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FOR REFERENCE ONLY
INVERSE MICROSUSPENSION POLYMERISATION OF AQUEOUS ACRYLIC ACID USING REDOX INITIATORS

by

ZUIFANG LIU

A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of

Doctor of Philosophy

of the Loughborough University

28 November, 1997

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TO MY WIFE AND SON
ACKNOWLEDGEMENT

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SUMMARY

In an inverse microsuspension polymerisation initiated by a redox pair, at least one component of the redox pair must be segregated from the monomer initially to restrict the extent of polymerisation before the dispersion is established. Normally, the monomer and the oxidant in aqueous solution are dispersed in an oil phase, and the aqueous reductant is separately added to start polymerisation. Thus, the reaction system initially consists of two types of aqueous drop and the distribution of reactants is heterogeneous in nature. In the literature, no report to date has been found concerning the mechanistic aspects of this polymerisation process. The present work concerns polymerisation of aqueous acrylic acid in drops that are dispersed in a paraffinic oil and stabilised with a non-ionic surfactant. A sodium metabisulphite/potassium bromate redox initiation system is used. Drop mixing in agitated dispersions has been investigated by examining the aqueous drop behaviour in simulation systems using various developed techniques. The evolution of aqueous drop size and size distribution has been characterised throughout the course of polymerisation using a freeze-fracture technique with electron microscope. The variations of polymerisation rate, limiting conversion, final particle size and size distribution have been investigated by altering several key parameters, such as agitation intensity, volume and composition of the aqueous reductant and ways of adding the aqueous reductant. Aqueous polymerisation of acrylic acid in a single-phase, initiated by the redox pair, has been also studied and a reaction scheme has been proposed. Kinetic relationships for polymerisations in both an aqueous homogeneous medium and a heterogeneous medium have been obtained and rationalised in terms of mechanism. A new hypothesis for the polymerisation process has been developed which differs from both conventional suspension and emulsion polymerisations. It is believed that the polymerisation takes place in the aqueous drops as a result of continuous simultaneous coalescence and break-up of the different types of aqueous drops. The surfactant has important effects on the course of polymerisation. A preliminary model has been developed for describing this specific polymerisation process. The publications arising from the present project are listed in Appendix VIII.
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CHAPTER 1

INTRODUCTION

1.1 DEFINITION OF TERMS

It is well known that the polymerisation of a vinyl monomer is an addition polymerisation in which "the polymers are formed by the stepwise addition of small molecules to an entity that is commonly, but not necessarily, a specially reactive species such as a free radical or ion" (Allen and Patrick, 1974). A redox system for initiating an addition polymerisation is made of an oxidising agent and a reducing agent, termed oxidant and reductant respectively. "The essential feature in redox initiation is a single-electron transfer, generating free radicals which are sufficiently active to initiate" (Bamford, 1989). Therefore, the polymerisation of acrylic acid initiated by sodium metabisulphite/potassium bromate redox pair follows the mechanism of a free radical initiated addition polymerisation.

The research addressed in this project is mainly concerned with redox pair initiated polymerisation of aqueous acrylic acid in aqueous drops that are dispersed in a hydrocarbon oil and stabilised with a non-ionic surfactant. This polymerisation system can be referred to as a heterogeneous polymerisation according to the classification based on the number of phases (Kucera, 1992). In contrast, the polymerisation of acrylic acid in aqueous solution, termed aqueous polymerisation, proceeds in a single-phase throughout the course of reaction and therefore is defined as homogeneous polymerisation.

In conventional heterogeneous polymerisations, hydrophobic monomers are dispersed in water using oil-in-water surface-active substances. The typical examples of this type of system are suspension and emulsion polymerisations. The former is "a
procedure whereby ... the polymerisation is allowed to proceed within the individual monomer drops ... and the reaction is best regarded as a ‘micro-bulk’ polymerisation”, whilst the latter is “a process in which the several concurrent propagating centres are isolated from one another” (Blackley, 1975). In the 1960's, patents concerning the polymerisation processes for producing water-soluble polymers in heterogeneous media appeared in the literature (Friedrich and Wiley, 1961; Vanderhoff and Wiley, 1966). In this type of heterogeneous polymerisation, aqueous solutions of hydrophilic monomer are dispersed in continuous hydrophobic oil media using surface-active substances promoting the formation of water-in-oil dispersions. To distinguish this from conventional definitions, the term “inverse” is employed to imply this type of heterogeneous polymerisation (Vanderhoff et al, 1962).

In the literature, a number of inverse heterogeneous polymerisations have been reported and various nomenclatures have been proposed for individual systems based on the specific process characteristics. In their pioneering work, Vanderhoff and co-workers (1962) proposed a schematic representation of an inverse emulsion polymerisation system, which was almost exact “mirror-image” of a conventional emulsion polymerisation system, and postulated an initiation procedure similar to that in conventional emulsions. Thereafter, the term of inverse emulsion polymerisation was used by a number of researchers (Kurenkov et al, 1978; McKechnie, 1982; Pichot et al, 1985). In the early 1980's, inverse microemulsion polymerisation was successfully performed in an inverse heterogeneous system which was optically transparent and thermodynamically stable (Leong and Candau, 1982). Baade and Reichert (1984) used a term of “dispersion polymerisation” for polymerisation in a water-in-oil system. The polymerisation was believed to occur in the aqueous monomer droplets initiated by free radicals transferring from the oil phase. Dimonie et al (1982) reported a polymerisation in a water-in-oil system with three distinct reaction stages. The term of “inverse suspension polymerisation” was employed, but the main features of this polymerisation process was quite different from that in a conventional suspension polymerisation. Hunkeler et al (1989) proposed the nomenclature “inverse microsuspension polymerisation” for the polymerisation in a
water-in-oil system based on two important features: the polymerisation took place in the aqueous monomer droplet; the aqueous droplet size was so small that the total interfacial area was large relative to the droplet volume and hence radical reactions within the interfacial layer were competitive with the reactions within the aqueous monomer droplets. Recently, the researchers from some major research groups working in the relative field jointly published a paper which categorised and distinguished water-in-oil polymerisation systems (Hunkeler et al, 1994).

In the present project, the research work revealed three specific features of the polymerisation process: (a) the two components of the redox pair were oil-insoluble and initially segregated in two types of aqueous drops; (b) the polymerisation occurred in the aqueous drops as simultaneous coalescence and break-up of the aqueous drops proceeded; (c) initially, the size of the aqueous drops (0.6 - 2.0 μm) was much smaller than that in conventional suspensions, but the aqueous reductant was present as big drops; the evolution of drop size and size distribution during the course of polymerisation had important effects on polymerisation kinetics and final product properties. Based on these, the term of inverse microsuspension polymerisation was employed for the present polymerisation process.

1.2 RESEARCH BACKGROUND AND OBJECTIVE

Water-soluble polymers have been used in a wide variety of fields such as adhesives, dispersants, flocculants, printing plates, viscosity modifiers and thickeners, fibre dying and modification, leather substitutes, paper sizing, protective colloids in photographic emulsions, surface coatings, textile treatments, gels for electrophoresis, improvement of cements, water purification, paper treatments, soil stabilisation, well drilling, boiler water treatment, hair sprays, ion-exchange resins, pigment binders and polyester-binding resins.

So far, numerous ways have been developed for producing water-soluble polymers in both homogeneous and heterogeneous media. Like conventional heterogeneous
polymerisations, inverse heterogeneous polymerisations provide many advantages. Firstly, the physical state of the systems makes it easy to control the processes. Thermal and viscosity problems are much less significant than in bulk and solution polymerisations. These are specially important for the production of acrylic polymers because of the extremely high viscosity of corresponding polymer solutions even at very low conversions, their relatively high propagation rates and the large exothermicities of polymerisation. Secondly, by performing an inverse heterogeneous polymerisation under proper conditions, for instance by an emulsion polymerisation mechanism, the molecular weight of produced polymer and polymerisation rate can be varied independently of each other due to the fact that the free radicals grow in relative isolation. The increasing demands for linear high molecular weight water-soluble polymers have intensively promoted the development of this kind of inverse heterogeneous polymerisation. Finally, the final products are colloidal dispersions of hydrophilic polymeric particles dispersed in continuous organic phases, which retain good stability and can be used either directly or be subjected to azeotropic distillation, solvent removal and drying. In some cases, the application of these final lattices is preferred to the use of dry polymers because of the former have lower viscosity and are more conveniently stored and easily dissolved on adding excess water.

The first academic research concerning the inverse heterogeneous polymerisation was performed by Vanderhoff and co-workers in the 1960's (Vanderhoff et al, 1962). From the 1980's, the rapid growth in the application of water-soluble polymeric materials has brought increasing interests from a number of research groups around the world, including the pioneering Vanderhoff's group in USA (Vanderhoff et al, 1984), Reichert's group in Germany (Baade and Reichert, 1984, 1986; Hubinger and Reichert, 1989), Candau's group (Candau et al, 1984; Candau et al, 1985; Carver et al, 1989 a, b; Candau, 1992) and Pichot's group (Graillat et al, 1986; Glukhikh et al, 1987; Graillat et al, 1990, Graillat et al, 1991) in France, Barton's group in Czech and Slovak (Vaskova et al, 1990 a, b; Barton, 1991, 1993), Hamielec's group in Canada (Hunkeler et al, 1989; Hunkeler and Hamielec, 1991), Kurenkov's group in former USSR (Kurenkov and Myagchenkov, 1980, 1991; Kurenkov et al, 1982; Kurenkov et al, 1986; Kurenkov et al, 1991), Dimonie's group in Romania (Dimonie et al, 1982;
Dimonie et al, 1992) and Hunkeler and co-workers (Barajas, J. H-. and Hunkeler, D, 1997 a, b).

One of the most important features in the inverse heterogeneous polymerisations is the usage of initiators in a broad range of miscibility with water, from water-soluble to oil-soluble. This has brought new information which could not be readily described by the conventional concepts. Various hypotheses of process mechanism have been developed for specific systems. Regarding the initiation of polymerisation, particle formations have been postulated to take place in aqueous monomer drops, inverse micelles and continuous oil phase. However, the majority of attention so far has been focused on the inverse heterogeneous polymerisations using single-component initiators.

Redox polymerisations are normally characterised by (i) very short induction period, (ii) high yield of polymers with a comparatively high molecular weight in a short time, (iii) relatively low activation energy, and (iv) the possibility of performing polymerisations at room temperature or lower (Konar and Palit, 1961). Scott Bader Company Limited has been commercially manufacturing a series of water-soluble polymeric products via inverse heterogeneous polymerisations using redox initiators. A literature search revealed that there was no report to date concerning the mechanistic aspects of this kind of processes in spite of simple descriptions in a few papers and patents (see Chapter 2).

When a water-soluble redox pair is used to initiate an inverse heterogeneous polymerisation, at least one of the two components must be segregated from the monomer to restrict the extent of polymerisation before the inverse dispersion is established. Normally, an aqueous solution containing the monomer and the oxidant are initially dispersed in the oil and stabilised with surfactant(s). The reductant in aqueous solution is then introduced to start polymerisation. Therefore, in the initial state, the reaction system consists of two different types of aqueous drops and the distribution of the reactants is heterogeneous in nature. Obviously, sharp distinctions exist between this polymerisation system and that using a single-component initiator.
The main objective of this project is to elucidate the mechanism of redox pair initiated polymerisation of aqueous acrylic acid dispersed in a hydrocarbon oil and stabilised with a non-ionic surfactant. The steps towards this objective are envisaged as follows:

Firstly, the aqueous drop behaviour in the inverse dispersion was investigated using simulation systems. Because the two components of the redox pair are segregated in the two different types of aqueous drops in the initial stage, it was supposed that the drop coalescence and break-up in the turbulence field of agitation could play an important role in generation of primary radicals and in determination of main polymerisation locus. In order to characterise the intermixing of reactants in different aqueous drops via simultaneous drop coalescence and break-up, several techniques were developed by conducting simulation experiments.

Secondly, a hypothesis for the mechanism of the present inverse microsuspension polymerisation process was proposed based on the observations in simulation experiments and the specific features of the reaction system.

Thirdly, kinetics of polymerisations in both aqueous solution and inverse dispersion were studied. It was expected that the rationalisation of experimental kinetic relationships in terms of mechanism could reveal the existence of some important reactive species or/and reactions in the aqueous polymerisation of acrylic acid initiated by sodium metabisulphite/potassium bromate redox pair. In addition, the comparison of kinetic relationships between the polymerisations in homogeneous medium and in inverse heterogeneous medium helped in verifying the new hypothesis for the inverse microsuspension polymerisation process. The successful performance of kinetic studies required the construction of an isothermal polymerisation apparatus and the development of techniques for monomer conversion determination. Special efforts were made to overcome the difficulties arising from the high exothermicity and rapid reaction in the present polymerisations.

Fourthly, the variation of polymerisation rate, limiting conversion, particle size and size distribution in the final lattices in the inverse microsuspension polymerisation
were examined by altering some key parameters that were believed to have important influences on drop mixing, such as agitation intensity, composition and volume of the reductant aqueous solution and methods of adding the reductant aqueous solution.

Finally, a preliminary model was developed for describing this specific inverse microsuspension polymerisation system.

1.3 THESIS ORGANISATION

The literature survey is presented in Chapter 2. In view of the complicated features of the present polymerisation system which differs from the definitions of both conventional suspension and emulsion polymerisations, the literature search covers the major fields of inverse heterogeneous polymerisations. In addition, the aqueous polymerisations of acrylic acid and the research on the use of redox systems containing sodium metabisulphite or potassium bromate are reviewed. Moreover, the published work in the area of drop mixing is also briefly summarised.

Chapter 3 is concerned with the preliminary investigations on aqueous drop behaviour in the inverse dispersion. The detailed development of techniques for characterising aqueous drop coalescence and break-up is described and the observations are discussed.

Chapter 4 is about the construction of the isothermal polymerisation apparatus and the operation of polymerisation in both homogeneous and heterogeneous media by using the constructed apparatus. The developments of techniques for following polymerisation, including temperature monitoring (for non-isothermal polymerisation only) and monomer conversion determination, are also presented.

In Chapter 5, the work that focuses on exploring the general features of the inverse microsuspension polymerisation is presented. Combined with the observations in the simulation experiments discussed in Chapter 3, it leads to a hypothesis for the mechanism of the inverse microsuspension polymerisation using the redox initiators.
Chapter 6 is relatively independent, but interconnects with the others. It deals with the mechanistic aspects of aqueous polymerisation of acrylic acid initiated by sodium metabisulphite/potassium bromate redox pair in the absence and in the presence of the surfactant. The mechanisms of elementary reactions involved in the polymerisation are elucidated and a reaction scheme is proposed. The kinetic models are established and compared with the experimental relationships.

Chapter 7 presents the kinetic studies of the polymerisation of acrylic acid in inverse heterogeneous medium using sodium metabisulphite/potassium bromate redox pair. The differences in the experimental kinetic relationships between the polymerisations in inverse heterogeneous medium and in aqueous solution were discussed in respect to the new hypothesis for the process mechanism presented in Chapter 5.

In Chapter 8, the effects of some key parameters on polymerisation rate, limiting conversion, final particle size and size distribution are investigated and discussed in terms of drop mixing.

Chapter 9 details the modelling of the inverse microsuspension polymerisation using redox initiators.

Finally, Chapter 10 highlights the main conclusions drawn in the present research work and recommends some possible work required to be done in the further research.
CHAPTER 2

LITERATURE REVIEW

2.1 POLYMERISATION OF ACRYLIC ACID

Acrylic acid \( (\text{CH}_2=\text{CHCOOH}) \) can be regarded as a derivative of ethylene with a substituent carboxyl group. Its reactivity stems from the presence of the two different unsaturated centres situated in a conjugated position. The polarisation of the terminal olefinic bond by the proximity of the carbonyl group imparts a strong electrophilic character which favours the addition of a nucleophile (Luskin, 1970). It can readily undergo polymerisation by a free radical mechanism.

\[
\text{CH}_2=\text{CHCOOH} + R\cdot \rightarrow R\text{CH}_2\cdot \text{CHCOOH} \\
\text{+ n CH}_2=\text{CHCOOH} \rightarrow \{ \text{CH}_2\text{CHCOOH} \}_{n+1}
\]

The polymerisation in solution can proceed at a very high rate depending on pH and solvent (Evans and Tyrrell, 1947). The polymerisation heat is approximately 77.5 kcal/mol in water (Busfield, 1989).

The strongly polar carboxyl group can associate via hydrogen bonds, with polyacrylic acid and with some solvents to form complexes. This association could cause changes in polymerisation kinetics and even in the properties of the generated polymer.

Galperina et al (1975, 1976) performed kinetic studies of photosensitised polymerisation of acrylic acid in water, formamide and dimethylsulphoxide. By using the rotating sector technique, they observed a strong solvent dependence for the rate
constant for propagation. At 293 K, $k_p$ (mol$^{-1}$dm$^3$s$^{-1}$) was 22,500 in water, 4,200 in formamide and 500 in dimethylsulphoxide.

A systematic investigation of solvent effects of on the radiation initiated polymerisation of acrylic acid was conducted by Chapiro and Dulieu (1977). It was found that solvents of the first group (water, methanol and dioxane) did not affect significantly the rate of polymerisation at moderate dilutions nor the stereoregularity of the resulting polyacrylic acid, which remains largely syndiotactic; in solvents of the second group (hydrocarbons and their chlorinated derivatives), the rate of polymerisation dropped steeply on dilution and the stereoregularity disappeared. The authors established the dominant role of molecular associations in the system for these phenomena. Acrylic acid associated by hydrogen bonds to form cyclic dimers (structure I) or linear oligomers (structure II):

\[
\text{cyclic dimer (I)} \quad \text{linear oligomer (II)}
\]

Structure I and II were in dynamic equilibrium, depending on the solvents.

The first group of solvents stabilised the oligomers whilst the second group of solvents did not associate with acrylic acid and shifted the above equilibrium to the left. The oligomeric aggregates associated via hydrogen bonds to the polymer matrix which was formed in the early stages of the reaction. In this way an organised structure was formed suitable for rapid "zip" propagation along the oriented double bonds generating a stereoregular polymer:
In the second group of solvents, the cyclic dimers did not form an oriented structure with the polymer and the “matrix effect” disappeared.

Kabanov et al (1973) obtained a crystalline, syndiotactic polyacrylic acid by free radical polymerisation of acrylic acid in aqueous solution at pH 10.2-10.8. It was postulated that the participation of ion pairs (involving ionised monomer, propagating radical anion and introduced cation) in the propagation step led to a stereochemical effect and, in certain circumstances, to the formation of stereospecific polymers.

The carboxyl on the acrylic acid molecule is an ionisable group. Therefore, the physical and chemical properties of acrylic acid and its macroradical formed in free-radical polymerisation are rather sensitive not only to variation in solvent type, but also to composition. Compared with polymerisation of non-ionisable monomers, a number of additional factors, such as dissociation, specific and non-specific binding of ions, electrostatic and hydrophobic interactions, etc., could strongly influence the state of acrylic acid and its macroradical in solution (Kabanov et al, 1973). Pinner (1952) and Blauer (1953) reported a significant effect of pH value of reaction mixture on the reaction rate in aqueous polymerisations of methacrylic acid initiated by potassium persulphate and AIBN respectively. Both authors attributed the effects to the variation of ionisation of monomer and propagating radicals with pH and believed that the addition of monomer to propagating radicals varies with the percentage of ionisation. Kabanov et al investigated the aqueous polymerisation of acrylic acid in the pH range of 1-13 (Kabanov et al, 1973). It was found that the dependence of the initial polymerisation rate on pH was nonmonotonous. The polymerisation rate and polymer molecular weight decreased rapidly with pH increasing from 1 to 6 and
showed minimum values at pH 6-7. They attributed these effects to the increase in the concentration of the acrylate (pKa 4.2 for acrylic acid) anion with increased pH value, based on the hypothesis that the addition of acrylate anion to unionised macroradical (pKa 6.4 for polyacrylic acid) is slower than that of unionised acrylic acid. When the pH was increased from 7 to 11, considerable increases in the rate and the molecular weight were observed. This was interpreted by a hypothesis about the ion pair playing an important part in the kinetics of polymerisation of ionisable monomers. In the case of polymerisation of acrylic acid using NaOH as neutraliser, the increase in the rate was assumed to be caused by an increase in the local concentration of Na\(^+\) in the vicinity of ionised propagating radicals. In this way, the electrostatic repulsion between the like charged anions of the propagating radical and the monomer would be diminished if the ionisable groups at the ends of the growing chains were involved in the formation of such ion pairs:

\[
\text{CH}_2=\text{CH}^+ \quad \text{CH}_2=\text{CH}
\]

In addition, the polymerisation rate was also dependent on the type of cation and cation concentration for pH > 7.0. This is in agreement with the above mentioned hypothesis. The influence of cation type on the polymerisation rate was connected with the different capabilities of respective cations to form ion pairs at the ends of negatively charged macroradicals.

For radical polymerisation of acrylic acid, different methods have been employed for generating reactive centres. Chapiro and Dulieu (1977) conducted solution polymerisations of acrylic acid in various solvents by radiation initiation using gamma-rays at 20 °C. Kabanov et al (1973) performed aqueous polymerisation of acrylic acid sensitised by photochemical decomposition of AIBN under UV irradiation at the wavelength of 365 nm at 23 °C. Mishra and Bhadani (1983, 1985) found that acrylic acid readily underwent polymerisation using nitrogen dioxide as initiator in
different solvents. Avela et al (1989) initiated the precipitation polymerisations of acrylic acid in toluene by decomposing ADVN in temperature range of 40 to 60 °C.

A number of papers have been found in the literature concerning the use of redox initiation systems in solution polymerisations of acrylic acid, including Fe\(^{2+}/\text{H}_2\text{O}_2\) (Evans and Tyrall, 1947; Fergusin and Eboatu, 1989), hydrosulphite/oxygen (Igarashi et al, 1989) and persulphate/sulphite pairs (Hafiz et al, 1990). The chemistry of redox polymerisation of acrylic acid will be presented in the following section.

### 2.2 REDOX INITIATORS

The first discovery of vinyl polymerisations initiated by redox initiation systems was made in the 1940s. Bacon (1946), Baxendale et al (1946) and Morgan (1946) independently observed that addition of small quantities of a reducing agent greatly increased the rate of initiation by peroxy compounds. They indicated the specific features of this system of high reaction rate and low reaction temperature. Thereafter, the research in this area has received much attention and numerous redox initiation systems have been developed. The early history of redox initiation was reviewed by Bacon (1959). The use of redox initiation systems in radical polymerisations have been extensively summarised in the literature. (Bovey et al, 1955; Duck, 1996; Vanderhaff, 1969; Konar and Palit, 1961; Cooper, 1974; Bamford, 1989).

The classic most intensively studied redox system is Fenton's reagent which is a mixture of hydrogen peroxide and a ferrous salt (Fenton, 1894). Subsequent research on the mechanism of this system has revealed a chemical reaction scheme shown below (Bamford, 1989):

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH} \quad (2-5) \\
\text{Fe}^{2+} + \cdot\text{OH} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (2-6) \\
\cdot\text{OH} + \text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O} + \text{HO}_2 \cdot \quad (2-7) \\
\text{Fe}^{2+} + \text{HO}_2 \cdot & \rightarrow \text{Fe}^{3+} + \text{HO}_2^- \quad (2-8)
\end{align*}
\]
In the presence of a vinyl monomer, the hydroxyl radical generated in reaction \((2-5)\) initiates polymerisation.

Peroxy and persulphate compounds coupled with reducing metal ions (e.g. \(\text{Ag}^+, \text{Co}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}\) and \(\text{Ti}^{3+}\), etc.) can undergo reactions similar to reaction \((2-5)\), which are essentially one electron transfer with concomitant rupture of the \(-\text{O-O-}\) or \(-\text{S-S-}\) bonds.

In addition, a variety of organic compounds have been developed in conjunction with metal ions to form redox initiation systems. This was summarised by Bamford (1989).

Another type of redox system for initiating radical polymerisation, which has been widely used in emulsion polymerisation, is the combination of oxidising and reducing agents free from transfer metals. Normally single electron transfer in these systems leads to two free radicals, both of which may initiate polymerisation, although the behaviour in a given system depends on the radicals and monomer reactivities. Compared with Fenton's reagent, this type of redox initiation system is insufficiently studied and "often the detailed chemistry involved is somewhat obscure" (Bamford, 1989). A typical widely used redox initiation system of this type is the persulphate/metabisulphite redox pair (Bamford, 1989; Kurenkov et al, 1987; Graillat et al, 1991; Elhakim et al, 1992; Ebdon et al, 1994a, b).

A proposed reaction scheme for this redox pair is (Bamford, 1989):

\[
\text{S}_2\text{O}_3^{2-} + \text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_4^{2-} + \text{S}_2\text{O}_5^{2-} \tag{2-10}
\]

Here the metabisulphite ion functions as a reductant and a metabisulphite radical ion is generated.
In the aqueous polymerisation of acrylamide initiated by potassium permanganate/sodium metabisulphite redox pair, Bajpai et al (1992) proposed a reaction scheme for initiation:

\[
\begin{align*}
S_2O_3^{2-} + H_2O & \leftrightarrow 2HSO_3^- \\
HSO_3^- + Mn^{4+} & \rightarrow Mn^{3+} + HSO_3^- \\
HSO_3^- + Mn^{3+} & \rightarrow Mn^{2+} + HSO_3^- 
\end{align*}
\]

The reductant here is bisulphite ion rather than metabisulphite ion. This suggestion was supported by recent end-group studies of polyacrylonitrile produced by using an ammonium persulphate/sodium metabisulphite redox pair in aqueous polymerisation (Ebdon et al, 1994 a). By using FTIR, high-field \(^{13}\)C and \(^{1}H\) NMR techniques, Ebdon et al found that the produced polymer possessed predominantly sulfonate end-group derived from initiation by bisulphite radicals and non-sulphur containing end-group by transfer to the bisulphite ion (Ebdon et al, 1994 b). Small amounts of sulphate and hydroxyl end-groups were also present. This was believed to be raised from initiations by sulphate radical ions and by hydroxyl radicals deriving from transfer of radicals to water respectively. Based on these results, they proposed a reaction scheme for the initiation:

\[
\begin{align*}
S_2O_3^{2-} + H_2O & \rightarrow 2HSO_3^- \\
S_2O_8^{2-} + HSO_3^- & \rightarrow SO_4^2- + SO_4^- + HSO_3^- \\
S_2O_8^{2-} & \rightarrow 2SO_4^- \\
R - + H_2O & \rightarrow RH + HO^- 
\end{align*}
\]

Here \(R^-\) represents the radicals produced in reactions (2-14) to (2-17). It was believed that reaction (2-15) was the dominant radical producing reaction at polymerisation temperature of 40°C.
Potassium bromate is a powerful oxidising agent and has been widely used for initiating aqueous polymerisations of vinyl monomers in conjunction with reducing agents. The most intensive studied reducing agents coupled with potassium bromate have been, so far, the thio- compounds, such as thiourea (Mishra et al, 1981), thioacetamide (Baral et al, 1982) and thiomalic acid (Shukla et al, 1984). These redox initiation systems have recently received considerable interest in the initiation of grafting polymerisations (Hebeish et al, 1996; Bajpai and Jain, 1993; Devarajan et al, 1993). Some compounds containing heavy metal ions (Fe$^{2+}$ and Co$^{2+}$) were also used as reducing agents to form redox initiation pairs with potassium bromate (Mishra et al, 1981; Elangovan and Saccubai, 1994; Barr, 1995).

In 1951, an US patent reported the use of potassium bromate coupled with a series of reducing sulfoxyl compounds in initiation of aqueous polymerisations of acrylonitrile, methyl methacrylate and vinyl chloride (Howard, 1951). However, this type of redox initiation system is still insufficiently studied in spite of the work performed by Palit and co-workers concerning the end-group studies of the polymers using potassium bromate/sodium bisulphite and potassium chlorate/sodium bisulphite redox pairs (Mukherjee et al, 1966). By using a dye technique, the authors found that the produced polymers contained about 2 nonhydrolysable sulfoxyl end-groups per chain. Some hydroxyl groups were also found to be incorporated particularly when the potassium chlorate or potassium bromate concentration was very low. The mechanism of radical generation by potassium chlorate/sodium bisulphite was suggested as:

$$H$SO$_3^-$ + $ClO_3^-$ $\rightarrow$ \[
\begin{bmatrix}
ClO_3^{-} \\
O \\
HO-S-O^{-}
\end{bmatrix}
\rightarrow ClO_2^- + \cdot OH + SO_3^- \cdot
\] 

The initiations by both sulphite radical ion and hydroxyl radical were in agreement with the views of Gleason et al based on their kinetic studies on chlorate/bisulphite reaction (Gleason et al, 1957).
However, in the polymerisation of vinyl chloride initiated by potassium chlorate/sodium bisulphite, Firsching and Rosen (1959) reported much lower content of initiator fragments chemically combined in each molecule of the resultant polymer. Using radioactive-tracer method, they found that about 0.3 to 0.5 atom of sulphur was combined with each polymer molecule depending on the concentration of the initiators. They also detected about 0.08 atom of chlorate-derived chlorine per polymer molecule chemically incorporated. The redox reactions were supposed to be complex and the following possibilities were suggested:

\[
SO_3^{2-} + ClO_2^- \rightarrow [O_3SOClO_2]^{3-} \rightarrow SO_4^{2-} + ClO_2^- \quad (2-19)
\]

\[
[O_3SOClO_2]^{3-} + 2H^+ + CH_2 = CHCl \rightarrow CHClCH_2SO_3 + ClO_2 + H_2O \quad (2-20)
\]

\[
SO_3^{2-} + ClO_2^- \rightarrow [O_3SOClO]^{3-} \rightarrow SO_4^{2-} + ClO^- \quad (2-21)
\]

It can be seen that the intermediate \([O_3SOClO_2]^{3-}\) could lead to formation of free radical only in the presence of vinyl monomer.

Hypochlorite ions could then react with sulphite ions to produce free radicals:

\[
ClO^- + H^+ \Leftrightarrow HOCl \quad (2-22)
\]

\[
SO_3^{2-} + HOCl \rightarrow SO_4^{2-} + HO \cdot + Cl \cdot \quad (2-23)
\]

or \[
SO_3^{2-} + HOCl \rightarrow SO_4 \cdot + HO^- + Cl \cdot \quad (2-24)
\]

Firsching and Rosen provided evidence to suggest that reactions (2-23) and (2-24) were not important for the initiation of polymerisation. The presence of chlorate-derived chlorine fragment in the polymer molecule could be due to the termination by the chlorine radicals produced in reactions (2-23) and (2-24). An alternative explanation was transfer with molecular chlorine which might be formed by combination of the chlorine radicals, or by reaction between hypochlorous acid and
the hypochloric acid which could in turn be formed by further reduction of the hypochlorous acid by the sulphate anion.

2.3 INVERSE HETEROGENEOUS POLYMERISATION

Water-soluble monomers were conventionally polymerised by mass or solution techniques. Both of these methods have disadvantages, such as thermal and viscosity problems. In 1960's, patents concerning inverse heterogeneous polymerisation processes (water-in-oil) for preparing water-soluble polymers appeared in the literature (Friedrich and Wiley, 1961; Vanderhoff and Wiley, 1966). In an inverse heterogeneous polymerisation system, an aqueous solution of hydrophilic monomer was dispersed in continuous hydrophobic oil phase and emulsified using a water-in-oil stabiliser. The polymerisation could be initiated by using either oil-soluble or water-soluble initiators. The final product was a kind of colloidal dispersion of polymer aqueous solution particles in a continuous oil phase. In the 1980's, the studies on this kind of polymerisation process began to be renewed because of the major new applications of water-soluble polymers with high molecular weight in many fields.

In the literature, the first detailed study on inverse heterogeneous polymerisations was performed by Vanderhoff and co-workers (1962). The authors proposed a schematic representation of an inverse emulsion polymerisation system, which appeared an almost exact "mirror-image" of a conventional emulsion polymerisation system (oil-in-water). It was postulated that the initiation of polymerisation proceeded by a mechanism analogous to that of a conventional system and submicroscopic particles of water-swollen hydrophilic polymer were generated in the continuous oil phase. However, the applications of water-soluble initiators and the uncertainty of existence of inverse emulsifier micelles in some circumstances have brought a lot of new information and made the mechanism of inverse heterogeneous polymerisation much more complex. In the literature, different nomenclatures, such as "inverse emulsion", "inverse microemulsion", "inverse suspension", "inverse microsuspension" and
“dispersion polymerisation” have been appropriately employed (see Chapter 1). All these inverse heterogeneous polymerisations will be covered in this section.

2.3.1 Main Components and Their Effects

2.3.1.1 Monomer

In their pioneering work, Vanderhoff and co-workers (1962) listed the followings as typical hydrophilic monomers which were suitable as subjects for the reaction: sodium \(\alpha\)-vinylbenzene sulfonate, sodium vinylbenzyl sulfonate, 2-sulfoethyl acrylate, acrylic acid, acrylamide, vinylbenzyl-trimethylammonium chloride, and 2-aminoethyl methacrylate hydrochloride. So far, the majority of research work reported in literature has focused on the polymerisation of acrylamide and on its copolymerisation with other hydrophilic monomers. The inverse heterogeneous polymerisation of acrylamide was reviewed by Kurenkov and Myagchenkov (1991). In contrast, the work on inverse heterogeneous homopolymerisation of acrylic acid is few (Volk et al, 1970; Brooks and Liu, 1996; Liu and Brooks, 1997 a, b).

In addition to undergoing chain propagation, monomers could have influences on the polymerisation systems in some circumstances. Candau and coworkers (1984) reported that the addition of acrylamide to a ternary toluene/Aerosol OT/water system had a profound effect on its properties, that is, the inverse microemulsion domain was extended upon the addition of acrylamide. This effect was attributed to a preferential location of acrylamide at the water/oil interface due to the strong polar interaction between acrylamide and toluene molecules. In this case, acrylamide acted as a co-surfactant in this inverse microemulsion system leading to an increase of micellar solubilisation capacity. This would favour the location of the initiation of acrylamide by emulsifier radicals at the water-oil interface. The co-surfactant function of acrylamide resulted in a monomer-rich region in the surface layer (shell) of the “water pool” of the inverse micelle, which provided the main locus of propagation for the polymerisation of acrylamide in inverse microemulsion (Barton, 1991). The co-
emulsifier function of a monomer could increase the stability of the emulsion (Buchert and Candau, 1990).

On the other hand, Kobyakova et al (1993) found that the introduction of 50 wt% acrylamide into the aqueous phase resulted in an approximately four-fold decrease of the value of maximal adsorption of Span 60 onto the surface of the aqueous phase. This was attributed to the decrease in interfacial tension at the oil/water interface by the presence of polar monomer and interpreted by the Gibbs equation of adsorption:

\[ \Gamma \Delta \mu = \sigma_{12} - \sigma_a \]  

Here \( \sigma_{12} \) is the initial interfacial tension, \( \sigma_a \) is the interfacial tension after adsorption of the emulsifier, \( \Gamma \) is the Gibbs adsorption and \( \Delta \mu \) is the difference in chemical potentials of the emulsifier in bulk and at the interface. A decrease in \( \sigma_{12} \) always leads to a decrease in the adsorption of the emulsifier (\( \Gamma \)) on the surface of aqueous droplets and hence reduces the stability of the emulsion.

In the case of AIBN as initiator, the polymerisation rate of acrylamide/Span 60/heptane system was found to be 1.30-1.34 order dependant on the acrylamide concentration. The high order with respect to the monomer concentration, as compared with that of conventional emulsion polymerisation, was attributed to the increase in the solubility of AIBN in the aqueous phase with the growth in the monomer content (Gromov et al, 1988). The promotion of AIBN solubility in the aqueous phase in the presence of acrylamide was also found by the partitioning experiment in an acrylamide/toluene system with a mixture of Montane 83 and Montanox 85 as emulsifier. An increase by a factor of 2.4 in the solubility of AIBN in the aqueous phase was observed (Graillat et al, 1986).
2.3.1.2 Emulsifier (Surfactant, Stabiliser)

Emulsifier is employed in a heterogeneous polymerisation system to stabilise the initial monomer droplets and the growing polymer particles during the polymerisation by generating the barrier between two particles due to the competition between Van der Wales interactions and repulsive double layer forces. In conventional emulsion polymerisations, another important role of emulsifiers is to form emulsifier micelles which provide locus for particle nucleation.

The molecule of an emulsifier consists of both hydrophilic and hydrophobic groups. Both ionic and non-ionic emulsifiers have been successfully used. The ratio of the respective weight percentage of these two groups, represented by hydrophilic-lipophile balance (HLB), has a strong influence on emulsification behaviour. For inverse heterogeneous polymerisations, oil-soluble emulsifiers with relatively low HLB value are normally used, such as oxyethylated alkylphenols, Aerosol OT (sodium bis(2-ethylhexyl sulfosuccinate)), sorbitan esters of fatty acids (Spans) and their oxyethylated derivatives (Tweens). The applications of two-emulsifier blends were reported in the literature because of the benefit of giving a wide range of HLB values. An experimental study of emulsion stability of aqueous acrylamide in xylene was carried out by varying the ratio of Span 80 and Tween 80 (McKechnie, 1982). The steady state interfacial tension results based on a Wilhelmy Plate method and "jar testing" indicated that an 8 wt% solution of 3 : 1 blend of San 80/Tween 80 was required to stabilise the emulsion, whereby the particle size is 150 nm. Graillat et al (1986) investigated the stability of the dispersions of aqueous acrylamide and other water-soluble comonomers in toluene and found it possible to keep the droplet size (as measured by dynamic light scattering) unchanged for one hour or more by using a mixture of two emulsifiers: Monane 83 (sorbitan sesquioleate) with low HLB and Montanoxa 85 (polyoxyethylene sorbitan trioleate) or C18-mercapto-terminated acrylamide oligomers with high HLB. The best stability of aqueous acrylamide-toluene emulsion was obtained using 10 wt% Montane 83 (based on toluene) and 5-10 wt% either Montanoxa 85 or acrylamide oligomers. The average monomer droplet size was 200 nm.
Compared with oil-in-water dispersions, the stability of inverse dispersions (water-in-oil) is normally rather low. Albers and Overbeek (1959) calculated that the length of the hydrocarbon chains of common emulsifiers was less than 20 Å, but the distance to which mutual attraction between two aqueous droplets acted in non-polar media was about 40 Å. Therefore, the common emulsifier was insufficient to prevent aqueous droplets from sticking at their approach. The presence of an electrical charge at the surface of the aqueous droplets could not create a potential barrier against droplet flocculation, because the maximum of the potential energy of repulsion between two charged particles was only slightly pronounced and was located at a distance more than 40 Å from the particles. This author’s calculations also suggested that the energy of attraction between aqueous droplets in non-polar media significantly exceeded the energy of Brownian motion of droplets. The energy of Brownian motion might be greater than that of attraction only when particles were less than 0.1 μm in diameter.

Kobyakova et al (1993) related the number of droplets $N$ in a dispersion to emulsifier concentration $c$ by the following equation:

$$N = N_{\text{max}} \left( \frac{c}{c + A} \right)^3$$  \[2-2\]

Here $N_{\text{max}}$ is maximum number of droplets and $A$ is adsorption characteristic of emulsifier:

$$A = \Gamma_{\text{max}} RT / \left( \frac{d\sigma}{dc} \right)_{c \rightarrow 0}$$  \[2-3\]

Here $\left( \frac{d\sigma}{dc} \right)_{c \rightarrow 0}$ is surface activity of emulsifier and $\Gamma_{\text{max}}$ is value of its maximum adsorption onto a droplet’s surface.
It is seen from equation [2-2] that the number of droplets initially increases with increased concentration of emulsifier and then reaches a maximum value. Increasing $N_{\text{max}}$ and $A$ leads to a stronger dependence of droplet number on emulsifier concentration. It should be mentioned that the authors, in deriving the equation, did not take into account for the fact that the adsorption of emulsifier on droplets surface can change the interfacial tension. Equation [2-2] suggests that the maximum order of droplet number with respect to emulsifier concentration can not be greater than 3. However, a higher order was reported by Vanderhoff et al (1962).

It is now well established that the aqueous droplet size in an inverse dispersion is directly related to emulsifier nature and concentration. Candau and coworkers (1984) obtained a clear and highly stable inverse microemulsion system of aqueous acrylamide dispersed in toluene with Aerosol OT as emulsifier. In the inverse emulsion polymerisation of acrylamide in toluene stabilised with a blend of Span 80 and Tween 80, Graillat et al (1986) found that the system was composed of two populations of particles in both initial monomer emulsion and final inverse latex: one with very tiny particles (20 nm diameter) and the other with larger particles (80-400 nm diameter).

