CHAPTER 2

THEORETICAL CONSIDERATIONS

2.1 Description of Dispersion Polymerization

Dispersion polymerization generally involves the polymerization of a monomer dissolved in an organic diluent to produce insoluble polymer dispersed in continuous phase in the presence of an amphipathic graft copolymer as dispersant. The conditions for successful dispersion polymerization require an inert diluent which dissolves the monomer but precipitates the polymer and a polymeric dispersant to stabilize the polymer particles as they are formed by the attachment of a dissolved protective layer around them. The followings are a number of features that can be regarded as characteristic of dispersion polymerization [9].

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

b) Polymer particles are formed at a very early stage of 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 auto-acceleration of polymerization rate is quite distinct from the delayed onset of polymerization during the induction period, which results from inhibition due to impurities. Thorough purification and deoxygenation eliminates the induction period but leaves the auto-acceleration 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.

2.2 The Scope of Dispersion Polymerization [10]

In dispersion polymerization, polymer dispersions may be prepared using any type of polymerization mechanism-free radical and ionic addition, condensation, ring opening and so on. Since the main field of practical application has so far been with free radical dispersion polymerization, detailed study of kinetics and mechanism has largely been confined to this area. Free radical addition polymerization has been the most widely applied and many of the commonly used monomers, such as vinyl acetate and methyl methacrylate, are entirely miscible in all proportions with aliphatic diluents allowing a wide range of dispersions of polymers and copolymers to be prepared. Ionic initiation can also be used and has been applied to both addition and ring-opening polymerizations. Since the polymerizations are carried out in non-polar media, those involving water or alcohol-sensitive reactants or catalysts whose use would normally be precluded from aqueous emulsion polymerization techniques, can readily be carried out by dispersion polymerization. Techniques of condensation polymerization can also be utilized, using soluble reactants in the usual ways. However, in cases in which the reactants are insoluble in the required organic medium, it is possible to use additional methods to emulsify or disperse the reactant using the same graft copolymer dispersants which are required for the dispersed polymer produced. The disperse nature of the reactants often allows the removal of the by-products of the condensation polymerization at a more rapid rate than the corresponding process under bulk conditions.

Although aliphatic liquids, such as n-heptane or cyclohexane, have been most used as the organic diluent in dispersion polymerization, more polar liquids such as fluoro- or chloro-substituted hydrocarbons, esters and even alcohols can readily be used if required. Normally, the hydrocarbon or mixture of hydrocarbons to be used is selected on the basis of suitable boiling point for the type of polymerization and initiation to be used since the dispersion polymerization is usually carried out under reflux conditions. However, if necessary, the choice can also be based on the requirements of the subsequent applications of the polymer dispersions. In the case of surface coatings, this would require a suitable diluent mixture to achieve the correct rate of evaporation for film formation, or if polymer powders are produced subsequently, a diluent of suitably low latent heat of evaporation to be distilled off readily with a low heat input.

With the use of the appropriate reactive comonomers in dispersion polymerization, dispersions of reactive polymers may be obtained, which undergo subsequent cross-linked or microgel polymer particles. Heterogeneous polymer particles, which contain separate inclusions of one polymer within the matrix of another, have also been prepared by dispersion polymerization. Other materials, for example inorganic pigments, have also been encapsulated within a dispersed polymer by a similar means.

2.3 The Role of the Dispersant [11]

The function of the dispersant in a sterically-stabilized colloidal dispersion is to provide a layer of material solvated by the dispersion medium on each particle surface. Every particle is thus surrounded by a tenuous cloud of freely moving polymer chains which are, in effect, in solution, in the continuous phase. This layer prevents the particles from coming into direct contact and also ensures that the distance of closest approach of the two particles, the attraction between them is so small that thermal energy renders contact reversible. The nature of the stabilization process can be explained in simple terms in the following way. When two particles which have polymer molecules firmly attached to their surfaces approach one another in a medium in which the polymer molecules are soluble, a change in free energy (ΔG_{R}) occurs as the polymer molecules interpenetrate or are compressed. The resulting increase in the concentration of the polymer segments in the layers of adsorbed polymer generates an osmotic pressure, i.e. ΔG_{R} is positive. To counteract this effect, solvent diffuses into the regions of higher polymer concentration forcing the particles apart until the steric barriers are no longer in contact. An effective stabilizer must therefore be able to maintain a complete coverage of the particle surface. In addition, the solvated cloud surrounding the particles must be concentrated enough to generate sufficient osmotic pressure to resist the inherent attractive forces, yet shows no tendency to form a separate phase. The solvated sheath is localized at the surface of the particle only because it is adsorbed or attached in some other way to the surface.

