shown in figure 6.18. A rather steep increase in the surface tension is observed if no monomer is present in the initial reactor charge.

Table 6.4: Number ($D_n$), weight ($D_w$), volume ($D_v$), intensity ($D_i$) average diameters and PDI obtained by calibrated TEM and average diameter ($D_0$) obtained by PCS of final latexes for different monomer distribution ratio.

<table>
<thead>
<tr>
<th>Run (R/F)$_M$</th>
<th>PCS nm</th>
<th>Overall Peak $D_n$</th>
<th>SEM $D_0$ nm</th>
<th>Primary peak $D_n$</th>
<th>Secondary peak $D_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$D_{w}$ $D_{v}$ $D_{i}$</td>
<td></td>
<td>$D_{w}$ $D_{v}$</td>
<td>$D_{w}$ $D_{v}$</td>
</tr>
<tr>
<td>BM 0</td>
<td>153</td>
<td>112 131 119 137 1.17</td>
<td>- - -</td>
<td>- - -</td>
<td>- - -</td>
</tr>
<tr>
<td>BW 10</td>
<td>205</td>
<td>137 202 164 211 1.48</td>
<td>201 209 1.04</td>
<td>74 83 1.12</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6.19 reveals that the surface coverage ratio of particles for the reaction using initial monomer charge drops to a low value and then approaches the saturation value at the end of reaction, while it stays practically constant for the run with no initial monomer charge. Such a trend is more obvious if the size correction for both experiments are carried out using the same factor, as discussed in appendix E and shown on the small graph of figure 6.19. Particle size distributions for latexes are shown in figure 6.20. The corresponding micrographs are shown in figure G.4 of appendix G. The PSD curve indicates that secondary nucleation occurred and a broader PSD was obtained for the run with initial monomer charge. The particle size averages and polydispersities are given in table 6.4. The formation of secondary particles for the run with monomer charge is supported by the figure 6.18 which shows that surface tension levels off early in the reaction and shows a slight decrease in the later stage of the reaction. The variations of surface tension with time corroborates with particle formation trend.
Effect of Monomer Distribution Ratio

Fig. 6.16: Time evolution of overall (filled symbols) and instantaneous (empty symbols) conversions for different monomer distribution ratios (R/F)m.

Effect of Monomer Distribution Ratio

Fig. 6.17: Number of particles versus overall conversion for different monomer distribution ratios (R/F)m.
Effect of Monomer Distribution Ratio

Fig. 6.18: Surface tension versus overall conversion for different monomer distribution ratios (R/F)m.

Fig. 6.19: Surface coverage ratio versus overall conversion for different monomer distribution ratios (R/F)m (The small figure shows the variations when the same correction factor, 1.10, is applied for both runs).
Fig. 6.20: The PSD curves for latexes with different monomer concentrations in the feed and 1.0 g SLS in the initial charge; a) (R/F)m = 10%, b) (R/F)m = 0%, c) both together (for corresponding micrographs see fig. G.4).
6.3.4 Effect of emulsifier distribution

The effect of emulsifier distribution between initial charge and the feed, $(R/F)_E$, on the course of reaction has been studied at two overall emulsifier concentrations, 2.50 and 10 g/litre. In these series of experiments the initial emulsifier loading was kept at 0, 20, 50, and 75 wt % of overall emulsifier concentration. The remaining emulsifier was fed to the reactor at a constant flow rate of 185 g/h (based on the monomer).

*Rate of polymerisation:* The conversion-time curves are shown in figures 6.21-24. For the higher SLS concentration, most of the reactions were carried out at monomer-starved conditions, while for the lower SLS concentration, most of the reactions proceeded at monomer flooded conditions. The steady-state rate of reaction was only achieved for a few reactions which will be discussed later.

*Particle nucleation:* Figures 6.25 and 6.26 show the time evolution of polymer particles formed at various $(R/F)_E$ ratios for overall emulsifier concentration of 10 and 2.5 g/litre, respectively. For all runs carried out using SLS concentration of 10 g/litre, an initial sharp increase in the number of particles was observed. The higher the $(R/F)_E$ ratio, the longer the initial nucleation period. The rate of nucleation slowed down after this stage. For the $(R/F)_E = 0$ and 20 wt %, nucleation continued up to high conversion. While, for the high $(R/F)_E$ ratios, nucleation ceased almost around medium conversion. The results obtained show that for SLS = 10 g/litre, primary particle nucleation occurred at distinctly monomer-starved conditions for all $(R/F)_E$ ratios but the $(R/F)_E = 0.0$. For experiments using 2.50 g/litre SLS, primary nucleation occurred at monomer-starved conditions for the two highest $(R/F)_E$ ratios.

Figures 6.27 and 6.28 show the variation in surface tension with the progress of the reaction for the two series. A distinct curve was obtained for SLS = 10 g/litre when no emulsifier was initially placed in the reactor, as discussed before. Despite the different number of polymer particles formed by using various emulsifier distribution ratios, all surface tension-time curves followed almost the same trend specially for the lower overall SLS concentrations used. Figure 6.29 shows that for SLS concentration of 10 g/litre as $(R/F)_E$ increases, particle surface coverage ratio decreases during the feeding,
indicating that secondary nucleation has less chance to occur. For the SLS concentration of 2.50 g/litre, particles were found to be less covered by emulsifier molecule (not shown).

Table 6.5: Number($D_\text{a}$), weight($D_\text{w}$), volume($D_\text{v}$), intensity ($D_\text{I}$) average diameters and PDI obtained by calibrated TEM and average diameter ($D_\text{a}$) obtained by PCS of final latexes for different emulsifier distribution ratios.

<table>
<thead>
<tr>
<th>Run</th>
<th>$(R/F)_E$</th>
<th>$X_e$</th>
<th>Viscosity</th>
<th>PCS $nm$</th>
<th>SEM $nm$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>mPa.s</td>
<td>$D_a$</td>
<td>$D_w$</td>
</tr>
<tr>
<td>SLS = 10 g/litre</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BK</td>
<td>0</td>
<td>89</td>
<td>44.1</td>
<td>213</td>
<td>156</td>
</tr>
<tr>
<td>BM</td>
<td>20</td>
<td>95</td>
<td>59.0</td>
<td>153</td>
<td>112</td>
</tr>
<tr>
<td>BN</td>
<td>50</td>
<td>89</td>
<td>69.4</td>
<td>136</td>
<td>112</td>
</tr>
<tr>
<td>BO</td>
<td>75</td>
<td>98</td>
<td>82.2</td>
<td>134</td>
<td>83</td>
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<td>SLS = 2.50 g/litre</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>BP</td>
<td>20</td>
<td>93</td>
<td>35.6</td>
<td>256</td>
<td>211</td>
</tr>
<tr>
<td>BQ</td>
<td>50</td>
<td>94</td>
<td>43.5</td>
<td>226</td>
<td>212</td>
</tr>
<tr>
<td>BR</td>
<td>75</td>
<td>87</td>
<td>43.6</td>
<td>180</td>
<td>151</td>
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</tbody>
</table>

Figures 6.30-31 shows the PSD of final latexes for the experiments of both series. The corresponding micrographs are presented in the figures G.5-6 of appendix G. The PSDs of series have been grouped in figures 6.32-33. Table 6.5 details the average particle sizes and distributions. The variation of PDI of final latexes with $(R/F)_E$ ratios show a minimum at a medium $(R/F)_E$ ratio for both overall SLS concentrations. A bimodal distribution curve was obtained for $(R/F)_E = 0$ at SLS concentration of 10 g/litre which has been explained before. For $(R/F)_E = 20 \%$, the number distribution curve skewed toward small particle sizes which is indicative of long nucleation period. A normal distribution was observed for $(R/F)_E = 50 \%$. For $(R/F)_E = 75 \%$ the distribution curve slightly skewed toward large particle sizes. For overall emulsifier concentration of 2.50 g/litre, shorter initial nucleation periods and no or little secondary nucleation were observed for all $(R/F)_E$ ratios studied. Table 6.5 shows that for both overall SLS concentrations studied, the viscosity of final latexes increased with $(R/F)_E$ ratio. The experimental procedure for viscosity measurements is given in appendix D.
Effect of SLS Distribution Ratio

Fig. 6.21: Time evolution of overall conversion for different emulsifier distribution ratios \((R/F)e\), using 10 g/litre SLS.

Fig. 6.22: Time evolution of instantaneous conversion for different emulsifier distribution ratios \((R/F)e\), using 10 g/litre SLS.
Effect of SLS Distribution Ratio

<table>
<thead>
<tr>
<th>Emulsifier</th>
<th>Charge, g</th>
<th>Feed, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA</td>
<td>0</td>
<td>250</td>
</tr>
<tr>
<td>DDI</td>
<td>100</td>
<td>400</td>
</tr>
<tr>
<td>KPS</td>
<td>0.054</td>
<td>0.216</td>
</tr>
<tr>
<td>SBc</td>
<td>0.054</td>
<td>0.216</td>
</tr>
</tbody>
</table>

SLS=2.5 g/litre, Ra = 185 g/h

Effect of SLS Distribution Ratio

Fig. 6.23: Time evolution of overall conversion for different emulsifier distribution ratio (R/F)e, using 2.5 g/litre SLS.

Effect of SLS Distribution Ratio

<table>
<thead>
<tr>
<th>Emulsifier</th>
<th>Charge, g</th>
<th>Feed, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA</td>
<td>0</td>
<td>250</td>
</tr>
<tr>
<td>DDI</td>
<td>100</td>
<td>400</td>
</tr>
<tr>
<td>KPS</td>
<td>0.054</td>
<td>0.216</td>
</tr>
<tr>
<td>SBc</td>
<td>0.054</td>
<td>0.216</td>
</tr>
</tbody>
</table>

SLS=2.5 g/litre, Ra = 185 g/h

Effect of SLS Distribution Ratio

Fig. 6.24: Time evolution of instantaneous conversion for different emulsifier distribution ratios (R/F)e, using 2.5 g/litre SLS.
Effect of SLS Distribution Ratio

![Graph](image)

Fig. 6.25: Number of polymer particles versus relative time for different emulsifier distribution ratios $(R/F)_e$ using SLS concentration of 10.0 g/litre.

Effect of SLS Distribution Ratio

![Graph](image)

Fig. 6.26: Number of particles versus relative time for different emulsifier distribution ratios $(R/F)_e$ using SLS concentration of 2.50 g/litre.

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Effect of SLS Distribution Ratio

Fig. 6.27: Evolution of surface tension with relative time for different emulsifier distribution ratios at SLS concentration of 10.0 g/litre.

Fig. 6.28: Evolution of surface tension with relative time for different emulsifier distribution ratios at SLS concentration of 2.50 g/litre.

Fig. 6.29: Particle surface coverage ratio versus relative time for different emulsifier distribution ratios at SLS concentration of 10.0 g/litre.
Fig. 6.30: PSD of final latexes for different emulsifier distribution ratios using 10 g/litre SLS conc.; (R/F)e = a) 0 %, b) 20 %, c) 50 %, d) 75 %. For corresponding micrographs, see fig. G.5 from appendix G.
Fig. 6.31: PSD of final latexes for different emulsifier distribution ratios using 2.50 g/litre SLS concentration; (R/F)e = a) 20 %, b) 50 %, c) 75 %. For corresponding micrographs, see fig.G.6 from appendix G.
Effect of SLS Distribution Ratio

Fig.6.32: The PSD curves for latexes with different SLS distribution ratios using SLS overall concentration of 10.0 g/litre.

Effect of SLS Distribution Ratio

Fig.6.33: The PSD curves for latexes with different SLS distribution ratios using SLS overall concentration of 2.50 g/litre.
6.3.5 Effect of overall initiator concentration and its distribution

In this series of experiments the effect of overall initiator concentration and its distribution between the charge and the feed was studied. The experiments were conducted at standard (base) conditions. In one experiment the initiator concentration in the charge and the feed was doubled, while the other variables were fixed. In the second experiment the initiator concentration in the charge was doubled, while the overall initiator concentration was kept constant at 0.54 g/l. No emulsifier was placed in the reactor charge for all three experiments.

Polymerisation rate: Figure 6.34 shows the time evolution of conversions. A slight increase in the rate of polymerisation was observed when overall initiator concentration was doubled. The polymerisations were carried out virtually at monomer-flooded conditions for all runs since instantaneous conversion did not exceed 0.45 during the feeding which is the conversion in the beginning of interval III of a batch or monomer-starved semibatch process.