Hunkeler (1991) proposed an identification of inverse heterogeneous polymerisation regimes according to the threshold emulsifier concentration as the primary criterion. Above this concentration, for given oil and aqueous phases, a thermodynamically stable inverse "microemulsion" spontaneously forms. Below this concentration, a thermodynamically unstable inverse "macroemulsion" is produced. The prefix "macro" is often omitted for brevity. The inverse macroemulsion can be sub-classified according to a secondary criterion, i.e. the level of emulsifier with respect to the critical micelle concentration (CMC). At emulsifier concentrations below the CMC, an inverse suspension of a dispersed monomer aqueous phase in a continuous oil media forms without the presence of emulsifier micelles. In these suspension systems, nucleation takes place predominantly in the monomer droplets and each particle therefore behaves as an isolated batch polymerisation reactor. By contrast, at
emulsifier concentrations above the CMC, micelles are formed and the system is designated as inverse emulsion. In these cases, the nucleation and propagation normally occur in emulsifier micelles. However, it is difficult to determine the CMC for oil-soluble emulsifiers (Davies et al, 1987; Ruckenstein and Nagarajan, 1980).

For inverse suspension polymerisation, the monomer droplet size is inversely related to the emulsifier level. If emulsifier concentration is high enough and the droplet size is reduced to such an extent that the total interfacial area is large relative to the droplet volume, radical reactions within the interfacial layer, in this case, become competitive with the propagation, termination and transfer reactions occurring within the monomer droplets. In order to distinguish these systems from "inverse macrosuspension" the nomenclature "inverse microsuspension" has been proposed.

Dimonie et al (1982) reported a phase inversion in an inverse suspension of aqueous acrylamide in white spirit when using 2 - 6 wt% of emulsifier (ethoxylated stearic acid or ethoxylated nonphenol). However, polymerisation proceeded without phase inversion when 12 wt% emulsifier was introduced.

Besides the stability function, it has been found that emulsifier(s) could have some complex effects on polymerisation. In an aqueous acrylamide in toluene system with Aerosol OT as emulsifier, Candau et al (1985) found that the addition of AIBN or K₂S₂O₈ as initiator contributed only slightly to the rate of initiation; on the other hand, Aerosol OT evidently played the major role in generating free radicals by forming bisulphite ion which initiated the polymerisation of acrylamide. The phenomenon of participation of emulsifier in the initiation reaction was also observed in acrylamide/Sintamide-5/toluene system by Kurenkov et al (1978). The authors proposed a scheme for the reaction between the emulsifier and the initiator ammonia persulphate:

\[
S_2O_8^{2-} + \sim CH_2-O-CH_2 \rightarrow HSO_4^- + SO_4^{2-} + \sim CH_2-O-\dot{CH}^- \quad (2-25)
\]
As a result, the polymerisation rate increased and the molecular weight decreased with increasing emulsifier concentration.

A number of independent results observed in inverse heterogeneous polymerisations of acrylamide showed the inverse relationships between polymerisation rate and emulsifier concentration (Baade and Reichert, 1984; Candau et al., 1985; Hunkeler et al., 1989). These were contrary to what would be expected by the traditional emulsion polymerisation theories. If the emulsifier sole function was stabilisation, the increase in its concentration would reduce the surface tension and produce larger number of smaller particles. Since the total interfacial area would be larger, the capture efficiency of primary radicals would rise and the overall polymerisation rate would increase.

Hunkeler et al (1989) attributed the inverse relationship between the polymerisation rate and the emulsifier concentration to the reaction between primary radicals and the emulsifier molecules resulting in an increase in the radical scavenging efficiency and a reduction in polymerisation rate. Experiments of polymerisation of acrylamide in aqueous solution were conducted both with and without sorbitan monooleate to confirm the transfer activity of the emulsifier. The result showed that the molecular weight of final product polymerised with emulsifier was 19% larger than that without emulsifier because of the branching polymerisation of emulsifier radicals through their double bond. The hypothesis of chain transfer to emulsifier molecules was supported by the first order dependence of the polymerisation rate in initiator concentration, implying the monomolecular chain termination mechanism in such cases.

However, based on their experimental results, Kobyakova et al (1993) assumed that, for different systems, inverse heterogeneous polymerisation for a rather narrow interval of emulsifier concentration would show variable reaction orders with respect to the emulsifier concentrations. When the emulsifier concentration was relatively low, a growth in emulsifier concentration increased the number of the aqueous droplet and hence resulted in increase in polymerisation rate (positive order). However, to a certain extent, the maximum number of aqueous droplet was attained and the
adsorption of emulsifier molecules on droplet surface became more compact with increased emulsifier concentration. In this case, the adsorption layers retarded the diffusion of initiating radicals from the continuous oil phase into the dispersed aqueous monomer phase and the polymerisation rate decreased as emulsifier concentration increased (negative order).

2.3.1.3 Initiators

Both single-component initiators and redox initiation systems have been widely used in inverse heterogeneous polymerisations.

With redox initiation systems (Li and Ruckenstein, 1996; Carver et al, 1989; Kurenkov et al, 1986; Dimonie et al, 1982), radicals can be produced at a reasonable rate at very moderate temperatures. This allows a greater freedom of choice of the polymerisation temperature than is possible with the thermal decomposition of single-component initiators. This advantage should have potential for controlling polymerisation rate and improving heat removal by performing polymerisation at a relative lower temperature, which is specially important for the polymerisation of acrylic monomers because of their high polymerisation rate and large exothermocity. However, compared with single-component initiators, the utilisation of redox initiators in inverse heterogeneous polymerisation is insufficiently studied.

As mentioned in the proceeding sections, when using single-component initiators, both oil- and water-soluble initiators have been used in inverse heterogeneous polymerisations. The choice of hydrophobic or hydrophilic initiator could directly control the predominate locus for production of primary free and hence influence the polymerisation mechanism.

In the case of using a water-soluble initiator, the major initiation occurs in the aqueous phase. Baade and Reichert (1984) investigated the polymerisation of aqueous acrylamide/Span 80/Isopar M using AIBEA (2,2'-azobis [N-(2-hydroxyethyl) butyramidine]) as a water-soluble initiator. The polymerisation rate was 0.5 order with
respect to the initiator concentration, 1.0 order to the monomer concentration, and independent of the emulsifier concentration. This corresponded to the kinetics of polymerisation in aqueous solution. The square root dependence of polymerisation rate on initiator concentration was also reported by Kurenkov et al (1982) for the polymerisation of aqueous acrylamide in toluene using ammonium persulphate as initiator. In these systems, each aqueous monomer droplet acted as a micro-batch reactor and the kinetics resembled the polymerisation in aqueous solution. However, for the polymerisation of sodium p-vinylbenzene sulfonate initiated by potassium persulphate, Vanderhoff and coworkers (1962) reported a considerable difference in rate between the polymerisation in heterogeneous medium and the polymerisation in aqueous solution. When o-xylene was used as the dispersion medium and Span 60 as emulsifier, the rate of inverse heterogeneous polymerisation was significantly faster than that in the aqueous solution. This suggested differences in polymerisation mechanism.

The polymerisation of water-soluble monomers has been mostly studied in the presence of oil-soluble initiators. The components in such an inverse dispersion corresponds exactly to that in a conventional emulsion with negative hydrophilic-lipophilic properties, except for the existence of water as monomer solvent. It is believed that, in a conventional emulsion system, the polymerisation takes place almost exclusively in the interior of the emulsifier micelles, so that each growing radical is isolated and both high polymerisation rate and high molecular weight can be achieved. Micellar initiation in inverse emulsion polymerisation was postulated by Hubinger and Reichert (1989). However, the main particle nucleation loci of inverse heterogeneous polymerisations were believed to be in aqueous monomer droplets (Hunkeler et al, 1989; Baade and Reichert, 1986; Graillat et al, 1986; Vanderhoff et al, 1984). In inverse heterogeneous polymerisations, there is so far no direct evidence that nucleation occurs in inverse micelles. Because of the specific features of intermolecular interactions, it was believed that, in non-polar media, the aggregation of molecules was possible even at very low concentrations of surface-active agents ($10^{-7} - 10^{-6}$ mol/l) and aggregation number was also small (Ross and Olivier, 1959).
The most favourable form for the aggregation of amphillic molecules in non-polar solvents is lamellar (Ruckenstein and Nagarajan, 1980). Polar groups tend to acquire a compact arrangement in one plane owing to dipole-dipole interactions, whereas hydrocarbon chains stick outside. It seems difficult to form submicron globular particles from lamellar aggregates less than 100 nm in size (Davies et al, 1987). Moreover, micellar polymerisation requires a significant transfer of monomer through oil phase. However, the diffusion of hydrophilic monomers from aqueous droplets to inverse micelles is energetically unfavourable because of the strong hydrogen bonding between them and water molecules (Yastremskii et al, 1988).

When AIBN was employed as an oil-soluble initiator, Reichert and Baade (1984) observed that the molecular weight obtained was as twice that produced using water-soluble initiator AIBEA under the same polymerisation conditions. However, the dynamic and static light scattering measurement did not show the existence of micelles. In the case of oil-soluble initiator, it was proposed that the concentration of primary radicals, and to a lesser extent of initiator molecules, in the aqueous phase was much smaller. Therefore, the growing polymer radicals had a longer life-time, leading to larger molecular weight.

The reaction between initiator radicals and emulsifier molecules were reported by several workers (Hunkeler et al, 1989; Baade and Reichert, 1986). This reaction can be influenced by the nature of initiators. In an inverse system of acrylamide/Span 80/Isopar M, the order dependence of polymerisation rate on the emulsifier concentration varied with different initiators. For AIBN and ADVN (2, 2'-azobis(2, 4-dimethyl valeronitrile), both were oil-soluble, the order in emulsifier concentration were -0.2 and -0.1 respectively. This was attributed to the size difference of these two types of initiator radicals. AIBN radical had smaller size so that their capability to reach the reactive centres of emulsifier was larger (Baade and Reichert, 1986).

2.3.1.4 Dispersion Media

Unlike in conventional heterogeneous polymerisation systems (oil-in-water), a variety
of organic solvents, normally referred as "oil", have been employed in inverse heterogeneous polymerisation systems. So far, the majority of inverse heterogeneous polymerisations have been conducted using aromatic and paraffinic liquids as dispersion media. The former is widely used in research work whilst the latter is used more frequently in industry (Baade and Reichert, 1986).

It was reported that the application of toluene or Isopar M as dispersion medium had direct effects on the mechanism and kinetics of polymerisation of aqueous acrylamide with Span 80 as emulsifier and ADVN as oil-soluble initiator (Baade and Reichert, 1986). When Isopar M was used as the dispersion medium, the maximum polymerisation rate was dependent on the first order of initiator concentration and 0.2 order of emulsifier concentration. No micelles were detectable in the system and the polymerisation was a mass transfer controlled reaction. However, a great difference was observed when using toluene. In the latter case, the maximum polymerisation rate was proportional to the square root of the initiator concentration and the order in emulsifier concentration was also in the range of a square root dependency. This indicated a characteristic of common emulsion polymerisation. Under the same conditions, the change of dispersion medium from toluene to Isopar M resulted in a decrease in the polymerisation rate by a factor of 3.5 and an increase in the average size of latex particles from 0.23 to 1.12 μm.

In a photo-polymerisation of aqueous acrylamide in microemulsion using Aerosol OT as emulsifier and AIBN as initiator (Candau et al, 1984), the order dependence of polymerisation rate on the light intensity decreased according to

\[
toluene (1.06) > \text{heptane} (0.73) > \text{benzene} (0.55)
\]

This sequence corresponded to the decreasing susceptibility of hydrogen atoms in the oil molecules to abstraction by free radicals. The growing polymer radical could transfer to toluene at the water/oil interface, followed by the diffusion of the new benzylic radical which was too stable to reinitiated polymerisation. So, the
polymerisation was thought a monomolecular termination reaction. Benzene has no labile hydrogen so that termination was almost exclusively bimolecular. The value of 0.73 for heptane suggested a mixture of both monomolecular and bimolecular termination.

The authors found that, in an oil/Aerosol OT/H₂O system, the addition of acrylamide extended the inverse microemulsion domain when oil was toluene. However, the opposite result was observed if toluene was replaced by heptane. This effect was attributed to a preferential location of acrylamide at the water/oil interface when the dispersion medium was toluene which is more polar than heptane.

2.3.1.5 Other Components

In the polymerisation of aqueous acrylamide in white spirit stabilised with MYRJ 45 or IGEPAL CO-430, a significant increase in the molecular weight was found in the presence of mono-, di- or polycarboxylic acid salts (Dimonie et al, 1982). The magnitude of the effect was dependent on the nature of the salt and reached a maximum for sodium polyacrylate. The effect was supposed to occur by interaction between the salts and the ethylene oxide groups of the emulsifier, thus limiting the chain transfer reactions (Dimonie et al, 1992).

In the inverse emulsion copolymerisation of acrylamide with acidic monomers, such as acrylic acid and methacrylic acid, the pH value of the aqueous phase had a significant effect on the polymerisation kinetics and final latex properties (Glukhikh et al, 1987; Pichot et al, 1985). The overall polymerisation rate of acrylamide and methacrylic acid inverse emulsion copolymerisation using AIBN as initiator was higher in alkaline condition than in acidic condition. The partitioning results showed that the solubility of both acrylamide and methacrylic acid in toluene were greatly promoted at low pH. The pH value also affected the monomer reactivity ratios. As pH increased from 4 to 10, the reactivity ratio of methacrylic acid decreased considerably from 4.4 to 0.15, while that of acrylamide changed slightly from 0.58 to 0.59.
The particle size of final latex formed at low pH increased with increased content of acidic monomer in the comonomer mixture, and the latex exhibited a poor stability.

The variation of the ratio of aqueous and oil phase also influenced the inverse emulsion polymerisation. It was shown that the rate of acrylamide polymerisation increased and the molecular weight decreased with the growth in the ratio of toluene to water (Kurenkov et al., 1978).

### 2.3.2 Mechanism, Kinetics and Modelling

Following the early description of the main features of an inverse emulsion polymerisation reported by Vanderhoff et al. (1962), the studies have been continuously and intensively performed towards the understanding of this kind of polymerisation process. The effects have been generally successful in modelling the behaviour of specific systems under specific conditions with various assumptions and adjustment of mechanistic parameters. Some kinetic studies of inverse heterogeneous polymerisation in the literature are listed in Table 2-1. The kinetics of each polymerisation system is dependent upon the level and type of initiator(s), emulsifier(s), and even dispersion medium. However, no unified quantitative theory has been developed so far and uncertainties still exist. One reason for this is the sub-reactions (physical or chemical), for instance, the reactions between macroradicals and the components in the system. This was described in the proceeding sections. The other is that the complex mechanism is still far from being understood.

So far, several concepts have been developed to describe the mechanism of polymerisations in inverse heterogeneous media. The main difference between these concepts involves the definition of polymerisation locus and the way of nucleation of polymer particles. The most significant feature is the use of various kinds of initiators (see Section 2.3.1.3). The successful performance of inverse microemulsion polymerisation (Candau, 1992) has generated a new research field which does not fit into the conventional concepts.
Table 2-1  Some Kinetic Studies of Acrylamide Inverse Heterogeneous Polymerisation

<table>
<thead>
<tr>
<th>research group</th>
<th>initiator</th>
<th>emulsifier(s)</th>
<th>dispersion medium</th>
<th>particle size</th>
<th>temp.</th>
<th>kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>V. F. Kurenkov</td>
<td>Na₂S₂O₆</td>
<td>Sintamide-5</td>
<td>toluene</td>
<td>---</td>
<td>---</td>
<td>Rp α [M]^{1.7} [T]^{0.9}</td>
</tr>
<tr>
<td>(1978)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V. F. Kurenkov</td>
<td>(NH₄)₂S₂O₅</td>
<td>AIBN</td>
<td>toluene</td>
<td>---</td>
<td>303-313K</td>
<td>Rp α [M]^{1.7} [T]^{0.5}</td>
</tr>
<tr>
<td>(1982)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Rp α [M]^{1.7} [T]^{0.48}</td>
</tr>
<tr>
<td>V. F. Kurenkov</td>
<td>K₂S₂O₄ +</td>
<td>Sorbitol C-20</td>
<td>toluene</td>
<td>---</td>
<td>30-60°C</td>
<td>Rp α [M]^{1.4} [K₂S₂O₄]^{1.0}</td>
</tr>
<tr>
<td>(1986)</td>
<td>Na₂S₂O₆</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Na₂S₂O₆]^{1.5}</td>
</tr>
<tr>
<td>J. W. Vanderhoff</td>
<td>BP</td>
<td>Tetronic 1102</td>
<td>xylene</td>
<td>---</td>
<td>60°C</td>
<td>Rp α [M]^{1.0} [T]^{2.0} [E]^{1.0}</td>
</tr>
<tr>
<td>(1984)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K. -H Reichert, W.</td>
<td>AIBEA</td>
<td>Span 80</td>
<td>Isopar M</td>
<td>1-2 μ</td>
<td>42-57°C</td>
<td>Rp α [M]^{1.9} [T]^{0.3}</td>
</tr>
<tr>
<td>Baade (1984)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Rp α [M]^{1.0} [T]^{0.1} [E]^{0.2}</td>
</tr>
<tr>
<td>K. -H Reichert, W.</td>
<td>ADVN</td>
<td>Span 80</td>
<td>Isopar M</td>
<td>1.12 μ</td>
<td>42-57°C</td>
<td>Rp α [M]^{1.0} [T]^{0.1} [E]^{0.1}</td>
</tr>
<tr>
<td>Baade (1986)</td>
<td></td>
<td></td>
<td></td>
<td>0.23 μ</td>
<td></td>
<td>Rp α [M]^{1.0} [T]^{0.2} [E]^{0.45}</td>
</tr>
<tr>
<td>K. -H Reichert, W.</td>
<td>AIBN</td>
<td>PEM</td>
<td>Isooctane</td>
<td>150-200 nm</td>
<td>60°C</td>
<td>Rp α [M]^{1.0} [T]^{0.4} [E]^{0.3}</td>
</tr>
<tr>
<td>Hubinger (1989)</td>
<td>ADVN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Rp α [M]^{1.0} [T]^{0.1} [E]^{0.9}</td>
</tr>
<tr>
<td>D. Hunkeler, W.</td>
<td>AIBN</td>
<td>Span 80</td>
<td>Isopar M</td>
<td>1.0 μ</td>
<td>47°C</td>
<td>Rp α [M]^{1.0} [T]^{0.1} [E]^{0.2}</td>
</tr>
<tr>
<td>Baade (1989)</td>
<td>ADVN</td>
<td>Span 60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F. Candau</td>
<td>AIBN</td>
<td>K₂S₂O₆</td>
<td>toluene</td>
<td>15-25 nm</td>
<td>45°C</td>
<td>Rp α [M]^{1.1} [T]^{0.1} [E]^{0.45}</td>
</tr>
<tr>
<td>(1985)</td>
<td></td>
<td>AOT</td>
<td></td>
<td></td>
<td></td>
<td>Rp α [M]^{1.5} [T]^{0.10}</td>
</tr>
</tbody>
</table>

2.3.2.1 Polymerisations Using Oil-Soluble Single-Component Initiator

In an aqueous acrylamide/pentaerythritol myristate/isooctane inverse emulsion in the presence of AIBN and ADVN as initiators, Hubinger and Reichert (1989) found that the polymerisation took a course similar to Smith-Ewart case 1 kinetics (n << 0.5) with the nucleation in the inverse micelles. The low value of average radical number in each inverse particle was attributed to the reaction between the macroradicals and the emulsifier molecules resulting in an increase in monomolecular termination. This
unusual termination reaction produced variations of the order of polymerisation rate with respect to the initiator concentration from 0.4 to 1.0. The authors developed an inverse emulsion polymerisation model under the supposition of uniform latex particles and chain-termination step with emulsifier. The only parameter in this model to fit was the rate constant for chain termination with emulsifier. The experimental variation of polymerisation rate with time was in good agreement with the prediction by the model. It was stated that this model could be used to predict polymerisation rate, conversion, particle size and number at various concentration of initiator, monomer and emulsifier.

In contrast, Hunkeler et al (1989) proposed a different mechanism for inverse heterogeneous polymerisation of water-soluble monomer in paraffinic media with oil-soluble initiators. In such polymerisations, the primary radicals and the macroradicals formed in the oil phase diffused into the monomer droplets and then the nucleation occurred there. This was verified by the absence of micelles in the system and the constant particle morphology throughout the course of polymerisation. The mechanism consisted of the initiation, propagation, transfer and termination reactions that were common to all free-radical polymerisation. It also included three newly proposed steps: the reaction between macroradicals and interfacial emulsifier molecules, which dominated the conventional bimolecular termination; a long-chain branching reaction with terminal unsaturated carbons; and the mass transfer of primary radicals and oligomer radicals between organic and aqueous phase. It was believed that these three steps had strong influence on the polymerisation kinetics, where the polymerisation rate was found to depend on the initiator concentration to an order greater than one-half, and to be inversely proportional to the emulsifier concentration. The developed kinetic model based on this polymerisation mechanism was compared with the experimental results of an acrylamide/Span 80/Isopar M inverse microsuspension system using AIBN as initiator. It was found that the model predicted the polymerisation conversion, molecular weight and particle characteristics quite well. In fact, this work is a development in depth of the earlier investigation performed by Baade and Reichert (1984, 1986). Based on the kinetic results of acrylamide/Span 80/Isopar M system in the presence of AIBN oil-soluble initiator,
Baade and Reichert (1984) postulated the following reaction scheme: the initiation of polymerisation took place in the monomer droplets as primary radicals, which were produced in the oil phase by the decomposition of initiator, diffused into the monomer droplets. The termination was a result of the reaction between the propagating macroradical and a newly entering primary radical. Here the diffusion of primary radicals through the boundary layer of the emulsifier into the monomer droplets was considered as rate controlling. A film model was developed to describe the mass transfer of the primary radicals through the boundary layer of emulsifier. It was believed that the diffusion was affected by the diffusion coefficients which depended on the emulsifier type and its position in the boundary layer. The whole diffusion was dependent on the specific concentration gradients and the Nernst distribution coefficient. However, the theoretical kinetic equation derived from this model was only able to describe the experimental kinetic data at low conversions. At higher concentrations, it was proposed that mainly the influence of the gel effect and the influence of the volume contraction should be taken into account for correction over the whole range of conversion. Later on, the same authors postulated a modified reaction scheme (Baade and Reichert, 1986). This time, they took account of the other two factors: (a) formation of oligomer radicals in the oil phase which could be extracted into the monomer droplets when reaching a certain molecular size and becoming oil-insoluble; and (b) the diffusion of the initiator molecules into the monomer droplets which was promoted by the presence of acrylamide. Hence, the polymerisation rate was determined by the mass transfer of primary radicals and oligomeric radicals and also of initiator molecules from the oil phase through the emulsifier boundary layer into the aqueous monomer phase. The hydrodynamics strongly affected the reaction rate and the true activation energy had a typical value of diffusion controlled reactions. The effect of emulsifier on the polymerisation rate was simply treated as the dependence of the diffusion coefficient on the emulsifier concentration. However, the interactions with emulsifier, which was verified by several workers, was not taken into account. The above model could not be used to satisfactorily explain the first order of polymerisation rate with respect to the initiator concentration.
In a recent paper, Barajas and Hunkeler (1997b) reported a hybrid inverse-emulsion/inverse-microemulsion polymerisation process. The polymerisations of acrylamide were conducted in aqueous droplets dispersed in Isopar M using blends of non-ionic stabilisers. The initial monomeric system was located outside the inverse-microemulsion domain, yet close to the inverse-macroemulsion phase boundary. A turbid, viscous and unstable dispersion was obtained at the outset and during the intermediate stages of the polymerisation. The system evolved to a non-settling dispersion at high conversions.

When Isopar M was replaced by toluene as oil phase, the experimental kinetic relation changed under the same conditions (Baade and Reichert, 1986). In this case, for an oil-soluble azo-initiator the maximum polymerisation rate was found to be dependent on the square root of the initiator concentration. The order of polymerisation rate with respect to the emulsifier concentration was also in the range of a square root dependency, but the actual value showed a tendency to values a little below one-half, whilst the first order with respect to the monomer concentration remained. This was in agreement with the dependencies in common emulsion polymerisation. The authors attributed this change to the different polymerisation mechanisms in these two cases with paraffinic and aromatic liquids as oil phase respectively. In the former case, the monomer droplets were dispersed in the paraffinic oil phase with relative large size and no inverse emulsifier micelles existed. In the latter case, the dynamic light scattering gave hints at associations of the emulsifier in toluene, which were regarded as water swollen vesicles. Therefore, it was thought that, when using aromatic liquid as oil phase, particle nucleation occurred in both monomer droplets and inverse micelles.

An interesting polymerisation mechanism was postulated by Vanderhaff et al. (1984). For an aqueous acrylamide/Tetronic 1102/xylene system initiated by benzoyl peroxide, a high order (2.0) of polymerisation rate with respect to the initiator concentration was observed. This was attributed to the specific polymerisation mechanism, that is, the primary locus of particle nucleation was the monomer droplets. The polymerisation was initiated by the primary radicals formed in the
aqueous monomer droplets by the decomposition of the initiator molecules. Although several papers reported the particle nucleation in monomer droplets, Vanderhoff and co-worker's conclusion was still surprising because of the insolubility of benzoyl peroxide in water. The conclusion for the locus of particle nucleation in monomer droplets was based on the analysis of TEM images of the monomer droplets and of the polymer particles. Firstly, the monomer droplets were extremely small (about 20 nm) and therefore could compete effectively with monomer-swollen micelles (at least 10 nm) in capturing radicals. Secondly, the morphologies and the size of droplets in the initial inverse emulsion were similar to that of polymer articles in the produced latex. Finally, the particle size and morphology varied with stirring rate as expected for initiation in monomer droplets. The strong influence of initiator concentration on polymerisation rate could not be related to a change in the number of particles initiated, which was found to be proportional to only 0.3 power of the initiator concentration. Therefore, the kinetic results diverged strongly from the Smith-Ewart case 2, according to which the rate of emulsion polymerisation was independent of the initiator concentration and the number of particles was proportional to 0.4 power of initiator concentration. The reaction order of 2.0 with respect to initiator concentration could not be attributed to a monomolecular termination favoured usually by a high viscosity of the reaction medium, because the polymerisation occurred within monomer droplets having small volumes. The observed significant increase in polymerisation rate with increased initiator concentration could also be expected to involve a considerable decrease in the molecular weight of the polymer formed. However, $[\eta]$ was just proportional to 0.2 power of initiator concentration. This conclusion was also supported by the successful polymerisation in aqueous acrylamide solution using benzoyl peroxide, both neat and in xylene solution, as initiator. It was believed that the interfacial area between benzoyl peroxide and the aqueous acrylamide phases was insufficient for the diffusion of a significant number of radicals formed in the benzoyl peroxide phase into the aqueous phase. Furthermore, the acrylamide polymerisation in aqueous solution was carried out in the presence of a water-insoluble inhibitor in the xylene phase, so that the radicals in the xylene phase would be quickly scavenged, precluding their diffusion into the aqueous acrylamide.
phase. The acrylamide still polymerised. It must be mentioned that this system was a multiple oil-in-water-in-oil emulsion.

2.3.2.2 Polymerisation Using Water-Soluble Single-Component Initiator

Compared with using oil-soluble initiators, the inverse heterogeneous polymerisations using water-soluble single-component initiators have been much less investigated. In the polymerisation of aqueous acrylamide dispersed in toluene in the presence of ρ-styrene sulphonates of sodium (SSN) or ρ-styrene sulphonates potassium (SSK) as comonomer, Kurenkov et al (1982) found that, by using ammonium persulphate as an initiator, the polymerisation rate was dependent on the 1.3 power of acrylamide concentration and 0.5 power of initiator concentration. In the later published papers, Baade and Reichert (1984 and 1986) reported that the maximum polymerisation rate, in the aqueous acrylamide/Span 80/Isopar M system initiated by a water-soluble azo-initiator (AIBEA), was proportional to 1.0 power of acrylamide concentration and 0.5 power of initiator concentration. This kinetic dependence exactly corresponded to the polymerisation in aqueous solution. Obviously, the particle nucleation occurred in aqueous monomer droplets initiated by radicals formed by decomposition of initiator molecules dissolved in the aqueous phase. Each monomer droplet acted as an individual tiny reactor of batch polymerisation in aqueous solution and the process could be defined as an inverse suspension polymerisation.

A higher order dependence of polymerisation rate on the concentrations of monomer and initiator with values of 1.7 and 0.9 respectively was observed by Kurenkov et al (1978) in the acrylamide/Sintamide-5/toluene system using sodium persulphite as initiator. The higher order with respect to concentrations of monomer and initiator, compared with the observation by Baade and Reichert (1984), indicated the difference in polymerisation mechanism. The 0.9 order of polymerisation rate with respect to the initiator concentration suggested an increase in the fraction of monomolecular chain termination in the total balance of the kinetic termination reactions. Furthermore, the
polymerisation rate also increased with increasing emulsifier concentration up to 2%. This showed the characteristics of emulsion polymerisation.

A series of polymerisations of sodium p-vinylbenzene sulfonate were conducted by using potassium persulfate as an initiator at 40-70 °C in both aqueous solution and inverse emulsion emulsified with Span 60 in o-xylene (Vanderhoff et al, 1962). It was observed that the polymerisation rate was significantly more rapid in emulsion than in solution. Clearly, the mechanism for these two types of polymerisation process were different. The particle nucleation in the emulsion polymerisation was postulated to occur in both aqueous monomer droplets (20 nm) and inverse micelles. The results were consistent with Smith-Ewart case 2 kinetics \( n = 0.5 \) at 40 °C and 50 °C, but deviated slightly at 60 °C and 70 °C.

### 2.3.2.3 Polymerisation Using Redox Initiators

Kurenkov et al (1986) successfully carried out polymerisation of aqueous acrylamide/Sorbital C-20/toluene using potassium persulphate and sodium metabisulphite as redox initiators. The product was a polyacrylamide latex with high molecular weight \( (0.3-6.0 \times 10^6) \) offering a good flocculating activity. The order of polymerisation rate in monomer concentration was found to be 1.4. The power dependencies of polymerisation rate on the concentrations of potassium persulphate and sodium metabisulphite were different with values of 1.0 and 1.5 respectively. The influence of concentrations of monomer and initiators on both molecular weight and percentage of polymer yield were also investigated. The molecular weight of produced polymer increased with an increase in the monomer concentration and with a decrease in the contents of the redox initiators components. However, the details about the polymerisation mechanism was not discussed in this paper.

Dimonie et al (1982) investigated the influences of various factors upon the molecular weight of polyacrylamide, including the concentrations of two components of a persulphate-bisulphate redox pair, the nature and the concentration of emulsifier, the
procedure of adding aqueous phase and the salt concentration. The oil phase consisted of white spirit as dispersing medium and ethoxylated stearic acid with 8 mol ethylene oxide (MYRJ 45) or ethoxylated nonylphenol with 4 mol ethylene oxide (IGEPAL CO-430) as non-ionic emulsifier. The polymerisation in aqueous solution was conducted within a thin film of reaction mixture of about 1 mm for result comparison. For the polymerisation in inverse medium, both components of the redox pair were introduced as aqueous solutions (K₂S₂O₅ in the aqueous phase and NaHSO₃ after mixing the two phases. The polymerisation proceeded with three distinct stages at emulsifier concentrations between 3 to 12 wt%:

a. An inverse suspension was formed when the aqueous phase was dispersed into the oil phase. This suspension was unstable and tended to separate without agitation at low or moderate emulsifier concentrations (2-6 wt% in the mixture) However, the oil phase remained the continuous phase.

b. The starting of the polymerisation, by addition of NaHSO₃ in aqueous solution, was closely associated with an increased viscosity, with gel formation and with a sudden inversion of the phases.

c. Later in the reaction, when enough polymer was formed, the gel was broken up into small particles (0.5 - 1.2 mm in diameter) under agitation and the oil phase was partially removed from the particles which settled down.

It should be mentioned that if more than 12 wt% emulsifier was used, polymerisation occurred without gel formation and a relatively stable suspension of polyacrylamide was obtained.

The more resent research (Dimonie et al, 1992) revealed that very small amounts of polymer were enough to transform the dispersion into a gel because the polymerisation conversion at the gel formation was less than 1 %. However, no concentration for the gel break-up was given.
The ratio of the two components of the redox pair, $K_2S_2O_8/NaHSO_3$, had an effect on the molecular weight of produced polymer. Insoluble polymers were produced when the molar ratio exceeded 3.5 - 4.0. The molecular weight of polymers prepared in inverse suspension was considerably lower than that prepared in aqueous solution. However, there was a sharp increase in the molecular weight of polyacrylamide prepared in inverse suspension if mono-, di- or polycarboxylic acid salts was present. It was suggested that the low molecular weight of polymers prepared in inverse medium would be due to the chain transfer to the emulsifier molecules. The authors correlated this unusual polymerisation behaviour with the physical-chemical interface phenomenon and with the fact that "the continuous phase" (the gel here) where polymerisation took place had a rather complex heterogeneous structure.

2.3.2.4 Inverse Microemulsion Polymerisation

One of the very important characteristics of inverse microemulsion is that the mass ratio of monomer to emulsifier is much lower than that of inverse macroemulsion. In consequence, the monomer droplets sizes are very small. To a certain extent, the system consists of a single class of monomer-swollen micelles (Candau, 1992). In an acrylamide/Aerosol OT/toluene system (Candau et al, 1984), the number of monomer-swollen micelles at the beginning of the polymerisation was of the order of $10^{21}$ per litre, whereas the number of polymer particles in the final latex was much lower and about $10^{18}$ per litre. Calculations showed that only about 1/5 of the emulsifier was required to stabilise the latex polymer particles. As a result, there was an excess of emulsifier which formed small micelles (about 3 nm) coexisting with the polymer latex particles (about 40 nm) at the end of polymerisation.

A continuous particle nucleation mechanism was proposed by Candau et al (1984) based on the above characteristics of microemulsion and the experimental result of average one polymer molecule per particle in the final product of acrylamide/Aerosol OT/toluene system with AIBN as initiator. Because the number of inverse micelles in the system was far greater than the number of polymerising particles, the initiating
radicals formed in the continuous phase were at any time preferentially captured by un-nucleated micelles rather than by polymer particles. This feature was totally different from that of conventional emulsion polymerisation. In the latter case, the particle number was constant throughout the course of polymerisation after the nucleation stage.

Studies (Candau, 1992) showed that the size of final polymer particles was somewhat dependent upon the initial composition of the system, but was in most cases of order of 25 to 50 nm which was much larger than that of the initial micelles (5-10 nm). This indicated that nucleated particles grew by addition of monomer from other micelles, either by coalescence with neighbouring micelles, or by diffusion of monomer through the continuous phase. Monomer diffusion from inactive micelles acting as reservoirs towards active particles should be the dominant process in view of the low average number of polymer chains per particle. This led eventually to a reduction in the number of particles and an increase in their size.

The photo-polymerisation of aqueous acrylamide/Aerosol OT/toluene was conducted using AIBN as initiator (Carver et al, 1989). The kinetic study showed the following laws for polymerisation rate ($R_p$) and degree of polymerisation ($DP$):

$$R_p \propto [I_a]^{1.06} [I]^{1.00}[M]^{0.95} \quad [2-4]$$

$$DP \propto [I_a]^{2.00} [I]^{0.00}[M]^{1.07} \quad [2-5]$$

Where $I_a$ was the absorbed light intensity. This result indicated a monomolecular termination mode. The monomolecular termination resulted from the degradative chain transfer to toluene molecules to form stable benzyl radicals. The reaction occurred at the water/oil interface by transfer of the growing macroradicals to toluene, followed by the exo-diffusion of the new benzyl radical. The latter was too stable to reinitiated polymerisation.
Vaskova et al (1990 a, b) investigated the influence of initiators with various solubilities in water on the inverse microemulsion polymerisation rate in aqueous acrylamide/Aerosol OT/toluene system. It was found that, under the same conditions, the polymerisation rates using AIBN (partial water-soluble) and ammonium persulfate (water-soluble) were almost the same. This was attributed to the loci of initiation. Initiation with AIBN was shown to take place predominately in the water/oil interfacial layer where the encounter with acrylamide cosurfactant was facilitated. With ammonium persulfate, the initiation occurred in the micellar water-pools. A later research result of this system in the absence and presence of Fremy's salt (potassium nitrosodisulfonate) provided a more clear picture of the locus of initiation and propagation for different initiators with various water-solubility (Barton, 1991). For oil-soluble initiator (dibenzoyl peroxide), the initiation occurred in the oil phase. Because the relative low level of acrylamide dissolved in the toluene phase, the polymerisation rate was slow in this stage. After reaching their limit of solubility in toluene, the acrylamide oligomeric radicals and its oligomers precipitated and were captured by the inverse micelles of Aerosol OT or formed aggregates which were finally also captured by the micelles. The oligomer radicals penetrated through the interface of the inverse micelle into the acrylamide-rich region in the surface layer (shell) of the water-pool. The propagation of these oligomeric radicals continued in there and resulted in a sharp increase of polymerisation rate. In the case of water-soluble initiator, the loci of initiation was the water-pool and the loci of propagation was the acrylamide-rich region because of their high acrylamide level. In the case of partially water-soluble initiator (AIBN), the main initiation in toluene and the initiation in water-pool occurred simultaneously. The propagation also proceeded in the acrylamide-rich region. This polymerisation mechanism was further confirmed by a more recent investigation in percolating inverse microemulsion polymerisation (Barton, 1993).

2.4 Drop Mixing in Agitated Liquid-liquid Systems

In an agitated system consisting of two immiscible liquids, a dispersion normally forms: one liquid is split up into individual drops, whilst the other remains continuous.
It is now well established that the dispersion proceeds gradually (Gopal, 1968). The dispersed liquid is first divided by the action of the agitation into “chunks” which are then extended into thin strips. These liquid strips are split up into globules which are then broken up into small drops. At the same time, the drops move and collide with one another in the turbulent flow. When a pair of drops come in contact, coalescence may occur if the condition is right. At the early stages, the number of drops is small and the drop break-up dominates the scene. As the break-up proceeds, more drops are generated and the collisions among them become more frequent. After a certain stage, a dynamic balance between disruption by break-up and recombination by coalescence is reached so that prolonging the agitation does little to change average drop size and size distribution (Valentas and Amundson, 1966; Coulaloglou and Tavlarides, 1977; Narsimham et al, 1979).

The simultaneous drop break-up and coalescence lead to intermixing of the dispersed drops, which is important in a variety of chemical engineering operations. Therefore, great effort has been made to improve the understanding of the mechanisms of break-up and coalescence in liquid-liquid dispersions.

Although the globules may be split up in a number of different ways, Hinze (1955) summarised the three basic patterns of deformation of the sphere and the flow fields causing such deformations: (i) A sphere may elongate as a prolate spheroid, the shape obtained by rotating an ellipse about its major axis. As the elongation further increases, the globule become a long cylindrical thread and then disintegrates into small droplets. (ii) The spherical drop may be flattened into an oblate spheroid, the shape obtained by rotating an ellipse about its minor axis. As the drop is further flattened, it forms a sheet of liquid which undergoes disintegration because of unstable surface disturbances. (iii) The drop deformation may be completely irregular. Local depressions and bulges occur on the drop and some protuberances may separate bodily from the globule to form separate droplets. The actual forces causing deformation of the globules may arise from viscous or dynamic pressures, although one or the other type will dominate under given conditions. Hinze (1955) correlated the deformation and break-up of drops with the Weber number, a dimensionless ratio giving the
preponderance of the dynamic energy over the interfacial energy of the drop. When
the Weber number exceeds a critical value (critical Weber number), drop break-up
will occur.

Compared with break-up, drop coalescence is intrinsically more complex, involving
an interaction consisting of two drops and the continuous phase. Many primary
investigations were concerned with the behaviour of single drops in two-phase liquid-
liquid systems (Cockbain and McRoberts, 1953; Gillespie and Rideal, 1956; Charles
and Mason, 1960a, b; Sonntag and Klare, 1963). In a typical experiment (Gillespie
and Rideal, 1956), a liquid drop was formed at a capillary tip and fell through another
liquid to an interface. As the drop approached the interface, it was deformed. At the
same time, the liquid between the drop and the interface drained. When the drop first
reached the interface, it could bounce, float or coalesce depending on the physical
properties of the two liquids, the size of the drop and the distance it had fallen. The
final rupture of the liquid film between the drop and the interface was attributed to
capillary waves.

Charles and Mason (1960a, b) and Jeffreys and Hawksley (1962) reported a
phenomenon of partial coalescence. Coalescence involved a series of partial
coalescences. A large drop coalesced and left behind a smaller drop. This process
continued until coalescence was complete. The proposed reason for this phenomenon
was a competition between interfacial tension forces which tended to smooth the
interface and Rayleigh waves or disturbances which tended to form a new smaller
drop.

