Studies of stabilization of non-aqueous polymer dispersions with diblock copolymers

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STUDIES OF STABILIZATION OF NON-AQUEOUS
POLYMER DISPERSIONS WITH DIBLOCK COPOLYMERS

BY

SA'ED AKRAM SHAKIR

A doctoral thesis
submitted in partial fulfilment of the requirements
for the award of Doctor of Philosophy of the
Loughborough University of Technology

Supervisor: Prof. J.V. Dawkins

May 1987 Department of Chemistry

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I acknowledge the value of discussion with colleagues in the Chemistry Department.
ORIGINALITY

The work presented in this thesis has been carried out by the author, except where otherwise acknowledged, and has not previously submitted to this University or any other Institution.
To my wife Faiza
and
my daughter Dena
ABSTRACT

A diblock copolymer of Poly(Styrene-b-[ethylene-co-propylene]) has been used as a stabilizer in non-aqueous dispersion polymerizations of methyl methacrylate and vinyl acetate in n-heptane. The particles thus produced were stabilized by well defined surface layers of ethylene-propylene copolymer chains. The dependence of the particle size on the stabilizer, monomer and initiator concentrations was studied. Both seeded and one-shot polymerization techniques were investigated. Polymer particles were characterized by transmission electron microscopy to determine particle shape and size. The long term stability of both types of polymer particles suggests that the anchoring efficiency in both systems was good. Rheological studies confirmed the sphericity of the particles and showed the particles to be non-flocculated under shear. The thickness of the surface layer was determined from viscosity studies of the dispersions at 298, 308 and 318K. Solution viscosities of a narrow distribution standard of ethylene-propylene copolymer in n-heptane and in a binary liquid mixture of n-heptane and n-propanol (79:21, v/v) at 298, 308 and 318K were obtained in order to estimate the root-mean-square end-to-end distance of free ethylene-propylene copolymer chains. The thickness of the surface layer was observed to increase on raising the temperature and to decrease on changing the
solvent of the dispersion medium from a good solvent to almost a theta solvent for the ethylene-propylene copolymer chains. The dimensions of the surface layer were slightly larger than the dimensions of the free ethylene-propylene copolymer chains in solution suggesting that long ethylene-propylene chains terminally anchored at the interface are only slightly extended over random coil dimensions. Calculations of the mean separation distance between adjacent stabilizing ethylene-propylene copolymer chains indicated close-packing of ethylene-propylene copolymer chains at the particle-liquid interface which may contribute to the slight extension of the ethylene-propylene copolymer chain conformation.

The theta-conditions for ethylene-propylene copolymer in a mixture of n-heptane and n-propanol were determined using samples obtained by hydrogenating polyisoprene standards. The solvency of the dispersion medium for the stabilizing ethylene-propylene copolymer chain on the polymer particles was reduced until flocculation occurred, and this was achieved by cooling the dispersion system to find the critical flocculation temperature or by adding a non-solvent (n-propanol) for the ethylene-propylene copolymer chains at constant temperature to find the critical flocculation volume. The polymer dispersions just retained stability at theta conditions and started to lose stability when the dispersion medium was changed to slightly worse than a theta system for the ethylene-
propylene chains. The close correspondence of the flocculation conditions to the theta conditions for free ethylene-propylene copolymer chains confirms that the steric stabilization mechanism is operative for these dispersions.
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INTRODUCTION
INTRODUCTION

The formation of colloidal polymer particles has become an important area of scientific study largely because of their industrial importance. By far the most exploited system is that of aqueous emulsion polymerization [1], which has been widely studied over the past four decades. Emulsion polymerization provides aqueous dispersions of polymers which serve as the basis of an extensive range of aqueous emulsion paints, adhesives and similar products. Thermal and viscosity problems are much less significant than in bulk polymerization. Emulsion polymerization is an important process in that it affords a means of increasing the polymer molar mass without decreasing the polymerization rate, so that it has the advantage of being able to simultaneously attain both high molar mass and high reaction rate. Water is odourless, cheap and non-toxic but it is disadvantageous because of a large latent heat of evaporation (2428 Jg\(^{-1}\)) compared with most organic liquids (<418.6 Jg\(^{-1}\)) so that a correspondingly larger input of heat is required for its evaporation during film formation i.e., slow and uncontrollable rate of evaporation. Attention was therefore, focussed in the surface coatings industry on the development of methods for preparing polymer dispersions in non-aqueous media which make use of the advantages of dispersed particles but without the concomitant
disadvantages of water as the continuous phase [2].

Nearly all of the methods used to produce polymer dispersions involve precipitation of polymer from solution at some stage in the process, and the different heterogeneous polymerization techniques will be discussed in section 2.3. When polymer particles are to form in a non-aqueous dispersion, rather than ill-defined agglomerates, then there has to be present some means of conferring stability on the growing particles which prevent their uncontrolled aggregation or flocculation. This can be achieved by surrounding the particles with surface layers of "swollen" polymeric stabilizer. The term stabilizers and stabilization, where used in this work, imply the use of a method for producing polymer dispersions which are stable towards aggregation processes. This is, of course, quite different from the definition in which these terms are frequently used in other branches of polymer science where they refer to processes and additives which confer on treated polymers an enhanced stability towards thermal oxidative and photolytic degradation processes [3].

Rehbinder et al, were among the first to show that long chain carboxylic acids could generate stable dispersions of powders in benzene [4]. Subsequently, Verwey and de Boer in 1938 gave an account of the stabilization of several powders, such as iron by oleic acid in non-aqueous dispersion media [5]. Verwey and de Boer surmised that the particles were surrounded by an oriented layer of oleic
acid molecules. These have their polar carboxylic acid groups adsorbed at the surface of the particles and their non-polar tails oriented toward the non-aqueous dispersion medium, and they even represented the particles by a schematic diagram that would be immediately recognizable today as depicting steric stabilization as seen in Fig. 1.1.

**FIGURE 1.1**

THE STABILIZATION OF COLLOIDAL PARTICLES

AS DEPICTED BY VERWEY AND DE BOER

Van der Waarden's work [6] was really the first to indicate that charge stabilization is unnecessary. He showed that carbon black particles could be stabilized in hydrocarbon media by substituted aromatic hydrocarbons containing aliphatic chains of sufficient length.

One of the earliest works with polymeric materials used as dispersion stabilizers reported in literature, was
that of Romo [7] who studied the stability of titanium (IV) oxide dispersions in xylene with added linseed oil or melamine.

The most successful type of stabilizer devised for use in dispersion polymerization has been based on a block or graft copolymer which consists of two essential polymeric components, one soluble and one insoluble in the continuous phase [2]. These types of stabilizers are extremely effective since by virtue of the insolubility of one of their components, they are strongly adsorbed onto a particle surface, so that they are neither desorbed from the surface nor displaced laterally when two particles collide. In this way the soluble components are firmly attached at the surface and so provide a swollen layer covering the surface of the particle. It is often preferable but not necessary for the adsorbed component to be identical in composition with the disperse phase polymer produced in the polymerization process [8].

The main requirement for the anchor component is that it be insoluble in the dispersion medium and have sufficient molar mass. For example, in the stabilization of polymer particles in n-alkanes, the polystyrene (PS) anchor blocks in stabilizing diblock copolymers should have a molar mass of at least $10^4$ g mol$^{-1}$ [9]. The soluble chain attached to such an anchoring block must have a molar mass of at least 3000 g mol$^{-1}$, otherwise a stable micellar solution of copolymer cannot be formed in the dispersion
Various types of polymerization mechanism are adaptable to dispersion polymerization, such as addition polymerization. Almost all the kinetic and mechanistic studies reported have concerned radical addition polymerization [2] particularly of acrylic monomers. Theoretical considerations were largely motivated by the work of Fischer [10] and Meier [11] and the major contributions have come from Dutch and British colloid schools and from Napper in Australia. There is currently much discussion in the literature as to the nature of steric interactions. The various theories have been reviewed [12]. Most of the theoretical work was developed in isolation from the practical systems studied largely in industrial laboratories. Some attempts to correlate theory and experiment have been made recently [12].

With this aim in mind, the present work sought to prepare well-defined, sterically stabilized dispersions of polymer particles in a non-aqueous medium. Studies based on such systems would lead to a better understanding of the stabilizing mechanism.

A simple AB-type of block copolymer stabilizer was chosen, consisting of a polystyrene (PS) block and ethylene-co-propylene (EP) copolymer block. The difference in the solubility of PS and EP copolymer in hydrocarbon, suggested that poly (styrene-b-[ethylene-co-propylene]) (S-EP) would be useful for stabilizing particles in aliphatic
hydrocarbon media. The soluble EP block would provide the stabilizing layer, and would be anchored to the particle by the insoluble PS anchor block. The use of S-EP as stabilizer in the radical dispersion polymerization of methyl methacrylate (MMA) and vinyl acetate (VA) in aliphatic hydrocarbon media was studied. In order to prepare a model system, a knowledge of the characteristics of dispersion polymerization involving adsorbed block copolymer stabilizer is described. A study of such a dispersion polymerization was, therefore, made.

The preparation of dispersions of poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVA) particles stabilized by S-EP block copolymer represent novel systems, although PMMA stabilized with S-EP block copolymer has been described in a very brief paper by Price and co-workers [13]. They prepared one sample of PMMA stabilized with an adsorbed layer of EP copolymer. Here, the effects of varying polymerization conditions have been extensively studied. The behaviour of the block copolymer stabilizer in a selective solvent was considered and a micellar dispersion was prepared. The stability of the dispersed particles of PMMA and PVA in a medium which is a θ-solvent for EP copolymer was studied by examining the flocculation behaviour of non-aqueous PMMA and PVA dispersions stabilized by S-EP block copolymer. PMMA and PVA particles in a dispersion medium consisting of a binary liquid mixture of n-heptane and n-propanol have been
studied. Results for critical flocculation volume (CFV) by adding n-propanol at constant temperature and critical flocculation temperature (CFT) by cooling have been obtained.

Rheological measurements were carried out in n-heptane and in a binary liquid mixture of n-heptane/n-propanol (79:21%, v/v) (slightly better than \( \theta \)-solvent mixture for EP copolymer) at three different temperatures. These rheological studies gave an indication of the state of dispersions and particle behaviour, and were used to provide an estimate of the hydrodynamic surface layer thickness of the stabilizing EP chain, and therefore, the effective volume of the particles. This study was combined with surface coverage information to suggest the configuration of the stabilizing EP chain at the interface and to compare these results with that of the configuration of the free EP chains in the same liquid media.
CHAPTER TWO

THEORY
2.1 STABILIZATION OF COLLOIDAL PARTICLES

For a dispersion to be stable it is necessary to provide a repulsive interaction which must be greater than the van der Waals attraction between the colloidal particles. This can be achieved practically by only a small number of different mechanisms.

(i) electrostatic stabilization, which exploits the Coulombic repulsion operative between charged, colloidal particles and their respective double layers. Electrostatic stabilization is often effective in aqueous medium but it is less effective in non-aqueous media.

(ii) polymeric stabilization, which for nonionic polymers can be accomplished in at least two distinct ways.
   (a) steric stabilization, whereby stability is imparted by polymers adsorbed or attached to the colloidal particles.
   (b) depletion stabilization, which is imparted by polymer chains in free solution.

2.1.1 STERIC STABILIZATION

Electrostatic stabilization requires an aqueous medium for effective repulsion of particles. Furthermore, charge stabilized latices in water are more sensitive to added electrolytes than sterically stabilized latices. Consequently steric stabilization is exploited industrially and biologically because it operates for a
wide range of experimental conditions, for non-aqueous media steric stabilization is the preferred mode of stabilization [14].

Steric stabilization can be maintained at both high and low volume fractions of the dispersed phase. Sterically stabilized dispersions can usually be flocculated by the addition of non-solvent for the stabilizing chains to the dispersion medium, dilution of the concentration of the non-solvent to a suitably low value is often sufficient to induce the particles to redisperse spontaneously [15-17]. Moreover, particles can be redispersed after drying. Everett and Stageman [18] have demonstrated the spontaneous redispersion in n-alkane of freeze-dried PMMA particles stabilized by poly(dimethyl siloxane) (PDMS). Sterically stabilized dispersions also often display good freeze-thaw stability, which makes them very useful in many technological applications.

2.1.2 FORCES OF ATTRACTION

Non-aqueous polymer dispersions are prepared by polymerizing a monomer dissolved in a suitable dispersion medium, which is a precipitant for the polymer. This precipitated polymer is in the form of a sub-micron dispersion and the particles collision frequency is such that the number of free particles is quickly reduced to zero. This behaviour, which is known as aggregation, is due to the mutual attractive forces which arise as particles approach each other. In order to appreciate the
mechanism of stabilizing such a system against aggregation, it is useful to consider firstly, the origin and magnitude of the attractive forces between particles.

Interactions between the atoms and molecules of two adjacent particles give rise to an attractive force between the particles. The origin of such forces was described by London [19], who showed that the interaction between the two atoms of an inert gas was a quantum mechanical effect. Applying the Heisenberg uncertainty principle, he showed that the fluctuation in the electron charge distribution around the atom (electrical field), could result in the formation of a transient dipole able to induce dipoles in another atom. Since the total energy involved was less than one quantum, no actual dissipation of energy occurred. The random fluctuations of the electrical fields of the two atoms become coupled and oscillate together, thus reducing the total free energy of the system. These fluctuations produced an instantaneous dipole so that one atom in the neighbourhood of another experiences an attraction, and they approach each other. Since random fluctuations of the electrical fields are involved, one atom is able to participate in London oscillations with several other atoms at the same time. This effect is seen in a gas where one gas atom attracts all its neighbouring atoms simultaneously. This quantum mechanical effect is essentially additive, based on "pair-wise" interactions, and it can be shown that the attractive potential energy
\( (V_A) \) varies inversely as the sixth power of the separation distance between the two atoms \((r)\)

\[
V_A = -\frac{L}{r^6} \tag{2.1}
\]

where \( L \) is the London interaction constant which depends upon the properties of the specific atoms.

The magnitude of the attractive potential energy \((V_A)\) generated by the above concepts, based upon gaseous systems, was applied to condensed bodies in a vacuum by Hamaker [20]. The theory of Hamaker is based on the assumption that the "pair-wise" additivity concept used in calculating the London attraction between gas atoms can be applied to the corresponding interactions between atoms in different condensed bodies and the attractive force between two particles, each consisting of a large number of molecules, is simply the sum of the interaction between all the pairs of molecules on different particles and can be replaced by a double integral. In this way, an integration of all the possible interactions between the attracting elements of a pair of particles results in an expression of the form.

\[
V_A = A.H \tag{2.2}
\]

The Hamaker constant \(A\) is a function of the strength of attraction between two elements, and is proportional to
L (London interaction constant) and their concentration \( q \) (the number of elements per unit volume) as follows

\[
A = \frac{2}{7} q^2 L
\]

(2.3)

\( H \) is a geometrical function which for equal-sized spheres, where the distance between their surfaces \( h \) is much less than their radius \( a \), is given by an approximate expression of the form

\[
H = a/12h
\]

(2.4)

The Hamaker integration predicts that the van der Waals interactions between two atoms or molecules is relatively short range extending only over a few tens of nanometers. For colloidal particles, however, each atom or molecule in one particle attracts every atom or molecule in the other particle. Typically, a colloidal particle is composed of \( 10^6 - 10^{16} \) atoms. The net effect of adding all of the myriad of possible atomic interactions is to generate a long range attraction between the particles that is of considerable strength.

Hamaker [21] extended London's treatment [22] of the dispersion forces between atoms to calculate attractive forces between colloidal particles. The result for the attraction \( (V_A) \) between two spheres each of radius \( a \) is

\[
V_A = -(A^* / 6) G
\]

(2.5)
where $A^*$ is the effective Hamaker constant and the geometrical term $G$ is given by

$$G = 2/(S^2-4) + (2/S^2) + 1n(|S^2-4|/S^2)$$  \hspace{1cm} (2.6)$$

Here, the parameter $S = (H_o + 2a)/a$, where $H_o$ is the minimum distance of separation between surfaces of the particles. If $H_o$ is small compared with the particle radius, then the first term in the expression for $G$ is dominant, and equation (2.5) reduces to

$$V_A = -A^* a/12H_o \hspace{0.5cm} (a >> H_o)$$  \hspace{1cm} (2.7)$$

It should be noted that the Hamaker approach is based upon interactions of microscopic elements and is therefore subject to errors when applied to macroscopic particulate systems. In such systems the attractive forces between elements just below the particle surface will be modified by the particle material. The Hamaker constant is not really a constant, in general, but a function of the distance between the particles and the temperature [18,23].

2.2 STABILIZATION OF COLLOIDAL DISPERSION AGAINST FLOCCULATION

Naked, uncharged colloidal particles at concentrations of interest in experiments undergo rapid coagulation, with the number of separate particles being halved in a matter of only a few seconds, as particles are
mutually attracted by the forces described earlier. Studies of the electrostatic stabilization of colloidal dispersion against flocculation have been largely confined to aqueous systems, both in theoretical and experimental considerations and the nature of stabilization is well understood.

Over recent years, a large body of experimental and theoretical research has been published in this area and numerous reviews show clearly the rapid expansion in understanding of steric stabilization, but the level of understanding is still below that of electrostatic stabilization.

2.2.1 INTERACTION FORCES BETWEEN PARTICLES WITH ADSORBED POLYMERS

Consider two spherical particles surrounded by surface layers of soluble polymer chains as in Figure 2.1.

FIGURE 2.1

SCHEMATIC REPRESENTATION OF STERIC STABILIZATION
A polymeric stabilizer chain may be attached to the particle surface at one or more points and may adopt the so-called loop, train and tail configurations as seen in Figure 2.2.

**FIGURE 2.2**

**CONFIGURATION OF ADSORBED POLYMERS**

In order to understand the stability of colloidal dispersions in the presence of adsorbed polymer layers, it is necessary to consider the possible interactions between the particles. When two particles with adsorbed polymer layers approach each other at distances of separation of their surfaces of less than twice the thickness of the adsorbed layer, interactions of the two layers take place. The degree of stabilization can be defined quantitatively in terms of the energy change occurring upon the interaction of the adsorbed layers. The Gibbs free
energy change $\Delta G$ of the overlap interaction of the adsorbed layers is expressed as

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (2.8)

If $\Delta G$ is negative upon the overlap of the adsorbed layers, flocculation or coagulation will result, and if $\Delta G$ is positive, stabilization will result.

Many theories for explaining the steric stabilization mechanism have been proposed, and many theoretical equations for calculating the energy change within the overlap of the adsorbed layers have been devised. Most of these theories classify the interaction between the particles approximately into two categories: "entropic" and "mixing" interactions. The "entropic" interactions result from the loss of configurational freedom of the adsorbed macromolecule on approach of the second particle. This is the result of the compression of the chain as shown in Figure 2.3a, and since the total volume available to each chain is reduced, the configurational entropy of the chain is also reduced. This reduction in entropy increases $\Delta G$, producing the net effect of repulsion between particles and thus preventing the particles from flocculation. This is called the "entropic" or volume restriction effect, and the total free energy change due to the entropic effect is represented by $(\Delta G_{VR})$. The "mixing" interactions arise from the interpenetration of the adsorbed layers of two particles, when the particles
FIGURE 2.3

INTERACTION OF STERICALLY STABILIZED PARTICLES

(a) COMPRESSION OR VOLUME RESTRICTION MODEL
(b) MIXING OF ADSORBED LAYERS
collide resulting in a build-up in the segment concentration in the interaction zone as shown in Figure 2.3b. This leads to an increase in the local osmotic pressure and free energy. This term is the "mixing" interaction and therefore, the total free energy change due to this interaction is $(-\Delta G_M)$.

Various problems arise when analysing the interaction forces between the particles as the adsorbed layers approach each other closely. The first problem is the question of equilibrium between the stabilizing chains at the interface and those in the dispersion medium. Clearly, for weakly adsorbed chains equilibrium can be maintained by desorption of the chains on particle-particle approach. However, with polymers, with many segments adsorbed to the surface, desorption is highly unlikely and, therefore, constant adsorption is maintained during particle collision. The segments protruding into the bulk solution, as loops and tails, may redistribute themselves during contact. This now imposes the second problem, the question of interpenetration versus compression. Clearly, interpenetration of the adsorbed layers, without compression, only applies for separations greater than one adsorbed layer thickness. However, at smaller separations compression should be the mode of interaction. Indeed, whether, interpenetration or compression or both occurs depends to a large extent on the segment density distribution. For example, if the segment concentration is relatively high and uniform, compression rather
than interpenetration may occur. This is usually the case with relatively low molar mass or branched chain polymers. On the other hand, with high molar mass polymers, where the segment density at the periphery of the layer is small, and also at low coverage, interpenetration is the dominant mode. However, it is highly likely that the two processes take place simultaneously, one being more dominant than the other depending on the particle separation and the segment concentration in the adsorbed layer.

2.2.1.1 ENTROPIC INTERACTIONS

Mackor [24] was perhaps the first to endeavour to calculate the repulsive potential energy in steric stabilization in order to explain the stability of carbon black dispersions in hydrocarbon media in the presence of long-chain alkyl benzenes [6]. Mackor assumed that a sizeable repulsive force results from the potential loss in configurational entropy occurring when molecules adsorbed on approaching particles begin to interact. He assumed a simple model based on inflexible rods anchored at one end to the surface by hinged joints, and calculated the reduction in entropy resulting from restriction of movement of rods by a similar opposed surface. The number of configurations, \( W_a \), available to the molecules was assumed to be proportional to the surface area of a hemisphere swept out by the free rod of length \( l \) when planes A and B are well separated, but as the planes are brought closer
together the gyration of the rod on the surface is restricted as shown in Figure 2.4.