Particle nucleation: Figure 6.35 shows the evolution of number of particles with the relative time. Figure 6.36 shows that surface tension variation with time for all three runs follow the same trend; initial drop and then increase due to primary nucleation, and finally slowly decreasing with time. The variation in surface coverage ratio with relative time is given in figure 6.37. PSD data are given in the figures 6.38-39 and the table 6.6. The corresponding micrographs are shown in figures G.7. For the base experiment (the lower initiator concentration, run BK), a distinct bimodal particle size distribution was obtained. For the reaction with the twice initial initiator charge but the same overall initiator concentration, run BBD, a larger number of particles were nucleated early in the reaction, compared with base run. A distinct bimodal PSD was obtained in which the first peak shrank and the second peak expanded, compared with the base experiment. This shows that initiator concentration in the feed effectively contributes to the nucleation process. A sharper increase in the number of polymer particles in the initial stage and finally a larger number of polymer particles was observed for twice the initiator concentration in the charge and the feed, compared
Effect of KPS Conc. and Distribution

Fig. 6.34: Time evolution of overall (filled symbols) and instantaneous (empty symbols) conversions for different initiator concentrations and distribution ratios.

Effect of KPS Conc. and Distribution

Fig. 6.35: Number of polymer particles versus relative time for different initiator concentrations and distribution ratios.
Fig. 6.36: Evolution of surface tension versus relative time for different initiator concentrations and distribution ratios.

Fig. 6.37: Surface coverage versus relative time for different initiator concentrations and distribution ratios.
Fig. 6.38: PSD of final latexes for different initiator concentrations and distribution ratios using 10 g/litre SLS concentration, a) KPS = 0.27 g, (R/F)i = 20%; b) KPS = 0.27 g, (R/F)i = 40%; c) KPS = 0.54 g, (R/F)i = 20%. For corresponding micrographs, see fig. G.7 from appendix G.
Table 6.6. Number \((D_n)\), weight \((D_w)\), volume \((D_v)\), intensity \((D_i)\) average diameters and PDI obtained by calibrated TEM and average diameter \((D_i)\) obtained by PCS of final latexes for different initiator concentrations and distributions, and temperatures.

<table>
<thead>
<tr>
<th>Run</th>
<th>KPS</th>
<th>((R/F)_{h} )</th>
<th>Temp. (^{\circ}C)</th>
<th>(X_r)</th>
<th>PCS nm</th>
<th>SEM nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(g)</td>
<td>%</td>
<td></td>
<td>(D_n)</td>
<td>(D_w)</td>
</tr>
<tr>
<td>(R_a = 185) g/h</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BK</td>
<td>0.27</td>
<td>20</td>
<td>50</td>
<td>89.0</td>
<td>213</td>
<td>156</td>
</tr>
<tr>
<td>BBD</td>
<td>0.27</td>
<td>40</td>
<td>50</td>
<td>85.0</td>
<td>207</td>
<td>155</td>
</tr>
<tr>
<td>BBC</td>
<td>0.54</td>
<td>20</td>
<td>50</td>
<td>88.0</td>
<td>179</td>
<td>156</td>
</tr>
<tr>
<td>(R_a = 85) g/h</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BH</td>
<td>0.27</td>
<td>20</td>
<td>50</td>
<td>0.94</td>
<td>284</td>
<td>181</td>
</tr>
<tr>
<td>BI</td>
<td>0.27</td>
<td>20</td>
<td>70</td>
<td>0.95</td>
<td>124</td>
<td>102</td>
</tr>
</tbody>
</table>

with the other two. Secondary nucleation occurred at a low extend. As a result a monomodal PSD with a skewness toward small sizes was obtained.

Fig. 6.39: The PSD curves for latexes with different KPS overall concentrations and distribution ratios.
6.3.6 Effect of Temperature

Effect of temperature has been investigated by carrying out the experiment BI at the higher temperature, 70 °C. No initial emulsifier was used in the initial charge. Monomer emulsion feed rate of 85 g/h, based on monomer, was used. The results obtained were compared with those from run BI which was carried out at the same conditions, but at the lower temperature of 50 °C.

**Polymerisation rate:** Figure 6.40 shows the time evolution of conversions for experiments carried out at two temperature 50, and 70 °C. The overall rate of polymerisation increased with temperature, as was expected. For the run using the higher temperature, the rate of polymerisation reached the steady-state early in the reaction. The overall rate of polymerisation for both runs converged at the later stage of the reactions.

**Particle formation:** Figure 6.41 depicts the variation of $N_p$ with relative time. A much larger number of particles is obtained for the higher temperature, as was expected. The PSD curves of the final latexes is shown in figure 6.42. A bimodal PSD was obtained from the final latexes at low temperature 50 °C, while a rather broad monomodal PSD was obtained for the higher temperature 70 °C. This indicates that at a higher temperature the possibility of secondary nucleation decreases. Figure 6.43 confirms that for the higher temperature, surface tension stabilised at a higher value which accounts for less amount of secondary nucleation.
Effect of Temperature

Fig. 6.40: Time evolution of overall (filled symbols) and instantaneous (empty symbols) conversions for different reaction temperatures.

Fig. 6.41: Number of polymer particles versus relative time for different reaction temperatures.
Effect of Temperature

**Fig. 6.42:** The PSD curves for the final latexes prepared at different temperatures.

**Fig. 6.43:** Evolution of surface tension with relative time for different reaction temperatures.

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6.3.7 Effect of Inhibition period

In order to investigate the effect of inhibition on the kinetic features of BA semibatch emulsion polymerisation, runs 4 and 10 from table 6.1 have been repeated once and twice, respectively. These are the runs with a high and a low emulsifier concentrations in the feed. In both of these runs, no initial monomer and no emulsifier charge was used. The reproducibility of the run with high emulsifier concentration was found to be satisfactory and the results are not given here. The reproducibility result for the run 10, BS, are given in figures 6.44-46 for the time evolution of overall conversion, number of polymer particles, and surface tension. The duplicate run was labelled BS1.

The lower the inhibition time, the smaller the number of particles. The polymerisation starts earlier for the lower inhibition time, but soon it falls behind of that for the higher inhibition time. In order to assimilate the run with low inhibition time which can be used for comparative study with the experiments using higher SLS concentration as BK and BT, a third run, labelled BS2, was carried out by stopping the feeding after 3.0 minutes from the beginning. As soon as the reaction started, the monomer feeding was activated again. As it is depicted in figures 6.44-45, a much smaller number of particles and rate of polymerisation were obtained for this short-inhibition period experiment, compared with the other two. This will be discussed later.

![Graph](image-url)

**Fig. 6.44:** Time evolution of overall conversion for three similar runs for the conditions susceptible to inhibition period.
Fig. 6.45: Number of polymer particles versus relative time for the three runs conducted using the same formulation.

Effect of Inhibition Period

![Graph showing the number of polymer particles versus relative time for the three runs conducted using the same formulation.](image)

Fig. 6.46: Variation in surface tension with relative time for the three runs conducted using the same formulation.
6.4 DISCUSSION

6.4.1 Rate of polymerisation

6.4.1.1 The steady state rate of polymerisation

The steady state rate of polymerisation was only established if the initial rate of polymerisation was rather high. This was achieved by using either a high SLS concentration (10 g/litre) or a low SLS concentration (2.50 g/litre) with high (R/F)_E ratio. The following experiments gave steady-state conditions; BH, BBF, BM, BN, BO, BW, BP, and BQ. For the runs BH, BBF, and BI steady state was reached so that \( R_p = R_a \), while for the other runs steady state was established at a lower value of \( R_p/R_a \) \( (R_p/R_a < 1) \). The remaining runs were carried out under monomer-flooded conditions due to low initial rate of polymerisation.

Equations 5.12 and 5.13, initially derived by Wesseling, apply to seeded systems with a constant number of polymer particles and constant radical concentration in the polymer particle phase, respectively. In the chapter 5 it was shown that in the semibatch emulsion polymerisation of BA with monomer feed, polymerisation rate follows the equation 5.12. However as shown by Wesseling, if the average radical concentration in the polymer particles remains constant, the equality equation \( R_p = R_a \) holds. No analytical equation has been derived for semibatch process with secondary or continuous nucleation. Battaile et al (1971) used the Wesseling expression for semibatch emulsion polymerisation of vinyl acetate with monomer emulsion feed. Such an application is under question as shown below. Monomer emulsion add semibatch polymerisation processes differ from monomer add semibatch process in two important ways:

- Firstly, particle nucleation may continuously occur in the course of reaction through secondary nucleation due to continuous addition of emulsifier.
- Secondly, the average radical number in polymer particles may increase due to addition of initiator.
Both or either of these two factors can increase the total number of radicals ($N_p \bar{n}$) with time and then could enhance the rate of polymerisation so that $R_p = R_a$ holds. It was shown in the *chapter 5* that although BA polymerisation is a high-$\bar{n}$ system, the rate of polymerisation is quite sensitive to the number of particles. In the *chapter 5* it was also confirmed that steady-state rate of polymerisation in BA semibatch polymerisation with neat monomer feed is dependent on the number of polymer particles (SLS concentration in the initial charge). For the two BH and BBF runs, which were carried out at high SLS concentration and with no emulsifier in the initial charge, the number of particles increased considerably in the course of reaction due to secondary nucleation (see *figures 6.3* and *6.6*). This, together with acceleration in the rate of polymerisation due to SLS addition, are perhaps the main reasons that the equation $R_p = R_a$ holds, as depicted in *figure 6.1*. It should be noted that, although for the runs BT and BW a massive secondary nucleation occurred, for these two experiments, polymerisation reactions occurred at virtually flooded conditions. For the other runs secondary nucleation was not important and number of particles reached constant value early in the reaction. The variations in $R_p/R_a$ versus $(R/F)_E$ ratio for the two overall SLS concentrations are shown in *figure 6.47*.

---

**Fig. 6.47:** Variation in steady state rate of polymerisation over monomer addition rate, $R_p/R_a$, with emulsifier distribution ratio, $(R/F)_E$, for two overall emulsifier concentrations, 2.50 and 10.0 g/litre.
Figure 6.47 shows that the steady-state rate of polymerisation slightly increases with $(R/F)_E$ ratio, especially for the lower SLS concentration. This is caused by the larger number of particles formed for the higher initial emulsifier concentration in the reactor charge. As it was discussed before in the chapter 5, the SSRR increases with number of polymer particles (SLS concentration) at a constant monomer feed rate.

The presence of monomer in the initial charge causes a rapid consumption of emulsifier molecules and enhances the initial rate of polymerisation, as depicted in figure 6.16. Elimination of monomer from initial charge reduces the initial rate of polymerisation, but increases the rate of particle nucleation at the cost of lower rate of particle growth (see figure 6.17). This results in a higher SSRR for polymerisation, as was reported in the chapter 5.

6.4.1.2 Inhibition period

Semibatch emulsion polymerisation processes may have inhibition periods since a monomer or monomer emulsion feed is continuously added to the reactor. Any impurities in the monomer, such as inhibitors, and other ingredients could easily affect polymerisation features. Semibatch emulsion polymerisation processes with monomer emulsion feed are more prone to inhibition effects, compared with the monomer add process, since a larger proportion of ingredients, and possibly inhibitors, are continuously added to the reactor. Furthermore, water dissolves oxygen which behaves as an inhibitor to the reaction. Although all feeds are continuously purged with nitrogen, the possibility of the presence of small amount of oxygen or other inhibitors in the feed can not be eliminated.

When no initial monomer is present in the reactor, the incoming monomer first saturates the water and diffuses into emulsifier micelles before any reaction can effectively occur. The excess monomer will form monomer droplets in the aqueous phase. This process, which is an emulsification process, will continue until polymerisation starts. This might impose a short delay in the start of polymerisation reaction. If both emulsifier and monomer were missing from the initial charge, the
Chapter Six

ME Add Semibatch Process

Inhibition period would be expected to be longer. If homogenous nucleation is not very effective, monomer emulsion feeding has to be continued until the CMC value is reached and particle nucleation starts. It was shown in chapter 5 that in BA batch emulsion polymerisation system, the exponent of particle number in terms of SLS concentration remains constant below the CMC value. This means that the nucleation rate is quite appreciable even for a very low concentration of SLS. Therefore, it is expected that particle nucleation easily start from the first minute of monomer addition for the BA polymerisation system. However, the results obtained indicate that all experiments with no initial emulsifier charge suffered an inhibition period. For the experiments carried out using monomer and emulsifier in the initial charge, it is easy to avoid inhibition error since feeding can be activated after polymerisation starts (for example, by observing an increase in the temperature of the reaction mixture). It is believed that the inhibition period does not affect the subsequent features of polymerisation reactions in batch processes. The elimination of inhibition period is not completely possible in semibatch processes with no initial monomer in the charge since the polymerisation reaction starts by feeding the monomer. Any inhibition effect during feeding, which can be caused by the impurities in the feed and especially dissolved oxygen in the water, can inhibit the reaction and leads to the accumulation of incoming ingredients in the reaction vessel. This makes the polymerisation reaction susceptible to inhibition error because once the reaction starts, the polymerisation features would not always follow the same trend.