The behaviour of two drops approaching each other in a liquid medium was also
investigated (Charles and Mason, 1966b; Frankel and Mysels, 1962; Lindblad, 1964;
Platikanov, 1964). In the case of relatively large drops, when inertial forces were large
compared with surface forces, the flow pattern known as “dimpling” was observed,
liquid being temporarily trapped near the line of approach of the drops, because of
concave depression in their surfaces. In a dimpling system, the thinnest regions of
liquid separating the drops were in the ring forming the periphery of the dimple and it
was here that collapse and coalescence would occur if the drops were not protected by a surfactant. In the case of small drops or large drops approaching very slowly, dimpling did not occur. The surfaces of the drops were depressed while the medium was squeezed from between them. However, the drops remained convex. The place of closest approach of the surfaces of the two drops was on the line of centres. Therefore, in the absence of surfactant, the coalescence took place at this point as soon as the intervening liquid had drained away. When surfactants were present, the time for coalescence was found to be considerably extended. A thin liquid lamella was formed between the two drops.

Compared with single drop investigation, the drop mixing in agitated systems is much more complicated. For an agitated liquid-liquid system, Shinnar (1961) considered that two drops were unlikely to coalesce immediately on collision, but that they might cohere together and be prevented from coalescing by a film of the continuous-phase liquid trapped between them. The film separating cohering drops was supposed to drain or diffuse away until it collapsed, and coalescence followed. During the drainage process of the film, the cohering drops might be parted by the agitation turbulent forces. The cohesion of the drops was assumed to be due to attractive forces, but the nature of the forces was not discussed. It was believed that the cohesive forces were dependent on drop diameter and the cohering drops could not be parted at a given intensity of turbulence if their size was smaller than a minimum value.

The existence of forces of attraction strong enough to cause drainage of the liquid film separating two drops was argued by Howarth (1964). The forces referred to by Shinnar were considered to be the forces of molecular attraction. However, such forces were known to be of very short range and hence would be unlikely to provide a cohesion force of any significance in relation to other forces to which drops in a turbulent field were subject. Therefore, the drainage of the liquid film is unlikely to proceed to any appreciable extent before the cohering drops were separated, so that the probability of ultimate drop coalescence was small. Howarth applied the knowledge of single drop investigation (Gillespie and Rideal, 1956) to the turbulent flow field and suggested that immediate coalescence would occur when the velocity of
approach along the line of centres at the instant of collision exceeded a critical value. Colliding drops with a velocity of approach less than the critical value might cohere, but the probability that cohering drops eventually coalesce was small. Based on this, an equation for the frequency of coalescence of uniformly sized drops in a homogeneous isotropic turbulent-flow dispersion of infinite extent was derived. The equation was tentatively confirmed by comparison with the experimental data of Madden and Damerell (1962).

It is technically difficult to tackle break-up and coalescence of drops in an agitated system. However, the simultaneous break-up and coalescence of drops can be monitored by following the intermixing of dispersed phases. Vanderveen (1960) used a dye which was soluble only in the dispersed phase to measure the drop mixing rate. After injecting a small volume of dye into an agitated dispersion, the dye intensity response was measured at time intervals using a light probe. Because the dye was soluble only in the dispersed phase, its distribution could take place only through repeated simultaneous coalescence and break-up of drops. Zerfa and Brooks (1996b) used a tracer dye technique for examining the drop mixing of vinyl chloride monomer droplets in an agitated liquid-liquid dispersion. Matsuzawa and Miyauchi (1961) studied an agitated system of water-in-benzene. Two different types of drops containing FeCl$_3$ and SnCl$_2$ in aqueous solution respectively were fed to the agitated benzene and then the drop mixing was followed by determining the amount of FeCl$_2$ which was the product of chemical reaction between FeCl$_3$ and SnCl$_2$. Madden and Damerell (1962) evaluated drop mixing by following the reaction between thiosulfate ion in dispersed aqueous drops and iodine in organic continuous phase. A small amount of aqueous thiosulfate ion drops was added to a dispersion of water in toluene. Because the reaction between thiosulfate ion and iodine was dependent on the number of aqueous drops containing thiosulfate, the drop mixing was monitored by determining the disappearance of iodine.

Research on the behaviour of agitated dispersions has revealed that drop mixing is dependent not only on external conditions, but also on internal properties. The former
includes agitator type, agitation speed, apparatus dimensions and residence time (Shinnar, 1961; Miller et al, 1963; Coulaloglou and Tavlarides, 1977; Brooks, 1979; Lee and Tasakorn 1979; Hong and Lee, 1983; Skelland and Kanel, 1990). The later involves volume fraction of dispersed phase (hold-up), viscosities and desities of the two phases, interfacial tension and size of drops (Vanderveen, 1960; Madden and Damerell, 1962; Stamatoudis and Tavlarides, 1985; Calabrese et al, 1986; Wright and Ramkrishna, 1994). The presence of surface active agents has strong effects on drop mixing (Church and Shinnar, 1961; Borwankar et al, 1986; Konno et al, 1993, Zerfa and Brooks, 1996b). The work published in the area of drop mixing was reviewed by Tavlarides and Stamatoudis (1981).

In order to describe drop break-up and coalescence in agitated dispersions, homogeneous and non-homogeneous models have been developed using simulation and population balance concepts. The former assumes the dispersion properties to be uniform throughout the vessel, while the latter relax these assumptions (Zeitlin and Tavlarides, 1972). Homogeneous models have been successfully applied to the dispersions in which coalescence frequency is very low relative to the circulation frequency of the dispersion (Coulaloglou and Tavlarides, 1976). The population balance concept was proposed by Hulbert and Katz in 1964 and developed later by a number of investigators (Valentas and Amundson, 1966; Ramkrishna, 1974; Bajpai et al, 1976; Coulaloglou and Tavlarides, 1977; Chatzi and Lee, 1987; Tsouris and Tavlarides, 1994). This model describe the history of a drop population in terms of drop properties, such as size, age and concentration, during the course of drop interaction events with themselves and with the surrounding environment.

Coulaloglou and Tavlarides (1977) derived a breakage model by considering drop deformation and break-up under the influence of local pressure fluctuations and the time needed for a critically deformed drop to break-up in a locally isotropic field. The model predicted correctly the effect of impeller speed on maximum stable size for drops greater than the microscale of turbulence. Recently, a drop breakage function was introduced as the product of the drop-eddy collision frequency and breakage
efficiency which reflected the energetic of turbulent liquid-liquid dispersion (Tsouris and Tavlarides, 1994).

A coalescence model was developed by Coulaloglou and Tavlarides (1977), assuming that the coalescence rate was proportional to the product of collision rate and coalescence frequency of deformable drops in the kinetic regime of locally isotropic turbulent fields. Das et al (1987) developed a White-noise model for drop coalescence which considered the film drainage between two colliding drops as a stochastic process driven by a suitably idealised random process for the fluctuating force applied on the drops. A conceptual framework for modelling drop coalescence was described by Chesters (1991). The framework split coalescence process into an internal and an external field. The former was characterised by deformation of the approaching interfaces and by rupture and confluence, while the latter was concerned with the frequency, force and duration of collisions.

Although numerous models have been presented in the literature, they are only valid for specific systems. Inconsistencies have been observed between the existing models and there is no universal model to date which can be used to describe all dispersions.
CHAPTER 3

PRELIMINARY INVESTIGATIONS ON DROP BEHAVIOUR IN INVERSE DISPERSION

3.1 INTRODUCTION

In the present project, the inverse microsuspension polymerisation is initiated by using a redox pair (sodium metabisulphite/potassium bromate). The oxidant is initially dissolved in the aqueous monomer drops which are dispersed in oil and stabilised with surfactant; then an aqueous solution of the reductant is added to start polymerisation. Therefore, the inverse dispersion consists of two different types of aqueous drops in the early stages of polymerisation and the distribution of the two components of the redox pair in the aqueous phase is heterogeneous in nature.

In the literature, three loci of initiation for inverse heterogeneous polymerisation have been reported, i.e. emulsifier micelles, interfacial layer and monomer droplets (see Chapter 2). In the present inverse microsuspension polymerisation, the initiation of polymerisation could occur only when the two components of the redox pair are intermixed. Among the possible ways for the intermixing of the two redox components, drop coalescence between the two different types of aqueous drops is supposed to play an important role.

Under agitation, the drops in a dispersion will strike one another as they move in the turbulent field. If the condition is right, the striking drops could coalesce and a larger new drop would be formed. The newly formed drop can either exist as it is or be torn apart into smaller drops. If it exists as it is, it could further coalesce with other drops and after a certain extent it will become too large to exist in the turbulent stream and
be broken up eventually. In other words, the drop coalescence and break-up always take place simultaneously. This will result in the intermixing of dispersed phase.

In order to obtain a basic knowledge of drop coalescence and break-up in the present inverse microsuspension polymerisation, preliminary work has been done for developing some experimental techniques and simulating the drop behaviour. In these preliminary experiments, components for polymerisation were absent. The results are presented in this chapter.

3.2 METHODOLOGY

The details of materials used in the following experiments are listed in Appendix I.

3.2.1 Optical Microscopy

Optical microscopy provides a fast and convenient method for drop/particle analysis. However, its application is restricted by the nature of light which imposes a limit to the resolution (normally drop diameter not smaller than 0.5 \mu m) even of optical systems completely free of defects. A preliminary experiment of dispersing water in Isopar M stabilised with Witcamide 511 showed that the majority of aqueous drops were in a size range of about 1.0 to 2.0 \mu m in a typical inverse dispersion. Therefore, optical microscopy might be a useful method in the present work for drop behaviour characterisation.

An OLYMPUS BH-2 optical microscope equipped with a camcorder was employed. In order to obtain clear images of individual drops, samples of the inverse dispersion were diluted prior to optical microscope observation. The use of neat oil dispersion medium as dilution solvent could cause coagulation of aqueous drops due to the new equilibrium of surfactant molecules in the dispersion. Therefore, the samples were diluted using the same mixture of oil and surfactant as used for dispersion preparation. Each diluted sample was then put into a glass cell covered with a glass
slide and observed under the optical microscope. The images were recorded on video tape and the photographs were taken.

For drop behaviour characterisation in the present system, it is essential to distinguish the two different types of original aqueous drops and the coalesced aqueous drops (derived from the coalescence of the two different types of drops). To achieve this, different techniques were developed, including colouring, acid indication and precipitation.

3.2.1.1 Colouring Method

In a previous research project performed in this laboratory, Zerfa (1994) developed a colouring technique which was successfully used for investigating drop behaviour in suspension polymerisations. It is expected that the mixing of coloured and uncoloured drops could result in a colour change of the latter as coalescence proceeds and give information of drop mixing between the two types of drops.

Methylene blue, which is water-soluble and oil-insoluble, was used as a dye in this experiment. The experimental composition is showed in Table 3-1.

<table>
<thead>
<tr>
<th>material</th>
<th>function</th>
<th>weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylene blue aqueous solution</td>
<td>simulating aqueous monomer</td>
<td>200.0</td>
</tr>
<tr>
<td>Isopar M</td>
<td>dispersion medium</td>
<td>61.0</td>
</tr>
<tr>
<td>Witcamide 511</td>
<td>surfactant</td>
<td>4.7</td>
</tr>
<tr>
<td>Span 80</td>
<td>surfactant</td>
<td>3.0</td>
</tr>
<tr>
<td>water</td>
<td>simulating aqueous reductant</td>
<td>10.0</td>
</tr>
</tbody>
</table>

The experiment was conducted as follows:

Firstly, the oil phase was prepared by agitating the hydrocarbon oil and the surfactants
in a 500 ml round-bottom glass reactor using a propeller stirrer at 1000 rpm for 5 minutes. Next, the methylene blue saturated aqueous solution was added slowly to the oil phase and the mixture was agitated continuously for about 30 minutes for emulsification. Then, the agitation speed was reduced to 300 rpm and the designated amount of water was injected using a glass syringe. After this, samples were withdrawn from the reactor at various time intervals and observed under the optical microscope. The experiment was carried out at room temperature (about 23 °C).

Unfortunately, the image contrast between the coloured and uncoloured drops was poor. In addition, the solubility of methylene blue in the oil phase was significantly enhanced by the presence of the surfactants. As a result, the image contrast was reduced.

3.2.1.2 Acid Indication Method

This experiment was based on the colour change of an acid indicator once being mixed with an acid solution.

By using aqueous acrylic acid (20 wt% solution) simulating the aqueous monomer and methyl red indicator simulating the aqueous reductant, it was expected that the coalescence of these two types of drops could change the colour of methyl red drops from yellow to red. The experimental composition and conditions were similar to the colouring experiment.

However, the colour change of methyl red drops was not distinguishable under the optical microscope although the dispersion became red after adding the methyl red indicator. This implicated that the colour of drops might be not dark enough in this case. To improve image contrast, a precipitation method was developed.
3.2.1.3 Precipitation Method

It was expected that precipitation reaction by mixing two types of drops containing different chemicals to produce a dark precipitate could increase the image contrast. Chemicals for this method must meet three criteria. Firstly, the reaction must produce heavy dark colour precipitates. Secondly, they must be water-soluble and oil-insoluble to produce dark colour drops rather than a coloured continuous phase. Finally, the reaction must have high sensitivity so that the coalescence is detectable as soon as it occurs.

Cupric sulphate and rubeanic acid were used in this experiment. The reaction of these two chemicals produces a black precipitate and has high sensitivity.

The experimental procedure was similar to the colouring experiment. The composition is showed in Table 3-2.

<table>
<thead>
<tr>
<th>material</th>
<th>function</th>
<th>weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>saturated cupric sulphate aqueous solution</td>
<td>simulating aqueous monomer</td>
<td>176.0</td>
</tr>
<tr>
<td>Isoper M</td>
<td>dispersion medium (oil)</td>
<td>61.0</td>
</tr>
<tr>
<td>Witcamide 511</td>
<td>surfactant</td>
<td>2.4</td>
</tr>
<tr>
<td>Span 80</td>
<td>surfactant</td>
<td>1.5</td>
</tr>
<tr>
<td>saturated rubeanic acid aqueous solution</td>
<td>simulating aqueous reductant</td>
<td>61.0</td>
</tr>
</tbody>
</table>

As soon as the rubeanic acid aqueous solution was added under agitation, the colour of dispersion of aqueous cupric sulphate changed immediately to black. Under the optical microscope, some drops with a black layer were observable but there were no black drops (Figure 3-1). An inspection of the image of a big drop produced by directly mixing a cupric sulphate aqueous drop and a rubeanic acid aqueous drop showed that the precipitate coagulated instead of filling the drop. This is probably why only drops with black layers were observed.
Figure 3-1 Optical microscope image of aqueous drops containing black precipitates

23 °C, propeller stirrer at 1000 rpm for 30 minutes emulsification

Table 3-3 Composition for Experiment B

<table>
<thead>
<tr>
<th>Experiment B-1</th>
<th>Experiment B-2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>material</strong></td>
<td><strong>weight (g)</strong></td>
</tr>
<tr>
<td>potassium permanganate</td>
<td>150.0</td>
</tr>
<tr>
<td>aqueous solution</td>
<td></td>
</tr>
<tr>
<td>Isopar M</td>
<td>40.0</td>
</tr>
<tr>
<td>Wicamid 511</td>
<td>1.6</td>
</tr>
<tr>
<td>Span 80</td>
<td>1.0</td>
</tr>
</tbody>
</table>

3.2.1.4 Limitation of Optical Microscopy

The foregoing experiments suggested that the microscopy technique is limited by poor image contrast in distinguishing between coloured and uncoloured drops. To verify the limitation of this technique, a series of experiments were conducted using potassium permanganate as “dye”. Because potassium permanganate is completely insoluble in the oil phase, the problem of enhancement of dye solubility in the oil
phase by the surfactants can be avoided (see Section 3.2.1.1). The preparation of dispersion was similar to that described in Section 3.2.1.1 and the compositions are listed in Table 3-3.

![Image of big drops](image)

Figure 3-2. Optical microscope image of big aqueous potassium permanganate drops

23 °C, propeller stirrer at 1000 rpm for 30 minutes emulsification

Figure 3-2 is an image of big drops of aqueous potassium permanganate dispersed in the oil phase produced by using lower surfactant level (Experiment B-1). The drop colour was distinguishable under the optical microscope. However, the drop colour paled with decrease in drop size. In Experiment B-2, the majority of drops were smaller than 10 μm (Figure 3-3). In this case, there was no significant difference between the small aqueous potassium permanganate drops and pure aqueous drops. In addition, the colour of small drops changed with the adjustment of microscope focus due to the resolution limitation of optical microscope. When a tiny drop was in focus with the maximum magnification, it looked like a “dark dot” (Figure 3-3, a). However, this dark dot changed to a “white dot” with just a little adjustment of
microscope focus (Figure 3-3, b). These indicated that the direct characterisation of drop mixing using an optical microscope is limited if the drop size is too small.

Figure 3-3 Optical microscope images of small aqueous potassium permanganate drops

(a), (b) images on different focus conditions see Figure 3-2
3.2.2 Light Scattering

A number of papers in the literature reported the use of light scattering techniques for size analysis of both initial monomer drops in dispersions and polymer particles in final lattices (Pichot et al, 1985).

Two Malvern instruments (Malvern 4600 Photon Correlation Particle Analyser and Zeta Master S) were employed for light scattering measurement.

Samples of inverse dispersion/latex were diluted using the same oil phase as used for inverse dispersion/latex preparation. In order to obtain well-dispersed drops/particles, the diluted samples were vigorously shaken and then put in an ultrasonic bath for about 5 minutes. Each sample was measured five times and the average value was calculated as the result. All measurements were performed at room temperature (23 °C).

Table 3-4 shows the light scattering results from a latex of slightly cross-linked polyacrylic acid particles dispersed in paraffinic oil (Texipol TD 6043, produced in Scott Bader Co Ltd) obtained using Malvern 4600 Photon Correlation Analyser. It is seen that the data of measured particle size are scattered with very poor reproducibility. A similar result was obtained by using the Zeta Master S. This poor result is probably caused by particle coagulation or/and the presence of some very large particles (see the following section).

<table>
<thead>
<tr>
<th>Table 3-4 Light Scattering Result from Texipol TD 6043</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample 1</td>
</tr>
<tr>
<td>measurement</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
</tbody>
</table>
3.2.3 Electron Microscopy

Theoretically, the electron microscope is based on very similar principles to those of an optical microscope. In an optical microscope, glass lenses are used to obtain a magnified image of a specimen. Magnetic fields are used, in an electron microscope, as lenses to establish and direct the path for the type of radiation used in the system, namely, the electrons. Because the wavelength of an electron beam is smaller than that of visible light, higher resolution can be attained by using an electron microscope than an optical microscope.

3.2.3.1 Transmission Electron Microscopy (TEM)

A transmission electron microscope (JEM-100 CX) was used to examine the size and size distribution of latex particles.

![TEM image of polyacrylic acid latex](image_url)

Figure 3-4 TEM image of polyacrylic acid latex

sample provided by Scott Bader Co Ltd
The polymer latex was firstly diluted with the same oil phase as used in polymerisation. A specimen substrate, stainless-steel grid coated with carbon film, was then covered with a hemispherical drop of the diluted polymer latex. Most of the drop was removed by contacting it with a piece of filter paper, leaving a thin film of the diluted latex on the specimen substrate. The prepared sample was finally placed in the specimen chamber of the TEM and its image photographs were taken. Figure 3-4 shows a TEM image of polyacrylic acid latex.

By measuring individual particle sizes in an image, the average particle size and size distribution can be obtained.

A high vacuum is maintained in the specimen chamber of the TEM. Liquid drops in dispersion can not be examined directly because they are volatile before polymerisation begins. To prevent liquid drop from evaporating in the vacuum chamber, a freeze technique is normally employed. However, it is not available with this TEM.

3.2.3.2 Scanning Electron Microscopy (SEM)

To examine aqueous drops in the inverse dispersions, a Crytrans freeze-fracture equipment was recently purchased from Oxford Instruments and installed on a scanning electron microscope (Cambridge Instrument Steroscan 360).

A series of experiments were performed for the development of this new technique. The sample preparation for obtaining the best images was eventually identified as follows:

1. A drop of inverse dispersion/latex was placed on the top of a specimen rivet and then it was frozen in liquid nitrogen.

2. The specimen rivet was quickly transferred into the Cryo chamber (about -160 °C) using a rivet holder.
3. The frozen hemispherical sample drop was broken using a fracture-knife in Cryo chamber under vacuum.

4. The fresh surface of the frozen sample was coated using a sputter coater which generates a cloud of gold in an argon plasma.

5. The coated sample was transferred into SEM chamber and image photographs were taken.

Figure 3-5 shows a typical SEM image of aqueous acrylic acid dispersed in paraffinic oil (Isopar M) stabilised with surfactant (Witcamide 511). No crystals were observed in the image of Isopar M with Witcamide 511 by using this technique. Therefore, the clearly visible drops in the image shown in Figure 3-5 are the aqueous acrylic acid drops.

Figure 3-5 Freeze-fracture SEM image of dispersion of aqueous AA in oil phase (after 2 hours emulsification at 1000 rpm)

aqueous phase 28 wt% AA, oil phase 10 wt% Witcamide 511 in Isopar M 23 °C, crossed-paddle + “U” blade stirrer and baffles (see Chapter 4)
3.2.4 Viscosity Method

In Scott Bader Company Limited, during the emulsification, the aqueous drop size is estimated by measuring the viscosity of the inverse dispersion. This is based on the observation that dispersion viscosities are generally proportional to reciprocals of mean drop sizes. However, dispersion viscosities are dependent on a large number of factors besides drop size, including dispersion composition, physical and chemical properties of stabiliser, disperse phase and continuous phase (Sherman, 1968). The viscosity measurements, therefore, do not give true drop sizes. Nevertheless, comparable results can be obtained for the dispersions having the same compositions provided the measurements are performed under identical conditions.

In the present work, the viscosity method was used for characterising the variation of the aqueous drop size with emulsification time and for comparing the dispersion efficiencies of different stirrers (see Section 4.1.2). The results were in good agreement with the observations by SEM.

The viscosity measurements were performed by using a coaxial cylinder viscometer (Rotovisco RV2 with sensor system NV, Haake Viscometers). The viscosity values were calculated by the following equation (see the instrument manual):

\[ \eta = \frac{G \cdot Q}{n} \quad \text{(mPa} \cdot \text{s)} \quad [3-1] \]

Here \( n \) and \( Q \) are testing head speed (min\(^{-1}\)) and resulting torque (scale grade) respectively. \( G \) is a constant (mPa \cdot s/scale grade \cdot min) and equals 329 when using sensor system NV.

The inverse dispersions of aqueous acrylic acid in Isopar M stabilised with Witcamide 511 exhibited non-Newtonian behaviours, i.e. their viscosities varied with shear rate. Therefore, the viscosities were measured over a range of testing head speed from 64 to 256 min\(^{-1}\).
3.3 RESULTS AND DISCUSSION

3.3.1 Stability of Inverse Dispersion

In a dispersion of one liquid in another, the interface between two phases is the seat of surface free energy, and there is a net reduction in interfacial area if two drops coalesce. Therefore, drop coalescence is a thermodynamically spontaneous process in such dispersions (except for spontaneously emulsifying systems). In other words, these dispersions are never completely stable in the absolute sense. Stability of such dispersions, thus, is a relative concept; and "there is no sharp transition from the ‘stable’ to the ‘unstable’ condition" (Kitchener and Musselwhite, 1968).

By shaking together DI water and Isopar M at a weight ratio W/O=3/1 (the weight ratio of aqueous phase to oil phase in the present inverse microsuspension polymerisation is 3 : 1), a dispersion of Isopar M in water formed. When left to stand, this dispersion separated into two phases (breaking) within seconds, indicating an extremely low stability. However, an inverse dispersion (water-in-oil) was obtained when 5 wt% (based on oil phase) non-ionic surfactant Witcamide 511 was present. The inverse dispersion appeared so stable that no breaking was observed when left to stand for 24 hours. When diluted using the oil phase (Isopar M containing 5 wt% Witcamide 511) and left to stand, the inverse dispersion, however, underwent creaming in minutes, i.e. the aqueous drops sank down under the action of gravity but remained separate. SEM observation revealed that the average drop size of the dispersion of aqueous AA in the oil phase, after emulsification, increased with standing time (Figure 3-6). This implied a slow coalescence of the aqueous drops on standing.

3.3.2 Addition of Pure Water to Inverse Dispersion

An experiment of drop mixing (experiment C) was conducted by using the same composition as in Experiment B-2, but DI water was used instead of aqueous potassium permanganate. Emulsification was performed using the propeller stirrer at 1000 rpm for 30 minutes, then the agitation speed was reduced to 400 rpm. About 15
minutes later, 15.0 g DI water was added and then a sample was withdrawn and observed under the optical microscope (Figure 3-7). It is seen that small aqueous drops adsorb on the surface of a big aqueous drop. Obviously, the big aqueous drop was derived from the newly added water under the rotation stress of agitation. It was observed under the optical microscope that some adsorbed small drops joined in the big drop. This observation suggested that the coalescence between the two different aqueous drops was probably a procedure of adsorption of the stabilised small drops by the newly introduced unstabilised big aqueous drops, followed by the joining of the former with the latter. Because the big drops were derived from pure water, they were unstable in the inverse dispersion and tended to adsorb surfactant molecules for reducing their interfacial tension. In addition to adsorbing the free surfactant molecules in the oil phase, they could acquire surfactant molecules by “capturing” stabilised small drops coming in contact with them in the turbulent field.

Figure 3-6 Freeze-fracture SEM image of dispersion of aqueous AA in oil phase (standing for 2 hours after emulsification)

compositions and conditions see Figure 3-5
In the experiment of using acid indicator (see Sections 3.2.1.2), it was found that the colour of the inverse dispersion of aqueous acrylic acid dispersed in Isopar M changed to red as soon as the methyl red indicator was added under agitation. A similar phenomenon was observed in the precipitation experiment (see Section 3.2.1.3). These indicated that the coalescence between newly introduced drops and the stabilised aqueous drops was very quick under agitation.

Figure 3-7 Optical microscope image of aqueous drops in oil phase conditions see Figure 3-2

3.3.3 Evolution of Drop Size and Size Distribution

In Experiment C, samples were withdrawn at various time intervals, followed by dilution and observation under the optical microscope. Figure 3-8 shows a series of optical microscope images of the samples withdrawn before and after adding a shot of water at different time.
Chapter 3  Preliminary Investigations on Drop Behaviour

(a) before adding a shot of DI water

(b) 5 minutes after adding a shot of DI water

(c) 30 minutes after adding a shot of DI water

Figure 3-8 Optical microscope images of inverse dispersion before and after adding water
It is seen that the aqueous drop sizes were fairly uniform before the addition of DI water (Figure 3-8a). Some big drops appeared after adding DI water (Figure 3-8b). As discussed in the preceding section, these big drops were generated by the break-up of DI water and/or by coalescing with the small stabilised drops. The size of the big drops decreased with continuous agitation (Figure 3-8c), indicating their further break-up.

3.4 Conclusion

Preliminary work has been done with the aim of developing appropriate techniques for investigating aqueous drop behaviour in inverse dispersions.

Optical microscopy is a fast and convenient method for examining drops/particles with relatively large size. However, its use is limited by its relatively low resolution. The drop mixing in the inverse dispersion can not be directly monitored by using this technique.

Light scattering measurement of the drop/particle size showed a very poor reproducibility. It is probably due to the coagulation of the aqueous drops/particles in the inverse dispersions/lattices.

Transmission electron microscopy is useful for examining the particles in the inverse lattices. However, it can not be used for analysing the aqueous drops in the inverse dispersions.

Scanning electron microscopy with freeze-fracture equipment provides a powerful method for examining drop/particle size and size distribution. Therefore, the evolution of drop/particle size and size distribution can be investigated throughout the course of emulsification and polymerisation.
The investigations of the inverse dispersions before and after adding a shot of water/aqueous solution have been made using an optical microscope. The major points are summarised as follows:

A fairly stable inverse dispersion was obtained by dispersing water or an aqueous solution in Isopar M using Witcamide 511 as surfactant.

After being added to the inverse dispersion as a shot, water or the aqueous solution was broken into big drops under the rotation stress of agitation. These big drops were unstable and could coalesce with the stabilised small drops to reduce their surface tension. The coalescence would be very quick. At the same time, the big drops would undergo further break-up under continuous agitation.
CHAPTER 4

POLYMERISATION APPARATUS
AND ITS OPERATION

4.1 DESIGN OF POLYMERISATION APPARATUS

4.1.1 Design of Reactor

It is essential, for kinetic studies, to conduct polymerisation under isothermal conditions. As stated in Chapter 2, the polymerisation of acrylic acid is a highly exothermic reaction and can be very quick under certain circumstances. Therefore, the removal of the heat of polymerisation released is a key factor in the design of an isothermal polymerisation installation. The most common reactors used in practice for fast and highly exothermic reactions are jacketed-reactors. By circulating a controlled cooling liquid through the jacket, the reaction heat can be removed quickly and the reaction temperature can be maintained at a constant value with a reasonable fluctuation.

Initially, a commercially available 1.0 litre glass jacketed-reactor was used for an inverse microsuspension polymerisation using a typical formulation which is the same as that listed in Table 4-1, except that the total amount of reaction mixture was about 300 g. In spite of using ice water as the cooling liquid, there was about 12 °C temperature increase at the early stages of polymerisation. One possibility to solve this problem is to reduce the total volume of the reaction mixture. However, the smallest commercially available glass jacketed-reactor is 1.0 litre, which had been demonstrated to be too big for the polymerisation. A 500 ml flat-bottom glass jacketed-reactor, therefore, has been manufactured and installed. It consists of a jacketed reaction tank and a commercially available glass lid with 5 necks.
Figure 4-1 Dimensions of reaction tank

units are given in mm (not to scale). material: glass
In order to improve heat transfer, reactors are normally designed so that large surface to volume ratios can be obtained, for instance, by choosing larger ratios of depth to diameter of cylindrical reactors. The ratio of effective depth to inner diameter of the jacketed reaction tank is about 6/5. The main dimensions of the reaction tank are shown in Figure 4-1.

The reaction tank jacket carries an inlet port and an outlet port. The cooling or heating water was pumped into the jacket from the inlet port (lower one) and out from the outlet port (upper one).

4.1.2 Design of Stirrer and Baffles

In two-phase liquid-liquid systems, agitation by rotating stirrers inside the liquid mixtures has the following functions (Nagata, 1975):

1) Increase of interfacial surface area by dispersing one liquid into another.
2) Reduction of diffusion resistance outside the dispersed drops.
3) Promotion of mass transfer by inducing convection current inside the dispersed drops.
4) Repetition of coalescence and redispersion of drops.

For the present inverse microsuspension polymerisation, both coalescence and break-up of drops are very important because the aqueous reductant is added separately after emulsification of the monomer and oxidant. The preliminary investigations on the drop behaviour (see Chapter 3) revealed simultaneous break-up and coalescence of the aqueous drops which were strongly dependent on the agitation. Therefore, in order to promote the intermixing of the aqueous phase in the inverse microsuspension polymerisation, an ideal construction of the agitation should facilitate not only effective dispersion but also frequent coalescence of drops. In addition, the desire for a fast heat removal requires that the agitation should provide an efficient convection current of the inverse dispersion in the reaction tank.
Harnby et al (1992) summarised four basic types of stirrer: propeller, turbine, paddle and anchor impeller. The application of these types of stirrer depends mainly on the viscosity of the liquid system.

The propeller-shaped stirrer impels liquid axially up and down so that the flow becomes turbulent throughout the vessel and the mixing can be effective. However, it is normally suited for making low or medium viscosity dispersions. The turbine stirrer tolerates somewhat higher viscosity than the propeller-shaped stirrer. The centrifugal forces throw the liquid to all parts of the vessel to achieve efficient mixing. But it must rotate at much higher speed (Gopal, 1968). For dispersing a lighter liquid into water, Nagata (1975) proposed the optimum dimensions of a 4-bladed paddle stirrer with a diameter of 1/3 of tank diameter and a width of 0.05-0.1 of tank diameter. However, this rule does not apply to the present inverse microsuspension polymerisation because of the relatively high viscosity of the inverse dispersion which increases significantly as polymerisation proceeds. Therefore, a crossed-paddle stirrer (with 4 equal size and equally placed blades) was constructed with a diameter of about 1/2 of the reaction tank inner diameter. When the crossed-paddle stirrer was rotated, the liquid was set in rotation and the free surface attained a rough parabolic shape. This swirling motion resulted in a large circular path with little vertical motion. In order to produce lateral and vertical flows which distribute the liquid rapidly to all parts of the vessel, four equally placed baffles were mounted near the wall of the reaction tank. The dimensions of the crossed-paddle stirrer and the baffles are shown in Figure 4-2.

The position of the stirrer in the reaction tank is also important for mixing (Nagata, 1975). Weinstein and Treybal (1973) reported that the smallest drops were found near the tip of the impeller and the largest drops presented at the bottom of the vessel. This provided a general image of drop coalescence and break-up in an agitated vessel. In the inverse microsuspension polymerisation, the heavier aqueous phase with larger volume fraction is dispersed in the lighter oil phase. To achieve an efficient dispersion and to obtain fairly uniform drops, the crossed-paddle stirrer was placed close to the bottom of the reaction tank with a gap of about 10 mm between the lower sides of the
stirrer blades and the bottom of the reaction tank, so that the agitation intensity was concentrated at the bottom of the tank where the heavier aqueous phase was locally in larger fraction.

Figure 4-2 Dimensions of crossed-paddle stirrer and baffles
(a) stirrer  (b) baffles
units are given in mm (not to scale). material: stainless steel
Figure 4-3 shows the viscosity variation of the inverse dispersion of aqueous acrylic acid in Isopar M stabilised with Witcamide 511, prepared by using the crossed-paddle stirrer and the baffles, with emulsification time. It is seen that, by applying 1000 rpm agitation, the viscosity of the inverse dispersion increased initially and reached a limiting value after about 1.5 hour emulsification. The SEM images of the inverse dispersion also revealed that there was no significant change in the aqueous drop size after 1.5 hour emulsification (Figure 4-4). This happens because of the balance...
between the drop coalescence and break-up (Gopal, 1968). At the early stages of emulsification, only a small number of drops were present and the drop break-up dominated the scene. As emulsification proceeded, a large number of drops were formed and collisions among them became more frequent. After a certain stage, the increase in drop size by coalescence and the decrease in drop size by break-up were almost the same and a limiting mean drop size was attained.

(a) 30 minutes emulsification

(b) 60 minutes emulsification
In the early stages of this research project, the crossed-paddle stirrer and the baffles were used. However, visual observation showed that, when using this stirrer, the convection of the inverse dispersion in the reaction tank was getting poorer as
polymerisation proceeded because of a significant increase in the viscosity of the inverse dispersion. To solve this problem, a modified stirrer was constructed, which is a combination of a "U" shaped-blade and a crossed-paddle. The visual inspection showed that the "U" shaped-blade with a larger size could promote the convection current of the inverse dispersion in the reaction tank. The dimensions of the modified stirrer and the baffles are shown in Figure 4-5.

![Diagram of polymerisation apparatus](image)

Figure 4-5  Dimensions of crossed-paddle + "U" blade stirrer and baffles

(a) stirrer,  (b) baffles

units are given in mm (not to scale).  material: stainless steel
The viscosity measurements showed that the emulsification efficiency of the modified stirrer was higher than that of the crossed-paddle stirrer (Figure 4-6).

![Figure 4-6 Variations of viscosities of inverse dispersions with emulsification time using different types of stirrers](image)

Figure 4-6 Variations of viscosities of inverse dispersions with emulsification time using different types of stirrers

- viscosity measurement: testing head speed 64 rpm, 23 °C
- inverse dispersions preparation: stirrer speed 1000 rpm, 23 °C
- compositions: same as that in Figure 4-3
4.1.3 Temperature Controlling System

Figure 4-7 is the diagrammatic representation of the polymerisation installation. The temperature controlling system consists of one cooling water bath (300 mm x 200 mm x 200 mm), one heating water bath (300 mm x 200 mm x 200 mm) equipped with a thermo-regulator, two water pumps (Paratherm II, JULABO, England), two solenoid valves (440-789, RS, Germany), a control box with a digital temperature indicator (4801 Therma Flow Control, DIGITRON Instrumentation Ltd), a thermo-sensor and soft plastic connecting tubes (inner diameter 8 mm).

For an isothermal polymerisation, the cooling water bath was filled with ice water and the heating water bath contained "warm" water automatically kept at a temperature about 5 °C higher than the designated polymerisation temperature. The temperature of the polymerisation mixture was monitored using the thermo-sensor which is placed inside the reactor. The two valves were connected to the control box and the two pumps were switched on. When the temperature of the reaction mixture exceeded the pre-set value, the valves was switched to let the ice water go through the reactor jacket; and when the temperature was lower than the pre-set value, the valves were switched to let the warm water go through. In this way, the temperature of the reaction mixture was maintained automatically at a constant value with a fluctuation of ±1.0 °C.

For a non-isothermal polymerisation, the temperature of the reaction mixture was initially maintained at the designated starting temperature (unless otherwise stated, non-isothermal polymerisation starts at 23 °C) by the same way used for isothermal polymerisations. However, the water in the warm water bath was kept at the same temperature as the designated polymerisation starting temperature and was pumped through the jacket at a constant rate throughout the course of the polymerisation. As polymerisation occurred, the temperature of the reaction mixture was recorded at different time intervals.
Figure 4-7  Diagrammatic representation of the polymerisation installation

- a: reactor
- b: stirrer
- c: control box
- d: heating-water bath
- e: ice-water bath
- f: water pump
- g: solenoid valve
- h: nitrogen inlet and outlet
- j: thermo sensor
Chapter 4  Polymerisation Apparatus and Its Operation

4.2  Polymerisation in Inverse Microsuspension

4.2.1  Materials

A typical formulation for inverse microsuspension polymerisation, which is suggested by Scott Bader Company Limited, is listed in Table 4-1. The total weights of the aqueous phase and of the oil phase are 144 g and 50 g respectively. The details of the materials are listed in Appendix I.

<table>
<thead>
<tr>
<th>material</th>
<th>weight (g)</th>
<th>material</th>
<th>weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acrylic acid</td>
<td>41.40</td>
<td>2.5% aqueous KBrO₃</td>
<td>1.60</td>
</tr>
<tr>
<td>DI water</td>
<td>73.86</td>
<td>Versenex 80</td>
<td>0.10</td>
</tr>
<tr>
<td>ammonium hydroxide</td>
<td>25.00</td>
<td>Isopar M</td>
<td>45.00</td>
</tr>
<tr>
<td>N, N'- methylene-bisacrylamide (MBA)</td>
<td>0.02</td>
<td>Witcamide 511</td>
<td>5.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>aqueous Na₂S₂O₅*</td>
<td>2.02</td>
</tr>
</tbody>
</table>

* aqueous Na₂S₂O₅ — Na₂S₂O₅ : water = 1 : 100 (wt/wt)

Acrylic acid (supplied by Scott Bader Company Limited, UK) was purified by vacuum distillation prior to polymerisation. DI water (Distilled and de-ionised water) was used as solvent. Ammonium hydroxide (SP.GR. 0.88, BDH Chemicals Ltd., UK) and N, N'-methylene-bisacrylamide (Klaus F. Meyer GmbH, Germany) were used as received for neutralisation and cross-linking agent respectively. Potassium bromate (Berk Chemicals Limited, UK) and sodium metabisulphite (William Blythe & Co Limited, UK) are commercial compounds and were used as redox initiators without further purification. Versenex 80 (Kinsley & Keith Chemical Group Limited, UK), an aqueous solution of the pentasodium salt of diethylenetriamine-pentaacetic acid (Na₅DTPA), was used as chelating agent to eliminate trace heavy metal ions in the system. Isopar M (paraffinic solvent, Exxon Company, USA) was used as dispersion medium and Witcamide 511 (alkanolamide, Witco Chemical Corporation, USA) was used as a non-ionic surfactant.
4.2.2 Inverse Microsuspension Polymerisation Procedure

Unless otherwise stated, the isothermal inverse microsuspension polymerisations were conducted as follows:

1. The designated amount of ammonium hydroxide was added to a beaker containing about 90 wt% of designated DI water and the beaker was allowed to stand in an ice-water both. The designated amount of acrylic acid was slowly added under magnetic agitation, keeping the temperature below 35 °C.

2. 1.6 g potassium bromate solution of designated concentration and 0.1 g Versenex 80 were added.

3. The pH of the solution was measured, which should be within ±0.1 of the designated value (pH 5.1 for the standard formulation). If the pH is low, it was adjusted with ammonium hydroxide.

4. Some more DI water was added to make 144 g of the total weight of the aqueous phase.

5. 45 g Isopar M and 5 g Witcamide 511 were added to the glass jacketed-reactor to form the oil phase.

