Chapter 12
Emulsion and Suspension Polymerization

Introduction

In this chapter we consider two polymerization processes having in common the following features:

(1) The monomers are polymerizable by free radical routes;

(2) The monomer and polymer are nearly completely insoluble in water and are dispersed therein as very small to small spherical particles;

(3) The continuous phase throughout the polymerization is water, at a volume fraction of usually 0.70 or more, and thus the effective viscosity of the entire mixture, calculable as a suspension of spheres is not much greater than twice the viscosity of water.

These processes are emulsion polymerization and suspension ("bead", "pearl") polymerization which — except for the above shared features — are completely different in kinetics.

12.1 Emulsion Polymerization

12.1.1 Introduction

As noted above, the monomer(s) must be (a) insoluble or sparingly soluble in water (acrylamide is a counter example) and (b) polymerizable by free radicals. The initiator is soluble *only* in the water phase, and it decomposes in this phase forming radicals which to an overwhelming degree arrive at dispersed *micellar* or polymer particles.

Fig. 12.1 shows the species present in emulsion polymerization. Fig. 12.2 shows schematically the three stages which occur in succession.

I. Micellar Stage: Soap, for example sodium palmitate, is dissolved in water at a concentration well above *critical micelle concentration.* Monomer(s) is (are) added and dispersed as droplets (0.1 *mm* – 1 *mm*), in the presence of a water soluble initiator. Monomer diffuses from droplets through water into micelles. While some initiation occurs probably in the water phase, most polymerization ensues in the *micelles.* The micelles become polymer particles, i.e., polymer dissolved in monomer. They grow from micellar dimensions, a few tens of Ångström units, eventually to hundreds of Ångström units in diameter (up to ~0.4 μm).

II. After about 15 percent conversion of the monomer initially charged, the micelles are exhausted, no new particles are generated, and monomer diffuses into the growing polymer particles from the droplets, to maintain thermodynamic balance of the monomer and polymer.

III. After 40 to 60% conversion the monomer droplet phase disappears (centrifugation no longer yields a monomer layer) and the polymer particles now remain about constant both in number and diameter as their monomer, roughly 40 to 60% of the volume, is converted to polymer.

Throughout the three stages in the *Smith-Ewart model,* each micelle or ensuing polymer particle alternately receives from the aqueous phase a radical, which starts polymerization within, and another radical, which combines with the growing chain radical end, terminating the reaction. This is referred to as "red light-green light" polymerization. On the average, the interval between capture of radicals is between 1 and 100 seconds (set by initiator concentration and soap concentration). Thus the red light or green light period may be of the order of 1 to 100 seconds.

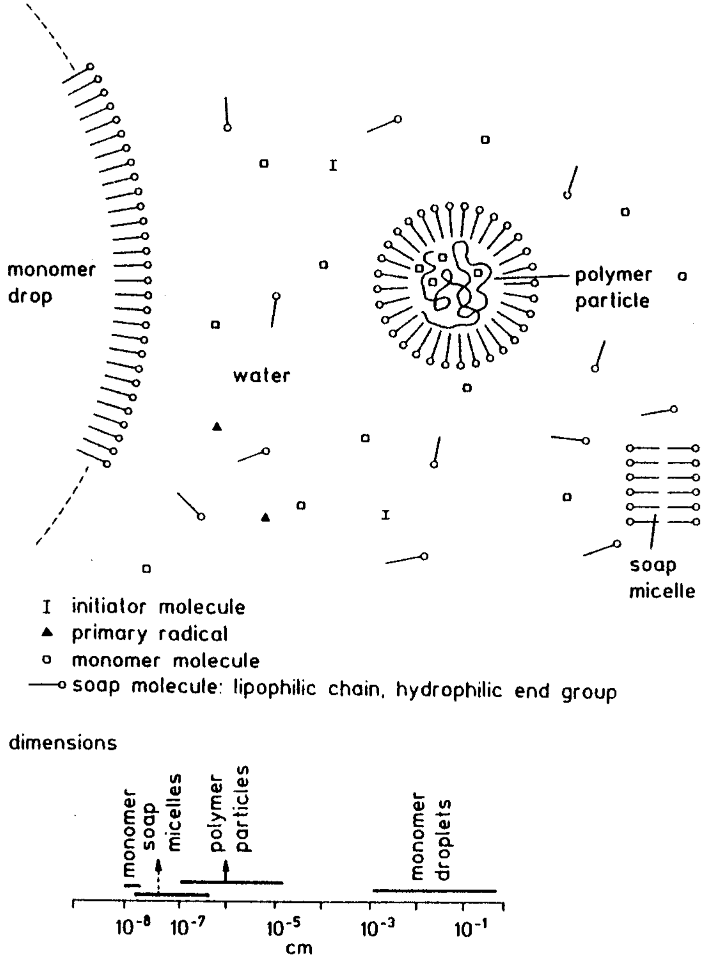


Fig. 12.1. Schematic representation of the reaction medium in an emulsion polymerization