Long inhibition periods in semibatch emulsion polymerisations can result in accumulations of large amount of emulsifier, initiator, and monomer in the reactor and affect the rate of reaction and latex properties. The effect of inhibition period on the regime of particle nucleation will be discussed later. The exact predictive expression for inhibition time can not be given here. But the experimental results show that inhibition time slightly increases with decreasing feed rate but largely decreases with SLS concentration in the feed. One possible reason for such an observation is the acceleration of initiation rate in the presence of SLS. The same observation has been reported by Capek et al (1984).
Since the run with lower overall emulsifier concentration (2.5 g/lit) was more prone to inhibition period, a couple of experiments were performed to study the reproducibility for these particular conditions. Figure 6.44 shows the variation of overall conversion with time for the runs. All necessary precautions were taken to prevent contamination of the feed with impurities and oxygen. Monomer was washed with caustic soda and distilled twice. All reactor lines were kept under nitrogen for an hour. In the first re-run, BS1, which was carried out exactly as the original run BS but with a more exhaustive purification stage, the polymerisation reaction did not start before 27 minutes, compared with 32 minutes obtained for the run BS. Such a low improvement over inhibition time suggests that the rate of KPS decomposition is highly affected by SLS concentration in the feed, as discussed above. Although the reaction for the run BS1 started earlier than that for experiment BS, a higher initial rate of polymerisation was obtained for the run BS, since a higher amount of SLS accumulated in the reactor before reaction started.

In the second re-run BS2, in order to reduce the inhibition time the polymerisation started with 4 wt % of the feed as a precharge, which was equivalent to 3 minutes of monomer emulsion feeding. The start of reaction was checked continuously by removal of samples form the reaction mixture and precipitating in methanol. The reaction started after 20 minutes. This gave enough time to the initial reaction mixture to start initiation through homogenous nucleation, since the instantaneous SLS concentration in the reactor was much lower than CMC value. A substantially different behaviour was observed for this run. It is obvious from figure 6.44 that the initial rate of polymerisation is very low for the second re-run since it started with a very low amount of emulsifier. The early formation of polymer particles by homogenous nucleation caused most of the incoming emulsifier molecules adsorbed on the growing polymer particles and hence a much smaller number of polymer particles was formed, as depicted in figure 6.45. The polymerisation reaction for this run occurred in the vicinity of CMC value (see figure 6.46) and a bimodal PSD with a very small peak formed. For evaluation of the effect of overall SLS concentration on the PSD of the latexes, the PSD curve from run BS2 (instead of BS) was used in generation of figures 6.14-15. A very important conclusion can be made from this
experiment; if polymerisation reaction starts from the first minute of feeding, the number of polymer particles formed are so low that they can not consume all incoming emulsifier molecules and polymerisation occurs in the vicinity of CMC for whole period of reaction.

6.4.1.3 Transition time

The impact of monomer or monomer emulsion feed on the transition time in semibatch emulsion polymerisation processes has not been treated so far in the literature. At a constant feed rate, the transition time in a semibatch emulsion polymerisation process with monomer emulsion feed, is highly dependent on the monomer, emulsifier, and initiator concentrations and distribution ratios, as well as other variables as monomer type and those in monomer addition semibatch process. For the BA semibatch emulsion polymerisation process with no initial emulsifier and monomer charge (and obviously no pre-period time) the following cases can be identified:

- Transition time is mostly influenced by those parameters which affect the initial rate of polymerisation. The shortest transition time was achieved for the highest monomer emulsion feed rate if steady state can be reached, as can be deduced from figure 6.1. This is because a larger number of polymer particles and hence a higher initial rate of polymerisation were obtained for the higher feed rates. This is in opposite to the results obtained for monomer addition process where the largest transition time was reported for the highest monomer feed rate.

- At a constant monomer emulsion feed rate, the higher the distribution ratios of emulsifier (and initiator) for the initial charge, the shorter the transition time, if the steady-state instantaneous conversion is not exceeded early in the reaction, as it is verified by figures 6.21-23.

The same classification of transition time as that in monomer add process can be put forward for a monomer emulsion process, if monomer is included in the initial charge.
At a constant feed rate with no pre-period time, a shorter transition time is required for the lower monomer distribution ratio, as can be deduced figure 6.16. This is similar to the results obtained for monomer add semibatch process.

6.4.2 Number of particles

Particle nucleation in the unseeded semibatch emulsion polymerisation can be divided, for simplicity, into two stages; primary nucleation and secondary nucleation. Primary nucleation occurs early in the initial reaction stage, while secondary nucleation mostly occurs later in the reaction due to continuous addition of emulsifier to the reactor. Correspondingly, the particles formed are called primary and secondary particles. Primary particles are bigger than secondary particles because they have formed earlier in the reaction, although in some circumstances there is no clear-cut boundary between them. In the terminology of this chapter, the “primary particles” refers only to the particles formed in the early stage of reaction. The same expression often used by many researchers, for small and unstable particles usually formed under homogenous nucleation, is not meant here.

Particle nucleation in semibatch emulsion polymerisation reactors with monomer emulsion feed is highly dependent on the distribution of the ingredients between the charge and the feed. If no emulsifier is initially present in the reactor, the emulsifier concentration in the feed and the feed rate will determine the number of polymer particles. A slightly larger final number of particles was formed if a higher monomer emulsion feed rate was used, as shown in figure 6.3. This can be better shown by particle size measurement by TEM as given in table 6.2. Similarly, application of a smaller amount of emulsifier in the feed resulted in the formation of fewer number of particles, as shown in figure 6.11 and table 6.3. For all feed rates and emulsifier concentrations used, bimodal PSDs were obtained if no emulsifier was present in the initial charge.

Similar to batch process, the overall number of particles increased with temperature, as shown in figures 6.41. At a constant KPS concentration, more particles were
nucleated if the KPS distribution ratio changed in favour of initial charge or the overall initiator concentration increased. However, the effect is trivial when no emulsifier was present in the initial charge, as depicted in figure 6.35 and table 6.6. Application of a high overall KPS concentration and temperature resulted in the formation of monomodal PSD.

![Graph](image)

Fig. 6.48: Variation in number of polymer particles with emulsifier distribution ratio, \((R/F)_E\), for two overall emulsifier concentrations, 2.50 and 10.0 g/litre.

As the emulsifier concentration in the initial charge increases, the behaviour of monomer emulsion add semibatch process becomes more similar to monomer add semibatch process where a single primary nucleation, although very long, may be observed during the reaction. Figure 6.48 shows the variation in the number of polymer particles versus emulsifier distribution ratio at two overall emulsifier concentrations, 10 and 2.5 g/litre, respectively. The two curves demonstrate slightly a different trend in variation of \(N_p\) versus \((R/F)_E\). It is observed that at the high emulsifier concentration the number of polymer particles initially increases with \((R/F)_E\) ratio and then at higher \((R/F)_E\) values (above 50 %) it remains almost constant and shows a little increase with \((R/F)_E\) afterwards. While at the lower overall SLS concentration \(N_p\) increases almost linearly with \((R/F)_E\) ratio. Then, it can be concluded
that final particle numbers may be controlled by overall emulsifier concentration and it is independent of the way it is added for high SLS concentrations and specially at the higher range of (R/F)_E ratio.

Another important conclusion can be drawn from figure 6.48. The two horizontal lines on this graph show the number of final particles for the equivalent batch processes using overall SLS concentration of 2.50 and 10.0 g/litre. This graph clearly shows that ME add semibatch emulsion polymerisation process can produce more particles than conventional batch process if suitable conditions exist, i.e., monomer-starved conditions (see section 4.4.1). This has not been reported before and is not in accord with the literature. According to figure 6.48 for low (R/F)_E ratios, batch process is superior to ME add semibatch process in terms of number of particles. However, above a critical (R/F)_E ratio for any fixed recipe and polymerisation conditions, the ME add semibatch process can produce more particles than batch process. The critical (R/F)_E ratio increases with overall SLS concentration, as depicted in the figure 6.48. The capability of ME add semibatch process to produce more particles than equivalent batch process increases with SLS concentration and decreases with the feed rate.

Monomer distribution between the charge and the feed could play an important role in the particle formation. The experiments for studying this effect were carried out at the conditions different from the base conditions; using 1 g/litre SLS in the initial charge. Application of an initial amount of monomer charge to a semibatch emulsion process with monomer emulsion feed, shifts the particle nucleation regime from monomer starved conditions to monomer flooded conditions where particles grow with a higher rate and as a result a smaller number of particles are formed, as shown in figure 6.17 and table 6.4 and discussed in the chapter 5.

Generally the size data obtained by PCS was found mostly in satisfactory agreement with those obtained with TEM. This has been shown in tables 6.1-7. However, the discrepancy increased with PDI of the latexes. In the chapter 3 it was mentioned that PCS is not sensitive to small particles. It should be added that although PCS is not
good at predicting the onset of secondary nucleation, it is useful in monitoring, at least qualitatively, the particle formation with some delay when secondary particles grow to a size that can be better detected by PCS. This is simply because small particles grow faster in terms of relative volume, assuming a constant volume growth rate for all particles. Furthermore at a low emulsifier concentration where homogenous nucleation is operative, small particles can grow both by monomer propagation in the particles and coagulation with other unstabilised particles. This will increase the growth rate of secondary particles. Obviously, PCS is not capable of particle formation monitoring, although with some delay, if secondary nucleation occurs very late in the reaction and particles do not undergo a big change in their volume. For example, figure 6.3 clearly depicts the occurrence of secondary nucleation in the course of reaction from which even the onset of nucleation can be inferred (see chapter 3 for more discussion).

6.4.3 Particle size distribution

It is important to determine the conditions under which a bimodal PSD can be obtained in semibatch emulsion polymerisation reactors. In batch emulsion polymerisation reactions usually a monomodal PSD is obtained. For a zero-one system, PSD becomes more polydisperse with reaction time due to stochastic broadening. For a high-$\bar{n}$ system, such as BA, the PSD tends to evolve uniformly in time in terms of volume and non-uniformly in terms of particle diameter. If the growth rate for particles is highly size dependent, then it might be possible that a bimodal PSD evolves in the course of reaction. This is the case where big particles contain more radicals and grow at a higher rate, compared with small particles. As a result, a bimodal PSD might evolve. The occurrence of bimodal PSD for batch emulsion polymerisations has been reported for MMA monomer (Gerrens, 1959). The high exit rate of radicals for small PMMA particles is understood to be the main reason for such a behaviour. For BA emulsion polymerisation, the exit rate was found to be small and particles contained more than one radical from early in the reaction (see chapter 4). Monomodal PSDs were observed for a few latexes examined from the batch experiment series. Then, the occurrence of bimodal PSDs in BA semibatch emulsion...
polymerisations can be attributed to the secondary nucleation brought about by addition of monomer emulsion feed.

Bimodal PSDs were obtained for all reactions at the base conditions (using no emulsifier in the initial charge). The average particle size of the peaks corresponding to the primary nucleation decreased with increasing monomer emulsion feed rate, as shown in figure 6.8, while their PDI increased with the feed rate indicating that the primary nucleation period increased with monomer feed rate. This clearly verifies that the initial rate of particle nucleation is greater if a higher monomer emulsion feed rate is used, as shown in figure 6.3. The reason is revealed by figure 6.4 which shows that surface tension stays at the CMC value for a longer period of time if the monomer emulsion feed rate increased, implying that more emulsifier molecules contribute to the particle formation. The average particle size of secondary nucleation peaks, similar to primary peaks, decreased with increasing monomer emulsion feed rate. However, the PSD of the secondary nucleation peaks broadened with decreasing monomer feed rate, indicating that secondary nucleation must have happened in a longer period of time as the feed rate decrease (see table 6.2). This is opposite to the PDIs obtained for primary nucleation peaks.