6. The pre-set temperature was set to the designated value and the two pumps on the warm-water and ice-water loops were switch on.

7. Surface nitrogen purge was applied at a slow and constant flow and the aqueous phase above prepared was added slowly and continuously under mechanical agitation of 1,000 rpm.

8. After about 1.5 hour emulsification, the agitation was adjusted to the designated speed and then 2.0 g sodium metabisulphite in aqueous solution of the designated concentration was injected to start polymerisation.

The polymerisation procedures for the non-isothermal inverse microsuspension polymerisations were the same as that for the isothermal inverse microsuspension polymerisations except for the temperature control (see Section 4.1.3).
4.3 Polymerisation in Aqueous Solution

In order to investigate the mechanism of chemical reactions involved in the aqueous polymerisation of acrylic acid using sodium metabisulphite/potassium bromate redox pair, polymerisations in aqueous solution were conducted and the kinetics were studied.

4.3.1 Materials

The total amount of reaction mixture for an aqueous polymerisation is 144 g which is the same as the amount of the aqueous phase in the inverse microsuspension polymerisation. Two typical formulations of the aqueous polymerisations with and without the surfactant are listed in Table 4-2 and Table 4-3 respectively. Unless otherwise stated, the pH values of the initial reaction mixtures were adjusted to $5.1 \pm 0.1$ using ammonium hydroxide as buffer.

Table 4-2 Typical Formulation of Aqueous Polymerisation without Surfactant

<table>
<thead>
<tr>
<th>material</th>
<th>weight (g)</th>
<th>material</th>
<th>weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acrylic acid</td>
<td>20.00</td>
<td>2.0 wt% KBrO₃ solution</td>
<td>1.60</td>
</tr>
<tr>
<td>ammonium hydroxide</td>
<td>15.50</td>
<td>Versenex 80</td>
<td>0.10</td>
</tr>
<tr>
<td>DI water</td>
<td>104.80</td>
<td>3.0 wt% Na₂S₂O₅ solution</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Table 4-3 Typical Formulation of Aqueous Polymerisation with Surfactant

<table>
<thead>
<tr>
<th>material</th>
<th>weight (g)</th>
<th>material</th>
<th>weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acrylic acid</td>
<td>20.00</td>
<td>2.0 wt% KBrO₃ solution</td>
<td>1.60</td>
</tr>
<tr>
<td>ammonium hydroxide</td>
<td>15.50</td>
<td>Versenex 80</td>
<td>0.10</td>
</tr>
<tr>
<td>DI water</td>
<td>99.79</td>
<td>MBA</td>
<td>0.01</td>
</tr>
<tr>
<td>Witcamide 511</td>
<td>5.00</td>
<td>3.0 wt% Na₂S₂O₅ solution</td>
<td>2.00</td>
</tr>
</tbody>
</table>
In the aqueous polymerisations with surfactant, MBA was used at the same concentration as used in the standard inverse microsuspension polymerisation to obtain comparable kinetic data.

### 4.3.2 Aqueous Polymerisation Procedure

Unless otherwise stated, the isothermal aqueous polymerisations were carried out as follows:

1. The aqueous phase was prepared by following the same procedure described in the forgoing section for the inverse microsuspension polymerisation (for aqueous polymerisation with surfactant, Witcamide 511 was added directly to the aqueous phase).
2. The aqueous solution was transferred to the glass jacketed-reactor with crossed-paddle stirrer, baffles, nitrogen inlet and outlet.
3. The pre-set temperature was set to the designated value and the two pumps on the warm-water and ice-water loops were switched on.
4. Surface nitrogen purge was applied for about 45 minutes under agitation of 400 rpm.
5. 2.0 g sodium metabisulphite in aqueous solution of the designated concentration was finally added to start polymerisation. The agitation speed was 400 rpm for the aqueous polymerisations.

### 4.4 Polymerisation Monitoring

#### 4.4.1 Determinations of Monomer Conversion and Polymerisation Rate

So far, a number of techniques have been developed for measuring monomer conversion. Useful summaries have been provided by Stickler (1989) and Gilbert (1995). Basically, monomer conversion may be determined in two different ways. One is by directly measuring the concentration of residual monomer level (such as chemical analysis, chromatographic methods and spectroscopic methods) or,
alternatively, by directly collecting and weighing the produced polymer (gravimetry). The other is by using indirect methods with the help of physical properties of the reaction system (such as dilatometry, densitometry, measurement of refractive index or dielectric constant, light-scattering, viscosity measurement and microcalorimetry).

In view of the features of polymerisations of acrylic acid in aqueous solutions and in inverse dispersions, chromatographic and gravimetric methods were employed in this project.

4.4.1.1 High Pressure Liquid Chromatography (HPLC)

HPLC is a combined separating and measuring system for liquid samples. Its high sensitivity and reproducibility make it useful for both qualitative and quantitative analysis.

The separation in liquid chromatography is achieved if the mutual interaction of sample components with stationary phase differs from that with mobile phase. The stationary phases normally possess one, or more, of four basic function characteristics: (i) the power physically to sorb solutes from solution; (ii) the power chemically to sorb solutes from solution; (iii) the ability to dissolve solutes when contacted with solutions in an immiscible solvent; (iv) a porous structure which can remain some, and reject other, solutes on the basis of solute size or shape. Based on these four characteristics, liquid chromatography can be referred to as adsorption chromatography, ion-exchange chromatography, partition chromatography and exclusion chromatography. Each of them uses different types of column and has specific suitability for sample separation (Perry et al, 1972).

The acrylic acid molecule possesses a polar group (-COOH). Therefore, a HYPERSIL 3 C18 reversed-phase HPLC column (octadecyl boned phase, PHENOMENEX) was employed.
There are four commonly used commercially available detectors which can be chosen for any particular application in liquid chromatography. They are, namely, the ultraviolet (UV) detector, the refractive index detector, the conductivity detector and the fluorescence detector. No detector can perform as a universal detector capable of handling all types of separation problems. UV detectors can be used for the analysis of those substances that absorb UV light at the wavelength of the source light. Many compounds absorb light in the UV range (180-350 nm) including all substances having one or more double bonds (π electrons) and substances having unshared electrons. Among the four types of detectors, the UV detector, with combined high sensitivity and wide linear dynamic range, is usually the first choice followed in popularity by the refractive index detector. The others are normally chosen for very specific applications.

An UV detector (UVICON 720LC, KONTRON Spectrophotometer) was employed in this project.

In order to separate the produced polymer from the residual monomer and to stop post-polymerisation, a precipitation technique was employed by using an organic solvent containing an inhibitor. The organic solvent must be one in which acrylic acid is soluble and polyacrylic acid insoluble; and the inhibitor must be soluble in the organic solvent. Initially, acetone and hydroquinone were chosen as the organic solvent and the inhibitor respectively. Both acetone and hydroquinone are soluble in aqueous solutions which are normally used as polar eluents of reversed-phase chromatography. Therefore, they may absorb the light in a certain UV range and give peaks in the chromatogram.

Figure 4-8 shows the UV spectrum of aqueous acrylic acid obtained by scanning the diluted aqueous acrylic acid at continuously varying wavelength (190 - 360 nm) using an UV/VIS spectrometer (Lambda 2, PERKIN ELMER). It reveals a maximum absorbance at a wavelength around 195 nm. In the absence of interference, the wavelength chosen for a quantitative determination is the wavelength of maximum
absorbance. However, if the detector is operated at 195 nm, interferences may arise from the absorbance of the organic solvent used for polymer precipitation, because the majority of organic solvents are not completely UV transparent below the wavelength of 200 nm. The HPLC chromatograms of acrylic acid and acetone are shown in Figure 4-10, a and b respectively. It is clear that an interference will be present because a complete resolution of these two solutes cannot be achieved in this case.

Figure 4-8  UV spectrum of aqueous acrylic acid

23 ºC
In quantitative spectrophotometric analysis, it is fairly common to use a wavelength at which the analytical substance absorbs rather strongly but at which the absorbance caused by the other reagent(s) is zero, or at least small (Fritz and Schenk, 1987). In order to eliminate the interference from the organic solvent, the UV detector was
operated at a wavelength of 210 nm and 2-propanol (UV cut-off 204) was used as solvent instead of acetone.

![HPLC chromatogram of a polymerisation sample](image)

**Figure 4-10** HPLC chromatogram of a polymerisation sample

- eluent: 1.5 wt% methanol aqueous solution, pH 2.5,
- flow rate: 0.24 ml/min
- column temp.: 30 °C
- Detector: UV spectrophotometer, 210 nm

In the primary experiments, methanol aqueous solution was used as the eluent. The pH of the eluent was adjusted to 2.5 using phosphoric acid as buffer. The column temperature was kept at 30 ± 0.1 °C by using the external heater of Waters 410 Differential Refractometer (MILLIPORE). A HPLC chromatogram of polymerisation sample is shown in Figure 4-10. A shoulder clearly appears in the peak of acrylic acid, an indication of an overlap of peaks. By an inspection of the chromatogram of hydroquinone obtained under the same conditions (Figure 4-11), it is apparent that the shoulder is due to the presence of hydroquinone.
A number of techniques were employed to obtain a complete resolution of acrylic acid and hydroquinone. The change of HPLC operation conditions, such as eluent flow rate and column temperature, had little effect. However, a remarkable improvement was achieved by changing the eluent composition. When an aqueous solution of 7.0 wt% THF at pH 3.0 was used, a very good resolution was obtained (Figure 4-12 and 4-13).
In some polymerisations, the cross-linking agent (MBA) may be also present in the samples. However, no absorbance was observed in the chromatogram at the concentration used for polymerisation.
In order to check the reproducibility of HPLC, six replications were performed for a sample under the conditions shown in Figure 4-12. The integrated areas are listed in Table 4-4. The standard deviation is 0.0441.

<table>
<thead>
<tr>
<th>run</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>area (relative unit)</td>
<td>3.4925</td>
<td>3.5460</td>
<td>3.5465</td>
<td>3.5520</td>
<td>3.5578</td>
<td>3.5806</td>
<td>0.0441</td>
</tr>
</tbody>
</table>

Figure 4-14 log-log plot of HPLC integrated area against AA concentration

same conditions as Figure 4-12
A series of standard aqueous acrylic acid solutions were characterised. Figure 4-14 shows the log-log plot of the corresponding HPLC integrated area against the acrylic acid concentration in the range of 10 to 150 ppm. The slope of the plot, namely, the response index, is 1.01. This accords with the definition: “the useful linear range of the detector is defined as that range of solute concentration over which the response index lies between 0.98 and 1.02” (Knox et al., 1978).

A calibration equation was obtained by least squares calculation (see Appendix II):

\[ C_{AA} = 4.77A + 0.61 \]  

[4-1]

Here \( C_{AA} \) and \( A \) represent acrylic acid concentration (ppm) and HPLC integrated area (relative unit) respectively.

The preparation of samples and the HPLC analysis were performed as follows:

1. Samples of reaction mixture (about 0.7 g of each) were drawn at different time intervals (1-2 minutes at early stages, about 5 and 10 minutes at middle and late stages respectively) using glass syringes and quickly injected into specimen tubes containing about 0.05 wt% hydroquinone 2-propanol solution (about 5.0 g weighed accurately in each tube), then the tubes were vigorously shaken. The specimen tubes were kept in a refrigerator below 8 °C prior to further analysis.

2. The liquid portion of the obtained samples were centrifuged at 13000 rpm for about 10 minutes, then about 0.05 g transparent supernatant liquid of each centrifuged sample was diluted to 25 ml with the HPLC eluent (7.0 wt% THF aqueous solution, pH 3.0). The acrylic acid concentrations in such prepared samples are in the range of 10 to 100 ppm.

3. The diluted samples were analysed using HPLC under the conditions shown in Figure 4-12. Two replications were normally performed for each sample and the average values were calculated.
4. The acrylic acid concentration in each diluted sample was calculated by the calibration equation [4-1] and the residual acrylic acid concentration was then calculated by correcting for the dilution used.

5. The monomer conversion was finally obtained using the following equation:

\[
\text{conversion} = 1 - \frac{C_{AA}}{C_{AA_0}} \tag{4-2}
\]

Here \(C_{AA_0}\) is initial acrylic acid concentration.

A typical result is shown in Appendix III.

### 4.4.1.2 Gravimetry

The gravimetric method is simple and has been widely used for measuring the monomer conversion of homopolymerisations. This method entails frequently withdrawing samples from the reactor, then drying and weighing them.

Because of its easy thermal-polymerisation (polyacrylic acid formed during vacuum distillation when the temperature exceeded 70 °C), the residual acrylic acid must be completely separated from the produced polymer. This was done by using the same precipitation technique as used in HPLC method. The procedure for determining the monomer conversion by gravimetric method is given below:

1. Precipitation procedure for produced polymers was similar to that for HPLC method, except that about 1.5 g of each sample was drawn at different time intervals and injected into about 15.0 g 2-propanol solution containing 0.05 wt% hydroquinone.

2. The precipitated polyacrylic acid samples were filtered using glass sinters, then were washed repeatedly with 2-propanol.
3. The polymer samples were dried in a vacuum oven at 70 °C to constant weight (about 48 hours).

4. The dried polymer samples were weighed and the monomer conversions were calculated according to:

\[ \text{conversion} = \frac{W_{\text{polym}}}{W_{\text{AAo}}} \]  \[4-3\]

Here \( W_{\text{polym}} \) and \( W_{\text{AAo}} \) are weight percentages of dried polymer portion in specimen withdrawn from reactor and of acrylic acid in initial inverse dispersion.

Typical monomer conversion curves of an aqueous polymerisation obtained by the gravimetric method and the HPLC method are shown in Figure 4-15. It is clear that the two results are in very good agreement with each other. However, for inverse microsuspension polymerisations, the gravimetric method usually led to considerably higher results than that obtained by the HPLC method. This is probably because of the difficulty in complete elimination of Isopar M and Witcamide 511 from the polymer produced by precipitation.

4.4.1.3 Determination of Polymerisation Rate

For kinetic studies, initial polymerisation rates were employed. First, the slopes of the tangent to the monomer conversion curves for zero polymerisation time were measured. Then the initial polymerisation rates were calculated by the following equation:

\[ R_{po} = l[M]_o \]  \[4-4\]

Here \( R_{po} \) is initial polymerisation rate, \( l \) the slope of the tangent to monomer conversion curve for zero polymerisation time and \( [M]_o \) is the corresponding initial monomer concentrations.
4.4.2 Measurement of Reaction Temperature

In Scott Bader Company Limited, the non-isothermal inverse microsuspension polymerisations were followed by monitoring the temperature variation inside the reactor. This technique was also employed for monitoring the reaction rates of the non-isothermal polymerisations in the present work.

The operation was described in Section 4.1.3.
4.5 Reproducibility of Polymerisation Control

To check the reproducibility of polymerisation control, replications of polymerisation were conducted for both inverse microsuspension polymerisation (non-isothermal) and aqueous polymerisation (isothermal). The polymerisation temperature profiles in Figure 4-16 and the monomer conversion curves in Figure 4-17 show that the polymerisations were well reproducible. These indicate a good polymerisation control and the reliability of the techniques for polymerisation monitoring.

Figure 4-16  Polymerisation temperature profiles of replications of non-isothermal inverse microsuspension polymerisations

\[
[AA]_0 = 4.24 \text{ mol/l}, \quad [KBrO_3]_0 = 8.77 \times 10^{-4} \text{ mol/l}, \\
[Na_2S_2O_3]_0 = 7.46 \times 10^{-4} \text{ mol/l}, \quad [S]_0 = 10 \text{ wt\% of oil phase, pH 5.1, 23 °C,} \\
crossed-paddle stirrer 1000 \text{ rpm for emulsification and 500 rpm for polymerisation}
\]
Figure 4-17  Monomer conversion curves of replications of aqueous polymerisation

the composition and conditions see Expt. W-2 in Appendix IV


CHAPTER 5

INVESTIGATIONS ON MECHANISM OF INVERSE MICROSPUSPENSION POLYMERISATION PROCESS

5.1 INTRODUCTION

Inverse heterogeneous polymerisations have been widely employed for producing water-soluble polymer lattices and colloids. Previously, attempts have been made to obtain understanding of individual systems and different mechanisms have been developed (see Chapter 2). So far, the most intensive studied systems have been those that use a single-component initiator, including oil-soluble and water-soluble initiators. The use of redox initiators in inverse heterogeneous polymerisations have been reported in the literature (see Chapter 2). However, no detailed studies to date have been found concerning the mechanistic aspects in these specific polymerisation systems.

In an inverse heterogeneous polymerisation using redox initiators, the two components of the redox pair are usually introduced separately. Normally, the oxidant is dissolved in the aqueous monomer which is then dispersed in an oil phase and the reductant is finally added to start polymerisation (Kurenkov, 1986, Dimonie et al, 1986 and Li and Ruckenstein, 1996). An alternative way is that both the oxidant and the reductant are introduced separately to the inverse dispersion of aqueous monomer in oil (Dimonie et al, 1992). Therefore, the polymerisation system may initially consist of two or three different types of aqueous drops and the distribution of the two components of the redox pair are heterogeneous in nature. Obviously, these inverse heterogeneous polymerisations have their specific features which are different from that of conventional suspension or emulsion polymerisations.
The present project concerns polymerisation of aqueous acrylic acid dispersed in a hydrocarbon oil (Isopar M) and stabilised with a non-ionic surfactant (Witcamide 511) using redox initiators (potassium bromate/sodium metabisulphite). The aim of the work presented in this chapter is to obtain an understanding of the mechanism of this polymerisation process.

5.2 EXPERIMENTAL

5.2.1 Polymerisation

Acrylic acid was purified by vacuum distillation prior to polymerisation. Distilled and de-ionised water was used as solvent. Other materials were used as received without further purification. The details of materials are shown in Appendix I.

Both the inverse microsuspension polymerisation and the aqueous polymerisation were conducted in the glass jacked-reactor with the mechanical crossed-paddle stirrer and baffles. The details of polymerisation apparatus and polymerisation procedures are described in Chapter 4.

For isothermal polymerisations, the variation of monomer conversion with time was obtained by measuring the residual monomer concentration using HPLC. For non-isothermal polymerisations, the polymerisation was monitored by measuring the variation of temperature of the reaction mixture with time. The details of the development of these techniques were discussed in Chapter 4.

5.2.2 Monomer Partitioning

Fourier transform infrared spectroscopy (FTIR) was used for characterising the solubility of acrylic acid in the oil phase (Isopar M containing Witcamide 511). An FTIR spectrophotometer (Mattson 300) was operated at a resolution of 2 cm\(^{-1}\) and 32 scans were accumulated. The liquid sample films were prepared using KBr windows.
Ultra-violet spectroscopy (UV/VIS spectrometer, Lambda 2, Perkin Elmer) was employed to measure the partitioning of acrylic acid between the aqueous phase and the oil phase. The acrylic acid concentrations in the aqueous samples were calculated using a standard calibration curve.

5.2.3 Drop Size Analysis

The aqueous drop size was examined at various stages throughout the course of polymerisation using SEM with freeze-fracture equipment. (See Chapter 3 for the development details of this technique)

5.2.4 Analysis of Solubility of Initiator in Oil Phase

The solubility of sodium metabisulphite in the oil phase was analysed by comparing the change in concentrations of sodium metabisulphite in aqueous solutions before and after mixing with the oil phase. Atomic absorption spectrophotometry (Perkin-Elmer 1100B) was employed for determining the concentration of sodium metabisulphite in aqueous solution.

5.3 RESULTS

5.3.1 General Features of Inverse Microsuspension Polymerisation

Figure 5-1 shows the variations of monomer conversion with polymerisation time in a typical inverse microsuspension polymerisation and in a typical aqueous polymerisation with surfactant. The two polymerisations were conducted using the same composition, except for the absence of Isopar M in the aqueous polymerisation, under identical conditions.
It can be seen that the polymerisations, in both cases, occurred as soon as sodium metabisulphite in aqueous solution was introduced. The rapid initiation by adding the aqueous reductant was also observed in non-isothermal polymerisations indicated by the immediate rise in temperature of the reaction mixtures. However, the polymerisation rate was slightly lower in the inverse microsuspension polymerisation than in the aqueous polymerisation with surfactant. This suggested differences in polymerisation mechanism.
5.3.2 Evolution of Drop Size and Its Distribution

Figure 5-2 shows a series of SEM images of the inverse dispersion at different polymerisation stages. The size of aqueous monomer-oxidant drop was in a range of 0.6 to 2.0 μm before adding the aqueous reductant. Like the observations in simulation experiment (see Chapter 3), big drops appeared after adding a shot of aqueous reductant. These big drops were obviously derived from the newly introduced aqueous reductant. It was also seen that the size of the big drops was getting smaller as polymerisation proceeded under continuous agitation. This indicated further break-up of these drops in the turbulent field. By a close inspection, it seems that the average particle size and size distribution in the final latex was larger than that of the aqueous monomer-oxidant drops in the initial inverse dispersion.

5.3.3 Role of Second Shot of Reductant Solution

In a non-isothermal inverse microsuspension polymerisation, a second shot of the aqueous reductant induced further initiation of polymerisation indicated by the appearance of a second temperature peak in the polymerisation temperature profile (Figure 5-3, a). However, a second shot of the oxidant in aqueous solution alone did not result in any significant temperature change. Here the second shot of the aqueous reductant or of the aqueous oxidant was added as the temperature of the inverse dispersion dropped from a peak value down near to the initial temperature.

Initially, it was thought that the above phenomenon might be because some unreacted oxidant molecules remained in the system, whilst the reductant molecules introduced by the first shot were almost consumed. However, this phenomenon was also observed when a higher mole ratio of the reductant to the oxidant was applied (Figure 5-3, b).
Figure 5-2 Freeze-fracture SEM images of inverse dispersion at various polymerisation time

emulsification at 1000 rpm for 1.5 hour, polymerisation at 500 rpm, 23 °C
In an aqueous polymerisation, an increase in monomer conversion was achieved only after the addition of a second shot of the aqueous reductant followed by a shot of the aqueous oxidant; but no significant change was produced by adding the second shot of the aqueous reductant alone (Figure 5-4). Here, the mole ratio of the reductant, introduced by the first shot, to the oxidant, existing in the aqueous monomer-oxidant drops, was lower than that in the forgoing two non-isothermal inverse microsuspension polymerisations. This indicated that the further initiation of polymerisation by adding a second shot of the aqueous reductant in the inverse
microsuspension polymerisations did not result from the complete exhaustion of the reductant molecules.

![Graph showing effects of second shots of initiators in aqueous polymerisation](image)

**Figure 5-4** Effects of second shots of initiators in aqueous polymerisation

\[
[AA]_0 = 1.99 \text{ mol/l}, \quad [KBrO_3]_0 = 7.59 \times 10^{-4} \text{ mol/l}, \quad [Na_2S_2O_3]_0 = 7.54 \times 10^{-4} \text{ mol/l},
\]

2nd shot: \([Na_2S_2O_3] = 7.54 \times 10^{-4} \text{ mol/l}, \quad [KBrO_3] = 7.59 \times 10^{-4} \text{ mol/l}\)

23 °C, crossed-paddle stirrer at 600 rpm for polymerisation

A number of papers in the literature reported that the reaction between bisulphite ion and oxygen could produce primary radicals to initiate polymerisations (Konar and Palit, 1961, Igarashi et al, 1989 and Bajpai et al, 1992). Because the aqueous reductant was added without pre-purge with nitrogen in the present polymerisations, a small
amount of atmospheric oxygen may introduced with the aqueous reductant. However, Figure 5-4 clearly indicated that the reaction between sodium metabisulphite and oxygen did not result in significant increase in monomer conversion. Therefore, the preceding phenomenon can not be simply attributed to the initiation by the reaction between sodium metabisulphite and oxygen alone.

5.3.4 Solubility of initiator in Oil Phase

In order to investigate the possibility of mass transfer of the initiator(s) through the oil phase, the solubility of sodium metabisulphite in the oil phase was characterised using atomic absorption spectrophotometry.

An inverse dispersion was prepared by slowly adding 20 g aqueous solution of sodium metabisulphite (9.6 x 10\(^3\) ppm) to 10 g oil phase (Isopar M containing 10 wt% Witcamide 511) in a 100 ml beaker under magnetic agitation. The inverse dispersion was then withdrawn at different time intervals and centrifuged for about 10 minutes at 13,000 rpm to separate the two phases. The separated aqueous solutions of sodium metabisulphite were diluted with DI water (0.1 ml aqueous solution in 500 ml DI water) and analysed using the atomic absorption spectrophotometer. The result showed no change in sodium concentration in these samples and hence indicated that sodium metabisulphite is insoluble in the oil phase.

5.3.5 Acrylic Acid Partition in Two Phases

144 g aqueous acrylic acid (4.24 mol/l acrylic acid in water) was slowly added to 50 g oil phase (Isopar M containing 10 wt% Witcamide 511) in the glass jacked reactor under 1,000 rpm agitation using the crossed-paddle stirrer. Samples were then withdrawn at various time intervals and centrifuged at 13,000 rpm for 60 minutes to separate the two phases.
The FTIR spectrum of one separated transparent oil phase was obtained and compared with that of the oil phase in Figure 5-5. Some differences, especially around wavenumbers 1500 to 1800 cm\(^{-1}\), are apparent. The peak at around 1700 cm\(^{-1}\) wavenumbers in spectrum (b) arises from C=O group which is neither present in Isopar M nor in Witcamide 511 (see Figure 5-6, a and b). This demonstrated the existence of acrylic acid molecules in the separated oil phase.

The subtraction technique was employed to obtain a subtracted FTIR spectrum (Figure 5-7, b) by subtracting the spectrum (a) from the spectrum (b) in Figure 5-5. The peak due to CH\(_3\) group which does not exist in acrylic acid was taken as the reference and reduced to zero. The subtracted spectrum is in very good agreement with the spectrum of acrylic acid (Figure 5-7, a).

The samples of separated aqueous phase obtained at various mixing time intervals were analysed using the UV spectrometer. The variation of weight percentage of acrylic acid in the separated aqueous phase with mixing time is shown in Figure 5-8. It can be seen that the equilibrium of acrylic acid partitioning between the two phases attained within about 1.0 hour and about 11.0 wt% of acrylic acid in the aqueous phase “lost” during mixing.

It must be mentioned that a complete separation of the two phases was unable to be achieved by the centrifugation. A thin liquid layer remained between the transparent oil (on the top) and the aqueous phase. The brown colour of this middle layer indicated that a large portion, if not total, of Witcamide 511 transferred from the oil phase to this layer (Witcamide 511 is brown and Isopar M is transparent).
Figure 5-5 FTIR spectra of oil phase before and after mixing with aqueous AA
Figure 5-6  FTIR spectra of Isopar M and Witcamide 511
On separating a mixture of pure acrylic acid with the oil phase, a transparent oil and a brown acrylic acid were obtained, an indication of transfer of Witcamide 511 from the oil phase to acrylic acid.

Figure 5-7  FTIR spectra of acrylic acid

(a) spectrum of AA        (b) subtracted spectrum of AA
These phenomena suggested a very strong interaction between acrylic acid molecules and the surfactant molecules. This interaction could favour the location of acrylic acid and Witcamide 511 molecules at the interface and lead to a monomer-rich interlayer in the inverse dispersion (Candau et al, 1984). Therefore, it seems reasonable to postulate that the concentration of acrylic acid in the above mentioned middle layer was higher than that in the separated aqueous phase and the 11.0 wt% acrylic acid "lost" from the aqueous phase was not completely present in the oil phase.
Unfortunately, the quantitative value of solubility of acrylic acid in the oil phase cannot be directly obtained by UV spectrometry because of the interference from Witcamide 511 molecules (Figure 5-9).

Figure 5-9 UV spectra of AA and Witcamide 511 in ethanol
5.4 DISCUSSION

5.4.1 Initiation Mode

For inverse heterogeneous polymerisations using single component water-soluble initiator, two kinds of initiation modes were proposed in the literature: initiation solely in aqueous drops or initiation in both aqueous drops and inverse micelles. In the polymerisation of acrylamide in Isopar M/Span 80 using 2,2'-azobis [N-(2-hydroxyethyl) butyramidine as initiator, Baade and Reichert (1984 and 1986) suggested that the initiation took place in each aqueous drop by decomposition of the initiator molecules dissolved in the aqueous phase. This hypothesis was supported by: (a) the absence of inverse micelles in the system; (b) the experimental results showing the same kinetic relationship for the polymerisations in inverse dispersion and in aqueous solution. In an early work in the polymerisation of sodium-p-vinyl benzene sulfonate in o-xylene/Span 60 initiated by potassium persulphate, Vanderhoff et al (1962) postulated a simultaneous initiation in both aqueous drops and inverse micelles. The emulsion polymerisation characteristics was also reported by Kurenkov et al (1978) in the polymerisation of acrylamide in toluene/Sintamide-5 using sodium persulphate as initiator.

In the present inverse microsuspension polymerisation, the two components of the redox pair were segregated in the two different types of aqueous drops. No polymer was produced during the nitrogen purge of the aqueous monomer containing potassium bromate. It has also been revealed that sodium metabisulphite could not initiate polymerisation alone (see Chapter 6). Therefore, the initiation could occur only when the oxidant and the reductant came together. The insolubility of sodium metabisulphite in the oil phase, revealed by the atomic absorption spectrometry analysis, indicated that the production of primary radicals could only be in the aqueous phase.
Based on the above analysis, it is apparent that the initiation in the inverse microsuspension polymerisation can initially occur in the aqueous drops only as a result of intermixing of the redox pair by coalescence between the added aqueous reductant drops (ARDs) and the dispersed aqueous monomer-oxidant drops (AMODs).

The coalescence between the ARDs and the AMODs could be, at the early stages, a procedure of "capture" of the small stabilised AMODs by the big unstable ARDs; similar to the mechanism suggested for the simulation experiments discussed in Chapter 3. The instantaneous initiation which occurred when the aqueous reductant was added gave evidence for the quick coalescence at this stage (see Figure 5-1). This is also in very good agreement with the observations in the simulating experiments of drop behaviour presented in Chapter 3.

Because they were still too big to exist in the turbulent field, the coalesced aqueous drops would undergo further break-up, thus, creating more unstabilised interface and inducing further coalescence. In this way, continuous coalescence and break-up of aqueous drops proceeded and more and more aqueous drops were initiated.

The evolution of drop size and size distribution revealed by the SEM images throughout the course of polymerisation suggested that the initiation in inverse micelles, if it existed, seems not to be of importance in this case. In a conventional emulsion polymerisation, monomer swollen micelles are the predominant locus of polymerisation and the monomer drops only act as reservoirs. As polymerisation proceeds, the number and the size of initiated micelles will increase whereas the number of monomer drops will decrease. The polymer particles in the final latex is normally much smaller than the initial monomer drops. However, no such evolution of drop/particle size and size distribution was observed during the present polymerisation. In contrast, the SEM images indicated a slight increase in the average size of aqueous drops/particles as polymerisation proceeded (Figure 5-2).
In addition, the difference between polymerisation rates of the inverse microsuspension polymerisation and of the aqueous polymerisation with surfactant under the identical conditions also gave implications of non-emulsion polymerisation characteristics of the present inverse microsuspension polymerisation (Figure 5-1). In the polymerisation of sodium p-vinyl benzene sulfonate initiated by potassium persulphate, Vanderhoff et al (1962) found that the polymerisation rate was significantly higher in inverse emulsion than in aqueous solution. However, in the present inverse microsuspension polymerisation, a contrary result was observed.

In the polymerisation of acrylamide in Isopar M/Span 80, Baade and Reichert (1984, 1986) observed that the polymerisation rate was proportional to the 1.0 power of monomer concentration and 0.5 power of initiator concentration. This kinetic relationship corresponded to that of an aqueous polymerisation. The authors, thus, postulated that each aqueous drop acted as an individual batch solution polymerisation reactor. Obviously, the inverse microsuspension polymerisation differs from this type of polymerisation. Although each coalesced aqueous drop could also undergo polymerisation as a tiny solution polymerisation reactor, all the AMODs seems unlikely to be initiated simultaneously at the beginning of polymerisation. This can probably account for the lower polymerisation rate in the inverse microsuspension than that in the aqueous solution with surfactant.

Apart from the initiation by aqueous drop coalescence, there might be another possibility for initiating the aqueous monomer drops. The partitioning experiment has revealed that a small amount of monomer dissolved in the oil phase. This suggested a transfer of the monomer molecules between the two phases. Some oligomeric radicals formed in the coalesced aqueous drops might also diffuse to the oil phase and then propagate there. They could be captured by the aqueous monomer drops and/or precipitate back to the aqueous drops when reaching a certain chain length. This could produce another kind of initiation. However, the kinetic studies revealed that this kind of initiation, if it existed, was not important (details will be discussed in Chapter 6 and 7).
5.4.2 Locus of Reactions

The insolubility of sodium metabisulphite in the oil phase clearly indicated that the production of primary radicals could only be in the coalesced aqueous drops. As soon as the primary radicals were produced in these coalesced aqueous drops, the polymerisation would start and aqueous polymer-monomer particles (APMPs) would be formed.

In the inverse dispersion polymerisation performed by Baade and Reichert (1984 and 1986), single component initiator was dissolved in the aqueous monomer before emulsification. The composition of reactants in each aqueous drop was, hence, homogeneous and each aqueous drop acted as the same solution polymerisation reactor. The composition in the locus of the present inverse microsuspension polymerisation might be much more complicated.

Because the reductant was added as a concentrated aqueous solution, the concentration of the reductant in the coalesced aqueous drops must be much higher than its apparent value (based on the overall aqueous phase) at the early stages. On the other hand, the concentrations of the monomer and the oxidant in these coalesced aqueous drops should be lower than their apparent values due to the dilution by the aqueous reductant. In addition, the polymer content in the APMPs varied as polymerisation and drop mixing proceeded. At the same time, these APMPs underwent further coalescence and break-up. The reductant concentration in the further-coalesced aqueous drops would be reduced by both dilution and the consumption in the redox reaction. Therefore, the composition in the coalesced aqueous drops was dependent on their drop mixing history and varied with time. This could have important consequences in the polymerisation kinetics.

The further polymerisation induced by the second shot of the aqueous reductant is in agreement with the above hypothesis. According to the hypothesis, polymerisation proceeded in the coalesced aqueous drops as a result of simultaneous coalescence and break-up of the different types of aqueous drops. The drop coalescence and break-up
are very complicated procedures and dependent not only on mixing conditions, but also on system internal properties (Zerfa and Brooks, 1996, and Sherman, 1968). The further coalescence and break-up of the coalesced aqueous drops could be restrained by the increase in the fluid viscosity inside them owing to the formation of polymer chains (Chesters, 1991). The balance between coalescence and break-up of aqueous drops during polymerisation was reported by Graillat et al (1986) in the inverse heterogeneous polymerisation of acrylamide in toluene. The authors found that polyacrylamide in aqueous solution simulating percent conversion higher than 10% could not be dispersed in toluene regardless of the agitation speed. In fact, polymerisation always results in a dramatic increase in the viscosity of the aqueous acrylic acid even at very low conversion. After a certain stage, an APMP might not be able to undergo any further coalescence and break-up because it became too "hard". Obviously, higher polymerisation rate always occurred in those coalesced aqueous drops containing higher concentrations of the reactants and resulted in slower coalescence and break-up. In view of the heterogeneous distribution of the reductant molecules in the aqueous phase, the coalesced aqueous drops containing the reductant at higher concentration would stop further coalescence and break-up at earlier stages. On the other hand, the volume ratio of the aqueous reductant to the aqueous monomer was quite small (about 1 : 66 for the majority of polymerisations), so that the intermixing of the reductant and the oxidant via coalescence was unlikely to be completely attained. As a result, both the reductant and the oxidant may not be completely consumed at the end of polymerisation. The residual oxidant might remain in uncoalesced or slightly polymerised drops, whilst the residual reductant could be "trapped" in highly polymerised drops. The new aqueous reductant drops, introduced by a second shot, could easily coalesce with the uncoalesced or slightly polymerised aqueous monomer drops to initiate further polymerisation. In contrast, the addition of new aqueous oxidant drops could hardly initiate further polymerisation because the newly formed coalesced aqueous drops will lack either the reductant or the monomer.

5.4.3 Hypothesis of Polymerisation Process

The experimental results have indicated the following specific features of the inverse-
microsuspension polymerisation:

i. The two components of the redox pair are initially segregated in two different types of aqueous drops, i.e. the oxidant in the surfactant stabilised aqueous monomer drops and the reductant in the newly introduced unstable aqueous drops.

ii. Both the oxidant and the reductant are unable to initiation polymerisation alone.

iii. The monomer is slightly soluble in the oil-phase, but the two components of the redox pair are not oil-soluble.

Based on the foregoing discussions, the process of this inverse microsuspension polymerisation might be postulated as follows:

After being added to the inverse dispersion under continuous agitation, the aqueous reductant is ruptured into big drops by the rotating stirrer and/or under the rotation stress. These ARDs are unstable and tend to reduce their interfacial tension by adsorbing the surfactant molecules. They could acquire stabiliser either by adsorbing the free surfactant molecules in the oil phase or by coalescing with the stabilised AMODs which collide with them in the turbulent field. The tendency to reduce the interfacial tension of the ARDs could promote their coalescence with the AMODs. As soon as the coalescence between the two different types of aqueous drops takes place, the two components of the redox pair join together and the initiation occurs in the coalesced aqueous drops leading to the formation of APMPs. At the same time, these APMPs are still too big to exist in the turbulent field and may undergo further break-up into smaller drops. As the further break-up proceeds, new unstabilised interface forms and further coalescence takes place.
As polymerisation proceeds in the APMPs, the monomer concentration in these drops decreases and the monomer molecules in the oil phase would transfer back to the aqueous drops.

The composition in individual aqueous drops would be very complex. At the beginning of adding the aqueous reductant, two types of aqueous drops co-exist, i.e. the AMODs and the ARDs. As soon as the coalescence occurs, a new type of aqueous drops forms — APMPs. The generation of new APMPs continues as a result of simultaneous further coalescence and break-up of the aqueous drops. However, the composition in these coalesced aqueous drops may not be the same. At the early stages, the APMPs are rich in the reductant. However, the reductant concentration will decrease quickly as coalescence and break-up proceed. Each cycle of coalescence and break-up will result in a composition change in those aqueous drops which are involved. Because of the statistical feature of coalescence and break-up, APMPs with various experience of coalescence and break-up would be generated. The difference in the composition should lead to a different polymerisation rate. The fluid viscosity inside the coalesced aqueous drops is directly correlated to the polymer content and, in turn, has an important influence on the coalescence and break-up. After a certain stage, the polymer content in some APMPs could be so high that they become glassy and can hardly undergo further coalescence and break-up. Therefore, aqueous drops/particles with different monomer conversion levels may be present throughout the course of polymerisation; at one extreme, the aqueous monomer drops without any polymer, and at the other extreme, completely polymerised particles containing some unreacted reductant.

In a conventional emulsion polymerisation, the propagating macroradicals are isolated from one another mainly in the monomer swollen micelles and are terminated with primary radicals which transfer into the micelles substantially. In a conventional suspension polymerisation, the composition in the dispersed phase is homogeneous and each drop acts as a tiny batch reactor in a manner of homogeneous solution polymerisation. However, the inverse microsuspension polymerisation has unique
characteristics and can be referred to neither as emulsion nor as suspension polymerisation.
6.1 INTRODUCTION

As mentioned in Chapter 5, in the inverse microsuspension polymerisation, polymerisation takes place in the aqueous phase; each coalesced drop acts as a tiny solution polymerisation reactor. Therefore, a knowledge of aqueous polymerisation of acrylic acid (in a single-phase) initiated by potassium bromate/sodium metabisulphite redox pair is required. The studies reported in the literature have revealed that the polymerisation of acrylic acid is a rather complex procedure. Apart from the normal features, this polymerisation seems very sensitive to some additional factors, such as solvent type, pH value and ionic strength. Different kinetic relationships were obtained under individual conditions and various hypotheses have been proposed for interpreting the specific observations. Although the redox initiation systems have been intensively studied, no report to date has been found in the literature concerning the mechanistic and kinetic aspects in the use of potassium bromate/sodium metabisulphite redox pair in aqueous polymerisations. Therefore, the study of aqueous polymerisation of acrylic acid by using this redox initiation pair is also of importance for understanding its initiation mechanism.

The role of surfactant in heterogeneous polymerisations is sometimes very complicated. In addition to drop stabilisation, it may participate in reactions with active centres, leading to changes in polymerisation rate, molecular weight and even product structure. The decline of polymerisation rate in the presence of surfactant suggested an “extra” function of the surfactant molecules in the polymerisation
system. Kinetic studies of aqueous polymerisation in the presence of the surfactant is expected to provide relative information; and the experimental kinetic relationship should be useful for verifying the new hypothesis of the mechanism for the inverse microsuspension polymerisation, which was presented in Chapter 5.

