Industrially Relevant Polymerization Processes

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In this chapter, industrially relevant polymerization methods are described in more detail. The focus is on chain growth polymerization, and special attention is paid to the heterogeneous methods—suspension and emulsion polymerization. Gas phase polymerization is dealt with separately in ▶ Sect. 11.5.

16.1 Overview

Polymerization can take place in bulk, from the gas phase, in suspension (monomer/water and, e.g., monomer/hexane), in solution, and in emulsion. Polymerization from the gas phase, but often from solution or bulk systems, is accompanied by the polymer precipitating and becoming a separate phase. The choice of method depends on the monomer, the resulting polymer, the conditions (e.g., temperature and pressure) necessary for the process, and the desired physical form of the product, so the industrial synthesis of polymers involves a broad range of methods (◘ Table 16.1).

16.2 Polymerization in Mass

Polymerization by opening the C=C double bond is an exothermal process, so polymerization in substance ("in bulk") involves substantial challenges to remove the heat generated. Moreover, viscosity problems arise, which are caused by increasing the viscosity by multiple orders (transition of a liquid to a solid). Local overheating is possible as a result of the gel effect. In this case the molar mass distribution of the product can change or the polymer becomes discolored as a result of oxidation or decomposition. One solution is to interrupt the polymerization at a conversion of 40–60% and recycling the residual monomer.

◘ **Table 16.1** Examples of the preferred industrial processes for a selection of large volume polymers

Polymer	B	S	L	P	G	E	Mechanism
High density polyethylene		+	+	+	+		z, (m)[1]
Low density polyethylene	+	+					r
Polypropylene	+	+	+		+		z, (m)[1]
Polystyrene	+	+				+	r, (m)[1]
Polymethyl methacrylate	+	+	+			+	r
Butyl rubber				+			c
ABS-polymers			+			+	r
SBS-polymers				+			a
Polyacrylonitrile				+			r

B Bulk polymerization, *S* Suspension polymerization, *L* Solution polymerization, *P* Precipitation polymerization, *G* Gas phase polymerization, *E* Emulsion polymerization, *a* Anionic polymerization, *c* Cationic polymerization, *m* Metallocene Catalyst, *r* Radical polymerization, *z* Ziegler–Natta Catalyst[1]To date, less important

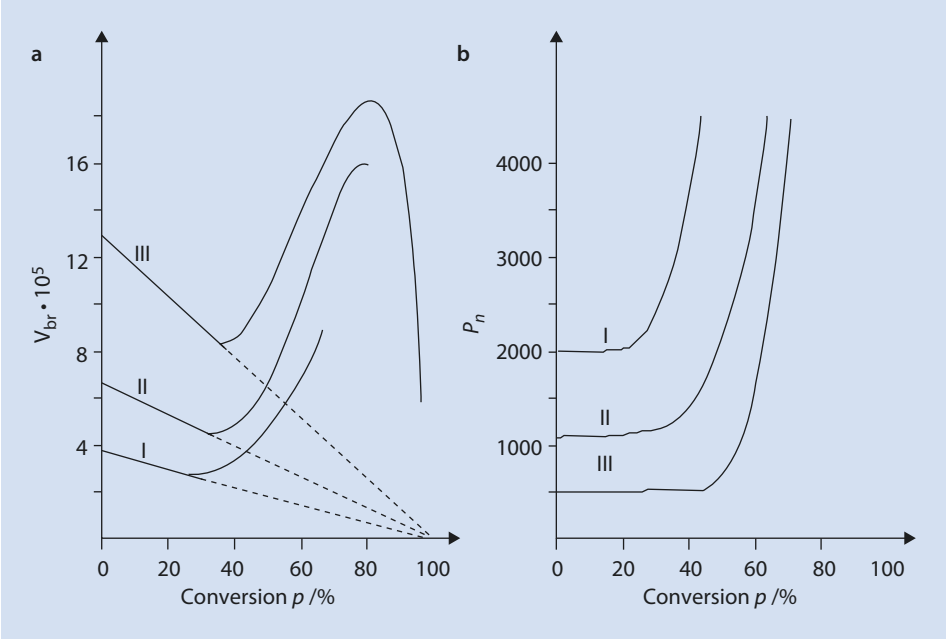


Fig. 16.1 Progress of (**a**) v_{br} and (**b**) P_n with time and the development of the gel effect ($[I]_I < [I]_{II} < [I]_{III}$). *Dashed line*: the bulk polymerization of styrene without a gel effect (Henrici-Olivé and Olivé 1958)

