radicals per milliliter per second. (The symbol ρ 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 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.

Polymerization takes place almost exclusively in the interior of the micelles. The micelles act as a meeting place for the organic (oil-soluble) monomer and the water-soluble initiator. The micelles are also favored as the reaction site because of their high monomer concentration (similar to bulk monomer concentration) compared to the monomer in solution and their high surface-to-volume ratio compared to the monomer droplets. 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 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 ○– to indicate one end (○) is polar or ionic and the other end (–) nonpolar.

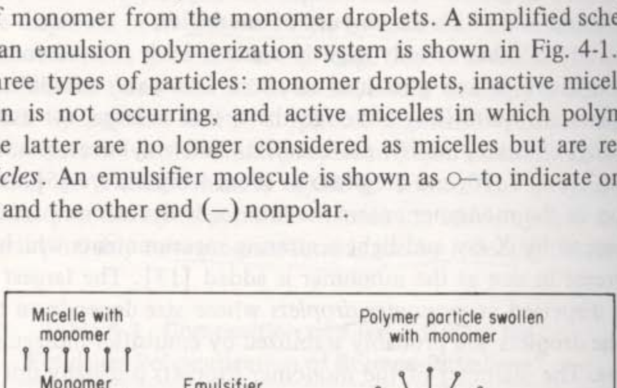

Fig. 4-1 Simplified representation of an emulsion polymerization system.

The mechanism for *particle nucleation* (i.e., formation of polymer particles) is best described as proceeding by two simultaneous processes. One is the entry of radicals (either primary radicals or oligomeric radicals formed by solution polymerization) from the aqueous phase into the micelles (*micellar nucleation*). The other, *homogeneous nucleation* [16,17], involves solution-polymerized oligomeric radicals becoming insoluble and precipitating on themselves (or on dead oligomer). The precipitated species become stabilized by absorbing surfactant (from solution and the monomer droplets) and upon subsequent absorption of monomer are the equivalent of polymer particles formed by micellar nucleation. The relative extents of micellar and homogeneous nucleation would be expected to vary with the water solubility of the monomer and the surfactant concentration. Higher water solubility and low surfactant concentration favor homogeneous nucleation; micellar nucleation is favored by low water solubility and high surfactant concentration. (That homogeneous nucleation occurs is evidenced by the emulsion polymerization of systems where the surfactant concentration is below the CMC [18].) Homogeneous nucleation may be the primary mechanism of particle formation for a relatively water-soluble monomer such as vinyl acetate [19], while micellar nucleation is the predominant mechanism for a highly water-insoluble monomer such as styrene [20].

4-1b-3 *Progress of Polymerization*

A variety of behaviors are observed for the polymerization rate vs conversion depending on the relative rates of initiation, propagation and termination which are in turn dependent upon 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 particles per milliliter) 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 in range 10^{13}–10^{15} particles per milliliter.) 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 which is 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

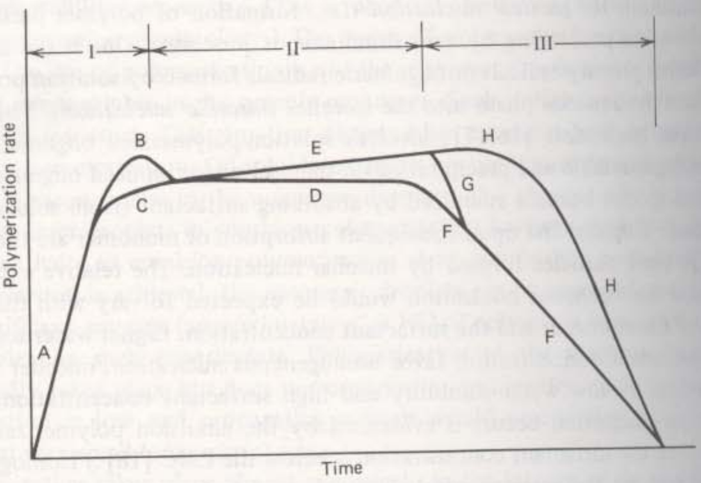

Fig. 4-2 Different rate behaviors observed in emulsion polymerization. After [5] (by permission of Wiley-Interscience, New York).

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 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 AC), arising from a transient high particle number and/or high proportion of particles containing propagating radicals, is often not 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 ϕ_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 [5]. 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 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 [4,5]. For monomers (e.g., vinyl chloride) with low water solubility and low ϕ_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% [19].