The evolution of bimodal PSD requires that particle formation occurs at two or more intermittent time intervals, or it is interrupted by a period with a low nucleation rate. Table 6.7 lists the number of particles formed after primary and secondary nucleation for the latexes having distinct bimodal PSDs. Since a larger number of primary particles is obtained at the higher feed rates, it is expected that a larger amount of emulsifier is needed to cover the particles and brings back the reaction mixture to the vicinity of CMC value. This means that secondary nucleation might occur at the later stage of the reaction in terms of relative time for the high monomer emulsion feed rate. Therefore, the period of time that secondary nucleation proceeds is expected to be shorter for the higher feed rate, leading to formation of less particles and a narrowing PDI. As it is seen from table 6.7, the number of primary particles for latexes using feed rates of 85 and 42.5 g/h are \(2.1 \times 10^{16}\) and \(9.0 \times 10^{15}\), respectively. While their corresponding number of secondary particles increased to \(3.0 \times 10^{16}\) and
3.4 \times 10^{16}, respectively. This again confirms that the number of secondary particles increases with decreasing number of primary particles.

Table 6.7: Number of primary, and secondary particles and overall number of particles for latexes having distinct bimodal distribution.

<table>
<thead>
<tr>
<th>RUN</th>
<th>x_1</th>
<th>W_{p2}/W_{p12}</th>
<th>PCS</th>
<th>TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>N_{p}</td>
<td>N_{p1}</td>
</tr>
<tr>
<td></td>
<td>x10^{-16}</td>
<td>x10^{-16}</td>
<td>x10^{-16}</td>
<td>x10^{-16}</td>
</tr>
<tr>
<td>BH</td>
<td>94.0</td>
<td>17</td>
<td>5.0</td>
<td>2.1</td>
</tr>
<tr>
<td>BBF</td>
<td>88.2</td>
<td>38</td>
<td>6.2</td>
<td>0.9</td>
</tr>
<tr>
<td>BBF17</td>
<td>50.3</td>
<td>17</td>
<td>4.1</td>
<td>1.1</td>
</tr>
<tr>
<td>BBF13</td>
<td>31.2</td>
<td>10</td>
<td>5.0</td>
<td>1.4</td>
</tr>
<tr>
<td>BBF9</td>
<td>13.5</td>
<td>0</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>BT</td>
<td>88.0</td>
<td>16</td>
<td>7.8</td>
<td>1.8</td>
</tr>
<tr>
<td>BW</td>
<td>88.0</td>
<td>5</td>
<td>10.0</td>
<td>3.9</td>
</tr>
</tbody>
</table>

N_{p1} = number of primary particles; N_{p2} = number of secondary particles; N_{p} = overall number of particles; W_{p2}/W_{p12} = weight ratio of secondary particles to all particles, calculated by the third moments of particle diameters in each population. Samples BBF17, BBF13, and BBF9 are those analysed from the run BBF at the different feeding times.

For a bimodal PSD curve, the overall PDI increases with the distance between the primary and secondary particle peaks. The magnitude of primary nucleation increased with monomer emulsion feed rate while, the magnitude of secondary peaks decreased with increasing monomer feed rate. This resulted in a higher PDI for the lower monomer emulsion feed rate. This can be easily deduced from figures 6.7-8.

The evolution of PSD with conversion for the lowest monomer emulsion feed rate, run BBF, is shown in figure 6.9. At the conversion of 0.14, a single peak with a slight skewness toward lower size and the PDI of 1.06 is obtained. As the reaction proceeded to the conversion 0.31, secondary nucleation occurred extensively and a relatively small second peak appeared at the lower size of the PSD curve with the PDI of 1.19. The PDI of primary peak decreased to 1.03. At the conversion 0.50, the secondary peak grew to a larger size with a broad width and PDI of 1.26, while the corresponding PDI of the primary peak almost stayed at the same level. Finally at the conversion of 0.88, the secondary peak grew to a much larger size compared with the primary peak with a high PDI as 1.19. The PDI of secondary peaks was found to
initially increase with conversion, but slightly narrowed afterwards. The PDI of the first peak slightly reduced with conversion. The overall PDI of the PSD curves increased with conversion. The particle size data for all stages are given in table 6.2. The number of primary and secondary particles with relative time for the run BBF are given in table 6.7. When secondary nucleation started, the number of newly borne particles constantly increased in the course of reaction. While, the number of primary particles showed a slight decrease with time. This suggests that primary particles undergo homo-coagulation. It has been suggested that small particles have more tendency to coagulate with large particles; hetero-coagulation (Hansen and Ugelstad, 1979a). This can not be experimentally verified when particle formation and coagulation simultaneously occur during secondary nucleation. The population of primary particles is not affected by hetero-coagulation due to their large size, but it is affected by homo-coagulation. In the other words, the formation of new particles might be accompanied by coagulation of mature particles and subsequent release of emulsifier molecules to the reaction mixture. Homo-coagulation is expected to occur more when particles are not fully covered by emulsifier molecules. Interestingly, homo-coagulation occurred late in the reaction according to the table 6.7.

The variation of overall emulsifier concentration in the context of the base conditions, also resulted in a formation of bimodal PSDs. As the emulsifier concentration in the feed decreased, the extend of both primary and secondary nucleations decreased. However, secondary nucleation appeared at a large time interval after primary nucleation due to lower emulsifier concentration in the feed, resulting in a broader PSD (see table 6.3).

Any variation in the conditions that improve the rate of primary particle nucleation, might result in a formation of monomodal PSD curves. Figure 6.30 and 6.32 show the PSD curves of latexes obtained using different \((R/F)_B\) ratios and overall SLS concentration of 10 g/litre. Particle size data and PDIs are tabulated in table 6.5. Obviously the number of particles increased with \((R/F)_B\) ratio. For all distribution ratios, the primary particles were formed initially through monomer flooded, and then monomer-starved nucleation (except \((R/F)_B = 0.0 \%)\), while the fresh emulsifier was
added to the reactor and contributed to the particle nucleation. Figure 6.30 shows that at the conditions studied a bimodal PSD can only be obtained if the emulsifier concentration in the initial charge is very low. This is the condition that satisfies a low rate of primary nucleation and a high rate of secondary nucleation. A bimodal PSD with the PDI equal to 1.25 was obtained for \((R/F)_E = 0\), as discussed before. At \((R/F)_E = 20\%\), a broad monomodal PSD curve with the PDI of 1.17 was obtained since the concentration of initial primary particles was not enough to hinder further nucleation by absorbing incoming emulsifier molecules onto their surfaces. However the secondary nucleation was not strong enough to generate a bimodal PSD. A PSD with negative skewness was obtained for this case. As \((R/F)_E\) increased to 50 \%, the primary nucleation increased to such an extend that a little secondary nucleation occurred and a narrower PDI equal to 1.13 was obtained. At \((R/F)_E = 75\%\), primary nucleation occurred for a long period of time at monomer starved conditions which eventually ended with a rather broad monomodal PSD with PDI of 1.23. Particles nucleated at different times have correspondingly different lengths of time to grow until the end of feeding. This gives rise to polydispersity of polymer particles. As \((R/F)_E\) increased, the contribution of monomer-flooded nucleation decreased and monomer-starved nucleation increased. Figure 6.22 shows that for the run with \((R/F)_E = 75\%\) particle formation occurred at highly monomer-starved conditions. More explanations about monomer-starved nucleation can be found in the chapter 5. Figures 6.25-26 corroborate with the discussion given above.

For the lower SLS concentration, 2.50 g/litre, PDIs show the same trend with \((R/F)_E\) ratio as that for the higher SLS concentration, but with lower variations. This is because, for this case, particle nucleation occurred briefly in the beginning of reaction at monomer flooded conditions. Figure 6.28 shows that surface tensions soon increased from near the CMC value to a value above 50 dyne/cm where particle coagulation is probable. It can be concluded that as the \((R/F)_E\) ratio increases, particle formation in monomer emulsion add semibatch process follows the same trend as that in the monomer add semibatch process.
The results obtained indicate that for a high overall emulsifier concentration the time evolution of the number of polymer particles can be characterised by a relatively short primary nucleation and a long secondary nucleation period for low \((R/F)_E\), and a long primary nucleation and a short, if any, secondary nucleation period for high \((R/F)_E\) ratios. For low overall emulsifier concentration the PSD curves can be characterised by a single primary nucleation peak. For both emulsifier concentrations, PDI initially decreased with increasing \((R/F)_E\) ratio and then after reaching a minimum, increased with \((R/F)_E\) ratio.

Any variation in initiator concentration in the initial charge or the feed can change the shape of PSD curves. The effect of the initiator concentration has been examined for the base conditions where a bimodal PSD was obtained. *Figures 6.38-39* show that as the initiator concentration increases, the rate of primary nucleation increases and secondary nucleation decreases. This is simply because, as the number of polymer particle increases, there is less chance for secondary nucleation to occur due to the large surface area of the particles formed. On the PSD curve, it is manifested by a dilation of the secondary peak and shrinkage of the primary peak. Eventually as the primary nucleation rate increases, a point is reached where the secondary nucleation is eliminated and a monomodal PSD is obtained, as shown in *figure 6.39* for the reaction with 1.08 g/litre KPS.

As discussed before, using emulsifier in the initial charge will reduce the possibility of formation of bimodal PSD curves by increasing the rate of primary nucleation. Application of an initial amount of monomer charge to a semibatch emulsion process with monomer emulsion feed reduces the extend of primary nucleation and hence increases the possibility of secondary nucleation. This is clearly manifested in the *figure 6.20* which shows a bimodal PSD for the run with monomer charge. The primary peak is rather sharp indicating a short nucleation period which is a characteristic of nucleation at monomer-flooded conditions. The PSD curve for the case with no monomer charge showed a unimodality with a slight skewness which is an indicator of particle nucleation at monomer-starved conditions.
6.4.4 Emulsifier adsorption

The emulsifier distribution between the aqueous phase and polymer particles could play an important role in the semibatch emulsion polymerisation. Kinetics of adsorption shows how fast the emulsifier molecules can adsorb and desorb. Any change in the balance of emulsifier concentration in aqueous media will influence particle formation and growth in the polymerisation process.

In a batch emulsion polymerisation as the polymer particles grow with increasing conversion, their surface coverage by emulsifier molecules diminishes and particles become less stable and more susceptible to coagulation with other particles. In a semibatch process with ME feed, the emulsifier associated with the incoming monomer emulsion can either remain in the aqueous phase or diffuse to the growing particles in order to stabilise them. The rate of growth of particles, which is a strong function of kinetics of polymerisation and the feed rate, also affects the rate of emulsifier adsorption from the aqueous phase to the oil phase. The free emulsifier concentration in the aqueous phase falls because of additional surfactant being adsorbed onto polymer particle surface. As the free emulsifier concentration falls, the surface tension of the aqueous phase rises above the value at the CMC. The free emulsifier concentration in the aqueous phase may increase if the emulsifier concentration in the feed is high. This might be associated with the formation of a second crop of particles and manifest itself in the decrease in the surface tension of the latex. Surface characteristics of the swollen polymer particles are very important in emulsifier adsorption isotherm. Rudin and co-workers (see chapter 2) reported that in situ emulsifier molecules have a large contribution to the surfactant concentration in the aqueous phase and hence surface tension.