It follows that since a positive value for ΔG_{R} ($= \Delta H_{\mathrm{R}} - T\Delta S_{\mathrm{R}}$) is necessary to achieve stability, this can arise from the separate enthalpic (ΔH_{R}) and entropic (ΔS_{R}) components. Napper [12] has classified the contributions to steric stabilization in the following way:

Enthalpic stabilization	*Entropic stabilization*	*Combined enthalpic-entropic stabilization*
ΔH_{R}, ΔS_{R} positive; $\Delta H_{\mathrm{R}} > T\Delta S_{\mathrm{R}}$	ΔH_{R}, ΔS_{R} negative; $T\Delta S_{\mathrm{R}} > \Delta H_{\mathrm{R}}$	ΔH_{R} positive, ΔS_{R} negative
Dispersions flocculate on heating	Dispersions flocculate on cooling	Dispersions stable throughout normal temperature range

2.4 Particle Formation in Dispersion Polymerization

2.4.1 Theories of particle formation

There is as yet no single definitive theory able to predict quantitatively the number of particles formed in a dispersion polymerization under defined conditions. Here are several approaches which can contribute to a theoretical treatment of particle formation [13].

2.4.1.1 Equilibrium Systems and Irreversible Process

Some systems are known in which a phase separates out in the form of particles or domains of well-defined size and number according to a true thermodynamic equilibrium. In contrast to such true equilibrium systems, the formation of particles in dispersion polymerization must clearly be regarded as an irreversible process: once formed, the particles are thermodynamically stable and continue to grow. Moreover, further polymerization within the particles lowers their solubility to a point where transfer of materials from one particle to another is virtually impossible. The numbers and sizes of particles are determined by the balance of several competing rate processes and the way they vary during the course of polymerization. The most importance of this process is the rate of nucleation, i.e., the rate of formation of new particle nuclei and the way in which this is related to the number and size of existing particles, the presence of a dispersant and the rate at which new polymer chains are initiated in the diluent phase.

2.4.1.2 Qualitative Models of Nucleation Process

The nucleation process starts in an essentially homogeneous solution containing monomer, initiator and usually a dispersant. Exactly as in conventional solution polymerization, the first steps involve production of radicals by break down of the initiator, which in turn react with monomer to form growing oligomeric chains with a reactive free radical at the end. Three different models have been proposed for the formation of particle nuclei from growing oligomeric 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, 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 associated 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, 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 oligomer chains therefore result in a sharply increasing rate of nucleation, but as in the previous model, capture by existing particles competes with the process of aggregation to form nuclei.

