

CHAPTER II

THEORETICAL CONSIDERATIONS

2.1 General Features of Dispersion Polymerization

Dispersion polymerization differs from emulsion and suspension polymerization in several features. These include the use of a polymeric steric stabilizer (matrix polymer) instead of the charged surfactant and the system is homogeneous prior to polymerization in contrast to emulsion methods. It is possible to prepare polymer dispersions by using any type of polymerization mechanism: free radical and ionic addition, condensation, ring-opening and so on (6). Free radical dispersion polymerization of vinyl and acrylic monomers, such as vinyl acetate, vinyl chloride, methyl methacrylate and acrylonitrile, in mainly aliphatic hydrocarbon diluents have been studied in detail of the kinetics and mechanism of the reaction.

Dispersion polymerization requires that the monomers, initiator, and stabilizer are all soluble in the starting medium. After the system is heated to reflux with stirring, the mixture is clear and transparent, but after 2-5 minutes a faint opalescence appears. Later stage, an opaque white latex is formed. Polymerization then continues without much further visible change and its progress can be monitored by a measure of total solid, density, heat output or unused monomer. Therefore, characteristics of free radical dispersion polymerization can be regarded as the following :

a) The insoluble polymer precipitates from a homogeneous reaction mixture.

b) Polymer particles are formed at a very early stage of the polymerization. Usually little or no polymerization can be detected before the first appearance of opalescence.

c) The rate of polymerization steadily increases to a maximum value. The autoacceleration of polymerization rate is quite distinct from the delayed onset of polymerization during the induction period, which results from inhibition due to impurities. Purification and deoxygenation can eliminate the induction period but leaves the autoacceleration unchanged.

d) In many cases, the rate of dispersion polymerization is much faster than the corresponding polymerization in solution using the same quantities of reactants. However, the degree of enhancement in rate depends very much on the nature of the monomer.

Dispersion polymerization may be regarded as a form of precipitation polymerization modified by the presence of a polymeric dispersant to prevent flocculation and aggregation of the precipitated particles. In contrast to emulsion polymerization, these particles are grown in a single step without the need for multiple swelling stages. A further major difference concerns the relation between the number of polymerization sites and the degree of polymerization. In emulsion polymerization, the rate and degree of polymerization depend on the number of polymer particles per unit volume (6).

In dispersion polymerization, however, the rate is virtually independent of both particle size and number over a very wide range. This is not only of theoretical significance in its own right but has an important practical outcome in that the rate of

dispersion polymerization is much more reproducible and readily controlled for this reason. It has certainly facilitated experimental kinetic studies in this field since the factors controlling a polymerization rate and the factors affecting particle size and number can be treated quite independently. A similar situation often exists in suspension polymerization since the polymer particles formed by polymerization within the emulsified monomer droplets containing oil-soluble initiator are usually large enough to contain many radicals simultaneously. This is clearly different from the situation in emulsion polymerization where the coarse emulsified monomer droplets merely serve as a reservoir of monomer while the much finer polymer particles are formed in the aqueous phase in which the initiator is dissolved. The differences between dispersion polymerization and the other types of heterogeneous polymerization described are summarized in Table 2.1.

Table 2.1 Comparison of Properties of Heterogeneous Polymerization Systems.

| Property | Dispersion | Suspension | Emulsion |
|--|------------|------------|----------|
| 1. Separate monomer phase | - | + | + |
| 2. Initiator dissolved in diluent | + | - | + |
| 3. Particles formed in diluent phase | + | - | + |
| 4. Particles stabilized | + | + | + |
| 5. Particle number dependent on stabilizer concentration | + | + | + |
| 6. Polymerization rate dependent on particle number | - | - | + |

+ means positive results and - means negative results.

2.2 Theories of Particle Formation

The particle formation stage is the most important in dispersion polymerization process. It is restricted to the early stages of the polymerization. The ultimate particle size and distribution of polymer are also a function of the amount of coalescence that occurs during and after the particle formation stage. There is as yet no single definitive theory able to predict quantitatively the number of particles formed in a dispersion polymerization under defined conditions. Several approaches which can contribute to a theoretical treatment of particle formation are examined (6).