The number of possible configurations is reduced to \( W_H \), and by calculating the loss in the number of configuration upon bringing the planes A and B to a distance of \( H \), the change in configurational entropy, \( \Delta S \), is given by

\[
\Delta S = S_H - S_\infty
\]  

(2.9)

The number of configurations of molecules is related to entropy by

\[
S = k \ln W
\]  

(2.10)

Where \( k \) is Boltzmann's constant, then

\[
\Delta S = k \ln \frac{W_H}{W_\infty} = k \ln \left( \frac{W_H}{W_\infty} \right)
\]  

(2.11)

Assuming that the degree of freedom of the adsorbed molecules of length \( r \) decreases linearly with approach of two planes, the repulsive energy \( \Delta G_{VR} \), due to the entropy change is

\[
\Delta G_{VR} = -T \Delta S = kT \ln \left( \frac{W_\infty}{W_H} \right) = kT \ln \left( \frac{1}{H} \right)
\]  

(2.12)

If there are \( N_s \) adsorbed molecules in a unit surface area, the repulsive energy per unit surface area is

\[
\Delta G_{VR} = N_s kT \theta_\infty \left( \frac{1}{H} \right)
\]  

(2.13)

Where \( \theta_\infty \) is the surface coverage when \( H = \infty \).
MACKOR'S MODEL FOR THE CALCULATION OF ENTROPIC TERM

(a) WHEN THE TWO PLANES A AND B ARE WELL SEPARATED.

(b) WHEN THE TWO PLANES A AND B BROUGHT CLOSER TOGETHER.
The lateral interactions between neighbouring rods were not taken into account in this model and, hence, the theory only applies to very low coverages. Although this theory was later extended to higher surface coverages [25], it was restricted to the case of dilute solutions, where the interaction between adsorbed and unadsorbed molecules may be neglected. Clearly these theories are too crude to be applied to the case of higher molar mass, flexible macromolecules, so that computer simulation methods have been developed to calculate the reduction in the configuration entropy of chains with several links. Clayfield and Lumb [26] used such simulations to calculate the steric repulsion for flexible terminally adsorbed macromolecules containing up to 100 links. However, segment-solvent interactions were not considered and the adsorbed layers were assumed not to interpenetrate each other. These numerical calculations were in the spirit of the Mackor approach; however, the flexibility of the polymer chains was now incorporated into the theory by simulating random flight chains. These chains were placed on a cubic lattice, containing a valence angle of 90°. Both terminally attached homopolymers and random copolymers that gave a loopy type adsorption were studied. The results of these simulations relate entirely to the loss of configurational entropy of the polymer chains on close approach of the particles, due either to the presence of the impenetrable surface of the opposite particle or the
polymer chains that are attached to that particle. The results of these calculations confirm the experimental observations that a random copolymer of the same root mean-square adsorbed layer thickness as a linear homopolymer which adsorbs terminally at one end group produces a better stabilizing effects because of the larger number of copolymer anchor points at the interface.

Another modification to Mackor's theory of the collision of two spherical particles was due to Bagchi and Vold [27], which taking the steric hindrance between neighbouring molecules into account, who derived a theoretical equation for entropic repulsion between two particles with adsorbed polymers which are extending into a \( \theta \)-solvent. Their conclusions were similar to those reported by Clayfield and Lumb [26].

### 2.2.1.2 MIXING INTERACTION

As mentioned in section 2.2.1, \( \Delta G_M \) is the result of the interpenetration, and hence the mixing of the polymer segments, when the adsorbed layers approach to distances shorter than twice their thickness. The first theory to recognize clearly the prime importance of the interpenetration and the solvency of the dispersion medium in steric stabilization was that published by Fischer in 1958 [10]. Fischer considered the overlap of the steric layers attached to two spheres and he made the following basic assumptions: the segment concentration in the adsorbed layer is uniform, the segment concentration in the
overlap region is the sum of the individual concentrations from both adsorbed layers, and the free energy of mixing of the adsorbed layers is the same as that obtained for a dilute polymer solution using the Flory-Krigbaum theory of dilute polymer solutions [28]. Figure 2.5 illustrates the mixing interactions when two particles are brought together. The mixing free energy change $\delta(\Delta G_M)$ in the small volume $\delta V$ of the region of overlap is given by

$$\delta(\Delta G_M) = kT(\delta n_1 \ln \phi_1 + \delta n_1 \phi_2)$$

(2.14)

Where $\delta n_1$ is the number of solvent molecules contained in the overlap region $\delta V$, $\phi_1$ and $\phi_2$ are the volume fractions of solvent and polymer respectively; $\chi$ is the Flory-Huggins polymer-liquid interaction parameter.

The total change in the free energy of mixing for the whole interaction zone $V$ is therefore, obtained by summing over all the volume elements $\delta V$. The total repulsive force is therefore, a function of the degree of overlap of the soluble layers, so $\Delta G_M$ is given by

$$\Delta G_M = 2kTC^2BV$$

(2.15)

Where $C$ is the concentration of polymer in the adsorbed layer, $B$ is the second virial coefficient of polymer in solution [29,30]. The lens-shaped overlap volume $V$, which is represented by the area restricted by the symbols $A$ and $B$ in Figure 2.5, can be calculated from the equation
FIGURE 2.5

A GENERAL MODEL FOR THE CALCULATION OF MIXING FREE ENERGY IN STERIC STABILIZATION
\[ V = \frac{2}{3} \pi (a-H/2)^2 (3r+2a+H/2) \]  \hspace{1cm} (2.16)

Where \( a \) is the steric layer thickness, \( H \) is the minimum distance between the surfaces of the two spheres and \( r \) is the particle radius so

\[ \Delta G_M = \frac{4}{3} \pi kT C^2 B(a-H/2)^2 (3r+2a+H/2) \]  \hspace{1cm} (2.17)

The second virial coefficient \( B \) can be related to the interaction parameter \( \lambda \), and can be expressed by

\[ B = (\frac{1}{2} - \lambda)/V_1 P_2^2 \]  \hspace{1cm} (2.18)

Where \( P_2 \) is the density of stabilizing moieties, and \( V_1 \) is the partial molar volume of the solvent. So \( \Delta G_M \) will be expressed by

\[ \Delta G_M = \frac{4}{3} \pi kT C^2 (\frac{1}{2} - \lambda)(a-H/2)^2 (3r+2a+H/2) \]  \hspace{1cm} (2.19)

Ottewill and Walker [31] have used the relationship between the interaction parameter \( \lambda \) and the entropy and enthalpy dilution parameters, \( \phi_1 \), and \( \kappa_1 \) respectively via

\[ \frac{1}{2} - \lambda = \phi_1 - \kappa_1 \]  \hspace{1cm} (2.20)

so equation (2.19) will be

\[ \Delta G_M = \frac{4}{3} \pi C^2 (\phi_1 - \kappa_1)(a-H/2)^2 (3r+2a+H/2) \]  \hspace{1cm} (2.21)
One disadvantage of the approach by Fischer [10] and Ottewill and Walker [31] is that, as noted above, the formulae proposed by these authors are only valid for the segment density of the stabilizing layers in the interpenetration domain. In order to obtain an expression for the mixing term for particles with adsorbed or anchored macromolecules, the segment density distribution should be taken into account [32, 33].

As the surfaces containing adsorbed chains are brought closer together, the volume available to the chains decreases, as a result, some otherwise possible chain configurations are lost. The free energy change due to the decrease in this volume was calculated by Meier [34] who took into account the segment density distribution in the adsorbed layer on two parallel flat plates.

If $P_n(d)$ is the probability that all chain segments are within a distance $d$ of the surface on which the chain is adsorbed when the other surface is at infinity, and $\Gamma$ is the number of polymer chains per unit area of the surface, then the entropy change due to volume restriction, $\Delta S_{VR}$, per unit area is expressed in terms of the Boltzmann equation by:

$$\Delta G_{VR}(d) = -T\Delta S_{VR}(d) = -2\nu kT \ln P_n(d)$$ (2.22)

Note that the factor 2 occurs because the entropic effect involves two surfaces as seen in Figure 2.6.
Meier solved the diffusion equation with the appropriate boundary conditions, as first pointed out by Di Marzio [35]. This corresponds to the placement of adsorbing barriers at $x = 0$ and $x = d$, even though the physical surface at $x = 0$ corresponds to an impenetrable reflective surface. Meier obtained rather unwieldy expressions for the segment density distribution functions, which will not be reproduced here. Results were, however, obtained for both low and high surface coverage.

Meier's theory is based on the model in which the flexible linear polymer chains are adsorbed by one of their end segments onto planer surfaces. Although this model is considered to be closer to the real system than Mackor's model, the derivation of the segment density distribution is incorrect [32], due to the inclusion of certain
configurations that actually penetrate the impenetrable adsorbent. These conformations should not be allowed, of course. Hesselink [32, 33] corrected this and extended Meier's idea to loop adsorption. The segment density distribution calculated by Hesselink for the segments of polymer terminally adsorbed at one end (tail adsorption) and at both ends (loop adsorption) shows that the segment density distribution calculated by Meier for tail adsorption is more inclined toward the adsorbent than that of Hesselink and that the density of looped segments is more compressed toward the interface than a tail of the same number of segments. Hesselink, Vrij and Overbeek [36] (HVO) again extended Meier's model to systems in which the polymer molecules are adsorbed with many segments and connected by loops dangling into solution.

The procedure adopted by Meier [34] and Hesselink et al. [36] assumed the superposition of the mixing contribution to the total steric interaction free energy. Their respective values were calculated separately. Dolan and Edwards [37], Gerber and Moore [38] and Levine et al. [39] have all attempted to by-pass this artifice and to evaluate the steric repulsion in its totality in one coordinated attack on the problem. This approach was pioneered by Dolan and Edwards [37]. They treated the interaction between segments as an excluded volume effect and estimated the whole of the free energy as a configurational entropy term.
The formulae derived by Dolan and Edwards demanded heavy numerical computations to estimate the magnitude of the repulsion. Subsequently, Gerber and Moore [38] and Levine et al. [39] showed how the interaction free energy can be evaluated more readily. Note that the theory presented by Dolan and Edwards applies to dispersion media that are θ-solvents or better than θ-solvent for the stabilizing chains. No discussion of the predictions of their theory for worse than θ-solvents has yet been published. This is unfortunate in light of the flocculation behaviour observed for some sterically stabilized dispersions in marginally worse than θ-solvents.

2.2.1.3 THE MAGNITUDE AND RANGE OF TOTAL INTERACTION

The total interaction \( \Delta G_T \) between two polymer-covered particles is given by

\[
\Delta G_T = V_A + V_R + \Delta G_S
\]

(2.23)

where \( V_A \) is the attractive potential energy, \( V_R \) is the repulsive potential energy (small for uncharged polymer particles) and \( \Delta G_S \) is the total steric interaction. It is assumed that the two contributions to \( \Delta G_S \) are additive, i.e.

\[
\Delta G_S = \Delta G_{VR} + \Delta G_M
\]

(2.24)

Where \( \Delta G_{VR} \) and \( \Delta G_M \) are the total energy change due to the
volume restriction and the mixing terms of the stabilizing chains respectively. Napper [8,40] claims that $\Delta G_M$ describes completely the total interaction.

In a thermodynamically "good" solvent, the mixing term will be the dominant repulsive term, at least for conditions of low overlap. This can be derived from a consideration of the geometry involved and the fact that most of possible configurations are lost as a result of interactions between polymer chains before the stage of half-overlap is reached.

The variation of net potential energy with interparticle distance, for sterically stabilized spheres in a "good" solvent for the stabilizing layer, is shown in Figure 2.7. The potential energy of repulsion exceeds that of attraction by an ever increasing amount as particles approach one another. The net repulsive energy is therefore, always positive and increases rapidly with decreasing particle separation. The attractive forces between uncharged polymer particles are relatively small and as pointed out by Evans and Napper [41] may be conveniently neglected in a consideration of the total repulsive energy. It is conceivable that for certain combinations of layer thickness and particle size, a significant attractive force might exist in this region, giving rise to a secondary minimum corresponding to a weak flocculation. The idea that repulsive forces are generated
FIGURE 2.7

FORM OF NET POTENTIAL ENERGY (V) CURVE AS A FUNCTION OF PARTICLE SURFACE SEPARATION (h).

Steric stabilization

Secondary minimum

Steric stabilization
only when the soluble layers interact is fundamental to the concept of steric stabilization, and both the predictions of theoretical model [36, 42] and experimental measurements [43, 44] are in agreement.

2.3 POLYMERIZATION PROCESS

Radical polymerization may be carried out by homogeneous and heterogeneous processes. This classification is often based on whether the initial reaction mixture is homogeneous or heterogeneous. Some homogeneous systems may become heterogeneous as polymerization proceeds due to insolubility of the polymer in the reaction medium.

2.3.1 BULK POLYMERIZATION

Bulk or mass polymerization of a pure monomer offers the simplest process with a minimum of contamination of the resulting polymer. Bulk polymerization requires careful control because of the need to dissipate the heat of reaction and because the viscosity of the reaction system increases rapidly at relatively low conversion. The viscosity and exotherm effects make temperature control difficult. Local hot spots may occur, resulting in degradation of the polymer product and a broadened molar mass distribution.

2.3.2 SOLUTION POLYMERIZATION

Polymerization of a monomer in a solvent overcomes many of the disadvantages of the bulk process. The solvent acts as a diluent and aids in the transfer of the heat of polymerization. The solvent also allows easier stirring,
since the viscosity of the reaction mixture is decreased. Thermal control is much easier in solution polymerization compared to bulk polymerization. On the other hand, the solvent may enter into chain transfer reactions, thus reducing the molar mass of the polymer, and the resulting polymer may be contaminated if solvent removal is difficult.

2.3.3 EMULSION POLYMERIZATION

Emulsion polymerization is perhaps the most commonly used heterogeneous polymerization technique, and the subject has been reported extensively in the literature [1]. The polymerization is carried out in a system which comprises monomer, the reaction medium (usually aqueous) in which the monomer is either virtually insoluble or sparingly soluble, an initiator which is soluble in the reaction medium and ionic or non-ionic surfactants. It is possible to obtain a very high molar mass at a relatively fast rate, owing to radical isolation within the particles. The particles produced are typically 0.1 - 0.3 \( \mu \text{m} \) diameter.

2.3.4 SUSPENSION POLYMERIZATION

A somewhat similar technique is that of suspension polymerization which differs from emulsion polymerization, since the initiator is soluble in the monomer which itself is only sparingly soluble in the dispersion medium (water). Small amounts of protective colloid are usually added to stabilize the dispersion of monomer, and the reaction is
best regarded as a "micro-bulk" polymerization [45]. The particles produced by suspension polymerization are larger than those from emulsion polymerization, typically greater than 5 µm.

2.3.5 PRECIPITATION POLYMERIZATION

Precipitation polymerization [46] commences as a homogeneous process, but the polymer formed in aqueous or organic media precipitates. The initially soluble monomer is converted into insoluble polymer which precipitates in the form of an agglomerate or slurry. An auto-acceleration in polymerization (an increased rate of polymerization) is often observed after the precipitation of polymer since the radical termination processes are restricted by the low mobility of the growing polymer radical in the viscous reaction medium.

2.3.6 DISPERSION POLYMERIZATION

Dispersion polymerization involves the polymerization of a monomer dissolved in a diluent which is a precipitant for the polymer [2]. This is a special case of precipitation polymerization in that a stabilizer is added to prevent gross flocculation of the polymer and to control polymer particle size. The particle size obtained by this method is in the range of 0.05–10 µm. The term dispersion polymerization will now be taken as describing polymerization in non-aqueous media, which will be discussed in section 2.6.

2.4 THE ROLE OF THE STABILIZER
Steric stabilization is achieved by surrounding particles with a layer of soluble polymer. One of the main requirements for a suitable stabilizer for a dispersion of polymer particles is that the soluble polymer is firmly anchored to the polymer particle. The stabilizing polymer should ideally be not easily desorbed or internally displaced when particles approach each other closely. This requirement excludes the use of soluble homopolymers, and random copolymers, for use as stabilizers of polymer particles. Homopolymers soluble in the dispersion medium are too weakly and reversibly, adsorbed on the polymer particles surfaces and are ineffective as stabilizers necessary for good stabilization. Anchoring of a homopolymer, however, can be effective if the surfaces of the colloidal particles contain sites with which the homopolymer can be interact specifically, but the stabilizing layers then be very thin with low δ values. Attempts to disperse polymer particles in aliphatic hydrocarbons in the presence of homopolymers have generally been unsuccessful [2], although several homopolymers have been used to stabilize dispersion of inorganic materials [47].

The soluble component in random copolymers normally exists in short sequences and is unable to form loops large enough to provide a thick stabilizing barrier. The anchoring component in the copolymer may be chemically attached to the polymer particles by the incorporation of suitable functional groups, which interact with
complementary functional groups (e.g. acid-base interaction) on the particle surface. Alternatively, random copolymers or homopolymers having relatively few grafting sites on their chains may be covalently grafted in situ on to growing particles in dispersion polymerization. In these cases, it is often necessary to use excessive amounts of soluble polymers relative to the area of particle surface to be sterically stabilized. In some cases the grafting of the soluble polymer occur on the surface of more than one polymer particles (bridging) which leads to uneffective stabilization of the particles.

The most widely reported stabilizers used for non-aqueous polymer dispersions are those based upon block and graft copolymers. Such copolymers are chosen to comprise one component which is soluble, and one component which is insoluble, in the dispersion medium. The stabilizing copolymer is firmly attached to the polymer particle by its insoluble component or anchor (designated "A"), which is physically adsorbed onto the particle surface owing to its insolubility in the dispersion medium. The anchor component may be chemically reacted with the dispersed polymer after adsorption, if desired. The soluble stabilizing component of the copolymer (designated "B") is chosen to have little or no affinity for the particle surface and, therefore, extends into the dispersion medium to provide a stabilizing barrier. Figure 2.8a shows block and graft copolymers adsorbed in this way.
FIGURE 2.8

(a) BLOCK AND GRAFT COPOLYMERS USED AS STABILIZERS

(i)  (ii)  (iii)

(iv)  (v)  (vi)

(b) SUITABLE COMBINATIONS OF A AND B FOR USE AS STABILIZER
It is possible to combine suitable "A" and "B" components into many forms of block and graft copolymers. Figure 2.8b shows a few of these combinations which might be suitable for use as steric stabilizers. The present study concerns systems stabilized by simple AB block copolymer of type (ii) in Figure 2.8b.

2.5 THE BEHAVIOUR OF STABILIZERS IN SOLUTION

Block or graft copolymers dispersed in solvents which are selectively poor for one component and good for the other are well known to form micellar aggregates [48-50]. The formation of these aggregates is somewhat analogous to the micellar structures observed in aqueous soap solutions, and details of the theoretical background of micelle formation in solution have been given [51,52]. The aggregates, or micelles formed, can adopt a variety of configurations depending upon the concentration, size and composition of the copolymer, the solvent environment and the temperature. At very low concentrations, polymer molecules are unassociated as in a conventional homopolymer solution. At concentrations of a few percent, copolymer molecules aggregate to form a micelle in which the core is composed of the least soluble component of the copolymer, see Figure 2.9. At higher concentrations (>20%) these aggregate coalesce into regular and periodic structures of three main types spheres, rods or cylinders, and lamellae [2].

Dispersion polymerization usually involves block or
Figure 2.9

Block copolymer micelles

Unassociated block copolymer molecules ⇌ Block copolymer micelle
graft copolymer stabilizers at a concentration level of a few percent, and the dispersion medium is a selective solvent for the stabilizing B component. The size of the micelle formed depends largely upon the ratio of the A and B components, known as the anchor/soluble balance (ASB) which is analogous to the hydrophile/lipophile balance (HLB) for emulsifiers [53]. Generally, when the ASB is about unity, block or graft copolymers at concentrations of a few percent aggregate to form micelles in equilibrium with free copolymer molecules as shown in Figure 2.9.

At higher ASB values, the equilibrium in Figure 2.9 is displaced towards the aggregated structure, so that eventually the copolymer may be irreversibly associated in micelles. At very high ASB values; it becomes impossible to surround the insoluble component with a layer of the soluble component and the polymer forms a flocculated mass rather than spherical micelles.

It is possible to calculate the number of copolymer molecules required to form a continuous layer of soluble polymer around the insoluble core [2]. The so-called the micellization number "n" which is related to the radius of the micelle core by the following equation

\[ r = \left( \frac{3nM_A}{4\pi x 0.6023} \right)^{1/3} \]  

(2.25)

Where \( r \) is the micelle core radius.

\( M_A \) is the molar mass of the insoluble A chains.
\( \rho \) is the density of core polymer (1.04 g cc\(^{-1} \) [54] for bulk PS).

\( n \) is the number of copolymer molecules per micelle.

### 2.6 Dispersion Polymerization and Particle Formation

There are three basic theoretical treatments which have been proposed for dispersion polymerization, as follows:

(a) Polymerization occurs in solution, followed by precipitation onto the existing polymer particles.

(b) Polymerization of monomer adsorbed at the surface of polymer particles.

(c) Polymerization of monomer adsorbed into the interior of the polymer particles.

From a study of the dispersion polymerization of methyl methacrylate in n-dodecane [55], the following kinetic features were apparent.

(i) The increased rate of dispersion polymerization over that of an equivalent solution polymerization indicated that the polymer particle was the main site of polymerization.

(ii) The rate of dispersion polymerization was independent of particle size over a wide range, indicating that a surface polymerization mechanism was improbable.

(iii) The rate of dispersion polymerization was independent of the number of particles present and proportional to the square root of the initiator concentration. The isolation of radicals as in emulsion polymerization...
is therefore, not occurring.