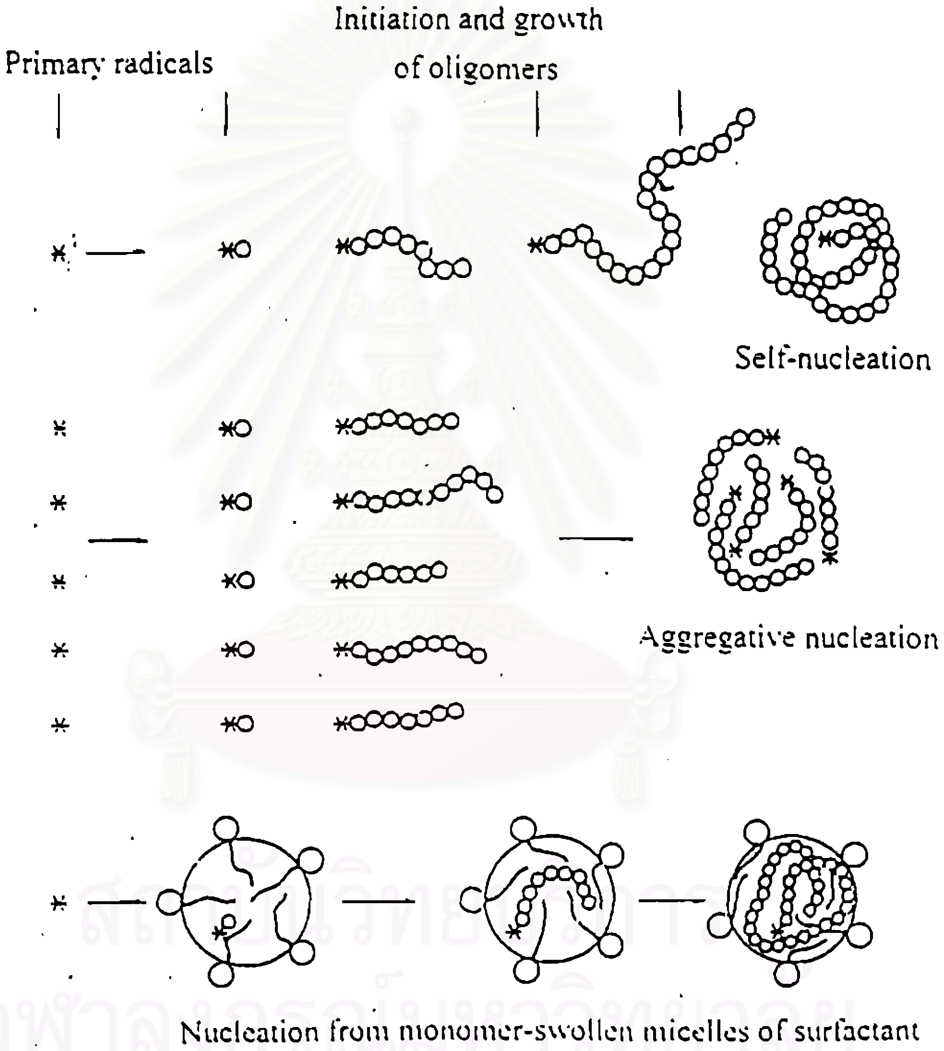


Figure 2.1. Three models for the formation of particle nuclei

Nucleation from micelles. Particle nuclei are formed by growth of oligomer chains initiated in monomer solubilized in micelles of surfactant or amphipathic dispersant. This, of course, is the model for emulsion polymerization. In aqueous emulsion polymerization, the micellar model appeared plausible in view of the very low concentration of molecularly dissolved monomer in the aqueous phase. However, it is now increasingly recognized that the primary initiation step probably takes place in the aqueous phase between a water-soluble radical and the low concentration of dissolved monomer; growing oligomers then either enter a micelle or acquire a layer of surfactant around them, provided there is excess surfactant present.

2.4.1.3 Suppression of Nucleation: Capture of Oligomers

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-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:

a) Diffusion capture: According to the model proposed by Fitch and Tsai [14], any oligomer which reaches an existing particle by diffusion before it has attained the criticle 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. 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 particle. The diffusion equations assume that the diffusing molecules are removed from the system irreversibly when they reach a particle surface and if they were rigorously true, far fewer particles could be formed than are found in practice.

b) Equilibrium capture: 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. In addition, there is the possibility of further interchange with temporary aggregations of oligomers on the one hand and the interior of particles on the other. Effectively irreversible removal of an oligomer from the diluent can then take place when it becomes part of an aggregation above the critical size for nucleation (or grows large enough for self-nucleation), or when 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. According to the equilibrium theory, the parameter which controls nucleation is the total surface area of the particles, although in a slightly different form. (A further nucleation parameter could be the total volume of particles if they are sufficiently fluid to allow a rapid equilibration with their interiors.)