The *gel effect* (also referred to as the *Trommsdorff effect*) is particularly relevant for the polymerization of methyl methacrylate and styrene at high conversions, at which both the overall rate of reaction v_{br} and the average degree of polymerization P_n increase exponentially (Fig. 16.1), despite the fact that both these parameters should decrease because $v_{br} \sim [M]$, $P_n \sim [M]$, and $[M]$ decrease as conversion progresses (▶ Sect. 9.3.1).

The degree of polymerization does not increase as expected because the initiating radicals also react with the polymer as soon as polymerization begins, causing branching and higher degrees of polymerization (Fig. 16.1b). One possible explanation lies in the fact that at higher conversions during bulk polymerization the viscosity increases and, as a result, the heat dissipation becomes less efficient and the temperature increases. At the higher temperature, more radicals are formed per unit time. Thus, because

$$v_{br} \sim \left[P^{\bullet}\right] \tag{16.1}$$

the overall rate of reaction (▶ Sect. 9.2.2) increases.

Furthermore, from (9.28) and (9.31) follows:

$$P_n \sim \frac{1}{\left[P^{\bullet}\right]} \tag{16.2}$$

However, this suggests that the degree of polymerization would decrease (▶ Sect. 9.3) and is contrary to what is observed (Fig. 16.1b).

That a gel effect can also be observed when temperature control is very effective suggests it is the flexibility of the polymers that is most affected at higher conversion and

increased viscosity, whereas the mobility of the monomer molecules is hardly affected. Thus, chain growth progresses unaffected, whereas termination is considerably impaired; the reaction rate of termination decreases significantly. The following equations, derived from ▶ Chap. 9, indicate that the molecules can grow "unobstructed," although both the degree of polymerization and the reaction rate increase:

$$v_{br} = k_p \cdot \sqrt{\frac{2k_d}{k_t} \cdot [I]} \cdot [M] \tag{9.5}$$

$$P_n = \frac{k_p [M]}{\sqrt{2k_t \cdot k_d \cdot [I]}} \tag{9.32}$$

The problems associated with the gel effect and bulk polymerizations lead to this approach being unsuitable if particularly pure products are wanted (PS, MMA).

16.3 Solution and Precipitation Polymerization

Solution polymerization is not significantly different to polymerization in bulk. The same kinetic laws apply. In both polymerization methods there are problems with viscosity and temperature control at higher conversion, although both problems are ameliorated by the added solvent. Formally, bulk polymerization can also be described as solution polymerization where the monomer is the solvent for the polymer rather than another, non-polymerizable solvent. Solution polymerization is a typical laboratory method.

Industrially it is used more for elastomer polymerizations (e.g., polybutadiene, EPDM recently for special SBS grades) than for thermoplasts; it is also often employed if the polymer is to be marketed as a polymer solution such as is often the case with functional water-soluble polymers (▶ Chap. 19).

In some cases the polymer is not or is only slightly soluble in its own monomer, so that with increasing conversion the polymer precipitates. This is therefore referred to as a precipitation polymerization. In most cases, the reason for the limited solubility is that the polymers are crystalline or semi-crystalline. The kinetics are not different to those in solution. However, different reaction rates can prevail in the liquid and solid phases. The most basic assumption that only different termination rate constants apply in the monomer-rich and the polymer-rich phases (impeded termination in the polymer phase) leads to a surprisingly good explanation of the experimental results. The chemical processes obviously overshadow the diffusion and mass-transfer processes. Popular examples are VC/PVC, VF/PVF, and ACN/PAN.