(iv) The polymer particles were significantly swollen by monomer during polymerization, which results in the smooth and spherical form of the particles, while those which formed by deposition from solution are asymmetrical and have a rough and granular surface. This suggests that polymerization in solution is unlikely.

2.6.1 MECHANISM OF PARTICLE FORMATION

The nucleation process starts in an essentially homogeneous solution containing monomer, initiator and a stabilizer. Radical chain polymerization leads to the formation of growing chains. These chains grow in solution until they reach threshold molar mass at which they precipitate and are involved in the formation of a particle nucleus. Three different models are proposed for the nucleation of the growing chains, and these models are illustrated in Figure 2.10.

2.6.1.1. SELF-NUCLEATION

Each individual polymer chain as it grows in solution has an extended configuration in solution, until it reaches a certain threshold molar mass at which the chain collapses into a condensed state. This condensed polymer chain therefore constitutes a new particle nucleus. The threshold molar mass is dependent upon the solvency of the dispersion medium. According to the view proposed by Fitch and Tsai [56], the behaviour of each oligomer chain is
FIGURE 2.10

PARTICLE NUCLEATION

Primary radicals

Initiation and growth of oligomers

Self-nucleation

Aggregative nucleation

Nucleation from monomer-swollen micelles of surfactant
unaffected by the presence of other oligomer molecules, so every chain initiated forms a new particle unless it is captured by diffusion to an existing particle before it reaches the threshold molar mass.

2.6.1.2 AGGREGATIVE NUCLEATION

This model suggests that the growing polymer chains tend to associate with each other increasingly as their molar mass and concentration rise, at first reversibly. Aggregates below a certain critical size are unstable, but above this critical size, they are stable and tend to grow, constituting new particle nuclei. According to this view, which corresponds to the classical theory of homogeneous nucleation developed by Becker and Doring [57], the rate of nucleation is dependent on the activation energy required to form a critical aggregate. The rise in concentration and molar mass of polymer chains therefore, result in a sharply increasing rate of nucleation. Again growing chains only form a nucleus if they are not firstly captured by existing particle.

2.6.1.3 NUCLEATION FROM MICELLES

The types of amphipathic copolymers used as stabilizers in dispersion polymerization are well known to form micelles [48-50]. It is suggested that chains are initiated and grow within monomer-swollen micelles until the critical threshold molar mass is reached when the nucleus is formed. This idea is very similar to a model proposed by Harkins [58] for aqueous emulsion polymerization.
which suggests that particle nuclei are formed by growth of oligomer chains initiated in monomer, solubilized in micelles of surfactant or stabilizer. Polymerization is started by the primary radicals formed from the thermal decomposition of water soluble initiator adsorbing into the micelles.

The model of nucleation from micelles may be disregarded in the situation where monomer is completely soluble in the dispersion medium. Both self-nucleation and aggregative nucleation models are thought to occur within a real system, with a bias towards one mechanism depending upon polymer solubility, its molar mass and the polymerization rate. In the absence of a competing process, the formation of particle nuclei would be expected to continue throughout the course of a polymerization until monomer is depleted. In practice, however, the rate of nucleation falls to a negligible level very early in the course of polymerization. It is, therefore, suggested that growing oligomers are captured by existing particles before they reach their threshold molar mass for precipitation.

The above models for nucleation represent systems in the absence of stabilizing copolymers. In the presence of such copolymers the nucleation process is enhanced and more nuclei are formed. This effect occurs since the stabilizing copolymer associates with the growing oligomers, which raises the probability of forming a nucleus and lowers the
probability of capture by existing particles. In the self-nucleation model, the stabilizing copolymer associates with a single growing chain, as shown in Figure 2.11a, protecting it from capture by existing particles. Therefore, the probability of the chain forming a nucleus is increased and more nuclei are produced. In the aggregative nucleation model Figure 2.11b, the stabilizing copolymer participates in forming incipient nuclei and reduces the interfacial tension. Thus, smaller nuclei are produced and the total number of nuclei is increased. It follows then that an increase in concentration of copolymer stabilizer in the dispersion medium will enhance the number of nuclei formed, with a consequent reduction in the particle size of the final dispersion.

2.6.2 KINETICS OF DISPERSION POLYMERIZATION

If dispersion polymerization is then a type of micro-bulk polymerization any kinetic model must be similar to ordinary bulk polymerization, and the kinetic model for bulk polymerization can be applied to dispersion polymerization. Free radical addition polymerization occurs in three stages, initiation, propagation, and termination. Initiation may be considered in two steps. Firstly, the initiator (I) decomposes to give free radical (R*).

\[
I \underset{k_d}{\rightarrow} 2R^* \tag{2.26}
\]

The radical then reacts with a monomer unit (M) to form a
FIGURE 2.11

MODIFICATION OF PARTICLE NUCLEATION IN THE PRESENCE OF STABILIZER

(a) Self-nucleation

(b) Aggregative-nucleation
chain radical \( (M_1^*) \)

\[
R^* + M \xrightarrow{k_p} M_1^* \tag{2.27}
\]

Where \( k \)'s are rate constant with subscripts designating the reactions to which they refer. Subsequent propagation steps, of the general form

\[
M_x^* + M \xrightarrow{k_p} M_{x+1}^* \tag{2.28}
\]

are assumed to have the same rate constant \( k_p \), since radical reactivity is taken as being independent of chain length. The termination step involves either combination of radicals.

\[
M_x^* + M_y^* \xrightarrow{k_{tc}} M_{x+y} \text{ (polymer)} \tag{2.29}
\]

or disproportionation:

\[
M_x^* + M_y^* \xrightarrow{k_{td}} M_x + M_y \text{ (polymer)} \tag{2.30}
\]

Now, if the rate of initiation within the whole system is \( R_i \) and the polymer particles at a given time occupy a volume fraction \( V \) of the whole dispersion, then the effective initiation rate within the particles \( (R_{ip}) \) will be given by

\[
R_{ip} = R_i / V \tag{2.31}
\]
If \([M_p]\) is the monomer concentration within the particles, the rate of polymerization within the particle \((R_{pp})\) is given by an expression similar to that for bulk polymerization

\[
R_{pp} = [M_p]k_p (R_i/k_t)^{1/2}
\] (2.32)

\[
R_{pp} = [M_p]k_p (R_i/k_tV)^{1/3}
\] (2.33)

since essentially all polymerization occurs within the particles in the volume fraction \(V\). The overall rate of polymerization in the whole dispersion is given by

\[
R_p = VR_{pp}
\] (2.34)

\[
R_p = [M_p]k_p (VR_i/k_t)^{1/3}
\] (2.35)

The concentration of monomer within the particles depends upon the monomer partition coefficient \((\alpha)\) between polymer and the dispersion medium, since the monomer is completely miscible with the hydrocarbon diluent. Thus the overall rate of dispersion polymerization, is therefore, given by

\[
R_p = \alpha [M_d]k_p (VR_i/k_t)^{1/3}
\] (2.36)

Where \([M_d]\) is the monomer concentration in the dispersion medium. Equation (2.36) is the general equation for dispersion polymerization and it takes into account the
principal features of the kinetics which have been established [55]. In principle, the partition coefficient $\alpha$ may also vary with monomer concentration but the variation is usually not great and a constant value is a sufficiently good approximation for use in most of the kinetic studies. Two limiting cases to describe the kinetic model have been derived [55] which must be considered. The first case is when $\alpha$ and $V$ are small, the $[M_{d}]$ may be taken as the overall monomer concentration $[M]$. Here, $V$ is roughly equal to $[M_{o}]x. V_p$ where $[M_{o}]$ is the initial monomer concentration, $x$ is the fractional conversion and $V_p$ is the value of polymer per mole of monomer and since

$$[M] = [M_{o}] - x[M_{o}]$$  \hspace{1cm} (2.37)

then $R_p$ after rearrangement will be

$$R_p = \alpha[M_o]x^{1/2}(1-x)([M_o]R_p V_p)^{1/2}k_p/k_{\ell}^{1/2}$$ \hspace{1cm} (2.38)

The second limiting case is when $\alpha$ is large and most of the monomer is found within the particles. Here, $V$ is approximately equal to $[M_o].V_m$ where $V_m$ is the molar volume of the monomer. $[M_p]$ is then roughly equal to $(1-x)/V_m$, then:

$$R_p = (1-x)[M_o]R_i/V_m k_{r}/k_{\ell}$$ \hspace{1cm} (2.39)

The overall kinetic model, therefore, depends upon
the system. It has been shown [2] that the model derived for low values of $\alpha$ describes well the kinetics of the dispersion polymerization of methyl methacrylate and vinyl acetate, whilst equation (2.39) describes the dispersion polymerization of more polar monomers such as acrylonitrile.

2.7 RHEOLOGICAL STUDIES OF DISPERSIONS

Investigations concerned with rheological properties of colloidal dispersions can provide a better understanding of the nature of the dispersion and its behaviour, such as flocculation, state and conformation of the steric stabilizer at the interface, the thickness of the steric barrier, and therefore the effective volume of the particles, and particle anisotropy. The viscosity of colloidal dispersion is greater than that of the medium in which the colloid is dispersed [59].

The dependence of viscosity on particle concentration was first investigated theoretically by Einstein [59]. The well-known Einstein relationship was derived assuming that the particles were spherical, rigid and uncharged, that interparticle separation in the medium is large, and that there is no slip at the particle medium interface. A dispersion with a solid phase volume of only a few percent are so diluted that the transfer of momentum between particles during flow is negligible. Therefore, the difference observed between the viscometric behaviour of the dispersion and its medium alone is due only to the
perturbation of the normal flow of the latter. The Einstein equation is only applicable for dispersion with a volume fraction less than 0.01. As the particle concentration is increased, interparticle interactions become important and the viscosity then becomes second order in the volume fraction. The viscosity ($\eta$) of the dispersion is proportional to the viscosity of the dispersion medium, ($\eta_0$) and the volume fraction ($\phi$) of the particles as in the following equation [60]

$$\eta = \eta_0 (1 + \frac{5}{2} \phi + 4 \phi^2 + \frac{11}{2} \phi^3 + 7 \phi^4 + \ldots)$$  \hspace{1cm} (2.40)

Assuming that at such low concentrations the hydrodynamic interaction between particles can be ignored, the increase in viscosity produced by one particle can be summed over the total number of particles. Hence, equation (2.40) gives

$$\eta = \eta_0 (1 + \frac{5}{2} \phi)$$  \hspace{1cm} (2.41)

by neglecting all terms in $\phi$ of higher order than unity.

This equation is the well known Einstein equation containing the Einstein coefficient ($\alpha_0$) of 2.5, and is only strictly applicable at volume fractions approaching infinite dilution. At higher volume fractions up to about 0.25, dispersions still show Newtonian behaviour, and much work has been devoted to extend Einstein's approach to higher concentrations. At volume fractions greater than
0.01 the viscosity of a dispersion is increased due to the formation of temporary doublets, triplets and higher orders of association which enhance the rate energy dissipation. The power series in volume fraction in equation (2.40) becomes for more concentrated systems, of the form

\[ \eta / \eta_0 = 1 + K_1 \phi + K_2 \phi^2 + K_3 \phi^3 + K_4 \phi^4 + \ldots \]  

This equation reduces to Einstein's equation for a dilute system of rigid non-interacting spheres; hence \( K_1 \) is taken as Einstein's coefficient 2.5. The coefficient \( K_2 \) describes the perturbation of streamlines by collision doublets, and \( K_3, K_4, \ldots \) describe higher order collisions. The values of \( K \) have been estimated by many workers, and their results have been reviewed [60, 61]. Values of \( K_2 \), which under Einstein conditions has a limit of 4.0, have been placed within the range 4 to 14.1 for a range of \( \phi \) of 0.48 to 0.74. The limitation of the power series to second order terms in the volume fraction is purely arbitrary and cannot be justified on fundamental ground.

At high values of \( \phi \), the cubic terms in equation (2.42) become important, although no vigorous hydrodynamic estimate of \( K_3 \) exists because of the difficulties in handling three-body interactions. The values of \( K_3 \) vary from 16 to 50 [60].

A large number of empirical and semi-empirical
equations have been proposed in the literature to account for the effect of particle concentration to the viscosity of the dispersion. One of the best known of these equations is due to Mooney [62] who proposed an equation of the form

$$\eta = \eta_0 \exp\left(\frac{2.5\phi}{1-k\phi}\right)$$

(2.43)

or

$$\ln\eta_r = \frac{2.5\phi}{1-k\phi}$$

(2.44)

Where $k$ is a self crowding factor.

Equation (2.44) was derived for rigid non-interacting spheres, and may be modified to study colloidal particles surrounded by an adsorbed polymer layer. It is then possible to calculate the thickness of the steric barrier ($\delta$) and thus infer the polymer conformation at the particle surface using such viscosity data.

If the volume fraction of the naked particles in the dispersion is $\phi_o$ and that for the particle with solvated layer is $\phi$, then the particle volume fraction is increased by a factor $f$ due to the solvated layer, where $f$ is defined as [63].

$$f = \frac{\phi}{\phi_o}$$

(2.45)

If the diameter of the particle is $D$, then by simple
geometrical arguments, Maron et al. [63] derived the value $f$ as

$$f = \left(1 + \frac{2\delta}{D}\right)^3$$  \hspace{1cm} (2.46)

or

$$f = 1 + \frac{6\delta}{D}$$ \hspace{1cm} (2.47)

Where equation (2.47) is, of course, the leading term in the expansion of equation 2.46. The dependence of relative viscosity $\eta_r$ on $\phi_o$ for sterically stabilized dispersions has been given by Saunders [64] who substituted the value of $f$ from equation (2.45) into equation (2.44) to give

$$\frac{\phi_o}{1n\eta_r} = \frac{1}{\alpha_o f} - \frac{k\phi_o}{\alpha_o}$$ \hspace{1cm} (2.48)

Where $\alpha_o f$ is the effective Einstein coefficient. For systems of very small particles, where the thickness of the adsorbed layer is significant compared with the particle diameter, the effective Einstein coefficient becomes [60].

$$\alpha_o f = \alpha_o (1 + \frac{2\delta}{D})^3$$ \hspace{1cm} (2.49)

2.8 THE CONFIGURATION OF POLYMER CHAINS

The stabilizing effects of polymer molecules are critically dependent upon their spatial extension and, therefore, upon their configuration. In general synthetic polymers do not exhibit relatively fixed configurations as do some biopolymers. A polymer molecule dissolved in a
solvent will be expanded depending on the degree to which solvent and polymer segments associate. If a polymer is in a "good" solvent, then the segments of the polymer will associate with the solvent molecules rather than with each other leading to the expanding of the total volume occupied by a single polymer chains. Then, the expansion factor $\alpha$ can be defined by

$$\alpha = \left( \frac{<r^2>}{<r_0^2>} \right)^{\frac{1}{2}}$$  \hspace{1cm} (2.50)$$

Where $<r^2>^{\frac{1}{2}}$ is the actual Root-mean-square (rms) end-to-end distance and $<r_0^2>^{\frac{1}{2}}$ is the distance when $\alpha = 1$ (unperturbed or un-swollen dimension). Values of $\alpha$ can be determined experimentally and fit a theoretical relationship [29].

$$\alpha^5 - \alpha^3 = C' M^{\frac{3}{2}} \left( 1 - \frac{\theta}{T} \right)$$  \hspace{1cm} (2.51)$$

Where $\theta$ is the theta temperature, $C'$ is a constant for a given polymer-solvent combination and $M$ is the molar mass. The $\theta$-temperature is the temperature at which polymer in the limit of infinite molar mass just starts to precipitate from solvent, and this is because the theta point occurs when polymer segments associate more with each other than they do with the solvent, reducing $\alpha$ to unity. The $\theta$-temperature is a characteristic temperature of a given polymer solvent combination. For a given polymer molecule
in solution, the intrinsic viscosity $[\eta]$ is proportional to the effective volume of the molecule in solution divided by its molar mass [29]. The effective volume is proportional to the cube of a linear dimension of the randomly coiling chain. If $<r^2>^{\frac{1}{2}}$ is the dimension chosen, then

$$[\eta] = \Phi \frac{<r^2>^{3/2}}{M} \tag{2.52}$$

Where $\Phi$ is a universal viscosity constant, which will be taken as $2.6 \times 10^{21}\text{mol}^{-1}$ [65]. By replacing $<r^2>^{\frac{1}{2}}$ by $\alpha<r^2>^{\frac{1}{2}}_o$ according to equation (2.50) and after rearrangement, equation (2.52) will be

$$[\eta] = \Phi <r^2>_o^{3/2} M^{3/2} \alpha^3 \tag{2.53}$$

The quantity $<r^2>_o^3$ is a function of chain structure independent of $M$ for a linear polymer of a given unit structure. Then

$$[\eta] = kM \frac{3}{2} \alpha^3 \tag{2.54}$$

Where $k = \Phi <r^2>_o^{3/2}$ is a constant for a given polymer, independent of solvent and molar mass.

Ordinarily, the intrinsic viscosity should depend on the molar mass not only owing to the factor $M^4$ according to equation (2.54) but also as a result of the dependence of the factor $\alpha^3$ on $M$. The influence of this expansion
resulting from intermolecular interactions may be eliminated by a suitable choice of solvent and temperature to give a $\theta$-solvent, when $\alpha = 1$ and equation (2.54) reduces to

$$[\eta]_\theta = K M^{1/2}$$

(2.55)
CHAPTER THREE

EXPERIMENTAL WORK
3.1 BLOCK COPOLYMER

Samples of the poly (styrene-b-[ethylene-co-propylene]) (S-EP) diblock copolymer were kindly provided by Dr B Wright, Shell Research Centre, Thornton, Chester, Dr A Bull, Shell Research BV, Amsterdam and Ms K F Churchley, Shell Centre, London. Characterization data for S-EP provided by Dr Wright were number average molar mass $M_n = 104,000$ g mol$^{-1}$, weight average molar mass $M_w = 118,000$ g mol$^{-1}$, and a styrene content of 38.5% by weight. Characterization experiments by gel permeation chromatography, see section 3.4.2, indicated that S-EP had a polydispersity $M_w/M_n \sim 1.1$. This S-EP diblock copolymer has therefore, a well-defined structure and had been produced by hydrogenating the polyisoprene block in a diblock copolymer of polystyrene-polyisoprene synthesised by anionic polymerization [66].

3.2 MICELLAR DISPERSIONS

Micellised solutions were prepared as follows. A known weight of a diblock copolymer stabilizer were dissolved in sufficient methylene chloride in a double-neck round-bottom flask equipped with a condenser, a suba-seal and magnetic stirrer. The required volume of the n-alkane was then added, and the methylene chloride removed by evaporation at high temperature leaving the micellar solution.

3.3 PREPARATION OF NON-AQUEOUS DISPERSIONS OF POLY (METHYL METHACRYLATE) AND POLY (VINYL ACETATE)
Methyl methacrylate (Aldrich Chemical Co Ltd, inhibited with 10 ppm hydroquinone monomethyl ether) was destabilized by washing twice with 10% KOH solution, then twice with distilled water and dried by stirring under vacuum for several days over ground calcium hydride. The monomer was degassed by the familiar freeze/degas/thaw cycles to ensure the removal of dissolved oxygen, and then distilled under vacuum immediately before use. Vinyl acetate (Aldrich Chemical Co Ltd, stabilized with 4 ppm hydroquinone and 300 ppm diphenyl amine) was degassed, and distilled under vacuum when required for use. The initiator azobisisobutyronitrile (AIBN) was double recrystallised from ethanol.

3.3.1 RADICAL DISPERSION POLYMERIZATION

The copolymer stabilizer was dispersed in an n-alkane, typically n-heptane (which had previously been dried over molecular sieve, degassed, and distilled under vacuum), by first leaving the mixture overnight at room temperature and then raising the temperature of the stirred mixture to 343 K. The entire solution was purged for 30 minutes with dry nitrogen to remove air, after which the purge was converted to a nitrogen blanket throughout the experiment. The polymerization apparatus fig 3.1 consisted of a round-bottom flask (100 cm$^3$) with side arm equipped with condenser and pressure equalized separating funnel. The temperature was controlled to ± 0.1 K by immersing the reactor in a thermostated bath. The stirring mechanism
was preformed by a magnetic bar inside the reactor and stirred through a magnetic stirrer placed under the water bath. Two polymerization techniques were used.

3.3.1.1 ONE-SHOT POLYMERIZATION TECHNIQUE

Monomer containing the dissolved initiator was added to the n-alkane dispersion medium containing the appropriate concentration of copolymer stabilizer at the desired polymerization temperature (usually 343K), and the initially clear solution soon became cloudy and then opaque white, as the dispersion was produced. After the required time (usually 10 hours for methyl methacrylate and 50 hours for vinyl acetate), the dispersion was cooled and transferred to a storage bottle at room temperature. The extent of monomer conversion was estimated by determining the polymer content of a sample (1.0 cm$^3$) of the final dispersion, by drying the sample to a constant weight under vacuum at room temperature.

3.3.1.2 SEEDED POLYMERIZATION TECHNIQUE

This technique consisted of two stages; a seed stage and growth stage. The seed stage was performed by adding monomer (20% by weight of the total monomer with the equivalent proportion of the initiator) to the dispersion medium containing the copolymer stabilizer at the polymerization temperature. After this addition, the seed dispersion was allowed to form for 2 hours for PMMA and 13 hours for PVA. When the seed stage had been accomplished,
the growth stage was started by adding the remaining monomer (with initiator) incrementally as a feed over a period of 30 minutes for MMA and 2 hours for VA. The total reaction time for the dispersion polymerization of MMA and VA was 10 and 50 hours respectively, after which the dispersion was cooled and stored as before. The effect of varying initiator, monomer and stabilizer was studied, and the results are summarized in tables 3.1 and 3.2.