2.4.1.4 Particle Formation in the Presence of Dispersants

The nature and the amount of 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. It is possible to propose a plausible role for the dispersant molecules in modifying each of the processes postulated in the various theoretical models. In each case, enchanced nucleation is accounted for by some form of association between the dispersant and the growing oligomer which raises 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 dispersant and 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:

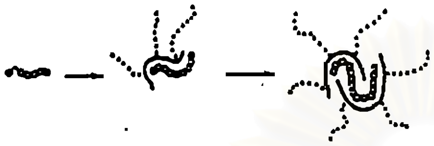
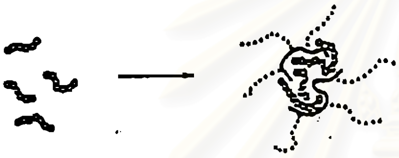
SELF-NUCLEATION 	Dispersant stabilizes growing oligomers against capture by particles at lower molecular weights ∴ Reduces probability of capture ∴ Produces more nuclei
AGGREGATIVE NUCLEATION 	Dispersant participates in forming incipient nuclei and reduces interfacial tension ∴ Lowers activation energy and threshold molecular weight ∴ Reduces probability of capture
MICELLAR NUCLEATION (probably only in aqueous systems) 	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
AGGLOMERATION 	Dispersant prevents or limits agglomeration of small particles to form larger ones ∴ Total particle surface area and hence number of particles, is limited by amount of dispersant

Figure 2.2 Probable roles of dispersant in modifying particle formation process

a) Dispersion-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. Whist this behavior 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.

b) 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 particle.

2.4.2 Methods of Investigation of Particle Formation [13]

It is obviously of the utmost importance to know how to control the particle size and particle size distribution in a polymer dispersion. This will affect the rheology of the latex and its tendency to settlement on storage, as well as other properties. The particle size distribution is essentially determined by the numbers of new particles which form at each moment during the course of polymerization, together with their subsequent growth and any aggregation which may occur.

The direct study of polymer particles as they are being formed presents great difficulty, since the decisive processes take place over a very short period of time on a submicroscopic scale. Some investigators have attempted to follow the formation and early growth of polymer particles in aqueous systems by measurement of light scattering but the interpretation of these measurements is not always clear-cut and estimates of particle size distribution are at best indirect. Consequently, nearly all knowledge of particle formation is based upon measurements of particle size and its distribution in samples of dispersions taken after the initial period of their information, and the way in which these change during the subsequent course of polymerization. Any of methods well known in the study of aqueous emulsion polymers can be readily used for dispersions in organic media: these include light scattering, sedimentation, centrifugation, etc. However, a much greater wealth of useful information can usually be obtained by electron microscopy. The following is important information obtained by a qualitative examination of electron micrographs:

a) A highly uniform particle size normally indicated that the particles have been formed within a very short period of time and subsequent growth has taken place without the formation of further particles or involving agglomeration processes (Figure 2.3 a).

b) A wide and fairly random distribution of particle size usually indicates that particle formation has continued over a long period of time, corresponding to a wide range of periods of growth (Figure 2.3 b). Occasionally, however, this distribution can also result from a process of agglomeration

c) The presence of many very small particles among a fairly uniform population of larger ones usually indicated that renucleation has occurred, i.e. a fresh crop of new particles has been formed long after the first period of particle formation (Figure 2.3 c)

d) Comparison of particle sizes at various stages during the course of polymerization, in conjunction with independent measurements of the amount of polymer formed, can distinguish between processes of agglomeration and extended periods of particle formation, depending on whether the total number