Surface tension has been found of great importance in on-line monitoring of particle formation in semibatch emulsion polymerisations with monomer emulsion feed, because it is directly related to the concentration of free emulsifier in the aqueous phase. Snuparek (1972) was the first to report surface tension monitoring of semibatch emulsion polymerisation reactors with monomer emulsion feed. He showed that for BA emulsion polymerisation with \((R/F)_E = 0\), similar to the current series, surface
tension decreased from a value over 60 dyne/cm to a value close to 30 dyne/cm and stayed there afterwards. Such a variation in surface tension is expected to result in a monomodal PSD curve. The current series of experiments revealed another type of surface tension variation with time; an initial decrease from values around 60 dyne/cm to value close to 30 dyne/cm followed by a sudden increase to values around 35-37 dyne/cm and then another fall which eventually over some period of time ended with a practically constant, but substantially low, surface tension. This trend of surface tension variation with time is shown in figure 6.4 for the three feed rates studied. In the later stage of reaction for the highest feed rate, surface tension decreased slightly with relative time till the last quarter of the feeding time and then increased again. For the lowest feed rate, the final surface tension stabilised at a slightly higher value compared with that for the highest feed rate. For the medium feed rate, surface tension stabilised at the highest value compared with those for the other two feed rates. The small variation of steady state surface tensions with feed rate can be partly explained by the monomer concentration in the aqueous phase; the higher the monomer concentration in the aqueous phase, the lower the steady state surface tension. It is well accepted that the surface tension of emulsifier solutions is reduced in the presence of monomers (see Appendix C). Figure 6.2 shows that for the highest feed rate, 185 g/h, monomer concentration in the polymer particles stayed close to the saturation level in most of the reaction time. Although surface tension is affected by monomer concentration in the aqueous phase, $M_w$, the decreasing trend of surface tension before the relative time of 0.75 can not be attributed to the $M_w$ because of constant or decreasing $M_w$ in that region. Then surface tension drop for this run is the sign of emulsifier accumulation in the reaction mixture. The increase in surface tension at relative time of 0.75 can be attributed to either the formation of another crop of particles or the decrease in $M_w$. The large increase in $N_p$ is observed later in the reaction according to figure 6.3. The inability of PCS to determine the onset of secondary nucleation has been discussed before. Generally, the surface tension for all three feed rates stayed within 30-37.5 dyne/cm which is the region that particle nucleation could strongly occur. This suggests that particle nucleation might be continuously occurring in the course of reaction for the three feed rates. However, the bimodal PSD obtained for all three feed rates clearly indicates that there must be a
time interval between primary and secondary nucleations where nucleation rate completely ceases or reduces to a very low value. PSD development for the lowest monomer feed rate is shown in figure 6.7 and was discussed before. The gradual PSD evolution from monomodal to bimodal confirms that reaction must have gone through such a time interval when the rate of particle nucleation reached to a very low level after primary and before secondary nucleation. Figure 6.5 can bring more insight into the discussion. The particle surface coverage drops from the full saturation value to the value well below CMC early in the reaction, a minimum, and then approaches to the CMC value afterwards. It is thought that the rate of particle nucleation is very low in such an interval.

It should be noted that at monomer-starved conditions if the reaction mixtures reaches the CMC value, it remains at CMC till the end of reaction. This is obviously because the emulsifier needed to cover the surface of particles varies roughly to the 2/3 power of monomer feed rate (Vandegaer, 1965). At such a condition, particle nucleation continues to the end of feeding. This is not true when nucleation occurs at monomer-flooded conditions, where free monomer droplets are available to consume all emulsifier molecules and derive the reaction to the emulsifier-starved conditions where surface of particles are not fully saturated with emulsifier molecules. As more emulsifier, along with monomer, is added to the reactor it is possible that the system approaches emulsifier-saturated conditions and secondary nucleation occurs.

Surface tension variation with relative time for the SLS concentration of 5.0 g/litre shows the same trend as that described above (see figure 6.12). After the initial rise, the surface tension stabilised at 40.0 dynes/cm and did not vary afterwards. The particle size data obtained by PCS shows a small increase in the number of particles in the course of reaction. The data obtained by TEM reveals a large number of secondary particles formed for this case. It can be concluded that secondary nucleation was operative during a time interval of feeding where surface tension was constant.

As the emulsifier concentration in the initial charged increased, the surface tension variation with time became more increasingly. Figure 6.27-28 show such variations
for different emulsifier concentrations in the initial charge using two overall emulsifier concentrations of 10.0 and 2.50 g/litre, respectively. Early in the reaction surface tension rose to 40.0 dyne/cm quickly and then increased above that in shorter increments, depending on the overall emulsifier concentration. Secondary nucleation was more appreciable for the higher overall SLS concentration where surface tensions stayed at lower values. However, the differences between surface tension variation with time for similar conditions but different overall emulsifier concentrations and distribution ratios were not appreciable, indicating that control policies for particle formation through surface tension measurements can not be generalised and should be closely adjusted to a particular system. In fact surface tension shows the concentration of free emulsifier molecules in the mixture and ignores the concentration of surfactants adsorbed on the particles which have contributions to the balance of emulsifier in the aqueous phase and particle formation.

In semibatch emulsion polymerisations at monomer-starved conditions, depending on the emulsifier concentration in the feed, the variation of surface coverage ratio with time could be declining or inclining. Due to nonlinearity between the growth rate of particle surface and emulsifier feed rate, the constant surface coverage ratio in the course of reaction is less probable. Correspondingly, the surface tension follows the same trend. A constant or decreasing surface tension in the range of 30-40 dyne/cm was found to be an indicative of particle formation. A rising surface tension above 50 dyne/cm could be a sign of particle instability and coagulation.

The surface tensions for all three KPS concentrations showed a decrease with conversion which is an indicator of secondary nucleation. The highest surface tension was obtained for the highest overall concentration of KPS used, 1.08 g/litre, in the range of 35.0 - 37.50 dyne/cm where secondary particle nucleation might be operative. However, almost no secondary nucleation was found for this run. It is thought that due to formation of a larger number of primary particles, most of the polymer radicals in the aqueous phase were swept up by particles. Furthermore, the high electrolyte concentration might suppress the particle stability and causes that newly borne particles flocculate with existing particles.
It is generally assumed that in a batch emulsion polymerisation emulsifier molecules adsorbed on the polymer particles and dissolved in the water phase are in thermodynamic equilibrium. In a semibatch emulsion polymerisation with a continuous emulsion addition, the thermodynamic equilibrium could be shifted toward the water phase. Static tension measurements are not capable of tracking the dynamic variation of surface tension with time.

6.4.5 Nucleation mechanism

In a seeded semibatch emulsion polymerisation it is possible to study the effect of monomer emulsion feed rate and number of seed (primary) particles on the rate of secondary nucleation, independently. Particle nucleation in unseeded semibatch emulsion polymerisation with monomer emulsion feed is more complex than the seeded one due to interaction of primary and secondary particle nucleations.

It was shown in the chapter 4 that homogenous nucleation is operative in BA emulsion polymerisation. Then it is expected that as soon as monomer and emulsifier are fed to the reactor, particle formation occurs. This did not happen as discussed before and instead a delay time comparable to the time required to reach the CMC value was obtained. It is thought that this delay only originates from contamination effect in the feed and low decomposition rate of KPS in the absence of SLS and BA.

In order to investigate the inhibition period and its possible effect on the regime of primary nucleation, the following calculations can be done. For the series with different feed rates at the base conditions (runs BK, BH, and BBF), a simple calculation shows that if 12.5 g of aqueous solution feed is fed to the reactor, the reaction mixture reaches the CMC value (1.0 g/lit). For the runs BK, BH, and BBF from the table 6.1 the feeding times of 2.5, 5.5, and 11.0 minutes, respectively, are theoretically required to reach CMC value. Experimentally these values were obtained as 4.0, 5.0, 6.0 minutes, respectively. The experimental values imply that the inhibition period slightly decreased with increasing monomer feed rates.
The same method can be used to study inhibition period in the series carried out using 3 different emulsifier concentrations with \((R/F)E = 0\) and a constant feed rate of 185.0 g/h (runs BK, BT, and BS from table 6.1). Since 100 g DDI water is present in the initial charge, the amount of aqueous solution of SLS needed to be fed to the reactor so that the reaction mixture reaches CMC value is 50.0, 25.0, and 12.5 g for SLS = 1.25, 2.5, and 5.0 g in the feed, respectively. This requires that feeding continues for 10.0, 5.0, and 2.5 minutes. The experimental results obtained are 27.0, 10.0, and 4.0 minutes, respectively, which show that polymerisations started long after reaching the CMC value. According to the above discussions, it is presumed that primary nucleation occurred mostly by micellar and partly by homogenous nucleation mechanisms for the base conditions. The surface tension graphs confirms that CMC value is reached early in the reaction for most of the runs with base conditions (for examples see figures 6.4 and 6.12). The primary nucleation for all reactions at the base conditions were carried out at monomer flooded conditions, as it is clear from figure 6.2. Because butyl acrylate solubility in the water is low, it can be assumed that monomer concentration in the aqueous phase quickly reaches the saturation value for all feed rates and hence does not play a different role in the kinetics of the water phase during primary nucleation of all three feed rates.

The secondary nucleation mostly occurred through homogenous nucleation. Figure 6.4 shows that the for the series using different feed rates, surface tensions of all the latexes never reached again to their initial values during primary nucleation. The disability to return to CMC value can be at least partly explained by the lower monomer concentration in the aqueous phase for the two lowest monomer feed rates. Figure 6.5 reveals that for all three runs although the particle surface coverage is close to full coverage, it is still around 80 - 90 % and lower than full saturation. This confirms that secondary particle formation occurred through homogenous nucleation. In such a case emulsifier molecules added to the reactor adsorb on the newly borne unstabilised particles to stabilise them and do not accumulate in the aqueous phase. This effectively hinders the approach to the region where micellar nucleation is more probable.
It is generally accepted that particles formed by a homogenous nucleation mechanism are comparatively unstable and subject to coagulation with other particles, if they are not further protected by adsorption of emulsifier molecules from the aqueous phase. The results obtained show that for BA emulsion polymerisation, stable particles can be formed even at the conditions lower than CMC. More evidences for particle nucleation through homogenous nucleation are provided by figures 6.4, 6.12, and 6.19 which show that secondary nucleation occurred even when the surface tension was in the range of 35-40 dynes/cm and particle surface coverage ratio above 50 %. It can be concluded that the critical surface coverage ratio for BA emulsion polymerisation at the conditions studied is around 50-60 % (see section 2.5.2.2 for the concept of critical surface coverage ratio).

According to the homogenous nucleation mechanism, the rate of particle nucleation is determined by the competition between the rate of formation of radicals, rate of radical capture and the rate of particle coagulation as:

\[
\frac{dN_p}{dt} = \rho_f - \rho_a - \rho_f
\]

Neglecting the coagulation term, the following expression has been suggested for the rate of particle nucleation through homogenous nucleation.

\[
\frac{dN_p}{dt} = k_p M_w R_{j2-1}
\]

\(M_w\) is the concentration of monomer in the aqueous phase. According to the above equation it is expected that the rate of homogenous nucleation is proportional to monomer concentration in the aqueous phase. For the calculation of partial swelling a general empirical equation has been suggested which is found to be valid for a number of monomers such as VA, MMA, and St as the following (Gilbert, 1996):

\[
\frac{M_w}{M_w^{sat}} = \left[\frac{M_p}{M_p^{sat}}\right]^{0.60}
\]
Using figure 6.2 for the average $M_p$ values for different feed rates in the second half of the reaction, it is possible to estimate that the rate of nucleation for the highest feed rate is twice more than that for the other feed rates. This might be another reason that PSD curve for the highest monomer emulsion feed approaches a monomodal curve.

One of the major challenges in the semibatch emulsion polymerisation with monomer emulsion feed is the prediction of onset of secondary nucleation. It should be added that polymer chains formed by homogenous nucleation in the aqueous phase can be swept by the existing polymer particles before they can adsorb enough emulsifier to protect them against coagulation with particles. It is expected that secondary nucleation through homogenous nucleation decreases as the number of existing particles increase (Hansen and Ugelstad, 1979a). A theoretical methodology for such a task has been reported for a batch process which can be equally applied to a semibatch process (see chapter 1). However, practically such an application is not easy and depends on the monomer type and polymerisation conditions. For a seeded semibatch polymerisation the onset of secondary nucleation can be independently studied. For unseeded semibatch polymerisation, this is more complicated due to interaction of primary and secondary nucleations.

For the base conditions as the emulsifier concentration in the feed decreases, a smaller number of primary particles are formed, and less emulsifier is available in the feed to cover the surface of polymer particles and bring the latex to the vicinity of CMC value. The former advances the onset of secondary nucleation and the latter delays it. The net effect will decide the onset of secondary nucleation. Figure 6.12 compares the PSD curves of latexes obtained using a constant feed rate of 185 g/h and SLS concentration of 10.0 and 5.0 g/litre, respectively. The number-average of primary peaks increased and secondary peak decreased with decreasing SLS concentration in the feed. This is because primary particle formation occurred with a lower SLS in the reactor and secondary nucleation was reached later in the reaction due to lower SLS concentration in the feed as explained above. The result is broadening of PSD curve, as is shown in table 6.3. However, the long inhibition period obtained for the low SLS concentrations in the feed causes an accumulation of emulsifier in the reactor which
boosts primary particle formation and hence delays secondary nucleation. This might slow down the development of a broad PSD for the latex using 5.0 g/litre SLS in the feed. The primary and secondary nucleation occurred at virtually monomer flooded conditions. The surface tension initially dropped to CMC value and then rose to 40 dyne/cm and stayed constant afterward. Figure 6.11 shows that particle surface coverage initially decreased to 50% and then gradually increased to 60% in the course of reaction.

