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# PRINCIPLES OF POLYMERIZATION

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Fourth Edition

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## CHAPTER 4

# EMULSION POLYMERIZATION

*Emulsion* polymerization refers to a unique process employed for some radical chain polymerizations. It involves the polymerization of monomers in the form of emulsions (i.e., colloidal dispersions). The process bears a superficial resemblance to suspension polymerization (Sec. 3-13c) but is quite different in mechanism and reaction characteristics. Emulsion polymerization differs from suspension polymerization in the type and smaller size of the particles in which polymerization occurs, in the kind of initiator employed, and in the dependence of polymer molecular weight on reaction parameters.

### 4-1 DESCRIPTION OF PROCESS

#### 4-1a Utility

Emulsion polymerization was first employed during World War II for producing synthetic rubbers from 1,3-butadiene and styrene. This was the start of the synthetic rubber industry in the United States. It was a dramatic development because the Japanese naval forces threatened access to the southeast Asian natural-rubber (NR) sources, which were necessary for the war effort. Synthetic rubber has advanced significantly from the first days of "balloon" tires, which had a useful life of 5000 mi to present-day tires, which are good for 40,000 mi or more. Emulsion polymerization is presently the predominant process for the commercial polymerizations of vinyl acetate, chloroprene, various acrylate copolymerizations, and copolymerizations of butadiene with styrene and acrylonitrile. It is also used for methacrylates, vinyl chloride, acrylamide, and some fluorinated ethylenes.

The emulsion polymerization process has several distinct advantages. The physical state of the emulsion (colloidal) system makes it easy to control the process. Thermal and viscosity problems are much less significant than in bulk polymerization. The product of an emulsion polymerization, referred to as a *latex*, can in many instances be used directly without further separations. (However, there may be the need for appropriate blending operations, e.g., for the addition of pigments.) Such applications include paints, coating, finishes, and floor polishes. Aside from the physical difference between the emulsion and other polymerization processes, there is one very significant kinetic difference. For the other processes there is an inverse relationship (Eq. 3-97) between the polymerization rate and the polymer molecular weight. This drastically limits one's ability to make large changes in the molecular weight of a polymer, from 25,000 to 100,000 or from 100,000 to 25,000. Large decreases in the molecular weight of a polymer can be made without altering the polymerization rate by using chain-transfer agents. However, large increases in molecular weight can be made only by decreasing the polymerization rate by lowering the initiator concentration or lowering the reaction temperature. Emulsion polymerization is a unique process in that it affords the means of increasing the polymer molecular weight without decreasing the polymerization rate. Because of a different reaction mechanism, emulsion polymerization has the advantage of being able to simultaneously attain both high molecular weights and high reaction rates.

#### 4-1b Qualitative Picture

##### 4-1b-1 Components and Their Locations

The physical picture of emulsion polymerization is based on the original qualitative picture of Harkins [1947] and the quantitative treatment of Smith and Ewart [1948] with subsequent contributions by other workers [Blackley, 1975; Casey et al., 1990; Gao and Penlidis, 2002; Gardon, 1977; Gilbert, 1995, 2003; Hawket et al., 1977; Piirma, 1982; Poehlein, 1986; Ugelstad and Hansen, 1976]. Table 4-1 shows a typical recipe for an emulsion polymerization [Vandenberg and Hulse, 1948]. This formulation, one of the early ones employed for the production of styrene-1,3-butadiene rubber (trade name: *GR-S*), is typical of all emulsion polymerization systems. The main components are the monomer(s), *dispersing medium*, *emulsifier*, and water-soluble initiator. The dispersing medium is the liquid, usually water,

**TABLE 4-1 Composition of a GR-S Recipe for Emulsion Polymerization of Styrene-Butadiene<sup>a</sup>**

Component	Parts by Weight
Styrene	25
Butadiene	75
Water	180
Emulsifier (Dresinate 731)	5
<i>n</i> -Dodecyl mercaptan	0.5
NaOH	0.061
Cumene hydroperoxide	0.17
FeSO <sub>4</sub>	0.017
Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> · 10 H <sub>2</sub> O	1.5
Fructose	0.5

<sup>a</sup>Data from Vandenberg and Hulse [1948].

in which the various components are dispersed by means of the emulsifier. The ratio of water to monomer(s) is generally in the range 70/30 to 40/60 (by weight). The action of the emulsifier (also referred to as *surfactant* or *soap*) is due to its molecules having both hydrophilic and hydrophobic segments. Various other components may also be present in the emulsion system. Thus, a mercaptan is used in the above formulation as a chain-transfer agent to control the polymer molecular weight. The initiator is the hydroperoxide-ferrous ion redox system and the function of fructose is probably to regenerate ferrous ion by reducing the ferric ion produced in the initiation reaction (Eq. 3-36c). The sodium pyrophosphate acts to solubilize the iron salts in the strongly alkaline reaction medium. The emulsion system is usually kept in a well-agitated state during reaction.