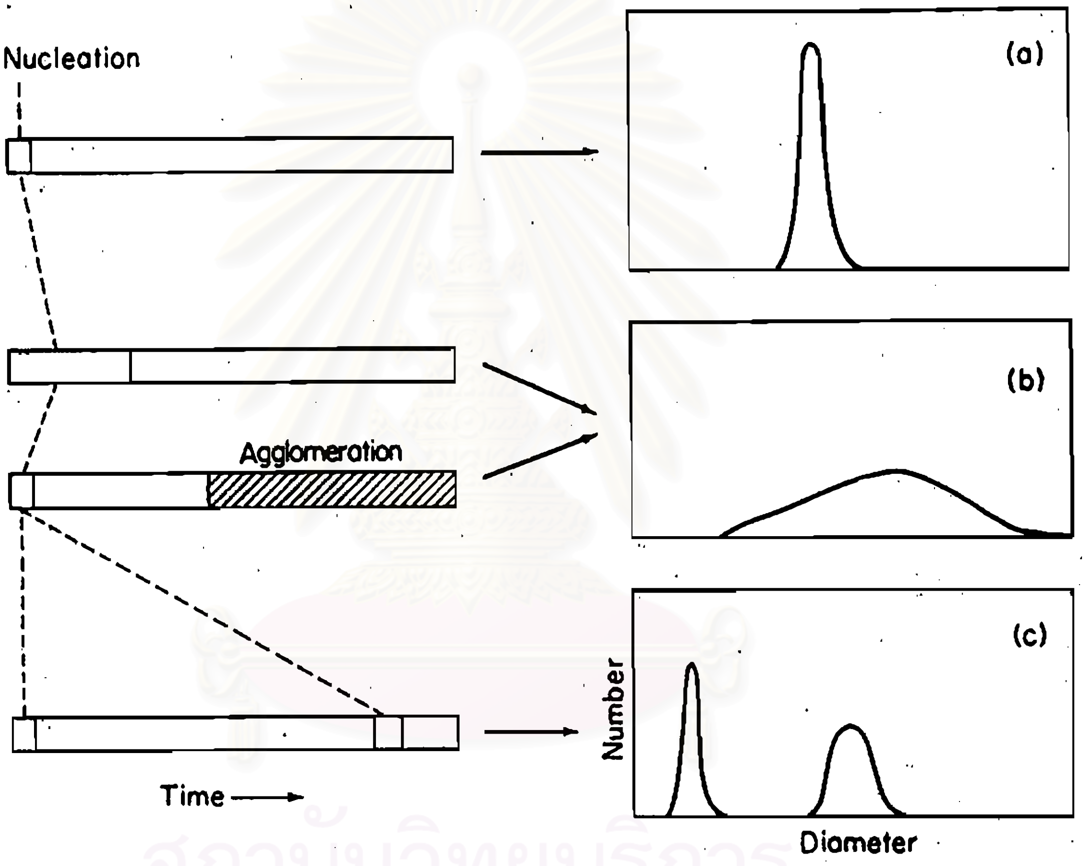


Figure 2.3. Schematic illustration of typical particle size distributions in dispersion polymerization (right) and characteristic course of the processes which give rise to them (left)

of particles decreases or increases. The time of renucleation and the conditions for its occurrence can be assigned with some precision, and the rates of growth of large and small particles compared.

e) In some cases, inferences can also be drawn from the appearance and microstructure of the particles, which provide clues to the manner of their formation. Spherical particles usually result from uniform growth of polymer, especially if it is fairly plastic under the conditions of polymerization. Irregular or protuberant particles may arise from processes of aggregation, or by growth from isolated points in a very rigid polymer matrix.

2.5 Particle Growth in Dispersion polymerization

2.5.1 The Mode of Polymerization

It has been a marked feature of dispersion polymerization in organic media that essentially no new polymer nuclei are formed after the initial precipitation of polymer particles. Following the nucleation stage, subsequent polymerization is confined to further growth of polymer particles formed initially. Three basic polymerization mechanisms have been considered as consistent this observation: [13]

1) Polymerization in solution, followed by precipitation onto the existing polymerization particles;
2) Polymerization in monomer adsorbed at the surface of the polymer particles;
3) Polymerization of monomer absorbed into the interior of the polymer particles.

All of the evidence from diagnostic tests for the mechanism of dispersion polymerization indicates that mechanism 3 is the predominant mode of polymerization, although mechanism 1 appears to operate in the dispersion polymerization of vinyl chloride under certain conditions.