16.4 Suspension Polymerization

For radical polymerizations, suspension technology is very often employed. With this method a monomer which is only slightly soluble in water is dispersed as droplets or pearls with diameters of 0.01–3 mm. To stabilize this emulsion (oil in water), protective colloids or inorganic suspension aids are added which inhibit the coalescence of the

droplets. The protective colloid in Fig. 16.2 is polyvinyl alcohol. Its hydrophobic backbone is positioned on the surface of the hydrophobic pearls and its polar functional groups, the –OH groups, face the water (Fig. 16.2).

With a monomer-soluble initiator, the polymerization is initiated by heating the reactor to the decomposition temperature of the initiator; a bulk polymerization takes place in the droplets. Each monomer droplet is a small, discontinuously operating batch reactor, optimally cooled by the surrounding water. Because of its two-phase nature, the reaction mixture—initially consisting of monomer droplets in water which becomes a mixture of polymer pearls in water with progressing conversion—retains a low viscosity similar to water even up to high monomer conversion. Thus, a considerably lower temperature gradient between the reactor contents and the coolant is observed than that existing for bulk polymerization (Fig. 16.3).

Whereas during a bulk polymerization (Fig. 16.3) the boundary layer (Fig. 16.3a) grows continuously with increasing conversion, the heat dissipation is aided significantly by carrying out the reaction as a suspension/pearl polymerization.

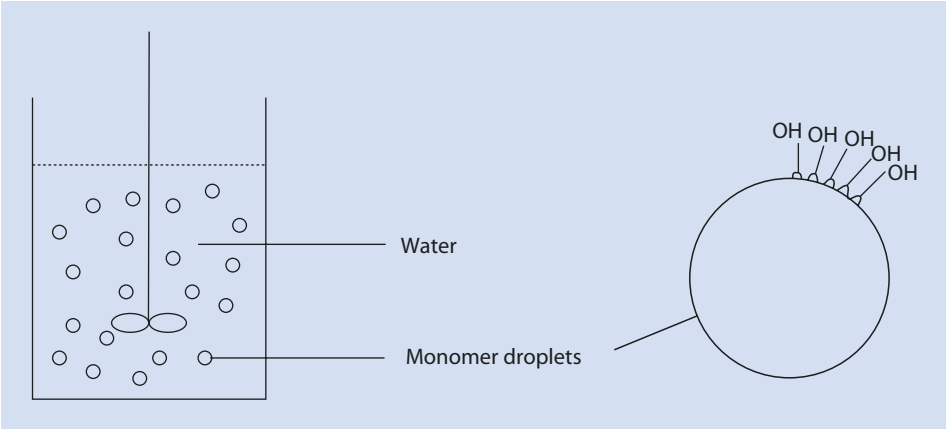


Fig. 16.2 Schematic diagram of a suspension polymerization and the mode of action of the stabilizer (polyvinyl alcohol)

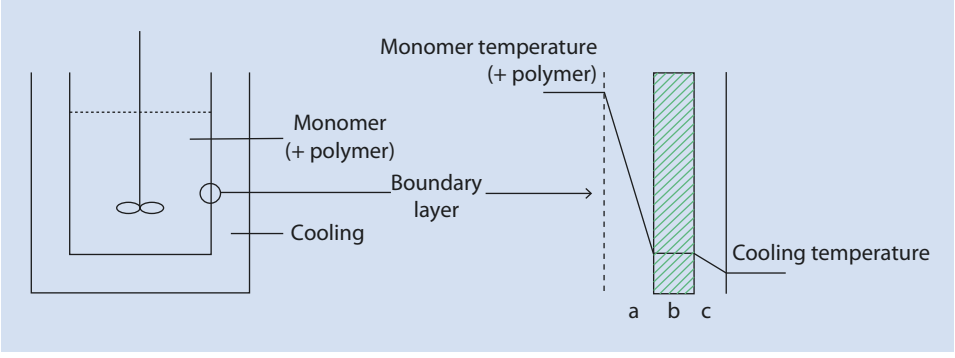


Fig. 16.3 Schematic diagram of a bulk polymerization and the temperature of the reactor zones. (**a**) Increasing temperature gradient in the monomer (and polymer) reaction mixture. (**b**) Reactor wall. (**c**) Boundary between the reactor wall and the coolant

The polymer forms as small, pearl-shaped particles which can be separated immediately. Suspension aids and protective colloids remain in the water or are easily removed from the polymer by washing. However, wastewater can, potentially, be a problem.