2.2.1 Qualitative Models of the Nucleation Process

The reaction mixture for dispersion polymerization is a single-phase (homogeneous liquid), consisting of a solution of monomer, initiator, and matrix polymer in a solvent that does not dissolve the resultant polymer. When the polymerization starts, free radicals formed by an initiator decomposition grow in the continuous phase until their size reaches a critical chain length with a reactive free radical at the end.

Three different models have been proposed for the formation of particle nuclei from these growing oligomer chains (Figure 2.1).

Self-nucleation: Each individual oligomer chain as it grows, at first has an extended configuration in solution, but then collapses into a condensed state when it reaches a certain threshold molecular weight depending on its solubility in the medium. This condensed oligomeric chain therefore constitutes a new particle nucleus. According to this view, proposed by Fitch and Tsai (7), the behaviour of each oligomer chain is 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 molecular weight.

Aggregative nucleation: Growing oligomer chains associate with each other increasingly as their molecular weight 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 Volmer, and by Becker and Doring (8), the rate of nucleation is dependent on the activation energy required to form a critical aggregate, which can in principle be calculated from the interfacial tension between the two phases and the relative supersaturation of the solute. Both rising concentration and rising molecular weight of the oligomer chains therefore result in a sharply increasing rate of nucleation, but as in the previous model, captured by existing particles competes with the process of aggregation to form nuclei.

Nucleation from micelles: Particle nuclei are formed by growth of oligomer chains initiated in monomer solubilized in micelles of surfactant or amphipathic dispersant.

2.2.2 Suppression of Nucleation: Capture of Oligomer

If no competing process came into action, the formation of particle nuclei might be expected to continue throughout the course of polymerization as long as free monomer remains. In the aggregation model, the build-up of oligomers above the supersaturation threshold would result in an initial burst of nucleation followed by a fall as supersaturation is lowered due to precipitation of particles, reaching a steady-