The strongest evidence for the polymerization of absorbed monomer within the polymer particles has come from the direct determination of the degree of swelling of preformed polymer particles dispersed in aliphatic hydrocarbons containing monomer under conditions representative of those in an actual dispersion polymerization. Such studies have shown that methyl methacrylate, at moderate concentrations, distributes itself between poly(methyl methacrylate) particles and aliphatic hydrocarbon diluents in approximately equal concentrations. A value near unity for the partition coefficient was also derived from the kinetic data. Similar values have also been reported from determinations on related systems. With vinyl acetate, the partition is somewhat more in favor of the polymer phase (about 2:1) and similar results have been obtained with other monomers. As far as the experimental data go, the distribution of monomer is independent of particle size as predicted by polymer solution theory. In fact, similar values are obtained using polymer in bulk form, providing sufficient time is allowed for equilibration. The levels of monomer absorption determined in this systems where the monomer is freely soluble in continuous phase, is much less than found in monomer-swollen particles undergoing aqueous emulsion polymerization. In the latter case, the monomer concentration can be as high as 60-70% by volume in the polymer particles when the aqueous phase is saturated with monomer of low solubility in water.

Supporting evidence for the interior of particles as the main site of polymerization has also emerged from the kinetic studies. For example, the rate of dispersion polymerization is essentially independent of both particle size and the amount of polymeric dispersant used (which controls particle size) over the range in which the polymer particles are fully stable to flocculation. This could hardly be the case if polymerization took place on the surface of the particles. In addition, the rate of dispersion polymerization accelerates rapidly as more polymer is formed. The extent of the acceleration runs closely parallel with the extent of acceleration in the corresponding bulk polymerization of monomer at high conversion (i.e. polymer swollen with monomer).

2.5.2 The Kinetic Model

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. The high viscosity of monomer-swollen polymer particle greatly hinders radical termination processes and the resulting increase in radical concentration due to the gel effect accelerates the rate of polymerization. The reduction in termination rate also allows the coexistence of many radicals within a single polymer particle. Any polymer radicals initiated in the diluent phase are rapidly swept up by existing particles before they have time to grow to more than a very few monomer units in length. Consequently, initiation can be considered as taking place as through all the initiator were confined within the particles, even though the types of initiator used are known to be distributed between the polymer particles and the diluent [15].

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

$$R_{ip} = R_i / V \tag{2.1}$$

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

$$R_{pp} = c_{mp} k_p (R_{ip} / k_t)^{1/2} \tag{2.2}$$

$$= c_{mp} k_p (R_i / k_t V)^{1/2} \tag{2.3}$$

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

$$R_p = V R_{pp} \tag{2.4}$$

$$= c_{mp} k_p (V R_i / k_t)^{1/2} \tag{2.5}$$

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 depend 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

$$R_p = \alpha\, c_{md} k_p (V R_i / k_t)^{1/2} \tag{2.6}$$

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 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 of importance 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 The Terminology of Dispersion Polymerization

The development of dispersion polymerization has utilized a blend of the disciplines of both polymer science and colloid science. Consequently, some of the terminology used for its description may be unfamiliar to some readers.

The term "polymer colloids" is now frequently used to describe polymer dispersions of colloidal dimensions, that is, in the size range of 0.01 to 10 μm in any medium. Colloidal dispersions in organic diluents are often called "organosols" with a corresponding term "hydrosols" for similar dispersions of particles in water. The term NAD (non-aqueous dispersions) is also frequency used in the literature on surface coatings to describe paint compositions which are based on polymer dispersions prepared in aliphatic hydrocarbons and similar diluents [16].

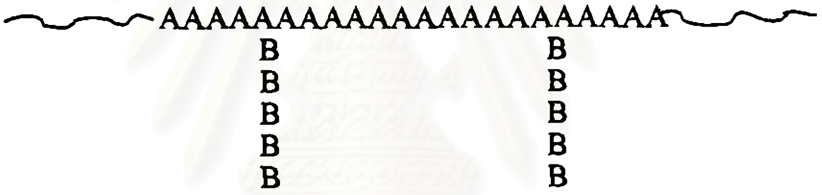
The terms "stabilizers" and " stabilization", which are used in this work, imply the use of a method for producing polymer dispersions which are stable towards aggregation processes. This is achieved in practice by the use of suitable amphipathic graft-copolymer dispersants, commonly called "stabilizers" in dispersion polymerization. However, in this system, dispersants will form a space or matrix between polymer dispersions that act as a skeleton for particle growth and preventing particle contact. In this way, dispersant is called the matrix polymer [17].