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 ϕ_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 have diameters of the order of 500 to 2000 Å and are intermediate in size between the initial micelles and initial monomer droplets.

4-2 QUANTITATIVE ASPECTS

4-2a Rate of Polymerization

An expression for the rate of polymerization can be 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^{18} per milliliter and the initiation rate is 10^{13} radicals per milliliter-second, a radical diffuses into a micelle every 10^5 sec 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 particle on an average of every 10 sec during Intervals II and III where N is typically 10^{14} particles per milliliter. 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.

$$r_p = k_p[\mathrm{M}] \tag{4-1}$$

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.

Consider now what occurs on the entry of a radical into a particle which already has a radical. For most reaction systems, the radical concentration in a polymer particle is 10^{-6} 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.

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

$$R_p = k_p[\mathrm{M}][\mathrm{P}\cdot] \tag{4-2}$$

[P·] is conveniently expressed by

$$[\mathrm{P}\cdot] = \frac{10^3 N'\bar{n}}{N_A} \tag{4-3}$$

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 $10^3/N_A$ in Eq. 4-3 and in the subsequent equations expresses [P·] in moles/liter and R_p in moles/liter-sec. Combination of Eqs. 4-2 and 4-3 yields the polymerization rate as

$$R_p = \frac{10^3 N'\bar{n}k_p[\mathrm{M}]}{N_A} \tag{4-4}$$

$N'\bar{n}$ 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 due to exhaustion of the initiator concentration. Most texts show

$$R_p = \frac{10^3 N\bar{n}k_p[\mathrm{M}]}{N_A} \tag{4-5}$$

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 Section 4-2, the discussions will be concerned only with these Intervals.

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*–1, 2, and 3–can be distinguished based upon the work of Smith and Ewart [1-3] and others [4-10]. 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 the initiation and termination processes 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 [1-10]. Our discussion will be in qualitative terms.

Case 2: $\bar{n} = 0.5$. This is the case usually described in texts as applicable to most emulsion polymerizations. It occurs when desorption of radicals does not occur or is negligible compared to the rate of radicals entering particles (*absorption*) and the particle size is too small, relative to the bimolecular termination rate constant, to accommodate more than one radical. Under these conditions, a radical entering a polymer particle is trapped within that particle and undergoes propagation until another radical enters, at which point there is essentially instantaneous termination. Any polymer particle will be active half of the time and dormant the other half of the time. In other words, at any given moment half of the polymer particles contain one radical and are growing while the other half are dormant. The number of radicals per particle $\bar{n}$ averaged over all the particles is 0.5. Case 2 behavior also requires the initiation rate not be excessively low and negligible termination of radicals in the aqueous phase.

Case 1: $\bar{n} < 0.5$. The average number of radicals per particle can drop below 0.5 if radical desorption from particles and termination in the aqueous phase are not negligible. The decrease in $\bar{n}$ is larger for small particle sizes and low initiation rates.

Case 3: $\bar{n} > 0.5$. Some fraction of the polymer particles must contain two or more radicals per particle in order for $\bar{n}$ to be larger than 0.5, since there will always be a fraction (a very significant fraction) which has zero radical per particle. This occurs if the particle size is large or the termination rate constant is low while termination in the aqueous phase and desorption are not important and the initiation rate is not too low.

Although most texts indicate that Case 2 is the predominant behavior for all monomers, this is not true. Certain monomers, especially vinyl acetate and vinyl chloride, follow Case 1 behavior under a variety of reaction conditions [4,5,9]. For example, $\bar{n}$ was observed to be approximately 0.1 or lower for vinyl acetate and vinyl chloride [5,22-24]. Values of $\bar{n}$ are calculated from Eq. 4-5 using the k_p value from bulk polymerization at the appropriate percent conversion, that is, at the conversion corresponding to the volume fraction of monomer in the polymer particles. The monomers which show strong Case 1 behavior are those with high monomer chain transfer constants. Chain transfer to monomer results in a small-sized monomer radical which can desorb from the polymer particle more readily than the large-sized propagating radical. This was verified by carrying out emulsion polymerizations with intermittent ionizing radiation. The polymerization rate decays to zero after irradiation ceases but before all of the monomer has polymerized [25-27]. If desorption of monomer radicals did not occur, polymerization should continue until monomer is exhausted. The polymerization rate decayed for all monomers but at very different rates. The decay rate, which follows the desorption rate, increased as the monomer chain transfer constant increased.