Semibatch emulsion polymerisation with monomer emulsion feed is known to produce a variety of PSDs. The results obtained show that a wide variety of PSDs can be produced. It was shown that monomer emulsion feed rate, monomer, emulsifier, initiator concentration and their distribution between initial charge and the feed play an important role in the PSD of the latex. It was found out that a high initial rate of particle formation could lead to elimination of secondary nucleation and hence formation of a monomodal PSD. This can be achieved by using high initiator and emulsifier concentrations, a high temperature, and a low monomer concentration in the charge. A low initial rate of nucleation increases the possibility of secondary nucleation and formation of a bimodal PSD, since enough particle surface area is not developed to adsorb all incoming emulsifier. Latexes with multimodal PSD can be easily produced by shot-addition of emulsifier at some time intervals of semibatch emulsion reactors. For semibatch emulsion polymerisation of BA using monomer-emulsion feed with a constant rate, the result obtained show that no process configuration led to a latex with multimodal PSD.
Chapter Seven

GENERAL CONCLUSIONS

7.1: CONCLUSIONS

The aim of this research work was to obtain a new insight into the particle formation and growth in semibatch emulsion polymerisation of butyl acrylate (BA). A fundamental understanding of BA emulsion polymerisation was obtained by studying the batch process. BA batch emulsion polymerisation using SLS as emulsifier and KPS as initiator was studied. It was found that the homogenous nucleation makes an important contribution to the particle formation. The steady-state rate of polymerisation and the final number of particles were found to be independent of monomer/water ratio at low emulsifier concentration. The rate of polymerisation was found to be influenced by the presence of SLS in the aqueous phase.

It was found that the traditional ranking of polymerisation processes in terms of number of particles is not always justified. The number of particles in semibatch emulsion polymerisation is mainly determined by two opposing factors:

- Monomer-starved nucleation
- Partitioning of ingredients between the initial charge and the feed

Particle formation at monomer-starved conditions would result in a larger number of particles, due to suppressed growth rate of particles. The partitioning factor might have opposing effects on the particle formation. For a fixed recipe, as more emulsifier and initiator are placed in the initial charge, the semibatch process approaches a batch
process and more particles are formed. While, the addition of monomer to the initial charge will favour monomer-flooded nucleation and reduces the number of particles. The net effect will decide the number of particles. The number of particles obtained by ME add semibatch process is usually lower than batch process due to portioning of emulsifier between the precharge and the feed. However, it is possible to enhance particle formation through monomer-starved conditions so that a larger number of particles is obtained for ME feed compared to batch and even M add semibatch process. The ranking of emulsion polymerisation processes can be best performed in terms of maximum number of particles which can be produced. An M add semibatch process provides the largest number of particles among the other processes studied. The ranking of Batch and ME add semibatch process in terms of number of particles depends on the polymerisation conditions and can not be generalised.

Monomer/Emulsifier ratio (M/E) was suggested as the best tool to recognise different regimes of particle formation in semibatch emulsion polymerisation processes. At a low M/E ratio, monomer starved nucleation and at a high M/E ratio reduced particle coagulation lead to the formation of a larger number of particles for a semibatch process, compared with a batch process. At medium M/E ratio, the number of particles obtained by both processes are virtually the same.

It was found that initial monomer charge can play a very important role in determining the number of particles. The region above which particle formation in M add semibatch process is not influenced by the monomer charge was defined. Generally, below this region the number of particles increases with decreasing initial monomer charge. The maximum number of particles can be obtained if polymerisation starts at highly monomer starved conditions with no monomer in the initial charge. This proves that for a fixed recipe, the semibatch process can produce a remarkably large number of particles compared with that which can be produced by batch process. However, it was shown that since initial monomer charge reduces the rate of primary particle formation, it promotes the rate of secondary nucleation for ME add semibatch process.
Chapter Seven

Conclusions

The indications are that the following features are important in particle formation in monomer-starved semibatch emulsion polymerisation:

- Monomer concentration in the aqueous phase could be much lower than the saturation value. This could affect the homogenous nucleation rate and radical capture efficiency.
- Micelles are lean monomer-swollen and might not be very effective in capturing radicals (or radical desorption may easily occur).
- Monomer droplets are not present in the reaction mixture and hence no emulsifiers are adsorbed by them, leading to the availability of emulsifier molecules for particle formation and stability, especially at low emulsifier concentrations.
- Since polymerisation time is usually longer than for a batch process, a larger proportion of initiator decomposes and contributes to the particle nucleation and stabilisation which is of great importance at a low emulsifier concentration.
- Particle coagulation is usually less than for a batch process since particles have passed the sticky stage. The adsorption of new incoming emulsifier molecules onto the surface of particles enhances the particle stability.
- Induced rate of initiator decomposition might be changing with emulsifier, or monomer concentration in the feed.

Generally, it was concluded that the concentration of ingredients in the initial reactor charge for the seeding stage has a determining effect on the particle formation stage, while their concentrations in the addition feed affect the particle growth stage. Initial emulsifier molecules mostly take part in particle formation, while the emulsifier molecules in the feed are mostly used for particle stabilisation. The initial initiator concentration plays an important role in particle nucleation, while its further addition ensures a supply of radicals for growing particles.

Secondary nucleation was found to occur for ME add semibatch process through homogeneous mechanism. The concept of “critical surface coverage” seems to be
acceptable for the current study. It was found that at the conditions studied the secondary particles can be formed when more than 60% of surface of particles are covered by emulsifier. The surface tension band above 45 dyne/cm was found to be a safe working region for avoiding secondary nucleation. However, it was shown that the variation of surface tension with monomer dissolved in the aqueous phase should be taken into consideration for defining any safe band.

Particle size distribution development was studied for the semibatch process. It was found that: an M add semibatch process usually produces a monomodal PSD which its skewness increases as the rate of monomer addition and monomer initial charge decrease. Above a critical initial monomer charge, PSD of an M add semibatch process resembles that of a equivalent batch process. Bimodal PSDs were obtained for ME semibatch process. It was found that:

- A high initial rate of particle formation could lead to elimination of secondary nucleation and hence produces a monomodal PSD, normal or negatively skewed, depending on the polymerisation conditions. A high initiator, and emulsifier concentrations in the feed result in the same effect.
- A low initial rate of nucleation increases the possibility of secondary nucleation and formation of a bimodal PSD.

The effect of variables such as feed rates and pre-period time on particle formation and kinetic features were studied. The steady-state rate of polymerisation was established for most of the experiments. The results obtained clearly show that although monomer feed rate controls the rate of polymerisation in monomer-starved semibatch emulsion polymerisation of BA, initial initiator and emulsifier concentrations and temperature are also important. The rate of polymerisation in M add and ME add processes follow the reciprocal and the equality expressions, originally derived by Wesseling, respectively. At high concentrations of initiator and emulsifier, and high temperature, along with a low monomer feed rate, the rate of polymerisation will approach the rate of monomer addition. The addition of SLS to the reaction mixture was also found to enhance the rate of polymerisation.
Chapter Seven

Conclusions

7.2 SUGGESTION FOR FURTHER WORK

The results obtained and the conclusions drawn from this research project have increased the understanding of particle formation and growth in semibatch emulsion polymerisation systems. It is recommended that the following tasks should be undertaken to widen the scope of understanding of semibatch emulsion polymerisation process.

1- Particle growth at monomer-starved conditions should be studied in order to arrive at a better understanding of size-dependent growth for a bidisperse polymer particle system.

2- Particle nucleation at monomer-starved conditions should be carried out in order to investigate the effect of micelle size, and low solubility of the monomer in the water phase, on particle formation.

3- Particle coagulation in semibatch polymerisation can be investigated by finding the optimal polymer/monomer ratio in the particles and feeding time which gives a monomodal PSD.

4- Particle formation and growth for semibatch process with a low particle stability, emulsifier-free emulsion polymerisation, will help to identify all parameters which might affect particle coagulation.

5- An investigation of the effects of composition of comonomer feed on secondary nucleation for a seeded semibatch process could clarify the effect of water solubility of comonomers on particle formation.
### Physical And Kinetics Data

#### Table A.1: Physical and kinetic data for butyl acrylate emulsion polymerisation system.

<table>
<thead>
<tr>
<th>Constants</th>
<th>Units</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propagation constant, (k_p), (\text{lit mol}^{-1}\text{sec}^{-1})</td>
<td>450 (50 °C)</td>
<td>Maxwell et al (1987)</td>
</tr>
<tr>
<td></td>
<td>200 (60 °C)</td>
<td>Kong et al (1987)</td>
</tr>
<tr>
<td></td>
<td>2100 (50 °C)</td>
<td>Song and Poehlin (1988)</td>
</tr>
<tr>
<td>Termination constant in the polymer phase, (k_{tp}), (\text{lit mol}^{-1}\text{sec}^{-1})</td>
<td>750 (50 °C)</td>
<td>Maxwell et al (1987)</td>
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<td>Termination constant in the water phase, (k_{tw}), (\text{lit mol}^{-1}\text{sec}^{-1})</td>
<td>(7 \times 10^7) (50 °C)</td>
<td>Maxwell et al (1987)</td>
</tr>
<tr>
<td></td>
<td>(3.3 \times 10^8) (50 °C)</td>
<td>Song and Poehlin (1988)</td>
</tr>
<tr>
<td>KPS decomposition rate constant, (k_{\text{KPS}}), (\text{sec}^{-1})</td>
<td>(1.3 \times 10^{-4}) (50 °C)</td>
<td>Maxwell et al (1987)</td>
</tr>
<tr>
<td>Desorption rate constant, (k_{\text{des}}), (\text{sec}^{-1})</td>
<td>(3 \times 10^{-3}) (50 °C)</td>
<td>Maxwell et al (1987)</td>
</tr>
<tr>
<td>PBA density, (\text{g cm}^{-3})</td>
<td>1.026</td>
<td>Maxwell et al (1987)</td>
</tr>
<tr>
<td>BA density, (\text{g cm}^{-3})</td>
<td>0.869</td>
<td>Maxwell et al (1987)</td>
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<tr>
<td>Surface area of SLS on PBA particles, (\alpha_{\text{SL}}), (\text{nm}^2)</td>
<td>0.56</td>
<td>Sutterlin et al (1976)</td>
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<td></td>
<td>0.67</td>
<td>Yeliseyev (1982)</td>
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<td></td>
<td>0.64</td>
<td>Emilie et al (1984)</td>
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<td></td>
<td>0.63</td>
<td>This work</td>
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<td>Equilibrium monomer conc. in PBA particles, (M_{p,\text{eq}}), (\text{mol lit}^{-1})</td>
<td>(4.45, (\varphi_m = 0.68))</td>
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<td></td>
<td>(\varphi_m = 0.65)</td>
<td>Gardon (1973)</td>
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<td>3.2, ((\chi_r = 0.58))</td>
<td>Maxwell et al (1987)</td>
</tr>
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<td>5.0</td>
<td>Gilbert (1995)</td>
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<tr>
<td></td>
<td>4.0, ((\chi_r = 0.45))</td>
<td>This work</td>
</tr>
<tr>
<td>Saturated monomer conc. in the water phase, (M_{w,\text{sat}}), (\text{mol lit}^{-1})</td>
<td>(11.0 \times 10^{3})</td>
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<td></td>
<td>(6.2 \times 10^{3})</td>
<td>Maxwell et al (1987)</td>
</tr>
<tr>
<td></td>
<td>(8.1 \times 10^{3})</td>
<td>This work</td>
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<tr>
<td>SLS Critical Micellar Conc. (CMC)</td>
<td>1.70 g/litre (6.0 mmol/l)</td>
<td>Sutterlin (1980)</td>
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<td></td>
<td>1.50-1.70 g/litre</td>
<td>Hansen and Uglestad (1979c)</td>
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<td></td>
<td>8-9 mmol/litre</td>
<td>Rosen (1978)</td>
</tr>
<tr>
<td></td>
<td>1.70 g/litre</td>
<td>This work</td>
</tr>
</tbody>
</table>
Appendix B

Chemicals

**Monomer**
Butyl acrylate (+99.0 %) was the monomer used. It was obtained from “Aldrich chemical company” in 2.50 litre glass bottles. The butyl acrylate (BA) contained hydroquinone as inhibitor. Before use butyl acrylate was freed from inhibitor as described in section 3.2.3.