6.2 EXPERIMENTAL

6.2.1 Polymerisation

Materials, apparatus and procedure for aqueous polymerisation have been described in Chapter 4. The polymerisation rates were obtained from the monomer conversion curves based on HPLC measurements (see Section 4.4.1.3).

6.2.2 Molecular Weight Measurement

A number of methods have been developed for measurement of polymer molecular weight, including viscosity method, gel permeation chromatography (GPC), and light scattering. In the literature, the molecular weight of polyacrylic acid is normally measured by the viscosity method, although there is a recent report of using the chromatographic technique (Igarashi et al, 1989). The solvents used in the viscosity measurements of diluted polyacrylic acid solutions have been, so far, dioxane (Newman et al, 1954; Mishra and Bhadani, 1983, 1985), 80/20 mixture of dioxane/water (Chapiro and Dulieu, 1977; Miller et al, 1962) and some sodium salt aqueous solutions (Kurata and Tsunashima, 1989).

In the work, the viscosity method was employed using an Ubbelohde viscometer. The solvent was 0.5 M aqueous sodium bromide and the measurements were made in a constant-temperature water bath at 25±0.01 °C. It was suggested that, “for highest precision, the efflux time must be kept long (preferably greater than 100 seconds) to minimise the need for applying corrections to the observed data” (Findlay, 1954). Therefore, an Ubbelohde viscometer was used which gave values of efflux time of
about 95 seconds for the solvent and of more than 100 seconds for the specimen of diluted polyacrylic acid in aqueous solution.

The preparation of dilute polyacrylic acid solutions and the determination of intrinsic viscosities were as follows:

1. The reaction mixture was precipitated in excess isopropanol containing 0.05% hydroquinone to stop post-polymerisation.
2. The precipitated polymer sample was washed with isopropanol repeatedly to eliminate unreacted monomer.
3. The sample was dried in a vacuum oven at 70 °C to constant weight.

Figure 6-1  A typical plot for intrinsic viscosity determination

experimental composition and conditions see L-d-1 in Appendix IV
4. The dried sample was dissolved in 0.5 mol/l aqueous sodium bromide. The values of polymer content in dried samples were recorrected using the monomer conversion data obtained by HPLC.

5. The above prepared polymer solution was diluted to 5 different concentrations. The concentrations of these diluted samples were controlled in the range that gave relative viscosities around 1.1 to 1.5 for accuracy in extrapolating to zero concentration (Findlay, 1954).

6. The efflux times of blank solution and individual dilute sample were measured using a stop-watch accurate to 0.1 second.

7. $\eta_p/c$ and $\ln\eta_p/c$ were plotted against $c$ (g/dl) and two extrapolations of two linear lines to $c = 0$ were obtained. The intrinsic viscosity $[\eta]$ was then calculated as a mean value of the two intercepts (Findlay, 1954).

The viscosity-average molecular weight were calculated using the following equation:
(Kurata and Tsunashima, 1989)

\[
[\eta] = 5.06 \times 10^{-4} M_v^{0.656}
\]  

[6-1]

Typical plots of $\eta_p/c$ and $\ln\eta_p/c$ against $c$ is shown in Figure 6-1.

6.3 RESULTS

6.3.1 General Features of Aqueous Polymerisation

Figure 6-2 shows a typical variation of monomer conversion with polymerisation time in an aqueous polymerisation of acrylic acid initiated by potassium bromate/sodium metabisulphite redox pair. The polymerisation occurred immediately after adding sodium metabisulphite in aqueous solution. The polymerisation rate gradually decreased with time and no auto-acceleration was observed in spite of a significant increase in the viscosity of the reaction mixture as polymerisation proceeded. It seems
that the polymerisation almost finished within 60 minutes at a monomer conversion of about 70%.

Figure 6-2  A typical monomer conversion curve of aqueous polymerisation
for experimental composition and conditions see Expt. L-d-I in Appendix IV. (c)

In non-isothermal polymerisations, Evans and Tyrrall (1947) reported 84% conversion of acrylic acid in 4.5 minutes initiated by Fenton's redox pair ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$). More recently, Ferguson and Eboatu (1989) observed up to 83% conversion in about 5 minutes in a polymerisation similar to Evans' system at 25 °C. However, in the polymerisations reported here, both the initial polymerisation rates and the limiting conversions were comparably lower.
6.3.2 Kinetics of Aqueous Polymerisation without Surfactant

Nowadays, it is well established that a radical-initiated vinyl polymerisation is a complex process consisting of several elementary reaction steps, namely, initiation, propagation, termination and transfer. The accumulation of data needed to predict the course of these reactions is often hindered by the presence of very reactive species which are difficult to determine analytically. Kinetic studies are often expected to reveal the existence of these species whose concentration and structure remain unknown and to describe the consequences.

The key parameter of kinetic studies is the instantaneous reaction rate which can be defined as change of molar concentrations of one reactant or one product at time \( t \). For kinetic studies of polymerisation, the reaction rate is normally defined as the disappearance rate of monomer. Theoretically, a simple chemical reaction rate \( R_r \) can be expressed as a product of two functions: (Margerison, 1969)

\[
R_r = kf(c_i)
\]  [6-2]

Here \( f(c_i) \) is solely a function of reactant concentrations; and \( k \), termed the rate constant, is dependent on the other reaction parameters, such as temperature, pressure etc..

In order to establish a kinetic relationship, the standard procedure is to follow the change with time of the concentrations of reactants and products in two distinct series of experiments. In the first series, the initial concentrations of the reactants are varied with the other reaction variables held constant. In the second series, the experiment are repeated at different values of the other reaction variables so that the dependence of the various rate constants on temperature, pressure, etc., can be found.
6.3.2.1 Effect of Polymerisation Temperature

Theories of reaction rate suggest that the rate constant $k$ is related to absolute temperature by the Arrhenius expression: (Margerison, 1969)

$$k = A \cdot e^{-E_a/RT} \quad [6-3]$$

here $E_a$ is the overall activation energy of the reaction, $A$ is the pre-exponential factor and $T$ is absolute temperature.

Theoretically, both $E_a$ and $A$ are dependent on reaction temperature. However, in the majority of rate studies, the temperature variation of the activation energy and pre-exponential factor can be disregarded over the small temperature ranges normally employed. Therefore, the overall activation energy of a polymerisation can be obtained from the slope of a least squares line through the points in the plot of $\ln k$ against $1/T$ according to the following expression which is derived by taking logarithms of each side in [6-3]:

$$\ln k = \ln A - E_a / RT \quad [6-4]$$

For a reaction of which the relationship between the rate and the concentrations of each reactant is known, the rate constant $k$ at a particular temperature can be elucidated by a set of experiments conducted at this temperature keeping all other factors which are liable to influence $k$ constant (Margerison, 1969).

In practice, the overall rate constant of a polymerisation can be sometimes obtained from the kinetic relationship of polymerisation: (Kurenkov et al, 1986)

$$R_p = kf(c_i) \quad [6-5]$$

Taking logarithms of both sizes of this expression, one has
\[
\ln R_p = \ln k + \ln f(c_i) \quad [6-6]
\]

Substituting [6-4] to [6-6], one obtains

\[
\ln R_p = -\frac{E_a}{RT} + \ln A + \ln f(c_i) \quad [6-7]
\]

A set of polymerisation rates can be obtained from the conversion cures at various temperatures. Suppose that the expression [6-6] is valid in the temperature range of the experiments and the temperature variations of reactant concentrations are negligible, the overall activation energy can be obtained from the slope of a least squares line through the points in the plot of \(\ln R_p\) against \(1/T\).
Isothermal aqueous polymerisations were conducted in the temperature range of 13 to 43 °C. From the conversion curves at different polymerisation temperatures (Figure 6-3), it is seen that the initial polymerisation rate increased with increased temperature. However, it is noteworthy that the polymerisation rate at 43 °C was lower than those at lower temperatures at late polymerisation stages. This indicates complicated effects of temperature on the polymerisation.

Figure 6-4 is the plot of $\ln R_{po}$ against $1/T$. The overall activation energy of polymerisation calculated from the slope of the least squares line is about 28.62 kJ/mol. This value is considerably lower than the activation energies of the polymerisations initiated by thermal decomposition of initiators (normally about 85 kJ/mol) (Cowie, 1989).

![Figure 6-4 Plot of $\ln R_{po}$ against $1/T$ for aqueous polymerisation](image-url)
6.3.2.2 Effect of Monomer Concentration

The high exothermicity and the large increase in the viscosity of reaction mixture even at low monomer conversions in aqueous polymerisation of acrylic acid make its isothermal polymerisation even more difficult than the inverse microsuspension polymerisation. Also, the high viscosity leads to an agitation problem. To solve these problems, a relatively low monomer concentration range, from 0.60 to 3.39 mol/l (1.10 to 4.20 mol/l in inverse microsuspension polymerisation), was used. The compositions of the initial reaction mixtures are listed in Appendix IV, (b).

Figure 6-5 Conversion curves of aqueous polymerisation without surfactant at varied concentrations of acrylic acid

data in legends are initial monomer concentration (mol/l)
Figure 6-5 shows the variations of monomer conversion with polymerisation time at various initial monomer concentrations. It is seen that the initial polymerisation rate increased with increased initial monomer concentration. The increase in initial monomer concentration also resulted in higher limiting monomer conversion.

\[ \text{Figure 6-6 log-log plot of } R_{po} \text{ against } [AA]_o \text{ for aqueous polymerisation without surfactant} \]

The log-log plot of initial polymerisation rate \( R_{po} \) versus initial monomer concentration \( ([AA]_o) \) is shown in Figure 6-6. A linear variation is observed, leading to the following relationship, derived from least squares fit of the data points.

\[ R_{po} \propto [AA]_o^{1.85} \]
6.3.2.3 Effect of Reductant Concentration

The compositions of the initial reaction mixtures with varied concentrations of Na$_2$S$_2$O$_5$ are listed in Appendix IV, (c).

Figure 6-7 shows the monomer conversion curves at different sodium metabisulphite concentrations from 3.95 to 23.20 x 10$^{-4}$ mol/l. Both the initial polymerisation rate and the limiting monomer conversion increased with increased sodium metabisulphite concentration.

![Conversion curves of aqueous polymerisation without surfactant at varied concentrations of sodium metabisulphite](image)

*Figure 6-7 Conversion curves of aqueous polymerisation without surfactant at varied concentrations of sodium metabisulphite*

Data in legends are initial reductant concentrations ([Na$_2$S$_2$O$_5$]$_i$ 10$^{-4}$ mol/l)
The least squares fit of the data points of log-log plot of initial polymerisation rate versus initial sodium metabisulphite concentration (Figure 6-8) leads to the following relationship:

$$R_{po} \propto [Na_2S_2O_5]_0^{0.50}$$  \[6-9\]

![Log-log plot of $R_{po}$ against $[Na_2S_2O_5]_0$ for aqueous polymerisation without surfactant.](image)

**6.3.2.4 Effect of Oxidant Concentration**

The compositions of the initial reaction mixtures with varied concentrations of KBrO$_3$ are listed in Appendix IV, (d).

The initial potassium bromate concentration was varied from 3.15 to 38.12 x $10^{-4}$. The variations of monomer conversion with polymerisation time at different oxidant
concentrations are shown in Figure 6-9. The higher initial oxidant concentration resulted in faster initial polymerisation and higher limiting monomer conversion.

Figure 6-10 represents log-log plot of initial polymerisation rate versus initial potassium bromate concentration. The following relationship is obtained by a least squares fit of the data points:

\[ R_{po} \propto [KBrO_3]_o^{0.74} \]  

[6-10]
6.3.3 Kinetics of Aqueous Polymerisation with Surfactant

The aqueous polymerisation in the presence of surfactant Witcamide 511 was carried out under the same conditions for aqueous polymerisations in the absence of surfactant. The initial reaction mixtures were kept at pH 5.1 for all polymerisations. Under continuous agitation, the surfactant was dispersed as tiny drops in the aqueous solutions.

The effects of concentrations of acrylic acid, sodium metabisulphite, potassium bromate and surfactant on polymerisation rate were investigated. The compositions of the initial reaction mixtures are listed in Appendix V. The influences of the
concentrations of acrylic acid, sodium metabisulphite and potassium bromate upon polymerisation rate and limiting monomer conversion are very similar to that in the aqueous polymerisations in the absence of surfactant.

![Conversion curves of aqueous polymerisation with surfactant at varied concentrations of surfactant](image)

Figure 6-11 Conversion curves of aqueous polymerisation with surfactant at varied concentrations of surfactant

data in legends are surfactant concentrations ([S]₀ wt% of system)
composition and conditions see Appendix V (d)

Figure 6-11 shows the variations of monomer conversion with polymerisation time at respective surfactant concentrations. It is clear that the presence of 1.71 wt% surfactant decreased initial polymerisation rate, suggesting the participation of surfactant molecules in the polymerisation reactions. However, this effect seems to be independent of the surfactant concentration in the investigated range of 1.71 to 6.49 wt% which are the same as used in the inverse microsuspension polymerisations (see Chapter 7).
Figure 6-12  log-log plot of $R_{po}$ against $[AA]_o$ for aqueous polymerisation with surfactant

Figure 6-13  log-log plots of $R_{po}$ against $[Na_2S_2O_5]_o$ and $[KBrO_3]_o$ for aqueous polymerisation with surfactant
The least squares fits of the data points of log-log plots of initial polymerisation rates versus initial concentrations of monomer, sodium metabisulphite and potassium bromate lead to the following relationship when surfactant concentration is larger than 1.71 wt\% (Figures 6-12, 6-13):

\[
R_{po} = [AA]_{0}^{1.94}[KBrO_3]_{0}^{0.74}[Na_2S_2O_3]_{0}^{0.51}[S]^{0.0}
\]  \hspace{1cm} [6-11]

\[\text{Figure 6-14} \quad \text{Conversion curves of aqueous polymerisation without surfactant at varied pH}\]
6.3.4 Effect of pH on Polymerisation

Polymerisations were conducted at initial pH values ranging from 3.8 to 7.1 using ammonium hydroxide as buffer under the same conditions for the aqueous polymerisations in the absence of surfactant. The compositions of initial reaction mixture are listed in Appendix IV, (e).

Figure 6-14 shows the influence of initial pH on the variations of monomer conversion with polymerisation time. It can be seen that the variation of pH of initial reaction mixture resulted in a significant change of initial polymerisation rate. The highest initial polymerisation rate occurred at the lowest pH value. This is in good agreement with the observations by Kabanov et al (1973) in the aqueous polymerisation of acrylic acid initiated by photochemical decomposition of AIBN.

In addition, higher limiting monomer conversion was attained at lower pH value. At pH of 3.8, up to about 85% monomer conversion was achieved in about 5 minutes.

6.3.5 Molecular Weight

In the aqueous polymerisations, the visual observation showed that the increase in viscosity of the reaction mixtures as polymerisation proceeded was promoted by reducing the concentrations of the redox initiators although the overall monomer conversion was decreased. This probably resulted from the increase in polymer molecular weight because less primary radicals were generated in the case of lower initiator concentration. Although the reduction in the concentrations of both sodium metabisulphite and potassium bromate promoted the increase of the reaction mixture viscosity, the former effect was likely much more significant. The kinetic studies have revealed a higher reaction order with respect to potassium bromate concentration than that with respect to sodium metabisulphite concentration (see the preceding sections). The more pronounced effect of sodium metabisulphite concentration on the viscosity of reaction mixture, therefore, suggests a special role of sodium metabisulphite molecules in polymerisation. In order to clarify this, the variations of molecular
weight with the concentrations of the two components of the redox pair were investigated. The results obtained by the viscosity method (see Appendix VI, (a) and (b)) are listed in Table 6-1.

Table 6-1 Variations of Molecular Weight with Initiators Concentrations*

<table>
<thead>
<tr>
<th>[KBrO₃]₀</th>
<th>[Na₂S₂O₅]₀</th>
<th>(\eta)</th>
<th>(M_v)</th>
<th>[Na₂S₂O₅]₀</th>
<th>(\eta)</th>
<th>(M_v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^4) mol/l</td>
<td>(10^4) mol/l</td>
<td>(10^{-6})</td>
<td>(10^4) mol/l</td>
<td>(10^4) mol/l</td>
<td>(10^{-6})</td>
<td></td>
</tr>
<tr>
<td>3.15</td>
<td>11.34</td>
<td>7.47</td>
<td>2.27</td>
<td>3.95</td>
<td>13.77</td>
<td>11.85</td>
</tr>
<tr>
<td>13.77</td>
<td>11.34</td>
<td>5.71</td>
<td>1.51</td>
<td>7.56</td>
<td>13.77</td>
<td>8.37</td>
</tr>
<tr>
<td>20.20</td>
<td>11.34</td>
<td>5.89</td>
<td>1.58</td>
<td>11.34</td>
<td>13.77</td>
<td>5.71</td>
</tr>
<tr>
<td>35.44</td>
<td>11.34</td>
<td>5.33</td>
<td>1.35</td>
<td>15.53</td>
<td>13.77</td>
<td>5.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>22.68</td>
<td>13.77</td>
<td>3.01</td>
</tr>
</tbody>
</table>

* \([AA]₀ = 1.99\) mol/l (for conditions see Appendix IV, (c) and (d)) polymer samples were prepared at 60 minutes polymerisation

The calculated results indicated that the increase in sodium metabisulphite concentration produced a significant decrease in the viscosity molecular weight whilst the change of potassium bromate concentration only resulted in a slight decrease. This agrees with the observation of effects of initiator concentrations on the reaction mixture viscosities.

The characterisation of the variation of intrinsic viscosities with polymerisation time was also performed (see Appendix VI, (c)). The calculated results are listed in Table 6-2.

Table 6-2 Variation of Molecular Weight with Polymerisation Time*

<table>
<thead>
<tr>
<th>(t) min</th>
<th>6</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\eta)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(M_v) (10^{-5})</td>
<td>3.45</td>
<td>3.53</td>
<td>4.20</td>
<td>4.52</td>
<td>5.63</td>
</tr>
</tbody>
</table>

* \([AA]₀ = 1.99\) mol/l, [Na₂S₂O₅]₀ = \(22.68 \times 10^{-4}\) mol/l, [KBrO₃]₀ = \(13.77 \times 10^{-4}\) mol/l
It can be seen that the polymer molecular weight gradually increased as polymerisation proceeded.

It was mentioned in Section 6.3.3 that the presence of the surfactant reduced the initial polymerisation rate. To clarify the specific function of the surfactant, the intrinsic viscosities of polymers produced in the presence of various surfactant concentrations were measured (see Appendix VI, (d)) and the molecular weights were calculated which are listed in Table 6-3.

<table>
<thead>
<tr>
<th>$[S]_0$ ** wt%</th>
<th>0.00</th>
<th>1.71</th>
<th>3.47</th>
<th>4.95</th>
<th>6.49</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\eta]$</td>
<td>3.01</td>
<td>2.94</td>
<td>2.91</td>
<td>2.93</td>
<td>2.95</td>
</tr>
<tr>
<td>$M_v \times 10^{-5}$</td>
<td>5.67</td>
<td>5.46</td>
<td>5.37</td>
<td>5.45</td>
<td>5.49</td>
</tr>
</tbody>
</table>

* $[AA]_0 = 1.99 \text{ mol/l}$, $[Na_2S_2O_3]_0 = 22.68 \times 10^{-4} \text{ mol/l}$, $[KBrO_3]_0 = 13.77 \times 10^{-4} \text{ mol/l}$ (see Appendix V (d))
* polymer samples were prepared at 60 minutes polymerisation
* $[S]_0$ is based on aqueous phase

It appears that the presence of 1.71 wt% of the surfactant slightly decreased the polymer molecular weight. The effect of further increase in the surfactant concentration on molecular weight, however, was not significant. This agrees well with the effect of the surfactant concentration on polymerisation rate.

### 6.3.6 Role of Atmospheric Oxygen

In the aqueous polymerisations, the two components of the redox pair were introduced separately. Before the addition of sodium metabisulphite aqueous solution, no polymerisation was observed in the aqueous monomer containing potassium bromate throughout the course of nitrogen purge (about 45 minutes). This clearly indicated that potassium bromate, the oxidising part of the redox pair, can not initiate polymerisation alone. On the other hand, polymerisation occurred, although relatively slowly, in an aqueous monomer containing sodium metabisulphite, but no potassium bromate, during the nitrogen purge (Figure 6-15). However, no polymer was produced when oxygen was removed from the aqueous monomer and the sodium metabisulphite in aqueous solution by purging them separately before mixing them together. This
indicates that the slow polymerisation was not initiated by sodium metabisulphite alone and that the atmospheric oxygen might have multiple functions in this case. Atmospheric oxygen could form a redox pair coupled with sodium metabisulphite to generate free radicals initiating polymerisation of acrylic acid. On the other hand, as well-known, it may also act as a radical scavenger. In the presence of a large amount of oxygen, the latter role is dominant so that the polymerisation was suppressed in the early stages of nitrogen purge of the aqueous monomer containing sodium metabisulphite (see Figure 6-15).

![Graph showing conversion vs. polymerisation time](image)

Figure 6-15  Polymerisation of aqueous AA initiated by sodium metabisulphite alone during nitrogen purge

\[ [\text{AA}]_0 = 1.99 \text{ mol/L}, \quad [\text{Na}_2\text{S}_2\text{O}_3]_0 = 2.21 \times 10^{-3} \text{ mol/L}, \quad \text{pH 5.1, } 23^\circ\text{C} \]
6.3.7 Effect of Cross-linking Agent

For the aqueous polymerisations in the presence of cross-linking agent, the MBA molecules would participate in the propagation reaction (Sandler, 1992):

\[
n \text{CH}_2=\text{CH}-\text{C}-\text{OH} + \text{CH}_2=\text{CH}-\text{C}-\text{NH}_2\text{NH}-\text{C}-\text{CH}=\text{CH}_2 \\
\rightarrow \text{(CH}_2\text{CH)}_n \text{(CH}_2\text{CH)} \\
\text{C}=\text{O} \quad \text{C}=\text{O} \\
\text{OH} \quad \text{NH}-\text{CH}_2\text{-NH-C-(CH}_2\text{H)}_2
\]

(6-1)

Figure 6-16 Effect of cross-linking agent on aqueous polymerisation

Data in legends are concentrations of MBA, $10^{-3}$ mol/l

$[AA]_0=1.99$ mol/l, $[Na_2S_2O_3]_0=2.27\times10^{-3}$ mol/l, $[KBrO_3]_0=1.38\times10^{-3}$ mol/l, pH 5.1, 23 °C
Therefore, this reaction is actually a copolymerisation of acrylic acid and MBA. However, no significant difference in polymerisation rate was observed between the polymerisations with and without MBA (see Figure 6-16). This is probably because of the very low concentration of MBA. In the inverse microsuspension polymerisations, the negligible effect of MBA at the lower concentrations was also found (see Chapter 7). These observations suggest that the polymerisations in the presence of a small amount of MBA could be treated as a homopolymerisation in kinetic studies.

Figure 6-17  Effect of Chelating agent on aqueous polymerisation
data in legends are concentrations of Versenex 80, g/l

$[AA]_o=1.99\text{ mol/l}$, $[Na_2S_2O_3]_o=2.27\times10^{-3}\text{ mol/l}$, $[KBrO_3]_o=1.38\times10^{-3}\text{ mol/l}$, pH 5.1, 23 °C
6.3.8 Effect of Chelating Agent

Figure 6-17 shows the comparison of the monomer conversion curves of aqueous polymerisations in the absence and in the presence of two different concentrations of the chelating agent. A pronounced increase in polymerisation rate was observed when 0.72 g/l chelating agent was employed, suggesting a special function of Versenex 80 in the polymerisation. However, further increase in the amount of chelating agent seems to have little effect on the polymerisation. This implies that the function of Versenex 80 molecules is probably confined to chelating the small amount of impurities which might act as a polymerisation retarder in the system.

6.3.9 Rate of Initiation

In the foregoing sections, it was shown that the aqueous polymerisations of acrylic acid was initially quite fast and then levelled off quickly to limiting monomer conversions. By a close inspection, it appears that the limiting conversions were attained in around 25 to 30 minutes for the majority of polymerisations (see Figures in Section 6.3.2 and 6.3.3). This suggests a connection between the limiting monomer conversion and polymerisation time. A knowledge of the disappearance rate of redox initiators or of the rate of initiation is expected to be helpful for understanding the reaction mechanism.

Unlike the initiators decomposed thermally or under radiation, the reaction between sodium metabisulphite and potassium bromate is very fast even at ambient temperature, so that direct measurement of their disappearance rate is difficult.

Numerous techniques have been developed for measuring rates of initiation in radical polymerisations (Stickler, 1989). In this work, one of the most common methods — estimation of the rate of production of free radicals by adding a radical inhibitor was employed (Bamford et al, 1958).
In using this method, it is essential to detect the start of polymerisation precisely. In view of the fast polymerisation of acrylic acid in aqueous solution, the polymerisations were followed by monitoring the temperature changes of the reaction mixtures in non-isothermal polymerisations instead of measuring the monomer conversions.

Figure 6-18  Inhibition of aqueous polymerisation of AA by hydroquinone

data in legends are concentrations of hydroquinone, mmol/l

Figure 6-18 shows the inhibition of the aqueous polymerisation of acrylic acid by hydroquinone. From the induction periods at different hydroquinone concentrations, the obtained average rate of consumption of hydroquinone was about $4.86 \times 10^{-5}$ mol/l·sec. Therefore, the initiation rate (defined as the rate of producing primary
radicals) of sodium metabisulphite/potassium bromate redox pair should be about 4.86 or 9.72 x 10\(^{-5}\) mol/l·sec assuming each hydroquinone molecule consumes one or two free radicals. This suggests a very quick consumption of the redox pair.

6.4 DISCUSSION

6.4.1 Mechanism

6.4.1.1 Redox Initiation

A literature search has revealed that both sodium metabisulphite and potassium bromate have been extensively used, as reductant and oxidant respectively, in conjunction with other compounds to form redox initiation systems in free-radical polymerisations. However, the utilisation of these two components as a redox pair is few.

In a kinetic study of the aqueous polymerisation of acrylamide using potassium permanganate/sodium metabisulphite as redox initiators, Bajpai et al (1992) proposed that the reducing part was bisulphite anion which was in equilibrium with metabisulphite anion. The derived polymerisation rate relationship was in agreement with the experimental results. The end-group studies performed by Ebdon et al (1994a) also supported the idea that the reducing part of the redox pair was the bisulphite anion rather than the metabisulphite anion in the polymerisation of acrylonitrile initiated by ammonium persulphate/sodium metabisulphite redox pair. On the basis of these reports, it is expected that, in the present work, the equilibrium reaction (2-11) could occur in the initiation reaction.

The mechanism of redox reaction between bisulphite anion and bromate anion is still insufficiently studied (see Chapter 2). Based on the hypothesis of redox reaction between bisulphite anion and chlorate anion proposed by Firsching and Rosen (1959), one possibility for the present redox reaction is:
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\[
\begin{align*}
\text{HSO}_3^- + \text{BrO}_3^- & \rightarrow [\text{HO}_3\text{SOBrO}_2^-]^{2-} \quad (6-2) \\
[\text{HO}_3\text{SOBrO}_2^-]^{2-} & \rightarrow \text{HSO}_4^- + \text{BrO}_2^- \quad (6-3) \\
[\text{HO}_3\text{SOBrO}_2^-]^{2-} + \text{CH}_2 = \text{CHCOOH} + \text{H}^+ & \rightarrow \\
& \quad \text{HOOCCHCH}_2\text{SO}_3^- + \text{H}_2\text{O} + \text{BrO}_2^- \\ 
\end{align*}
\]

The intermediate \([\text{HO}_3\text{SOBrO}_2^-]^{2-}\) produced in reaction (6-2) may undergo two competitive reactions and initiation only occurs when the monomer is present.

Palit and co-workers proposed a possible mechanism for the redox reaction (Mukherjee et al., 1966):

\[
\begin{align*}
\text{HO}_3^- + \text{BrO}_3^- & \rightarrow \begin{bmatrix} \text{BrO}_3^- \\ \text{O} \\ \text{HO}^- - \text{S} - \text{O}^- \end{bmatrix} \rightarrow \text{BrO}_2^- + \bullet\text{OH} + \text{SO}_3^- \bullet \\
\end{align*}
\]

It is well known that hydroxyl radical \(\bullet\text{OH}\) is very active for initiating polymerisation of vinyl monomers. The above redox reaction mechanism suggests that the primary free radicals for initiation could be hydroxyl radicals and anionic sulfoxy radicals. However, the author’s end-group studies indicated that the produced polymer contained about 2 nonhydrolysable sulfoxy end-groups per chain in spite of a very small amount of incorporated hydroxyl groups.

The kinetic studies also suggests that the mechanism proposed by Fisching and Rosen is likely the case in the present polymerisations (see the following sections).

6.4.1.2 Role of Oxygen

A number of authors reported that the bisulphite anion could couple with oxygen to form a redox pair. Palit and co-workers performed intensive studies on the mechanism of this redox pair (Konar and Palit, 1961; Mukherjee et al., 1966; Palit and Mandal,
The aqueous acrylic acid containing bisulphite anion was successfully polymerised by continuously pumping atmosphere air into the reaction mixture (Igarashi et al, 1989). More recently, Bajpai et al (1992) reported that acrylamide in aqueous solution underwent polymerisation readily under atmospheric oxygen by using potassium permanganate/sodium metabisulphite redox initiators. The following reaction scheme has been proposed:

$$4\text{HSO}_3^- + \text{O}_2 \rightarrow 4\text{SO}_3^-\cdot + 2\text{H}_2\text{O}$$  \hspace{1cm} (6-6)

On the other hand, it is well known that oxygen is a strong radical scavenger. Even a trace amount of residual oxygen can stop polymerisation completely and cause an induction period in free radical polymerisations (Hunkeler et al 1989). In the present work, the sodium metabisulphite aqueous solution was added without pre-purge with nitrogen. A small amount of oxygen, therefore, would be introduced at the same time. However, polymerisation occurred as soon as the sodium metabisulphite solution was added, indicated by the immediate temperature rise in non-isothermal polymerisations. This is probably attributed to the participation of atmospheric oxygen in the initiation reaction. The slow polymerisation of the aqueous acrylic acid containing sodium metabisulphite during nitrogen purge (see Figure 6-15) also provided evidence for this reaction. However, the induction period in Figure 6-15 suggests an inhibitor role of oxygen at the same time. This is in agreement with the observation that no polymerisation occurred if the concentration of bisulphite was lower than 0.005 mol/l (Igarashi et al, 1989).

The aqueous polymerisations were conducted at an initial pH of 5.1. Therefore, the ionic radical $\text{SO}_3^-\cdot$ could be involved in the following equilibrium (Firsching and Rosen, 1959):

$$\text{SO}_3^-\cdot + \text{H}^+ \Leftrightarrow \text{HSO}_3^-\cdot$$  \hspace{1cm} (6-7)
At pH 5.1, the ionisation of acrylic acid ($pK_a = 4.2$) (Kabanov et al, 1973) is expected. The initiation of acrylate anions by $\text{SO}_3^- \cdot$ must be much slower than that by $\text{HSO}_3^- \cdot$ owing to electrostatic repulsion between anions. This would shift the equilibrium (6-7) to the right side.

For the aqueous polymerisations in the presence of surfactant, the deduction of polymerisation rate suggested a participation of the surfactant molecules in the reactions with free radicals. The three major components of the surfactant are: oleic diethanolamide, linoleic diethanolamide and linolenic diethanolamide. These three unsaturated compounds might be involved in reactions with $\text{HSO}_3^- \cdot$ or $\text{SO}_3^- \cdot$:

$$S + R \cdot \rightarrow S \cdot$$  \hspace{1cm} (6-8)

Here $R \cdot$ represents $\text{HSO}_3^- \cdot$ or $\text{SO}_3^- \cdot$.

### 6.4.1.3 Propagation

The propagation of acrylic acid has been proved to be dependant on a number of factors (see Chapter 2). The present experimental results indicated a significant decrease in polymerisation rate as the initial pH increased (Figure 6-14). According to Kabanov's hypothesis (Kabanov et al, 1973), this is probably attributed to the variation of ionisation degree of acrylic acid with altered pH. At pH 5.1, at which the kinetic studies were performed, the propagation took place between ionised acrylic acid and the unionised propagating radicals ($pK_a$ of polyacrylic acid is 6.4).

In aqueous polymerisations of acrylic acid, Chapiro and Dulieu reported a very high polymerisation rate and auto-acceleration associated with the formation of oligomeric structures of acrylic acid and the matrix effect of polyacrylic acid leading to a rapid "zip" propagation (Chapiro and Dulieu, 1977). These phenomena, however, were not observed in the experiments reported here. The reason for this is probably that the
molecular associations through hydrogen bonds did not exist at pH 5.1 due to the ionisation of acrylic acid.

6.4.1.4 Transfer Reactions

As early as the 1930's, chain transfer to bisulphite ion was reported in the literature (Kharasch et al, 1938). However, a value of 2 sulphonate end-groups per chain was estimated by the end-group studies of polymethyl methacrylate initiated by bisulphite-containing redox initiators (Mukherjee et al, 1966). This did not support the chain transfer hypothesis because the number of sulphonate end-groups per chain should be much less than 2 if the chain transfer was predominant (Palit and Mandal, 1968). Recent end-group studies, however, provided new evidence for the chain transfer (Ebdon et al, 1994a, b). The variation of polymer molecular weight with pH also indicated a significant chain transfer to bisulphite ion in the aqueous polymerisation of acrylic acid in the presence of bisulphite (Igarashi et al, 1989).

In the current polymerisations, the variation of concentration of sodium metabisulphite showed a much stronger influence upon the molecular weight of produced polymer than that of the concentration of potassium bromate although the latter has a higher reaction order. An increase of just less than 600% in the concentration of sodium metabisulphite caused 88% decrease in the molecular weight whilst only a 50% decrease occurred with a 10 fold increase in the concentration of potassium bromate (see Table 6-1). This supports the views of chain transfer with bisulphite ion:

\[
M_n \cdot + \text{HSO}_3^- \rightarrow \text{polymer} + \text{SO}_3^- \cdot
\]  \hspace{1cm} (6-9)

The progressive increase of molecular weight as polymerisation proceeded is probably attributed to the same transfer reaction (see Table 6-2). At the early stages of the polymerisation, the chain transfer to bisulphite ions played an important role so that the molecular weight was comparably low. As polymerisation proceeded, the chain
transfer reaction decreased quickly as a result of fast decrease in the concentration of bisulphite ion by consumption in the redox reaction.

Reaction (6-9) leads to formation of an identical free radical formed in reaction (6-6). If this free radical undergoes further initiation, reaction (6-9) will not result in any change in kinetics, but a waste of bisulphite anion.

The influences of the surfactant on the polymerisation rate and on the molecular weight suggested another type of transfer in the system, that is, the transfer to the surfactant molecules:

\[
M_n \cdot + S \rightarrow \text{polymer} + S \cdot
\]  

(6-10)

The transfer to surfactant molecules has been reported in the literature (Glukhikh et al, 1987; Hunkeler et al, 1989). The composition of Witcamide 511 is very complex. Although the details of this transfer reaction is still not clear, the decrease in polymerisation rate in the presence of 1.71 wt% Witcamide 511 suggested that the produced surfactant radicals would be less active than the primary radicals and the macroradicals or terminate in the consequent reactions. However, the effect of the surfactant concentration on the polymerisation rate was negligible in the range from 1.71 wt% to 6.49 wt%. This is probably attributed to the very limited solubility of the surfactant in the aqueous phase and its slow diffusion rate from the surfactant drops to the aqueous phase.

6.4.1.5 Termination

As with most vinyl monomer polymerisations, the propagating radicals may undergo bimolecular termination in the aqueous polymerisation of acrylic acid:

\[
M_m \cdot + M_n \cdot \rightarrow \text{polymer}
\]  

(6-11)
In addition, the high orders of polymerisation with respect to the concentrations of both oxidant and reductant suggested the importance of monomolecular termination. In general, monomolecular termination is caused by combination of propagating radicals with radical scavenger molecules or involves a transfer of propagating radicals to small molecules resulting in virtual dead radicals.

Each chain transfer to a bisulphite anion always produces a new free radical $SO_3^{-}$ and hence does not lead to any change in kinetics provided that the new free radical is capable of initiating monomer polymerisation. Bajpai et al (1992) reported a possibility for the recombination of $SO_3^{-}$ to form an inert product. If this recombination were of significance in the present aqueous polymerisation, an inverse relationship between the polymerisation rate and the sodium metabisulphite concentration would have been observed.

The surfactant radicals formed in transfer reaction (6-10) could either initiate acrylic acid molecules or terminate mutually:

\[
S \cdot + M \rightarrow SM \cdot \quad (6-12)
\]

\[
S \cdot + S \cdot \rightarrow \text{inert product} \quad (6-13)
\]

Reaction (6-13) provides another possibility for monomolecular termination. However, high reaction order with respect to reactant concentrations in the aqueous polymerisation without surfactant suggested a reaction between the propagating radicals with impurity molecules:

\[
M_n \cdot + C \rightarrow \text{polymer} \quad (6-14)
\]

Here C represents impurity molecules.

In the aqueous polymerisation with surfactant, the surfactant radicals might also react with the impurity molecules:
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$$S \cdot + C \rightarrow \text{inert product} \quad (6-15)$$

#### Table 6-4 Reactions in aqueous polymerisation of AA using sodium metabisulphite/potassium bromate redox initiators

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiation</td>
<td></td>
</tr>
<tr>
<td>$S_2O_3^{2-} + H_2O \rightleftharpoons 2HSO_3^-$</td>
<td>(2-11)</td>
</tr>
<tr>
<td>$HSO_3^- + BrO_3^- \xrightarrow{k_\text{redox}} [HO_3SOBrO_2]^{2-}$</td>
<td>(6-2)</td>
</tr>
<tr>
<td>$[HO_3SOBrO_2]^{2-} \xrightarrow{k_d} HSO_4^- + BrO_2^-$</td>
<td>(6-3)</td>
</tr>
<tr>
<td>$[HO_3SOBrO_2]^{2-} + M + H^+ \xrightarrow{k_i} M_1 \cdot + BrO_2^- + H_2O$</td>
<td>(6-4)</td>
</tr>
<tr>
<td>$4HSO_3^- + O_2 \xrightarrow{k_{\text{ox}}} 4SO_3^- \cdot + 2H_2O$</td>
<td>(6-6)</td>
</tr>
<tr>
<td>$SO_3^- \cdot + H^+ \leftrightarrow HSO_3^- \cdot$</td>
<td>(6-7)</td>
</tr>
<tr>
<td>$M + R \cdot \xrightarrow{k_{i,s}} M_1 \cdot$</td>
<td>(6-16)</td>
</tr>
<tr>
<td>$S + R \cdot \xrightarrow{k_{i,s}} S \cdot$</td>
<td>(6-8)</td>
</tr>
<tr>
<td>$S \cdot + M \xrightarrow{k_{s,i}} M_1 \cdot$</td>
<td>(6-12)</td>
</tr>
<tr>
<td>Propagation</td>
<td></td>
</tr>
<tr>
<td>$M_n \cdot + M \xrightarrow{k_p} M_{n+1} \cdot$</td>
<td>(6-17)</td>
</tr>
<tr>
<td>Transfer</td>
<td></td>
</tr>
<tr>
<td>$M_n \cdot + HSO_3^- \xrightarrow{k_{p,r}} \text{polymer} + SO_3^- \cdot$</td>
<td>(6-9)</td>
</tr>
<tr>
<td>$M_n \cdot + S \xrightarrow{k_{r,s}} \text{polymer} + S \cdot$</td>
<td>(6-10)</td>
</tr>
<tr>
<td>Termination</td>
<td></td>
</tr>
<tr>
<td>$M_m \cdot + M_n \cdot \xrightarrow{k_i} \text{polymer}$</td>
<td>(6-11)</td>
</tr>
<tr>
<td>$M_n \cdot + C \xrightarrow{k'_i} \text{polymer}$</td>
<td>(6-14)</td>
</tr>
<tr>
<td>$S \cdot + S \cdot \xrightarrow{k_{i,s}} \text{inert product}$</td>
<td>(6-13)</td>
</tr>
<tr>
<td>$S \cdot + C \xrightarrow{k_{i,s}} \text{inert product}$</td>
<td>(6-15)</td>
</tr>
<tr>
<td>$R \cdot + R \cdot \xrightarrow{k_{i,s}} \text{inert product}$</td>
<td>(6-18)</td>
</tr>
</tbody>
</table>
6.4.2 Kinetic Models

Based on the foregoing discussions, the most probable reactions involved in the aqueous polymerisation of acrylic acid initiated by potassium bromate/sodium metabisulphite redox pair are summarised in Table 6-4.