The effect of reaction conditions on $\bar{n}$ (and R_p, of course) can be observed even with styrene which shows a very strong tendency toward Case 2 behavior under a wide range of reaction conditions [28,29]. *Seed* polymerization, involving the addition of monomer and initiator to a previously prepared emulsion of polymer particles, is especially useful for this purpose since it allows the variation of certain reaction parameters while holding N constant. Thus, $\bar{n}$ in seeded styrene polymerization drops from 0.5 to 0.2 when the initiator concentration decreases from 10^{-2} to 10^{-5} M. At sufficiently low R_i, the rate of radical absorption is not sufficiently high to counter-balance the rate of desorption. One also observes that above a particular initiation rate ($[\mathrm{I}] = 10^{-2}$ M in this case), the system maintains Case 2 behavior with $\bar{n}$ constant at 0.5 and R_p independent of R_i. A change in R_i simply results in an increased rate of alternation of activity and inactivity in each polymer particle. Similar experiments show that $\bar{n}$ drops below 0.5 for styrene when the particle size becomes sufficiently small. The extent of radical desorption increases with decreasing particle size since the travel distance for radical diffusion from a particle decreases.

Case 3 behavior occurs when the particle size is sufficiently large (about 0.1-1 μm) relative to k_t such that two or more radicals can coexist in a polymer particle without instantaneous termination. This effect is more pronounced as the particle size and percent conversion increase. At high conversion the particle size increases and k_t decreases, leading to an increase in $\bar{n}$. The increase in $\bar{n}$ occurs at lower conversions for the larger sized particles. Thus for styrene polymerization $\bar{n}$ increases from 0.5 to only 0.6 at 90% conversion for 0.7 -μm particles. On the other hand, for 1.4 -μm particles, $\bar{n}$ increases to about 1 at 80% conversion and more than 2 at 90% conversion [30,31].

Consider now the implications of Eq. 4-5. The values of k_p, [M] and, to a large extent, $\bar{n}$ are specified for any particular monomer. The polymerization rate is then determined by the value of N. Increasing the surfactant concentration and increasing R_i increases N (Sec. 4-2c) and, therefore, R_p. These trends are shown in Figs. 4-3 and 4-4 [32,33]. It should be noted that the polymerization rate is unaffected

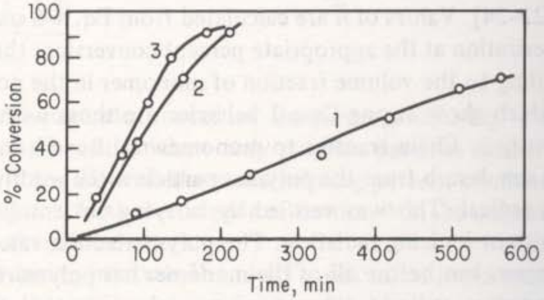

Fig. 4-3 Plot of percent conversion vs time for emulsion polymerizations of styrene with different concentrations of potassium laurate at 60°C. The moles of emulsifier per polymerization charge (of 180 g H_2O, 100 g styrene, 0.5 g $K_2S_2O_8$) are 0.0035 (curve 1), 0.007 (curve 2), and 0.014 (curve 3). After [32] (by permission of Wiley-Interscience, New York).

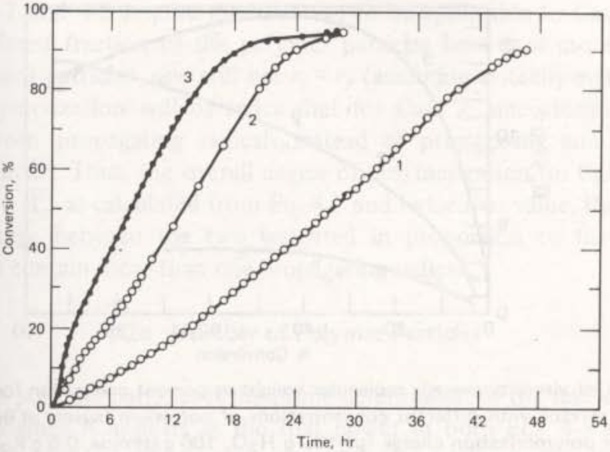

Fig. 4-4 Plot of percent conversion vs time for emulsion polymerization of vinyl chloride at 50°C for monomer/water ratio of 26/74 and 0.883% surfactant. The initiator concentrations are 0.0012% (curve 1), 0.0057% (curve 2) and 0.023% (curve 3). After [33] (by permission of Huthig and Wepf Verlag, Basel).

by changes in R_i once particle nucleation has ceased at the end of Interval I. Such changes would only result in changing the rate of alternation of activity and inactivity in each polymer particle.