In describing the structures of various copolymers used in dispersion polymerization, the usual terminology is followed [18].

The random copolymers are derived from two monomer units, A and B, which are distributed randomly, as represented by

The random copolymer are indicated by the prefix, -co-, as in poly(methyl methacrylate-co-styrene).

The graft copolymer is a branched copolymer with a backbone of one monomer to which are attached one or more side chains of another monomer, as represented by



The graft copolymer is indicated by the prefix, -g-, as in poly(methyl methacrylate-g-styrene)

In an unstable dispersion, the primary colloidal particles rapidly form loose clusters, usually known as “flocs”, which can associate further to form loosely-bound aggregates. The term “agglomerate” is sometimes used to denote more tightly-bound clusters of particles. However, in this work, the terms such as “flocculation”, “aggregation” and “coagulation” are used synonymously to describe such process unless reference is made to the detailed structure of the particular type of aggregate formed.

2.7 Literature Review

Barrett [19] has thoroughly described the dispersion polymerization method, the alternative route for the direct preparation of polymer dispersions of controlled particle size in organic media, this process involved the polymerization of a monomer dissolved in an organic liquid to produce insoluble polymer dispersed in the continuous phase, and included the use of polymeric dispersant instead of the charged surfactant that are present in an emulsion polymerization. The reaction medium must be selected not only because it is a non-solvent for the newly formed polymer but also because of its miscibility with the original monomer and its solubility properties for the dispersant. In this work, he also reviewed the general features of the process and the method used for stabilizing the polymer dispersion.

The kinetics of free-radical-initiated dispersion polymerization of MMA in *n*-dodecan were studied by Barrett [15]. The mode of polymerization was described in terms of a bulk polymerization within the monomer swollen particles. It was noted that all radicals produced in the diluent phase are transferred immediately to the polymer particles, monomer swells the polymer particles in partition equilibrium with monomer in the diluent, and polymerization proceeds within the polymer particle according to the kinetics of bulk polymerization, taking into account of Trommsdorff acceleration and plasticization effects.

Almog et al. [20] prepared both monosized polystyrene and poly(methyl methacrylate) particles as large as 6 μm by dispersion polymerization, using quaternary ammonium salt surfactants in conjunction with a polymeric steric stabilizer. The size was shown to be dependent on the polarity of the reaction medium and correlated well with the solubility parameters of the reagents.

Tseng et al. [21] succeeded in preparing uniform polystyrene particles in the size range of 1-10 μm by dispersion polymerization in ethyl alcohol with azo-type initiators and PVP stabilizer along with an anionic, nonionic or comonomeric co-stabilizer. The use of PVP in combination with co-stabilizers resulted in a stable dispersion with a narrow particle size distribution. Without co-stabilizer, dispersion with a broad particle size distribution was obtained. In their studies, functional groups such as hydroxyl, carboxyl, amine, amide, silane, polydimethylsiloxane, and silacrown have been successfully incorporated onto the particles by copolymerization. In addition, they also presented a mechanism for particle formation and growth in dispersion polymerization.

Ober et al. [2,22] produced micrometer-sized polystyrene particles up to 12 µm using hydroxypropylcellulose as a stabilizer in ethanol. They found that the stabilizer concentration had little effect on particle size or polydispersity. They also examined the effect of using different alcohols as the dispersion medium. Particle size increased from methanol to ethanol to 2-methyl-2-propoanol, and for polymerization in 2-methyl-2-propanol the particle size distribution was much wider. The effect of temperature and initiator levels was also investigated [23]. It was shown that the monodispersity can be achieved over a considerable range of temperatures provides that a particular level of initiator is used at a given concentration.

Williamsom and co-workers [24] investigated the dispersion polymerization of MMA using mixture of carbon tetrachloride and 2,2,4-trimethylpentane as the medium and polyisobutylene as the stabilizer. They suggested that the locus of the particle polymerization changes as the solvency of the dispersion medium for the resulting polymer is varied with a concomitant change in the size of the final particle.