For a typical suspension polymerization, the following chemicals are required:

- Monomer(s) insoluble in water (styrene, methyl methacrylate, …)
- Initiator, soluble in the monomer
- Stabilizer (which preferably accumulates in the oil-water boundary layer)
- Water as dispersion agent (continuous phase)

Polyvinyl alcohol and partially saponified polyvinyl acetate, polyvinyl pyrrolidone, and methyl cellulose are typical protective colloids. As suspension agents, $BaSO_4$, $CaCO_3$, talcum, and hydroxyl apatite are often used.

The advantage of suspension polymerization over bulk or solution polymerization is emphasized in Figs. 16.2 and 16.3.

16.5 Emulsion Polymerization

The finest distribution of one liquid in another which is not miscible with it, e.g., a water insoluble monomer in water, is called an emulsion. Resulting from the effects of the emulsifier, the polymerization of a monomer which is emulsified in water is a special case and is discussed in the following section.

16.5.1 Differences Between Emulsion and Suspension Polymerization

As in suspension polymerization, in an emulsion polymerization the monomer is dispersed in water but in this case the dispersion aids are surfactants (e.g., sodium dodecyl sulfate—molecules with a hydrophilic head and hydrophobic tail). In addition, the initiators employed for the emulsion polymerization are soluble in water. The following chemicals are usually also included in a typical emulsion polymerization recipe:

- Monomer(s) not soluble in water
- Initiator soluble in water (frequently redox systems)
- Emulsifier(s) (surfactant(s))
- Buffer, complexing agent
- Water as a continuous phase

Buffers are used to maintain a stable pH level in the system because redox initiators are frequently only effective over a narrow pH range and only react via radical transition stages within this range. Hydroxyl ions (OH^-) (Fig. 16.7) may also form, for example from the reaction of H_2O_2 with Fe^{2+}, which also needs to be buffered. Complexing agents serve to control the concentration of the metal ion components of the redox system.

Recipes such as these lead to a number of features which distinguish the emulsion polymerization appreciably from a bulk or suspension polymerization.

One fundamental difference to the suspension polymerization is that the polymerization does not take place in the monomer drop but in micelles which are formed from surfactants above the so-called *critical micelle concentration* (CMC).

16.5.2 Mode of Action of a Surfactant

Surfactants are only partially soluble in water. If the threshold of molecular solubility is exceeded, the surfactant molecules occupy the air/water interface with the hydrophobic tail facing the air and the hydrophilic head in the water (Fig. 16.4a, c_1). The surfactant reduces the surface tension of the water. If the interface is completely occupied by surfactant molecules, the surface tension is at a minimum and the CMC is reached. Any further increase in the surfactant concentration (Fig. 16.4a, c_3) leads to the formation of micelles, structures of ca. 100 surfactant molecules made up of a hydrophobic middle and a hydrophilic surface, which are often spherical in shape.

Because of the relatively large range of emulsifier concentrations which have to be examined, it can prove more useful to plot a log-log-graph rather than the linear