6.4.2.1 Kinetics in Presence of Surfactant

Assuming that the reaction rate constants of a given type of reaction are independent of the radical size and the degree of conversion of the reaction mixture, one can denote \([R\bullet], [M\bullet]\) and \([S\bullet]\) as total concentrations of primary radicals (HSO\(_3\) • or SO\(_3\) •), propagating monomer radicals and surfactant radicals.

Applying the stationary state approximation to primary radicals \(R\bullet\), monomer radicals \(M\bullet\) and surfactant radicals \(S\bullet\), one has:

\[
\frac{d[R\bullet]}{dt} = 0 = R_{ox} + k_{tr}[M\bullet][HSO_3^-] - k_i'[R\bullet][M] - k_{t,s}[R\bullet][S] - k_{i,R}[R\bullet]^2
\]

\[
\frac{d[M\bullet]}{dt} = 0 = R_i + k_i'[R\bullet][M] + k_{s,i}[S\bullet][M] - k_{tr,s}[M\bullet][S] - k_t[M\bullet]^2 - k_{t,s}[M\bullet][C]
\]

\[
\frac{d[S\bullet]}{dt} = 0 = k_{i,s}[R\bullet][S] + k_{tr,s}[M\bullet][S] - k_{s,i}[S\bullet][M] - k_{t,s}[S\bullet]^2 - k_{t,s}[S\bullet][C]
\]

Here \(R_{ox}\) is the rate of producing free radicals by reaction (6-6) and \(R_i\) is the rate of monomer initiation by reaction (6-4).

The resolution of \([M\bullet]\) from equations [6-12] to [6-14] gives a very complex equation. For simplicity, it might be permissible to neglect the mutual terminations of the
surfactant radicals ($S\bullet$) and primary radicals ($R\bullet$) because the concentration of surfactant radicals is small and the mutual termination of primary radicals is always much less important compared with initiation reactions.

Adding equations [6-12], [6-13] and [6-14] and ignoring the items containing $k_{t,s}$ and $k_{t,R}$:

$$k_t[M\bullet]^2 + k_t[M\bullet][C] + k_{t,s}[S\bullet][C] - (R_t + R_{ox}) = 0 \quad [6-15]$$

Rearranging equation [6-14] and [6-12]:

$$[S\bullet] = \frac{k_{tr,s}[M\bullet][S] + k_{i,s}[R\bullet][S]}{k_{s,i}[M] + k_{t,s}[C]} \quad [6-16]$$

$$[R\bullet] = \frac{R_{ox} + k_{tr}[M\bullet][HSO_3^-]}{k_t[M] + k_{i,s}[S]} \quad [6-17]$$

Substituting equations [6-16] and [6-17] into equation [6-15], then rearranging it gives:

$$k_t[M\bullet]^2 + \left(k_i + k_{t,s}\right)\left(\frac{k_{tr,s}[S]}{k_{s,i}[M] + k_{t,s}[C]} + \frac{k_{tr}[HSO_3^-]}{(k_{s,i}[M] + k_{t,s}[C])\left(1 + \frac{k_t[M]}{k_{i,s}[S]}\right)}\right)[M\bullet][C]$$

$$- 1\frac{k_{t,s}[C]}{(k_{s,i}[M] + k_{t,s}[C])\left(1 + \frac{k_t[M]}{k_{i,s}[S]}\right)}R_{ox} - R_t = 0 \quad [6-18]$$
The above equation can be further simplified by assuming that the reaction between the primary radicals and the surfactant molecules is negligible compared with the initiation of monomer. This assumption is permissible because the production of the primary radicals is in the aqueous phase where the amount of the surfactant molecules is sufficiently low. Therefore, one has:

$$k_t[M\bullet]^2 + \left( k'_t + \frac{k_{ts}k_{fr,s}[S]}{k_{s,i}[M] + k_{ts}[C]} \right) [C][M\bullet] - (R_{ox} + R_t) = 0 \quad [6-19]$$

The long chain approximation can be applied. This assumes that the monomer is consumed entirely in propagation and that the monomer consumed in the following reactions is negligible:

(a) transfer to the monomer
(b) reaction between the surfactant radicals and the monomer
(c) monomer initiation by the primary radicals

Therefore, the polymerisation rate, expressed in terms of mole of monomer converted to polymer per unit volume in unit time, is:

$$R_p = k_p[M][M\bullet] \quad [6-20]$$

Combining equation [6-19] with equation [6-20]:

$$\frac{k_t}{k_p^2[M]^2} R_p^2 + \left( k'_t + \frac{k_{ts}k_{fr,s}[S]}{k_{s,i}[M] + k_{ts}[C]} \right) \frac{[C]}{k_p[M]} \cdot R_p - (R_t + R_{ox}) = 0 \quad [6-21]$$

This equation seems much more complex than a classical rate expression for simple polymerisations. However, it is clear that the first item on the left side is a contribution from bimolecular termination and the second item from monomolecular termination. Therefore, one can examine two extreme cases:
Case I — bimolecular termination dominates

Ignoring items involving $k_i$ and $k_i'$ in equation [6-21], one has:

$$R_p = \frac{k_p}{k_t^{1/2}} (R_i + R_{ox})^{1/2} [M]$$  \[6-22\]

This is a typical rate expression for bimolecular termination polymerisations. From reactions (6-4), (6-6), one has:

$$R_i = k_i [\text{HO}_3\text{SOBr}_2^{2-}] [M][H^+]$$  \[6-23\]

$$R_{ox} = 4k_{ox} [\text{HSO}_3^-]^4 [O_2]$$  \[6-24\]

According to reactions (6-2), (6-3) and (6-4) and applying steady state assumption to $[\text{HO}_3\text{SOBr}_2^{2-}]$, one has:

$$[\text{HO}_3\text{SOBr}_2^{2-}] = \frac{k_{\text{redox}}[\text{HSO}_3^-][\text{BrO}_3^-]}{k_d + k_i[M][H^+]}$$  \[6-25\]

From reaction (2-11), one has:

$$[\text{HSO}_5^-] = K^{1/2} [S_2\text{O}_5^{2-}]^{1/2} [\text{H}_2\text{O}]^{1/2}$$  \[6-26\]


$$R_p = \frac{k_p}{k_t^{1/2}} [M] \cdot$$

$$\left( \frac{k_{\text{redox}} K^{1/2} [S_2\text{O}_5^{2-}]^{1/2} [\text{BrO}_3^-] [\text{H}_2\text{O}]^{1/2} [M][H^+] + 4k_{ox} K^2 [S_2\text{O}_5^{2-}]^2 [O_2][\text{H}_2\text{O}]^2}{k_d / k_i + [M][H^+]} \right)^{1/2}$$  \[6-27\]
This equation suggests that the presence of initiation through the reaction between bisulphite anion and oxygen leads to a very complicated kinetic relationship. It also leads to a high order of polymerisation with respect to sodium metabisulphite concentration, varying from 0.25 to 1.0 as the contribution from the reaction with oxygen increases in initiation. The order in potassium bromate concentration is about 0.5. The order with respect to monomer concentration varies from 1.0 to 1.5 depending on the competition between reaction (6-3) and reaction (6-4). Only in the case of \( k_d \ll k_i \), the majority of the intermediate \([\text{HO}_2\text{SOBr}_2\text{O}_2]^-\) reacts with the monomer and the order in monomer concentration is unity.

Case II — monomolecular termination dominates

Ignoring the item involving \( k_i \) in equation [6-21], one has:

\[
R_p = k_p \left( k_i + \frac{k_{s,i}k_{r,s}[S]}{k_{s,i}[M] + k_{i,s}[C]} \right)^{-1} [C]^{-1}[M](R_i + R_{ox})
\]  

[6-28]


\[
R_p = k_p \cdot \left( \frac{k_{s,i}[M] + k_{i,s}[C]}{k_i k_{s,i}[M] + k_{i,s}[C] + k_{i,s}k_{r,s}[S]} \right) [C]^{-1}[M] 
\left( \frac{k_{\text{redox}}K^{1/2}[S_2O_5^{2-}]^{1/2}[BrO_3^-][H_2O]^{1/2}[M][H^+]}{k_d / k_i + [M][H^+]} \right)
\left( 4k_{ox}K^2[S_2O_5^{2-}]^2[O_2][H_2O]^2 \right)
\]

[6-29]

Equation [6-29] suggests that complicated kinetic relationship is due to the oxidation of bisulphite anion by oxygen and the chain transfer to the surfactant molecules. The order with respect to the sodium metabisulphite concentration varies from 0.5 to 2.0 as the contribution of the reaction with oxygen increases in initiation; the order in the monomer concentration varies from 1.0 up to 3.0 depending on the competition of the
two reactions involving the intermediate \([\text{HO}_3\text{S}O\text{Br}_2\text{O}_2]^{2-}\) and the transfer to the surfactant molecules; the order with respect to the potassium bromate concentration is 1.0.

### 6.4.2.2 Kinetics in Absence of Surfactant

Analogous to that in the above section, the following relationship is derived by ignoring the reactions involving the surfactant molecules:

\[
\frac{k_t}{k_p[M]^2} \cdot R_p^2 + \frac{k'_t[C]}{k_p[M]} \cdot R_p - (R_i + R_{ox}) = 0 \tag{6-30}
\]

In the case of bimolecular termination dominant:

\[
R_p = \frac{k_p}{k'_t/2} (R_i + R_{ox})^{1/2} [M] \tag{6-31}
\]

This rate expression is the same as equation [6-22].

In the case of monomolecular termination dominant:

\[
R_p = \frac{k_p}{k'_t[C]} (R_i + R_{ox}) [M] \tag{6-32}
\]

\[
R_p = \frac{k_p[M]}{k'_t[C]} \cdot \left( \frac{k_{\text{redox}} K^{1/2} [S_2O_5^{2-}]^{1/2} [BrO_5^{-}] [H_2O]^{1/2} [M][H^+]}{k_d / k_i + [M][H^+]} + 4k_{ox} K^2 [S_2O_5^{2-}]^2 [O_2] [H_2O]^2 \right) \tag{6-33}
\]
This equation suggests that the order of polymerisation with respect to the monomer concentration varies from 1.0 to 2.0 depending on the competition of two reactions involving the intermediate \([HO_3SOBrO_2]^-\); the order in the sodium metabisulphite concentration varies from 0.5 to 2.0 as the reaction with oxygen increases; and the order with respect to the oxidant concentration is 1.0.

### 6.4.2.3 Comparison of Kinetic Models with Experimental Relationships

The experimental kinetic studies led to the following relationships (see the preceding sections):

**aqueous polymerisation in the absence of surfactant**

\[
R_{po} \propto [AA]_o^{1.85} [KBrO_3]_o^{0.74} [Na_2S_2O_3]_o^{0.50}
\]

**aqueous polymerisation in the presence of surfactant**

\[
R_{po} \propto [AA]_o^{1.94} [KBrO_3]_o^{0.74} [Na_2S_2O_3]_o^{0.51} [S]^{0.0}
\]

It is seen from the above relationships that the orders of polymerisation with respect to the concentrations of potassium bromate and sodium metabisulphite are almost identical for the polymerisations with and without the surfactant whilst the order in acrylic acid concentration is higher in the presence of the surfactant. This is in very good agreement with the prediction by the kinetic models.

The kinetic models suggest that the order of polymerisation with respect to potassium bromate concentration is 0.5 and 1.0 in the two extreme cases of bimolecular termination and monomolecular termination respectively. The experimental value of about 0.74 implies a combination of the two termination modes.
If the reaction (6-4) predominates in initiation, the kinetic models will lead to values of 0.25 and 0.5 for the order in sodium metabisulphite concentration in the two extreme cases of bimolecular termination and monomolecular termination respectively. If the reaction (6-6) is dominant, the orders in sodium metabisulphite concentration will be 1.0 and 2.0 in the cases of bimolecular termination and monomolecular termination respectively. The experimental order in sodium metabisulphite concentration, around 0.5, implies that the contribution of the reaction between oxygen and bisulphite anion to the initiation is probably small. This is not difficult to explain in view of the very small amount of oxygen in the polymerisation systems. Moreover, it also gives an implication of combination of two termination modes.

For a simple ideal solution polymerisation, the order in monomer concentration is always unity regardless the termination mode (Compton, 1992). The current kinetic studies revealed that the orders of polymerisation with respect to monomer concentration were higher than unity in both the presence and absence of surfactant. Different explanations for the high order in monomer concentration have been reported in the literature. Josefowitz and Mark (1945) attributed the high order in monomer concentration to the formation of a complex between the initiator with the monomer. No polymerisation was observed during the nitrogen purge of the aqueous acrylic acid containing potassium bromate alone, indicating the absence of reaction between acrylic acid and potassium bromate. Palit and co-workers (Mukherjee et al, 1964) reported the initiation of polymerisation of methyl methacrylate, ethyl methacrylate and methacrylic acid by bisulphite anion. A slow polymerisation was observed when the aqueous acrylic acid containing sodium metabisulphite was purged with nitrogen. However, this has been proved to result from the reaction of sodium metabisulphite with atmospheric oxygen rather than from an initiation by sodium metabisulphite alone (see Section 6.3.6). Burnett and Loan (1955) obtained a kinetic equation with a high order of polymerisation with respect to monomer concentration on the basis that radicals formed from the transfer to solvent were capable of reacting with the propagating radicals as well as of re-initiating the monomer. In this case, an inverse relationship between the polymerisation rate and the solvent concentration
was established. The solvent used in the current polymerisations was water which has been proved to have a negligible transfer effect in free radical polymerisations of acrylic monomers (Dainton and Collinson, 1952; Brandrup and Immergut, 1989). Although the transfer to the surfactant molecules in the present polymerisations can lead to a high order in monomer concentration, as discussed in the preceding section, it can not account for the high order in monomer concentration in the absence of surfactant. Matheson (1945) attributed high order in monomer concentration to a cage effect, that is, the competition between the diffusion of primary radicals out of the “cage” and the reaction of primary radicals with “wall monomer”. For the validity of cage effect hypothesis, the primary radicals must be produced in pairs and recombine to form an inert product. In the mechanism proposed by Palit and co-workers (Mukherjee et al, 1966), the redox reaction between bisulphite anion and bromate anion produces free radical pairs (see reaction (6-5)). Gleason et al (1957) proposed a possible reaction between the primary radical pairs produced in reaction (6-5):

\[
\text{SO}_3^- \cdot + \cdot \text{OH} \rightarrow \text{HSO}_4^- 
\]

(6-19)

By considering initiation by the primary radicals produced in reaction (6-5), the following equation was obtained for aqueous polymerisation without surfactant by the same reasoning as that in Section 6.4.2.2:

\[
\frac{k_i}{k_p[M]^2} \cdot R_p^2 + \frac{k_i[C]}{k_p[M]} \cdot R_p - fI = 0 
\]

[6-35]

Here \(f\) and \(I\) are efficiency of initiation and overall rate of producing primary radicals respectively.

From equation [6-35], it is clear that the order in monomer concentration will be always unity if the efficiency of initiation \(f\) is independent of monomer concentration. Therefore, the high order with respect to monomer concentration in the experimental kinetic relationships led to a hypothesis of significant cage effect in the
polymerisations (Brooks and Liu, 1995; Liu and Broods, 1996). However, the factors relating to cage effect have not been well defined in the literature although it is well accepted that all primary radicals are unlikely to be able to initiate monomer in many circumstances. The cage effect for the primary radicals produced in reaction (6-6) can not be significant because of the electrostatic repulsion. The kinetic models obtained in the preceding sections indicated that the high order with respect to monomer concentration is unnecessarily attributed to significant cage effect. If the competition between the two reactions involving the intermediate \([\text{HO}_3\text{SOBrO}_2]^2-\) and the transfer to the surfactant molecules are not negligible, the order in monomer concentration will be higher than 1.0 and be different in two termination cases. The experimental orders in monomer concentration in the polymerisations with and without the surfactant imply a combination of the two termination modes again. The higher value in the presence of the surfactant than that in the absence of the surfactant is probably attributed to the transfer to the surfactant molecules.

6.5 CONCLUSIONS

The following points have arisen from the studies of aqueous polymerisations of acrylic acid initiated by potassium bromate/sodium metabisulphite redox pair in the absence and in the presence of non-ionic surfactant.

The aqueous polymerisation of acrylic acid can be characterised as a free radical mechanism by using potassium bromate/sodium metabisulphite redox pair as an initiation system. The polymerisation is probably dominantly initiated by the intermediates formed in the reaction between bisulphite anion and bromate anion. There is a competition between the two reactions involving the intermediates: one leading to initiation of acrylic acid polymerisation and the other producing inert products. The activation energy of this redox reaction is much lower than that of typical thermal decomposition initiators. The redox reaction proceeds very fast even at ambient temperature. However, the effect of temperature on the polymerisation rate has not been well understood.
A small amount of atmospheric oxygen introduced by adding the sodium metabisulphite aqueous solution probably couples with bisulphite anion to form a redox pair. Apart from the reductant role, bisulphite ion functions as a chain transfer agent and its concentration has a significant effect on the polymer molecular weight. In the presence of surfactant, a transfer to alkanolamide molecules might occur.

The termination in this polymerisation is probably a combination of monomolecular and bimolecular terminations. It is postulated that the monomolecular termination takes place between the propagating radicals and some impurity molecules. However, the details of this termination reaction is still not clear.

The pH value of the initial reaction mixture has a strong influence on the polymerisation rate. The effect of cross-linking agent (N, N'-methylene-bisacrylamide) on the polymerisation rate appears to be negligible at the experimental concentration.

The developed kinetic models based on the proposed reaction scheme are in very good agreement with the experimental relationships.
As it is well known, each free radical polymerisation of a vinyl monomer consists of elementary reactions: initiation, propagation, termination and transfer. These elementary reactions determine the course of polymerisation when they simultaneously occur and hence the overall polymerisation kinetics is a manifestation of features of individual elementary reaction. Because the kinetics of a reaction are not only a function of reactant concentrations, but also a function of reaction conditions, any difference in mechanism always leads to variations in kinetic relations.

The polymerisation of acrylic acid in aqueous solutions have been shown to be homogeneous, i.e. all elementary reactions proceeded in homogeneous media (see Chapter 6). In the inverse microsuspension polymerisations using the redox initiators, the reactants were separated in two types of aqueous drops in the initial stage. The different polymerisation rates between these two kinds of polymerisations suggested difference in mechanisms (see Section 5.3.1).

Kinetic studies have been performed for the inverse microsuspension polymerisations of acrylic acid initiated by sodium metabisulphite/potassium bromate redox pair. The results were compared with that obtained in the aqueous polymerisations (presented in Chapter 6) and related to the hypothesis of the mechanism for the inverse
microsuspension polymerisation process, which differs from both conventional emulsion polymerisations and suspension polymerisations (see Chapter 5).

7.2 EXPERIMENTAL

The details of the materials used for the kinetic studies of inverse microsuspension polymerisation were described in Section 4.2.1.

All inverse microsuspension polymerisations presented in this chapter were conducted by following the procedures described in Section 4.2.2.

The crossed-paddle stirrer was used in the polymerisations concerning the effect of temperature on polymerisation. The stirrer of crossed-paddle combined with a "U"-shaped blade was employed for investigating the effects of individual reactant concentration on polymerisation.

The monomer conversions were calculated from the residual monomer level obtained using HPLC.

7.3 RESULTS

7.3.1 Effect of Polymerisation Temperature

Isothermal inverse microsuspension polymerisations of acrylic acid initiated by potassium bromate/sodium metabisulphite redox pair were carried out in the temperature range of 13 to 43 °C. The variations of monomer conversion with polymerisation time at different temperatures are shown in Figure 7-1. It is clear that these conversion curves are very similar to those in the aqueous polymerisations presented in Chapter 6, an indication of analogous effects of temperature on polymerisation for these two polymerisation processes. It is interesting that the
polymerisation performed at 43 °C proceeded in the same manner as that in the aqueous polymerisation at the same temperature.

By using the same technique employed for the aqueous polymerisations, \( \ln R_{po} \) is plotted against \( 1/T \) (Figure 7-2). The slope of the least squares line through the points in the graph leads to an activation energy of about 26.96 kJ/mol for the inverse microsuspension polymerisation. This value is almost identical with that for the aqueous polymerisation (28.62 kJ/mol) in the same temperature range.

SEM images of the final lattices produced at different temperature showed no significant difference in the particle size, an indication of little influence of temperature upon the aqueous drop/particle size in the temperature range of
investigation. This was different from the observations by Baade and Reichert (1984) who found a progressive decrease in the aqueous droplet size with increasing temperature in the systems of aqueous acrylamide/Span 80/Isopar M.

![Figure 7-2 Plot of lnR_p0 against 1/T for inverse microsuspension polymerisation](image)

7.3.2 Effect of Cross-linking Agent

About 9.59 x 10^{-4} mol/l of cross-linking agent (MBA) was used in each inverse microsuspension polymerisation. In the aqueous polymerisation, the presence of 1.87 x 10^{-3} mol/l of cross-linking agent showed negligible influence upon the polymerisation rate (see Section 6.3.7). From this point of view, for the inverse microsuspension polymerisation, the aqueous polymerisation of acrylic acid inside the
coalesced aqueous drops, in the presence of a small amount of cross-linking agent, could also be studied as a homopolymerisation in respect to the kinetics. However, the presence of the cross-linking agent in the inverse microsuspension polymerisation might have more complicated effects. In addition to the copolymerisation with acrylic acid, the cross-linking reaction would result in more rapid increase in the fluid viscosity in the coalesced aqueous drops. Any significant change in the fluid viscosity in a coalesced aqueous drop might affect its further coalescence and break-up. As a consequence, the overall polymerisation rate would be varied.

Figure 7-3 Effect of cross-linking agent on inverse microsuspension polymerisation
data in legends are MBA concentrations, $10^{-4}$ mol/l

$[AA]_0 = 4.24$ mol/l, $[Na_2S_2O_3]_0 = 7.77 \times 10^{-4}$ mol/l, $[KBrO_3]_0 = 8.08 \times 10^{-4}$ mol/l,
$[Si]_0 = 10$ wt% of oil phase
pH 5.1, 23 °C, crossed-paddle + "U" blade stirrer at 1000 rpm
Figure 7-3 shows the variations of monomer conversion with polymerisation time in the presence and in the absence of the cross-linking agent. It was observed that the presence of cross-linking agent had little influence on the polymerisation rate and limiting monomer conversion. The very low concentration of the cross-linking agent ([AA] : [MBA] = 4.42 x 10^3 : 1 mol/mol) is probably the main reason for this. Moreover, the fluid viscosity of a coalesced aqueous drop can rise very quickly as polymerisation proceeds in it, even when only a small amount of polyacrylic acid is produced. In this case, the increase in the viscosity resulting from the cross-linking reaction might be of little importance.

Figure 7-4 Conversion curves of inverse microsuspension polymerisation at various concentrations of acrylic acid

Data in legends are acrylic acid concentrations, mol/l
Experimental compositions and conditions see Appendix VII (b)
7.3.3 Effect of Monomer Concentration

Isothermal inverse polymerisations were conducted at 23 °C in a range of initial monomer concentration from 1.09 to 4.24 mol/l.

Figure 7-4 shows the variations of monomer conversion with polymerisation time at different initial monomer concentrations. Both the initial polymerisation rate and the limiting monomer conversion increased with increased monomer concentration, a similar phenomenon to that in the aqueous polymerisations.

![Figure 7-5 log-log plot of $R_{po}$ versus $[AA]_o$ for inverse microsuspension polymerisation](image)
Chapter 7  Kinetics of Inverse Microsuspension Polymerisation

Figure 7-5 shows the log-log plot of initial polymerisation rate versus initial monomer concentration. The least squares fit to the data points leads to:

$$R_{po} = [AA]_0^{2.01}$$  \[7-1\]

7.3.4 Effect of Reductant Concentration

Figure 7-6 shows the conversion curves at various initial sodium metabisulphite concentrations from 1.95 to 31.61 x 10^{-4} mol/l. The increase in sodium metabisulphite concentration resulted in rises in both initial polymerisation rate and limiting monomer conversion.

![Conversion Curves](image)

Figure 7-6 Conversion curves of inverse microsuspension polymerisation at varied concentrations of sodium metabisulphite

data in legends are concentrations of sodium metabisulphite, 10^{-4} mol/l
experimental compositions and conditions see Appendix VII (c)
The following relationship was obtained by least squares fit to the data points in log-log plot of initial polymerisation rate versus initial concentration of sodium metabisulphite (Figure 7-7):

\[
R_{po} \propto [Na_2S_2O_3]^{0.70}
\]

Figure 7-7  log-log plot of \( R_{po} \) versus \([Na_2S_2O_3]\) for inverse microsuspension polymerisation

7.3.5  Effect of Oxidant Concentration

Polymerisations were conducted at initial concentrations of potassium bromate which varied from 2.50 to 32.96 x 10^{-4} mol/l. The variations of monomer conversion with
polymerisation time (Figure 7-8) indicated faster polymerisation rate and higher limiting monomer conversion at higher concentration of potassium bromate.

Figure 7-9 shows the log-log plot of the initial polymerisation rate versus the initial concentration of potassium bromate. The reaction order with respect to the concentration of potassium bromate was obtained by least squares method:

\[ R_{po} \propto [KBrO_3]_o^{0.76} \]  

[7-3]

Figure 7-8 Conversion curves of inverse microsuspension polymerisation at varied concentrations of potassium bromate
data in legends are concentrations of potassium bromate, \(10^{-4}\) mol/l
experimental compositions and conditions see Appendix VII (d)
7.3.6 Effect of Surfactant Concentration

The effect of Witcamide 511 concentration, varied from 5 to 10 wt% of the oil phase, on the monomer conversion is shown in Figure 7-10. Pronounced decreases in the initial polymerisation rate and the limiting monomer conversion were observed as the surfactant concentration increased, an indication of complicated functions of the surfactant molecules.
Figure 7-10  Conversion curves of inverse microsuspension polymerisation at varied concentrations of Witcamide 511

data in legends are concentrations of Witcamide 511, based on oil phase experimental compositions and conditions see Appendix VII (e)

The following relationship was obtained by least squares fit to the log-log plot of the initial polymerisation rate and the surfactant concentration (Figure 7-11):

\[ R_{po} \propto [S]_o^{0.47} \]  \[7-4\]
Figure 7-11

log-log plot of $R_{po}$ versus $[S]_o$ for inverse microsuspension polymerisation

Figure 7-12 shows the SEM images of the final lattices at two different surfactant concentrations. It is seen that smaller particles were obtained at a higher surfactant concentration.
Figure 7-12 Freeze-fracture SEM images of final lattices at different surfactant concentrations
7.4 DISCUSSION

In a simple homogeneous polymerisation, the overall rate constant is a function of the rate constants for individual elementary reactions. Therefore, the effect of temperature on the polymerisation rate is solely due to the influences of temperature upon the individual elementary reactions. On the other hand, in some heterogeneous polymerisations (except for conventional suspension polymerisations), the distributions of the reactants or of the intermediates are not homogeneous. In a conventional emulsion polymerisation, for instance, the initiator is normally segregated from the chain propagation locus and the initiation and termination reactions differ from that in homogeneous polymerisations (Blackley, 1975). In these cases, the effects of temperature on the polymerisation rates are more complicated. Baade and Reichert (1984) carried out inverse dispersion polymerisations of acrylamide by using both water-soluble and oil-soluble initiators. They found that the kinetic dependencies for water-soluble initiator (AIBEA) corresponded to that of solution polymerisations in water. When oil-soluble initiator (AIBN) was used, the polymerisation rate was much more sensitive to the temperature variations. In the latter case, an overall activation energy of 88.2 kJ/mol was obtained from the slope of the Arrhenius plot. However, the overall rate constant was also a function of the interfacial area of spherical droplets/particles related to the volume. This itself was dependent on temperature. When corrections were made by using the values of overall rate constant at constant interfacial area, an overall activation energy of 26 kJ/mol was obtained.

In the inverse microsuspension polymerisations, the effect of temperature on polymerisation was exactly the same as that in the aqueous polymerisation (see Section 6.3.2.1). The values of overall activation energy in the two kinds of polymerisations were almost identical. These suggested that the inverse microsuspension polymerisations were, at least predominantly, initiated by the primary radicals generated in the aqueous phase. It was mentioned in Chapter 5 that the oligomeric radicals formed in the polymer-monomer particles may transfer through the oil phase and lead to another kind of initiation. It is expected that the
temperature dependence of this kind of initiation should be different from that of the
initiation by primary radicals in the aqueous phase. However, this was not supported
by the experimental results. Therefore, the initiation attributed to the transfer of
oligomeric radicals through the oil phase, if it existed, could not be of any importance
in the inverse microsuspension polymerisations.

In spite of the identity in the overall activation energy and the similarity in the
temperature dependence of the overall polymerisation rate and limiting monomer
conversion, the kinetic relationships of the two kinds of polymerisations were
different (see Section 6.3.3 and Section 7.3). This was in agreement with the
difference in the overall polymerisation rate under the identical conditions (see
Chapter 5) and suggested the differences in polymerisation mechanism again.

In the aqueous polymerisations, the distributions of the reactants and the produced
polymer molecules were homogeneous throughout the course of the polymerisation.
As soon as the aqueous reductant was introduced, the reactions took place in a single
phase. In contrast, in the inverse microsuspension polymerisations, the reactants were
initially segregated in the two different types of aqueous drops and the polymerisation
only occurred in the coalesced aqueous drops. Therefore, in the latter case, the real
initial compositions for polymerisation in the reaction loci differed from the apparent
values. At the initial stage, the reductant concentration in a coalesced aqueous drop
was always higher than the apparent value based on the overall volume of the aqueous
phase because the reductant was introduced as a concentrated aqueous solution.
Similarly, atmospheric oxygen introduced with the aqueous reductant would be
concentrated in the coalesced aqueous drops. Therefore, the reaction between the
bisulphite anion and the oxygen molecules (reaction (6-6)) would be more significant
than that in the aqueous polymerisations. This probably accounts for the higher order
with respect to reductant concentration in the inverse microsuspension polymerisation
than that in the aqueous polymerisation with surfactant.

The orders with respect to the oxidant concentration were almost identical for the two
kinds of polymerisations. This is in agreement with the prediction by the kinetic
models which suggest that the order of polymerisation rate with respect to oxidant concentration is only dependent on the termination modes, but independent of variations in reactant concentrations.

The inverse relationships between the polymerisation rate and the surfactant concentration have been reported in the various inverse heterogeneous polymerisations. In the polymerisation of aqueous acrylamide in Isopar M using AIBN as an oil-soluble initiator, Baade and Reichert (1984) postulated two effects for the inverse dependence of polymerisation rate on the surfactant (Span 80) concentration. One was the physical effect, i.e. the probability of an increase in the thickness and the density of the boundary layer of surfactant with increase in its concentration. Fewer primary radicals forming in the oil phase could diffuse into the aqueous monomer droplets. The other was the chemical effect, i.e. the possibility of a reaction between the primary radicals and the surfactant molecules. This reaction increased to a larger extent with increasing concentration of the surfactant and could control the concentration of the primary radicals for initiating the chain propagation. In a latter published paper, Hunkeler et al (1989) believed that the high levels of Span 80 molecules, which saturated the interface at relatively low levels, with the remainder residing in the continuous oil phase, could increase the radical scavenging efficiency due to the reaction through their double bond in the oleic acid backbone. In the present inverse microsuspension polymerisation, the physical effect proposed by Baade and Reichert could not be of any importance because the redox initiation reaction only occurred in the coalesced aqueous drops. The decline of polymerisation rate with increased surfactant concentration confirmed the hypothesis of participation of Witcamide 511 molecules in the polymerisation reactions (see Section 6.4.1.4). In view of the limited solubility of the Witcamide 511 molecules in the aqueous phase, the reaction between the primary radicals and the surfactant molecules would predominantly take place in the interfacial layer. SEM images revealed that higher surfactant concentration produced more aqueous drops with smaller size and larger interfacial area (Figure 7-12). The larger interfacial area could have provided more opportunities for the surfactant molecules to participate in the reactions with the free radicals.
In determining the order with respect to the surfactant concentration, the surfactant concentration was calculated based on the overall oil phase. However, the surfactant molecules were not uniformly dispersed in the aqueous phase, instead, they were mostly present in the interfacial layer. Therefore, the real concentration of surfactant in the reaction locus would differ from the apparent value. This probably accounts for the difference in the orders with respect to the surfactant concentration between the kinetic model and the experimental relationship.

Taking into account experimental error, the orders with respect to monomer concentration are very close in the inverse microsuspension polymerisation and the aqueous polymerisation with surfactant. The slightly higher order in monomer concentration in the inverse microsuspension polymerisation is probably attributed to more transfer to the surfactant molecules in this case as discussed above.

7.5 CONCLUSIONS

The inverse microsuspension polymerisation of acrylic acid initiated by sodium metabisulphite/potassium bromate redox pair showed very similar dependences of polymerisation rate and limiting monomer conversion on temperature to the aqueous polymerisation of acrylic acid using the same redox initiation system in the same temperature range. The values of activation energy of the two kinds of polymerisations were almost identical. These supported the hypothesis of initiation in the aqueous phase as a result of coalescence between the two different types of aqueous drops.

The kinetic studies led to a relationship for the inverse microsuspension polymerisation which is different from that for the aqueous polymerisation in the presence of the surfactant. This confirms the difference in process mechanisms of these two kinds of polymerisation and hence supports the hypothesis that the inverse microsuspension polymerisation differs from a conventional suspension polymerisation. The inverse relationship between the polymerisation rate and the surfactant concentration confirms the transfer function of the surfactant molecules and
clearly indicates a mechanism different from a conventional emulsion polymerisation. The reaction between the bisulphite ion and atmospheric oxygen seems more significant than that in the aqueous polymerisations, probably due to the higher levels of these two components in the polymerisation locus.
CHAPTER 8

DROP MIXING IN INVERSE MICROSPUSPENSION POLYMERISATION USING REDOX INITIATORS

8.1 INTRODUCTION

It has been shown in the forgoing chapters that the inverse microspusension polymerisation proceeds in the aqueous drops generated by drop mixing via simultaneous coalescence and break-up of the different types of aqueous drops in the system. It is thus expected that the drop mixing could have strong influence not only on polymerisation kinetics, but also on product properties, such as limited monomer conversion, particle size and size distribution. The literature survey has revealed that the drop mixing is a very complex procedure depending on a number of factors (see Chapter 2). In the present inverse microspusension polymerisation, the drop mixing is even more complicated because (i) there are two types of aqueous drops at the beginning: the AMODs are stabilised with surfactant and small in size and the ARDs are unstable and big; (ii) the composition in individual aqueous drops/particles varies with time, thereby, altering their physical properties. The work presented in this chapter is concerned with the inverse microspusension polymerisation performed by varying some parameters which have effects on drop mixing.

8.2 RESULTS AND DISCUSSIONS

8.2.1 Effect of Agitation Intensity

Inverse microspusension polymerisations were conducted at different agitation
intensities by varying agitation speed and using different types of stirrer. Figure 8-1 shows the temperature profiles of non-isothermal inverse microsuspension polymerisations at agitation speed of 200 and 400 rpm respectively. It is clear that the agitation speed had a significant effect on the polymerisation rate. The maximum temperature was reached in about 3.0 minutes at 400 rpm agitation whilst it was reached in about 4.5 minutes at 200 rpm agitation. The maximum temperature at 400 rpm agitation (about 38 °C) was higher than that at 200 rpm agitation (about 35 °C).

![Temperature profiles of inverse microsuspension polymerisations at different agitation speeds](figure8-1.png)

Figure 8-1  Temperature profiles of inverse microsuspension polymerisations at different agitation speeds

[AA]_o=4.24 mol/l, [Na_2S_2O_3]_o=7.85 x 10^{-4} mol/l, [KBrO_3]_o=1.73 x 10^{-3} mol/l, [S]_o=10 wt% of oil phase, pH 5.1

propeller stirrer, 1000 rpm emulsification for 2 hours
Figure 8-2 Freeze-fracture SEM images of final lattices prepared at varied polymerisation agitation speed

experimental composition is the same as that in Figure 8-1

crossed-paddle stirrer, 1000 rpm for emulsification, 23 °C
Dependence of polymerisation rate on agitation speed is one of the main characteristics of drop initiation. Vanderhoff and coworkers (1984) observed a strong influence of agitation speed upon the induction period of inverse heterogeneous polymerisation of acrylamide using benzyl peroxide as initiator. They believed that the initiation took place in aqueous monomer droplets by decomposition of benzyl peroxide dissolved or solubilised in the aqueous phase. Therefore, the shorter induction period at higher agitation speed was attributed to the smaller aqueous droplet size because larger interfacial area resulted in faster-starting polymerisation. In the present inverse microsuspension polymerisation, the increase in polymerisation rate with increased agitation speed supports the polymerisation process hypothesis presented in Chapter 5. It is well established that the frequency of drop coalescence and break-up are strongly dependent on agitation speed (Nagata, 1975). More frequent simultaneous coalescence and break-up of the aqueous drops at higher agitation speed could generate more polymerising aqueous drops and hence result in higher overall polymerisation rate. The faster break-up of aqueous reductant drops at higher agitation speed was confirmed by the SEM images of the final inverse lattices prepared at different polymerisation agitation speed (Figure 8-2). Some big particles were present in the final latex when an agitation of 500 rpm was applied (Figure 8-2, a). In contrast, big particles were hardly observed in the final latex obtained using 700 rpm agitation (Figure 8-2, b).

Figure 8-3 shows the variations of monomer conversion with polymerisation time in inverse microsuspension polymerisations using different types of stirrer. It has been shown that the agitation efficiency of the crossed-paddle stirrer combined with “U” shaped-blade is higher than that of the crossed-paddle stirrer alone (see Section 4.1.2). The monomer conversion curves clearly indicated that a higher polymerisation rate was obtained by using the stirrer with a higher agitation efficiency. This provides further evidence for that simultaneous coalescence and break-up of the aqueous drops play very important role in the inverse microsuspension polymerisation.
In addition to agitation speed, it has been shown in Chapter 4 that the particle size in the final inverse lattices are also dependent on the type of stirrer. The significant effects of agitation intensity on the particle size and size distribution in final inverse lattices are consistent with the hypothesis of polymerisation process presented in Chapter 5. It is not known whether the surfactant molecules form inverse micelles in Isopar M at the experimental surfactant concentrations. However, it is postulated that they are of little importance in polymerisation. This is because, as discussed in Chapter 5, there was no significant decrease in the size of AMODs during polymerisation and this suggested that there was little diffusion of monomer through the oil phase. The observation that the higher agitation intensity led to a smaller size
of latex particle and narrower size distribution also suggests that the nucleation of particles could not be attributed to initiation in inverse micelles or in the continuous phase because the size of micelles is usually insensitive to agitation intensity. In contrast, the strong correlation between agitation intensity and the latex particle size and size distribution could be reasonably explained by the effect of agitation intensity on simultaneous coalescence and break-up of the aqueous drops.

8.2.2 Effect of Aqueous Reductant Volume

According to the hypothesis of inverse microsuspension polymerisation, the polymerisation takes place in the aqueous drops as a result of coalescence between different types of aqueous drops. It is not difficult, therefore, to predict that the volume of the reductant aqueous solution may have effects on polymerisation.

Isothermal inverse microsuspension polymerisations were carried out under identical composition and conditions except that the volume of the reductant aqueous solution was varied. Figure 8-4 shows the variations of monomer conversion with polymerisation time at different volumes of the reductant aqueous solution while the reductant mass was kept constant. The small increase in the volume of the reductant aqueous solution seems not to change polymerisation significantly. However, pronounced increases in both polymerisation rate and limiting monomer conversion were evident when a larger volume was employed.

The growth in the volume of the reductant aqueous solution should increase the number of aqueous reductant drops at early stages of polymerisation and hence increase the frequency of collision between the two different types of aqueous drops. As a result, more coalesced aqueous drops could be generated and the overall polymerisation rate could be increased. On the other hand, the polymerisation rate in each coalesced aqueous drop can be reduced by increasing the volume of the aqueous reductant. This is because the reductant concentration in its aqueous solution decreases with increased volume. It has been shown in the aqueous polymerisation that the reductant concentration has a pronounced influence on the polymerisation rate.
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Drop Mixing in Inverse Microsuspension Polymerisation

(see Section 6.3.2 and 6.3.3). Therefore, the effect of aqueous reductant volume on
polymerisation could be complicated as a combination of these two conflicting
factors.

1.0
o

O.B
0
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0.6

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Cl)
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~

u

rnl
I!l 4.0 rnl
a 2.0 rnl

I2J 9.0

0.2
0.0

r
0

10

20

30

40

polymerisatln time
Figure 8-4

50

60

70

(minutes)

Conversion curves of inverse microsuspension polymerisation
at different aqueous reductant volumes

data in legends are aqueous reductant volumes

[AAl o=4.24 molll, [Na2S20s1o=7.94 x 10-4 moVI, [KBr031o=1.77 x 10-3 molll,

[SJ o=1O wt% of oil phase, no MBA, pH 5.1
crossed-paddle + "U" blade stirrer at 1000 rpm, 23°C

8.2.3

Effect of Cross-linking Agent

The influence of the cross-linking agent (MBA) on the rate of the inverse
microsuspension polymerisation has been presented in Section 7.3.2.