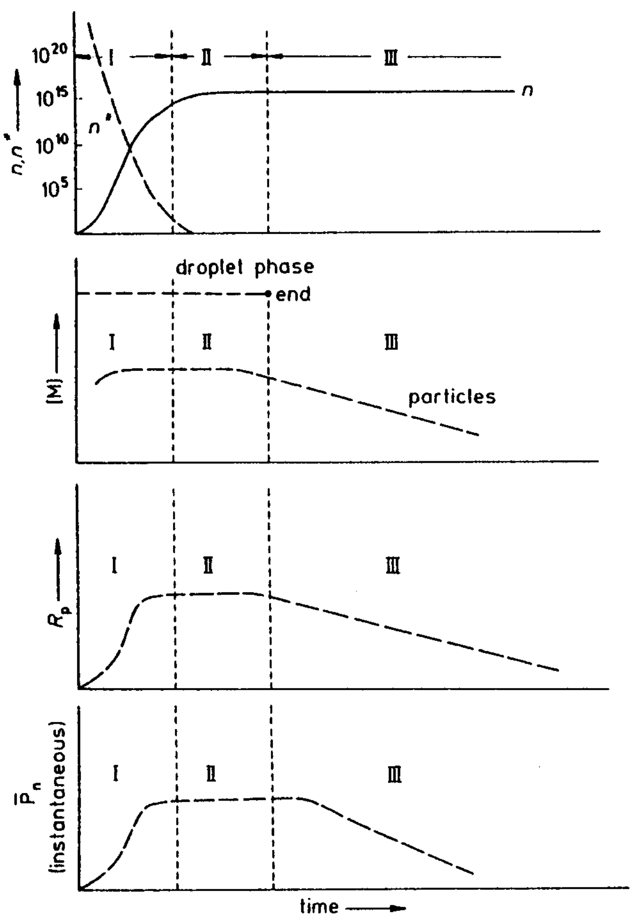


Fig. 12.2. Diagrams showing the three stages of emulsion polymerization: (I) Micelles increasing; (II) micelles exhausted, droplet phase remains; (III) droplet phase exhausted.
n number of particles per unit volume
n^* number of micelles per unit volume
[M] monomer concentration in the droplets and in the particles
R_p overall rate of polymerization
$\bar{P}_n$ instantaneous degree of polymerization

12.1.2 Advantages and Disadvantages

Advantages

(1) Termination is controlled externally by reason of the initiator's insolubility in the organic phase. The rate of arrival of radicals at the polymer particles is established *independently* of propagation, by regulation of soap content, which sets the number of micelle/polymer particles at 10^{14} to 10^{17} per *ml* of emulsion, and by the redox initiator concentration in the aqueous phase, which establishes the rate of generation of radicals.

Thus for example butadiene, which cannot be economically polymerized *homogeneously* by radical initiation (k_t being very high compared to k_p), is readily polymerized by emulsion polymerization.

(2) Because at least 50% of the volume is water, *viscosity is always low*, and heat removal rates are easily managed. It would be difficult to provoke runaway, explosive polymerizations in emulsion polymerization.

(3) In many cases the emulsion finally produced, ~0.1 *μm* polymer particles at around 50% volume fraction in water, is a product *immediately applicable* as a coating, e.g., a paint or barrier coating layer: poly(vinylidene chloride) on polyethylene.

Disadvantage

The polymer will contain *residues* of the soap which are hard to eliminate, even if the polymer has been precipitated from the emulsion and washed. If the emulsion is used directly as a coating, all the soap will be present.

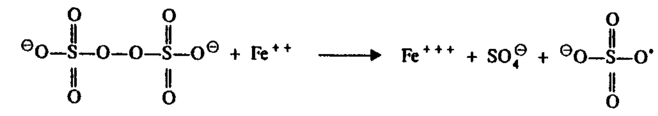
12.1.3 Initiators

Reduction-oxidation (redox) initiators are particularly useful in emulsion polymerization because they can produce high rates of radical generation at the moderate temperature levels common to emulsion polymerization. A primary requirement is that they be insoluble in the monomer droplet phase and insoluble in the polymer particles: Thus, they must be highly water soluble.

As examples of redox systems, cumyl hydroperoxide reacts with ferrous ion to produce one radical:

$$(C_6H_5){-}C(CH_3)_2OOH + Fe^{++} \longrightarrow Fe^{+++} + OH^{\ominus} + (C_6H_5)C(CH_3)_2O^{\bullet}$$

Persulfate reacts with ferrous ion to give:



$$^{\ominus}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}O{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}O^{\ominus} + Fe^{++} \longrightarrow Fe^{+++} + SO_4^{\ominus} + {}^{\ominus}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}O^{\bullet}$$

Another redox system is the ferrous-hydrogen peroxide mixture:

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH^- + OH^{\bullet}$$

In general, the rate of production of radicals by redox initiators, $+d[R^{\bullet}]/dt$, given in [$mole \cdot l^{-1} \cdot s^{-1}$], in a single phase medium, is given by the rate equation:

$$+\frac{d[R^\bullet]}{dt} = k_{d,r}[X][Y] \tag{12.1}$$

wherein $[X]$ = molar concentration of peroxide
$[Y]$ = molar concentration of reducing agent (e.g., Fe^{++})
$k_{d,r}$ = dissociation constant for redox pair

The factors 2 and f (efficiency factor), found in the equation for homolytic dissociation of a *single* initiator I,

$$+\,d[R^\bullet]/dt = 2fk_d[I] \tag{12.2}$$

are absent in redox initiation.

Because in each initiation step only one radical is produced, recombination of this radical species is not favored.

As applied to emulsion polymerization, in which the volume fraction of organic phase is ϕ, and that of water $(1-\phi)$, the rate ρ of production of initiator radicals (number of radicals per *cm*³ and per *s*) must therefore be, from eq. (12.1):

$$\rho = \frac{N_A}{10^3}(1-\phi)k_{d,r}[X][Y] \tag{12.3}$$

wherein $[X]$ and $[Y]$ are calculated as moles per litre in the aqueous phase, and N_A is Avogadro's number.

12.1.4 Smith-Ewart Kinetic Scheme

There are three premises central to the Smith-Ewart theory:

(1) All radicals generated in the aqueous phase arrive at the surface of micelles, or of polymer particles derived therefrom.

(2) When a radical arrives at a micelle or a particle surface, it instantly initiates a single chain propagation, if there is not already radical activity within.