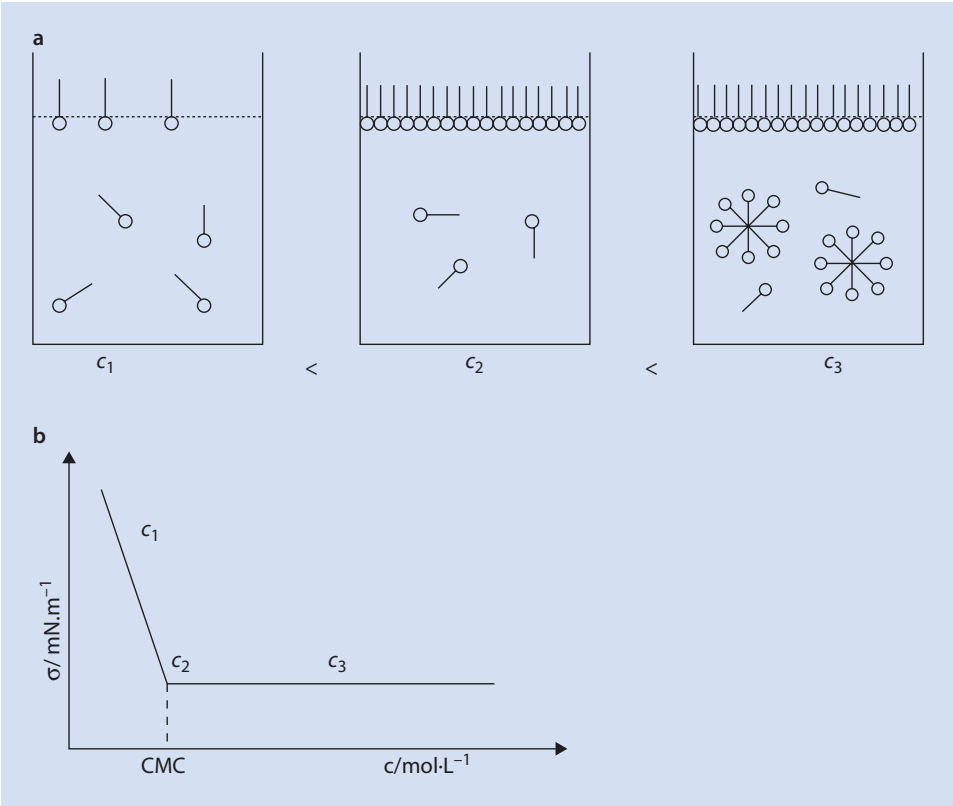


Fig. 16.4 (**a**) Localization of the surfactant at different concentrations c_1, c_2, and c_3. (**b**) Determining a surfactant's critical micelle concentration (CMC) by surface tension measurements

graph of the surface tension as a function of the emulsifier concentration shown in ◘ Fig. 16.4b.

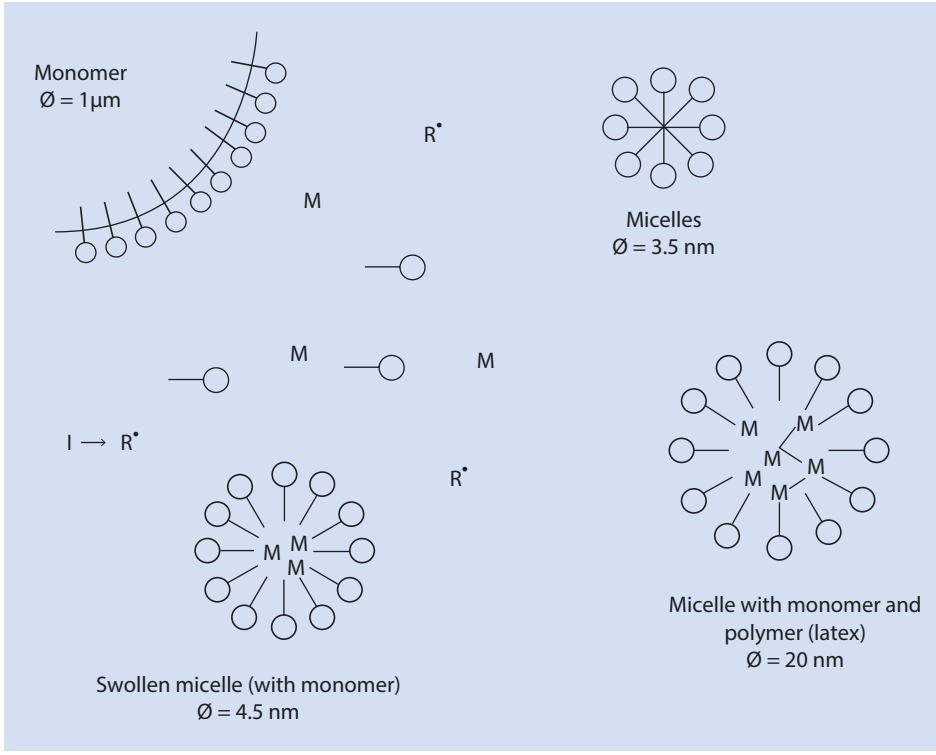
16.5.3 Kinetics of Emulsion Polymerization

A snapshot of an emulsion polymerization is shown in ◘ Fig. 16.5. In this diagram all species, the monomer droplets, micelles, micelles filled with monomer, and micelles containing polymer are shown.