Figure 8-5


shows the SEM images of the final lattices prepared in the absence and in the presence of a small amount of the cross-linking agent. Little difference in the particle size and size distribution was observed. This is in consistent with the kinetic results.

Figure 8-5 Freeze-fracture SEM images of lattices with and without cross-linking agent

experimental compositions and conditions see Figure 7-3
Generally, cross-linking reactions lead to increase in molecular weight or even produce insoluble polymers and hence increase the fluid viscosity. The coalescence and break-up of dispersed drops, as is well known, are strongly dependent on their internal fluid viscosity. According to the hypothesis proposed in Chapter 5, the further coalescence and break-up of the APMPs formed by coalescence between the different types of aqueous drops are accompanied by polymerisation in these APMPs. The cross-linking reaction in these polymerising APMPs could promote the growth of fluid viscosity and hence restrict the further break-up of them. If this effect is important enough, the further break-up of the coalesced aqueous drops may virtually stop after a certain stage and some big particles may remain in the final latex. The foregoing result suggests that this effect is negligible with the experimental concentration of the cross-linking agent. As discussed in Section 7.3.2, the very low concentration of the cross-linking agent or/and the significant increase in the fluid viscosity as polymerisation proceeds even in the absence of cross-linking agent could be the main reason.

8.2.4 Presence of Monomer in Aqueous Reductant

A polymerisation was conducted by adding a reductant aqueous solution containing the monomer at the same concentration as in the AMODs to start polymerisation, while the total monomer mass in the system was kept unchanged. The monomer conversion curves with and without the monomer in the reductant aqueous solution are shown in Figure 8-6.

In the case of adding the reductant as an aqueous solution without the monomer, it is anticipated, according to the hypothesis, that the monomer concentration in the coalesced aqueous drops would be lower than the apparent value based on the total aqueous phase owing to a dilution effect. This dilution effect can be eliminated by the presence of monomer in the aqueous reductant drops. As a result, the polymerisation rate in the coalesced aqueous drops should be higher due to the higher monomer concentration. However, the experimental result showed that both the overall
polymerisation rate and the limiting monomer conversion were lower in the latter case.

![Conversion curves of inverse microsuspension polymerisations with and without monomer in reductant aqueous solution](image)

**Figure 8-6**  Conversion curves of inverse microsuspension polymerisations with and without monomer in reductant aqueous solution

data in legends are monomer concentrations in reductant aqueous solution
experimental composition and conditions are the same as that in Figure 8-4

The effects of acrylamide conversion on the viscosity of polymer-monomer aqueous solution and on the dispersibility of this solution in toluene were investigated by Graillat et al (1986). It was found that the viscosity of polymer-monomer aqueous solution increased very quickly as the monomer conversion increased. A polymer-monomer aqueous solution which simulated 10 % monomer conversion could not be dispersed in toluene regardless of the agitation speed. In the above experiment (Figure 8-6), the higher polymerisation rate in the coalesced aqueous drops in the latter case
resulted in faster growth of fluid viscosity inside them and hence restricted their further coalescence and break-up. Therefore, the overall polymerisation rate and monomer conversion were reduced although the polymerisation rate in individual APMPs might be faster.

SEM imaging revealed the existence of big drops in the final latex although the polymerisation was conducted at 1000 rpm agitation (Figure 8-7), confirming a slower break-up of aqueous drops/particles in the case of adding the reductant aqueous solution containing the monomer.

This result supports the hypothesis for the process of inverse microsuspension polymerisation and indicates again the crucial role of drop mixing in this specific process.

![Figure 8-7](image_url)

**Figure 8-7** Freeze-fracture SEM image of final latex prepared by adding reductant aqueous solution containing monomer experimental composition and conditions see Figure 8-6
8.2.5 Adding Aqueous Reductant as Stabilised Dispersion

In view of the crucial role of coalescence between the different types of aqueous drops, inverse microsuspension polymerisations were performed by adding the aqueous reductant in different ways. In an inverse microsuspension polymerisation, the aqueous reductant was pre-dispersed in Isopar M stabilised with the surfactant and then added to the aqueous monomer dispersion to start polymerisation. The phase ratio and the concentration of the surfactant in the inverse dispersion of aqueous reductant are the same as that in the inverse dispersion of the aqueous monomer containing the oxidant. Figure 8-8 shows the temperature profiles of inverse microsuspension polymerisations by adding the aqueous reductant as an aqueous solution and as a stabilised inverse dispersion.

In the case of introducing the reductant as an aqueous solution, it has been shown that the aqueous reductant was broken into aqueous drops after being added to the agitated aqueous monomer dispersion, but the drop sizes were relatively large at the early stages of polymerisation (see Section 5.3.2). When the aqueous reductant is added as an inverse dispersion, the opportunity of collision between the ARDs and the AMODs should increase, at least at the early stages, due to the higher interfacial area of the ARDs. However, the experimental result indicated that the polymerisation was retarded rather than being promoted in this case. This is probably due to the stabilisation function of the surfactant molecules adsorbed on the surface of the aqueous reductant drops.

In an agitated two phase liquid-liquid system, the dispersed drops move in the turbulent field and collide one another. However, coalescence only occurs when the colliding drops remain together for a time long enough to enable the rupture of the interfacial film entrapped between them. On the other hand, some of the collisions do not result in coalescence and the colliding drops rebound owing to the elastic properties of the interfacial film. The strength of this film can be increased by the presence of surfactant molecules (Nagata, 1975). The preceding result suggests that the coalescence frequency between the AMODs and the ARDs was reduced by pre-
stabilising the latter with the surfactant molecules although the collision frequency might be increased. This is in very good agreement with the hypothesis that, in the case of adding the reductant as an aqueous solution, the unstabilised aqueous reductant drops are unstable at the beginning and tend to require the surfactant molecules to reduce their surface tension by coalescing with the surrounding stabilised AMODs (see Chapter 5).

![Figure 8-8](image)

**Figure 8-8** Temperature profiles of inverse microsuspension polymerisations by adding aqueous reductant in different ways

\[ [AA]_o = 4.24 \text{ mol/l}, \ [Na_2S_2O_5]_o = 8.05 \times 10^{-4} \text{ mol/l}, \ [KBrO_3]_o = 1.79 \times 10^{-3} \text{ mol/l}, \ [S]_o = 10 \text{ wt\% of oil phase, pH 5.1} \]

crossed-paddle + "U" blade stirrer at 1000 rpm
In spite of the retardation of coalescence, the presence of the surfactant molecules on the aqueous reductant surface did not completely inhibit the coalescence, indicated by the immediate raise of temperature as the stabilised dispersion of the aqueous reductant was added (Figure 8-8). This suggests a very important fact that the coalescences not only involve the unstabilised aqueous drops, but also take place between the stabilised aqueous drops. This supports the hypothesis that the generation of the polymerising APMPs could continue through simultaneous coalescence and break-up between the polymerising APMPs and the uncoalesced AMODs, provided the fluid viscosity in the former is not too high (see Chapter 5). This is probably why a relatively high yield of polymer can be achieved although only a small volume of the reductant aqueous solution was introduced in the present inverse microsuspension polymerisation.

8.2.6 Continuous Addition of Aqueous Reductant

An inverse microsuspension polymerisation was conducted by adding the aqueous reductant continuously over a period of 25 minutes at an approximately constant rate. According to the conventional definitions, this process may be termed as a semi-batch polymerisation, in contrast to the batch polymerisation in which the aqueous reductant is added as a shot.

Figure 8-9 shows the conversion curves of batch and semi-batch polymerisations conducted under the identical conditions. It is clear that the batch polymerisation rate is much higher than the semi-batch polymerisation rate at the early stages. This is obviously because more ARDs were present in the system and more reductant molecules were available for initiation at the early stages of the batch polymerisation. It is noteworthy that a higher limiting monomer conversion was attained in the semi-batch polymerisation. This is also in agreement with the hypothesis of the polymerisation process. Compared with the batch polymerisation, the number ratio of the AMODs to the ARDs is higher at the early stages of semi-batch polymerisation. Therefore, the opportunity for the coalescence between these two different types of drops is higher. This is beneficial for the quick distribution of the reductant molecules
in the aqueous phase and reduces the possibility of trapping them in highly polymerised particles. As polymerisation proceeds, APMPs with various monomer conversion levels form. In view of the effects of the fluid viscosity of an aqueous drop on its break-up and coalescence with other aqueous drops, the newly added ARDs could thus prefer coalescing with the unpolymerised AMODs or with the APMPs with lower monomer conversion. Therefore, the overall residual monomer concentration can be reduced by continuously adding the aqueous reductant at an appropriate rate.

![Figure 8-9](image)

**Figure 8-9** Conversion curves of batch and semi-batch inverse microsuspension polymerisations

experimental composition and conditions are the same as that in Figure 8-4

the volume of aqueous reductant is 9.0 ml
8.3 CONCLUSIONS

The results indicated a crucial role of drop mixing in the inverse microsuspension polymerisation. The improvement of drop mixing, for instance, by increasing agitation intensity, improves the generation of polymerising particles and the quick break-up of the big ARDs. The effect of volume of the aqueous reductant on polymerisation might be a combination of the increase in collision frequency of the two types of aqueous drops and the reduction in the concentration of the reductant in individual coalesced aqueous drops. The presence of monomer in the aqueous reductant lowers the polymerisation rate, probably due to the restriction of further coalescence and break-up of the generated polymerising APMPs by the quick growth of fluid viscosity in them. The stabilisation of aqueous reductant reduces the polymerisation rate mainly because of the decrease in drop coalescence. However, the coalescence between two stabilised aqueous drops is also feasible. The continuous addition of the aqueous reductant facilitates the distribution of the reductant molecules in the aqueous drops and hence increases the limiting monomer conversion. The effect of the cross-linking agent is negligible with the experimental concentration used here.
CHAPTER 9

MODELLING OF INVERSE MICROSPSUSPENSION POLYMERISATION USING REDOX INITIATORS

9.1 INTRODUCTION

A hypothesis was proposed in Chapter 5 for the mechanism of the inverse microsuspension polymerisation of acrylic acid using redox initiators based on some specific features of the system. The proposed mechanism differs from the conventional concepts for both suspension polymerisation and emulsion polymerisation. The kinetic studies with both a single-phase aqueous medium and a heterogeneous medium (presented in Chapter 6 and 7) have clearly revealed the differences between these two kinds of polymerisation processes. The rationalisation of the kinetic results in terms of mechanism is in good agreement with the hypothesis. The investigations presented in Chapter 8 on the variations of polymerisation rate, limiting monomer conversion, final particle size and size distribution by altering some key parameters, such as agitation intensity, volume and composition of the aqueous reductant and the ways of adding the aqueous reductant, have provided further evidence for the hypothesis. This Chapter is concerned with the development of a general model for describing inverse microsuspension polymerisation using redox initiators.

The work presented in this Chapter will deal exclusively with theoretical predictions, with no attempt to confirm the model experimentally. The purpose is twofold: to obtain further understanding of the process; and to predict some phenomena in the course of polymerisation.
9.2 MECHANISTIC MODEL

In developing the mechanistic model for inverse microsuspension polymerisation using redox initiators, the work is based on the hypothesis proposed in Chapter 5. The model only concerns the system which satisfies the following conditions:

The two components of the redox pair are virtually oil-insoluble and can not initiate polymerisation alone. Therefore, the generation of primary free radicals can only occur in the aqueous phase as a result of mixing of the two components of the redox pair. The reductant of the redox pair is introduced after the inverse dispersion of the aqueous monomer containing the oxidant in the oil phase has been established, so that it is initially segregated from the oxidant and monomer. The diffusion of all kinds of free radicals through the oil phase is negligible.

The polymerisation process is illustrated diagrammatically in Figure 9.1. Here the reductant is supposed to be introduced as an unstabilised aqueous solution. The separate parts of this figure relate to the various stages of the reaction system from before addition of the aqueous reductant up to complete conversion. At stage (a), an inverse dispersion is established. The monomer and oxidant in aqueous solution are present as aqueous drops in the oil and stabilised with the surfactant. These AMODs are moving and colliding one another in the turbulent field of agitation. They may experience coalescence and break-up, but an equilibrium between the drop coalescence and break-up has been established. Therefore, the size of the AMODs is fairly uniform. At (b) is shown the addition of the aqueous reductant to the system. Because the aqueous reductant is added as a shot, it must be initially present as aqueous drops much larger than the AMODs. These ARDs are unstable and tend to acquire surfactant to reduce their surface tension. At (c) is shown the deformation of the ARDs under the rotational stress. At the same time, the ARDs will collide with the AMODs. Some AMODs may stick with the ARDs after collision and subsequently join together (coalescence).
As soon as the coalescence occurs, the two components of the redox pair mix together and primary free radicals are generated within these coalesced aqueous drops. In consequence, some ARDs disappear and some APMPs are now formed. At (d) is
shown the break-up of big ARDs or APMPs into smaller aqueous drops or particles. It must be mentioned that there is probably no sharp distinction between stage (c) and (d). The coalescence and break-up of the ARDs are more likely to take place simultaneously. The time which elapses between the addition of the big ARDs and their break-up into the same size as AMODs is normally long relative to the time for the coalescence and the initiation of polymerisation. Therefore, the big ARDs will soon become APMPs before they are all broken into small aqueous drops. These APMPs are still too big to exist in the system and will undergo further break-up. At the same time, they will coalesce with the remaining AMODs. Provided the reductant is added in an amount equal to or larger than that required for the redox reaction, polymerisation will continue within the newly formed APMPs derived from the coalescence between the AMODs and the APMPs. In an ideal system, all AMODs experience coalescence with ARDs or APMPs and eventually the polymerisation within every APMP is complete. Finally, the system comprises an inverse dispersion of small polymer particles stabilised with the surfactant molecules. This is represented at the end stage (e).

9.3 QUANTITATIVE DESCRIPTION OF MODEL

From the mechanistic model presented in the preceding section, it is clear that the polymerisation proceeds in the aqueous phase as a result of intermixing of the dispersed aqueous phase by continuous coalescence and break-up involving the different types of aqueous drops and APMPs. Therefore, the overall polymerisation rate is a function of two terms: (a) the polymerisation rate in each polymerising APMP, and (b) the volume percentage of the aqueous phase undergoing polymerisation (generated by coalescence between two different types of drops).

According to the model, it is not difficult to predict that the polymerisation rate in individual polymerising APMPs is different depending on its history of coalescence and break-up. This is because the composition varies as intermixing and reaction proceed.
Let

\[ V = \text{total volume of aqueous phase (litre)} \]
\[ v_i = \text{volume of APMPs polymerising at rate } r_{pi} \text{ (litre)} \]
\[ R_p = \text{overall polymerisation rate (mol·l}^{-1}·\text{min}^{-1}) \]

From the definition of polymerisation rate (see Section 6.4.2), one has

\[ R_p = \frac{d[M]}{dt} = \frac{1}{V} \cdot (v_1 r_{p1} + v_2 r_{p2} + \cdots + v_i r_{pi}) \quad [9-1] \]

or

\[ R_p = \frac{1}{V} \sum v_i r_{pi} \quad [9-2] \]

Here

\[ r_{p1} \neq r_{p2} \neq \cdots \neq r_{pi} \quad [9-3] \]

Obviously, \( v_i \) is directly dependent on the coalescence and break-up of the ARDs, AMODs and APMPs. In addition, it is well known that \( r_{pi} \) can be expressed as a product of two functions: the rate constants of the elementary reactions and the reactant concentrations in the corresponding polymerising aqueous phase. As mentioned above, the reactant concentration is dependent on the intermixing. Moreover, the changes in composition caused by continuous coalescence and break-up may lead to variation of the rate constants of elementary reactions due to some specific effects, such as 'gel effect'. Therefore, \( r_{pi} \) is also strongly dependent on the intermixing of the dispersed aqueous phase. In this case, the polymerisation kinetics can be very complicated. The resolution of equation [9-2] requires knowledge of variations of both \( v_i \) and \( r_{pi} \) with time.

Let \( r_c \) denote intermixing rate, expressed in terms of volume percentage of aqueous phase initiated (generated to polymerising APMPs) in unit time, \( \frac{1}{V} \cdot \frac{dv}{dt} \text{ (1/min)}. \)

Now let us consider two extreme cases:
If \( r_c \gg r_p \), in one extreme case, the intermixing of all the reactants has been completed and the composition of the aqueous phase becomes homogeneous at an extremely low polymerisation conversion.

Therefore

\[ r_{p1} = r_{p2} = \ldots = r_{pn} = r_p \]

and

as \( dt \to 0 \), \( \Sigma v_i \to V \)

Then, equation [9-2] becomes

\[ R_p = r_p \] \[ \text{[9-4]} \]

In this case, the effects of intermixing of the dispersed aqueous phase on the overall polymerisation rate are negligible and the kinetics of the inverse microsuspension polymerisation is the same as that of a conventional inverse suspension polymerisation. The overall polymerisation rate is polymerisation-controlled.

If \( r_c \ll r_p \), in the other extreme case, all monomer in a coalesced aqueous drop has been converted to polymer in a very short time relative to the time which elapses between the two coalescences. The total moles of monomer converted to polymer in unit time will be the monomer within the volume of intermixed aqueous phase in unit time. Therefore, the overall polymerisation rate will have the following form:

\[ R_p = [M] r_c \] \[ \text{[9-5]} \]

In this case, the overall polymerisation rate will be intermixing-controlled.

Although a number of works on modelling of drop coalescence have been reported in the literature (see Chapter 2), the quantitative modelling of \( r_c \) in the present system can be very complex. Three difficulties arise: (a) the coalescence is accompanied by a continuous break down of the ARDs and the derived APMPs; (b) the surface tension of the ARDs and derived APMPs varies as they coalesce with the AMODs; and (c) the
fluid viscosity in the polymerising APMPs also varies as polymerisation within them proceeds. The variations in surface tension and fluid viscosity may, in turn, influence the drop mixing. For simplicity, one can model a system in which the ARDs are introduced as a stabilised inverse dispersion (see Section 8.2.6). This will be presented in the following Section.

9.4 MODELLING OF DROP MIXING

9.4.1 Drop-mixing Model

The model presented here only concerns the system which satisfies the following assumptions:

1. the system initially consists of two different types of drops: AMODs and ARDs; and the total volume of ARDs is small relative to that of AMODs.
2. all drops in the system are the same size.
3. the dispersion and distribution of all drops is homogeneous.
4. all coalescence is binary (involving only two drops).
5. all binary coalescence is equally likely.
6. all binary coalescence takes place one by one and is followed immediately by breaking up into two equal size drops.
7. intermixing within coalesced drops takes place instantaneously once coalescence occurs.

Under the above assumptions, the coalescence can be described in terms of "event". An event is defined in the following sequence:

- beginning of coalescence
- intermixing
- break-up
- unmolested travel
- beginning of next coalescence
It must be stressed that, in an event, the beginning of further coalescence does not necessarily involve the same two newly formed drops.

Under assumptions 1 and 2, the system can be divided into small groups: each group consists of one ARD and the same number of AMODs. The number of AMODs in each group depends on the total volume ratio of the two different aqueous phases. Because it is assumed that all drops are the same in size, the number ratio of ARD to AMODs in each group naturally equals their total volume ratio.

For simplicity, let us consider a system in which the total volume ratio of aqueous reductant to aqueous solution of monomer and oxidant is 1 : 3. So each group consists one ARD and three AMODs at the beginning:

\[ \text{R} \quad \text{M} \quad \text{M} \quad \text{M} \]

Here \( \text{R} \) and \( \text{M} \) are an ARD and an AMOD respectively.

Under assumption 6, after a first event, the system will still contain four same-size drops. But the configuration might be altered. If the coalescence takes place between unlike drops (one ARD and one AMOD in the first event), defined as a "heterogeneous event", the new configuration will be the following:

\[ \text{P} \quad \text{P} \quad \text{M} \quad \text{M} \]

Here \( \text{P} \) is an APMP resulting from the coalescence between the ARD and one of the AMODs followed by break-up into two same-size drops. Under the assumption 7, the composition in the two newly formed APMPs is the same.
If the event involves two like drops (two AMODs in the first event), defined as “homogeneous event”, the configuration will remain unchanged.

If we let the reductant molecules in the system be in excess of oxidant molecules required by the redox reaction so that every APMP contains unreacted reductant molecules, a further heterogeneous event involving an APMP and an AMOD will lead to formation of one more polymerising APMP in the group. In this case, all possible configurations of the four drops can easily be shown and numbered:

(1) \[ \text{R} \quad \text{M} \quad \text{M} \quad \text{M} \]
(2) \[ \text{P} \quad \text{P} \quad \text{M} \quad \text{M} \]
(3) \[ \text{P} \quad \text{P} \quad \text{P} \quad \text{M} \]
(4) \[ \text{P} \quad \text{P} \quad \text{P} \quad \text{P} \]

9.4.2 Drop-mixing Rate

It is clear that any particular configuration which is attained in a group is directly influenced by the present configuration and is independent of how the present configuration is achieved. Moreover, the character of this influence remains unchanged as the event proceeds. In the four-drop group, for example, if the group is in configuration 3, the next configuration after another event can only be configuration 3 or 4. This does not depend on how the group arrives in configuration 3. This transition process between configurations can be described as a Markov chain with four possible states (Kurtz, 1991). Here, each configuration corresponds to a specified state.
The conditional probabilities of a Markov chain are defined as (Parzen, 1960):

\[ P(i, j) = \text{conditional probability that the Markov chain is in state } j \]
\[ \text{at time } t, \text{ given that at time } t-1 \text{ it was in state } i \]

The \( m \)-step conditional probabilities are defined as:

\[ P_m(i, j) = \text{conditional probability that the Markov chain at time } t+m \text{ is in} \]
\[ \text{state } j, \text{ given that at time } t \text{ it was in state } i \]

The transition probability \( P \) of a Markov chain with \( r \) states can be conveniently exhibited in the form of a \((r \times r)\) matrix:

\[
P = \begin{bmatrix}
P(1,1) & P(1,2) & P(1,3) & \ldots & P(1, r-1) & P(1, r) \\
P(2,1) & P(2,2) & P(2,3) & \ldots & P(2, r-1) & P(2, r) \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
P(r-1,1) & P(r-1,2) & P(r-1,3) & \ldots & P(r-1, r-1) & P(r-1, r-1) \\
P(r,1) & P(r,2) & P(r,3) & \ldots & P(r, r-1) & P(r, r) 
\end{bmatrix}
\]  

[9-6]

The \( m \)-step transition probability matrix is an \( m \) power matrix:

\[
P_m = P^m
\]

[9-7]

here \( m \) can be 1, 2, 3 \ldots etc, representing the 1st, 2nd, 3rd \ldots etc step transition probability matrix.

For the foregoing described four-drop group, the transition from one configuration (state) to another is step-by-step. For instance, the configurations 3 and 4 can not directly achieved from configuration 1, but are possible from configurations 2 and 3 respectively. Furthermore, the transition can not go backwards, such as from configuration 3 to 2 or 1. Therefore, in the transition probability matrix, one has
\[ P(i, j) = 0 \quad \text{if} \quad j \neq i, \; i + 1 \]  
[9-8]

\[ i = 1, 2, 3 \text{ and } 4 \]

In each transition of configuration, the total possible number of events in a group composing \( N \) drops, denoted by \( N_e \), is the number of possible combinations of \( n \) items taken 2 at a time. For the four-drop group

So,

\[ N_e = \binom{N}{2} = \binom{4}{2} = \frac{4!}{(4-2)!2!} = 6 \]  
[9-9]

In configuration \( i \), the group contains \( i \) ARDs or APMPs and \( (4 - i) \) AMODs. The possible number of heterogeneous event, denoted by \( N_{ihe} \), is \( i(4 - i) \).

Thus,

\[ P(i, j) = \frac{N_{ihe}}{N_e} = \frac{i(4-i)}{6} \quad \text{if} \quad j = i + 1, \; i = 1, 2 \text{ and } 3 \]  
[9-10]

It is apparent that the possible number of homogeneous events, denoted by \( N_{ihho} \), can be obtained by \( N_e - N_{ihe} \).

So,

\[ P(i, j) = 1 - \frac{N_{ihe}}{N_e} \quad \text{if} \quad j = i, \; i = 1, 2, 3 \text{ and } 4 \]  
[9-11]

From [9-8], [9-10] and [9-11], it is clear that the transition probability matrix of this four-drop group is given by

\[
P = \begin{bmatrix}
P(1,1) & P(1,2) & 0 & 0 \\
0 & P(2,2) & P(2,3) & 0 \\
0 & 0 & P(3,3) & P(3,4) \\
0 & 0 & 0 & P(4,4)
\end{bmatrix} = \begin{bmatrix}
1/2 & 1/2 & 0 & 0 \\
0 & 1/3 & 2/3 & 0 \\
0 & 0 & 1/2 & 1/2 \\
0 & 0 & 0 & 1
\end{bmatrix} \]  
[9-12]
According to [9-7], any given step transition probability matrix can be calculated. The 3rd step, for instance, is as follows:

\[
P_3 = P^3 = \begin{bmatrix}
1/8 & 19/72 & 4/9 & 1/6 \\
0 & 1/27 & 19/54 & 11/18 \\
0 & 0 & 1/8 & 7/8 \\
0 & 0 & 0 & 1
\end{bmatrix}
\] [9-13]

This means that after 3 generations

\[
P_3 (1, 1) = 1/8, \quad P_3 (1, 2) = 19/72, \\
P_3 (1, 3) = 4/9, \quad P_3 (1, 4) = 1/6
\]

In order to find the absolute probabilities that the group is in configurations 1, 2, 3 or 4, a knowledge of the original probability distribution is necessary. In the case of the above four-drop group, it is apparent that the configuration 1 is the only configuration present originally. Therefore, the original probability is:

\[
P_0 = \begin{bmatrix} 1 & 0 & 0 & 0 \end{bmatrix}
\] [9-14]

The absolute probabilities that the group is in any given configuration after \(i\) events, denoted as \(P_{ai}\), can be calculated by

\[
P_{ai} = P_0 \cdot P_i
\] [9-15]

For instance, the absolute probabilities that the four-drop group is in each configuration after 3 events can be calculated by
This means that after 3 events

\[ P(\text{in configuration 1}) = \frac{1}{8} \]
\[ P(\text{in configuration 2}) = \frac{19}{72} \]
\[ P(\text{in configuration 3}) = \frac{4}{9} \]
\[ P(\text{in configuration 4}) = \frac{1}{6} \]

Let \( E_{mix} \) denote the extent of drop-mixing, defined as a volume percentage of mixed aqueous phase. Under assumption 2, the extent of drop-mixing can be easily assigned to each group configuration:

- (1) \( E_{mix} = 0 \)
- (2) \( = \frac{2}{4} \)
- (3) \( = \frac{3}{4} \)
- (4) \( = 1 \)
The possibilities of the group being in each configuration after $m$ (can be 0, 1, 2, ....) events can be calculated. For the whole system, therefore, an average extent of drop-mixing after any event can be obtained.

The average extent of drop-mixing after 3 events, for instance, is

$$E_{mix} = [(1/8) (0) + (19/72) (2/4) + (4/9) (3/4) + (1/6) (1)] \times 100\%$$

$$= 63\% \quad [9-17]$$

This means that about 63% volume of aqueous phase becomes APMPs in the system after 3 events.

From the preceding discussion, for a system composing $N$ drops in each group, the extent of drop-mixing after $m$ events can be obtained by the following equation:

$$E_{mix} = P_o \cdot P^m \cdot P_e \quad [9-18]$$

Here $P_o$ is the original probability matrix:

$$P_o = \begin{bmatrix} 1 & 0 & 0 & \cdots & 0 \\ \hline N \end{bmatrix} \quad [9-19]$$

$P$ is the transition probability matrix $P (N \times N)$, in which

$$P(i, j) = \begin{cases} 0, & \text{if } j \neq i, \ i + 1 \quad i = 1, 2, 3, \ldots, N \\ \frac{i(N - i)}{\binom{N}{2}}, & \text{if } j = i + 1 \quad i = 1, 2, 3, \ldots, N - 1 \\ \frac{i(N - i)}{\binom{N}{2}}, & \text{if } j = i \quad i = 1, 2, 3, \ldots, N \\ \end{cases} \quad [9-20]$$
$P^m$ is $m$ power of $P$

$P_e$ is a matrix with its elements corresponding to the extents of drop-mixing for each group configuration:

$$
P_e = \begin{bmatrix}
0 \\
2 / N \\
3 / N \\
\vdots \\
1
\end{bmatrix}^N \quad [9-21]
$$

By using this method, the extent of drop-mixing in a system can be calculated after each event. If the time which elapses between two adjacent events is known, then, the variation of $E_{\text{mix}}$ with time can be obtained. If the volume ratio of the aqueous reductant to the aqueous solution of monomer and oxidant is so small that the increase in volume of mixed aqueous phase via each heterogeneous event is small relative to the total volume of aqueous phase, the variation of $E_{\text{mix}}$ with event or time could be approximately treated as a continuous function and the drop-mixing rate $r_e$ can be obtained by drawing a tangent to the curve of drop-mixing extent versus time (Figure 9-2).

However, the time interval for events is a complicated function of physical properties of the two phases, equipment geometry and operating variables. This treatment requires further work, which is beyond the main objective of the present project.

### 9.4.3 Determination of Expected Drop-mixing Life

As mentioned before, the group configurations can not go backwards. All aqueous drops in a group will become APMPs after a certain number of events and then no change in the group configuration occurs in further events. In this case, the Markov chain is considered to have terminated. A chain which has a capacity to terminate
itself is called an absorbing chain (Kurtz, 1991). The four-drop group, for example, will terminate when it reaches the configuration 4.

An absorbing chain will end eventually, but the length of the chain is a random variable. The length for which an absorbing Markov chain will remain active is defined in terms of expected life and can be calculated. Therefore, for the drop-mixing in the polymerisation system, it is possible to calculate after how many events all the AMODs have become APMPs. The calculation is as follows (Kurtz, 1991):

Firstly, form the matrix $S$:

$$S = (I - P)^{-1}$$  \[9-18\]

![Figure 9-2 Variation of extent of drop-mixing with time](image-url)
here \( I \) is unit matrix and \( p \) is the matrix derived from the transition probability matrix \( P \) (see equation [9-6]) by deleting the row and column pertaining to the final configuration.

Then, set the expected life \( E(\chi) \) equal to the sum of the elements in the first row of matrix \( S \).

For the four-drop group

\[
S = (I - p)^{-1} = \begin{bmatrix}
2 & 3/2 & 2 \\
0 & 3/2 & 2 \\
0 & 0 & 2
\end{bmatrix}
\]

[9-19]

So

\[
E(\chi) = 2 + 3/2 + 2 = 5.5 \text{ (events)}
\]

[9-20]

This means that it will require about 5 to 6 events to bring the group from configuration 1 to 4.

If the time which elapses between two adjacent events is known, it is possible to calculated how long it will take to complete drop-mixing.

9.5 SOME PREDICTIONS FROM MODEL

9.5.1 Difference in Kinetics between Aqueous Polymerisation and Inverse Microsuspension Polymerisation

Equation [9-2] indicates clearly that the kinetic relationship for the inverse microsuspension polymerisation is much more complicated than that for the aqueous polymerisation.

In the kinetic studies (see Chapter 6 and 7), the experimental relationships were obtained by using the initial polymerisation rates and the initial concentrations of the
reactants. For inverse microsuspension polymerisation, in the initial stage, it might be reasonable to assume that both the monomer conversion and the drop-mixing extent are low so that difference of the reactant concentrations between the polymerising APMPs due to the reaction consumption and the dilution are negligible. Thus, the polymerisation rates in all polymerising APMPs can be approximately treated as the same. Then, equation [9-2] becomes:

$$R_p = \frac{\sum v_i}{V} \cdot r_p$$  \[9-22\]

Here, $\sum v_i$, the total volume of polymerising APMPs, is a function of drop-mixing. $r_p$ is the polymerisation rate in a polymerising APMP.

The equation suggests that the overall polymerisation is a product of two functions: polymerisation in polymerising APMPs and drop-mixing. Assume that the polymerisation in the APMPs resembles the kinetics of aqueous polymerisation and that the drop-mixing is independent of the concentrations of the reactants (in fact, the changes in the reactant concentrations may result in variations in some properties of the aqueous drops and particles and hence influence drop-mixing). Then, the relationship of overall polymerisation rate with the concentrations of the reactants has the same form as that for the aqueous polymerisation. The kinetic models presented in Section 6.5.2 suggest that, for aqueous polymerisation, the orders with respect to the reactant concentrations vary with the reactant concentrations. Especially, the reductant concentration plays an important role in determining the reaction orders (see equations [6-27] and [6-29]). In the inverse microsuspension polymerisation, the reductant was added as concentrated aqueous solution without nitrogen pre-purge. So, the real concentration of reductant in the polymerisation locus (APMPs) was much higher than the apparent value in the initial stage. Therefore, it can be expected from the model that the kinetic relationship for the inverse microsuspension polymerisation differs from that for the aqueous polymerisation. The model prediction is in good agreement with the experimental results.
9.5.2 Expected Drop-mixing Life

In the present inverse microsuspension polymerisation system, the volume ratio of the aqueous reductant to the aqueous monomer containing oxidant is about 1 to 66. If the aqueous reductant is introduced as a stabilised dispersion, it is possible to calculate the expected life for drop-mixing.

By using equations [9-6], [9-9], [9-10] and [9-11], the transition probability matrix will be a 67 x 67 matrix:

\[
P = \frac{1}{2211} \begin{bmatrix}
2145 & 66 & 0 & 0 & 0 & \ldots & 0 & 0 \\
0 & 2081 & 130 & 0 & 0 & \ldots & 0 & 0 \\
0 & 0 & 2019 & 192 & \ldots & 0 & 0 \\
0 & 0 & 0 & 1959 & 252 & \ldots & 0 & 0 \\
0 & 0 & 0 & 0 & 1901 & \ldots & 0 & 0 \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
0 & 0 & 0 & 0 & 0 & \ldots & 2145 & 66 \\
0 & 0 & 0 & 0 & 0 & \ldots & 0 & 2211
\end{bmatrix}
\]

From this transition probability matrix, the value of expected life of the system is calculated using equation [9-18]:

\[
E(X) = 315 \quad \text{(events)}
\]

This means it will need about 315 events to convert all AMODs to APMPs.

The time interval for events cannot be directly measured in the experiment. However, it is possible to obtain an approximate value by using the following technique.
As discussed in the above section, the variation of average drop-mixing extent with event can be obtained using equation [9-21]. The calculated drop-mixing extent against event number for the current system is shown in Figure 9-3.

![Figure 9-3 Calculated extent of drop-mixing vs events](image)

From this curve, the number of events for a designated drop-mixing extent can be obtained. If the time for attaining a designated drop-mixing extent can be obtained, for instance, by simulation experiment, the average time interval for events can be worked out.

It is assumed that the reductant concentration in ARDs is high enough to initiate polymerisation in all consequential coalescences involving an AMOD and an ARD or an APMP. In fact, this is not the case in the present inverse microsuspension polymerisation. The reductant concentration in the two APMPs formed after the first
heterogeneous event will be diluted to a half value of that in an ARD regardless the consumption in the initiation reaction with oxidant. When these two APMPs undergo further heterogeneous events with other AMODs, the reductant concentration will be further reduced, and so on. After $n$ continuous heterogeneous events, the reductant concentration in an APMP will be reduced to a value of $[I_r]_0/2^n$ ($[I_r]_0$ represents initial reductant concentration in the ARDs). In the present inverse microsuspension polymerisation, for instance, the highest experimental reductant concentration in the ARDs is about 0.16 mol/l, while the oxidant concentration in the AMODs is about $1.38 \times 10^{-3}$ mol/l. In this case, the reductant concentration will be lower than the oxidant concentration in an APMP which experiences only 7 continuous heterogeneous events regardless of the consumption in the redox reaction. This suggests that an APMP derived from continuous heterogeneous events may lose its capability of further initiation soon and thereafter its coalescence with other AMODs is no longer valid for generating new polymerising APMPs. Therefore, the real expected polymerisation life would be longer than the calculated value.
CHAPTER 10

GENERAL CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

10.1 GENERAL CONCLUSIONS

Work has been performed with the aim of elucidating the mechanism of polymerisation of aqueous acrylic acid dispersed in parafinic oil stabilised with non-ionic surfactant using redox initiators. The major results and achievements are summarised as follows:

In order to examine drop behaviour in the inverse dispersion, efforts have been made to develop appropriate techniques. Scanning electron microscopy with freeze-fracture equipment has been developed for characterising both aqueous drops and polymeric particles in the system throughout the course of emulsification and polymerisation. Transmission electron microscopy has been shown to be an useful technique for examining the polymeric particles in the final inverse lattices although it is not suitable for analysing the unpolymerised aqueous drops in the inverse dispersions due to the volatility of the samples in the vacuum chamber.

A polymerisation apparatus has been constructed. It consists of a glass jacketed reactor, a mechanical stirrer, baffles and a temperature controlling system. The temperature of the inverse dispersion can be automatically controlled at a constant value with a fluctuation of ± 1 °C during polymerisation.

A technique has been developed for measuring monomer conversion by using high pressure liquid chromatography. A reversed-phase HPLC column and an ultra-violet
detector have been employed. It has good sensitivity and reproducibility and hence provides a powerful method for kinetic studies.

The preliminary investigation on drop behaviour in the simulation systems has revealed (1) that the newly introduced big unstabilised aqueous drops coalesce very quickly with the small aqueous drops stabilised with the surfactant in the inverse dispersion; (2) that the drop coalescence and break-up take place simultaneously under agitation.

For the polymerisation of aqueous acrylic acid dispersed in Isopar M stabilised with Witcamide 511 initiated by sodium metabisulphite/potassium bromate redox pair, the research has indicated that (1) the two components of the redox pair, which are initially segregated in two types of aqueous drops, are oil-insoluble; (2) acrylic acid is slightly soluble in the oil phase; (3) neither sodium metabisulphite (reductant) nor potassium bromate (oxidant) are able to initiate polymerisation of aqueous acrylic acid alone; (4) after being added to the inverse dispersion of aqueous monomer-oxidant drops in the oil phase, the aqueous reductant drops undergo continuous break-up under agitation; (5) agitation intensity has pronounced influences on polymerisation rate, particle size and size distribution in the final lattices; (6) polymerisation occurs as soon as the aqueous reductant is added; (7) a second shot of the aqueous reductant induces further initiation of polymerisation whilst a second shot of the aqueous oxidant does not; however, this phenomenon is not observed in the aqueous polymerisation; (8) the initial polymerisation rate is lower in the inverse microsuspension polymerisation than in the aqueous polymerisation with surfactant under identical conditions. These results lead to a hypothesis for the mechanism of inverse microsuspension polymerisation using a redox pair: polymerisation takes place in the aqueous drops generated by simultaneous coalescence and break-up of the different types of aqueous drops. This differs from the mechanisms for both conventional emulsion polymerisation and suspension polymerisation.

A chemical reaction scheme has been proposed, based on the kinetic studies, for the aqueous polymerisation of acrylic acid using sodium metabisulphite/potassium
bromate redox pair. This shows that (1) the reaction mechanism is a free radical polymerisation; (2) the redox reaction is complex and probably produces intermediates which may undergo two competitive reactions: one leads to initiation (which involves the monomer) and the other produces inert products; this redox reaction has much lower activation energy and proceeds very fast at ambient temperature; (3) the chain transfer to the bisulphite anion, which is in equilibrium with the metabisulphite anion, is significant, especially in the case of high mole ratio of reductant to oxidant; (4) oxygen may act as an oxidant in conjunction with the bisulphite anion to initiate polymerisation in addition to its well-known function of free radical scavenger; (5) the surfactant molecules, when present, also function as a kind of transfer agent, resulting in reductions in both polymerisation rate and molecular weight of the produced polymer; (6) the termination is a combination of bimolecular and monomolecular modes.

Kinetic models for the aqueous polymerisations in the presence and in the absence of the surfactant have been developed based on the proposed reaction scheme and are in good agreement with the experimental kinetic relationships.

The kinetic studies on the inverse microsuspension polymerisation have led to a relationship which is different from the experimental kinetic relationship of the aqueous polymerisation in the presence of surfactant. The differences support the hypothesis for the mechanism of the inverse microsuspension polymerisation. However, the overall activation energies for the two kinds of polymerisations are almost identical. This leads to a conclusion that, in the inverse microsuspension polymerisation, the initiation predominantly takes place in the coalesced aqueous drops by the redox reaction and the initiation via transfer of oligomeric radicals or/and surfactant radicals through the oil phase, if it occurs, is of no importance.

