

INTRODUCTION

Emulsion polymerization involves the reaction of free radicals with relatively hydrophobic monomer molecules within submicron polymer particles dispersed in a continuous aqueous phase. Nevertheless, this unique polymerization process that is heterogeneous in nature exhibits very different reaction mechanisms and kinetics compared to bulk or solution free radical polymerization. Surfactant is generally required to stabilize the colloidal system; otherwise, latex particles nucleated during the early stage of polymerization may experience significant coagulation in order to reduce the interfacial free energy. This feature may also come into play in determining the number of reaction loci (i.e., polymer particles) available for the consumption of monomer therein. The objective of this chapter is therefore to provide readers with an overview of those subjects such as the free radical polymerization mechanisms and kinetics, the general features of emulsion polymerization, the role of surfactants in emulsion polymerization, and the importance of colloidal stability that is sometimes ignored in this research area.

1.1 FREE RADICAL POLYMERIZATION

1.1.1 Free Radical Polymerization Mechanisms

Free radical polymerization of vinyl monomers containing carbon–carbon double bonds has been widely used in industry to manufacture a variety of polymeric materials such as low-density polyethylene, polystyrene, polyvinyl

chloride, polyvinyl acetate, acrylic polymers, and synthetic rubbers, which can be accomplished in bulk, solution, suspension, or emulsion processes. The generally accepted free radical polymerization mechanism involves three kinetic steps in sequence, namely, initiation, propagation, and termination [1, 2].

Initiation



Propagation



Termination



where I , R^* , M , P_n^* ($n = 1, 2, 3, \dots$), and P_n represent the initiator, initiator radical, monomer, free radicals with n monomeric units, and dead polymer chains with n monomeric units, respectively. The kinetic parameters k_d , k_i , k_p , k_{tc} , and k_{td} are the thermal decomposition rate constant for the initiator, the initiation rate constant for the primary radical, the propagation rate constant for the reaction between one free radical with n monomeric units and one monomer molecule, the combination termination rate constant, and the disproportionation termination rate constant for the reaction between two free radicals, respectively.

The above three-reaction mechanism reflects its characteristic chain addition polymerization; the rate of consumption of monomer is relatively slow, but the molecular weight of polymer builds up rapidly, as shown schematically in Figure 1.1.

Chain transfer reactions are also a part of the free radical reaction system. These reactions, as the name implies, transfer the radical activity from a growing chain to another species such as monomer, polymer, initiator, solvent, or a deliberately added chain transfer agent. For example, chain transfer of a propagating radical to monomer or polymer can be represented as follows:



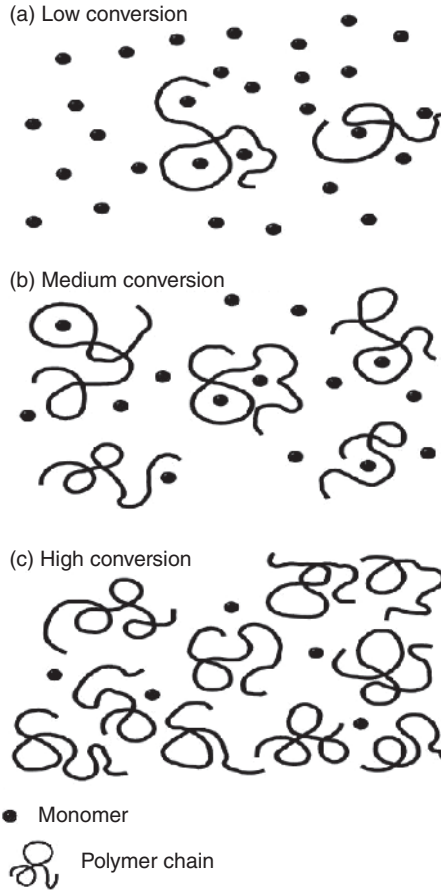


Figure 1.1. A schematic model for free radical polymerization at different levels of monomer conversion.

where $k_{tr,m}$ and $k_{tr,p}$ are the rate constants for the chain transfer reaction of a propagating radical with monomer and polymer, respectively. Both P_1^* and P_m^* may reinitiate the free radical chain polymerization to form linear and branched polymer chains, respectively, or participate in the termination reactions.