(3) If there is a chain propagation underway, the arriving radical stops it instantly by mutual termination.

These premises were reached by considering typical values of k_t for bulk polymerization (10^6 to 10^8 [$l \cdot mole^{-1} \cdot s^{-1}$]), and calculating the time that two radicals could coexist in a typical particle of 1 000 Å diameter (between 10^{-2} and 10^{-3} *s*). *In the aqueous phase*, the average time between radical formation from initiator and arrival at a micelle or polymer particle is very much shorter than the average time required to terminate with another radical in the aqueous phase.

These three central assumptions concerning radical generation and termination are combined with the additional assumption that monomer *homogeneously dissolved in water* is at *negligibly* small concentration, therefore not polymerizable in the water phase. With these four assumptions, the following results are obtained:

(1) The number of monomer molecules converted to polymer per second, $-dm/dt$, in a single particle in which monomer concentration is $[M]$, is:

$$-\frac{dm}{dt} = \frac{1}{2}k_p[M] \tag{12.4}$$

The factor 1/2 arises from the "red light-green light" effect (on the average, *one* chain is growing half the time), and $k_p[M]$ has the dimensions: monomers per second per radical.

Thus if there are n particles per *cm*³, the rate per *cm*³ is $-n(dm/dt)$.

(2) *The degree of polymerization* $\bar{P}_n$ is

$$\bar{P}_n = k_p[M]\,\Delta t \tag{12.5}$$

where Δt, the "green light" period, is n/ρ, ρ being the rate of generation of radicals per *cm*³ per *second.* (The killing radical is assumed to terminate by *coupling* with the previously growing chain.)

(3) The number of particles per *cm*³, n, finally generated depends on the rate ρ of generation of radicals per *cm*³ and on the number of soap molecules available per *cm*³ of total volume, thus, upon the initial concentration of soap, c_s, given in [g/cm^3], and the area of a soap molecule in a packed monolayer a_s (as deduced for example in a Langmuir trough). The result is:

$$n \approx 0.53(c_s a_s)^{3/5}\rho^{2/5}\left(\frac{dv}{dt}\right)^{-2/5} \tag{12.6}$$

The rate of generation of radicals ρ in the aqueous phase per *cm*³ per *s* is set by concentration and type of initiator, and by temperature (cf. eq. 12.3). The volumetric rate of growth dv/dt of the particles is:

$$\frac{dv}{dt} = -\,v_u q\,(dm/dt)\ \text{, where} \tag{12.7}$$

v_u = volume of a monomer unit as polymerized.
$-v_u \cdot \frac{dm}{dt}$ = volume increase of polymer chain per *s*.
q = volume of (polymer + monomer)/volume of polymer alone, which during stage I and II is around 1.5 to 3.0, depending on thermodynamic affinity of monomer/polymer.

Solubility of Monomer in Water

When a monomer like vinyl acetate is soluble to the extent of a fraction of a weight percent, the initiator generated in the aqueous phase in effect sets off a *solution* polymerization of the dissolved monomer, but the growing polymer chains quickly become insoluble in the water and tend to cluster as colloidal aggregates. Since the soap molecules can diffuse from particle to particle throughout the medium, these can rapidly become stabilized and thereafter act as growing polymer particles, being fed with monomer from the monomer droplets, together with particles which were generated from true micelles.

Equilibrium between monomer drops and particles

One might speculate that the rate of growth of the polymer particles could be diffusion limited, that is, that the rate of diffusion of monomer from the droplets into the growing polymer particles through the aqueous phase would limit the rate at which polymerization could occur. One can readily show, assuming a diffusion coefficient (for the monomer through water) of around 10^{-5} [cm^2/sec], that, under any conceivable conditions and even with concentrations of monomer in the aqueous phase as low as 100 parts per million, the rate of flux between the monomer droplets and the polymer particles would be several orders of magnitude greater than the rate at which the monomer could be used up by polymerization in the polymer particles.

If this is true, it would seem that the monomer in the droplet phase (which, as noted above, is free of polymer) should diffuse indefinitely into the growing polymer particles.

This does *not* occur because the polymer particles are in fact in equilibrium with monomer droplets. The reason is the following: (a) the interfacial tension σ on these very small particles of radius r produces an effective excess pressure $P_{excess} = 2\sigma/r$ according to the Laplace equation. (b) This excess pressure P_{excess} increases the thermodynamic activity a_1 of the monomer of molar volume V in the particles, according to the Poynting relation:

$$\ln a_1 = P_{excess} \cdot V/RT$$

(R, T gas constant, temperature), but (c) this value of $\ln a_1 > 0$ is exactly balanced by the reduction of the thermodynamic activity of the monomer by reason of dilution from the pure state by the contained polymer of volume fraction ϕ_2, according to the Flory Huggins equation:

$$\ln a_1 = \ln(1 - \phi_2) + \phi_2 + \chi_1\phi_2^2$$

where χ_1 is the monomer-polymer interaction parameter.

Thus in combination equilibrium occurs when:

$$\frac{2\sigma}{r}\bar{V}/RT + \ln(1 - \phi_2) + \phi_2 + \chi_1\phi_2^2 = 0 \tag{12.8}$$

Because the rate of polymerization is found to be constant in many emulsion/polymerizations during stage II (see next section), it is to be inferred that the concentration of monomer in the particles: $[M_0](1 - \phi_2)$ is constant, therefore that ϕ_2 is constant, and therefore that σ/r is approximately constant. Representative values are for $r = 5 \times 10^{-6}$ cm, $\sigma \simeq 30$ dyn/cm; $\bar{V} \sim 100$ cm^3/mol; χ_1 ranges from ~ 0 to ~ 0.4, and ϕ_2 is found to range from ~ 0.25 to ~ 0.5.