The locations of the various components in an emulsion system will now be considered. When the concentration of a surfactant exceeds its *critical micelle concentration* (CMC), the excess surfactant molecules aggregate together to form small colloidal clusters referred to as *micelles*. The transformation of a solution to the colloidal state as the surfactant concentration exceeds the CMC occurs to minimize the free energy of solution (heat is liberated) and is accompanied by a sharp drop in the surface tension of the solution. Electrical conductivity, ion activities, viscosity, and other solution properties also show marked changes at CMC. CMC values are in the range  $0.001\text{--}0.1\text{ mol L}^{-1}$ , with most surfactants having values in the lower end of the range. Since surfactant concentrations in most emulsion polymerizations (0.1–3 wt% based on the aqueous phase) exceed CMC by one or more orders of magnitude, the bulk of the surfactant is in the micelles. Typical micelles have dimensions of 2–10 nm ( $1\text{ nm} = 10\text{ \AA} = 10^{-3}\text{ }\mu\text{m}$ ), with each micelle containing 50–150 surfactant molecules. Most authors show the shape of micelles as being spherical, but this is not always the case. Both spherical and rodlike micelles are observed depending on the surfactant and its concentration. The surfactant molecules are arranged in a micelle with their hydrocarbon portion pointed toward the interior of the micelle and their ionic ends outward toward the aqueous phase. The number of micelles and their size depends on the amount of emulsifier. Large amounts of emulsifier yield larger numbers of smaller-sized micelles.

When a water-insoluble or slightly water-soluble monomer is added, a very small fraction dissolves in the continuous aqueous phase. The water solubilities of most monomers are quite low, although the spread is large; for example, styrene, butadiene, vinyl chloride, methyl methacrylate, and vinyl acetate are soluble to the extent of 0.07, 0.8, 7, 16, and  $25\text{ g L}^{-1}$ , respectively, at  $25^\circ\text{C}$  [Gardon, 1977]. An additional but still small portion of the monomer enters the interior hydrocarbon portions of the micelles. This is evidenced by X-ray and light-scattering measurements showing that the micelles increase in size as monomer is added. The amount of monomer in micelles compared to that in solution is much greater for the water-insoluble, nonpolar monomers. For example, the amount of micellar monomer is 2-, 5-, and 40-fold larger for methyl methacrylate, butadiene, and styrene, respectively, than the amount in solution [Bovey et al., 1955]. For vinyl acetate, the amount of micellar monomer is only a few percent of that in solution [Dunn, 1985].

The largest portion of the monomer (>95%) is dispersed as *monomer droplets* whose size depends on the stirring rate. The monomer droplets are stabilized by surfactant molecules adsorbed on their surfaces. Monomer droplets have diameters in the range  $1\text{--}100\text{ }\mu\text{m}$  ( $10^3\text{--}10^5\text{ nm}$ ). Thus, in a typical emulsion polymerization system, the monomer droplets are much larger than the monomer-containing micelles. Consequently, while the concentration of micelles is  $10^{19}\text{--}10^{21}\text{ L}^{-1}$ , the concentration of monomer droplets is at most  $10^{12}\text{--}10^{14}\text{ L}^{-1}$ . A further difference between micelles and monomer droplets is that the total surface area of the micelles is larger than that of the droplets by more than two orders of magnitude. The size, shape, and concentration of each of the various types of particles in the

emulsion system are obtained from electron microscopy, light scattering, ultracentrifugation, photon correlation spectroscopy, and other techniques [Debye and Anacker, 1951; Kratochvil, 1964; Munro et al., 1979].

#### 4-1b-2 Site of Polymerization

The initiator is present in the water phase, and this is where the initiating radicals are produced. The rate of radical production  $R_i$  is typically of the order of  $10^{13}\text{ radicals L}^{-1}\text{ s}^{-1}$ . (The symbol  $p$  is often used instead of  $R_i$  in emulsion polymerization terminology.) The locus of polymerization is now of prime concern. The site of polymerization is not the monomer droplets since the initiators employed are insoluble in the organic monomer. Such initiators are referred to as *oil-insoluble initiators*. This situation distinguishes emulsion polymerization from suspension polymerization. Oil-soluble initiators are used in suspension polymerization and reaction occurs in the monomer droplets. The absence of polymerization in the monomer droplets in emulsion polymerization has been experimentally verified. If one halts an emulsion polymerization at an appropriate point before complete conversion is achieved, the monomer droplets can be separated and analyzed. An insignificant amount (approximately <0.1%) of polymer is found in the monomer droplets in such experiments. Polymerization takes place almost exclusively in the micelles. Monomer droplets do not compete effectively with micelles in capturing radicals produced in solution because of the much smaller total surface area of the droplets.