1.1.2 Free Radical Polymerization Kinetics

Assuming that the concentration of free radicals remains relatively constant during polymerization (the pseudo-steady-state assumption), the rate of polymerization (R_p) for bulk or solution polymerization can be expressed as

$$R_p = k_p[M](fk_d[I]/k_t)^{1/2} \quad (1.10)$$

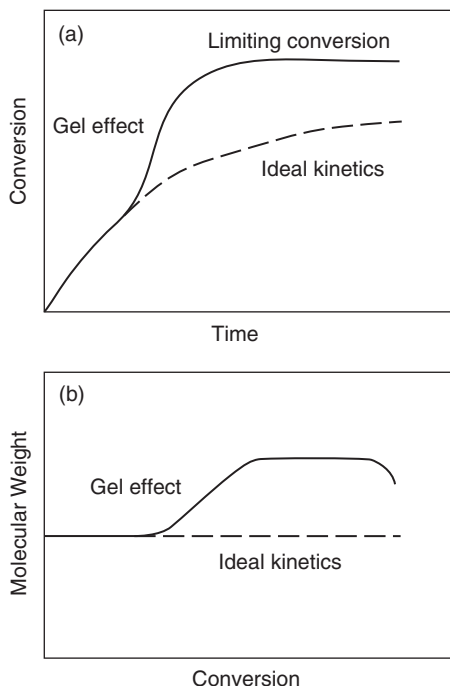


Figure 1.2. (a) Monomer conversion as a function of time. (b) Weight-average molecular weight as a function of conversion for free radical polymerization.

where f is the initiator efficiency factor and $[M]$ and $[I]$ are the concentrations of monomer and initiator, respectively. It should be noted that the term $(fk_d[I]/k_t)^{1/2}$ represents the concentration of free radicals. At low monomer conversions, the rate of polymerization can be adequately predicted by Eq. (1.10). The conversion first increases and then gradually levels off with the progress of polymerization (Figure 1.2). However, for many free radical reactions, after a certain conversion, the termination rate constant (k_t) becomes chain length dependent due to the influence of diffusion of free radicals on the bimolecular termination reaction. Under these circumstances, k_t decreases significantly with increasing conversion, thereby leading to the severely retarded bimolecular termination reaction and then autoacceleration of the polymerization rate. This is termed the gel effect or Trommsdorff effect [3–6]. In general, k_p is relatively independent of the chain length of P_n^* because the rather mobile monomer predominates in the propagation reaction. Nevertheless, when the reaction temperature is below the T_g of the polymerizing medium, the propagation reaction may also become diffusion-controlled at very high conversions. Thus, k_p decreases continuously toward the end of polymerization and complete conversion cannot be achieved (termed the limiting conversion) [5, 6]. Mechanistic models based on the concept of free volume adequately describe

the key features of the diffusion-controlled polymer reactions [3–6]. These peculiar kinetic phenomena are shown in Figure 1.2a.

The kinetic chain length (ν) can be calculated according to the following equation:

$$\nu = k_p[M]/[2(fk_dk_t[I])^{1/2}] \quad (1.11)$$

It should be noted that ν is inversely proportional to $[I]^{1/2}$, and thus any attempt to increase the rate of polymerization (i.e., to shorten the batch cycle time) by increasing the concentration of initiator inevitably results in polymer with a shorter chain length. Equation (1.11) predicts that molecular weight will change with the ratio $[M]/[I]^{1/2}$ during the course of the reaction if the rate constants are indeed constant. By contrast, molecular weight is strongly dependent on conversion due to the diffusion-controlled polymer reactions (Figure 1.2b).

1.2 EMULSION POLYMERIZATION

1.2.1 Conventional Emulsion Polymerization

Emulsion polymerization, which is a heterogeneous free radical polymerization process, involves emulsification of the relatively hydrophobic monomer in water by an oil-in-water emulsifier, followed by the initiation reaction with either a water-soluble initiator (e.g., sodium persulfate (NaPS)) or an oil-soluble initiator (e.g., 2,2'-azobisisobutyronitrile (AIBN)) [7–15]. This polymerization process was first commercialized in the early 1930s, and since then it has been widely used to produce environmentally friendly latex products with a variety of colloidal and physicochemical properties. If desired, these water-based polymer dispersions can be readily converted into bulk resins. Some representative monomers used to synthesize emulsion polymers include ethylene, butadiene, styrene, acrylonitrile, acrylate ester and methacrylate ester monomers, vinyl acetate, and vinyl chloride. Because the compatibility between the polymer produced and water is very poor, an exceedingly large oil–water interfacial area is generated as the particle nuclei form and grow in size with the progress of the polymerization. Thus, effective stabilizers such as ionic surfactants, nonionic surfactants, or protective colloids (e.g., hydroxyethyl cellulose, polyvinyl alcohol, polyvinyl pyrrolidone and dextrin), which can be physically adsorbed or chemically incorporated onto the particle surface, are generally required to prevent the interactive latex particles from coagulation. Satisfactory colloidal stability can be achieved via the electrostatic stabilization mechanism [16], the steric stabilization mechanism [17, 18], or both. Latex products comprise a very large population of polymer particles ($\sim 10^1$ – 10^3 nm in diameter) dispersed in the continuous aqueous phase. Although the performance properties of most of the water-based polymers are often inferior to

their solvent-based counterparts, there has been an even stronger demand for these environmentally friendly products in recent years. The continuously increased pressure for environmental protection and a hike in crude oil price are the primary factors responsible for this constant trend. The major competitive technologies in the marketplace include high-solids solvent-based polymers, UV coatings, and powder coatings.