12.1.5 Rate of Conversion According to Stage

Fig. 12.3 illustrates the three stages of a typical batch emulsion polymerization. In Stage I, the micellar stage, the rate of polymerization increases as particles are generated from micelles, but the increase stops at about 15% conversion of the monomer, depending of course on the total amount of soap charged to the system initially.

In Stage II, "constant rate", the monomer droplets continue to exist and the monomer concentation [M] in the polymer particles remains almost constant as noted in the preceding section.

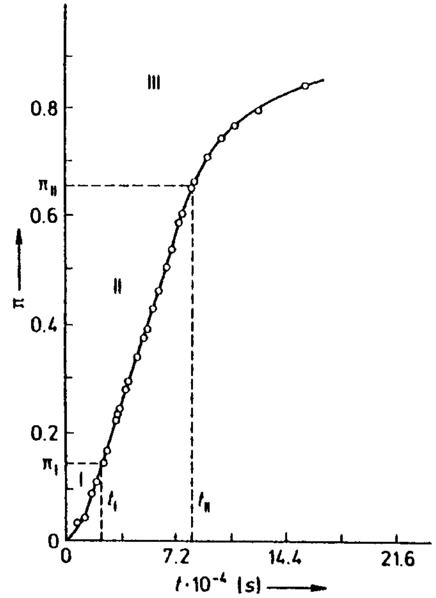


Fig. 12.3. Conversion versus time diagram for a typical batch emulsion polymerization

In Stage III, the falling rate period, the monomer droplets have been exhausted, and the monomer present in the polymer particles is the only monomer (other than the trivial amount dissolved in water) now left in the system, and this becomes progressively converted into polymer. Define π as the number of polymer units formed, divided by the total number of polymer units plus monomer units present. Thus, π is percent yield divided by 100.

Let t_I represent the time necessary to reach the end of the micellar period, at which time the fraction of monomer polymerized is π_I, and t_{II} the time at which the droplet phase is exhausted, at which time the fraction of monomer converted is π_{II}. Thus, in Stage II the difference $\Delta t \equiv t_{II} - t_I$ is the total period of operation at the constant rate condition. Consequently,

$$\int_{\pi_I}^{\pi_{II}} d\pi = \frac{1}{C}\int_{t_I}^{t_{II}} k_p [M_0] (1 - \phi_2) \frac{n}{2} dt \tag{12.9}$$

wherein k_p = propagation rate constant, $l \cdot mol^{-1} \cdot s^{-1}$
$[M_0]$ = molar concentration of undiluted pure monomer, $mol \cdot l^{-1}$
$(1 - \phi_2)$ = volume fraction monomer in particles (ϕ_2 vol. fraction dissolved polymer)
n = number of particles per cm^3 of total mixture
t = time, s
C = number of monomer molecules initially present per cm^3 of total mixture

In turn,

$$C = (f\, N_A)/(\bar{v}\, m_0) \tag{12.10}$$

where f = cm^3 of monomer charged per cm^3 of total mixture
N_A = Avogadro's number
$\bar{v}$ = specific volume of monomer, $cm^3 \cdot g^{-1}$
m_0 = monomer molecular weight, $g \cdot mol^{-1}$

If as is usually found, ϕ_2 remains constant in Stage II, (droplet phase present), equation 12.9 upon integration becomes:

$$\pi_{II} - \pi_I = \frac{k_p[M_0]\,(1 - \phi_2)}{2C}\,(t_{II} - t_I) \tag{12.11}$$

At the end of stage II the only monomer present is in the particles.
Thus *at this time* the monomer concentration in the particles is:

$$[M_0]\,(1 - \phi_2) = [M_0]\,(1 - \pi_{II}),$$

whereas throughout stage II, ϕ_2 was assumed constant while π increased.
Thus in stage III the conversion π as a function of time becomes:

$$\int_{\pi_{II}}^{\pi} d\pi = \frac{1}{C} \int_{t_{II}}^{t} k_p[M_0]\,(1 - \pi)\,\frac{n}{2}\,dt \tag{12.12}$$

which can be rearranged to give:

$$\int_{\pi_{II}}^{\pi} \frac{d\pi}{1 - \pi} = \frac{k_p[M_0]\,n}{2C} \int_{t_{II}}^{t} dt$$

from which we find

$$-\frac{\Delta \ln(1 - \pi)}{\Delta t} = \frac{k_p[M_0]\,n}{2C} \tag{12.13}$$

To illustrate the application of these calculations, we can determine from Fig. 12.4 — in which $\ln(1 - \pi)$ is plotted versus t (from the data of Fig. 12.3) — that the slope $\frac{\Delta \ln(1 - \pi)}{\Delta t}$ is -1.04×10^{-5} [s^{-1}]. Let us assume that in this experiment the number of particles n was $10^{14}/cm^3$ and that ϕ was 0.3 cm^3 of organic phase per cm^3 of total

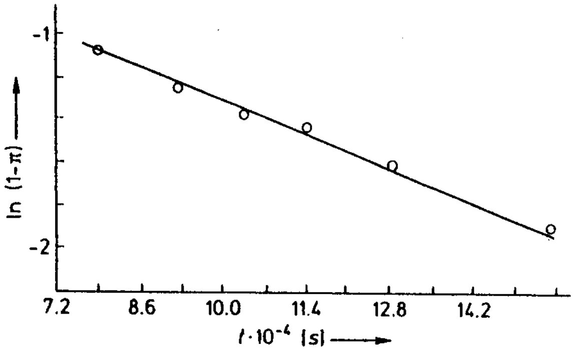


Fig. 12.4. Semi-logarithmic plot, $\ln(1 - \pi)$ versus time, of the data of Fig. 12.3

phase. The specific volume $\bar{v}$ for isoprene is about 1 [cm^3/g] and with a molecular weight of 62, the initial molarity $[M_0]$ would have been about 1,000/62 = 16 [$mol \cdot l^{-1}$]. From eq. 12.13. and these numerical values the propagation rate constant k_p should be 36 [$l \cdot mol^{-1} \cdot s^{-1}$].