3.3.2 RATE OF POLYMERIZATION STUDIES

The extent of monomer conversion was followed as a function of time for each of the dispersion polymerization systems studied. Samples of dispersion (0.2 cm$^3$) at fixed time intervals were removed by a syringe to a small preweighed flat-bottom tube. After removing each sample, the tube was cooled in ice-cold water to stop the polymerization. The tube was then weighed again before allowing the diluent and the unpolymerized monomer to evaporate in a vacuum oven at room temperature to a constant weight.

3.3.3 PURIFICATION OF NON-AQUEOUS DISPERSION BY REDISPERSION

In order to remove unconverted monomer, unadsorbed stabilizer and initiator residues from the dispersions prepared, the dispersions were subjected to several redispersion cycles. The dispersion was centrifuged at 15000 rpm for 30 minutes and the supernatant above the sedimented polymer particles was replaced by fresh dispersion medium, such as n-heptane. The particles were
### TABLE 3.1

**REACTION CONDITIONS OF THE POLYMERIZATION OF MMA**

<table>
<thead>
<tr>
<th>No.</th>
<th>AIBN (wt%)</th>
<th>S-EP (wt%)</th>
<th>MMA (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DM1</td>
<td>0.5</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DM2</td>
<td>0.75</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DM3</td>
<td>1</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DM4</td>
<td>1.5</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DM5</td>
<td>0.3</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DM6(a)</td>
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<td>20</td>
</tr>
<tr>
<td>DM7</td>
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<td>6</td>
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</tr>
<tr>
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<td>4</td>
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</tr>
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<td>3</td>
<td>20</td>
</tr>
<tr>
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<td>2</td>
<td>20</td>
</tr>
<tr>
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</tr>
<tr>
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<td>5</td>
<td>30</td>
</tr>
<tr>
<td>DM13</td>
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<td>5</td>
<td>15</td>
</tr>
<tr>
<td>DM14</td>
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<td>5</td>
<td>25</td>
</tr>
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<td>DM20</td>
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<td>5</td>
<td>20</td>
</tr>
<tr>
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<td>0.75</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DM22</td>
<td>0.3</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DM23</td>
<td>0.5</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>DM24</td>
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<td>3</td>
<td>20</td>
</tr>
<tr>
<td>DM25</td>
<td>0.5</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DM26</td>
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</tr>
<tr>
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<td>20</td>
</tr>
<tr>
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<td>35</td>
</tr>
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<td>DM29</td>
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<td>5</td>
<td>10</td>
</tr>
<tr>
<td>DM31(a)</td>
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<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DM32</td>
<td>0.5</td>
<td>5</td>
<td>20</td>
</tr>
</tbody>
</table>

(a) one-shot polymerization
## TABLE 3.2

REACTION CONDITIONS FOR THE POLYMERIZATION OF VA

<table>
<thead>
<tr>
<th>No.</th>
<th>AIBN wt%</th>
<th>S-EP wt%</th>
<th>VA wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>DV1</td>
<td>2</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DV2</td>
<td>0.5</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DV3</td>
<td>0.75</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DV4</td>
<td>1</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DV5</td>
<td>1.5</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DV6</td>
<td>1</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>DV7</td>
<td>1</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>DV8</td>
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<td>4</td>
<td>20</td>
</tr>
<tr>
<td>DV9</td>
<td>1</td>
<td>6</td>
<td>20</td>
</tr>
<tr>
<td>DV10</td>
<td>1</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>DV11</td>
<td>1</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>DV12</td>
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<td>5</td>
<td>25</td>
</tr>
<tr>
<td>DV13</td>
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<td>5</td>
<td>30</td>
</tr>
<tr>
<td>DV14(a)</td>
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</tr>
<tr>
<td>DV20</td>
<td>1</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DV21</td>
<td>1</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DV22</td>
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<td>5</td>
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</tr>
<tr>
<td>DV23(a)</td>
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</tr>
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<td>DV24</td>
<td>1</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>DV25</td>
<td>1</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>DV26</td>
<td>1</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DV27</td>
<td>0.5</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DV28</td>
<td>1.5</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DV29</td>
<td>1</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>DV30</td>
<td>1</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>DV31</td>
<td>0.5</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>DV32</td>
<td>1</td>
<td>5</td>
<td>20</td>
</tr>
</tbody>
</table>

(a) one-shot polymerization
redispersed by vigorous shaking or ultrasonic vibration, and the redispersion cycle repeated. Analysis of the supernatant by infra-red spectroscopy demonstrated that six such redispersion cycles were usually sufficient to reduce the excess stabilizer to negligible proportions. Redispersion also provided a way of exchanging the dispersion medium for a different one, and products prepared were redispersed in n-hexane and n-heptane.

3.4 CHARACTERIZATION OF NON-AQUEOUS DISPERSIONS

3.4.1 PARTICLE SHAPE, SIZE AND SIZE DISTRIBUTION

Transmission electron microscopy (TEM) was used extensively to determine particle size, shape and size distribution. Samples were prepared by placing one drop of dilute redispersed dispersion (0.1% w/v, polymer content) directly onto a carbon-coated copper grid and evaporating to dryness. Samples were examined at magnifications of $10^4$ - $10^5$ times using a JEOL JEM 100 CX instrument calibrated with replica of 2160 lines mm$^{-1}$ grating. Particle size and size distribution were calculated from direct measurement of individual particles on the micrograph.

3.4.2 GEL PERMEATION CHROMATOGRAPHY

Gel permeation chromatography (GPC) was used to characterise the molar masses and the polydispersity of the S-EP samples supplied and the polymer produced in the dispersions. A modified Waters 502 ALC/GPC instrument, having a refractive index detector, was operated at room temperature using tetrahydrofuran (THF) as eluent at a
constant flow rate of 1 cm³ min⁻¹. The column (Polymer Laboratories) was a mixed bed PL gel column (60 cm) containing crosslinked polystyrene gels and was calibrated with polystyrene standards with a narrow molar mass distribution (Polymer Laboratories) having molar masses from 200 to 2 x 10⁶ g mol⁻¹. A calibration curve was plotted between the log (peak molar mass) and the percentage of elution volume of the polymer to the elution volume of the internal standard (toluene), and is presented in figure 3.2. Solution injection volumes were 100 µl with a sample concentration of 0.025% (w/v). Calculation of the number average and weight average molar masses $M_n$ and $M_w$ (g mol⁻¹) respectively, and the polydispersity $M_w/M_n$, were obtained from a chromatogram with a computer program employing a molar mass calibration established with polystyrene standards [67].

3.4.3 PERCENTAGE OF BLOCK COPOLYMER IN DISPERSIONS

Dried dispersion samples were analysed for copolymer content using a Kantron Uvikon 810 U.V. spectrophotometer. Absorbance values for the wavelength range 200-400 nm were obtained on several solutions of different copolymer content in chloroform, and a calibration curve of peak height at 272 nm against copolymer concentration was plotted in figure 3.3. Samples (2 mg cm⁻³) of dried dispersion in chloroform were prepared and from the peak height at 272 nm the exact concentration and as a consequence the percentage of copolymer can be calculated.
FIGURE 3.2

CALIBRATION CURVE FOR POLYSTYRENE STANDARDS IN THF
FIGURE 3.3

CALIBRATION CURVE BETWEEN THE PEAK HEIGHT AT 272 nm AND THE S-EP CONCENTRATION

[Graph showing a linear relationship between peak height in mm and concentration in $10^{-5}$ g cm$^{-3}$]
U.V. spectrophotometry was also used to calculate the polystyrene content in the block copolymer samples. A series of solutions of a polystyrene standard (molar mass = 32000 and $M_w/M_n = 1.04$) in chloroform was prepared. The peak height at 272 nm was plotted against polystyrene concentration as shown in figure 3.4.

3.4.4 ISOLATION AND ANALYSIS OF THE STABILIZER ADSORBED ON PMMA AND PVA PARTICLES

The stabilizer adsorbed on PMMA and PVA particles was isolated from washed and dried samples of the dispersed phase. Acetone and methanol (all Fisons S.L.R grade) were used individually as an extraction solvent in a Soxhlet apparatus and the extraction continued for 240 h. The residue left after extraction was washed with methanol, dried at room temperature, and then analysed for the polystyrene content, the percentage of the unextracted polymer and for the average molar masses.

3.4.5 SURFACE COVERAGE

The surface coverage of the polymer particles could be conveniently estimated from copolymer content. Samples of the dispersions were washed by redispersion cycles as described earlier in section 3.3.3 to remove unadsorbed stabilizer. The dispersion medium was then evaporated under vacuum and the dried dispersed phase subjected to U.V. spectroscopic analysis as described in section 3.4.3. The area A occupied by a single ethylene-propylene chain at
FIGURE 3.4

CALIBRATION CURVE BETWEEN THE PEAK HEIGHT AT 272 nm AND THE CONCENTRATION OF POLYSTYRENE
the surface of a particle was calculated from copolymer content and the transmission electron microscope estimate of particle diameter.

3.5 FLOCCULATION STUDIES

Dispersions were flocculated by reducing the solvency of the dispersion medium in two ways; first by adding n-propanol, a non-solvent for ethylene-propylene copolymer, and second by cooling a dispersion having a dispersion medium of a mixture of n-heptane and n-propanol (70:30%, v/v). The conditions at which incipient flocculation was observed are termed the critical flocculation volume (CFV) of added non-solvent and the critical flocculation temperature (CFT).

3.5.1 DETERMINATION OF CFV

Determinations of CFV were performed with dispersions in a cell designed and constructed to be accommodated in a Unicam SP 600 UV-visible spectrophotometer operating at 600 nm. The sample compartment containing the dispersion was surrounded by a jacket containing water circulated from an external thermostated bath. A rotating magnet beneath the cell rotated a bar stirrer in the sample compartment to ensure, constant and efficient mixing of the dispersion. A diagram showing the essential features of this cell is presented in figure 3.5. A dispersion (polymer content 2 x 10^{-3} g cm^{-3}) in n-heptane (10 cm^3) was contained in the cell at 298K. Addition of n-propanol (99.9% Aristar grade) to the stirred dilute dispersion was through a fine
FIGURE 3.5

THE CELL FOR FLOCCULATION STUDIES

1 - Water in
2 - Water out
3 - Glass cell
4 - Water jacket
5 - Light window
6 - Magnetic follower
7 - Rotated magnet
8 - Motor
9 - Gears
hypodermic needle from a microburette. Time for equilibrium was allowed between additions of n-propanol. The drop size was such that n-propanol could be added in increments of 0.001 cm$^3$. The addition was continued until the original solution started to show turbidity as measured by a significant change in transmittance, from which the solvet/non-solvent composition by volume at flocculation was calculated.

3.5.2 DETERMINATION OF CFT

Determination of CFT were performed with the same cell which was used for CFV experiments. A dispersion (polymer content $2 \times 10^{-3}$ g cm$^{-3}$) in n-heptane (10 cm$^3$) was added to the cell at 298K. n-propanol was added drop wise to this stirred dispersion to give a dispersion medium of n-heptane/n-propanol (70:30, v/v). The stirred contents of the cell were heated to at least 5° above the CFT and then allowed to cool at the rate of 1° per 360s, and the temperature at which a significant change in transmittance was observed was recorded as the CFT.

Flocculation was noticed to be reversible, and addition of further n-heptane or an increase in temperature produced de-flocculation. Stopping the stirrer at the flocculation point caused a remarkable decrease in the turbidity as the flocs settled.

3.6 ETHYLENE - PROPYLENE COPOLYMER STANDARDS

Narrow distribution ethylene-propylene copolymer standards (EP) for the phase separation experiments were
obtained by the hydrogenation of polyisoprene (PI) standards (Polymer Laboratories, Church Stretton, Shropshire, England) having a cis 1,4 content > 95%. The hydrogenation was performed with diimide generated in situ from p-toluene sulphonyl hydrazide (TSH) [68, 69] in the presence of the hindered phenol Irganox 1010 antioxidant (pentaerythritol-tetrakis-3-(3,5-di-tert. butyl-4-hydroxyphenyl)-propionate, M.P. = 110 — 125°C [70]), which was added to prevent incorporation of TSH fragments into any pendant vinyl groups in PI [71].

PI (1 gm) was dissolved in xylene (100 cm³). TSH (Aldrich Chemical Company) was recrystallized from ethanol, dried under vacuum at room temperature and then added to the PI solution to yield 3 moles of diimide per mole of double bonds. Irganox 1010 (0.01 gm) obtained from Ciba-Geigy Industrial Chemicals, was then added to the solution which was refluxed under nitrogen for 8 hours in order to thermally decompose TSH to produce the active hydrogenating diimide species. The product was precipitated with excess methanol, washed several times with hot distilled water, redissolved in xylene, reprecipitated with excess methanol, and dried at 313K under vacuum for 24 hours. Polymer characterization was performed by infra-red spectroscopy (Perkin-Elmer model 1310), ¹H nuclear magnetic resonance spectroscopy (Perkin-Elmer R32 instrument operating at 90 MHz), and thermal analysis (Perkin-Elmer model DSC4 operating at 20°
min\(^{-1}\)). Molar mass characterization by GPC was performed as described in sections 3.4.2.

### 3.6.1 PHASE SEPARATION OF EP COPOLYMERS

The apparatus and experimental procedure were similar to those described in the determinations of CFV and CFT. Phase separation was induced by adding the non-solvent, n-propanol, to a solution of EP copolymer in n-heptane at 298K and by cooling a solution of EP copolymer in a mixture of n-heptane/n-propanol (70:30% v/v).

In the determination of the \(\Theta\)-composition, n-propanol was added dropwise to a solution of EP copolymer in n-heptane (10 cm\(^3\)) until the original clear solution started to show turbidity as measured by a significant change in transmittance. The solvent/non-solvent composition by volume at phase separation was calculated. Experiments were performed for two EP copolymers over a range of copolymer concentrations (0.1 - 3.0%, w/v).

In the determination of the \(\Theta\)-temperature, EP copolymer was dissolved in n-heptane, and n-propanol was then added to give a mixture of n-heptane/n-propanol (70:30%, v/v) whilst maintaining the solution at a temperature above the cloud point. The temperature was then reduced at a rate of 1\(^\circ\) per 360s until phase separation occurred as detected by a significant change in transmittance, and the cloud point temperature \(T_p\) (K) was noted. Rigorous methods for determine \(\Theta\)-temperature are laborious [29], and so two rapid methods have been utilised.
3.6.1.1. SUH AND CLARKE METHOD [72]

This method involved the determination of the temperature at which turbidity developed on cooling the stirred solution of EP copolymer as a function of the concentration in a mixture of n-heptane/n-propanol (70:30,v/v). Experiments were performed for samples EP3 and EP4 (table 4.1) over a range of copolymer concentrations (0.5–3.0%, w/v).

3.6.1.2 TALAMINI AND VIDOTTO METHOD [73]

This method involved the determination of the cloud point on cooling as a function of the number average degree of polymerization $x_n$ of EP copolymer (calculated from $M_n$ with the molar mass of a repeating unit assumed to be 70 g mol$^{-1}$) for the same concentration of copolymer (1% w/v) in the mixture of n-heptane/n-propanol (70:30, v/v). Four EP copolymer samples (EP2, EP3, EP4 and EP5 in table 4.1) having a number average molar mass in the range 36900 – 233000 g mol$^{-1}$ were used in this method.

3.6.2 SOLUTION VISCOSITIES OF EP COPOLYMERS

Relative and specific viscosities, and as a result intrinsic viscosities, were determined for an EP copolymer dissolved in n-heptane and in a binary liquid mixture of n-heptane/n-propanol (79:21,v/v). The EP copolymer concentration was in the range 0.4 – 2.0 g dl$^{-1}$ and measurements were performed with an Ubbelohde viscometer grade 1. Sample EP3 (see table 4.1) was studied in n-heptane and in the binary liquid mixture of n-heptane/
n-propanol (79:21, v/v) at three temperatures 298, 308 and 318 ± 0.02K. Flow times for these solvents exceeded 150s, and so kinetic energy corrections were neglected [74]. At least five concentrations were used for each experiment by successive dilution in the viscometer. All solvents and solutions were filtered through a fine fibre glass filter paper before introducing them in the viscometer to eliminate any dust particles that may affect the results. Solution viscosity data were extrapolated to a common intercept to find the intrinsic viscosity.

3.7 RHEOLOGY

The relative viscosities of dispersions at dispersed phase volume fractions of 0.02 - 0.16 were measured with a Cannon-Fenske capillary viscometer having a capillary diameter of 0.55 mm. This diameter was very large compared to the diameter of the dispersion particles so that corrections for wall-effects could be neglected [74]. Relative viscosities were determined for dispersion particles in n-heptane and a mixture of n-heptane/n-propanol (79:21%, v/v) at the three temperatures 298, 308 and 318 ± 0.02K. Cumulative errors arising from dilution procedures were avoided by gravimetrically determining the polymer content of samples of the dispersion at each dilution. The viscometer was washed with filtered n-heptane and filtered chloroform and dried between each determinations.

Particles of the non-flocculated dispersions tend to
accumulate with time on the walls of the glassware used. A method proposed to prevent this involved the prior adsorption of block copolymer stabilizer on the glass [75], but no improvement here was noted. The problem was overcome completely by silylating all glassware with a solution of chlorotrimethylsilane (10% w/v) in chloroform [76]. Glassware was baked for several hours at 373K before cooling and filling with the silylating agent. After 24 hours exposure to this silylating agent, glassware was washed thoroughly with filtered chloroform and dried. The silylation of the viscometer in such manner remained effective for at least six months.
CHAPTER FOUR

RESULTS AND DISCUSSION
4.1 BLOCK COPOLYMER AND EP COPOLYMER STANDARDS

4.1.1 MICELLAR DISPERSIONS

Solutions of block copolymer by their bluish tint indicated the presence of molecular aggregated "micelles". A typical transmission electron micrograph of the micelles is shown in Figure 4.1. It is evident that the micelles appear spherical and have a narrow size distribution. During the preparation of the sample for TEM, the layer of EP chains collapsed onto the surface of the PS core when the solvent was removed. These collapsed layers are of negligible thickness, and so the diameter of the core was taken directly from the micrograph.

There is a possibility that the PS core may be swollen in n-alkane to some extent. Plestil and Baldrian [77] have studied the micelles formed by AB block copolymer of Polystyrene-polybutadiene in n-heptane by small angle x-ray scattering technique. They estimated that the swelling factor (ratio of the swollen to unswollen core volume) for a micelle core having a PS block with $\bar{M}_n$(PS) = 15700 was 1.1 at 291K. NMR studies have indicated that the PS cores in micelles of S-EP ($\bar{M}_n = 40000$) in n-octane are mainly glassy in nature [48]. The core diameter predicted in this work does not take into account any swelling behaviour, since the molar mass of the PS block in S-EP was sufficiently high enough for swelling to be neglected.

The micelle diameter for S-EP from Figure 4.1 was found to be 250Å and the number of copolymer molecules per micelle (micellization number "n" in equation 2.25) was found to be 129 in very good agreement with the micellar
FIGURE 4.1

S-EP MICELLES
core, and the number "n" of the same block copolymer determined from small angle neutron scattering studies [78].

4.1.2 HYDROGENATION OF POLYISOPRENE

The polyisoprene (PI) samples which were subjected to hydrogenation were within the molar mass range of 8000 - 305000 g mol⁻¹, and they are shown in table 4.1. The spectroscopic characterization of products formed from the treatment of PI with p-toluenesulphonyl hydrazide (TSH) indicated that hydrogenation proceeded to more than 99%.