Paine et al. [25] studied the effect of reaction parameters on particle size and molecular weight of polystyrene in alcoholic media in the presence of poly(*N*-vinylpyrrolidone) as a steric stabilizer. They produced monodisperse particles in the size range of 1-18 µm. Smaller particles were obtained at higher stabilizer concentrations and molecular weights and decreasing initiator concentrations. An inverse correlation between particle size and polymer molecular weight was reported, with the smallest particles having the highest molecular weights. They also proposed a simple mathematical model to predict the particle size in dispersion polymerization of styrene in polar solvent [26].

Similar studies were reported by Shen at el. [27] for the dispersion polymerization of MMA in alcoholic media using PVP as a stabilizer. They prepared PMMA particles ranging in diameter from 2 μm to 10 μm. Particle size was found to increase with increasing polymerization temperature, initiator concentration, and solvency of the dispersion medium. Smaller particles were also favored at increased stabilizer concentrations and molecular weights.

Shen et al. [28] also proposed the mechanism for the formation of micron-sized polymer particles in the dispersion polymerization of MMA by applying dynamic light scattering to monitor the evolution of the average particle size in the early stages of the polymerization. They described the coexistence of the adsorption of PVP and its graft copolymer in dispersion polymerizations based on the measurement of the amount of physically adsorbed PVP, IR examination of the "bound" graft copolymer, and these two effects were regarded as complementary rather than mutually exclusive.

Ho et al. [29] studied the effect of reaction parameters i.e. initiator concentration, type of solvent on dispersion polymerization of styrene. The results suggest the existence of two different kinetic regions: one at low conversions, where the reaction takes place primarily in the solution phase, and one at high conversions, where the reaction takes place primarily in the particle phase. It is also found that the rate of polymerization increases with the initiator concentration at 0% conversion level and becomes independent of it at higher monomer conversions. Significantly, the rate is also increased with solvent polarity.

Ober et al. [30] produced monodisperse copolymer particles consisting of styrene and *n*-butyl methacrylate in ethanol-water media. The resulting particles were 1-10 μm in the size range. It was observed that narrow size distributions could be obtained in all cases with essentially incoporation of the monomer at the feed composition. The polarity of the starting mixture as calculated from the solubility of the individual component was found to have significant effect on final particle size. The more polar the reaction mixture, the smaller the final particles. Changes in the polarity of the reaction medium with conversion of monomer to polymer was observed to broaden the particle size distribution.

Horak et al. [31] studied the dispersion copolymerization of styrene and butyl methacrylate in ethanol/water medium. It was shown that increasing concentration of monomers or increasing the relative percentage of butyl methacrylate in the mixture both lead to an increase in particle size. The nature of the stabilizer was found to have only a minor effect on particle size and distribution. Under the same condition, poly(*N*-vinylpyrrolidone), poly(acrylic acid) and hydroxypropyl cellulose yields beads of similar size and distribution. A novel stabilizing systems based on mixtures of stabilizers can be used to control the surface charging on the beads. Replacing benzoyl peroxide with azo-bisisobutyronitrile requires a concomitant reduction in initiator concentration from 4.1 to 1 wt %.

Apiwattananon [17] prepared the super-fine particles of poly(styrene-co-methyl methacrylate) up to 5 μm by a dispersion polymerization in the mixed solvent of ethanol/n-hexane where poly(methyl vinyl ether) was used as a polymer matrix. Solubility of the polymer matrix containing a good solvent is the main factor controlling the morphology of PMVE and providing different free volumes of the polymerizing system that leads to different particle sizes.

Recently, Kiatkamjornwong et al. [32] produced poly(styrene-co-methyl methacrylate) particles in the size range of 0.3-1.5 μm. The reaction was carried out in ethanol/water media in the presence of azo-bisisobutyronitrile initiator and PVP dispersant. When the systems were polymerized without PVP, the copolymers were aggregated and formed in lumps. A narrow size distribution was obtained in a mixture containing 10-30 parts of water. Influence of various reaction parameters on particle size and distribution were studied. They also elucidated the techniques for copolymer formation by theories of the solubility parameter, and dispersant anchoring.