12.1.6 Multiple Radical Effects in Emulsion Polymerization

The *Smith-Ewart* theory leads to the conclusion that in every polymer particle there is a *"green light" period* in which only one radical is present and is propagating, forming an increasingly long polymer chain, and that, following the entry of a second radical into this particle, the second radical immediately finds the growing macroradical and terminates it, whereupon a *"red light" period* sets in, in which there is no propagation at all in the particle. Considering typical values of the termination constant k_t as deduced from *bulk* polymerizations and calculating how long two radicals could coexist in a growing particle, if the growing particle were part of a bulk substance, one can show that the period of coexistence would be of the order of milliseconds, thus very short compared to the typical "green light" or "red light" periods, which are of the order of 1 to 100 seconds.

In reality, the polymer particle has an interface containing surfactant molecules, and the initiating radical which arrives from the aqueous phase is partially or strongly hydrophilic (a persulfate ion-radical is insoluble in an organic phase such as an isoprene-polyisoprene mixture, whereas a hydroxyl-radical might have limited solubility). In the case of a persulfate ion-radical, the arriving radical must start polymerization at the interface without invading the polymer particle, and thus the alleged termination step would have to be preceded by the growth of a short polymer chain which finally becomes long enough to drag the ionic end with its counterion into the interior of the polymer particle, and then find the end of the growing chain. This restriction might not be so severe with the hydroxyl radical, but since this radical would form an alcoholic hydroxyl, it is unlikely that it would immediately diffuse deeply into the polymer particle, until the chain which it initiated becomes sufficiently long, perhaps several ten's of monomer units. Thus, the assumption of instantaneous killing of the first radical by the second may not be exactly true under all conditions, but ordinarily the relative delay, as compared to the total propagation period or quiescent period, would be small.

However, as already noted in bulk polymerization, termination[*)] is profoundly affected as viscosity increases. In turn, viscosity in the polymer particle increases as polymer concentration increases, and as the glass transition of the monomer-polymer mixture rises (due to increasing polymer concentration) towards the polymerization temperature. In the example of isoprene cited, the glass transition would not be relevant, whereas it would become important in the polymerization of monomers such as styrene or methyl methacrylate. In all polymerizations, the concentration of polymer is bound to rise after the exhaustion of the droplet phase (stage III). Thus diffusion control of termination can lead to the existence of multiple growing radicals in a polymer particle. Monomer can still diffuse within the particle to arrive at (and be propagated by) macroradical chain ends, but the macroradicals cannot find each other because of the high viscosity of the continuum. This would correspond to the *autoacceleration* called the *Trommsdorf-Effect* in bulk polymerization. When the polymer concentration becomes such as to make the reaction temperature that of the glass transition, monomer diffusion to the radicals will diminish finally to zero.

Another way that multiple radicals could exist in a growing polymer particle, simultaneously propagating, would be if the particles have a diameter significantly greater than around 1/2 μm. In this case, because of the sheer volume of the polymer particle, a second radical arriving at the other side of the particle in which the first radical is growing may have some opportunity to propagate a chain before the two radicals find each other, even if the system is not encumbered by excessive viscosity. Ordinarily, polymer particles do not grow to diameters of this magnitude, but one can always expect to have complications if the polymer being produced has a glass transition above the temperature of polymerization.

In emulsion polymerization the temperature of polymerization effectively must exceed the freezing point of water and, at least in the micellar phase, it must be significantly less than the normal boiling point of water, since micelles are disrupted and stabilization is not obtainable if one operates close to the boiling point of water. In the third stage of an emulsion polymerization (post-micellar, and post-droplet), it is of course feasible to increase the temperature of the system above 100 °C by using a pressure vessel so as to overcome the problem of the glass transition, but this is not a problem of great industrial consequence, since most of the glassy polymers are made by methods other than emulsion polymerization and most of the polymers made by emulsion polymerization are homopolymers or copolymers whose glass transition lies well below 100 °C.

[*)] We have noted before that the true chemical reactivity is unchanged and thus k_t is not changed, but now diffusion becomes controlling.

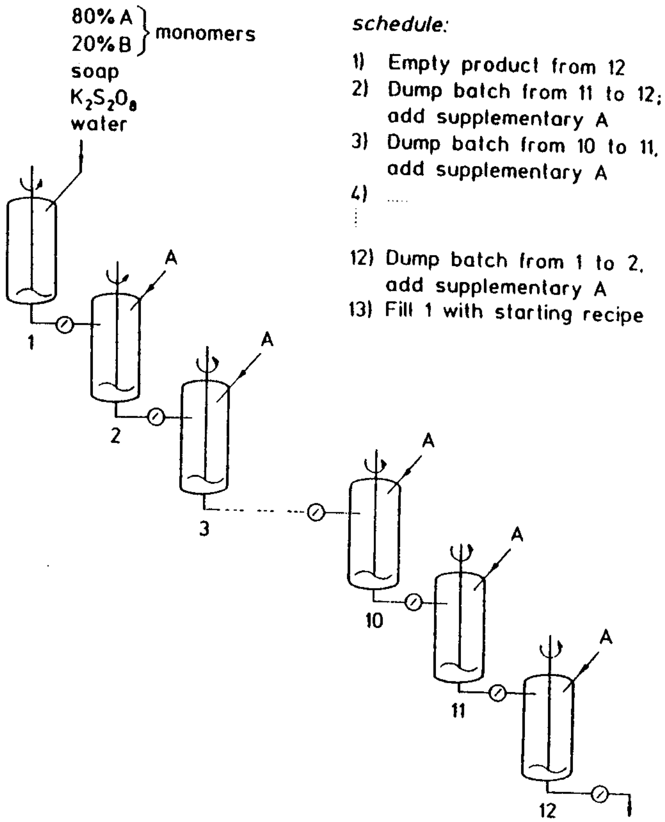
12.1.7 Emulsion Copolymerization

Emulsion copolymerization is particularly appropriate for the following monomers:

1. styrene-butadiene
2. styrene-acrylonitrile
3. acrylonitrile-butadiene-styrene
4. vinylidene chloride-vinyl chloride
5. vinyl acetate-methyl acrylate
6. acrylates-methacrylates

In order to maintain constant polymer composition (constant mole fraction of each type of unit), the monomer composition must be kept constant at a value determined by the reactivity ratios r_A and r_B.

As with emulsion homopolymerizations, this could be done using a single batch reactor, with a *feed of monomer* adjusted over the time of the process. An alternate way, used in production of butadiene styrene rubber, is illustrated schematically in Fig. 12.5.



schedule:

1) Empty product from 12
2) Dump batch from 11 to 12; add supplementary A
3) Dump batch from 10 to 11, add supplementary A
4) .....
⋮
12) Dump batch from 1 to 2, add supplementary A
13) Fill 1 with starting recipe

Fig. 12.5. Usage of a series of batch reactors to produce styrene (B) butadiene (A) rubber by emulsion copolymerization

A *series of batch reactors,* as many as twelve, are operated as shown. A batch of emulsion, starting with 80% butadiene and 20% styrene as mixed monomer, added to water, soap and initiator, is carried to a low degree of conversion, then transferred to a second reactor, to which some make-up butadiene is added, and the conversion is continued to a higher degree.

Small amounts of mercaptan may also be added to control molecular weight by promoting chain transfer. Sequential transfer of a batch of emulsion from reactor to reactor, accompanied by *correction* of the monomer composition through addition of butadiene, as the conversion is advanced, leads to a product copolymer in which all molecules have a ratio of A to B units (butadiene to styrene units) narrowly distributed around the intended average (e.g., 70:30).

It is not necessarily desirable to attain complete conversion. In diene copolymerization, branching and network formation will occur at high conversion. Thus polymerization is stopped usually at *60% to 70% conversion,* and the mixed residual monomer is recovered by steam stripping.

If two or more monomers are supplied in the *droplet* phase, their incorporation into polymer in the polymer *particles* will depend not only on reactivity ratios r_A and r_B but also on the relative *affinity* of each of the monomers for the copolymer, as measured for example by the Flory-Huggins interaction parameters $\chi_{A,\text{polymer}}$, $\chi_{B,\text{polymer}}$. Thus the problem of adjusting polymer composition is not as simple as in homogeneous copolymerizations.

12.1.8 Anomalous Emulsion Polymerization

Vinyl chloride is polymerized in large quantity by emulsion polymerization to produce *"paste grade"* resin, a fine powdered material useful in *"plastisol"* technology. Like vinylidene chloride, vinyl fluoride, vinylidene fluoride, and acrylonitrile, the polymer formed becomes insoluble in its monomer at low degrees of polymerization, and a *precipitation polymerization* ensues, as described in chapter 13. From consideration of equilibrium between monomer droplets and particles, if the monomer inside a polymer particle did not have its activity somehow reduced by interaction with polymer, diffusion from the drops could not occur. Thus we must postulate that the polymer in the particle is somewhat like a microcosmic network with some of the polymer segments being in an amorphous state, interacting with monomer.

Because of these profound differences, polymerization of the above listed monomers by emulsion polymerization differs in every respect from those in which the polymer particles are of a single phase.

12.2 Suspension Polymerization

12.2.1 Introduction

Suspension polymerization of water-insoluble monomers that can be initiated by radicals is preferred whenever it is desired to produce small spherical beads. This method is also called *pearl* or *bead polymerization.* Bead diameters range from 5 *μm* (thus one or two orders of magnitude greater than in emulsion polymerization) up to 1 *cm* (in rare cases). The organic phase, containing a single monomer (or mixed monomers) and a radical initiator, which is soluble in the monomer but not in water, is progressively added to a reaction vessel containing water, fitted with an impeller, until the volume fraction of organic phase is of the order 0.2 to 0.35. The impeller breaks this phase into drops, each of which becomes a miniature "chemical reactor", in which monomer is converted to polymer by the radicals *generated within.* Thus in terms of kinetics, those applicable to bulk radical homopolymerization or copolymerization must apply. There is no feature of emulsion polymerization present, since radical generation occurs in the same phase as the termination.

12.2.2 Problems of Fluid Mechanics

The process is one whose success depends primarily on fluid mechanics and on "fortification" of the organic-water interface. As a counter-example, if benzene were added to a volume of water progressively with stirring, droplets would result, but upon cessation of stirring the droplets would rise through buoyancy and coalesce into a supernatant layer.

Furthermore, as has been demonstrated with dye tracer experiments, if red-dyed benzene is introduced into a stirred tank of water, containing already blue-dyed benzene droplets, collision of droplets and coalescence, followed by resplitting of large drops into small, will soon lead to a population of drops uniformly purple.

If nothing were done in the case of polymerizable monomer dispersed as drops in water, the drops should become increasingly viscous during polymerization of monomer to polymer, but *redivision* after coalescence would become increasingly difficult, and finally impossible. Thus, small drops would grow into larger drops or clusters, defeating the purpose of the process.