The infrared (IR) spectra shown in Figure 4.2 of the PI before and after hydrogenation, show that the alkene band at 1680 cm⁻¹ and alkene C-H bands at 835 and 3050 cm⁻¹ in PI are removed by hydrogenation. Calculations of absorbance for EP copolymers were performed for the absorption band at 720-740 cm⁻¹, corresponding to ethylene content and for the band at 1160 cm⁻¹, arising from CH₃ groups and thus corresponding to propylene content. The calibration curve (see Figure 4.3) for the absorbance ratio of these two bands against the ethylene/propylene weight ratio proposed by Ng and co-worker [79] was extended up to weight ratio of 4 by calibration experiments with blends of homopolymers of polyethylene and polypropylene. The absorbance ratio for the two bands was consistent with a 1:1 composition for ethylene and propylene units in the samples under investigation. The ¹H nuclear magnetic resonance (NMR) spectra in Figure 4.4 show that the >C=CH-
TABLE 4.1
MOLAR MASS DATA FOR ETHYLENE-PROPYLENE COPOLYMERS

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_P^a$</th>
<th>MWD$_P^b$</th>
<th>MWD$_P^c$</th>
<th>$M_{EP}^d$</th>
<th>$M_n$(EP)</th>
<th>MWD(EP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP1</td>
<td>8000</td>
<td>1.03</td>
<td>1.05</td>
<td>9000</td>
<td>8800</td>
<td>1.05</td>
</tr>
<tr>
<td>EP2</td>
<td>34000</td>
<td>1.05</td>
<td>1.08</td>
<td>38700</td>
<td>36900</td>
<td>1.10</td>
</tr>
<tr>
<td>EP3</td>
<td>60000</td>
<td>1.05</td>
<td>1.19</td>
<td>54300</td>
<td>47400</td>
<td>1.31</td>
</tr>
<tr>
<td>EP4</td>
<td>135000</td>
<td>1.04</td>
<td>1.13</td>
<td>114000</td>
<td>100000</td>
<td>1.30</td>
</tr>
<tr>
<td>EP5</td>
<td>305000</td>
<td>1.05</td>
<td>1.07</td>
<td>275000</td>
<td>233000</td>
<td>1.39</td>
</tr>
</tbody>
</table>

a Peak molar mass for PI precursor supplied by Polymer Laboratories.

b Polydispersions supplied by Polymer Laboratories.

c Polydispersions found in this laboratory.

d Peak molar mass calculated according to the following equation:

$$\log M_{EP} - \log M_{PS} = \log C$$
FIGURE 4.2

INFRARED SPECTRA FOR PRECURSOR POLISOPRENE STANDARD (A)
AND ETHYLENE-PROPYLENE EP3 (B)
FIGURE 4.3

CALIBRATION CURVE OF ABSORBANCE RATIO A720/A1160 vs WEIGHT RATIO [ETHYLENE] / [PROPYLENE]
\( ^1H \) NUCLEAR MAGNETIC RESONANCE SPECTRA FOR PRECURSOR POLYISOPRENE STANDARD (A) AND ETHYLENE-PROPYLENE COPOLYMER EP3(B)
chemical shift $\delta = 5.04$ p.p.m. in PI is removed completely by treatment with TSH. The methyl protons which appeared as a singlet at 1.64 p.p.m. for the PI became a doublet shifted to 0.77 and 0.98 p.p.m. in the product which is consistent with the addition of a proton to a carbon atom adjacent to a methyl group. Finally, the CH$_2$ - doublet at 1.95 and 2.00 p.p.m. in the PI became a multiplet at 1.23 p.p.m. The spectrum for hydrogenated PI in Figure 4.4 is consistent with previous work [68, 69, 80]. The first spectroscopic studies [68, 69] of hydrogenated PI indicated that fragments of TSH could be incorporated at low levels because of reactions involving pendant unsaturated groups in the original PI sample. Cyclic structures may also be generated during hydrogenation [80]. The addition of the hindered phenol inhibitor (Irganox 1010) together with the appropriate reaction conditions as proposed by Wang and co-workers [71] appears to minimise side reactions and limit the number of structural imperfections in hydrogenated PI to very low and probably negligible concentrations. It was demonstrated that IR and NMR spectra for a blend of a PS standard ($\overline{M}_n = 35000$) and sample EP3, with a PS composition of 38.4% by weight, were identical with spectra obtained for S-EP as shown in Figures 4.5 and 4.6.

GPC characterization of the products from the hydrogenation reactions indicated changes in molar mass distribution. Chromatograms for the EP copolymers exhibited somewhat more tailing to low molar masses than
FIGURE 4.5

IR SPECTRA OF A BLEND OF PS AND EP3(a), AND AS-RECEIVED S-EP(b)
**FIGURE 4.6**

$^1$H NMR SPECTRA OF A BLEND OF PS AND EP3(a) AND AS-RECEIVED S-EP(b)
the PI standards. Tailing is also apparent on chromatograms reported by Wang and co-workers [71] who treated PI with TSH in xylene at 413K for up to 8 hours. The polydispersities increased as molar mass increased. These results indicate that during hydrogenations side reactions such as chain scission may be occurring.

Thermal analysis characterization showed that EP copolymers had a glass transition temperature (T_g) at 216K, which is in reasonable agreement with values reported for 1:1 alternating copolymers of ethylene/propylene [68, 81, 82]. This experimental glass transition temperature is somewhat higher than the predicted value of 197K obtained for an amorphous 1:1 copolymer by averaging the transition temperatures of the homopolymers, 148K (polyethylene) and 253K (polypropylene) [54].

The homogeneous hydrogenation of polyisoprene by "diimide" generated in situ is easy to perform at normal laboratory conditions and gives complete hydrogenation in a relatively short time with a very low level of side reactions such as chain scissions. Heterogeneous hydrogenations required extremely difficult conditions of temperature and pressure [83, 84], and only partial hydrogenation may be achieved after 24h treatment with Pd/CO_3 under laboratory conditions [85].
4.1.3 PHASE SEPARATION STUDIES

4.1.3.1 DETERMINATION OF $\Theta$-COMPOSITION FOR EP COPOLYMERS IN N-HEPTANE/N-PROPANOL MIXTURE

The $\Theta$-composition for EP copolymers in a n-heptane/n-propanol mixture was determined at 298K according to the Suh and Clarke method [72]. Plots of the square of the volume fraction of added n-propanol versus log volume fraction of EP copolymer ($v_2$) (density of EP copolymer = 0.862 gm cm$^{-1}$ [82]), were linear and extrapolation to pure polymer gave the $\Theta$-composition as percent volume. Figure 4.7 shows this plot for two EP copolymers (EP3 and EP4) and the common intercept gave a value of 22.25% added volume of n-propanol for the $\Theta$-composition.

4.1.3.2 DETERMINATION OF $\Theta$-TEMPERATURE FOR EP COPOLYMERS IN N-HEPTANE/N-PROPANOL MIXTURE

The $\Theta$-conditions for EP copolymers in a n-heptane/n-propanol mixture are given in table 4.2. Two methods were used for the determination of the $\Theta$-temperature. Method I is a modification of the cloud point method proposed by Cornet and Ballegooijen [86] who suggested a plot of the reciprocal phase separation temperature ($T_p^{-1}$) versus log $v_2$. Extrapolation of this plot to $v_2 = 1$ (i.e. at bulk copolymer) yields $1/\Theta$. Since the solubility parameters of EP polymer and n-heptane are very similar [54], a linear plot of ($T_p^{-2}$) versus log $v_2$, as proposed by Suh and Clarke [72] should be applicable. In Figure 4.8, the plots for two EP copolymers (EP3 and EP4) yielded a
DETERMINATION OF THETA COMPOSITION BY EXTRAPOLATING TO BULK ETHYLENE-PROPYLENE COPOLYMER ACCORDING TO SUH AND CLARKE METHOD, O = SAMPLE E3; • = SAMPLE EP4
**TABLE 4.2**

**THETA CONDITIONS FOR EP COPOLYMER IN N-HEPTANE/N-PROPA NOL**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>θ-condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theta composition at 298K</td>
<td>22.25% volume n-propanol</td>
</tr>
<tr>
<td>θ-temperature for n-heptane/n-propanol (70:30, v/v)</td>
<td>317.5K according to Suh and Clarke method, 317.5K according to Talamini and Vidotto method</td>
</tr>
</tbody>
</table>
FIGURE 4.6

DETERMINATION OF $T$ -TEMPERATURE(K) BY EXTRAPOLATING TO BULK ETHYLENE-PROPYLENE COPOLYMER ACCORDING TO SUH AND CLARKE METHOD. O = SAMPLE EP3; • = SAMPLE EP4
common intercept from which $\Theta = 317K$ for EP copolymer in the liquid mixture n-heptane/n-propanol (70:30, v/v). A second method of obtaining the $\Theta$-temperature was used to check on method I. This method involves plotting $(T_p)^{-1}$ versus the reciprocal number average degree of polymerization to the power of 0.6 $(x_n)^{-0.6}$, as proposed by Talamini and Vidotto [73]. This plot is shown in Figure 4.9, from which the intercept corresponding to $1/\Theta$ may be obtained by extrapolating to infinite $x_n$. A value of $\Theta = 317.5K$ as obtained by method II, and this value is in good agreement with the $\Theta$-value determined by method I despite the additional error introduced by using molar mass data to calculate $x_n$ values plotted in Figure 4.9.

4.1.4 SOLUTION VISCOSITY OF EP COPOLYMERS

The intrinsic viscosity [$\eta$] for EP3 in various solvents was obtained from the common intercept plots of $\eta_{sp}/C$ and $\ln \eta_r/C$ versus the polymer concentration $C$ (gdl$^{-1}$). $\eta_{sp}$ is the specific viscosity obtained from $\eta_r^{-1}$ where $\eta_r$ is the relative viscosity. Solution viscosity data for copolymer EP3 in n-heptane at 298,308 and 318K are plotted in Figure 4.10. Values of [$\eta$] deduced from the intercept of these plots permit the calculation of the root-means-square end-to-end distance $<r^2>^{0.5}$ of free EP copolymer chain in solution according to relation 2.52 [29] and the results are summarized in table 4.3. Since n-heptane may be considered to be a good solvent for EP copolymer (from values of solubility parameter [54],
FIGURE 4.2

DETERMINATION OF $\theta$-TEMPERATURE (K) BY EXTRAPOLATING TO INFINITE MOLAR MASS OF ETHYLENE-PROPYLENE ACCORDING TO TALAMINI AND VIDOTTO METHOD.
DEPENDENCE OF SOLUTION VISCOSITY ON THE CONCENTRATION OF COPOLYMER EP3 in n-HEPTANE
**TABLE 4.3**

CHAIN DIMENSIONS OF EP3 COPOLYMER IN N-HEPTANE AND IN A BINARY LIQUID MIXTURE OF N-HEPTANE/N-PROPANOL

<table>
<thead>
<tr>
<th>Temperature/K</th>
<th>([\eta])</th>
<th>(&lt;r^2&gt;^{0.5}/\text{Å}(a))</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.765</td>
<td>251(^{(b)})</td>
</tr>
<tr>
<td>308</td>
<td>0.725</td>
<td>247(^{(b)})</td>
</tr>
<tr>
<td>318</td>
<td>0.695</td>
<td>244(^{(b)})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature/K</th>
<th>([\eta])</th>
<th>(&lt;r^2&gt;^{0.5}/\text{Å}(a))</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.56</td>
<td>227(^{(c)})</td>
</tr>
<tr>
<td>308</td>
<td>0.595</td>
<td>232(^{(c)})</td>
</tr>
<tr>
<td>318</td>
<td>0.645</td>
<td>238(^{(c)})</td>
</tr>
</tbody>
</table>

- **a.** The values \(<r^2>^{0.5}\) calculated according to equation 2.52.
- **b.** Values of \(<r^2>^{0.5}\) in n-heptane.
- **c.** Values \(<r^2>^{0.5}\) in a mixture of n-heptane/n-propanol (79:21, v/v).
the change in $<r^2>^{0.5}$ over the temperatures range from 298 to 318K is expected to be very small [65].

Solution viscosity data for copolymer sample EP3 in a binary liquid mixture of n-heptane/n-propanol (79:21, v/v) which is just better than a theta system at 298K for the EP copolymer chain are plotted in Figure 4.11 at the three temperatures 298, 308 and 318K. Values of $[\eta]$ deduced from the intercepts of these plots are lower than the results in Figure 4.10 at the corresponding temperatures, confirming the decrease in coil size in solution when the good solvent n-heptane for the EP copolymer chain is replaced by the binary liquid mixture which is almost a theta solvent. The values of $[\eta]$ in Figure 4.11 and therefore $<r^2>^{0.5}$ is predicted to increase when a solution is heated just above theta condition [29].

4.2 DISPERSION POLYMERIZATION

Seeded polymerization was used in all experiments, unless other conditions are stated. The seed particles were allowed to form for 2 hours for PMMA and for 12 hours for PVA. When the seed stage had been accomplished, the remaining monomer with the initiator was added incrementally as a feed over a period of 30 minutes for MMA and 2 hours for VA, after which polymerization continued for 10 and 50 hours for MMA and VA respectively.

4.2.1 NON-AQUEOUS RADICAL DISPERSION POLYMERIZATION OF MMA

PMMA dispersions have been prepared and stabilized with S-EP diblock copolymer as described in section 3.3.
FIGURE 4.11

DEPENDENCE OF SOLUTION VISCOSITY ON THE CONCENTRATION OF COPOLYMER EP3 IN n-HEPTANE / n-PROPanOL (79:21, v/v)
The extent of monomer conversion was followed as a function of time for each dispersion polymerization. Although MMA is miscible in all proportions with most aliphatic hydrocarbons the solubility of PMMA in aliphatic hydrocarbons is almost negligible, so swelling of the polymer particles by the diluent could be neglected. The polymerization temperature of 343K was chosen to prepare stable colloidal dispersions for the following reasons. Below 323K the S-EP stabilizer molecules are in a strongly associated state (micelles) [48]. According to a general conclusion by Barrett [2], when the polymeric anchoring component of the dispersant strongly associates with itself, a higher reaction temperature is necessary for the dispersant to be effective in a dispersion polymerization. This leads in turn to the concept that the reaction temperature must be sufficiently high to enable the micellar aggregate of the dispersant molecules to dissociate freely. In practice, the polymerization temperature of 343K was high enough to allow the dispersant molecules to leave micellar associates and to move freely in the solution (the equilibrium shifts towards the free state in Figure 2.9), to give a reasonable rate of initiator decomposition and to be below the refluxing temperature of the dispersion medium to reduce evaporation, and minimize concentration changes.

In Figure 4.12 monomer conversion data are presented for dispersion polymerizations with S-EP stabilizer concentrations of 1, 3 and 5 Wt% in the presence of
FIGURE 4.12

MMA CONVERSION VERSUS TIME WITH DIFFERENT S-EP WEIGHT %

- 5 wt %
- 3 wt %
- 1 wt %

Monomer conversion / wt %

Time / hours
constant monomer concentration (20 Wt%) and constant initiator concentration (0.5 Wt%). It is apparent that the monomer conversion is highest with the highest stabilizer concentration. As the concentration of S-EP stabilizer is reduced, so the MMA conversion curve tends towards a form similar to an ordinary solution polymerization as shown in the polymerization with the 1 Wt% S-EP stabilizer in Figure 4.12. The gel-effect is evident for higher concentrations of the S-EP stabilizer. In many cases, the total MMA conversion for a given reaction time in radical dispersion polymerization was found to be higher than that of the equivalent solution polymerization, see for example the monomer conversion data for solution polymerization of MMA according to Schulz and Harborth [87]. The kinetics of dispersion polymerization processes have been interpreted in terms of a diffusion-controlled reaction of a polymeric radical trapped in a highly viscous polymer matrix [88] and the restricted termination of the polymeric radicals due to the retardation of diffusion of polymeric radicals within the swollen polymer particles. Once particles have formed they absorb monomer from the diluent phase. Within the particles, polymerization follows bulk monomer kinetics. The high viscosity of this monomer-swollen polymer phase greatly hinders radical termination. The resulting increase in radical concentration accelerates the rate of polymerization (gel-effect).

Any radicals initiated in the diluent phase are swept
up by particles before radicals have had time to grow more than a very few monomer units. This results in an enormous decrease in the effective radicals concentration in the diluent phase, suppressing both solution polymerization and the formation of new particles. Since all radicals formed rapidly find their way to the particles, this implies that initiation from the kinetic point of view can be treated as if it were all in the particle phase, even though common peroxide and azonitrile initiators are partitioned between particles and diluent.

Barrett and Thomas [55] studied the rate of dispersion polymerization of MMA in the presence of a graft copolymer which was compared with the solution polymerization of MMA in benzene. They found that the rate of dispersion polymerization was very much faster than that of solution polymerization (ratio of 12.5:1). They concluded that the greatly accelerated rate of dispersion polymerization is a characteristic of restricted radical termination, either by isolation, as in an emulsion system, or by diffusion control, as in high-conversion bulk polymerization.

Monomer conversion data are presented in Figure 4.13 with MMA concentrations of 10, 20 and 30 Wt% in the presence of constant S-EP stabilizer concentration (5 Wt%) and constant initiator concentration (0.5 Wt%). A higher rate of monomer conversion was observed for higher monomer concentration. Figure 4.14 shows the effect of using different initiator concentrations (0.3, 0.5, 0.75 and 1.0
FIGURE 4.13

MMA CONVERSION VERSUS TIME WITH DIFFERENT MMA WEIGHT %

- 30 wt%
- 20 wt%
- 10 wt%

Monomer conversion / wt %

Time / hours

Seed
Growth
FIGURE 4.14

MMA CONVERSION VERSUS TIME WITH DIFFERENT AIBN WEIGHT %

- 1 wt%
- 0.75 wt%
- 0.5 wt%
- 0.3 wt%

Monomer conversion / wt %

Time / hours

growth seed
Wt% on monomer conversion at constant monomer concentration (20 Wt%) and constant S-EP stabilizer concentration (5 Wt%). Again a higher rate of monomer conversion for higher initiator concentrations was observed in all experiments performed.

The shape of the conversion-time curves in Figures 4.12-4.14 have a sigmoidal form in common with similar work reported in the literature [55, 89]. The initial acceleration corresponds to increasing particle size due to the increase of the average number of free radicals per particle during polymerization. The tailing off in rate at high conversion corresponds to a gradual diminution of the residual monomer content.

4.2.2 NON-AQUEOUS RADICAL DISPERSION POLYMERIZATION OF VA

The preparation of dispersions of PVA in water by emulsion polymerization is a very large and a well-established industry having applications in the emulsion paint and adhesive fields. In organic media, a dispersion polymerization can be similarly employed to give dispersions of colloidal PVA particles [90]. Non-aqueous dispersion polymerization of VA has received relatively little attention in the scientific literature. Napper [8] used a graft copolymer of poly(12-hydroxystearic acid) to sterically stabilize PVA particles in aliphatic hydrocarbons. Croucher and co-workers in a series of papers [91-93] have prepared PVA particles stabilized by grafting polystyrene in cyclopentane [91], poly(isobutylene) in
n-heptane [92] and poly(2-ethyl hexyl methacrylate) in isopar G (aliphatic hydrocarbon) [93]. Poly(ethylene oxide-b-vinyl acetate) have been used as a stabilizing dispersant for the dispersion polymerization of VA [89]. The only work involving the use of block copolymers in organic media was reported by Dawkins and co-workers [94, 95] who employed PS-PDMS to stabilize PVA particles in a non-aqueous medium. In the present work PVA dispersions have been prepared and stabilized with S-EP copolymer which has a well-defined molar mass and low polydispersity, so that the produced particles were expected to be spherical and to have a narrow particle size distribution and a uniform surface layer of the stabilizing EP chains.

In Figure 4.15 VA conversion data are presented for dispersion polymerizations with S-EP stabilizer concentrations of 1, 3 and 5 Wt% in the presence of constant monomer concentration (20 Wt%) and constant initiator concentration (1 Wt%). It is observed that monomer conversion is highest for the lowest concentration of S-EP stabilizer. This was a surprising observation and is clearly the reverse of the experimental results reported for MMA in Figure 4.12. It is difficult to explain the VA results in Figure 4.15, and only several very tentative contributory reasons (which require further experimental study) can be proposed as follows:

1. If the dispersion polymerization of VA is mainly confined to the dispersion medium rather than in the
FIGURE 4.15

VA CONVERSION VERSUS TIME WITH DIFFERENT S-EP WEIGHT %
particles, and if most of the VA monomer is in the S-EP micelles (the partition coefficient $\alpha$ of VA monomer between PVA particles and diluent is equal to 1.5-1.7 [96]), then in the presence of higher S-EP concentrations more VA monomer will be removed from the dispersion medium and solubilized in micelles. Therefore, polymerization in the dispersion medium may be starved of VA monomer which might lead to lower monomer conversions.

2. As the oligomeric free radicals start to diffuse through the EP chains into micelles and particles, any surface layer repulsion between PVA radicals and the EP stabilizing chains might influence the extent of monomer conversion. Higher S-EP concentrations will increase this repulsion and reduce the monomer conversion.

3. A higher S-EP stabilizer concentration will raise the viscosity of the dispersion medium. It is possible that the rate of diffusion of the oligomeric VA radicals might be retarded, in particular radical diffusion through a highly viscous swollen surface layer of EP chains, leading to a lower rate of entry of the free radicals into the particles, so polymerization proceeds more slowly. This type of explanation has been proposed in aqueous emulsion polymerization [89].

4. As the oligomeric free radicals diffuse through the surface layer of EP chains, some degradative chain transfer of PVA radicals with EP chains might occur reducing the conversion of the monomer.
Monomer conversion data are presented in Figure 4.16 with VA concentrations of 10, 20 and 30 Wt% in the presence of a constant S-EP stabilizer concentration (5 Wt%) and constant initiator concentration (1 Wt%). Higher VA conversions were observed for the higher monomer concentrations. Figure 4.17 shows the effect of using different initiator concentrations of 0.5, 1 and 1.5 Wt% on monomer conversion at constant monomer concentration (20 Wt%) and S-EP stabilizer concentration (5 Wt%). Again, higher monomer conversions for higher initiator concentrations were observed in all experiments performed. The shape of conversion-time curves in Figures 4.15-4.17 have a sigmoidal form as for PMMA in Figures 4.12-4.14 and the rate of VA conversion was found in all cases to be much slower than that of an equivalent MMA polymerization. The lower rate for VA polymerization is surprising in view of the literature data for $K_p$ and $K_p/K_t^{0.5}$ in radical polymerizations of MMA and VA [54]. It is possible that PMMA and PVA radicals behave differently in n-heptane in the presence of S-EP stabilizer because of the reasons 1-4 mentioned earlier. It is seen in Figure 4.18 that the number of particles produced at the end of dispersion polymerization (and therefore the constant number of particles growing during dispersion polymerization) is much higher for PMMA than for PVA (number of particles is calculated from the total monomer conversion and the volume of a single particle estimated from its diameter). Since
FIGURE 4.16
VA CONVERSION VERSUS TIME WITH DIFFERENT VA WEIGHT %

[Graph showing monomer conversion versus time with different VA weight% (30 wt%, 20 wt%, and 10 wt%) over a time span of 48 hours.]
FIGURE 4.17

VA CONVERSION VERSUS TIME WITH DIFFERENT AIBN WEIGHT %

![Graph showing VA conversion versus time with different AIBN weight percentages.](image-url)

- 1.5 wt%
- 1.0 wt%
- 0.5 wt%

Monomer conversion (wt%) vs Time (hours)
FIGURE 4.18

THE TOTAL NUMBER OF PARTICLES PRODUCED VERSUS % AIBN AS A TOTAL WEIGHT.