Polymerization of the monomer in solution undoubtedly takes place but does not contribute significantly, since the monomer concentration is low and propagating radicals would precipitate out of aqueous solution at very small (oligomeric) size. The micelles act as a meeting place for the organic (oil-soluble) monomer and the water-soluble initiator. The micelles are favored as the reaction site because of their high monomer concentration (similar to bulk monomer concentration) compared to the monomer in solution. As polymerization proceeds, the micelles grow by the addition of monomer from the aqueous solution whose concentration is replenished by dissolution of monomer from the monomer droplets. A simplified schematic representation of an emulsion polymerization system is shown in Fig. 4-1. The system consists of three types of particles: monomer droplets, inactive micelles in which

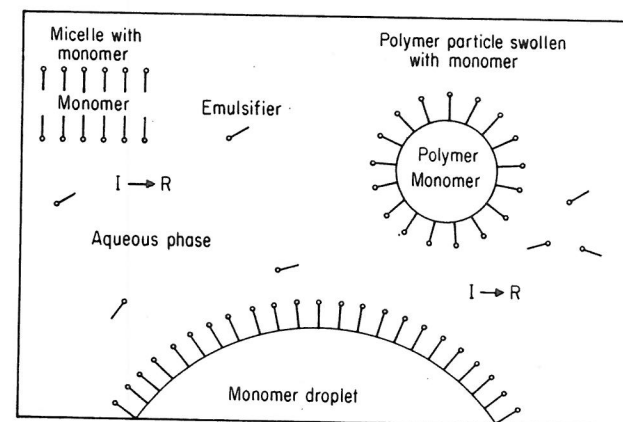


Fig. 4-1 Simplified representation of an emulsion polymerization system

polymerization is not occurring, and active micelles in which polymerization is occurring. The latter are no longer considered as micelles but are referred to as *polymer particles*. An emulsifier molecule is shown as  $\circ-$  to indicate one end ( $\circ$ ) is polar or ionic and the other end ( $-$ ) nonpolar.

Two mechanisms for *particle nucleation* (i.e., formation of polymer particles) have been discussed. The process described above, called *micellar particle nucleation*, occurs when radicals from the aqueous phase enter the micelles. (The term *heterogeneous particle nucleation* has been proposed as an alternative to the term *micellar particle nucleation*.) The radicals may be primary radicals or, much more likely, oligomeric radicals formed by solution polymerization with degrees of polymerization of  $\sim 2$ – $5$  [De Bruyn et al., 2002; Dong and Sundberg, 2002]. *Homogeneous particle nucleation* involves solution-polymerized oligomeric radicals becoming insoluble and precipitating onto themselves (or onto dead oligomer in solution) [Fitch et al., 1969; Hansen and Ugelstad, 1978]. The precipitated species become stabilized by absorbing surfactant (from solution, monomer droplets, and micelles) and on subsequent absorption of monomer are the equivalent of polymer particles formed by micellar nucleation. The relative extents of micellar and homogeneous nucleation are expected to vary with the surfactant concentration and the solubility of monomer in water. Micellar nucleation is the predominant nucleation process when the surfactant concentration is well above CMC. For styrene and methyl methacrylate, more than 99% of particle nucleation occurs by micellar nucleation [Herrera-Ordonez and Olayo, 2000, 2001; Saldivar et al., 1998]. Since MMA is much more water-soluble than styrene ( $16$  vs.  $0.07$  g L $^{-1}$ ), solubility in water is not important in determining the mechanism for nucleation well above CMC. Whether this is the case for vinyl acetate and other monomers more water-soluble than MMA is unclear. Around CMC, micellation nucleation is still the predominant mode of nucleation, but homogeneous nucleation is present—more for vinyl acetate and methyl methacrylate and less for styrene. The situation is much different for all monomers when the surfactant concentration is well below CMC. Micelles are absent below CMC and only homogeneous nucleation occurs. In fact, the occurrence of emulsion polymerization in the absence of micelles is evidence for the homogeneous nucleation mechanism.

It has been suggested that an important growth process for the first-formed polymer particles, sometimes called *precursor particles*, is coagulation with other particles and not polymerization of monomer. This coagulation, called *coagulative nucleation*, is then considered as part of the overall nucleation process for the formation of *mature* polymer particles whose subsequent growth occurs entirely by polymerization [Feeney et al., 1984]. Coagulative nucleation is probably important below CMC. The driving force for coagulation of precursor particles is their relative instability compared to larger particles, that is, there is insufficient surfactant to stabilize a larger number of smaller-sized particles. Once the particles reach a larger size, sufficiently large to be stabilized by the available surfactant, there is no longer a driving force for further coagulation and further growth occurs only by polymerization. Coagulative nucleation is much less important, if at all, above CMC since there is sufficient surfactant to stabilize smaller-sized particles.