To circumvent this, two kinds of additives are commonly used, each of which greatly enhances the stability of the organic-water interface against coalescence upon contact of two drops. One type of additive includes platelet-like mineral particles, that preferentially concentrate at the organic-water interface. It is of course essential that the proposed stabilizing particle *not* become dispersed inside the organic phase droplets, since as such it will serve no protective purpose and only contaminate the polymer.

The second kind of additive is macromolecular. These are polymers which are soluble in water, insoluble in the monomer, and capable of concentrating at the interface between the two phases. The literature abounds with examples, but *poly(vinyl alcohol)* and starch products are mostly cited.

With either type of additive, the interface is converted from one characterized by high mobility (fluidity) and low interfacial tension, to one characterized by a quasi-elastic, quasi-rigid surface of high effective interfacial tension.

Thus, once formed at the proper size, the stabilized droplets with such interfacial coatings cannot readily coalesce upon mutual contact, or further subdivide

Sometimes both mineral and polymeric additives are used together. It seems probable, but has not been conclusively demonstrated, that macromolecular additives function in yet a different way. Any solution of random coiling polymers (thus including poly(vinyl alcohol) in water) reacts so as to strongly oppose *extensional* flows. When a volume of fluid is pulled, rather than sheared, resistance is proportional to the product of extensional strain rate and of extensional viscosity (cf., resistance in shear flow is proportional to the product of *shear* strain rate and *shear* viscosity). The two viscosities are strain rate dependent but in *opposite* directions: Shear viscosity drops as strain rate increases, but extensional viscosity increases. Furthermore, even in the dilute aqueous polymer solution that constitutes the continuous phase in suspension polymerization, the *extensional viscosity* can increase by one or more orders of magnitude in regions of high strain rate. Owing to the extension of originally randomly coiled macromolecular chains, they expand to a length ultimately near that of their full contour value and thereby exert much greater drag on the solvent adjacent to it. This means that in the fluid volume near the moving tip of the impeller, where the extensional strain rate otherwise might be very high, the polymer dissolved in the water (in excess of that adsorbed at the drop-water interface) acts to reduce this strain rate, and thus the velocity (energy) with which one droplet can be impelled toward another is reduced.

12.2.3 Preferred Sequence of Operations

In view of these considerations, it is clear that for success in a suspension polymerization process, where regular spherical particles within a specified range of diameters are desired, the following sequence should be used:

(1) Premix initiator and monomer(s) to form initial organic phase.
(2) Add the organic phase to water (up to 35 *vol.-%*) under conditions of impeller agitation sufficient to produce the particle diameters desired — the smaller the particle, the higher the impeller speed needed.
(3) Add the stabilizers (mineral and/or polymeric), which should concentrate at the interface between organic drops and water.
(4) Reduce impeller speed so as to maintain gentle circulation in the vessel, adequate to prevent gravitational separation of particles from water.
(5) Raise temperature to that intended for polymerization (typically 50° to 80 °*C*) and maintain it until conversion has brought the glass transition of the bead mixture (polymer-monomer) near the polymerization temperature.
(6) Increase temperature towards 100 °*C*, sufficient to complete conversion.
(7) Lower temperature to ambient, and dump the batch onto a screen, retaining the polymer particles.

As one of the final processing steps, the collected beads may be cleared of stabilizer. For example, if carbonates were used, dilute hydrochloric acid rinse will destroy them. Polymeric stabilizers are *not* so easily removed, but hydrolysis can be employed in certain cases: For example, amylase digestion of starch.

In virtually every case, the product of suspension polymerization is glassy, rigid, and non-adhesive at room temperature.

12.2.4 Special Bead Polymerized Materials

Three products deserve special comments: "Foamable" poly(styrene), ion exchange beads, and chromatographic packings.

If styrene is suspension-polymerized in the presence of a limited quantity of cyclohexane, a poor solvent for the polymer, beads are produced which are glassy at room temperature, but contain residual *entrapped* cyclohexane, in significant percentage.

The beads can subsequently be charged into a mold cavity and rapidly heated, which causes their expansion into a closed cell foam that forms an insulating layer, after cooling to the glassy state.

In this example, it is particularly convenient to use suspension polymerization, because large cavities can be readily charged with the free flowing beads, and because the "packaging" with entrapped cyclohexane is so readily accomplished.

Uniform spherical beads of *controlled* and *narrow size* distributions are particularly desirable for packing *chromatographic* or *ion exchange columns*, since uniformity of filling space without entraining voids is essential for high efficiency. Particle diameters range from 5 *μm* in chromatographic colums to 1 to 2 *mm*, in ion exchange columns.

The polymers are invariably crosslinked for dimensional stability against pressure and changing solvents in chromatography, and to prevent dissolution in the case of ion exchange resins, following reactions which produce fixed ionic groups on the polymer.

Many of these materials are generated from divinyl benzene, or divinyl benzene and styrene. Others are generated from acrylates and divinyl benzene. Thus, to the extent that *copolymerization* is involved, these systems correspond to single charge reactions carried to completion without adjustment of monomer composition.

Inherent to many of the chromatographic and ion exchange polymer bead syntheses is the technique of introducing internal porosity by *syneresis*.

According to this principle, any polymeric network can hold an amount of solvent limited by its degree of crosslinking. The higher the degree of crosslinking, or the more adverse the solvent, the less the network can hold. Thus, for example, in a mixture of divinyl benzene and a poor solvent, e. g., cyclohexane, as polymerization and crosslinking proceeds, the polymeric material reaches a critical condition after which the cyclohexane is expelled, as the polymer becomes concentrated in strands that form the walls of pores. Further polymerization consolidates the polymer-rich phases, from which even more solvent is expelled, until in the end the polymeric material is distributed as shown in a typical scanning electron micrograph Fig. 12.6.