4-2b Degree of Polymerization

The number-average degree of polymerization in an emulsion polymerization can be obtained by considering what occurs in a single polymer particle. The rate r_i at which primary radicals enter a polymer particle is given by

$$r_i = \frac{R_i}{N} \tag{4-6}$$

This is the same as the rate of termination r_t of a polymer chain for Case 2 behavior, since termination occurs immediately upon the entry of a radical into a polymer particle in which a polymer chain is propagating. The degree of polymerization is then the rate of growth of a polymer chain divided by the rate at which primary radicals enter the polymer particle, that is, Eq. 4-1 divided by Eq. 4-5.

$$\overline{X}_n = \frac{r_p}{r_i} = \frac{Nk_p[\mathrm{M}]}{R_i} \tag{4-7}$$

Figure 4-5 shows the viscosity-average molecular weights in the emulsion polymerizations of styrene of Fig. 4-3. The results are in line with Eq. 4-7 in that the polymer size increases with the emulsifier concentration.

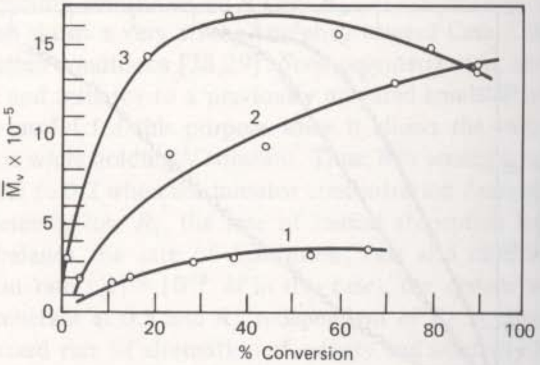

Fig. 4-5 Plot of viscosity-average molecular weight vs percent conversion for emulsion polymerizations of styrene with different concentrations of potassium laurate at 60°C. The moles of emulsifier per polymerization charge (of 180 g H_2O, 100 g styrene, 0.5 g $K_2S_2O_8$) are 0.0035 (curve 1), 0.007 (curve 2), and 0.014 (curve 3). After [32] (by permission of Huthig and Wepf Verlag, Basel).

It should be noted that the degree of polymerization in an emulsion polymerization is synonymous with the kinetic chain length. Although termination is by bimolecular coupling, one of the radicals is a primary (or oligomeric) radical, which does not significantly contribute to the size of a dead polymer molecule. The derivation of Eq. 4-7 assumes the absence of any termination by chain transfer. If chain transfer occurs the degree of polymerization will be given by

$$\overline{X}_n = \frac{r_p}{r_i + \Sigma r_{tr}} \tag{4-8}$$

where Σr_{tr} is the sum of the rates of all transfer reactions. The rate of a chain transfer reaction in a polymer particle would be given by an equation of the type

$$r_{tr} = k_{tr}[\mathrm{XA}] \tag{4-9}$$

analogous to the case of transfer in homogeneous polymerization (Eq. 3-113).

The degree of polymerization, like the polymerization rate, varies directly with N, but the degree of polymerization also varies indirectly with R_i. A consideration of Eqs. 4-5 and 4-7 with their analogues for homogeneous, radical chain polymerization (Eqs. 3-25 and 3-109) shows the significant characteristic of the emulsion process. In homogeneous polymerization, one can increase the polymerization rate by increasing the rate of initiation, but the result is a simultaneous lowering of the polymer molecular weight. No experimental variable is available to increase R_p without decreasing $\overline{X}_n$. The situation is quite different in emulsion polymerization. The rate and degree of polymerization can be simultaneously increased by increasing the number of polymer particles at a constant initiation rate. These conclusions have been verified by a number of studies [5,6,9,10].

Equations 4-7 and 4-8 require modification to be applicable to Case 3 behavior where a significant fraction of the polymer particles have 2 or more radicals per particle. For such particles, one still has $r_i = r_t$ (assuming a steady-state $\overline{n}$) but the degree of polymerization will be twice that for Case 2, since termination is by coupling between propagating radicals instead of propagating and primary (or oligomeric) radicals. Thus, the overall degree of polymerization for Case 3 behavior will be between $\overline{X}_n$ as calculated from Eq. 4-7 and twice that value, the exact value being the average between the two weighted in proportion to the fraction of particles which contain more than one propagating radical.