According to the generally accepted model (Smith and Ewart 1948) (▶ Sect. 16.5.5), a batch emulsion polymerization involves three stages: particle formation (I), particle growth (II), and monomer depletion (III). The changes in the overall reaction rate and surface tension as the reaction progresses through these three stages are shown in ◘ Fig. 16.6 and are explained in more detail below.

16.5.3.1 Particle Formation

The monomer molecules diffuse into the hydrophobic nucleus of the micelles and become solubilized. The generation of radicals from thermally induced decomposition of initiator molecules or redox initiators is the same as for conventional radical polymerization (▶ Chap. 9). The example redox initiators as shown in ◘ Fig. 16.7 play a significant role because of their solubility in water and their effectiveness at and below room temperature.



◘ **Fig. 16.5** Schematic snapshot of an emulsion polymerization

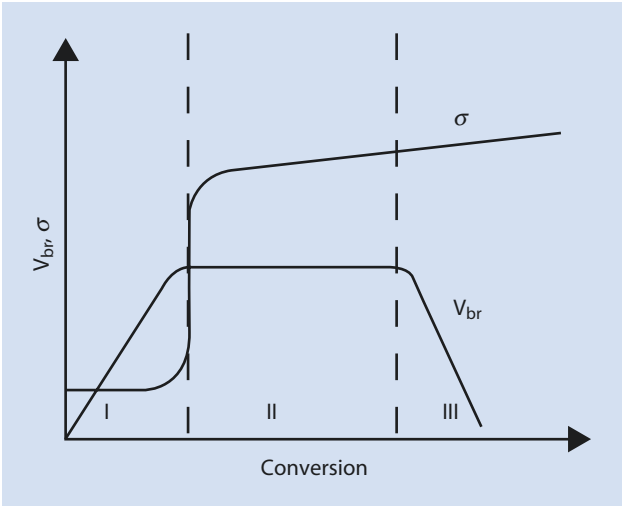


Fig. 16.6 Overall reaction rate v_{br} and the surface tension σ variation as a function of monomer conversion

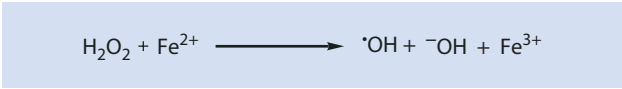


Fig. 16.7 Formation of initiator radicals by the oxidation of iron(II) with hydrogen peroxide

The –OH• radicals attack the monomers dissolved in water to form oligomer radicals. These oligomers now possess the same, and growing, impetus as a "surfactant" as the oligomer grows to diffuse into the micelle where it can continue to grow by consuming the monomer in the micelle (they become increasingly hydrophobic (the oligomer chain) and less hydrophilic (terminal –OH group)). An alternative theory is based on the concept that the growing oligomer radicals are no longer soluble in water as of a certain chain length and are stabilized by surfactant molecules which hinder their precipitation. Monomer then diffuses into the new micelle and can be polymerized. Oligomer radicals can also enter into the monomer droplets but, because the ratio of monomer droplets to micelles per cubic centimeter of emulsion is 10^{10}:10^{18}, this is highly unlikely.

The overall reaction rate steadily increases up to a total conversion of 10–15 % (Fig. 16.6). According to the assumptions above, one after another the (nano-)reactors, the monomer-filled micelles, are "switched on" by the oligomer radicals. When 50 % of all micelles are activated, the probability of an oligomer diffusing into an active or an inactive micelle is equal. A radical entering, an active micelle reacts with the radical present and the micelle is "switched off"; an inactive micelle is "switched on" by the entering radical. Thus, at this stage the overall reaction rate no longer changes[1] and the particle growth stage begins.

1 It is known from many studies that the assumption of merely one radical per micelle is extremely simplified and that multiple radicals can indeed coexist in the latex.