To gain an insight into emulsion polymerization mechanisms and kinetics is a must in the development of quality products that fulfill customers' requirements. Unfortunately, this heterogeneous polymerization system is a very complex process because nucleation, growth, and stabilization of polymer particles are controlled by the above-mentioned free radical polymerization mechanisms along with several colloidal phenomena. There is no doubt that the most striking feature of emulsion polymerization is the segregation of free radicals among the discrete monomer-swollen polymer particles during the reaction. This unique behavior greatly reduces the probability of bimolecular termination of free radicals, thereby resulting in a faster polymerization rate and, in the absence of significant chain transfer reactions, producing a polymer with a higher molecular weight. This advantageous characteristic of emulsion polymerization cannot be achieved simultaneously in bulk or solution polymerization (see Section 1.1). Although the particle nucleation period is relatively short, formation of particle embryos during the early stage of polymerization plays an important role in determining the final latex particle size and particle size distribution, and it also affects quality control and application properties (e.g., colloidal stability, rheology, and film formation) of latex products. How to effectively control the particle nucleation process then represents a very challenging task to those who are involved in this fascinating research area. Beyond the particle nucleation stage, transport of monomer molecules, free radicals, and stabilizer molecules to the growing particles and partition of these reagents among the continuous aqueous phase, emulsified monomer droplets (monomer reservoir), monomer-swollen polymer particles (primary reaction loci), and oil-water interface are the key factors that govern the particle growth stage. The colloidal properties of latex products are of great importance from both academic and industrial points of view. Some representative properties include the particle size and particle size distribution, particle surface charge density (or zeta potential), particle surface area covered by one stabilizer molecule, conformation of the hydrophilic polymer physically adsorbed or chemically coupled onto the particle surface, type and concentration of functional groups on the particle surface, particle morphology, optical and rheological properties, and colloidal stability. Table 1.1 summarizes the primary characteristics of bulk free radical polymerization and emulsion polymerization.

1.2.2 Emulsion Polymerization Processes

Three types of reactors that are used to produce latex products and will be briefly discussed here are the batch reactor, semibatch reactor, and continuous

Table 1.1. Primary Characteristics of Bulk Free Radical Polymerization and Emulsion Polymerization

Parameter	Bulk Polymerization	Emulsion Polymerization
Reaction system	Homogeneous	Heterogeneous
R_p /MW ^a	Slow/high or fast/low	Fast/high
Temperature control	Poor	Good
Viscosity of medium	High	Low

^a R_p and MW are the rate of polymerization and molecular weight of polymer, respectively.

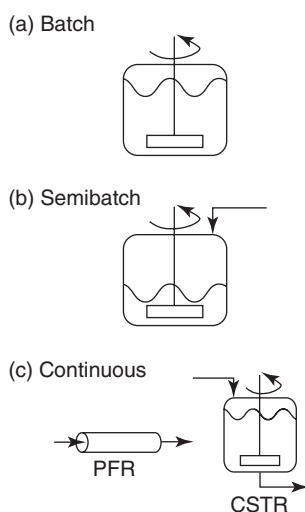


Figure 1.3. Three types of reactors commonly used to produce latex products: **(a)** batch reactor, **(b)** semibatch reactor, and **(c)** continuous reactor.

reactor (Figure 1.3). The reader is referred to an excellent book dealing with these three polymerization systems [19]. Batch emulsion polymerization is generally used in the laboratory to study reaction mechanisms, develop new latex products, and obtain kinetic data for process development and reactor scale-up. To the best of the author's knowledge, only very few latex products are manufactured in large-scale batch polymerization systems. As expected, severe problem in controlling the reaction temperature is often experienced because free radical polymerization is highly exothermic in nature and the heat transfer capacity is rather limited due to the very small surface-to-volume ratio of large-scale batch reactors. Most of the commercial latex products are thus produced by semibatch or continuous reaction systems. Continuous reaction systems include plug flow reactors (PFR), continuous stirred tank reactor trains (CSTR) and any combinations of PFR and CSTR. One major difference among the above polymerization processes is the residence time distribution

of the growing particles within the reactor system. The broadness of residence time distribution in decreasing order is a single CSTR > semibatch > batch. As a result, the broadness of the resultant particle size distribution in decreasing order is single CSTR > semibatch > batch. It should be noted that PFR behaves much like the batch reactor in terms of residence time distribution, provided that the length of PFR is long enough. Nevertheless, the very different fluid dynamics patterns observed in the PFR and batch reactor may have an influence on the properties of latex products to some extent. The rate of polymerization generally follows the following trend: batch > semibatch > CSTR. In addition, the versatile semibatch and continuous emulsion polymerization systems offer the operational flexibility to prepare latex products with controlled particle size distribution, polymer composition, and particle morphology. This may serve as an effective tool for chemists to design specialty emulsion polymers exhibiting performance properties that meet the sometimes contradictory requirements of customers. For the continuous emulsion polymerization systems that are only suitable for large-volume latex products, more efforts should be devoted to the development and understanding of different reactor designs and operating procedures, especially related to characteristics of latex products and start-up and product changeover strategies. Only a small number of professional journal papers dealing with these two important industrial processes are available in the open literature. More research efforts are required to further advance the semibatch and continuous emulsion polymerization technology. For those who are interested in the previous studies on semibatch and continuous emulsion polymerizations, refer to those cited in the review articles [20–25].