4-2c Number of Polymer Particles

The number of polymer particles is the prime determinant of the rate and degree of polymerization since it appears as the first power in both Eqs. 4-5 and 4-7. The formation (and stabilization) of polymer particles by both micellar nucleation and homogeneous nucleation involves the adsorption of surfactant from the micelles, solution, and monomer droplets. The number of polymer particles which can be stabilized is dependent on the total surface area of surfactant present in the system a_sS where a_s is the interfacial surface area occupied by a surfactant molecule and S is the total concentration of surfactant in the system (micelles, solution, monomer droplets). However, N is also directly dependent on the rate of radical generation. The quantitative dependence of N on a_sS and R_i has been derived as

$$N = k\left(\frac{R_i}{\mu}\right)^{2/5} (a_sS)^{3/5} \tag{4-10}$$

where μ is the rate of volume increase of a polymer particle (which can be determined from r_p and geometrical considerations). The value of k is between 0.37 and 0.53 depending on the assumptions made regarding the relative efficiencies of radical capture by micelles versus polymer particles and which geometric parameter of the particle (radius, surface area or volume) determines the rate at which polymer particles capture radicals. We should note that high particle numbers are associated with small particle size and low particle numbers with large particle size. Equation 4-10 leads to the prediction that the particle radius will be inversely dependent on the 0.20- and 0.13-order of S and R_i, respectively [5].

A consideration of Eq. 4-10 together with Eqs. 4-5 and 4-7 shows that both R_p and $\overline{X}_n$ depend on the $\frac{3}{5}$-power of the total surfactant concentration. The polymerization rate varies with the $\frac{2}{5}$-power of R_i while the degree of polymerization varies inversely with the $\frac{3}{5}$-power of R_i. The dependence of R_p on R_i does not contradict the earlier conclusion regarding the independence of the polymerization rate on the rate of radical production. The rate of radical generation affects the number of polymer particles formed which in turn determines the polymerization rate. However, once an emulsion polymerization system has reached a steady-state with regard to N, the rate of radical generation no longer has any effect on the polymerization rate as long as initiation is taking place. Further and very significantly, it should be noted that the number of polymer particles can be increased by increasing the emulsifier concentration while maintaining a constant rate of radical generation. Thus from the practical viewpoint one can simultaneously increase R_p and $\overline{X}_n$ by increasing N. Increasing N by increasing R_i increases R_p but at the expense of decreasing $\overline{X}_n$.

Equation 4-10 is generally followed by monomers such as styrene which show little tendency toward radical desorption. Considerable deviations are usually observed for monomers such as vinyl acetate and vinyl chloride which show Case 1 behavior. For these monomers the order of dependence of N on S is generally greater than predicted and approaches first-order, while the dependence on R_i approaches zero-order. When extensive radical desorption occurs the large bulk of nucleation is initiated by desorbed radicals with the result that N is little affected by R_i and the dependence on S is higher than predicted. Thus, the order of dependence of N on R_i is 0.64 for styrene, 0.86 for methyl methacrylate and 1.0 for vinyl chloride and vinyl acetate, while the orders of dependence on S are 0.36, 0.20, and ~0, respectively [34]. Further, for Case 1 monomers, the N values are considerably higher than predicted (i.e., k is larger than predicted) due to the increased nucleation by desorbed radicals.

The polymer particles decrease in stability during Intervals II and III since the total particle surface area increases and the coverage of the surface with emulsifier decreases. The relative decrease in particle stability appears not to be sufficient to cause coalescence as long as stirring is maintained since N is generally observed to be constant. In some systems, however, the stability decreases sufficiently to cause the particles to coalesce and N decreases with conversion [9,10].

4-3 OTHER CHARACTERISTICS OF EMULSION POLYMERIZATION

4-3a Initiators

The initiators used in emulsion polymerization are water-soluble initiators such as potassium or ammonium persulfate and hydrogen peroxide. Partially water-soluble peroxides such as succinic acid peroxide and *t*-butyl hydroperoxide and azo compounds [9,35] have also been employed. The most commonly used initiators are the redox systems (Sec. 3-4b) such as persulfate with ferrous ion

$$S_2O_8^{2-} + Fe^{2+} \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-}\cdot \tag{4-11}$$

often with a second reducing agent (glucose, fructose, tetraethylenepentamine) to recycle the ferric back to ferrous. Redox systems are advantageous in yielding desirable initiation rates at very moderate to low temperatures (+50 to -50°C). Other useful redox systems include cumyl hydroperoxide or hydrogen peroxide with ferrous, sulfite or bisulfite ion.