**Emulsifier**
The emulsifier used was sodium Lauryl sulphate (SLS), an anionic soap, obtained from “Fison Scientific”. The soap was of reagent grade quality and was used directly as received.

**Initiator**
Potassium persulphate (KPS) was used as initiator. It was obtained from “BDH” and was used without further purification.

**Water**
Distilled-deionised water (DDI) was used for all experiments.

**Inhibitor**
Hydroquinol was obtained from “BDH” and used without further purification.

**Potassium bicarbonate**
Potassium bicarbonate was used for adjustment of the pH. It was obtained from "BDH" and used without any further purification.

**Other chemicals**
The other chemicals used were the followings:

1-Methanol
2-Acetone
3-Dioxane
4-Sodium hydroxide
5-Osmium trioxide
6-Phosphotungestic acid

They were all analytical grades and were used directly as received. High purity nitrogen (99.0 %) was used for all experiments.
Appendix C

Surface Tension Measurements

C.1 Critical Micellar Concentration of SLS in water

Critical micellar concentration of SLS was measured using du Nouy tensiometer and also conductometric method. *Figure C.1* shows the variation of conductivity of water with SLS from which the CMC value, the point that conductivity does not vary much with further addition of SLS, can be obtained. CMC obtained was around 1.7 g/litre which is in a very good agreement with literature values as reported in *appendix A*. All measurements were done after equilibrium was reached. However, the specific conductivity of emulsifier (defined as conductivity per unit weight of SLS) shows that micelles might form above 1.10 g/litre of SLS (shown by dotted line on the *figure C.1*). The CMC value obtained by surface tension measurements is in accord with that from conductivity measurements, as shown in figure C.2. Similarly, the surface tension variation with SLS concentration was very slow above 1.0 g/litre, indicating that micelles might form in this region. Vanderhoff (1985) reported that the aggregates of SLS are present at concentrations well below the physically measured CMC.

![Conductometric Measurement of CMC](image)

*Fig.C.1: Conductivity and specific conductivity of water versus the concentration of SLS in the water phase.*
C.2 CMC of SLS in water at the polymerisation conditions

CMC is not a fundamental property of a surfactant and is a characteristic of aqueous phase. The degree of ionisation of the surfactant will be reduced by the addition of its common ions. It is also known that the dissolved monomer in the water phase will drop the surface tension. Figure C.3 shows the variation of surface tension of pure water with dissolved BA. A small drop in surface tension is seen with BA at low concentration. But at a high BA concentration, an appreciable decrease in the surface tension is observed.

Fig.C.2: Surface tension of water versus the concentration of SLS in the water phase

Fig.C.3: Surface tension of water versus the amount of BA in the water phase in relative to saturation value.
Figure C.4 shows the variation in surface tension of water containing 0 and 0.25 g/litre BA with SLS concentration. For both cases the water phase contains 0.54 g/litre of KPS and SBc. The CMC value for both cases were obtained around 0.8-1.0 g/litre which is smaller than CMC in the pure water. Ionic strength can change the CMC. For example, it was reported that the CMC of SDS (SLS) dropped from 8 mmol/litre in a pure system to 2 mmol/litre in the presence of $1.4 \times 10^{-2}$ mol/litre of KPS. Monomer can also promote micelle formation in the aqueous phase and hence suppress CMC value. The CMC of SDS measured with styrene present is 4.5 mmol/litre (Morrison and Gilbert, 1995).

For a low SLS concentration in the water, the surface tension is suppresses by the BA dissolved in the water, compared with that for pure water. But as the SLS concentration in water increases, the surface tension becomes more controlled by the SLS concentration and the effect of BA diminishes. It can be concluded that the effect of BA on the surface tension is more pronounced at lower SLS concentrations in the water. The CMC measured physically, however, does not really correspond to the critical point at which the micelles are formed for particle nucleation (Vanderhoff, 1985).

Fig.C.4: Surface tension of water containing 0.0 and 0.25 g/litre BA versus the amount of SLS in the water phase. The water phase contained 0.54 g/litre of KPS and SBc.
C.3 Determination of molecular area of surfactant

The method developed by Maron et al. (1954), which originally was introduced to measure particle size, was utilised to determine the area occupied by the surfactant molecule on PBA particles at saturation adsorption. A surfactant titration curve is obtained by plotting surface tension as a function of added surfactant titer for a known mass of polymer latex with a known particle size. A given volume of a diluted latex was titrated by adding dropwise sodium lauryl sulphate solutions of known concentration. The latex was stirred for a few minutes and left for 20 minutes before the surface tension value is recorded. Three samples of 2.5, and 5, and 10 percent solid contents were prepared by diluting a seed latex of the size \( D_s = 109.0 \, nm \). No purification was done on the seed particles and it contained SLS, KPS, and SBC. The measurements were carried out using an aqueous solution of 0.54 g/litre KPS and SBC. A family of curves similar to figure C.4 were obtained (not shown).

Surfactant titration results determine the amount of added surfactant required to initiate micellisation which is composed of two components; \( E_a \) moles of surfactant adsorbed on the polymer particles, and \( E_w \) moles of surfactant in the aqueous phase.

\[
a_s E_a N_a / \pi D_s^2 N_p = 1.0 \quad \text{then} \quad a_s = \pi D_s^2 N_p / E_a N_a \quad \text{C.1}
\]

If above equation is multiplied and divided by \( D_s \rho_p / 6 \), Then;

\[
a_s = 6 / (E_a / m_s) D_s \rho_p N_a \quad \text{C.2}
\]

where \( E_a / m_s \) is the total moles of surfactant needed to cover \( m_s \) gram of polymer particles with the surface average size \( D_s \). For all three experiments \( C_a \) for the break-even point was taken as critical micellar concentration of SLS in the water and equal to 1.0 g/litre at polymerisation conditions. From the amount of SLS required to get the constant surface tension, the \( E_a \) was calculated \( E_a = E - E_w \) and from equation C.2 \( a_m \) was calculate as 0.625 \pm 0.025 \, nm^2. This is in good agreement with the literature values (see appendix A).
Appendix D

Viscosity Measurements

The viscosity measurements of selected latexes has been carried out using HAAKE viscometer at 25 °C temperature. For each latex sample, shear stress was measured at different shear rates and from those the shear rate- shear stress curves were generated. The viscosities were determined from the slope of shear stress versus shear rate curves in the linear region. Figures D.1-2 show shear stress-shear rate curves for the two series of semibatch emulsion polymerisation experiments with ME feed. The viscosities are given in table 6.5.

Fig. D.1: Shear rate - shear stress curves for final latexes using different emulsifier distribution ratios, (R/F), at SLS overall concentration of 2.50 g/litre (see figures 6.21-29 and table 6.5 for corresponding kinetic results).
For the lower overall SLS concentration, 2.50 g/litre, shear rate - shear stress curve is virtually linear in whole range of shear rate applied. As the emulsifier concentration increased to 10 g/litre, the linear relationship disappeared at low shear rates, indicating that the emulsion samples deviate from Newtonian models at low shear rates. The deviation region widened as the higher emulsifier distribution ratio, (R/F)_E, was used as shown in figure D.2. The comparison of the two sets of shear stress-shear rate obtained clearly demonstrates that PBA latexes shows non-Newtonian behaviour at low shear rates as the number of particles increases.
Appendix E

Experimental Errors and Reproducibility

E.1 ERRORS IN EXPERIMENTAL WORK

E.1.1 Inhibition effect

Due to continuous addition of ingredients, semibatch emulsion polymerisations are very prone to contamination effects. Contamination effects are more appreciable when they are associated with particle nucleation. For more discussion on inhibition effects see section 6.4.1.2. For batch process and M add semibatch process contamination effect is minor. Figures E.1 shows the reproducibility analysis of the conversion-time and number of particles-time curves for a M add semibatch process. A very good agreement is observed for both conversion and number of particles. The same degree of confidence was obtained for batch process (not shown). The reproducibility of results for the ME add semibatch process with no emulsifier charge has been discussed in chapter 6. It is expected that for ME add semibatch process with initial emulsifier charge, like M add semibatch process, the contamination effect is minor.

Fig. E.1: The reproducibility results for a typical M add semibatch run (run BU from table 5.2) Filled symbols and empty symbols represent the results for the two runs.
E.1.1 Conversion

Errors in the solid content analysis, including sampling, weighing, and drying can be safely avoided by careful treatment. The reproducibility results for batch experiments confirm that such errors can be eliminated. For chromatography analysis, the application of an internal standard eliminates the uncertainty regarding the varying volume of samples.

E.1.2 Particle size

Error in particle size measurements by PCS and TEM were reduced by identifying the source of possible errors and avoiding them in the course of measurements. These are discussed in section 3.3.2. For PCS measurements, 10 runs were carried out for each sample and the mean average was assigned as the mean size of particles (intensity average). The difference between these runs were within ± 2.0 % of the average size. Measurements usually made the day after the experiments.

The possibility of particle coagulation during sample preparation for TEM was avoided by analysing the samples within a few days after the experiment. Errors in TEM measurement were avoided or at least reduced by taking pictures from different parts of the grids and counting more than 1500 particles for polydisperse samples. The results showed that for monomodal distributions, as those obtained from batch process or M add semibatch process with a high M/E ratio, the PSD approached a constant (final) shape as the number of particles counted increased to 250. For multimodal samples, the PSD curve took its shape within ± 5.0 variation from the average size when at least 750 particles were counted. The errors induced by the hardening technique was avoided by ignoring ill-conditioned samples. These are samples with very big or distorted particles. The agreement of PCS and TEM size data approve that such an error is not appreciable. However, the possibility of a limited coagulation can not be eliminated.
E.2 ERROR IN ANALYSIS

E.2.1 Particle size

Errors in particle size measurement may have occurred in analysis procedure. The discussions about the particle size calibration and measurements has been already pointed out in section 6.3.3.2. The major source of error in the calculations of number of particles, according to equation 3.9, was in the estimation of average volume of polymer particles from PCS measurements. This was particularly significant when the correction factor obtained by the comparison of final particle size by PCS and TEM was applied to whole particle sizes in the course of reaction. The error increased with the PDI of the samples. However, it is thought that direct application of z-average, obtained by PCS, for calculation of $N_p$ could have led to a higher degree of error in the estimation of number of particles.

E.2.2 Conversion

Although sampling does not affect the course of reaction in a batch process, it might influence a semibatch process. The removal of reaction mixture from a semibatch reactor will result in a slight decrease in the number of particles in the reactor which might affect the polymerisation rate and other kinetic features. In order not to influence the polymerisation reaction, the volume of samples should be very small. In all experiments, aliquots of 2-3 mls latex were taken from the reaction mixture for particle size analysis, surface tension measurements and conversion measurements.

If the correction is allowed for such a decrease in reaction volume, the real conversion and number of particles obtained are slightly smaller than those uncorrected. Figure E.2 shows the variation of conversion and number of particles with relative time when the correction is made for a typical run. It should be noted that the error originates from neglecting the variation of $M/W$ ratio with sampling for conversion calculations. The results shows only a negligible increase in conversions and number of particles. The error slightly builds up with conversion as more samples are taken out of the reactor in the course of reaction. The maximum error due to this effect is 1.0 % for $M$
Appendix E

Experimental Errors

add semibatch process. For ME add semibatch process the same degree of error, or even less since M/W remains almost constant, is obtained. It can be concluded that due to large amount of reaction volume, 750 mls, sampling effect is trivial and then no corrections have been made for the effect of sampling.

Error Analysis in a semibatch run

Fig.E.2: The comparison of conversion, and number of particles versus time for corrected and uncorrected semibatch run. Filled symbols represent corrected and empty symbols represent uncorrected results.
Appendix F

Particle Size Measurements

F.1 Photon Correlation Spectroscopy

During the past two decades the technique of quasi-elastic light scattering (QELS) has been used extensively to characterise colloidal-sized particles in the size range from a few nanometers to a few microns. In this range, particles exhibit significant random motion from collisions with the surrounding liquid medium known as “Brownian motion”. The motion arises as particles are bombarded by the surrounding molecules of suspending medium. The random motion gives rise to fluctuations in the scattered light intensity which is usually analysed with a digital correlator. As a result the name photon correlation spectroscopy (PCS) is often used.