1.2.3 Miniemulsion Polymerization

Miniemulsion, microemulsion, and classical emulsion polymerizations show quite different particle nucleation and growth mechanisms and kinetics. This is primarily attributed to the different initial conditions (i.e., the conditions immediately before the start of polymerization) that have a profound influence on the subsequent particle nucleation and growth mechanisms. In the conventional emulsion polymerization, the most widely accepted particle nucleation mechanisms include micellar nucleation [26–31] and homogeneous nucleation [32–36]. Emulsified monomer droplets (>10 μm in diameter) generally do not contribute to particle nucleation to any appreciable extent due to their very small droplet surface area (Figure 1.4a). However, after intensive homogenization, submicron monomer droplets containing a hydrophobic, low-molecular-weight compound [e.g., hexadecane (HD) or cetyl alcohol (CA)] may become the predominant particle nucleation loci if the total monomer droplet surface area becomes large enough to compete effectively with the continuous aqueous phase, in which particle nuclei are generated to capture radicals (i.e., monomer droplet nucleation). The hydrophobic, low-molecular-weight species is used as a costabilizer to impart the osmotic pressure effect

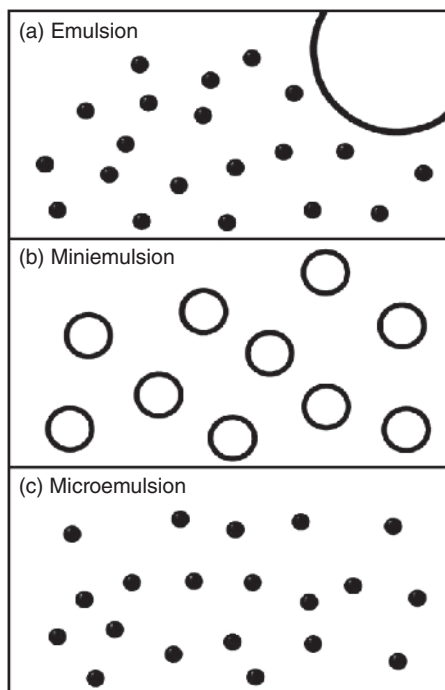


Figure 1.4. Initial conditions for (a) the conventional emulsion polymerization, (b) miniemulsion polymerization with the surfactant concentration lower than its critical micelle concentration, and (c) microemulsion polymerization. \circ ($>10^4$ nm in diameter for the conventional emulsion polymerization and $<10^3$ nm in diameter for miniemulsion polymerization) and \bullet ($\sim 10^0$ nm in diameter) represent emulsified monomer droplets and monomer-swollen micelles, respectively.

to the emulsion system to retard the diffusion of monomer molecules from smaller droplets to larger ones (i.e., the degradation of monomer droplets or Ostwald ripening effect). As a result, kinetically stable miniemulsion droplets are produced for the subsequent free radical polymerization (Figure 1.4b). This unique technique has been termed the miniemulsion polymerization [37–42], and new industrial applications based on miniemulsion polymerization have been continuously developed. One major potential advantage of miniemulsion polymerization is the ability to utilize highly water-insoluble monomers and other reagents because with droplet polymerization those ingredients do not need to be transported through the aqueous phase.

1.2.4 Microemulsion Polymerization

Unlike the conventional milky white emulsion, the transparent or translucent reaction system comprising microemulsion droplets is thermodynamically

stable in nature, and these tiny droplets ($\sim 1\text{--}10\text{ nm}$ in diameter) have an extremely large oil–water interfacial area ($\sim 10^5\text{ m}^2\text{ dm}^{-3}$), as shown schematically in Figure 1.4c. An anionic surfactant (e.g., sodium dodecyl sulfate (SDS)) in combination with a cosurfactant (e.g., 1-pentanol) is the most popular stabilization package. Incorporation of amphiphatic 1-pentanol into the adsorbed layer of SDS around an oil droplet greatly reduces the electrostatic repulsion force between two anionic SDS molecules, minimizes the oil–water interfacial tension, and enhances the flexibility of interfacial membrane. All these synergistic factors promote the spontaneous formation of a transparent one-phase microemulsion. Relatively stable polymer particles ($\sim 10\text{ nm}$ in diameter) consisting of only a few polymer chains per particle are produced, and therefore the resultant polymer molecular weight is very high ($\sim 10^6\text{--}10^7\text{ g mol}^{-1}$) [43–47]. This cannot be achieved readily by the conventional emulsion polymerization or miniemulsion polymerization. In addition, the particle nucleation and growth mechanisms and kinetics associated with microemulsion polymerization are quite different from those of emulsion and miniemulsion polymerization systems. Research interests in such a polymerization technique have grown rapidly since the 1980s because of its potential applications in the preparation of fine latex particles, ultrahigh-molecular-weight water-soluble polymers (flocclants), novel porous materials, polymeric supports for binding metal ions, conducting polymers, colloidal particles containing various functional groups for the biomedical field, and transparent colloidal systems for photochemical and other chemical reactions [45].