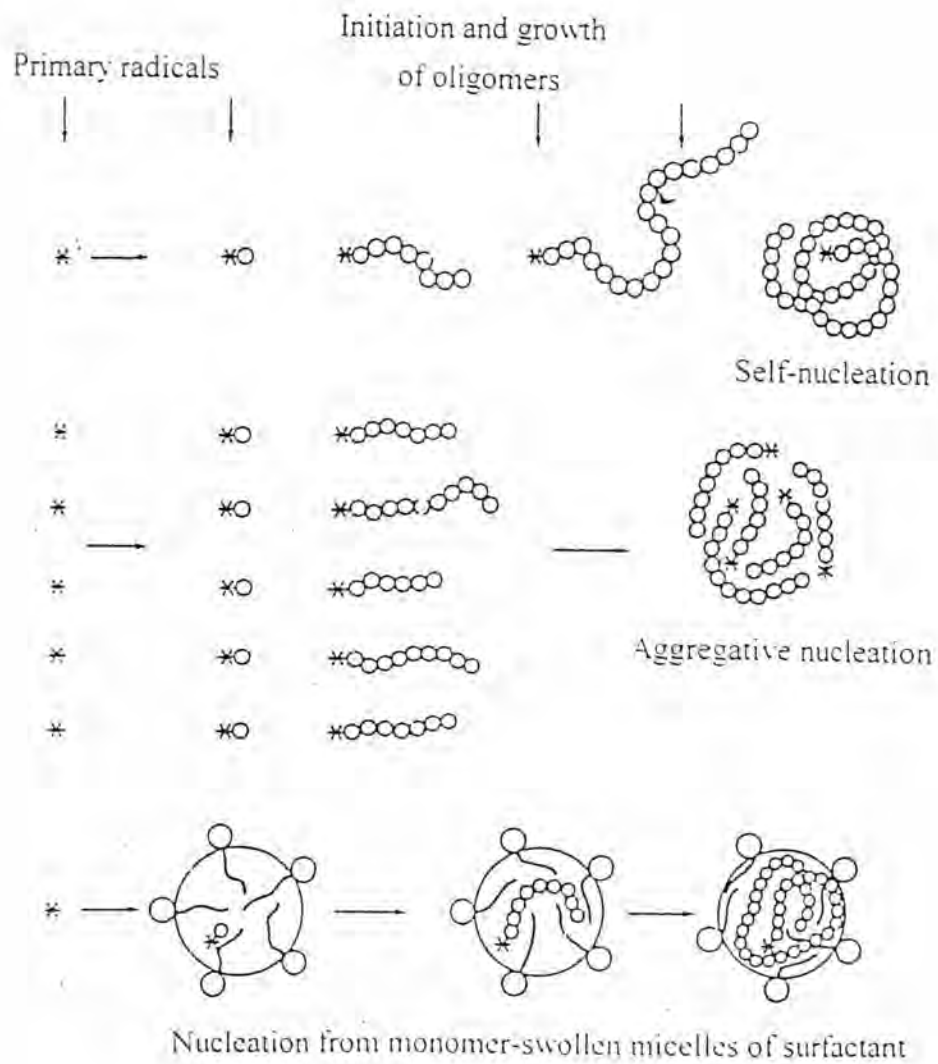


Figure 2.1 Three models for the formation of particle nuclei

state level in which the rate of initiation of the oligomers is balanced by their rate of loss to form nuclei. Alternatively, according to the self-nucleation model, the rate of nucleation would follow the rate of initiation throughout, falling gradually as monomer becomes depleted.

In practice, of course, the rate of formation of particles usually falls to a negligible level very early in the course of polymerization, unless conditions are substantially altered : once many particles are present, the formation of new particles is strongly inhibited. The most likely reason is that nearly all the oligomer molecules forming in the diluent phase are captured by existing particles before they can form new nuclei. Indeed they are probably captured while still very small and continue to grow within the particles, serving essentially as a source of radicals from the diluent. The rate of oligomer capture clearly increases with the rising number and the size of particles and since it must largely determine the number of particles formed it is obviously important to try and quantify such relationships. Two approaches have been adopted, depending on whether capture is regarded as controlled by a diffusion or by an equilibrium process:

2.2.2.1 Diffusion Capture: According to the model proposed by Fitch and Tsai, any oligomer which reaches an existing particle by diffusion before it has attained the critical size for self-nucleation, is irreversibly captured. They derive an expression for the rate of capture which is proportional to the surface area of the particle and the number of particles; the difference between this and the rate of initiation defines the rate of nucleation. The result incorporates a parameter representing the average distance an oligomer can diffuse before attaining the critical

size for self-nucleation, which therefore, characterizes the solubility of the polymer. With minor modifications the theory can be adapted to allow for nucleation by aggregation of oligomers.

However, the method of deriving the basic equation for rate of capture appears to be at variance with classical diffusion theory, which would indicate that a very much higher proportion of oligomers is captured, at a rate proportional to the number and the diameter, rather than the surface area, of the particles. The diffusion equations assume that the diffusing molecules are removed from the system irreversibly when they reach a particle surface and if this were rigorously true, far fewer particles could be formed than are found in practice.

2.2.2.2 Equilibrium Capture: In fact, there is every reason to believe that at least the lower oligomers of growing polymer chains are subject to a dynamic equilibrium between diluent and surface, perhaps moving from one to the other many times between the addition of each monomer unit. There is, in addition, the possibility of further interchange with temporary aggregations of oligomers on one hand and the interior of particles on the other hand. Effectively irreversible removal of an oligomer from the diluent can then take place when (a), it becomes part of an aggregation above the critical size for nucleation (or grows large enough for self-nucleation), or when (b), it passes from the loosely adsorbed surface layer to the interior of a particle when it is sufficiently large and insoluble that its chance of escape before adding another monomer unit is negligible.

The proportions of oligomer molecules undergoing capture or nucleation are therefore decided by their equilibrium distribution immediately prior to

this process of irreversible removal, rather than by diffusion. This approach is essentially analogous to the treatment of chemical reaction rates by transition state theory.

According to the equilibrium theory, the parameter which controls nucleation is the total surface area of the particles, as in the theory of Fitch and Tsai, although in a slightly different form. (A further nucleation parameter could be the total volume of the particles if they are sufficiently fluid to allow a rapid equilibration with their interiors).

All of the approaches described above of course, require a knowledge of the rate of growth of particles before they can be applied to actual situations, and plausible assumptions can be made about this in the light of the mechanism of polymerization. However, the theories postulated also involve parameters which cannot easily be estimated independently, although Fitch and Tsai attempted to measure the molecular weight of polymer just prior to precipitation. Nevertheless, useful conclusions can be drawn about the general form of the relationships to be expected.