#### 4-1b-3 Progress of Polymerization

A variety of behaviors are observed for the polymerization rate versus conversion depending on the relative rates of initiation, propagation, and termination, which are in turn dependent on the monomer and reaction conditions (Fig. 4-2). Irrespective of the particular behavior observed, three *intervals* (I, II, III) can be discerned in all emulsion polymerizations based on the *particle number*  $N$  (the concentration of polymer particles in units of number of

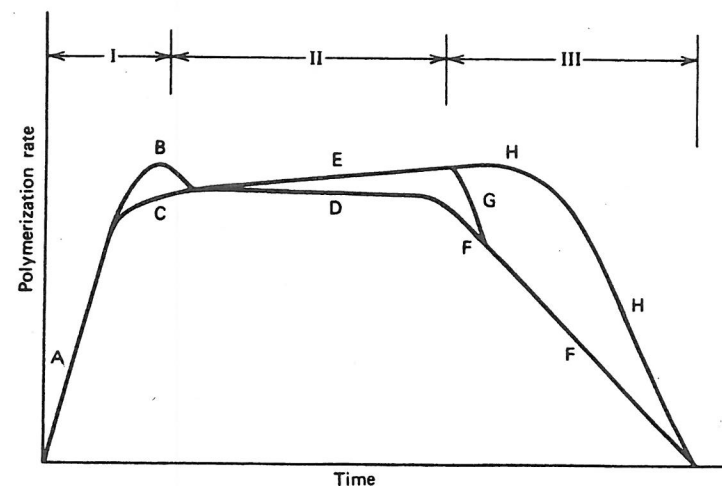


Fig. 4-2 Different rate behaviors observed in emulsion polymerization. After Gardon [1977] (by permission of Wiley-Interscience, New York).

particles per liter) and the existence of a separate monomer phase (i.e., monomer droplets). There is a separate monomer phase in intervals I and II but not in III. The particle number increases with time in interval I and then remains constant during intervals II and III. Particle nucleation occurs in interval I, with the polymerization rate increasing with time as the particle number builds up. Monomer diffuses into the polymer particles to replace that which has reacted. The reaction system undergoes a very significant change during interval I. The particle number stabilizes at some value which is only a small fraction, typically about 0.1%, of the concentration of micelles initially present.  $N$  is the range  $10^{16}$ – $10^{18}$  particles L $^{-1}$ . As the polymer particles grow in size and contain polymer as well as monomer, they absorb more and more surfactant (in order to maintain stability) from that in solution. The point is quickly reached at which the surfactant concentration in solution falls below its CMC, the inactive micelles become unstable and disappear with dissolution of micellar surfactant. By the end of interval I or very early in interval II all or almost all of the surfactant in the system has been absorbed by the polymer particles. As a consequence, the monomer droplets are relatively unstable and will coalesce if agitation is stopped. Interval I is generally the shortest of the three intervals, its duration varying in the range 2–15% conversion. Interval I is longer for low initiation rates as more time is needed to attain the steady-state particle number. The more water-soluble monomers such as vinyl acetate tend to complete interval I faster than do the less water-soluble monomers. This is probably a consequence of the significant extent of homogeneous nucleation occurring simultaneously with micellar nucleation, resulting in achieving the steady-state particle number sooner. The predicted maximum in Fig. 4-2 (curve AB), arising from a transient high particle number and/or high proportion of particles containing propagating radicals, is seldom distinguishable experimentally, since it is not a high maximum. The maximum is observed for many monomers when the initiation rates are sufficiently high.

Polymerization proceeds in the polymer particles as the monomer concentration in the particles is maintained at the equilibrium (saturation) level by diffusion of monomer from solution, which in turn is maintained at the saturation level by dissolution of monomer

from the monomer droplets. The monomer concentration in the polymer particles is high; the volume fraction of monomer  $\phi_m$  is 0.2, 0.3, 0.5, 0.6, 0.71, and 0.85 for ethylene, vinyl chloride, butadiene, styrene, methyl methacrylate, and vinyl acetate, respectively [Gardon, 1977]. The polymerization rate either is constant (behavior *D*) or increases slightly with time (*E*) during interval II. The latter behavior, which may begin immediately as shown in Fig. 4-2 or after a constant rate period, is a consequence of the gel or Trommsdorff effect (Sec. 3-10a). The polymer particles increase in size as the monomer droplets decrease. Interval II ends when the monomer droplets disappear. The transition from interval II to interval III occurs at lower conversions as the water solubility of the monomer increases and the extent of swelling of the polymer particles by monomer increases. For monomers (e.g., vinyl chloride) with low water solubility and low  $\phi_m$ , the transition occurs at about 70–80% conversion. The transition occurs at progressively lower conversion as the proportion of the total monomer in the system that is contained in the droplets decreases: styrene and butadiene at 40–50% conversion, methyl methacrylate at 25%, and vinyl acetate at 15% [Zollars, 1979].