Control of pore size and pore volume is gained by choice of solvent/monomer ratio and the thermodynamic relation of solvent to the polymer segments. The greater the solvent content, the higher the final porosity. The poorer the solvent, the earlier syneresis occurs and the larger the pores become.

While the generation of porosity in a network by syneresis follows thermodynamic principles, unrelated to any particular form of copolymerization, the practical consequences are most commonly realized in connection with the production of chromatographic and ion exchange materials. It is also important to note that it is impractical to attempt a rigorous application of network swelling theory.

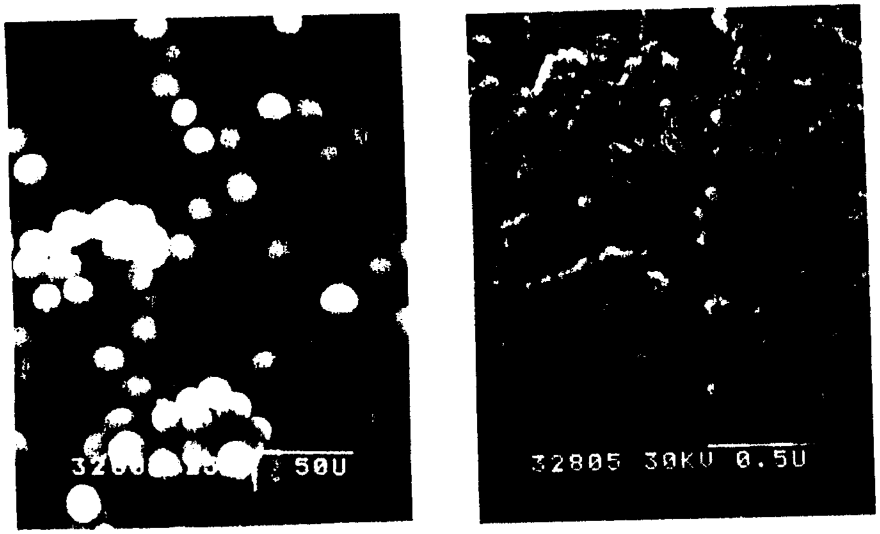


Fig. 12.6. Scanning Electron Microscope Photograph of Chromatography Packing made by suspension polymerization

Problem 12.1

Compare a homogeneous, single phase radical polymerization (*SP*) of butadiene with an emulsion polymerization (EP), and for convenience consider 1 *ml* of volume. The molar concentration of *undiluted* butadiene $[M_0] = 14.8$. Let us consider in each process a time, at which 25% of the initial butadiene has be converted to polymer. In each case the temperature will be 60 °*C* at which $k_p = 100\ [l \cdot mol^{-1} \cdot s^{-1}]$ and $k_t = 36 \times 10^7\ [l \cdot mol^{-1} \cdot s^{-1}]$.

To make a reasonable basis of comparison, we will say that in the *SP* case we start with 1 *ml* which contains 0.33 *ml* butadiene and 0.67 *ml* benzene as solvent, and we use sufficient azo compound to produce by decomposition 1×10^{12} *effective* radicals per second and per *ml*.

In the EP case, we will start with 0.33 *ml* butadiene and 0.67 *ml* water, enough sodium palmitate soap to create 1×10^{14} polymer particles per *ml*, and sufficient potassium persulfate to generate 1×10^{12} radicals per *ml* per second.

When 25% of the monomer has been converted, the micellar phase has disappeared, droplets still exist, and in the growing polymer particles the monomer concentration [M] remains steady at 7 [*mol*/*l*].

In both cases let us assume termination is exclusively by coupling. At this time in the respective processes,

— determine the rate of polymerization, i. e., the consumption of monomer per *ml* and per *s*.

— determine $\overline{P_n}$, assuming C_M and C_s are zero.

Problem 12.2

Consider two hypothetical cycles B and C relevant to emulsion polymerization, in the frame of reference of what can go on in a single particle. It is assumed that, at the instant under consideration, k_p [M] = 500 monomer units/second are being polymerized.

Time in [*s*]	*Cycle B* *Event*	*Time in* [*s*]	*Cycle C* *Event*
0	Initiating radical enters and propagation starts	0	Initiating radical enters and propagation starts
5	Chain transfer to monomer occurs	15	Second radical enters, cannot find first radical end
10	Chain transfer to monomer occurs	20	Second radical, having grown by addition, couples with end of first
15	Second radical enters, terminates chain by coupling		
30	Cycle starts again	30	Cycle starts again

Compare cycle B and C with an ideal cycle A in which *no* transfer occurs, and the red light period is exactly equal to the green light period, each being 15 seconds.

a) How does $\overline{P_n}$ differ?

b) How does the rate of polymerization differ, this being reported as monomers polymerized per particle per second of total elapsed time (red light and green light combined)?

Problem 12.3

In an emulsion polymerization of butadiene at 60 °*C*, let us assume the green light-red light period of Problem 12.1. Further assume that at the time in question a typical particle has a diameter of 1 000 Å and has a concentration of butadiene monomer of 7 molar, i. e., half of the volume is monomer and the other half polymer.

Case I: The time is just *before* exhaustion of droplet phase. Droplets exist.
As a result of one "green light" period, by what percentage will the volume of the particle increase?

Case II: The time is just *after* exhaustion of the droplets phase.
What fraction of the monomer molecules existing in the particle will be formed into polymer during one green light period?

Problem 12.4

In the emulsion polymerization of 80% butadiene (A) and 20% styrene (B), at 60 °*C*, to produce SBR, the rate of generation of radicals is 10^{13} ml^{-1} s^{-1} and th