Total number of particle produced x 10^{-15}

AIBN / wt%
the sizes of PMMA and PVA particles produced at given conditions (see Figures 4.23 and 4.24) are approximately the same, it follows that the volume fraction \( V \) of particles in dispersion will be much higher for PMMA than for PVA from equations 2.34 and 2.35, it is concluded that \( R_p \) for MMA will be higher than \( R_p \) for VA.

4.2.3 DEPENDENCE OF PARTICLE SIZE ON POLYMERIZATION CONDITIONS

A controlled particle size coupled with a narrow size distribution of the produced particles was the main aim of this study. In Figures 4.19 and 4.20 typical transmission electron micrographs of PMMA and PVA particles produced from a one-shot polymerization technique show clearly the variation of particle sizes and the difficulties of producing a narrow particle size distribution. Consequently, it is necessary to use seeded polymerizations in all the studies to produce smaller particles of relatively narrow size distribution as presented in Figures 4.21 and 4.22. The amount of the monomer polymerized in the seed stage did, however, have a marked effect on the final particle size. This effect will be discussed later in section 4.2.3.2.

4.2.3.1 THE EFFECT OF THE S-EP STABILIZER CONCENTRATION

The concentration of the S-EP stabilizer is one of the most important factors controlling nucleation. Figures 4.23 and 4.24 demonstrate the effect on the mean particle size of dispersions of different concentrations of S-EP
<table>
<thead>
<tr>
<th>TABLE No.</th>
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<th>COVERS</th>
<th>DATE</th>
<th>SERVED BY</th>
<th>DRINK</th>
<th>FOOD</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>10 25</td>
<td>27.80</td>
</tr>
</tbody>
</table>

VAT REGISTRATION
232 2014 27

TOTAL INCLUDING VAT
37.25

VAT %

TOTAL EXCLUDING VAT

GUEST'S SIGNATURE:

ACCOUNT TO:

THE RESTAURANT PRICES INCLUDE SERVICE & VALUE ADDED TAX
Thank you - we hope to welcome you back soon.

Trusthouse Forte Hotels

Registered Office: Trusthouse Forte (U.K.) Ltd.
188 High Holborn, London WC1V 6TT.
In 1 gm, how many particles \( \text{PEV} \) are occupied per unit area?

16 & 17

215579

Note: electrons, protons, neutrons, and other subatomic particles and their interactions with each other.
FIGURE 4.19

PMMA PARTICLES FROM ONE SHOT-POLYMERIZATION

0.5 μm
FIGURE 4.20

PVA PARTICLES FROM ONE-SHOT POLYMERIZATION
FIGURE 4.21

PMMA PARTICLES FROM SEEDED POLYMERIZATION
FIGURE 4.22

PVA PARTICLES FROM SEED POLYMERIZATION
Log$_{10}$ (Copolymer concentration)

Particle diameter (μm) vs. Copolymer concentration (wt%) graph.

Figure 4.23: The effect of stabilizer concentration on particle diameter of PMA dispersions.
FIGURE 4.24

THE EFFECT OF STABILIZER CONCENTRATION ON
PARTICLE DIAMETER OF PVA DISPERSIONS.
stabilizer. As the stabilizer concentration increased, smaller particles were produced as predicted by the mechanism of particle formation (section 2.6.1).

The initiation step in dispersion polymerization results in the formation of oligomeric chains which grow in solution until they reach a critical molar mass which is dependent upon the solubility of these oligomers in the dispersion medium. The chains then either collapse upon themselves producing particle nuclei (self-nucleation) or alternatively, several growing oligomeric chains may associate with each other to form an aggregate which, above a certain critical size, precipitates forming a new stable nucleus (aggregative nucleation). In either case these nuclei can grow by capture of further oligomers from solution and by absorption of monomer which subsequently polymerizes within the particle matrix. The stability of the resulting colloidal system is achieved by adsorption of S-EP stabilizer from solution. The initial high number of particle nuclei and their small particle size result in a very large total particle surface area. At low S-EP copolymer stabilizer concentrations the amount of S-EP is insufficient to effectively cover the available surface area. Some unstable particles, therefore, agglomerate until the total surface area has decreased to produce a stable dispersion. This process may lead to a grossly flocculated system with a wide particle size distribution; however, controlled agglomeration and the growth of
narrowly dispersed particles is possible by introducing a seed into the polymerization. After the initial seed stage, the rest of the monomer and initiator can be added incrementally to a relatively stabilizer rich solution, so that the particle surfaces will be effectively covered with S-EP stabilizer, until most of the stabilizer is consumed. At increased S-EP stabilizer concentrations it is possible to stabilize effectively a larger total particle surface area, resulting in the formation of stable particles of lower particle size. The data in Figures 4.23 and 4.24 when replotted on logarithmic axes gave straight lines which obeyed the relationships

\[ D \propto C^{-0.98} \quad \text{for PMMA} \]
\[ D \propto C^{-0.615} \quad \text{for PVA} \]

in which \( D \) is the average particle diameter and \( C \) is the concentration of the S-EP stabilizer in solution. Dawkins and Taylor [97] have reported a similar relationship for dispersions of PMMA stabilized with diblock copolymers of polystyrene-poly(dimethyl siloxane), finding that \( D \propto C^{-0.77} \). Barrett [2] found that the value of the exponent was in the range -0.5 to -0.6 for dispersions of PMMA stabilized by a graft copolymer of poly(12-hydroxy stearic acid).

Dispersion polymerizations of both PMMA and PVA were usually performed in the presence of 5 Wt% S-EP stabilizer in solution. It should be noted despite this relatively high concentration, only up to 60% of the S-EP stabilizer was actually incorporated onto the polymer particles.
Higher concentrations were required to prepare stable dispersions since the adsorption of the block copolymer stabilizer onto the particle surface occurs less readily than a chemical grafting of the stabilizer onto the surface and also due to the low miscibility of polymer core and the PS anchor block.

4.2.3.2 THE EFFECT OF MONOMER CONCENTRATION

Stable dispersions of PMMA and PVA in n-alkanes were prepared in the presence of S-EP stabilizer. Figures 4.25 and 4.26 show the variation of particle size of dispersion prepared with an increasing proportion of monomer in the seed stage. As the monomer content of the seed stage increased, larger particles were produced, until in the limit all the monomer in the seed stage corresponds to a one-shot polymerization when particle sizes of 0.54μm for PMMA and 0.48μm for PVA were produced.

The process of particle formation is strongly influenced by increasing the solvency of the medium for the polymer which is being produced. For a given polymer, solvency may be raised by an appropriate choice of diluent, addition of strong solvents or by increasing monomer concentration. The process of particle formation begins when a polymer chain grows in solution until it reaches a threshold molar mass at which it collapses into a condensed state and forms a particle nucleus. The threshold molar mass is dependent upon the solvency of the dispersion medium. Hence for poor solvency, the threshold molar mass
FIGURE 4.25

VARIATION OF PARTICLE DIAMETER OF PMMA DISPERSIONS

WITH THE % TOTAL MMA IN THE SEED STAGE

0.6

0.5

0.4

0.3

0.2

0.1

0.0

0

20

40

60

80

100

Monomer in the seed stage / wt %

Particle diameter / μm
FIGURE 4.26
VARIATION OF PARTICLE DIAMETER OF PVA DISPERSIONS
WITH % TOTAL VA IN THE SEED STAGE
will be low and as a result a high number of short polymer chains (oligomers) will precipitate from the dispersion medium. So, more nuclei will be formed during the course of polymerization, i.e. a higher number of nuclei produced at constant concentration of monomer so that each particle obtains less monomer throughout the polymerization and ends up smaller. At high solvency the threshold molar mass is higher and the growing chains increase in size and spend more time in the continuous phase before they precipitate. As a consequence, fewer nuclei were formed and they grow bigger so the resulting particles will be fewer and bigger than in the case for poor solvency.

However, in dispersion polymerization there are important additional effects of solvency in modifying the operation of the S-EP stabilizer and its influence on the number of particles formed. Higher solvency for the polymer moiety which anchors the S-EP copolymer to the polymer particles probably reduces the tendency of the stabilizer to associate with the growing polymer chains during the process of particle formation, as well as reducing the efficiency of anchoring to the particles which have been formed. The practical outcome is fewer and larger particles. Figures 4.27 and 4.28 represent the effect of the monomer concentration as weight per cent of the total weight, on the particle size. In these experiments 1/5 of the total monomer was used as a seed (variable seed). As the monomer concentration increased
FIGURE 4.27
A PLOT OF PARTICLE DIAMETER AND THE % OF MMA AS A TOTAL WEIGHT. (VARIABLE SEED)
FIGURE 4.28

A PLOT OF PARTICLE DIAMETER AND THE % OF VA AS A TOTAL WEIGHT. (VARIABLE SEED)
the particle size increased from 0.0625\(\mu\)m for 10 Wt\% to 0.48\(\mu\)m for 30 Wt\% MMA and from 0.13\(\mu\)m for 10 Wt\% to 0.292\(\mu\)m for 30 Wt\%. Figures 4.29 and 4.30 represent the effect of monomer concentration as weight per cent on the particle size; these experiments were performed with a fixed amount of monomer and initiator in the seed stage (fixed seed). Again, as the total monomer increased the particle size increased. The effect of monomer concentrations on particle size in Figure 4.27 and 4.28 are greater than that in Figures 4.29 and 4.30. In the variable seed experiments, higher monomer concentrations were used at the start of polymerization and the presence of the higher monomer concentration increases the solvency of the dispersion medium and as a consequence, larger particles were formed.

4.2.3.3. THE EFFECT OF INITIATOR CONCENTRATION

Variation of the initiator concentration is perhaps the most appropriate parameter one might choose for the control of nucleation and therefore particle size during dispersion polymerization. However, the effect of varying the initiator concentration on the mean particle size of the produced dispersions has not been fully investigated previously. The dependence found in this study is shown in Figure 4.31 and 4.32 which show that the particle size decreases with increasing initiator concentration. Every attempt was made to ensure that all conditions except the initiator concentration were identical for each prepar-
FIGURE 4.29
A PLOT OF PARTICLE DIAMETER AND THE % OF MMA AS A TOTAL WEIGHT (FIXED SEED)
FIGURE 4.30

A PLOT OF PARTICLE DIAMETER AND THE % OF VA AS A TOTAL WEIGHT. (FIXED SEED)
FIGURE 4.31

A PLOT OF PARTICLE DIAMETER OF PMMA DISPERSIONS AND THE % OF AIBN AS A TOTAL WEIGHT.

\[ \log_{10}(D \times 10) \]

Particle diameter / \(\mu\text{m}\)

AIBN / wt %
FIGURE 4.32

A plot of particle diameter of PVA dispersions and the % of AIBN as a total weight.

\[
\log_{10}(1 \times 10)
\]

Particle diameter / \(\mu m\)

AIBN / wt %

\[
\log_{10}(D \times 10)
\]
ation. The phenomenon of decreased mean particle size with increased initiator concentration is consistent with competitive growth. As the initiator concentration increased the number of particles initiated increased, i.e. a higher number of nuclei produced at constant monomer concentration as seen in Figure 4.18. Thus, each particle obtains less monomer throughout polymerization and ends up smaller.

Increasing the initiator concentration leads to an increase in the rate of initiation and as a result increases the number of polymer chains and consequently the number of particles produced. This will usually lead to an increase in the total surface area of the resulting particles, and if there is enough S-EP stabilizer to cover and stabilize all the particles produced in dispersion polymerization, then a stable dispersion with small particle size will be produced.

When the data in Figures 4.31 and 4.32 are replotted on logarithmic axes, the mean particle size \( D \) and initiator concentration \( I \) are related by

\[
D \propto I^{-0.32} \quad \text{for PMMA}
\]

\[
D \propto I^{-0.41} \quad \text{for PVA}
\]

4.3 CHARACTERIZATION OF NON-AQUEOUS DISPERSIONS

4.3.1. PARTICLE SIZE AND SHAPE

Transmission electron microscopy (TEM) was used as the principle method of determining particle size and shape. The soluble EP stabilizing layer which surrounds
the particles, collapses onto the particle surface when the dispersion medium is removed during the preparation of a sample, Choi and Krieger [98] have estimated the thickness of the collapsed layer of Poly(dimethyl siloxane) ($\bar{M}_n = 5400$) on a PMMA particle and found that it is below 1 nm, which represents less than a 1% increase in the diameter of the smallest particles. In the present work, the thickness of the collapsed layer of EP ($\bar{M}_n = 65000$) was calculated for both PMMA and PVA and found to be 2 nm which represents 3.14% increase in the diameter of the smallest particles (62.5 nm). Thus, the thickness of the collapsed layer could be neglected, and the core diameter measured from electron micrographs was taken as the core diameter.

Although the instrument was calibrated with a replica of a diffraction grating, electrical fluctuation can generate up to 5% error in the recorded magnifications. A more fundamental source of error might result from a change in the sample during preparation of the microscope grids. It is not expected that particles will be swollen by the dispersion medium for PMMA and PVA in n-alkanes. Depolymerization of polymer particles has been reported under the rather hostile conditions of high vacuum and electron bombardment within an electron microscope [56].

4.3.2. SURFACE COVERAGE

The surface coverage of the polymer particles can be calculated from the copolymer content and the particle diameter estimated directly from TEM micrographs. Surface
coverage results can be interpreted in terms of the surface area $A$ occupied or stabilized by each EP chain and the mean separation distance $d$ between adjacent EP chains, assuming that the PS block in the S-EP stabilizer does not extend significantly into the dispersion medium, that each EP chain is terminally anchored at the particle surface, and that EP chain is anchored at the centre of a regular hexagon of area $A$. These results for $A$ are presented in tables 4.4 and 4.5 for PMMA and PVA particles respectively.

The results in tables 4.4 and 4.5 suggest that the area $A$ occupied or stabilized by a given EP chain was constant for each polymer particle type with no obvious dependence of $A$ on particle size for PMMA and PVA. This implies that total surface coverage may be assumed for all dispersions. It can be seen that different areas were stabilized by a given EP chain (40-48 nm$^2$ for PMMA and 28-32 nm$^2$ for PVA particles). This could give the impression that the PS anchor block might be extended into the dispersion medium for PVA but not for PMMA. However, the amount of the block copolymer surrounding the PVA particles was higher than that for PMMA particles (see Figure 4.33 and Tables 4.6 and 4.7). Consequently, it can be concluded that the EP stabilizing chains are packed more closely for PVA particles than for PMMA particles (suggested by the mean separation distance $d$ between adjacent EP chains for PMMA being in the range of 68-73\AA and that for PVA in the range of 57-61\AA). These results
FIGURE 4.33

VARIATION OF BLOCK COPOLYMER PERCENTAGE vs. PARTICLE SIZE
**TABLE 4.4**

SURFACE COVERAGE DATA FOR PMMA DISPERSIONS

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>Area A stabilized by EP chain (nm²)</th>
<th>d / R</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.063</td>
<td>45.2</td>
<td>72.2</td>
</tr>
<tr>
<td>0.132</td>
<td>43.8</td>
<td>71.1</td>
</tr>
<tr>
<td>0.152</td>
<td>46.1</td>
<td>73.0</td>
</tr>
<tr>
<td>0.177</td>
<td>47.3</td>
<td>73.9</td>
</tr>
<tr>
<td>0.186</td>
<td>41.2</td>
<td>69.0</td>
</tr>
<tr>
<td>0.287</td>
<td>40.6</td>
<td>68.5</td>
</tr>
</tbody>
</table>
### TABLE 4.5

**SURFACE COVERAGE DATA FOR PVA DISPERSIONS**

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>Area A stabilized by EP chain/nm²</th>
<th>d / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.136</td>
<td>30.7</td>
<td>59.5</td>
</tr>
<tr>
<td>0.158</td>
<td>29.1</td>
<td>58.0</td>
</tr>
<tr>
<td>0.180</td>
<td>29.0</td>
<td>57.9</td>
</tr>
<tr>
<td>0.203</td>
<td>32.3</td>
<td>61.0</td>
</tr>
<tr>
<td>0.250</td>
<td>28.9</td>
<td>57.7</td>
</tr>
<tr>
<td>0.309</td>
<td>28.1</td>
<td>56.9</td>
</tr>
</tbody>
</table>
indicate that it is possible to explain why EP chains because of closer packing extend further into the dispersion medium for PVA particles than for PMMA particles, whilst retaining the assumption that the PS block in S-EP does not extend into the dispersion medium for both PVA and PMMA particles.

The proposal that close-packing of EP chains occurs at the particle-liquid interface is indicated by comparing values of $d$ with the root-mean-square radius of gyration $\langle s^2 \rangle^{0.5}$ of a free EP copolymer chain which was calculated with the equation $6\langle s^2 \rangle = \langle r^2 \rangle$ for theta conditions [29, 65]. It is expected that the value of $\langle s^2 \rangle^{0.5}$ will be at least 90Å based on the values of $\langle r^2 \rangle^{0.5}$ for the free EP chain as calculated in section 4.1.4. The calculated values of $d$ for PMMA and PVA particles in tables 4.4 and 4.5 are slightly lower than that of $\langle s^2 \rangle^{0.5}$ for the free EP chain. If the values of $d$ had been greater than twice the radius of gyration, few interactions between neighbouring chains would occur as illustrated in Figure 4.34a. The thickness of the adsorbed layer might in this case be expected to be about equal to twice the radius of gyration of the stabilizing chains. With $d \geq 2\langle s^2 \rangle^{0.5}$ adjacent EP chains might be represented as in Figure 4.34b. This close-packing of the stabilizing chains at the interface within the shaded area could lead to interaction if the chains adopt a conformation similar to the conformation of a free chain in solution. Such interactions may lead to
FIGURE 4.34

MODELS FOR TERMINALLY ADSORBED POLYMER MOLECULES

[a] $d > 2 \langle S^2 \rangle^{1/2}$

[b] $d < 2 \langle S^2 \rangle^{1/2}$

[c] Prolate ellipsoid model

$2 \langle S^2 \rangle^{1/2}$
excluded volume effects which may restrict overlap between neighbouring chains. Therefore, the terminal anchoring of the stabilizing chains and excluded volume considerations may determine the preference for EP chains to adopt a conformation which is slightly extended over random coil dimensions. PDMS chains at the particle-liquid interface [76] were found to be significantly extended, and it was therefore proposed that the volume of each PDMS chain and associated solvent could be represented by a prolate ellipsoid as seen in Figure 4.34C. It is possible that a similar ellipsoid with the major axis slightly larger than the minor axis might represent the behaviour of EP chains at a particle-liquid interface.

4.3.3 BLOCK COPOLYMER STABILIZER AND POLYSTYRENE CONTENTS

Tables 4.6 and 4.7 show the percentage of block copolymer stabilizer and the anchor block polystyrene in a series of PMMA and PVA dispersions. The values of copolymer stabilizer were calculated from U.V. spectra of clean and dry dispersion samples in chloroform as described in section 3.4.3. PS on the other hand was obtained from the block copolymer composition and percentage of PS in the copolymer.

It can be seen that the percentage of block copolymer stabilizer and PS contents is increased as the particle size decreased. On the basis of block copolymer to the monomer in the original dispersions, these values are less than 50% of the total block copolymer used in the prepar-
### TABLE 4.6

**COPOLYMER CONTENTS OF PMMA PARTICLES**

<table>
<thead>
<tr>
<th>D/µm</th>
<th>Copolymer Contents (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0625</td>
<td>26.25</td>
</tr>
<tr>
<td>0.0676</td>
<td>25.25</td>
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<tr>
<td>0.0947</td>
<td>17.62</td>
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<tr>
<td>0.132</td>
<td>15.31</td>
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<tr>
<td>0.1321</td>
<td>15.12</td>
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<td>0.1364</td>
<td>14.95</td>
</tr>
<tr>
<td>0.1521</td>
<td>12.81</td>
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<tr>
<td>0.1771</td>
<td>10.97</td>
</tr>
<tr>
<td>0.1858</td>
<td>11.87</td>
</tr>
<tr>
<td>0.25</td>
<td>10.95</td>
</tr>
<tr>
<td>0.2875</td>
<td>8.12</td>
</tr>
<tr>
<td>0.3833</td>
<td>8.12</td>
</tr>
<tr>
<td>0.4525</td>
<td>7.75</td>
</tr>
<tr>
<td>Particle diameter (µm)</td>
<td>Copolymer contents (% w/w)</td>
</tr>
<tr>
<td>------------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>0.1365</td>
<td>19.75</td>
</tr>
<tr>
<td>0.1538</td>
<td>17.5</td>
</tr>
<tr>
<td>0.158</td>
<td>18.31</td>
</tr>
<tr>
<td>0.1699</td>
<td>18.00</td>
</tr>
<tr>
<td>0.18</td>
<td>16.5</td>
</tr>
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<td>0.2025</td>
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</tr>
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<td>12.50</td>
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<td>11.75</td>
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<td>0.2944</td>
<td>10.87</td>
</tr>
<tr>
<td>0.3089</td>
<td>10.62</td>
</tr>
</tbody>
</table>
ation of the dispersions. The excess of the block copolymer was removed by redispersion (see section 3.3.3).

4.3.4 DISPERSION STABILITY AND STABILIZER ANCHORING MECHANISM

PVA dispersions remained stable for longer periods of time (many months) under normal laboratory conditions than PMMA dispersions, after the excess S-EP stabilizer was removed. This may be due to the thicker surface layer in the case of PVA particles (section 4.3.6) or the S-EP stabilizer may be anchored differently on PVA and PMMA particles. Both types of polymer particles which had been sedimented in the ultracentrifuge were easily redispersed upon shaking. This suggests that there was no significant desorption of S-EP stabilizer with time. The stability was to be expected if the PS anchor block of the S-EP stabilizer was firmly anchored to the core polymer with the surface layer of EP chains stabilizing the particles.