The particle number remains the same in interval III as in interval II, but the monomer concentration decreases with time, since monomer droplets are no longer present. The decrease in  $\phi_m$  is slower with the more water-soluble monomers as the monomer in solution acts as a reservoir. The presence of a gel effect continues in interval III. The quantitative interplay of a decreasing monomer concentration with the gel effect determines the exact behavior observed in this interval (*GF* or *H*). Polymerization continues at a steadily decreasing rate as the monomer concentration in the polymer particles decreases. Final conversions of essentially 100% are usually achieved. The final polymer particles, spherical in shape, usually have diameters of 50–300 nm, which places them intermediate in size between the initial micelles and monomer droplets.

## 4-2 QUANTITATIVE ASPECTS

### 4-2a Rate of Polymerization

An expression for the rate of polymerization is obtained by considering first the rate in a single polymer particle in which propagation is occurring (i.e., a particle containing a radical) and then the number of such particles. At the start of polymerization in a typical system where the concentration of micelles is  $10^{21} \text{ L}^{-1}$  and the initiation rate for the formation of radicals is  $10^{16} \text{ L}^{-1} \text{ s}^{-1}$ , a radical diffuses into a micelle every  $10^5 \text{ s}$  at the start of interval I. As the system progresses through interval I, this time period decreases sharply, since the concentration of micelles is decreasing. A radical enters each polymer particle on an average of every 10 s during intervals II and III, where  $N$  is typically  $10^{17} \text{ L}^{-1}$ . Once inside the micelle or polymer particle, a radical propagates in the usual manner at a rate  $r_p$  dependent on the propagation rate constant  $k_p$  and the monomer concentration  $[M]$  in the particle.

$$r_p = k_p[M] \quad (4-1)$$

The monomer concentration is usually quite high since in many cases the equilibrium swelling of the particle by monomer is of the order 50–85% by volume. Values of  $[M]$  as high as 5 *M* are common.  $[M]$  varies only weakly with the size of the polymer particles.

Consider now what occurs on the entry of a radical into a particle that already has a radical. For most reaction systems, the radical concentration in a polymer particle is  $10^{-6} \text{ M}$  or higher. This is a higher radical concentration than in the homogeneous polymerization systems and the radical lifetime here is only a few thousandths of a second. The entry of

a second radical into the polymer particle results in immediate bimolecular termination. Thus the polymer particle will have either one or zero radicals. The presence of two radicals in one particle is synonymous with zero radicals, since termination occurs so quickly. The particle is then dormant until another (the third) radical arrives. The particle is again activated and propagation proceeds until the next radical. The cycle of alternate growth and inactivity of the polymer particle continues until the monomer conversion is essentially complete.

*Compartmentalization* (or *segregation*) of a propagating radical in a polymer particle isolates it from other propagating radicals and allows growth to higher molecular weight than might be achieved in solution polymerization, provided that the rate of entry of another radical from the aqueous phase is sufficiently slow.

The rate of polymerization  $R_p$  at any instant is given by the product of the concentration of active particles  $[P\cdot]$  and the rate of propagation in a particle.

$$R_p = k_p[M][P\cdot] \quad (4-2)$$

$[P\cdot]$  is conveniently expressed by

$$[P\cdot] = \frac{N'\bar{n}}{N_A} \quad (4-3)$$

where  $N'$  is the concentration of micelles plus particles,  $\bar{n}$  is the average number of radicals per micelle plus particle, and  $N_A$  is the Avogadro number. The use of  $N_A$  in Eq. 4-3 and in subsequent equations expresses  $[P\cdot]$  in  $\text{mol L}^{-1}$  and  $R_p$  in  $\text{mol L}^{-1} \text{ s}^{-1}$ . Combination of Eqs. 4-2 and 4-3 yields the polymerization rate as

$$R_p = \frac{N'\bar{n}k_p[M]}{N_A} \quad (4-4)$$

$N'\bar{n}$  is zero at the start of interval I, since  $\bar{n} = 0$ .  $N'$  decreases,  $\bar{n}$  increases, and the product  $N'\bar{n}$  increases with time during interval I. At the start of interval II,  $N'$  has reached its steady-state value  $N$ .  $\bar{n}$  may or may not reach an absolutely constant value. Behavior *D* in interval II usually involves a steady-state  $\bar{n}$  value, while behavior *E* usually involves a slow increase in  $\bar{n}$  with conversion.  $\bar{n}$  will remain approximately constant or increase in interval III although a decrease will occur if the initiation rate decreases sharply on exhaustion of the initiator concentration. Most texts show Eq. 4-5 for the polymerization rate instead of the more general Eq. 4-4. Equation 4-5 applies to intervals II and III where only polymer particles exist (no micelles). It is during intervals II and III that the overwhelming percent of monomer conversion to polymer takes place. In the remainder of Sec. 4-2, the discussions will be concerned only with these intervals.