In summary, there has been a tremendous effort devoted to the fundamental aspects of emulsion polymerization mechanisms, kinetics and processes since the early twentieth century. Representative review or journal articles concerning the conventional emulsion polymerization can be found in literature [20–25, 48–60]. The research areas related to both miniemulsion [42, 61–64] and microemulsion [44–47, 65] polymerizations have received increasing interest recently.

1.2.5 Inverse Emulsion Polymerization

Inversion emulsion polymerization involves the dispersion and then polymerization of hydrophilic monomers, normally in aqueous solution, in a nonaqueous continuous phase. The emulsifier systems primarily based on the steric stabilization mechanism (see Section 1.3.3) are quite different from those of the more conventional oil-in-water emulsion polymerization processes. This is simply because the electrostatic stabilization mechanism (see Section 1.3.2) is not effective in stabilizing inverse emulsion polymerization comprising an aqueous disperse phase and a nonaqueous continuous phase with a very low dielectric constant. The unique anionic surfactant bis(2-ethylhexyl) sulfosuccinate (trade name: Aerosol OT) that can be dissolved in both oil and water

has been widely used in the stabilization of inverse emulsion or microemulsion polymerization systems. Both oil-soluble and water-soluble initiators have been used to initiate the free radical chain polymerization in this water-in-oil type of colloidal systems.

The inverse emulsion polymerization mechanisms and kinetics can be found in the literature [10, 66–68]. The area of inverse emulsion polymerization has not been studied extensively, except perhaps for the inverse microemulsion polymerization of acrylamide. The most important applications for these acrylamide-based products are as polymeric flocculants in water treatment. The two major advantages of this polymerization process are the very high polymer molecular weight and a colloidal system that results in rapid dissolution of the polymer in water.

1.3 COLLOIDAL STABILITY

1.3.1 A Critical but Often Ignored Issue

The product obtained from (conventional) emulsion polymerization is a colloidal dispersion comprising a very large population of submicron hydrophobic polymer particles dispersed in the continuous aqueous phase. This colloidal system is not thermodynamically stable because of the incompatibility between polymer and water (i.e., the very low solubility of polymer in water) in nature. As a matter of fact, the fate of most common latex products is the coagulation of polymer particles in order to minimize the particle–water interfacial area. Moreover, the monomer-swollen particles may even lose their colloidal stability and flocculate with one another in the course of emulsion polymerization. This will inevitably make the particle nucleation and growth mechanisms more complicated.

The level of surfactant used in emulsion polymerization is generally kept at a minimum for the manufacture of polymeric materials with excellent water resistance and adhesion properties. However, polymer particles that are inadequately stabilized by stabilizers (anionic and nonionic surfactants and protective colloids) may lose their colloidal stability, and coagulation of these unstable particles occurs upon aging. This represents an extremely challenging task for those who deal with the surfactant-free emulsion polymerization technique. Therefore, the shelf life of latex products is an important issue for successful product development. Furthermore, intensive coagulation of the latex particles to form filterable solids and scraps adhering to the reactor wall and agitator could become a serious problem in plant production. This annoying production problem not only increases the cost significantly but also makes the task of quality control much more difficult. Thus, the colloidal stability issue that has sometimes been ignored must be addressed from both the theoretical and practical points of view.

1.3.2 Electrostatic Interactions

Adequate colloidal stability of the emulsion polymerization system can be achieved by the adsorption of surfactants and protective colloids onto the growing polymer particle surfaces with the progress of polymerization. For example, the interactions between two negatively charged colloidal particles originating from anionic surfactant molecules adsorbed on their particle surfaces can be described schematically in Figure 1.5 [16, 69]. The total potential energy of interaction is the resultant of the competitive van der Waals attraction force and electrostatic repulsion force between the two adjacent particles. The driving force for coagulation of colloidal particles to take place is van der Waals attraction force. The positive and negative signs of the total potential energy of interaction represent the net repulsive interaction and the net attractive interaction between two particles, respectively.