Samples of S-EP copolymer stabilizer adsorbed onto PMMA and PVA particles were isolated and analysed as described in section 3.4.4. The concentrations of the S-EP stabilizer adsorbed on both types of particles before and after the extraction and their GPC analyses are presented in table 4.8. For all the anchoring studies acetone was used to extract PMMA core polymer from its dispersion, while PVA core polymer was extracted from its dispersion by methanol.

The GPC chromatograms of the PMMA dispersion before
<table>
<thead>
<tr>
<th>Polymer</th>
<th>S-EP wt%</th>
<th>wt/g</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_p$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA dispersion</td>
<td>12.8</td>
<td>0.49a</td>
<td>53800</td>
<td>78100</td>
<td>52900</td>
<td>2.18</td>
</tr>
<tr>
<td>Residue of</td>
<td>97.5</td>
<td>0.07b</td>
<td>104900</td>
<td>113700</td>
<td>109200</td>
<td>1.08</td>
</tr>
<tr>
<td>PVA dispersion</td>
<td>17.5</td>
<td>0.87a</td>
<td>73200</td>
<td>164300</td>
<td>109700</td>
<td>2.24</td>
</tr>
<tr>
<td>Residue of</td>
<td>96.25</td>
<td>0.06c</td>
<td>76500</td>
<td>165400</td>
<td>112500</td>
<td>2.16</td>
</tr>
<tr>
<td>S-EP</td>
<td></td>
<td></td>
<td>105000</td>
<td>113700</td>
<td>109300</td>
<td>1.08</td>
</tr>
<tr>
<td>S-EP heated in n-heptane for 48 hours at 343K</td>
<td></td>
<td></td>
<td>102900</td>
<td>116300</td>
<td>109400</td>
<td>1.08</td>
</tr>
<tr>
<td>S-EP extracted with acetone for 240 hours</td>
<td></td>
<td></td>
<td>103900</td>
<td>116300</td>
<td>109600</td>
<td>1.08</td>
</tr>
<tr>
<td>S-EP extracted with methanol for 240 hours</td>
<td></td>
<td></td>
<td>102300</td>
<td>113800</td>
<td>107900</td>
<td>1.09</td>
</tr>
</tbody>
</table>

a. Initial weight of dispersion.
b. Weight of residue after 96 hours.
c. Weight of residue after 216 hours.
the extraction process started and the residue left after extraction with acetone for 96 hours are shown in Figure 4.35a and b. When the chromatogram of the residue in Figure 4.35a is compared with that of the original S-EP stabilizer as shown in Figure 4.35c, it appears that they were almost identical. This observation is confirmed by comparing the values in table 4.8 for $\overline{M}_n$, $\overline{M}_w$, $\overline{M}_p$, and $\overline{M}_w/\overline{M}_n$ for the extraction residue with values for the as-received S-EP sample. Furthermore, the extraction residue as a percentage of the original dried dispersion was 14.3\% (w/w) which corresponds with the S-EP content (12.8\%) in the original dispersion. These results suggest that there was no grafting of the stabilizer chains onto the particle surface by a chain transfer mechanism. This was not surprising as the chain transfer constant for PMMA radicals onto PS is very small ($29 \times 10^{-5}$ at 353K) [54]. The IR spectrum of the PMMA dispersion before extraction is displayed in Figure 4.36a, and that of the residue left after extraction is displayed in Figure 4.37a. A comparison of the IR spectrum of the residue in Figure 4.37a with that of the as-received S-EP stabilizer in Figure 4.37c showed that the IR spectrum of the residue contained a very small peak at about 1750 cm$^{-1}$ indicating C=0 groups. U.V. spectrophotometric analysis on the residue indicated that it consisted of 97.5\% S-EP stabilizer with the remainder presumed to be either unextracted PMMA or possibly some impurities left due to
FIGURE 4.35

GPC CHROMATOGRAMS OF PMMA DISPERSION (A), S-EP EXTRACTED FROM PMMA DISPERSION (B) AND AS-RECEIVED S-EP (C)
(a) IR spectrum of the residue of PMMA dispersion left after extraction.

(b) IR spectrum of a blend of PMMA homopolymer and S-EP.

(c) IR spectrum of as-received S-EP.
extraction such as acetone. A blend of 97.5% S-EP stabilizer and 2.5% PMMA showed a much higher absorbance at about 1750 cm\(^{-1}\) in Figure 4.37b than that of the extraction residue example in Figure 4.37a. The above results suggest that the S-EP stabilizer had not been grafted onto the particles, which is also indicated by the dispersity of the original S-EP stabilizer and the extraction residue being identical (see table 4.8). In the absence of covalent grafting of the S-EP stabilizer to the particles, these results suggest that for PMMA particles having a glass transition temperature (\(T_g\)) above the dispersion polymerization temperature, PS block of the S-EP stabilizer becomes trapped within a hard polymer matrix, as shown in Figure 4.38a, and stabilize polymer particles after the removal of excess block copolymer by redispersion. This anchoring mechanism is postulated despite a possible incompatibility effect between the PS block and the PMMA core. It is possible at temperatures above \(T_g\) of PMMA that the PS blocks may diffuse through the soft PMMA matrix to the particle surface. If the PS block is soluble in the \(n\)-alkane diluent at elevated temperatures, then flocculation of the dispersion may occur above the \(T_g\) of the core polymer owing to the desorption and dissolution of the PS anchor blocks. So, PMMA particles were redispersed in \(n\)-dodecane and such a dispersion, when heated to 463K for 6 hours, did not show any sign of flocculations; this suggests that the PS anchor blocks are firmly anchored to
FIGURE 4.38
POSSIBLE STABILIZER ANCHORING MECHANISMS

(a) PMMA
   Below $T_g$

(b) PVA
   Above $T_g$
It is interesting to compare the stabilization of PVA particles with PMMA particles, since PVA core polymer has a $T_g$ below the dispersion polymerization temperature. PVA particles stabilized with S-EP showed a good stability during and after redispersion cycles to remove excess S-EP stabilizer, even though on mixing solutions of PS and PVA homopolymers, phase separation tends to occur [99, 100]. For $T_g$ below the polymerization temperature, it could be assumed that for soft polymer particles the PS anchor block is rejected from the particle surface as shown in Figure 4.38b. In view of the incompatibility effect of PS in the soft PVA matrix and the possible diffusion of the PS blocks to the particle-liquid interface where desorption of the block copolymer may occur, effective anchoring of EP chains may require covalent grafting of the S-EP stabilizer to the particles by reaction between PVA particles and S-EP during dispersion polymerization. Literature values for the chain transfer constant of PVA radicals to PS ($190 \times 10^{-5}$ at 348K) is relatively high when compared with $29 \times 10^{-5}$ for PMMA radicals to PS [54], suggesting a possible grafting reaction between PVA radicals and PS is possible. The GPC chromatograms of the PVA dispersion sample before extraction process and the residue left after extraction for 216 hours with methanol are shown in Figure 4.39a and b. When the chromatogram of the residue (Figure 4.39b) is compared with that of the dispersion (Figure 4.39a) and the
FIGURE 4.39

GPC CHROMATOGRAMS OF PVA DISPERSION(A), S-EP EXTRACTED FROM PVA DISPERSION(B) AND AS-RECEIVED S-EP(C)
original S-EP stabilizer (Figure 4.39c), it is evident that the chromatogram of the residue spans a similar molar mass range to the range for the dispersion and is much broader than the chromatogram for the S-EP stabilizer. The molar mass data for the residue and the dispersion in table 4.8 are very similar. Extraction experiments on as-received S-EP, see molar mass data in table 4.8, suggest that S-EP chains are not soluble in methanol. The PVA which remains in the residue is presumed to be non-extractable because of grafting to insoluble S-EP. These results suggest that there is some sort of grafting reaction of the S-EP stabilizer chain onto the PVA particle surface. The IR spectrum of the residue in Figure 4.40a when compared with the PVA dispersion (Figure 4.36b) and that of as-received S-EP (Figure 4.40c) clearly demonstrates an intense absorption at about 1750 cm\(^{-1}\), indicating the presence of C=O groups in the residue. U.V. spectrophotometric analysis of the residue suggests an S-EP stabilizer content of 96.25%, so a blend of 96.25% S-EP stabilizer and 3.75% PVA was prepared and its IR spectrum in Figure 4.40b shows the same intensive absorption band at about 1750 cm\(^{-1}\). The relative absorbance values for the infrared bands due to C=O, C-H (aliphatic) and C-H (aromatic) are very similar for the residue and the blend in Figure 4.40a and b. This provides strong support for the occurrence of non-extractable PVA which is presumed to be grafted to S-EP in the residue. When the residue was subjected to longer
(a) IR spectrum of the residue of PVA dispersion left after extraction.

(b) IR spectrum of a blend of PVA homopolymer and S-EP.

(c) IR spectrum of as-recieved S-EP.
periods of extraction with methanol, there was no increase in the percentage of the S-EP stabilizer existing in the residue. It is concluded that for particles containing a soft PVA core polymer effective anchoring of the S-EP stabilizer onto the particle surface is aided by covalent grafting. When a PVA dispersion was redispersed in n-dodecane and heated to 463K for 6 hours, there was no sign of flocculation, so it is suggested that the PS blocks anchored very strongly to the particle surface. The thicker surface layer may be generated if the PS block is anchored to one point onto the PVA surface.

It should be stated that heating the S-EP stabilizer in n-heptane (343K for 48 hours), and extracting with acetone (240 hours) and methanol (240 hours) in order to simulate the experimental conditions during dispersion polymerization and extraction appeared not to change the S-EP chain length. Molar mass data given in table 4.8 demonstrate that the heated sample and as-received S-EP are identical. There was hardly any change in weight in the S-EP samples before and after the extraction experiments.

4.3.5 FLOCCULATION STUDIES

The behaviour of sterically stabilized dispersions in a medium which is a θ-solvent for the stabilizing chains will be discussed in section (4.3.6). Consideration of the "mixing term" gave equation 2.19 from which it was predicted that under θ-conditions (i.e. $\chi = 0.5$), $\Delta G_M$ becomes zero. In the absence of a repulsive force, the
particles would flocculate. If an additional "volume restriction" term is considered, such systems would still experience a repulsive force under \( \Theta \)-conditions.

Well-defined non-aqueous dispersions of PMMA and PVA particles prepared in the present work were studied as a function of the solvency of the dispersion medium. Adding a non-solvent for EP chains (e.g. n-propanol) to a dispersion eventually produced flocculation. The minimum volume fraction of non-solvent added to produce flocculation was recorded as the critical flocculation volume CFV. The solvency of the dispersion medium was also reduced by lowering the temperature to give the critical flocculation temperature CFT. Flocculation could not be induced by cooling dispersions based on aliphatic hydrocarbons, so the dispersion medium was changed to a mixture of n-heptane/n-propanol. All these studies were based upon stirred samples of dispersions, so that any inherent weak flocculation was removed. It was found that if flocculation of both polymer particles is induced by decreasing the solvency of the dispersion medium for the stabilizing chains, spontaneous redispersion occurs on making the dispersion medium a better solvent for the stabilizing EP chains by adding n-heptane or an increase in temperature, if the particles are not allowed to stay in the flocculated state for too long, in common with the previously reported work [8, 15, 18, 101].

Values of CFV and CFT for dispersions of PMMA and PVA
of different particle size are given in tables 4.9 and 4.10. These results may be compared with the theta conditions given in table 4.2. The observed CFV and CFT values were found to be independent of the volume fraction of the dispersed phase within the limit of the experimental error for up to $2 \times 10^{-2}$ g cm$^{-3}$ in agreement with the observations reported previously [8, 15, 18, 92]. Furthermore, the flocculation data in table 4.9 and 4.10 were obtained with the spectrophotometer operating at 600 nm, but the same CFV and CFT results were obtained for wavelengths down to 425 nm. The results in tables 4.9 and 4.10 suggest that flocculation behaviour is independent of particle size for D over the range 132-288 nm for PMMA and over the range 136-309 nm for PVA. Little or no dependence of flocculation behaviour on D over the particle diameter 96-480 nm was reported for PDMS stabilizing chains [15].

These observations together with flocculation occurring close to the theta conditions are consistent with Napper's view [12] on steric stabilization of colloidal particles with long chains in the interfacial layer. When the interfacial layer thickness exceeds 10 nm, the attractive forces between particle cores will not influence stabilization/flocculation behaviour. The PDMS chains with $\bar{M}_{\text{PDMS}} > 10^4$ g mol$^{-1}$ [15] have surface layer thickness $> 10$ nm [76], and the stabilizing EP chains ($\bar{M}_{\text{EP}} \approx 6.4 \times 10^4$ g mol$^{-1}$) provide a thick steric barrier, estimated by rheological measurements to be about 30 nm for PMMA
TABLE 4.9

CFV AND CFT RESULTS FOR PMMA DISPERSIONS

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>CFV % n-propanol</th>
<th>CFT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.063</td>
<td>24.81</td>
<td>42.93</td>
</tr>
<tr>
<td>0.132</td>
<td>25.48</td>
<td>42.77</td>
</tr>
<tr>
<td>0.152</td>
<td>25.82</td>
<td>42.35</td>
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<tr>
<td>0.177</td>
<td>25.61</td>
<td>42.38</td>
</tr>
<tr>
<td>0.186</td>
<td>25.59</td>
<td>42.15</td>
</tr>
<tr>
<td>0.287</td>
<td>25.98</td>
<td>42.25</td>
</tr>
<tr>
<td>Particle size (µm)</td>
<td>CFV % n-propanol</td>
<td>CFT °C</td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------</td>
<td>-------</td>
</tr>
<tr>
<td>0.136</td>
<td>26.79</td>
<td>39.85</td>
</tr>
<tr>
<td>0.158</td>
<td>26.52</td>
<td>40.05</td>
</tr>
<tr>
<td>0.180</td>
<td>26.68</td>
<td>40.10</td>
</tr>
<tr>
<td>0.203</td>
<td>26.94</td>
<td>39.95</td>
</tr>
<tr>
<td>0.250</td>
<td>26.90</td>
<td>39.94</td>
</tr>
<tr>
<td>0.309</td>
<td>26.74</td>
<td>39.95</td>
</tr>
</tbody>
</table>
particles and about 40 nm for PVA (section 4.3.6).

All the flocculation results in tables 4.9 and 4.10 indicate that both PMMA and PVA dispersions retained stability at theta conditions, with flocculation occurring when the dispersion medium was just worse than a theta system for the EP chains in free solution (see table 4.2). However, the experimental errors in determining $T_p$ (and CFT) and the errors inherent in the theoretical assumptions for the extrapolations in Figures 4.8 and 4.9 suggest that it is not possible to distinguish values of $\theta$ and CFT which differ by $1K$, and so the CFT must be close to the $\theta$-temperature. Similar errors were reported previously [15]. On the other hand, the CFV data clearly indicate that the composition of the dispersion medium at flocculation is somewhat worse than the theta composition of the EP chains. This observation is consistent with the proposal cited by Napper [12] that flocculation is induced by attractive interaction between segments in interfacial chains attached to different particles. Such attractions between EP segments only arise when the dispersion medium is just worse than a theta system. It is important to recognise that this hypothesis does not correspond to the stabilizing chains causing flocculation by a phase separation process. Thus, the values of $T_p$ in Figure 4.8 are all below 310K, and therefore well below the CFT values in tables 4.9 and 4.10. Furthermore, the volume fraction of n-propanol of phase separation for sample EP3 in
a mixture with $V_2 \simeq 10^{-3}$ in Figure 4.7 is $>0.3$, i.e. higher in n-propanol than the CFV results (see tables 4.9 and 4.10) which were obtained for dispersions having a volume fraction of EP chains $<10^{-3}$ in the dispersion medium.

CFV results should be interpreted cautiously because preferential sorption of one liquid component by the stabilizing chains or by the particle cores may change the solvency of the dispersion medium around the stabilizing chains. Taylor [102] observed for his polymer dispersions stabilized in a mixture of n-heptane and ethanol by PDMS chains that when the CFT corresponded closely to the $\theta$-temperature for PDMS the CFV occurred at slightly worse than theta conditions for PDMS. Since the polymers PMMA and PVA are present in the CFV experiments, but absent from the phase separation studies to find the theta composition of EP copolymer, the CFV results might be interpreted by the observation that more n-propanol is required in flocculation than the theta composition for EP copolymer because of preferential sorption of n-propanol by the polymers PMMA and PVA in particles. However, there was no change in the composition of the dispersion medium when the PMMA and PVA particles were dispersed in a mixture of n-heptane/n-propanol (with composition fixed at 70:30, v/v) for the time scale typical of a flocculation experiment. Napper's studies [8] of the correlation between the flocculation behaviour of PMMA particles and the theta
conditions of the stabilizing chains did not show any dependence on the alcohol (ethanol, propanol and butanol) employed in the CFV experiments. In both PMMA and PVA dispersions in the present work, the significant quantity of PS blocks per particle (see surface coverage data for S-EP in tables 4.4 and 4.5) may provide a barrier against sorption of n-propanol by PMMA and PVA.

The values of CFV in tables 4.9 and 4.10 demonstrate that the volume fraction of n-propanol required to cause flocculation of PVA dispersions is higher than that used for PMMA dispersions. This may be due to the mode in which the block copolymer stabilizer is attached to the particles, since the anchoring studies (section 4.3.4) suggested that there is some grafting of the block copolymer to the PVA particles while there appears to be no grafting of S-EP to PMMA polymer. Furthermore, the packing of EP chains at the particle-diluent interface appears to be somewhat different for PMMA and PVA dispersions. The viscosity studies of dispersions suggest that the surface layer thickness of EP chains is 40 nm for PVA particles and 30 nm for PMMA particles (see section 4.3.6). Surface coverage data (section 4.3.2) indicates that more block copolymer anchors on PVA particles than on PMMA particles, resulting in the computed area A stabilized per EP chain being 40-48 nm$^2$ for PMMA particles and 28-32 nm$^2$ for PVA particles. The closer packing of EP chains on PVA particles
may generate a more extended chains conformation, and therefore a thicker surface layer as suggested by viscosity measurements. These observations suggest that the segment density of EP chains at the particle-liquid interface will be higher for PVA particles which might explain why more n-propanol is required for flocculation than for PMMA particles.

4.3.6 RHEOLOGY OF PMMA AND PVA PARTICLES

The rheology of dispersed particles of PMMA surrounded by short polydispersed chains of Poly(12-hydroxystearic acid) has been reported in the literature [75, 103]. These studies were based on Polymer particles surrounded by a surface layer of low molar mass polymer (1600 g mol\(^{-1}\)). Measurements of the viscosity of the dispersed phase were combined with a knowledge of the particle core dimensions to estimate the thickness of the adsorbed layer \(\delta\). Such estimation was complicated by the ill-defined nature of the soluble polymer, which was branched and short and was prepared by step-growth polymerization so that the polydispersity of the stabilizing chains tends toward 2. Hence, it is unlikely that the thickness of the surface layer will be constant over the whole particle. Also, the thickness of the layer was small compared to the particle diameter, since the molar mass of the stabilizing chain was low.

The most thorough viscometric studies of dilute sterically stabilized dispersions have been carried out by Dawkins and Taylor [56]. They prepared dispersions of PMMA
particles in organic media stabilized with the diblock copolymer Poly(styrene-b-dimethyl siloxane) (PS-PDMS) which can be produced with well-defined block lengths and a narrow chain length distribution. The values of $\delta$ were determined for the stabilizing chains (PDMS) from viscosity studies of PMMA particles in n-alkane as a function of the molar mass of PDMS in the range of $(3-48) \times 10^3$ g mol$^{-1}$. The results indicated that the size of PDMS chains at a PMMA particle-n-alkane interface is somewhat extended over random coil dimensions. Recently, Choi and Krieger [98] used the same technique to determine $\delta$ of PDMS chains on PMMA particles and their results agree very well with those reported by Dawkins and Taylor [76].

The polymer dispersions prepared in the present work have made possible a more comprehensive study of the adsorbed layer. The rheological behaviour of non-aqueous PMMA and PVA dispersions stabilized with the diblock copolymer S-EP which has a much lower polydispersity of any block copolymer investigated for rheological studies to date has been examined. PMMA and PVA particles in dispersion media consisting of n-heptane and a binary liquid mixture of n-heptane and n-propanol have been studied as a function of temperature. These studies permitted the determination of surface layer thickness $\delta$ of EP copolymer chains at the polymer-diluent interface as the dispersion medium was changed from a good solvent to almost a theta solvent for the terminally anchored EP
chains. The adsorbed layer thickness \( \delta \) was measured for a series of dispersions of varying particle size for both PMMA and PVA systems. The values of \( \delta \) were compared with the dimensions determined for free EP copolymer chains in solution from viscometric measurements.