$$R_p = \frac{N\bar{n}k_p[M]}{N_A} \quad (4-5)$$

The value of  $\bar{n}$  during intervals II and III is of critical importance in determining  $R_p$  and has been the subject of much theoretical and experimental work. Three cases can be distinguished—cases 1, 2, and 3. The major differences between the three cases are the occurrence of radical diffusion out of the polymer particles (*desorption*), the particle size, modes of termination, and the rates of initiation and termination relative to each other and to the other reaction parameters. The quantitative interplay of these factors leading to case 1, 2, or 3 behavior has been discussed [Gao and Penlidis, 2002; Gilbert, 1995; Nomura, 1982;

stearate, laurate, palmitate), sulfates, and sulfonates (sodium lauryl sulfate and sodium dodecylbenzene sulfonate). The sulfates and sulfonates are useful for polymerization in acidic medium where fatty acid soaps are unstable or where the final product must be stable toward either acid or heavy-metal ions. Nonionic surfactants such as poly(ethylene oxide), poly(vinyl alcohol) and hydroxyethyl cellulose are sometimes used in conjunction with anionic surfactants for improving the freeze-thaw and shear stability of the polymer or to aid in controlling particle size and size distribution. The presence of the nonionic surfactant imparts a second mode of colloidal stabilization, in addition to electrostatic stabilization by the anionic surfactant, via steric interference with the van der Waals attraction between polymer particles. Non-ionic surfactants are also of use where the final polymer latex should be insensitive to changes in pH over a wide range. Nonionic surfactants are only infrequently used alone, since their efficiency in producing stable emulsions is less than that of the anionic surfactants. Anionic surfactants are generally used at a level of 0.2–3 wt% based on the amount of water; nonionic surfactants are used at the 2–10% level. Cationic surfactants such as dodecylammonium chloride and cetyltrimethylammonium bromide are much less frequently used than anionic surfactants because of their inefficient emulsifying action or adverse effects on initiator decomposition. Also, cationic surfactants are more expensive than anionic surfactants.

Surfactants increase particle number and decrease particle size as their concentration in the initial reaction charge is increased. However, one can use delayed addition of surfactant after nucleation is complete to improve particle stability, without affecting the particle number, size, and size distribution.

#### 4-3c Other Components

The quality of the water used in emulsion polymerization is important. Deionized water may be used since the presence of foreign ions or ions in uncontrolled concentrations can interfere with both the initiation process and the action of the emulsifier. Antifreeze additives are used to allow polymerization at temperatures below 0°C. These include inorganic electrolytes as well as organics such as ethylene glycol, glycerol, methanol, and monoalkyl ethers of ethylene glycol. The addition of inorganic electrolytes often affects the polymerization rate and stability of the emulsion. Sequestering agents such as ethylenediamine tetraacetic acid or its alkali metal salts may be added to help solubilize a component of the initiator system or to deactivate traces of calcium and magnesium ions present in the water. Buffers such as phosphate or citrate salts may be used to stabilize the latex toward pH changes.

#### 4-3d Propagation and Termination Rate Constants

Emulsion polymerization proceeds in a polymer particle where the concentration of polymer is quite high throughout the reaction. This type of system is similar to a bulk polymerization in the later stages of reaction where there is a strong Trommsdorff effect. The propagation rate constant for an emulsion polymerization can be obtained for case 2 systems from the polymerization rate using Eq. 4-5, where  $\bar{n} = 0.5$ . One can ascertain that case 2 behavior is present by observing whether the polymerization rate in interval II is insensitive to changes in the initiation rate. The value of  $k_p$  can also be obtained from the degree of polymerization using Eq. 4-7. This is often a more reliable measure of  $k_p$  since there is no need to make any assumption on the value of  $\bar{n}$ . The propagation rate constant is generally found to have the same value in emulsion polymerization as in the corresponding bulk polymerization at high conversion—more specifically, at a conversion corresponding to the volume fraction of polymer in monomer that exists in the emulsion system.

#### 4-3e Energetics

The heat of an emulsion polymerization is the same as that for the corresponding bulk or solution polymerization, since  $\Delta H$  is essentially the enthalpy change of the propagation step. Thus, the heats of emulsion polymerization for acrylic acid, methyl acrylate, and methyl methacrylate are  $-67$ ,  $-77$ , and  $-58$  kJ mol $^{-1}$ , respectively [McCurdy and Laidler, 1964], in excellent agreement with the  $\Delta H$  values for the corresponding homogeneous polymerizations (Table 3-14).