For particles smaller than around 1 micron, measuring methods based on single particle detection generally break down because the signals (e.g. scattered light, etc.) obtainable from individual particles below this size are simply too small to detect. Photon correlation spectroscopy, which is based on a new principle, has been commercialised for measurements of mean particle sizes in the submicron range. PCS circumvents the problem of inadequate signal level for individual particles by simultaneously detecting thousands to many million of particles.

Consider light of wavelength $\lambda$ (in the medium) of the intensity $I_0$ propagating in the medium of refractive index $n_0$ which encounters a particle of radius $R$ and refractive index $n_1$ ($n = n_1/n_2$, relative refractive index). A detector some distance $r$ away from the scatterer will then receive a signal with an intensity $I$. For the particles smaller than the wavelength of light, Rayleigh showed that

$$I = I_0 \frac{16 \pi^4 R^6 ((n^2 - 1)/(n^2 + 2))^2}{(r^2 \lambda^4)}$$  \hspace{1cm} F.1
Then the measurement of intensity could lead to knowledge of the size of particles smaller than, and comparable to the wavelength of light. The PCS method depends on the fact that a photon counting detector can track rapid change of intensity. For a system of Brownian particles of uniform size and shape, the autocorrelation function will be a decaying exponential:

\[ g(\tau) = A e^{-2\Gamma \tau} + B \]

where \( \Gamma \) is a decay constant characteristic of particles of that size and \( A \) and \( B \) are constants dependent on the sample, experimental geometry and counting efficiency of the optics and electronics.

The decay constant is related to the diffusion constant of the particles through the equation,

\[ \Gamma = q^2 D \]

where \( q \) is the magnitude of so called "scattering vector", and \( D \) is the diffusion constant of the particles. The scattering vector is given by the following equation:

\[ q = 4 \pi n \sin (\theta/2) / \lambda \]

where \( n \) is the refractive index of the dispersion medium, \( \theta \) is the scattering angle, \( \lambda \) is the wavelength of the laser in the vacuum. In turn, for spherical particles, the diffusion constant is related to the particle diameter through the Stokes-Einstein equation:

\[ D = kT / (3\pi \eta D_p) \]

where \( k \) is Boltzmann's constant, \( T \) is absolute temperature, \( \eta \) is the viscosity of the dispersion medium and \( D_p \) is the particle diameter. Using equations G.3-5, the measured decay constant \( \Gamma \) can be directly related to the particle diameter.

When the sample contains particles of different sizes, the autocorrelation function will be a sum of decaying exponential weighted by the intensity of light scattered from particles of each characteristic size. This can be described in general by the equation:

\[ g(\tau) = \int_a^b X(s) e^{-\Gamma(\tau)s} ds \]
where the index, \( s \), labels the size of particles and \( X(s) \) is the particle size distribution, which gives the relative proportion of the scattering from particles of size \( s \). The constants \( a \) and \( b \) are the lower and upper limits of particle size. This integral equation must be numerically inverted to extract the size distribution, \( X(s) \), from the measured autocorrelation function. This is mostly done by using a FORTRAN program called CONTIN. CONTIN has been reported to be a program particularly successful at detecting widely spaced bimodal distributions and is usually available as an option with Malvern PCS software.

The CUMULANT calculation is the best starting point for studying an unknown sample. This gives a good idea of mean size and spread (for a monomodal distribution). The CUMULANT method assumes nothing about the distribution form, it simply fits a polynomial to the LOG of normalised correlation function. According to the CUMULANT method, the correlation function is written in a log form and it is fitted with a power series to the data:

\[
Y(t) = A + Bt + Ct^2
\]

where \( Y(t) \) is the log of correlation function, \( t \) is the delay time, and \( A, B, \) and \( C \) are constants which are fitted by the analysis.

\( A \) is related to the signal to the noise ratio. \( B \), the initial slope, gives the "z-average mean". This mean size is weighted by the amount of light scattered by each size of particles in the sample. \( C \) is related to the width of the PSD, in fact \( C/B^2 \) is the polydispersity.

The raw size distribution obtained in PCS is intensity weighted. Most particle sizing results are either mass, area, or number weighted. Therefore to compare results, the PCS data would have to be transformed. An intensity distribution is related to a number distribution by

\[
X(s, \theta) = N(s) C_1(s, \theta)
\]

\( C_1(s, \theta) \) is a conversion factor of number to intensity, i.e. the amount of scattering from the particles of size \( s \). \( C_1 \) and \( X \) both show an explicit dependence on \( \theta \).
In a concentrated solution the diffusion process may be hindered by the effect of other particles. Depending on the whether the particles attract or repel each other the diffusion coefficient can increase or decrease over the dilute value.

At high concentrations, multiple scattering, a process where light is, on average, scattered by several particles before reaching the detector will often interfere before particle interaction becomes dominant. This normally manifest itself as a reduction in the apparent size of the particles. Generally this and interaction effects can best be avoided experimentally.

PCS benefits from exact theory (no model) for z average and fast sampling. However, since sample usually must be diluted, chemistry of the sample can be altered. Moreover, reliable PSD can not be obtained.

**F.2 Electron Microscope**

Because of the limit of resolution of the light microscope - visible light has wavelengths from about 400 to 800 nm, larger than colloidal particles - the electron microscope is of great importance in visualisation and measurement of colloid particles. Microscopy represents the only method of obtaining particle size and size distribution by direct measurement of individual particles. Transmission electron microscopy (TEM) is the most reliable method for the measurement of PSD. The electron microscope with its great resolution is useful in sizing particles below 1000 nm. The main advantage of electron microscopy is that the application of short wavelengths allows for resolution of details down to few nanometers. The main disadvantage of electron microscope is that electron beams can be destructive of polymers, causing depolymerisation or degradation. The other disadvantage is that organic polymers are not very electron-dense, with the results that small diameter polymer particles are difficult to see.

One of the chief problems in electron microscopy is the difficulty in obtaining a representative sample. Usually a large number of particles, 1000-2000, should be counted for a full PSD or hundreds just for an average size. The temperature of the sample in electron microscope is about 100 °C, but can reach as high as 200-275 °C. Under these conditions many latexes will shrink and give diameters about 20-25% low (Collins, 1975).
Sample preparation for electron microscopy involves putting a drop of highly diluted sample on a carbon grid and allowing to dry. The dried sample is then examined in the microscope. In the case of polymers where the glass transition temperature is close to or below room temperature, the particles will be too soft to retain their shape on drying. Such latexes must be hardened, by bromination, cross-linking with UV or other radiations, or coated with carbon, gold, osmium trioxide, or other staining agents before measurement are made.

F.3 Particle size averages and analysis

The most useful averages are given below as

\[ D_n = \frac{\sum n_i D_i}{\sum n_i} \]  
\[ D_w = \frac{\sum n_i D_i^4}{\sum n_i D_i^3} \]  
\[ D_v = \left[ \frac{\sum n_i D_i}{\sum n_i} \right]^{1/3} \]  
\[ D_s = \frac{\sum n_i D_i^3}{\sum n_i D_i^2} \]

Where \( D_n \) is number average, \( D_w \) weight average, \( D_v \) volume average, and \( D_s \) surface average. \( n_i \) is the number of particles of diameter \( D_i \), and \( n \) the number of particles counted. The weight average is strongly influenced by small numbers of large particles, while it is not very sensitive to a large number of tiny particles. If the distribution data are available, then it is possible to compute any of particle size averages.

The surface average is of interest in latex technology since it can be easily obtained by soap titration. The particle size average given by light scattering instruments (for example Malvern), the z-average mean size, in effect is the size of particle that corresponds to the mean of intensity distribution for a narrow distribution. Polydispersity index is usually calculated from fitting a 3 parameter polynomial to the log correlation function, interpreted as the variance of a supposed log-normal model.
The dependence of z-average on the particle size is not well elaborated in the literature. Many light scattering methods give a value close to weight average (Collins, 1975). It has been also reported that z-average is proportional to particle volume (Fitch, 1996; Gilbert, 1995). Higher order dependence has been also reported (Gerrens, 1969; Gardon, 1968b). Perhaps the reason for this discrepancy is that though the term "z-average mean" has been initially adopted from polymer physics, it is not well correlated with the other averages. The z-average mean for a polymer molecule is also weighted by the amount of light scattered from each species present. However, because polymer molecules are small and transparent, a simple mathematical expression relates their z-average mean to other means weighted by number or mass. This is not generally the case for the larger, non-transparent particles measured by PCS and the equations found in polymer physics for the z-average mean do not apply.

The Rayleigh equation shows a very strong dependence (sixth power) on particle size. Therefore, scattering from a particle of twice the size will give 64 times the intensity emphasising the importance of PSD of the sample.

Using such a dependence the z-average diffusion coefficient was estimated as (Van der Meeren, 1992):

\[ D = \frac{\sum n_i D_i^7}{\sum n_i D_i^6} \]  

From the above equation and equation F.5, the z-average diameter is calculated as follows:

\[ D_z = \frac{\sum n_i D_i^6}{\sum n_i D_i^5} \]  

The following expression has been also reported for the average particle diameter obtained by light scattering methods (Gardon, 1969b; Gerrens, 1969):
Several parameters have been used in the literature to define the breadth of the particle size distribution. The standard deviation, \( \sigma \), is defined as the difference of particle diameters from their number average value to power two.

\[
\sigma = \left( \sum_{i=1}^{n} n_i (D_i - D_n)^2 \right) / \left( \sum_{i=1}^{n} n_i - 1 \right)
\]  

The other two important measures of breadth are coefficient of variation, \( C_v \), and polydispersity index, \( PDI \), as shown below, respectively:

\[
C_v = \sigma / D_n \quad \text{F.17}
\]
\[
PDI = D_w / D_n \quad \text{F.18}
\]

\( C_v \) and \( PDI \) are weighted or relative values, while \( \sigma \) is an “unweighted” measure of the breadth of the distribution. In practice, it has been observed that as the average size of a population of particles increases, the breadth of distributions increases as well. Then a comparative study of different distribution can be made more meaningfully if the weight measures of breadth of distribution are used.

In general, since scattering of a particle varies with its diameter to the power six, then the following expression holds; \( D_z > D_w > D_n \). Only for perfectly monomodal distributions the average values on number-, weight-, volume-, or intensity basis are identical. As the \( PDI \) of a distribution increases, the number average diameter decreases, whereas the intensity average value increases.
Appendix G

Micrographs

The micrographs of some selected samples are shown here. References are made to the corresponding PSDs curves obtained by particle sizing of the micrographs shown in the text. The micrographs shown are all from ME add semibatch latexes which have broad particle size distributions.
Fig G.1: Micrographs for the final latexes from different feed rates (runs BK, BH, and BBF) corresponding to figure 6.6; a) 185 g/h; b) 85 g/h, c) 42.5 g/h.
Fig. G.2: Micrographs for the latexes from the run BBF using 42.5 g/h monomer feed rate at different relative times and corresponding to figure 6.7; a) 23.3 %, b) 68.0 %, c) 108 % (Note that the micrograph for the sample BBF13 has been replaced by that of the final sample BBF).
Fig. G.3: Micrographs for the final latexes form the runs using different overall emulsifier concentrations (runs BK, and BT), and corresponding to figure 6.14; a) SLS = 10.0 g/litre, b) SLS = 2.50 g/litre.
Fig.G.4: Micrographs for the final latexes from the runs using different monomer concentrations in the initial charge (runs BM, and BW), corresponding to figure 6.20; a) (R/F)_{M} = 10 \% ; b) (R/F)_{M} = 0 \%.
Fig G.5: Micrographs for the final latexes using different emulsifier distribution ratios at SLS concentration of 10 g/litre (runs BK, BM, BN, BO), corresponding to figure 6.30; a) $(R/F)_E = 0\%$, b) $(R/F)_E = 20\%$, c) $(R/F)_E = 50\%$, d) $(R/F)_E = 75\%$. 

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Appendix G Micrographs

Fig. G. 6: Micrographs from the final latexes using different emulsifier distribution ratios at SLS concentration of 2.50 g/litre (runs BR, BP, and BQ), corresponding to figure 6.31; a) (R/F)E = 20%, b) (R/F)E = 50%, c) (R/F)E = 75%.
Fig. G.7: Micrographs from the final latexes using different initiator concentrations and distributions (runs BK, BBD, and BBC), corresponding to figure 6.38; a) KPS = 0.54 g/litre, (R/F)₁ = 20 %; b) KPS = 0.54 g/litre, (R/F)₁ = 40 %; c) KPS = 1.08 g/litre, (R/F)₁ = 20 %.
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