Except for the micellar nucleation model, all of the mechanisms discussed so far would yield unstabilized particle nuclei, which rapidly flocculate while continuing to grow, followed by coalescence or agglomeration to an extent dependent upon the physical properties of the polymer and its plasticization by monomer etc. The typical product of an unstabilized precipitation polymerization is therefore a coarse aggregate of particles which themselves consist of smaller primary particles largely fused together.

2.3 Particle Formation in the Presence of Dispersants

The nature and the amount of amphipathic dispersant used in a dispersion polymerization has a profound effect on the occurrence of nucleation and the numbers of particles formed as well as preventing flocculation (9). It is possible to propose a plausible role for the dispersant molecules in modifying each of the processes postulated in the various theoretical models, and a great deal of further work is needed to establish exactly the complete role which a dispersant plays in any given polymerization system. In each case, enhanced nucleation is accounted for by some form of association between the dispersant and the growing oligomer which rises the probability of forming a nucleus and in turn, lowers the probability of capture by existing particles. The effects of increasing polarity and insolubility of both the anchoring portion of the dispersant and the polymer being formed therefore fall naturally into place since these will increase the tendency to associate and hence increase the rate of nucleation (Figure 2.2).

So far, it has been tacitly assumed that nucleation is brought to a halt by prior capture of oligomers while there is still excess unused dispersant present, so that the concentration of dispersant can be taken as roughly constant throughout the nucleation period. However, there are two possible situations in which depletion of dispersant could become the limiting factor determining particle size and number.

2.3.1 Dispersant-limited Nucleation: The dispersant is so efficient that nucleation continues at a high rate until there is very little dispersant remaining unattached to particles; thereafter nearly all oligomers are captured by particles. This is essentially the model proposed by Roe for emulsion polymerization (10). Whilst this behaviour

has been taken as the normal situation in emulsion polymerization, there is little evidence for its widespread occurrence in organic media, at any rate in such an extreme form.

2.3.2 Dispersant-limited Agglomeration: Primary particles grow in size and in number until the dispersant available is insufficient to cover the surface effectively and prevent flocculation. In principle, this may occur either while nucleation is still under way, or well after it has been brought to a halt by prior capture of oligomers. The usual practical result of running out of dispersant in a dispersion polymerization is gross flocculation throughout the dispersion, but in certain circumstances controlled agglomeration occurs instead, to form fewer and larger particles with a smaller total surface. In its extreme form, this model assumes that the dispersant serves merely to prevent secondary aggregation and plays no part in the formation of primary particles.

2.4 Factors Controlling Particle Number and Size

2.4.1 Period of Particle Formation: Constancy of Numbers

In a typical dispersion polymerization producing polymer which is very insoluble in the diluent, such as methyl methacrylate in an aliphatic, the stage of particle formation is normally completed very quickly, within a few seconds or tens of seconds after the start of reaction (11). All the evidence from electron micrographs indicates that very few particles form after this stage unless the solvency of the medium is drastically altered or substantial amounts of additional dispersant are added. The number of particles therefore, remains virtually unchanged throughout the remaining course of the polymerization, unless some form of aggregation intervenes, as may

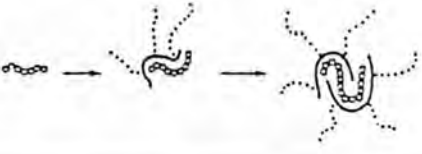
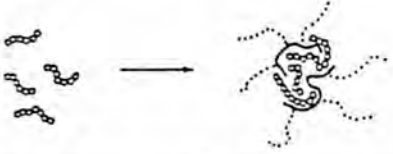