The effect of temperature on the rate of emulsion polymerization, although not extensively studied, is generally similar to that on homogeneous polymerization with a few modifications. The overall rate of polymerization increases with an increase in temperature. Temperature increases the rate by increasing both  $k_p$  and  $N$ . The increase in  $N$  is due to the increased rate of radical generation at higher temperatures. Opposing this trend to a slight extent is the small decrease in the concentration of monomer in the particles at higher temperatures. Thus, the value of  $[M]$  for styrene decreases  $\sim 15\%$  in going from 30 to 90°C [Smith and Ewart, 1948]. The overall activation energy for emulsion polymerization is, thus, a combination of the activation energies for propagation, radical production, and  $[M]$ . For the few systems studied, the overall activation energies for emulsion polymerization are approximately the same as or less than those for the corresponding homogeneous polymerization [Stavrova et al., 1965].

Carrying out an emulsion polymerization requires an awareness of the *krafft point* of an ionic surfactant and the *cloud point* of a nonionic surfactant. Micelles are formed only at temperatures above the Krafft point of an ionic surfactant. For a nonionic surfactant, micelles are formed only at temperatures below the cloud point. Emulsion polymerization is carried out below the cloud temperature of a nonionic surfactant and above the Krafft temperature of an ionic surfactant.

#### 4-3f Molecular Weight and Particle Size Distributions

Theoretical considerations indicate that compartmentalization of radicals in polymer particles does not change the polydispersity index  $PDI (= \bar{X}_w/\bar{X}_n)$  in emulsion polymerization from its value of 2 in homogeneous polymerization when termination takes place by transfer to monomer, chain-transfer agent, or other substance [Butte et al., 2002a,b; Giannetti et al., 1988; Gilbert, 1995; Lichti et al., 1980, 1982; Mendizabal et al., 2000]. However, emulsion polymerization results in molecular weight broadening when termination involves bimolecular reaction between radicals. While short propagating chains are likely to couple or disproportionate with longer chains in homogeneous polymerization ( $PDI = 1.5$  and 2 for coupling and disproportionation, respectively) (Sec. 3-11), any two chains that undergo bimolecular termination in emulsion polymerization are not random. The broadening of PDI in emulsion polymerization is greater for disproportionation than for coupling. For case 2 behavior, coupling of the propagating chain in a polymer particle with the low-molecular-weight entering radical does not greatly affect PDI. Such coupling is equivalent to termination by chain transfer and PDI has a value of 2 compared to 1.5 for homogeneous polymerization. When termination is by disproportionation, PDI has a value of 4 at  $\bar{n} = 0.5$  compared to 2 for homogeneous polymerization [Butte et al., 2002a,b]. Low-molecular-weight radicals entering the polymer particles disproportionate with propagating radicals and increase the number of low-molecular-weight molecules;  $\bar{X}_n$  is decreased while  $\bar{X}_w$  is essentially unchanged and  $\bar{X}_w/\bar{X}_n$  increases. When  $\bar{n} > 0.5$  (case 3), the tendency toward molecular weight broadening decreases as the size of the radicals undergoing coupling or disproportionation

become more nearly the same size. PDI tends toward the values in homogeneous polymerization (1.5 and 2 for coupling and disproportionation, respectively) as  $\bar{n}$  increases from 0.5 to 2.

The preceding discussion relates primarily to polymerization in stage II of an emulsion polymerization. Since this constitutes the major portion of an emulsion polymerization and the reaction conditions ( $N$ ,  $R_i$ ,  $k_p$ ,  $[M]$ ) are relatively constant during stage II, the molecular weight distribution is considerable narrower than in homogeneous polymerization [Cooper, 1974; Lin and Chiu, 1979]. However, there is molecular weight broadening with conversion as reaction proceeds through stage III where various reaction parameters are no longer constant. Also, the molecular weights produced during stage I are not the same as in stage II. The PDI for a batch polymerization taken to complete conversion can be as high as 5–7 [Butte et al., 2002a,b], which is still lower than for a typical homogeneous polymerization.

In addition to the molecular-weight distribution, there is a particle size distribution in emulsion polymerization [Chen and Wu, 1988; Gardon, 1977; Lichti et al., 1982]. The particle size distribution (PSD) is expressed, analogously to the molecular weight distribution, as the ratio of the weight-average particle size to number-average particle size. (Different particle sizes are calculated depending on whether one uses the particle radius, diameter, or volume as the measure of particle size.) The particle size distribution is a consequence of the distribution of times at which different polymer particles are nucleated. The polydispersity is maximum during interval I and narrows considerably during the subsequent period. There has been an effort to produce narrow-particle-size distributions (PSD) by controlling the nucleation process, choice and amount of surfactant, temperature and other reaction variables, and the use of seed emulsion polymerization. Narrow particle size distributions are useful in applications such as calibration of electron microscope, ultracentrifuge, aerosol counting, and light-scattering instruments and the measurement of pore sizes of filters and membranes. Narrow particle distributions, with PSD values of 1.1 and lower, have been obtained by choosing reaction conditions with short nucleation times (short interval I relative to intervals II and III), increased latex stability (to prevent coagulation), and decreased interval III times.