The studies on the inverse microsuspension polymerisation by varying some parameters, which have influences on drop mixing, have revealed that (1) the volume of aqueous reductant has a pronounced effect on polymerisation even though the mass of the reductant remains unchanged; (2) the presence of monomer in the aqueous
reductant drops reduces the polymerisation rate and limiting conversion; (3) by adding
the aqueous reductant as a stabilised dispersion, polymerisation occurs with no
retardation, but the polymerisation rate is reduced; (4) continuous addition of the
aqueous reductant increases the limiting monomer conversion; (5) the effect of the
cross-linking agent is negligible in the range of experimental concentrations. These
experimental results provide further evidence for the mechanism hypothesis of the
inverse microsuspension polymerisation.

A preliminary model has been developed for describing inverse microsuspension
polymerisations which proceed by a mechanism described in the hypothesis. The
overall polymerisation rate of such a polymerisation is a function of polymerisation
rate in individual polymerising polymer-monomer drops and of volume percentage of
aqueous phase undergoing polymerisation. In one extreme case, where the drop-
mixing finishes at very low monomer conversion, the polymerisation kinetics is the
same as that of a conventional suspension polymerisation; in the other extreme case,
where the polymerisation in a coalesced aqueous drop completes as soon as the
coalescence between the two types of aqueous drops occurs, the overall
polymerisation rate is a product of drop-mixing rate and the monomer concentration.
The drop-mixing has been modelled by using Markov chain theory. A relationship
between drop-mixing extent and drop coalescence number has been derived. The
expected drop-mixing life, in terms of drop coalescence number, can be determined by
the model.

10.2 SUGGESTIONS FOR FURTHER WORK

For further investigation, work might be done on the following aspects:

1. Chemical reaction mechanism

A chemical reaction scheme has been proposed in the present work. However, the
details of some reactions are still not clear and further research is required. These
could include (1) verification of the proposed mechanism of redox reaction; (2) details
of monomolecular termination; (3) transfer reaction of free radicals to the surfactant molecules; (4) reason(s) for the relatively low limiting monomer conversion.

End-group studies can provide information of the structure of primary radicals and hence might be an useful technique for verifying the mechanism of the redox reaction. The current work has shown a possible reason for the limited monomer conversions in the polymerisation of acrylic acid using sodium metabisulphite/potassium bromate redox pair; that is, the quick consumption of the redox initiators under the experimental conditions. More precise determination of the half-life of the redox pair and a series of polymerisation which use initiators with different half-life values would provide more information.

2. Process mechanism and drop-mixing control

The current research has demonstrated a possibility of transfer of the oligomeric radicals through the oil phase although it seems not to be important in initiation. To clarify this kind of initiation, it might be helpful to perform and compare inverse microsuspension polymerisations in the presence and in the absence of an oil-soluble inhibitor. The oil-soluble inhibitor must be completely water-insoluble to avoid interference from inhibition in the aqueous phase.

In view of the complicated nature of drop-mixing and its crucial role in the inverse microsuspension polymerisation, some knowledge is required for the optimum control of the process:

(1) The aqueous drops in the system are unlikely to be initiated at the same time and the fluid viscosity in a polymerising polymer-monomer particle varies with monomer conversion inside the drops. Therefore, there is a need to clarify the effect of monomer conversion in a polymer-monomer particle on its break-up and coalescence with other aqueous drops/particles.
2) In industry, the majority of polymerisations are performed under non-isothermal conditions. The knowledge of drop-mixing at varied temperatures would be important in these cases.

(3) It has been shown that the continuous addition of the aqueous reductant has potential advantages, such as quick distribution of the reductant in the aqueous phase, increase in the limiting monomer conversion and better temperature control. A systematic study is required to establish the optimum feed policies for addition of the reductant to an agitated monomer dispersion.

3. Process modelling

The preliminary modelling in the present work leads to a possible way to construct a process model. Further work is required for this purpose.
NOTATION

\( A \)  
HPLC integrated area (relative unit)

\( A_a \)  
pre-exponential factor in Arrhenius equation

\( c \)  
polymer concentration in diluted aqueous solution for intrinsic viscosity measurement (g/dl)

\( C \)  
impurity molecules

\( C_{AA} \)  
concentration of acrylic acid in aqueous solution for HPLC measurement (ppm)

\( E_a \)  
overall activation energy (kJ/mol)

\( E_{mix} \)  
the extent of drop-mixing, defined as a volume percentage of mixed aqueous phase

\( f \)  
initiation efficiency

\( f(c) \)  
function of reactant concentrations

\( I \)  
overall rate of producing primary radicals (mol·l\(^{-1}\)·min\(^{-1}\))

\( [I_i]_0 \)  
initial reductant concentration in ARDs

\( K \)  
equilibrium constant between \( S_2O_5^{2-} \) and \( HSO_3^- \)

\( k \)  
overall reaction rate constant

\( k_d \)  
rate constant of decomposition of intermediate \( [HO_3SOBrO_2]^2- \) to inert products

\( k_i \)  
rate constant of monomer initiation by intermediate \( [HO_3SOBrO_2]^2- \)

\( k'_i \)  
rate constant of initiation of monomer by primary radical

\( k'_{i,s} \)  
rate constant of initiation of surfactant molecules by primary radical

\( k_p \)  
propagation rate constant

\( k_{redox} \)  
rate constant of redox reaction between \( HSO_3^- \) and \( BrO_3^- \)
Notation

\[ k_{ox} \quad \text{rate constant of reaction between HSO}_3^- \text{ and } O_2 \]
\[ k_{s,i} \quad \text{rate constant of initiation of monomer by surfactant radicals} \]
\[ k_t \quad \text{bimolecular termination rate constant} \]
\[ k_{t,s} \quad \text{rate constant of monomolecular termination by impurity molecules} \]
\[ k_{ir} \quad \text{rate constant of transfer to HSO}_3^- \]
\[ k_{t,R} \quad \text{rate constant of termination of primary radicals } R\cdot \]
\[ k_{ir,s} \quad \text{rate constant of transfer to surfactant molecules} \]
\[ k_{ts} \quad \text{rate constant of recombination of surfactant radicals} \]
\[ k'_{ts} \quad \text{rate constant of termination of surfactant radical by impurity molecules} \]
\[ l \quad \text{slope of tangent to monomer conversion curve for zero polymerisation time} \]
\[ M \quad \text{monomer} \]
\[ M\cdot \quad \text{monomer radical} \]
\[ M_n\cdot, M_m\cdot \quad \text{macroradicals containing } n \text{ and } m \text{ monomer units} \]
\[ M_v \quad \text{viscosity molecular weight} \]
\[ [M]_0 \quad \text{initial monomer concentration (mol·L}^{-1} \text{)} \]
\[ n \quad \text{testing head speed in viscosity measurement (min}^{-1} \text{)} \]
\[ N_e \quad \text{the total possible number of events in each group of drops in every transition of configuration} \]
\[ N_{ihe} \quad \text{possible number of heterogeneous event in each drop group in every transition of configuration} \]
\[ N_{iho} \quad \text{possible number of homogeneous events in each drop group in every transition of configuration} \]
\[ P \quad \text{transition probability} \]
<table>
<thead>
<tr>
<th>Notation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{ai}$</td>
<td>absolute probabilities of the drop group in any given configuration after $i$ events</td>
</tr>
<tr>
<td>$P_o$</td>
<td>original probability</td>
</tr>
<tr>
<td>$P_m$</td>
<td>$m$-step transition probability</td>
</tr>
<tr>
<td>$P(i, j)$</td>
<td>conditional probability that the Markov chain is in configuration $j$ at time $t$, given that at time $t-1$ it was in configuration $I$</td>
</tr>
<tr>
<td>$P_m(i, j)$</td>
<td>$m$-step conditional probability that the Markov chain is at time $t+m$ in configuration $j$, given that at time $t$ it was in configuration $i$</td>
</tr>
<tr>
<td>$Q$</td>
<td>resulting torque in viscosity measurement, scale grade</td>
</tr>
<tr>
<td>$R_i$</td>
<td>rate of monomer initiation by reaction between $[\text{HO}_3\text{SOBrO}_2]^{2-}$ and monomer</td>
</tr>
<tr>
<td>$R_{\text{ox}}$</td>
<td>rate of producing primary radicals by reaction between $\text{HSO}_3^-$ and $O_2$</td>
</tr>
<tr>
<td>$R_p$</td>
<td>overall polymerisation rate, expressed in terms of molar concentration of monomer convert to polymer in unit time, $-d[M]/dt$ (mol·l⁻¹·min⁻¹)</td>
</tr>
<tr>
<td>$R_{po}$</td>
<td>initial polymerisation rate, expressed in terms of molar concentration of monomer convert to polymer in unit time, $-d[M]/dt$ (mol·l⁻¹·min⁻¹)</td>
</tr>
<tr>
<td>$R.$</td>
<td>primary radicals</td>
</tr>
<tr>
<td>$r_c$</td>
<td>drop-mixing rate, expressed in terms of volume percentage of mixed aqueous phase (generated to polymerising APMPs) in unit time, $\frac{1}{V} \frac{dv}{dt}$ (min⁻¹)</td>
</tr>
<tr>
<td>$r_p$</td>
<td>polymerisation rate within polymerising APMPs at time $t$, expressed in terms of molar concentration of monomer convert to polymer in unit time, $-d[M]/dt$ (mol·l⁻¹·min⁻¹)</td>
</tr>
<tr>
<td>$S$</td>
<td>surfactant molecules</td>
</tr>
<tr>
<td>$S.$</td>
<td>surfactant radical</td>
</tr>
<tr>
<td>$T$</td>
<td>absolute temperature (K)</td>
</tr>
<tr>
<td>$V$</td>
<td>total volume of aqueous phase in inverse dispersion system (litre)</td>
</tr>
<tr>
<td>Notation</td>
<td>Description</td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\nu_i$</td>
<td>volume of the aqueous phase (APMPs) polymerising at rate $r_{pi}$ (litre)</td>
</tr>
<tr>
<td>$W_{polym}$</td>
<td>weight percentage of dried polymer portion in specimen</td>
</tr>
<tr>
<td>$W_{AAO}$</td>
<td>weight percentage of AA in initial inverse dispersion</td>
</tr>
<tr>
<td>$\eta_r$</td>
<td>relative viscosity</td>
</tr>
<tr>
<td>$\eta_{sp}$</td>
<td>specific viscosity</td>
</tr>
<tr>
<td>$[\eta]$</td>
<td>intrinsic viscosity</td>
</tr>
<tr>
<td>[ ]</td>
<td>concentration of reactant (mol·l$^{-1}$)</td>
</tr>
<tr>
<td>[ ]$_o$</td>
<td>initial concentration of reactant (mol·l$^{-1}$)</td>
</tr>
</tbody>
</table>
## ABBREVIATION

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA</td>
<td>acrylic acid</td>
</tr>
<tr>
<td>Aerosol OT</td>
<td>sodium bis(2-ethylhexyl) sulfo succinate</td>
</tr>
<tr>
<td>ADVN</td>
<td>2, 2'-azobis(2, 4-dimethyl valeronitrile)</td>
</tr>
<tr>
<td>AIBEA</td>
<td>2,2'-azobis [N-(2-hydroxyethyl) butyramidine]</td>
</tr>
<tr>
<td>AIBN</td>
<td>azobisisobutyronitrile</td>
</tr>
<tr>
<td>AMODs</td>
<td>aqueous monomer-oxidant drops</td>
</tr>
<tr>
<td>APMPs</td>
<td>polymer-monomer particles</td>
</tr>
<tr>
<td>ARDs</td>
<td>aqueous reductant drops</td>
</tr>
<tr>
<td>BP</td>
<td>benzoyl peroxide</td>
</tr>
<tr>
<td>CMC</td>
<td>critical micelle concentration</td>
</tr>
<tr>
<td>DI water</td>
<td>distilled and de-ionised water</td>
</tr>
<tr>
<td>DP</td>
<td>degree of polymerisation</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectrophotometry</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>HPLC</td>
<td>high pressure liquid chromatography</td>
</tr>
<tr>
<td>Isopar M</td>
<td>mixture of branched parafins</td>
</tr>
<tr>
<td>MBA</td>
<td>methylene bisacrylamide</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>PEM</td>
<td>pentaerythritol myristate</td>
</tr>
<tr>
<td>rpm</td>
<td>revolution per minute</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electronic microscope</td>
</tr>
<tr>
<td>Sintanide-5</td>
<td>oxyethylated amide of stearic acid</td>
</tr>
<tr>
<td>Sorbital C-20</td>
<td>mixture of polyethylene glycolic esters of mono- and distearates of hydrosorbites</td>
</tr>
<tr>
<td>Span 60</td>
<td>sorbitan monostearate</td>
</tr>
<tr>
<td>Span 80</td>
<td>sorbitan monooleate</td>
</tr>
<tr>
<td>SSK</td>
<td>ρ-styrene sulphonates potassium</td>
</tr>
<tr>
<td>SSN</td>
<td>ρ-styrene sulphonates of sodium</td>
</tr>
</tbody>
</table>
Abbreviation

Tetronic 102  polyoxyethylene adduct of polyoxypropylene-ethylene diamine adduct
THF         tetrahydrofuran
UV          ultra-violet
Versenex 80  an aqueous solution of pentasodium salt of diethylenetriamine-
             pentaacetic acid
Witcamide 511 surfactant (tall oil fatty acid diethanolamide)
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APPENDIX I  MATERIALS

1. Acrylic Acid (Scott Bader Company Limited)
   1) chemical nature  \(\text{CH}_2=\text{CH—COOH}\)
   2) physical data  form: liquid,  density: 1.046 g/cm\(^3\) (20 °C)
   melting point: ca. 13 °C,  boiling point: 141 °C

2. Potassium Bromate  (Berk Chemicals Ltd, UK)
   1) chemical nature  \(\text{KBrO}_3\)
   2) physical data  form: solid  melting point: 430 °C
   solubility: water-soluble (8 g/100g water at 20 °C)

3. Sodium Metabisulphite  (William Blythe & Co Limited, UK)
   1) chemical nature  \(\text{Na}_2\text{S}_2\text{O}_5\)
   2) physical data  form: solid  melting point: <100 °C
   solubility: water-soluble (40% w/w at 20 °C)
   3) specification  assay: > 96.5%  \(\text{SO}_2\): >65%  \(\text{Na}_2\text{S}_2\text{O}_3\): <0.03%
   Fe: <10 ppm  Pb: <10 ppm  Se: <30 ppm

4. Isopar M  (Exxon Chemical Company, USA)
   1) chemical nature  a mixture of paraffinic solvent, chemical formula is not known
   2) physical data  form: liquid  boiling point: 199 - 257 °C
   density: 0.79 g/ml at 15 °C  solubility in water: <0.1 wt% at 20 °C

5. Witcamide 511  (The Baxenden Chemical Co. Ltd, UK)
   1) chemical nature  tall oil fatty acid diethanolamide
   the 3 major components:  oleic diethanolamide \((\text{C}_{18})\) 1 double bond
   linoleic diethanolamide \((\text{C}_{18})\) 2 double bonds
   pinolenic diethanolamide \((\text{C}_{18})\) 3 double bonds
2) physical data  
form: liquid  
density: 0.96 g/ml at 25 °C  
solubility in water: insoluble at 25 °C

6. N, N'- methylene-bisacrylamide  (Klaus F. Meyer GmbH, Germany)
   1) chemical nature  
      \[ \text{CH}_2\text{CHCONH}-\text{CH}_2\text{-NHCOCH=CH}_2 \]
   2) physical data  
      form: solid  
solubility in water: 3.5 g/100 ml water at 30 °C  
      purity  98.3 wt%

7. Versenex 80  (The Dow Chemical Company, USA)
   1) chemical nature  
an aqueous solution of pentasodium salt of diethylenetriamine-pentaacetic acid
   \[ (\text{NaOOCCH}_2)_2\text{NCH}_2\text{CH}_2\text{-N-CH}_2\text{CH}_2\text{N(CH}_2\text{COONa})_2 \]
   \[ \text{CH}_2\text{COONa} \]
   2) physical data  
      form: aqueous solution  
      freezing point: -20 °C

8. Span 80  (ICI, Belgium)
   1) chemical nature  
sorbitan monooleate
   2) physical data  
      form: liquid  
      boiling point: >100 °C  
solubility in water: insoluble  
density: ca. 1.0 g/ml at 25 °C

9. Ammonium Hydroxide  (Fisher Scientific UK Ltd)
   1) chemical nature  
      \[ \text{NH}_4\text{OH} \]
   2) physical data  
      0.88 specific gravity  
      laboratory reagent

10. Hydroquinone  (Fisher Scientific UK Ltd)
    laboratory reagent

11. 2-Propanol  (Fisher Scientific UK Ltd)
    HPLC grade
12. Acetone (Fisher Scientific UK Ltd)  
   HPLC grade

13. Tetrahydrofuran (Fisher Scientific UK Ltd)  
   HPLC grade

14. Phosphoric Acid (Fisher Scientific UK Ltd)  
   85 wt% aqueous solution laboratory reagent

15. Methylene blue (Opkin & Williams Ltd, UK)  
   laboratory reagent

16. Methyl Red (The British Drug Houses Ltd, UK)  
   laboratory reagent

17. Potassium Permanganate (Fisher Scientific UK Ltd)  
   laboratory reagent

18. Cupric Sulphate (Fisher Scientific UK Ltd)  
   laboratory reagent

19. Rubeanic Acid (Aldrich Chemical Co. Ltd)  
   Laboratory reagent
Appendix

APPENDIX II

DETERMINATION OF HPLC CALIBRATION EQUATION BY LEAST SQUARES METHOD

A series of standard samples of aqueous acrylic acid were characterised by HPLC under the conditions described in Figure 4-12. The experimental results are listed in the following table:

<table>
<thead>
<tr>
<th>sample number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{AA}$</td>
<td>11.59</td>
<td>28.98</td>
<td>57.95</td>
<td>86.93</td>
<td>115.91</td>
<td>144.89</td>
</tr>
<tr>
<td>$A$</td>
<td>2.32</td>
<td>6.19</td>
<td>12.01</td>
<td>17.96</td>
<td>23.45</td>
<td>30.77</td>
</tr>
</tbody>
</table>

Here $C_{AA}$ and $A$ represent acrylic acid concentration (ppm) and HPLC integrated area respectively.

Suppose $C_{AA}$ and $A$ have linear relationship:

$$C_{AA} = aA + b$$

Here $a$ and $b$ are constants.

According to least squares method, from the above table, we have:

$$\sum A = 92.70, \quad \sum C_{AA} = 446.25$$
$$\sum A^2 = 2007.20, \quad \sum C_{AA}^2 = 46317.44, \quad \sum A \cdot C_{AA} = 9639.87$$

So

$$l_{xx} = \sum A^2 - \frac{1}{n}(\sum A)^2 = 574.98$$
$$l_{xy} = \sum A \cdot C_{AA} - \frac{1}{n}(\sum A)(\sum C_{AA}) = 2745.31$$
$$l_{yy} = \sum C_{AA}^2 - \frac{1}{n}(\sum C_{AA})^2 = 13127.59$$
\[ a = \frac{l_{xy}}{l_{xx}} = \frac{2745.31}{574.98} = 4.77 \]
\[ b = \frac{1}{n} (\Sigma A - a \Sigma C_{AA}) = \frac{1}{6} (446.25 - 4.77 \times 92.7) = 0.61 \]

Therefore \[ C_{AA} = 4.77 A + 0.61 \] [4-1]
APPENDIX III  A TYPICAL RESULT OF MONOMER CONVERSION DETERMINATION USING HPLC (Expt. A-2)

<table>
<thead>
<tr>
<th>specimen No.</th>
<th>time (min)</th>
<th>$W_s$ (g)</th>
<th>$W_{s+p}$ (g)</th>
<th>$W$ (g)</th>
<th>HPLC integrated area</th>
<th>monomer conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>run 1</td>
<td>run 2</td>
</tr>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.3087</td>
<td>3.9364</td>
<td>0.0668</td>
<td>8.5697</td>
<td>8.5705</td>
</tr>
<tr>
<td>2</td>
<td>1.00</td>
<td>0.3630</td>
<td>4.0847</td>
<td>0.0659</td>
<td>9.2622</td>
<td>9.2492</td>
</tr>
<tr>
<td>3</td>
<td>3.00</td>
<td>0.4498</td>
<td>4.0668</td>
<td>0.0738</td>
<td>10.9018</td>
<td>10.9144</td>
</tr>
<tr>
<td>4</td>
<td>5.50</td>
<td>0.4522</td>
<td>3.5311</td>
<td>0.0754</td>
<td>10.9634</td>
<td>11.1056</td>
</tr>
<tr>
<td>5</td>
<td>7.00</td>
<td>0.3608</td>
<td>4.1916</td>
<td>0.0716</td>
<td>6.7723</td>
<td>6.8033</td>
</tr>
<tr>
<td>6</td>
<td>10.00</td>
<td>0.3673</td>
<td>4.1351</td>
<td>0.0741</td>
<td>6.6890</td>
<td>6.6736</td>
</tr>
<tr>
<td>7</td>
<td>15.00</td>
<td>0.4405</td>
<td>4.0859</td>
<td>0.0741</td>
<td>7.1081</td>
<td>7.1724</td>
</tr>
<tr>
<td>8</td>
<td>20.00</td>
<td>0.4937</td>
<td>4.0548</td>
<td>0.0762</td>
<td>7.6096</td>
<td>7.5994</td>
</tr>
<tr>
<td>9</td>
<td>25.00</td>
<td>0.6176</td>
<td>3.8000</td>
<td>0.0714</td>
<td>8.8134</td>
<td>8.8036</td>
</tr>
<tr>
<td>10</td>
<td>30.00</td>
<td>0.6716</td>
<td>3.9044</td>
<td>0.0725</td>
<td>9.0343</td>
<td>8.9065</td>
</tr>
<tr>
<td>11</td>
<td>35.00</td>
<td>0.6135</td>
<td>4.2989</td>
<td>0.0764</td>
<td>7.5981</td>
<td>7.5619</td>
</tr>
<tr>
<td>12</td>
<td>40.83</td>
<td>0.5135</td>
<td>3.4022</td>
<td>0.0738</td>
<td>7.1247</td>
<td>7.1561</td>
</tr>
<tr>
<td>13</td>
<td>45.67</td>
<td>0.5074</td>
<td>3.0989</td>
<td>0.0740</td>
<td>7.7783</td>
<td>7.7249</td>
</tr>
<tr>
<td>14</td>
<td>50.00</td>
<td>0.5013</td>
<td>3.6659</td>
<td>0.0751</td>
<td>6.4651</td>
<td>6.6157</td>
</tr>
<tr>
<td>15</td>
<td>55.00</td>
<td>0.4670</td>
<td>3.8554</td>
<td>0.0754</td>
<td>5.6225</td>
<td>5.6347</td>
</tr>
<tr>
<td>16</td>
<td>60.00</td>
<td>0.583</td>
<td>4.1049</td>
<td>0.0855</td>
<td>6.4853</td>
<td>6.4321</td>
</tr>
</tbody>
</table>

$W_s$ weight of specimen withdrawn from reactor

$W_{s+p}$ weight of mixture of specimen in 2-propanol

$W$ weight of transparent liquid of centrifuged mixture of specimen in 2-propanol, which is then diluted using the eluent for HPLC analysis

The monomer conversion is calculated by the following equation:

$$\text{conversion} = 1 - \frac{(C_{AA} \cdot W_{s+p} / W \cdot W_s)_i}{(C_{AA} \cdot W_{s+p} / W \cdot W_s)_o}$$

Here subscript $i$ and $o$ refer to $ith$ and initial specimens respectively. $C_{AA}$ is calculated using equation [4-1] (see Chapter 4 or Appendix II).
### Appendix

**APPENDIX IV  ORIGINAL DATA OF AQUEOUS POLYMERISATION WITHOUT SURFACTANT**

(a) **Effect of Polymerisation Temperature**

<table>
<thead>
<tr>
<th>expt. No.</th>
<th>temp. °C</th>
<th>$R_{po} \cdot 10^2$ mol/l·min</th>
<th>compositions and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-1</td>
<td>13</td>
<td>1.98</td>
<td>[AA]$_o$ = 1.99 mol/l</td>
</tr>
<tr>
<td>W-2</td>
<td>23</td>
<td>3.35</td>
<td>$[Na_2S_2O_3]_o = 2.61 \times 10^{-3}$ mol/l</td>
</tr>
<tr>
<td>W-3</td>
<td>33</td>
<td>4.62</td>
<td>$[KBrO_3]_o = 1.42 \times 10^{-3}$ mol/l</td>
</tr>
<tr>
<td>W-4</td>
<td>43</td>
<td>6.29</td>
<td>pH 5.1</td>
</tr>
</tbody>
</table>

(b) **Effect of Monomer Concentration**

<table>
<thead>
<tr>
<th>expt. No.</th>
<th>[AA]$_o$ mol/l</th>
<th>$R_{po} \cdot 10^2$ mol/l·min</th>
<th>other compositions and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-c-1</td>
<td>0.60</td>
<td>1.53</td>
<td>$[Na_2S_2O_3]_o = 7.56 \times 10^{-4}$ mol/l</td>
</tr>
<tr>
<td>L-c-2</td>
<td>1.05</td>
<td>4.23</td>
<td>$[KBrO_3]_o = 1.38 \times 10^{-3}$ mol/l</td>
</tr>
<tr>
<td>L-b-3</td>
<td>1.99</td>
<td>13.44</td>
<td>pH 5.1</td>
</tr>
<tr>
<td>L-c-4</td>
<td>3.39</td>
<td>37.59</td>
<td>temp. 23 °C</td>
</tr>
</tbody>
</table>

(c) **Effect of Reductant Concentration**

<table>
<thead>
<tr>
<th>expt. No.</th>
<th>$[Na_2S_2O_3]_o$ 10$^4$ mol/l</th>
<th>$R_{po} \cdot 10^2$ mol/l·min</th>
<th>other compositions and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-b-1</td>
<td>3.95</td>
<td>9.66</td>
<td>[AA]$_o = 1.99$ mol/l</td>
</tr>
<tr>
<td>L-b-3</td>
<td>7.56</td>
<td>13.44</td>
<td>$[KBrO_3]_o = 1.38 \times 10^{-3}$ mol/l</td>
</tr>
<tr>
<td>L-b-4</td>
<td>11.34</td>
<td>15.12</td>
<td>pH 5.1</td>
</tr>
<tr>
<td>L-b-5</td>
<td>15.53</td>
<td>----</td>
<td>temp. 23 °C</td>
</tr>
<tr>
<td>L-d-1</td>
<td>22.68</td>
<td>23.98</td>
<td></td>
</tr>
</tbody>
</table>
(d) Effect of Oxidant Concentration

<table>
<thead>
<tr>
<th>expt. No.</th>
<th>$[KBrO_3]_0 \times 10^4$ mol/l</th>
<th>$R_{po} \cdot 10^2$ mol/l·min</th>
<th>other compositions and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-a-1</td>
<td>3.15</td>
<td>5.41</td>
<td>$[AA]_0 = 1.99$ mol/l</td>
</tr>
<tr>
<td>L-b-4</td>
<td>13.77</td>
<td>15.12</td>
<td>$[Na_2S_2O_3]_0 = 11.34 \times 10^{-4}$ mol/l, pH 5.1</td>
</tr>
<tr>
<td>L-a-6</td>
<td>20.20</td>
<td>23.69</td>
<td></td>
</tr>
<tr>
<td>L-a-4</td>
<td>25.86</td>
<td>24.41</td>
<td>temp. 23 °C</td>
</tr>
<tr>
<td>L-a-5</td>
<td>35.44</td>
<td>29.75</td>
<td></td>
</tr>
<tr>
<td>L-a-7</td>
<td>38.12</td>
<td>37.36</td>
<td></td>
</tr>
</tbody>
</table>

(e) Effect of pH value of Initial Reaction Mixture

<table>
<thead>
<tr>
<th>expt. No.</th>
<th>pH</th>
<th>compositions and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA-1</td>
<td>3.8</td>
<td>$[AA]_0 = 1.99$ mol/l, $[Na_2S_2O_3]_0 = 2.27 \times 10^{-3}$ mol/l</td>
</tr>
<tr>
<td>AA-3</td>
<td>5.1</td>
<td>$[KBrO_3]_0 = 1.38 \times 10^{-3}$ mol/l, temp. 23 °C</td>
</tr>
<tr>
<td>AA-2</td>
<td>7.1</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX V
ORIGINAL DATA OF AQUEOUS POLYMERISATION WITH SURFACTANT

(a) Effect of Concentration of Acrylic Acid

<table>
<thead>
<tr>
<th>expt. No.</th>
<th>([AA]_0) mol/l</th>
<th>(R_{po} \cdot 10^2) mol/l·min</th>
<th>other compositions and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-a-1</td>
<td>0.98</td>
<td>4.07</td>
<td>([Na_2S_2O_3]_0 = 2.34 \times 10^{-3}) mol/l</td>
</tr>
<tr>
<td>P-a-2</td>
<td>1.54</td>
<td>8.76</td>
<td>([KBrO_3]_0 = 1.38 \times 10^{-3}) mol/l</td>
</tr>
<tr>
<td>P-a-3</td>
<td>1.99</td>
<td>16.30</td>
<td>([MBAl]_0 = 9.35 \times 10^{-4}) mol/l</td>
</tr>
<tr>
<td>P-a-4</td>
<td>2.50</td>
<td>21.85</td>
<td>([S]_0 = 1.71) wt%, pH 5.1, temp. 23 °C</td>
</tr>
<tr>
<td>P-a-5</td>
<td>3.02</td>
<td>37.14</td>
<td>pH 5.1, temp. 23 °C</td>
</tr>
</tbody>
</table>

(b) Effect of Reductant Concentration

<table>
<thead>
<tr>
<th>expt. No.</th>
<th>([Na_2S_2O_3]_0 \times 10^4) mol/l</th>
<th>(R_{po} \cdot 10^2) mol/l·min</th>
<th>other compositions and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-b-1</td>
<td>3.96</td>
<td>7.02</td>
<td>([AA]_0 = 1.99) mol/l</td>
</tr>
<tr>
<td>P-b-2</td>
<td>7.84</td>
<td>8.56</td>
<td>([KBrO_3]_0 = 1.38 \times 10^{-3}) mol/l</td>
</tr>
<tr>
<td>P-b-3</td>
<td>11.79</td>
<td>11.26</td>
<td>([MBAl]_0 = 9.35 \times 10^{-4}) mol/l</td>
</tr>
<tr>
<td>P-b-4</td>
<td>15.12</td>
<td>14.76</td>
<td>([S]_0 = 1.71) wt%, pH 5.1, temp. 23 °C</td>
</tr>
<tr>
<td>P-b-5</td>
<td>23.40</td>
<td>16.30</td>
<td>pH 5.1, temp. 23 °C</td>
</tr>
</tbody>
</table>

(c) Effect of Oxidant Concentration

<table>
<thead>
<tr>
<th>expt. No.</th>
<th>([KBrO_3]_0 \times 10^4) mol/l</th>
<th>(R_{po} \cdot 10^2) mol/l·min</th>
<th>other compositions and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-c-2</td>
<td>7.15</td>
<td>7.89</td>
<td>([AA]_0 = 1.99) mol/l</td>
</tr>
<tr>
<td>P-c-3</td>
<td>13.84</td>
<td>11.26</td>
<td>([Na_2S_2O_3]_0 = 1.18 \times 10^{-3}) mol/l</td>
</tr>
<tr>
<td>P-c-4</td>
<td>20.10</td>
<td>14.23</td>
<td>([MBAl]_0 = 9.35 \times 10^{-4}) mol/l</td>
</tr>
<tr>
<td>P-c-5</td>
<td>27.28</td>
<td>19.70</td>
<td>([S]_0 = 1.71) wt%, pH 5.1, temp. 23 °C</td>
</tr>
<tr>
<td>P-c-6</td>
<td>37.74</td>
<td>23.38</td>
<td>pH 5.1, temp. 23 °C</td>
</tr>
</tbody>
</table>
(d) Effect of Surfactant Concentration

<table>
<thead>
<tr>
<th>expt. No.</th>
<th>$[S]_o$ wt% on aqueous phase</th>
<th>other compositions and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-d-1</td>
<td>0.00</td>
<td>$[AA]_o = 1.99 \text{ mol/l}$</td>
</tr>
<tr>
<td>P-d-1</td>
<td>1.71</td>
<td>$[Na_2S_2O_3]_o = 2.27 \times 10^{-3} \text{ mol/l}$</td>
</tr>
<tr>
<td>L-e-2</td>
<td>3.36</td>
<td>$[KBrO_3]_o = 1.38 \times 10^{-3} \text{ mol/l}$</td>
</tr>
<tr>
<td>P-d-3</td>
<td>4.95</td>
<td>pH 5.1</td>
</tr>
<tr>
<td>P-d-4</td>
<td>6.49</td>
<td>temp. 23 °C</td>
</tr>
</tbody>
</table>
(a) Effect of Reductant Concentration on Intrinsic Viscosity

**Expt. L-b-1**

\[ y = 11.768 + 68.995x \quad r^2 = 0.979 \]

\[ y = 11.919 - 12.130x \quad r^2 = 0.738 \]

**Expt. L-b-3**

\[ y = 8.445 + 7.303x \quad r^2 = 0.992 \]

\[ y = 8.303 - 19.400x \quad r^2 = 0.994 \]

**Expt. L-b-5**

\[ y = 5.301 + 4.447x \quad r^2 = 0.989 \]

\[ y = 5.258 - 7.300x \quad r^2 = 0.987 \]

**Expt. L-d-1**

\[ y = 3.011 + 2.339x \quad r^2 = 0.997 \]

\[ y = 3.008 - 1.964x \quad r^2 = 0.998 \]
(b) Effect of Oxidant Concentration on Intrinsic Viscosity

Expt. L-a-1

\[ y = 7.467 + 21.603x \quad r^2 = 1.000 \]
\[ y = 7.477 - 7.221x \quad r^2 = 1.000 \]

Expt. L-b-4

\[ y = 5.728 + 5.199x \quad r^2 = 0.943 \]
\[ y = 5.885 - 8.947x \quad r^2 = 0.977 \]

Expt. L-a-6

\[ y = 5.924 + 0.000x \quad r^2 = 1.000 \]
\[ y = 5.853 - 12.962x \quad r^2 = 0.997 \]

Expt. L-a-5

\[ y = 5.338 + 7.187x \quad r^2 = 0.946 \]
\[ y = 5.315 - 5.926x \quad r^2 = 0.958 \]
Appendix

(c) Effect of Polymerisation Time on Intrinsic Viscosity

Expt. AA-3  6 minute polymerisation

Expt. AA-3  10 minute polymerisation

Expt. AA-3  20 minute polymerisation

Expt. AA-3  30 minute polymerisation
Expt. AA-3  60 minute polymerisation

\[ y = 2.986 + 3.970x \quad r^2 = 0.992 \]

\[ y = 3.005 - 0.944x \quad r^2 = 0.934 \]
(d) Effect of Surfactant Concentration on Intrinsic Viscosity

Expt. P-d-1
1.71 wt% surfactant

Expt. L-e-2
3.36 wt% surfactant

Expt. P-d-3
4.95 wt% surfactant

Expt. P-d-4
6.49 wt% surfactant
APPENDIX VII
ORIGINAL DATA OF INVERSE MICROSPUSPENSION POLYMERISATION

(a) Effect of Polymerisation Temperature

<table>
<thead>
<tr>
<th>expt. No.</th>
<th>temp. °C</th>
<th>$R_{po}$ · 10⁻² mol/l-min</th>
<th>compositions and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>13</td>
<td>1.84</td>
<td>$[AA]_o = 4.24$ mol/l, $[S]_o = 10$ wt% of oil phase,</td>
</tr>
<tr>
<td>A-2</td>
<td>23</td>
<td>2.56</td>
<td>$[Na_2S_2O_3]_o = 7.85 \times 10^{-4}$ mol/l,</td>
</tr>
<tr>
<td>A-3</td>
<td>33</td>
<td>3.85</td>
<td>$[KBrO_3]_o = 1.73 \times 10^{-3}$ mol/l,</td>
</tr>
<tr>
<td>A-4</td>
<td>43</td>
<td>5.29</td>
<td>pH 5.1, crossed-paddle stirrer at 1000 rpm</td>
</tr>
</tbody>
</table>

(b) Effect of Monomer Concentration

<table>
<thead>
<tr>
<th>expt. No.</th>
<th>$[AA]_o$ mol/l</th>
<th>$R_{po}$ · 10⁻² mol/l-min</th>
<th>other compositions and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-1</td>
<td>1.09</td>
<td>6.71</td>
<td>$[Na_2S_2O_3]_o = 7.85 \times 10^{-4}$ mol/l,</td>
</tr>
<tr>
<td>G-2</td>
<td>2.15</td>
<td>13.34</td>
<td>$[KBrO_3]_o = 1.73 \times 10^{-3}$ mol/l,</td>
</tr>
<tr>
<td>G-3</td>
<td>3.23</td>
<td>28.36</td>
<td>$[S]_o = 10$ wt% of oil phase, temp. 23 °C, pH 5.1,</td>
</tr>
<tr>
<td>E-1</td>
<td>4.24</td>
<td>57.88</td>
<td>crossed-paddle+“U” blade stirrer at 1000 rpm</td>
</tr>
</tbody>
</table>

(c) Effect of Reductant Concentration

<table>
<thead>
<tr>
<th>expt. No.</th>
<th>$[Na_2S_2O_3]_o$ 10⁻⁴ mol/l</th>
<th>$R_{po}$·10 mol/l-min</th>
<th>other compositions and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-1</td>
<td>1.95</td>
<td>1.98</td>
<td>$[AA]_o = 4.24$ mol/l, $[S]_o = 10$ wt% of oil phase,</td>
</tr>
<tr>
<td>F-2</td>
<td>4.21</td>
<td>3.46</td>
<td>$[KBrO_3]_o = 1.73 \times 10^{-3}$ mol/l, temp. 23 °C, pH 5.1,</td>
</tr>
<tr>
<td>E-1</td>
<td>7.85</td>
<td>5.79</td>
<td>crossed-paddle+“U” blade</td>
</tr>
<tr>
<td>F-4</td>
<td>14.93</td>
<td>8.25</td>
<td>crossed-paddle+“U” blade at 1000 rpm</td>
</tr>
<tr>
<td>F-5</td>
<td>31.61</td>
<td>14.22</td>
<td></td>
</tr>
</tbody>
</table>
(d) Effect of Oxidant Concentration

<table>
<thead>
<tr>
<th>expt. No.</th>
<th>$[KBrO_3]_o \times 10^4$ mol/l</th>
<th>$R_{po} \times 10$ mol/l·min</th>
<th>other compositions and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-5</td>
<td>2.50</td>
<td>1.19</td>
<td>$[AA]_o=4.24$ mol/l, $[S]=10$ wt%</td>
</tr>
<tr>
<td>E-4</td>
<td>5.00</td>
<td>2.18</td>
<td>$[Na_2S_2O_5]_o=7.85 \times 10^{-4}$ mol/l, pH 5.1, temp. 23 °C, crossed-paddle +“U” blade</td>
</tr>
<tr>
<td>E-2</td>
<td>8.62</td>
<td>3.25</td>
<td></td>
</tr>
<tr>
<td>E-1</td>
<td>17.25</td>
<td>5.79</td>
<td></td>
</tr>
<tr>
<td>E-3</td>
<td>32.96</td>
<td>8.44</td>
<td></td>
</tr>
</tbody>
</table>

(e) Effect of Surfactant Concentration

<table>
<thead>
<tr>
<th>expt. No.</th>
<th>$[S]_o$ wt% of oil phase</th>
<th>$R_{po} \times 10$ mol/l·min</th>
<th>other compositions and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-1</td>
<td>5</td>
<td>6.50</td>
<td>$[AA]_o=4.24$ mol/l, $[KBrO_3]_o=1.79 \times 10^{-3}$ mol/l, pH 5.1, temp. 23 °C</td>
</tr>
<tr>
<td>I-2</td>
<td>10</td>
<td>5.45</td>
<td>$[Na_2S_2O_5]_o=8.05 \times 10^{-4}$ mol/l, pH 5.1, temp. 23 °C</td>
</tr>
<tr>
<td>I-3</td>
<td>15</td>
<td>3.74</td>
<td>$[KBrO_3]_o=1.79 \times 10^{-3}$ mol/l, pH 5.1, temp. 23 °C</td>
</tr>
<tr>
<td>I-4</td>
<td>20</td>
<td>3.47</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX VIII

PUBLICATIONS ARISING FROM THE PRESENT PROJECT


(2) “Kinetics and Mechanism of Inverse Microsuspension Polymerisation Initiated by Water-soluble Redox System”, Z. Liu and B. Brooks, The 1997 IChemE Jubilee Research Event, April 7 - 9, 1997, University of Nottingham, UK