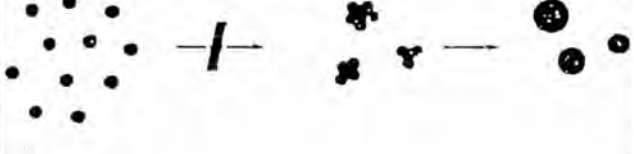
| | |
|---|---|
| <p>SELF-NUCLEATION</p>  | <p>Dispersant stabilizes growing oligomers against capture by particles at lower molecular weights</p> <p>∴ Reduces probability of capture</p> <p>∴ Produces more nuclei</p> |
| <p>AGGREGATIVE NUCLEATION</p>  | <p>Dispersant participates in forming incipient nuclei and reduces interfacial tension</p> <p>∴ Lowers activation energy and threshold molecular weight</p> <p>∴ Reduces probability of capture</p> |
| <p>MICELLAR NUCLEATION (probably only in aqueous systems)</p>  | <p>Dispersant forms micelles from which nuclei are formed by initiation of monomer solubilized in them. Dispersant migrates from micelles to cover particle surface ∴ Nucleation stops</p> |
| <p>AGGLOMERATION</p>  | <p>Dispersant prevents or limits agglomeration of small particles to form larger ones</p> <p>∴ Total particle surface area and hence number of particles, is limited by amount of dispersant</p> |

Figure 2.2 Probable roles of dispersant in modifying particles formation processes

indicates that very few particles form after this stage unless the solvency of the medium is drastically altered or substantial amounts of additional dispersant are added. The number of particles therefore, remains virtually unchanged throughout the remaining course of the polymerization, unless some form of aggregation intervenes, as may happen if the total particle surface formed outruns the amount of dispersant available.

2.4.2 Solvency of the Medium and Solubility of the Polymer

The process of particle formation are strongly influenced by increasing the solvency of the medium for the polymer which is being produced:

2.4.2.1 The onset of particle formation is often retarded;

2.4.2.2 The duration of particle formation is prolonged;

2.4.2.3 Fewer particles are produced;

2.4.2.4 They are correspondingly larger and usually of a wider particle size distribution.

For a given polymer, solvency may be varied by an appropriate choice of diluent, addition of strong solvents, or by altering the concentration of the monomer. In most polymer-diluent systems, the effects of changes in temperature are small compared with the results of even minor changes in composition, but solvency generally increases with rising temperature.

The monomer itself behaves as a strong solvent, and so relatively large particles are obtained at high monomer concentrations. The effect of a small increase in monomer content in coarsening and widening the range of particle sizes is particularly marked in the presence of fairly high concentrations of dispersant and near to the limiting concentration at which the polymer is soluble. At even higher monomer

concentrations, of course, polymerization takes place in solution until the monomer content falls to the threshold value of around 55% for methyl methacrylate in aliphatic hydrocarbons below which polymer precipitates as a very coarse dispersion of highly swollen particles with a wide range of sizes.

Addition of extra solvent or monomer after the first crop of particle nuclei has been formed does not usually reduce the number of particles, unless so much is added as to desorb stabilizer causing flocculation. On the other hand, a drastic fall in solvency, in an initially coarse latex may produce a fresh crop of fine particles; this may happen when the initial monomer concentration is very high and then falls as polymerization continues. This phenomenon has been utilized in a process for making polymer dispersions with a very wide range of particle sizes.

2.4.3 Concentration and Nature of the Dispersant

The concentration of the dispersant is one of the most important factors controlling nucleation: the number of particles increases and their size decreases as the stabilizer content is raised. In any given system, the exact relationship must be established empirically. The dependence on dispersant content is very marked up to a certain level, beyond which further additions have much less effect. In very high levels of the dispersion chain solvency, the efficiency of stabilization is seriously impaired and it is possible that secondary aggregation of primary particles occurs under these conditions, so that the final particle size is not very sensitive to dispersant concentration. At low levels of dispersant, the particles have a higher average size (12).

2.4.4 Reactivity of Dispersant Precursors

Whatever the type of dispersant used, a broadly similar relationship is found between its concentration and the particle size of the dispersion formed: examples have been drawn from both preformed comb-type grafts and precursor-type dispersants. However, in the latter case the true dispersant is formed only gradually from the precursor during polymerization, so that its effective concentration at the critical period when particles are forming depends on the relative rates of this grafting reaction and the polymerization of the monomer. For this reason, particle size falls as the proportion of reactive groups in the precursor is raised, or if the type of reactive group is replaced by one with reactivity ratios more favourable to copolymerization.

2.4.5 Renucleation, Agglomeration and Flocculation

Renucleation is the formation of fresh particles at a later stage in the polymerization. It is most likely to occur in feed processes, in which the original seed particles grow by further addition of monomer together with more dispersant, since the latter may at times exceed the amount required to protect the increasing surface area of the growing particles.