The total potential energy of interaction approaches zero, and this implies that the interactions are insignificant when the distance of separation between two particles is very large, as shown in Figure 1.5. As the distance of separation decreases, the attractive van der Waals force tends to pull the two particles together. Further decreasing the distance of separation, the pair of particles

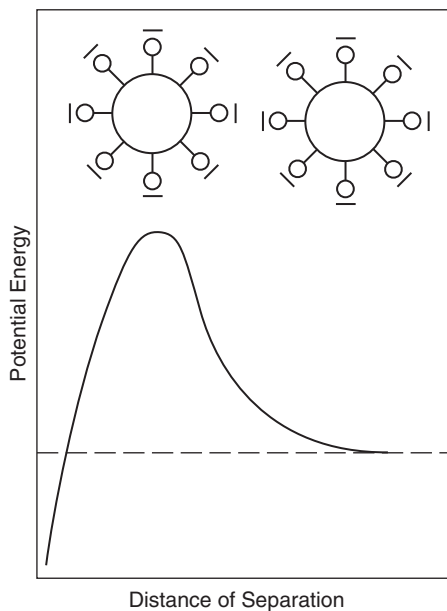


Figure 1.5. Interactions between two negatively charged colloidal particles. The abscissa and ordinate represent the distance of separation between two particles and potential energy barrier against coagulation as a result of the competitive van der Waals attraction force and electrostatic repulsion force between the two interactive particles.

starts to experience the electrostatic repulsion force to some extent. At close approach, the total potential energy barrier (if high enough) may oppose the continued approach of the interactive particles. The primary maximum observed in the total potential energy of interaction versus distance of separation curve represents an activation energy that must be overcome for coagulation to take place. It is dependent on the constituent materials in the disperse phase, the surface charge density (or zeta potential) of colloidal particles, the valency of counterions, and the concentration of electrolytes.

The DLVO theory predicts that decreasing the surface charge density, increasing the valency of counterions, and increasing the concentration of electrolytes tend to depress the primary maximum and thus reduce the colloidal stability [16, 69]. Another useful rule of thumb, the Shultz–Hardy rule, suggests that the critical coagulation concentration, defined as the concentration of counterions at which point visible aggregates start to form in the colloidal dispersion, is inversely proportional to the valency of counterions to the sixth power [70, 71]. This strongly suggests that the addition of counterions with a higher valency should be avoided during emulsion polymerization or in subsequent formulation work. On the other hand, a simple method based on the Shultz–Hardy rule can be developed to evaluate the effectiveness of the electrostatic stabilization of a particular colloidal dispersion.

1.3.3 Steric Interactions

In addition to the electrostatic stabilization mechanism, latex particles can be stabilized by adsorption of hydrophilic polymer chains on their particle surfaces. The physically adsorbed or chemically grafted polymer chains surrounding the colloidal particles and extending themselves into the continuous aqueous phase serve as a steric barrier against the close approach of the pair of particles. In this manner, coagulation of latex particles can be prevented via the steric stabilization mechanism [17, 18]. Typical nonionic surfactants and surface-active, nonionic block copolymers are quite effective in imparting such a steric stabilization effect to colloidal dispersions.

A schematic representation of the steric stabilization mechanism is shown in Figure 1.6. Considering the space of interaction between two hairy colloidal particles as the control volume, these particles are well separated and there is no overlap of adsorbed polymer layers initially (Figure 1.6a). In this case, the adsorbed polymer chain has the maximum number of conformations near the particle surface, and therefore the corresponding entropy is relatively large. Under these circumstances, no appreciable interactions between the pair of particles can be detected. However, at close approach, the concentration of polymer increases, and therefore the number of polymer chain conformations (i.e., entropy) decreases significantly due to the overlap of adsorbed polymer layers (Figure 1.6b). As a result, the change of entropy (i.e., the entropy of the final state (Figure 1.6b) minus that of the initial state

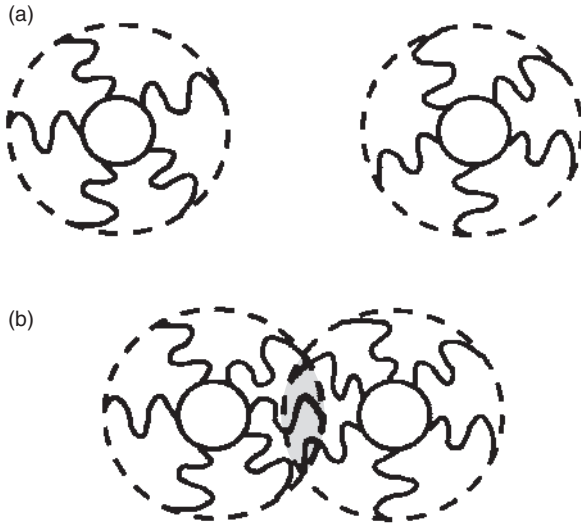


Figure 1.6. Interactions between two hairy colloidal particles: **(a)** Two particles with a relatively large distance of separation in the absence of overlap of adsorbed polymer layers and **(b)** two particles at close approach in the presence of overlap of adsorbed polymer layers.

(Figure 1.6a)) is negative. This implies that this process is not thermodynamically feasible, and repulsive steric interactions are established accordingly to pull the pair of particles apart. In general, the degree of steric interactions between two hairy particles is governed by the surface polymer concentration, the polymer chain length (or the adsorbed polymer layer thickness), and temperature. The primary features of models describing the steric stabilization mechanism include (a) a strong effect of temperature on the repulsive steric interactions, (b) a rapidly increased steric interactions with increasing polymer concentration in the adsorbed polymer layer, and (c) an increased steric interactions with decreasing distance of separation [17, 18, 70, 71]. The addition of a solvent or other ingredient that could cause polymer desorption from the particle surfaces could clearly destabilize a sterically stabilized system.