#### 4-3g Surfactant-Free Emulsion Polymerization

The presence of surfactant is a disadvantage for certain applications of emulsion polymers such as those involving instrument calibration and pore size determination. The presence of adsorbed surfactant gives rise to somewhat variable properties since the amount of adsorbed surfactant can vary with the polymerization and application conditions. Removal of the surfactant, either directly or by desorption, can lead to coagulation or flocculation of the destabilized latex. *Surfactant-free emulsion polymerization*, involving no added surfactant, is a useful approach to solving this problem [Chainey et al., 1987; Li and Salovey, 2000; Ni et al., 2001]. The process uses an initiator yielding initiator radicals that impart surface-active properties to the polymer particles. Persulfate is a useful initiator for this purpose. Latexes prepared by the surfactant-free technique are stabilized by chemically bound sulfate groups of the  $\text{SO}_4^-$ -initiating species derived from persulfate ion. Since the surface-active groups are chemically bound, the latexes can be purified (freed of unreacted monomer, initiator, etc.) without loss of stability, and their stability is retained over a wider range of use conditions than the corresponding latexes produced using surfactants. A characteristic of surfactant-free emulsion polymerization is that the particle number is generally lower by up to about 2 orders of magnitude compared to the typical emulsion polymerization, typically  $10^{12}$  versus  $10^{14}$  particles per milliliter. This is a consequence of the lower total particle surface area

that can be stabilized by the sulfate groups alone relative to that when added surfactant is present.

Another approach to producing latexes with chemically bound surface-active groups is to use a *reactive surfactant*—a surfactant with a polymerizable double bond, such as sodium dodecyl allyl sulfosuccinate [Wang et al., 2001a,b,c]. Copolymerization of the reactive surfactant with the monomer of interest binds the surface active groups into the polymer chains.

#### 4-3h Other Emulsion Polymerization Systems

In the conventional emulsion polymerization, a hydrophobic monomer is emulsified in water and polymerization initiated with a water-soluble initiator. Emulsion polymerization can also be carried out as an *inverse emulsion polymerization* [Poehlein, 1986]. Here, an aqueous solution of a hydrophilic monomer is emulsified in a nonpolar organic solvent such as xylene or paraffin and polymerization initiated with an oil-soluble initiator. The two types of emulsion polymerizations are referred to as *oil-in-water (o/w)* and *water-in-oil (w/o)* emulsions, respectively. Inverse emulsion polymerization is used in various commercial polymerizations and copolymerizations of acrylamide as well as other water-soluble monomers. The end use of the reverse latices often involves their addition to water at the point of application. The polymer dissolves readily in water, and the aqueous solution is used in applications such as secondary oil recovery and flocculation (clarification of wastewater, metal recovery).

Nonionic surfactants such as sorbitan monooleate yield more stable emulsions than do ionic surfactants. However, the latexes from inverse emulsion polymerizations are generally less stable than those from conventional emulsion polymerizations, and flocculation is a problem.

*Miniemulsion polymerization* involves systems with monomer droplets in water with much smaller droplets than in emulsion polymerization, about 50–1000 nm compared to 1–100  $\mu\text{m}$  in diameter [Antonietti and Landfester, 2002; Asua, 2002; Bechthold and Landfester, 2000; Landfester, 2001]. Micelles are usually not present because surfactant concentrations are generally below CMC. Water-insoluble costabilizers such as hexadecane and cetyl alcohol are present along with the surfactant to stabilize the monomer droplets against diffusional degradation (coagulation), referred to as *Ostwald ripening*. The droplet size depends not only on the amount of surfactant and costabilizer but also on the amount of energy used in the homogenization process. The final polymer particle size is similar to the monomer droplet size. Both water-soluble and oil-soluble initiators have been used in miniemulsion polymerization. The reaction approximates an emulsion or suspension polymerization depending on the monomer droplet size. Larger droplet sizes (>500 nm) lead to suspension polymerization; smaller droplet sizes lead to emulsion polymerization. Miniemulsion polymerizations are useful for producing high-solids-content latexes. *Inverse miniemulsion polymerizations* have also been studied [Landfester et al., 2001].

*Microemulsion polymerization* is an emulsion polymerization with very much smaller monomer droplets, about 10–100 nm compared to 1–100  $\mu\text{m}$ . Micelles are present because the surfactant concentration is above CMC. The final polymer particles generally have diameters of 10–50 nm. Although many of the characteristics of microemulsion polymerization parallel those of emulsion polymerization, the details are not exactly the same [Co et al., 2001; de Vries et al., 2001; Lopez et al., 2000; Medizabial et al., 2000]. Water-soluble initiators are commonly used, but there are many reports of microemulsion polymerization with oil-soluble initiators. Nucleation in emulsion polymerization occurs almost exclusively in the early portion of the process (interval I). Nucleation occurs over a larger portion of the process in microemulsion polymerization because of the large amount of surfactant present. Nucleation