Renucleation is inhibited by the presence of existing particles, and in this respect the total number of particles seems to be more important than the total polymer concentration, so that coarse dispersions renucleate much more readily than fine ones of equivalent concentration.

Renucleation is also promoted by all the factors which tend to produce fine particles as follows:

| Renucleation favoured by : | Renucleation inhibited by : |
|---|---|
| Coarse particle size | Fine particle size |
| Low total solids | High total solids |
| Low solvency medium | High solvency medium |
| Low free monomer content | High free monomer content |
| More polar monomers | Less polar monomers |
| High dispersant content | Low dispersant content |
| Strongly anchored dispersant (more polar anchor chain) | Weakly anchored dispersant (less polar anchor chain) |

The effect of renucleation, of course, is to produce a bimodal or polymodal particle size distribution, whilst at the same time preventing the original particles from growing to as large a size as if renucleation had not taken place.

The aggregation of polymer particles occurs in the absence of sufficient effective dispersant to protect the total particle surface, and can take the form of flocculation or agglomeration.

Agglomeration is the formation of new larger particles by the aggregation of limited numbers of primary particles, which may be followed by partial or completed fusion.

Flocculation is the formation of loose aggregates or flocs over extended regions, sometimes throughout the whole of a dispersion, which may then appear to gel or coagulate.

Agglomeration of primary particles can in principle afford a means of increasing the size of particles in a dispersion and reducing their number. Such controlled secondary aggregation has rarely been demonstrated conclusively in practice. It would not be expected to be revealed in the shape of the particles formed since agglomeration would usually be followed by complete coalescence in the conditions normally used in dispersion polymerization. It is therefore necessary to demonstrate that the particle size after aggregation has increased by an amount more than could be accounted for from the particle size before aggregation and the extra amount of monomer polymerized, or in other words, that the number of particles has decreased.

2.5 Kinetic Model for Dispersion Polymerization

Once polymer particles have been formed from the initially-homogeneous reaction mixture, they absorb monomer from the diluent phase and polymerization subsequently proceeds within the particles according to the laws of bulk polymerization kinetics. In the conditions used here, the high viscosity of this monomer-swollen polymer phase greatly hinders radical termination. The resulting increase in radical concentration accelerates the rate of polymerization (Trommsdorff effect), while the slow rate of termination also ensures that many radicals can coexist in each particle, in contrast to the situation envisaged in classical Harkins-Ewart-Smith emulsion polymerization kinetics (13).

A kinetic equation corresponding to this model for dispersion polymerization has been developed in the following manner. If the polymer particles at a given time

occupy a volume fraction V of the whole dispersion, and the rate of initiation in the whole dispersion is R_i , then the effective initiation rate in the particles will be given by

$$R_{ip} = R_i/V \quad (2.1)$$

If the monomer concentration in the particles is C_{mp} , the overall polymerization rate in the particles, R_{pp} , will be equivalent to the usual expression for bulk or solution kinetics in the form

$$\begin{aligned} R_{pp} &= C_{mp}k_p(R_{ip}/k_t)^{1/2} \\ &= C_{mp}k_p(R_i/k_tV)^{1/2} \end{aligned} \quad (2.2)$$

Since essentially all polymerizations take place within the particles in the volume fraction V , the overall rate in the whole dispersion is

$$\begin{aligned} R_p &= VR_{pp} \\ &= C_{mp}k_p(VR_i/k_t)^{1/2} \end{aligned} \quad (2.3)$$

In emulsion polymerization, the concentration of monomer in the polymer particles is usually taken as constant up to the stage in the polymerization where the monomer droplets disappear. In dispersion polymerization, since the monomer is completely miscible with the hydrocarbon diluent, the concentration of monomer in the polymer particles depends on its partition coefficient, α , between polymer and diluent. Thus, the overall rate of dispersion polymerization, where C_{md} is the monomer concentration in the diluent, is given by

$$R_p = \alpha C_{md}k_p(VR_i/k_t)^{1/2} \quad (2.4)$$

This is the general equation for dispersion polymerization and it takes into account the principal features of the kinetics which have been established, such as the

proportionality of the polymerization rate to the square root of initiator concentration, the acceleration in rate which follows the increase in the total volume of the polymer particles and the correlation of rate with that in the bulk polymerization of the monomer. It is important to note that the value of $k_p/k_t^{1/2}$ in this expression is not to be taken as constant but varies as the concentration of monomer in the polymer particles changes, in exactly the same manner as in bulk polymerization at high conversions. In principle, the partition coefficient α 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 experiments.