1.3.4 Mechanical Stability

The shear force used to provide the heterogeneous reaction system with efficient mixing and heat transfer also has an influence on the colloidal stability of latex particles during polymerization. The shear force is linearly proportional to the velocity gradient, the viscosity of the continuous phase, and the square of the colloidal particle size. This relationship can be used to determine

where the stability or instability boundaries are located for a particular colloidal dispersion (e.g., the mechanical stability map for a particular colloid dispersion as a function of shear rate and zeta potential) [70, 71]. It is also interesting to note that at constant velocity gradient and viscosity, the mechanical stability of larger colloidal particles is more sensitive to the hydrodynamic force than that of smaller particles.

The above discussion reflects an important fact that a variety of interfacial phenomena play important roles in heterogeneous reaction systems such as emulsion polymerization, but somehow this scientific discipline has not been studied as extensively of the reaction systems over the years. Therefore, the reader is encouraged to become familiar with the most basic concepts of colloid and interface science.

1.4 SOME PERFORMANCE PROPERTIES FOR INDUSTRIAL APPLICATIONS

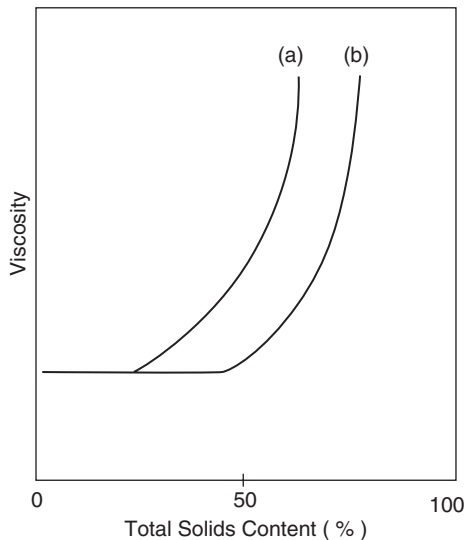
One distinct advantage of the emulsion polymerization technique is that latex products are often used directly without prior separation of polymer from water. For example, coatings formulated primarily with emulsion polymers are essential to the beauty and protection of many objects such as houses, furniture, leathern products, and packaging materials. The performance properties of emulsion polymers of major interest to this section include rheology and film formation related to the colloidal phenomena. These performance properties play a crucial role in determining the ultimate mechanical properties of the polymeric films.

1.4.1 Rheology

Rheology deals with the deformation or flow of materials subjected to forces [71, 72], and it has an influence on (a) mixing and heat transfer during emulsion polymerization, (b) transfer of latex products, (c) storage, handling, and mixing of emulsion polymers, cosolvents, and additives to manufacture water-based coatings, (d) application of the finished coatings products to a variety of substrates (e.g., brush coating, roll coating, and spray coating), and (e) film formation. For industrial coatings, satisfactory rheological properties are necessary to ensure the formation of polymeric films with excellent appearance and physical and chemical properties. The rheological characteristics of materials can be described by the dimensionless Deborah number De , defined as the ratio of the characteristic time τ to the experimental time t_{exp} . Table 1.2 summarizes the conditions corresponding to three types of rheological behavior. It should be noted that colloidal dispersions have De values close to unity, and therefore they can exhibit viscoelastic behavior.

Table 1.2. Ranges of Deborah Number Corresponding to Three Types of Rheological Behavior

De	Rheological Behavior	Examples
$\ll 1$	Liquid-like	Water
~ 1	Viscoelastic	Latex paints
$\gg 1$	Solid-like	Steel

**Figure 1.7.** Viscosity of the colloidal dispersion versus total solids content profiles with different particle sizes: **(a)** small particle size and **(b)** large particle size.

The viscosity of a colloidal dispersion is a rheological property that measures the resistance to flow in response to the applied shear force. It is dependent on the hydrodynamic interactions between the particles and the continuous aqueous phase and interparticle interactions. The viscosity increases exponentially with increasing total solids content of the emulsion polymer, as shown schematically in Figure 1.7. This general feature can be described by the Mooney equation [73]:

$$\eta = \eta_0 \exp \left\{ 2.5\phi / [1 - (\phi/\phi^*)] \right\} \quad (1.12)$$

where η and η_0 are the viscosity of the colloidal dispersion and the viscosity of the continuous aqueous phase, respectively. The parameters ϕ and ϕ^* represent the volume fraction of the colloidal particles and the critical volume fraction corresponding to infinite viscosity, respectively. For very dilute col-