Plots of the dependence of the absolute viscosity of PMMA and PVA particles of different sizes in n-heptane at 298 K against the volume fraction of the polymer particle core \( \phi_0 \) are shown in Figures 4.41 and 4.42. The values of \( \phi_0 \) was calculated from the total polymer content in the dispersion (obtained gravimetrically), the EP content (obtained from the percent of block copolymer found by U.V. spectrophotometry) and the density of particle core (assumed to be 1.19 g cm\(^{-3}\) for bulk PMMA [54] and for bulk PVA [104]). The viscosity of the dispersions appears to increase with decreasing particle size. As seen in tables 4.6 and 4.7, smaller particles contain more block copolymer, so the increase in the population of EP chains for smaller particles will contribute to an increase in the viscosity of the dispersions. The value of \( \delta \) for the EP surface layer may be calculated from the limiting slope of the curves \( \phi_0 = 0 \) in Figures 4.41 and 4.42 according to the method employed by Walbridge and Waters [103]. However, this method may not be accurate because of the errors in locating the curves in Figures 4.41 and 4.42 at low value of \( \phi_0 \), and so in the present work it is preferred to use the procedure involving relative viscosity (\( \eta_r \)) as
VARIATION OF VISCOSITY OF PMMA PARTICLES IN n-HEPTANE AT 298K WITH THE VOLUME FRACTION OF CORE POLYMER

**Figure 4.41**

- **D = 0.0625 μm**
- **D = 0.25 μm**

**Abscissa:** $\Phi_0$

**Ordinate:** Absolute viscosity $\eta / \eta_p$
FIGURE 4.42

VARIATION OF VISCOSITY OF PVA PARTICLES IN n-HEPTANE AT 298K WITH THE VOLUME FRACTION OF CORE POLYMER

- D = 0.1365 μm
- D = 0.292 μm
reported by Barsted et al [75] which was found to be more reliable. The dependence of $\eta_r$ on $\phi_o$ is given by equation 2.48 in section 2.7, which was proposed by Saunders [64] who modified the relation suggested by Mooney [62]. Viscosity data plotted according to equation 2.48 are shown in Figures 4.43 and 4.44 for PMMA particles and Figures 4.45 and 4.46 for PVA particles stabilized in n-heptane with S-EP at 298, 308 and 318K. The quantity $\alpha_o f$ in equation 2.48 may be though of as an effective Einstein coefficient which may be determined from intercepts in Figures 4.43-4.46. For dispersions of particles having a value of $(\delta)$ which is significant compared with $D$ Goodwin [60] proposed that the magnitude of $f$ was correctly given by equation 2.46. Values of $(\alpha_o f)^{1/3}$ determined from the intercepts in Figures 4.43 and 4.44 for PMMA particles and from Figures 4.45 and 4.46 for PVA particles were plotted against the reciprocal of $D$ as shown in Figures 4.47 and 4.48 which confirm the linear behaviour predicted by equation 2.49 for the range of particle core diameters (0.063-0.25 $\mu$m for PMMA particles and 0.13-0.29$\mu$m for PVA particles) examined. As $D^{-1}$ tend to zero, the surface layer becomes negligible relative to the core diameter and the effective Einstein approaches the true Einstein coefficient of 2.5. From the intercepts in Figures 4.47 and 4.48 the values of $\alpha_o$ were found to be in good agreement with the true Einstein value, suggesting that PMMA and PVA particles were spherical and free from aggreg-
FIGURE 4.43

PLOTS OF VISCOSITY DATA ACCORDING TO EQUATION (2.48) FOR PMMA PARTICLES IN n-HEPTANE AT 298K (Δ, △)
AT 308K (□, ▪), AND AT 318K (○, ●).

open symbols D = 0.12 μm
filled symbols D = 0.0625 μm
FIGURE 4.44

PLOTS OF VISCOSITY DATA ACCORDING TO EQUATION (2.48) FOR PMMA PARTICLES IN n-HEPTANE AT 298K (▲, ▲), AT 308K (□, □) AND AT 318K (○, ●)
FIGURE 4.45

Plots of viscosity data according to Equation (2.48) for PVA particles in n-heptane at 298K (Δ, ▴) at 308K (□, ■) and at 318K (○, ●).

Open symbols D = 0.2025 μm
Filled symbols D = 0.1365 μm
FIGURE 4.46

PLOTS OF VISCOSITY DATA ACCORDING TO EQUATION (2.48) FOR PVA PARTICLES IN n-HEPTANE AT 298K (∆, ▲), AT 308K (□, ■) AND AT 318K (○, ●)

open symbols  D = 0.2922 Ωm
filled symbols  D = 0.1699 μm
FIGURE 4.47

DEPENDENCE OF THE FUNCTION $(\alpha_0 f)^{1/3}$ ON THE RECIPROCAL OF PARTICLE DIAMETER FOR PMMA PARTICLES IN FIGS. 4.43 AND 4.44.
FIGURE 11.11

DEPENDENCE OF THE FUNCTION $(\alpha_0 f)^{1/3}$ ON THE RECIPROCAL OF PARTICLE DIAMETER FOR PVA IN FIGS. 11.115 AND 11.116

![Graph showing the dependence of $(\alpha_0 f)^{1/3}$ on the reciprocal of particle diameter for different temperatures.](image-url)
ation. The sphericity of the particles was indicated from TEM observations as seen in Figures 4.21 and 4.22. The linearity of the plots in Figures 4.47 and 4.48 implies that δ at each temperature was essentially constant over the particle size range considered. Therefore, from equation 2.49 values of δ at each temperature may be found from the ratio of the slope to the intercept for each plot in Figures 4.47 and 4.48 and the results are shown in tables 4.11 and 4.12.

Predicted values for $<r^2>^{0.5}$ from table 4.3 section 4.1.4 are compared with the results determined for δ from figures 4.47 and 4.48. This comparison of chain dimensions indicates that EP chains terminally anchored at the PMMA in n-heptane interface may be slightly extended over random coil dimensions for free chains in solution. Since n-heptane may be considered to be a good solvent for EP copolymer (from values of solubility parameters [54]), the change in $<r^2>^{0.5}$ over the temperature range from 298 to 318K is expected to be very small [29]. Consequently, the increase in δ over the same temperature range might arise from the terminally attached EP chains populating higher energy chain conformations which extended further away from the interface.

It is of interest to investigate whether the thickness of the stabilizing surface layer changes as the flocculation point is approached by changing the composition of the dispersion medium. As mentioned in the
TABLE 4.11

VALUES OF $\delta$ AND $\alpha_0$ FOR PMMA PARTICLES

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta$</th>
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<tbody>
<tr>
<td></td>
<td>298K</td>
<td>308K</td>
<td>318K</td>
</tr>
<tr>
<td>n-heptane</td>
<td>25.7</td>
<td>27.7</td>
<td>30.3</td>
</tr>
<tr>
<td>n-heptane/ n-propanol (79:21,v/v)</td>
<td>24.8</td>
<td>26.7</td>
<td>28.8</td>
</tr>
</tbody>
</table>

TABLE 4.12

VALUES OF $\delta$ AND $\alpha_0$ FOR PVA PARTICLES

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta$</th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>298K</td>
<td>308K</td>
<td>318K</td>
</tr>
<tr>
<td>n-heptane</td>
<td>36.1</td>
<td>41.1</td>
<td>45.2</td>
</tr>
<tr>
<td>n-heptane/ n-propanol (79:21,v/v)</td>
<td>35.0</td>
<td>39.5</td>
<td>43.0</td>
</tr>
</tbody>
</table>
flocculation studies (section 4.3.5), PMMA and PVA dispersions having surface layer of EP chains retained stability at 298K when n-propanol was added to the n-heptane dispersion medium to form a theta system (n-heptane/n-propanol, 77.75:22.25, v/v) for the EP chains, with flocculation occurring when the n-propanol composition was further increased. It was therefore, decided to examine the viscosity behaviour of particles in a dispersion medium (n-heptane/n-propanol, 79:21, v/v) which was just better than a theta system for the EP chains.

The relative viscosity data plotted according to equation 2.48 are shown in Figures 4.49 and 4.50 for PMMA and Figures 4.51 and 4.52 for PVA particles stabilized in the binary liquid mixture, with S-EP at 298, 308 and 318K. From the intercepts of these plots, values of \( (\eta_0 f)^{1/3} \) were determined and plotted against the reciprocal of D as shown in Figures 4.53 and 4.54 which confirm the linear behaviour predicted by equation 2.49 with an intercept close to the Einstein value. Values of \( \delta \) obtained from the plots in Figures 4.53 and 4.54 are shown in tables 4.11 and 4.12. Again an increase in \( \delta \) on raising the temperature is observed. Comparison of the results for \( \delta \) and \( \langle r^2 \rangle^{0.5} \) from table 4.3 indicates that EP chains terminally anchored at the interface of the polymer particle and the dispersion medium may be slightly extended over random coil dimensions for free chains in solution.

The data of the surface layer thickness of particles
FIGURE 4.49

PLOTS OF VISCOSITY DATA ACCORDING TO EQUATION (4.48) FOR PMMA PARTICLES IN n-HEPTANE/n-PROPAOL (79:21, v/v) AT 298K (Δ, ▲), AF 308K (□, ■), AND AT 318K (○, ●)

open symbols \( D = 0.12 \mu m \)
filled symbols \( D = 0.0625 \mu m \)
FIGURE 4.50

PLOTS OF VISCOSITY DATA ACCORDING TO EQUATION (4.48) FOR PMMA PARTICLES IN n-HEPTANE /n-PROPANOL (79:21, v/v)
AT 298K (Δ, ▲), AT 308K (□, ■) AND AT 318K (○, ●)

open symbols D = 0.25 μm
filled symbols D = 0.186 μm
FIGURE 4.51

Plots of viscosity data according to equation (4.48) for PVA particles in n-heptane / n-propanol (79:21, v/v) at 298K (Δ, ▲), at 308K (□, ■) and at 318K (○, ●)

open symbols D = 0.2025 μm
filled symbols D = 0.1365 μm
FIGURE 4.52

PLOTS OF VISCOSITY DATA ACCORDING TO EQUATION (4.48) FOR PVA PARTICLES IN n-HEPTANE / n-PROPANOL (79:21, v/v) AT 298K (△, ▲), AT 308K (□, ▻) AND AT 318K (○, ●).

open symbols \( D = 0.2922 \, \mu m \)

filled symbols \( D = 0.1699 \, \mu m \)
FIGURE 4.53

DEPENDENCE OF THE FUNCTION \((\alpha_0f)^{1/3}\) ON THE RECIPROCAL OF PARTICLE DIAMETER FOR PMMA PARTICLES IN FIGS. 4.49 AND 4.50.

\[
\begin{align*}
\Delta & \quad 298K \\
\square & \quad 308K \\
\circ & \quad 318K
\end{align*}
\]
FIGURE 4.54

DEPENDENCE OF THE FUNCTION $\left( \alpha_0 f \right)^{1/3}$ ON THE RECIPROCAL OF PARTICLE DIAMETER FOR PVA PARTICLES IN FIGS. 4.51 AND 4.52
stabilized by short Poly(12-hydroxystearic acid) (PSA) in n-alkanes when compared with r.m.s. end-to-end distance of free PSA chains suggest that the chains have adopted an extended conformation [75]. Results for the surface layer thickness of PDMS chains at an interface of PMMA particle-n-alkane suggested that very short chain of PDMS (\(M < 10^4\) g mol\(^{-1}\)) are in an extended chain conformation and longer chains have a conformation intermediate between random coil and extended chain conformation [76]. For \(M_{PDMS} = 48000\) g mol\(^{-1}\), the value of \((\delta)\) was about twice \(<r^2>^{0.5}\). The data for \(\delta\) in tables 4.11 and 4.12 indicate slight extension over random coil dimensions for EP chains having \(M_{EP} > 64000\) g mol\(^{-1}\). These observations may be considered in terms of the number \(n\) of main chain bonds. A PDMS chain with \(M = 48000\) g mol\(^{-1}\) has \(n \approx 1300\) whereas an EP chain with \(M = 64000\) g mol\(^{-1}\) has \(n \approx 3600\). From these data it would therefore appear that extending the end-to-end distance of a terminally attached chain at solid-liquid interface becomes less likely as the chain length (as defined by \(n\)) increases.
CHAPTER FIVE

NON-AQUEOUS RADICAL DISPERSION POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF THE DIBLOCK COPOLYMER POLY(STYRENE-B-METHYL METHACRYLATE)
5.1 INTRODUCTION

Dispersions of PMMA in n-alkanes have been stabilized with the well-defined diblock copolymers PS-PDMS [96] and S-EP [13, 105]. Because the critical flocculation point for non-aqueous polymer dispersions is close to the theta conditions for the stabilizing chains in free solution [12], there is a need for dispersions having stabilizing chains whose conformational and thermodynamic properties in solution are well documented. Consequently, dispersions stabilized with PS chains should be preferred for flocculation studies, and particles of polyacrylonitrile [43] and PVA [91], stabilized with PS graft copolymers, and particles of polyacetylene [106], stabilized with a PS block copolymer, have been reported. In this section the preparation of a dispersion of PMMA particles stabilized in organic media by the diblock copolymer poly(styrene-b-methyl methacrylate), abbreviated to PS-PMMA in which PS is the stabilizing block and PMMA is the anchor block are described.

5.2 EXPERIMENTAL WORK

A sample of the PS-PMMA diblock copolymer was kindly provided by Dr. T.G. Croucher, Polymer Laboratories Ltd, Church Stretton, Shropshire. Characterization data for PS-PMMA provided were number average molar mass $\bar{M}_n = 55000$ g mol$^{-1}$ and polydispersity = 1.13. The PS content of the diblock copolymer was estimated from U.V. spectroscopy of PS-PMMA in chloroform and found to be 45 Wt%. This PS-PMMA
diblock copolymer has therefore a well-defined structure and had been synthesised by anionic polymerization [107] performed under conditions of rigorous purity using a high vacuum technique similar to that described in the published literature [96].

MMA monomer was destabilized by repeated washing with 10% w/v KOH solution, distilled water and dried over magnesium sulphate and distilled before use. The initiator AIBN was recrystallized from ethanol. The PS-PMMA sample (1g) was dispersed in cyclohexane (15g), which had previously been dried over molecular sieves, degassed and distilled under vacuum, by first leaving the mixture overnight at room temperature and then raising the temperature of the stirred mixture to 338K for 30 minutes. The apparatus contained nitrogen gas throughout. The seed stage of the dispersion polymerization was then performed by adding MMA (0.8g which represented 20 Wt% of the total monomer with the equivalent proportion of the initiator). After this addition the seed dispersion was allowed to form for two hours, following which the remaining monomer (3.2g MMA with AIBN) was added incrementally as a feed over a period of one hour. The total reaction time for dispersion polymerization was 48 hours. The dispersion was stored at ambient temperature in a mixture of cyclohexane/dichloromethane (90:10, v/v) and this liquid mixture was used in repeated centrifuge/diluent exchange cycles to remove unadsorbed block copolymer and unconverted monomer. The
final redispersion with pure cyclohexane required storage of the PMMA dispersion at 313K. Values of the mean diameter of the PMMA particles were estimated from transmission electron micrographs. The PS content was determined by U.V. spectrophotometry of the dry particles in chloroform at 272 nm.

5.3 RESULTS AND DISCUSSION

The transmission electron micrograph in Figure 5.1 indicates that the produced PMMA particles were spherical and that narrow particle size distributions were obtained by incorporating a seed stage into the dispersion polymerization. The mean particle diameter of 0.1μm is higher than the dimensions of PS-PMMA micelles having diameters of about 300Å as shown in Figure 5.2. The stabilization of the particles in Figure 5.1 required a minimum concentration of PS-PMMA of 5 Wt% in the dispersion polymerization, as lower concentrations produced coarse particles and coagulation of PMMA. The PS content of a PMMA particle was estimated to be 10% (w/w) by U.V. spectrophotometry of particles dissolved in chloroform.

Dichloromethane was added to cyclohexane for storing the dispersions and during redispersion cycles because PMMA particles flocculated in cyclohexane (theta temperature = 307K for PS in cyclohexane [29]) at 301.6K. With a dispersion medium of cyclohexane/carbon tetrachloride (0.869:0.131, v/v) it was shown that PMMA particles on cooling lost stability at 283.8K. This flocculation
FIGURE 5.1

PMMA PARTICLES STABILIZED WITH PS-PDMA COPOLYMER
FIGURE 5.2
PS-PMMA MICELLES
temperature is near to the theta temperature of 288K for PS chains in the same binary liquid mixture [29], confirming effective stabilization of particles when the dispersion medium is a theta system or better than a theta system for the PS chains at the surfaces of the PMMA particles.
CHAPTER SIX

CONCLUSIONS AND RECOMMENDATION

FOR FURTHER WORK
CONCLUSIONS AND RECOMMENDATION FOR FURTHER WORK

Well-defined systems of sterically stabilized polymer particles have been prepared. PMMA and PVA particles were produced by radical dispersion polymerization and the stabilization mechanism was provided by a surface layer chains of EP copolymer. The two techniques of one-shot polymerization and seeded polymerization for the preparation of polymer particles were compared. Smaller particle sizes with a relatively narrow particle size distribution were obtained when the seeded polymerization technique was used, whereas a broad range of particle sizes was produced in one-shot polymerization. The mean particle size and particle size distribution were greatly influenced by the concentration of the S-EP stabilizer in the dispersion media, the solvency of the medium and the concentration of initiator used. Smaller particles were obtained as the concentration of the S-EP stabilizer was increased. When the solvency of the dispersion medium is decreased by lowering the concentration of the monomer used, smaller particles were produced and finally increasing the number of nuclei by increasing initiator concentration also produced smaller particles. The particle sizes were estimated by transmission electron microscopy.

During the course of dispersion polymerization, the nuclei formed by either self nucleation or aggregation of the precipitated oligomers adsorbed stabilizer from the
The driving force for this adsorption was the insolubility of the PS block of the S-EP stabilizer in the dispersion medium. Two models for the anchoring mechanism are proposed. One model involves the collapsed PS anchor block being trapped within the polymer matrix. In an alternative model, the anchor block is adsorbed onto the surface of particles. The long term stability of both PMMA and PVA particles suggests that the anchoring efficiency in both systems was good. The surface coverage, rheology and flocculation studies have suggested that the PS anchor block was not significantly extended into the dispersion medium, since these properties can be interpreted satisfactory in term of a surface layer of EP chains. Sterically stabilized dispersions may be flocculated by changing the temperature and by adding a miscible non-solvent (n-propanol) for the EP stabilizing chains to the dispersion medium (n-heptane). The common feature of these methods is that the solvency of the dispersion medium for the EP stabilizing chains must be reduced to break the stability, and eventually flocculation will occur. Comparison between the CFT and CFV results with $\theta$-conditions of EP copolymer chains in free solution shows that these non-aqueous dispersions of PMMA and PVA particles just retained stability at theta conditions and they start to lose stability when the dispersion medium was changed to a slightly worse than a theta system for the stabilizing EP chains. Flocculation of both types of polymer particles was observed to be reversible, and
addition of further n-heptane or an increase in temperature produce deflocculation. It was found that there was no variation in CFV and CFT values with particle concentration up to $2 \times 10^{-2} \text{g cm}^{-3}$. Furthermore, CFV and CFT results were insensitive to the particle size over the range studied. The above results suggest that for these systems, the London attractions between the core particles are not responsible for flocculation, and the observed flocculation behaviour is characteristic of long stabilizing chains.

The surface coverage of the polymer particles was calculated and it was represented as the surface area $A$ occupied or stabilized by each EP chain. The mean separation distance $d$ between adjacent EP chains was calculated assuming hexagonal close packing at the particle-liquid interface. The values of $A$ are constant for both PMMA and PVA particles with no dependence of $A$ on particle size, so total surface coverage may be assumed for all the dispersions. Different surface areas were stabilized with EP chains for PMMA and PVA particles.

Rheological studies of PMMA and PVA particles in n-heptane and in a binary liquid mixture of n-heptane and n-propanol have been studied as a function of temperature. Determinations of the surface layer thickness $\delta$ of the stabilizing EP chains from viscosity measurements of both PMMA and PVA particles in n-heptane and in the binary liquid mixture of n-heptane and n-propanol suggest that $\delta$ decreases as the temperature falls and as the solvency of the dispersion medium is changed from a good solvent to a
theta solvent for the EP copolymer chains. The surface layer thickness is larger than the root-mean-square end-to-end distance estimated for free EP copolymer chain in solution, suggesting that long EP copolymer chains terminally anchored at the interface between the polymer particle and the liquid are only slightly extended over random coil dimensions. Close packing of the EP copolymer chains at the interface may contribute to surface layer thickness which are slightly larger than random coil dimensions.

The present work has provided a method for preparing model sterically stabilized polymer dispersions. The stabilizing EP copolymer layers were well-defined and of sufficient thickness to prevent flocculation and agglomeration of the polymer particles. However, further studies are required to improve the understanding of dispersion polymerization and the behaviour of the dispersions. More experimental work is required in order to explain the slow rate of dispersion polymerization of VA in the presence of S-EP and the decrease in the rate of VA conversion as the concentration of S-EP is raised. The anchoring of S-EP to particles and the data for $\delta$, CFT and A for dispersions might be determined by the temperature chosen for the dispersion polymerization. Dispersion polymerizations performed at or below room temperature will involve the production of PMMA and PVA particles below $T_g$, which may be achieved by polymerizing with photochemical activation of an initiator or by promoting the decompos-
ition of benzoyl peroxide by adding an organic amine. Such temperature dependent polymerizations might change the mode of anchoring of S-EP to PVA particles, and similar studies could be performed for polyacrylonitrile having a high $T_g$, and for poly(ethyl acrylate), having a low $T_g$. The particle size distribution of PMMA and PVA particles is very sensitive to the state of solvency of the dispersion medium for the propagating polymer radicals during dispersion polymerization. This could be investigated by adding a good solvent (e.g. toluene) rather than raising the monomer concentration in a seeded polymerization. Finally, more information on chain conformation and its effect on $\delta$, CFT and A may be obtained by stabilizing particles with EP chains having shorter chain lengths. This may be achieved by preparing or purchasing a range of diblock copolymers of polystyrene and polyisoprene having different block lengths. Selective hydrogenation of the polyisoprene block will provide a range of S-EP samples for studies of the effect of the length of the stabilizing EP chain on dispersion properties.
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