2.6 Literature Survey

Barrett (14) prepared micron-sized particles with a very narrow size distribution in an organic phase. The stabilizing polymers used were usually graft or block copolymers which is used in conjunction with some quaternary ammonium salts. It was shown that the concentration of the stabilizing polymers is one of the most important factors controlling nucleation. The number of particles increases and their size decreases as the stabilizer content is raised.

Ugelstad et al. (15) developed a method to obtain monodisperse polymeric particles of micron-sized using a two-stage swelling method which is very efficient but very tedious and requires several reaction steps. This method was the first successful technique for preparing monodisperse polymeric particles of micron-size in the range of 0.2-1.5 μm .

Almog et al. (16) prepared micron-sized particles by breaking up monomer droplets into the micron-sized range by homogenization in the presence of a stabilizer, and subsequently, polymerized the monomer by suspension polymerization. This method prepared polymeric particles between about 50-100 μm with a wide particle size distribution because of the inherent size distribution in the mechanical homogenization step.

Ober et al. (17) presented the use of nonionic cellulosic derivatives as a steric stabilizers (matrix polymer) in the dispersion polymerization of styrene. It was shown that particles up to 10 μm can be prepared without the use of an electrostatic co-stabilizer.

Almog et al. (18) developed a method of dispersion polymerization by the use of a polymeric stabilizer (matrix polymer) in combination with a quaternary ammonium salt as a co-stabilizer. They prepared polymeric microspheres in the size range from as small as 0.1 μm , to as large as 12 μm . When Aliquat 336 which acts as an electrostatic co-stabilizer was used as a co-surfactant, monodisperse microspheres in the range of 1-6 μm were formed with the standard deviation (SD) ranging from 1.4 to 4.5%. The extent of monodispersity improvement by the electrostatic co-stabilizer depends on the type of monomer, nature, and amount of the surfactant. At high concentrations of surfactant the effect is less pronounced. A number of steric stabilizers (matrix polymer) in combination with the electrostatic co-stabilizer, were used in the polymerization of styrene. It is seen that the matrix polymers such as PVP, PMVE, PAA and PEI are effective but PVAc is only effective provided that it contains at least 82% VAc. Low molecular weight surfactants, such as Span 80 and Pluronic

P-103, resulted in agglomerative systems when it was used as a matrix polymer. When the system is used without any matrix polymer, agglomerative systems resulted.

Lok and Ober (19) developed a dispersion polymerization of styrene using nonionic cellulosic derivatives as steric stabilizers (matrix polymer) in a variety of solvent systems without the use of an electrostatic co-stabilizer. It was found that the particles obtained by using hydroxypropyl cellulose as a matrix polymer in a solvent mixture of MeCell to ethanol had a monodisperse size distribution in the size range of 3-9 μm . The particle size distribution (PSD) was 1 and molecular weight distribution of the monosized polymeric particles was 2 to 3. The molecular weights of the monodispersed particles produced in MeCell-EtOH were lower than those of polydisperse particles produced in the EtOH-water system.

Tseng et al. (20) expanded the approach of Almog et al. Polymerizations were carried out in ethyl alcohol using an anionic surfactant, a nonionic surfactant, a long-chain alcohol, or a comonomer in combination with a matrix polymer (PVP) instead of a cationic co-stabilizer. They have successfully prepared monosized polystyrene particles in the size range of 2.5-4.0 μm with a narrow size distribution when using PVP in combination with an anionic surfactant Aerosol OT, anionic surfactant Triton N-57, or cetyl alcohol as a co-stabilizer. When the polymerization was carried out in the presence of PVP K-30 without a co-stabilizer, the larger particle sizes in the size range of 4-15 μm with a bimodal particle size distribution was found. For dispersion polymerization of styrene in ethanol with several functional comonomers instead of the above co-stabilizers, it appeared that copolymerizations with comonomers including methacrylic acid (MMA), hydroxyethyl acrylate (HEA), acrylamide, allyltriethoxy

silane, vinyl poly(dimethyl siloxane), and vinyl silacrown resulted in polymer of a narrow particle size distribution. Polymer of a broad size distribution in the size range of 4-12 μm was found when methyl methacrylate was used as a comonomer.