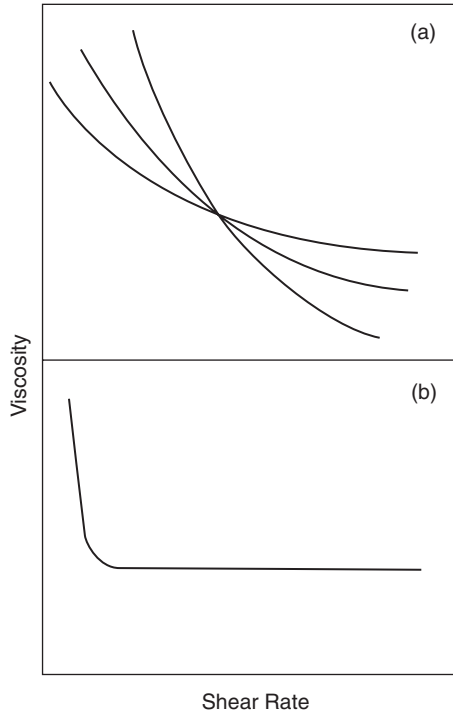


Figure 1.8. (a) Viscosity of the colloidal dispersion versus shear rate profiles that can be adjusted by a variety of rheology modifiers. (b) Viscosity versus shear rate curve for the rheology-controlled emulsion polymers.

colloidal dispersions, Eq. (1.12) can be reduced to the well-known Einstein equation:

$$\eta = \eta_0(1 + 2.5\phi) \quad (1.13)$$

The crowding effect is more pronounced for the dispersion with a smaller particle size (Figure 1.7a). At constant total solids content, the viscosity of the dispersion increases significantly with decreasing particle size. This is the major reason why it is very difficult to prepare latex products with high solids contents and small particle sizes simultaneously. High-solids-content latexes are often comprised of broad particle size distributions, including bimodal systems. In extreme cases, the numerous small particles act as part of the continuous phase for flow of the large particles. In addition, the viscosity of a colloidal dispersion decreases with increasing temperature.

Normally, emulsion polymers show a shear-thinning behavior; viscosity decreases with increasing shear rate (Figure 1.8a). Furthermore, the shape of

the viscosity versus shear rate curve can be adjusted by a variety of effective rheology modifiers to meet various application requirements of end-users. Typical rheology modifiers include cellulosic thickeners, alkali-soluble or -swellable thickeners, and advanced associative thickeners. It is also interesting to note that a Newtonian-like flow behavior illustrated in Figure 1.8b is observed for some latex products (e.g., a series of rheology-controlled emulsion polymers originally developed at S. C. Johnson Wax). The viscosity of this type of latex products first decreases rapidly and then levels off as the shear rate is increased.

1.4.2 Film Formation

After application, the liquid coating must be converted into a solid polymeric film (viscosity $> 10^6$ cps) in order to build up satisfactory performance properties (termed the film formation process) [74]. As water evaporates from a film of emulsion polymer, the distance of separation between the submicron particles continues to decrease and, ultimately, capillary tubes form. In a capillary tube, surface tension results in a force that tends to collapse the tube. Moreover, the smaller the diameter of the tube, the greater the destruction force. When the particles are so close to one another, the destruction force is strong enough to overcome the repulsion forces originating from either the electrostatic or steric interaction mechanism striving to push the neighboring particles apart. Coalescence of the particles to form a continuous film is thus possible.

To produce an integral film during the latter stage of the film formation process is primarily governed by the free volume of the coating materials. This is simply because polymer chains must be free to diffuse from particle to particle so that the individual particle boundaries disappear in the completely coalesced film. Above the glass transition temperature (T_g) of polymer, free volume increases (or viscosity decreases) significantly with increasing temperature. This then results in decreased viscosity and increased polymer chain mobility with temperature. In other words, the rate of coalescence is controlled by $T - T_g$, and it is much easier for film formation to occur when the temperature is much higher than the T_g . The following universal equation can be used to estimate the T_g required for a polymeric film to be “dry to touch” at a particular temperature T .

$$\ln \eta = 27.6 - \{40.2(T - T_g) / [51.6 + (T - T_g)]\} \quad (1.14)$$

For example, the T_g required for a polymeric film to be “dry to touch” (i.e., a solid-like film with $\eta = 10^6$ cps = 10^3 Pas) at 25°C is estimated to be -29°C [74]. However, a polymeric film with $T_g = -29^\circ\text{C}$ is kind of sticky,

and it is only useful in the area of adhesives. According to Eq. (1.14), satisfactory film formation apparently cannot be achieved for common latex paints with T_g in the range 0–30°C when applied at some temperature below 25°C. To resolve this problem, suitable coalescing solvents can be incorporated into the latex paint formulations to lower the minimum film formation temperature (MFFT). After the film formation process is completed, coalescing solvent molecules can migrate toward the coating surface layer and then evaporate.

It should be pointed out that satisfactory film formation is a prerequisite for the coating materials to fully exhibit their excellent mechanical properties. Finally, the mechanical properties (e.g., hardness, flexibility, impact resistance, solvent resistance, abrasion resistance, post-formability, and adhesion) of the polymeric film are closely related to the T_g , structure, molecular weight, and viscoelasticity of polymers.

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