Ober and Hair (21) studied the effect of temperature and initiator levels on the dispersion polymerization of polystyrene. The hydroxypropyl cellulose was used as a steric stabilizer and the solvent mixture is ethanol and 2-methoxyethanol, it could be concluded that the dispersion polymerization was carried out at 72°C, monodisperse particles with a diameter of 7 μm was produced. It was shown that monodispersity could be achieved over a considerable range of temperature provided that a particular level of initiator was used at a given temperature.

Lu et al. (22) investigated the dispersion polymerization of styrene in ethanol with azo-type initiators and a matrix polymer (PVP) along with an anionic or nonionic co-stabilizer. It was reported that the co-stabilizer was necessary for monodisperse particles to be formed. When using Triton N-57, Aerosol OT, and cetyl alcohol, the particle size was in the size range of 4, 2.5 and 3.2 μm , respectively while producing a monodisperse size distribution. The monodisperse particles had a value of coefficient of variation of 5-6% and molecular weight distribution was 3.69-4.13.

Kobayashi et al. (23) studied a dispersion polymerization of methyl methacrylate in an aqueous methanol solution by using poly(2-ethyl-2-oxazoline) (PEtOZO) and polyethylenimine (PEI) as a polymeric stabilizer. It was found that the monomer concentration increased from 5 to 15%, the average particle size increased from 2.3 to 3.4 μm of monodispersed poly(methyl methacrylate) particles and the value of polydispersity index was 1.02.

Tuncel et al. (24) prepared the monosized polymeric microbeads of polystyrene in the size range of 1.0-4.0 μm in isopropanol/water, 1-butanol/water and 2-butanol/water by using polyacrylic acid as a steric stabilizer. The average size and size distribution of microbeads decreased with increasing polarity of the dispersion medium. The increase in the stabilizer concentration resulted in a decrease in average size and size distribution of the microbeads. Isopropanol/water dispersion medium provided monosize microbeads with higher values of monomer/dispersion medium ratio.

Shen et al. (25) synthesized prepared monodisperse poly(methyl methacrylate) particles in the size range of 0.4-10 μm in methanol or a water/methanol mixture by using PVP as a steric stabilizer. It was found that the presence of the co-stabilizer was necessary to obtain monodisperse particles when the stabilizer concentration was lower than 2 wt%.

Saenz (26) studied the dispersion polymerization of styrene in ethanol and the dispersion copolymerization of styrene and butyl acrylate in a water-ethanol mixture. It was found that only at low stabilizer concentrations, the effect of co-stabilizer on the particle size distribution was significant. The monosized polymeric particles in a size range of 2.4-3.1 μm and a coefficient of variation 2.7-8% and polydispersity index 1.01 to 1.02 were found. In this work, it was found that purging with nitrogen was a necessary but it was not a condition to achieve monodispersity. The type of agitation had a weak effect on the monodispersity. A good dissolution of the stabilizer was necessary to obtain monodispersity in the dispersion polymerization of styrene and monomer purification was also of paramount importance to obtain a good monodispersity.

Horak et al. (27) studied the dispersion polymerization of styrene and butyl methacrylate in ethanol-water medium by using hydroxy propyl cellulose, poly(acrylic acid), and poly(N-vinyl pyrrolidone) as a steric stabilizers. It was observed that only beads ranging from 2 to 9 μm possessed a narrow size distribution. These beads were obtained in water contents not exceeding 13 vol%. The size distribution of the beads broadens dramatically at water contents lower than 6 vol%, while it remains relatively narrow at water contents between 6 and 11 vol%.

Apiwattananon (28) prepared the solution, bulk, and dispersion polymerization of poly(styrene-*co*-methyl methacrylate) by using PMVE as a matrix polymer and EtOH/n-hexane as a medium. The results indicated that the copolymers in solution and bulk polymerizations were aggregated and found in random shapes but the dispersion copolymer particles were obtained in a spherical shape with the size range of 1-5 μm and the value of standard deviation was 0.24-2.08. The appropriate temperature range for this dispersion polymerization was 50 to 64°C. The reaction did not occur at 40°C and it gave the agglomerated particles at 73°C.