16.5.3.2 Particle Growth

In this stage, all the initially formed monomer droplets remain. They are, however, decreasing in size as the monomer diffuses into the water phase. From the water phase the monomer molecules diffuse into the micelle because of their limited solubility and the Nernst distribution law. Because the concentration of the monomer remains constant in the monomer droplets (the molar concentration of the pure monomer does not depend on the size of the droplets) and in the water phase (the number of active micelles does not change), the overall reaction rate remains constant up to a conversion of 50–60 %. Monomer is replaced in the active micelles at the same rate as it is consumed.

The micellar nanoreactors are also referred to as *latex particles*. In this stage of the reaction their diameter increases from about 3.6 nm (micelle) to 20 nm (latex). During the particle formation (stage I) and particle growth (stage II), polymerization and, as a consequence, particle growth occur in the active micelles. The surfactant molecules required to stabilize the growing surface area of the growing particles are initially supplied by the inactive micelles until the supply of these is depleted. Thereafter the surfactants in the air/water interface and finally those surfactant molecules dissolved in the water phase are used. As a result, the surfactant concentration becomes ever smaller, and the surface tension increases, until the CMC is reached (◘ Fig. 16.6).

16.5.3.3 Monomer Depletion

When the monomer droplets have all been consumed, fresh monomer is no longer available and the monomer concentration in the latex particles decreases, leading to a decrease in the rate of polymerization.

In an emulsion polymerization the polymerization takes place almost exclusively in the micelles and only in exceptional cases in the monomer droplets, as is the case in a suspension polymerization.

This can be verified by:

- The characteristic kinetics
- The latex particle size at the end of polymerization whereby the largest particles are smaller than the smallest monomer droplets
- Direct observation of the increasing size of the micelles during polymerization with the aid of electron microscopy, light scattering, or ultracentrifugation
- Statistical considerations, according to which it is highly unlikely that an oligomer radical formed in water encounters a monomer drop instead of a micelle
- Interrupting polymerization after a conversion of 5% and breaking the emulsion by adding a few drops of aqueous HCI so that it separates into two phases; almost all the polymer can be found not in the oil phase, but in the water phase

16.5.4 Polymerization Rate and Degree of Polymerization

As for bulk and solution polymerization, the polymerization speed can be written as

$$-\frac{d[M]}{dt} = k_w [M][P^\bullet] \tag{9.4}$$

Because the polymerizing radicals are present in the micelles, $[P^\bullet]$ is proportional to the number of micelles N_{Mic} and the radicals $\bar{n}$ per micelle:

$$[P^\bullet] = \bar{n} \cdot \frac{N_{Mic}}{N_L} \tag{16.3}$$

$\bar{n}$	Average number of radicals per micelle
N_{Mic}	Number of micelles per liter
N_L	Loschmidt's number

With (9.4) and (16.3) one obtains for the rate of polymerization:

$$-\frac{d[M]}{dt} = k_p [M] \cdot \frac{N_{Mic}}{N_L} \cdot \bar{n} \tag{16.4}$$

Assuming that only one radical can exist per micelle, because any additional radical terminates the growing chain by combination and only a further radical can re-start chain growth, $\bar{n}$ equals 1/2. This assumption is reasonable for the beginning of polymerization. However, with increasing particle diameter and the viscosity within the particles, it becomes likely that multiple radicals can coexist inside a single latex particle and do not directly encounter one another.

If transfer reactions are ignored, the degree of polymerization P_n is given by (▶ Sect. 9.3)

$$P_n = \frac{v_p}{v_t} = \frac{k_p [M] \cdot N_{Mic} \cdot \bar{n}}{N_L \cdot 2k_z \cdot f \cdot [I]} \tag{16.5}$$

If more surfactant is added, the number of micelles N_{Mic} increases, so that both rate and the degree of polymerization increase. The initiator concentration does not have any influence on the polymerization speed, unlike in bulk and suspension polymerizations. However, more initiator means more frequent "turning off and on" of the polymerization in the micelles so that the degree of polymerization is decreased.

From a comparison between a polymerization of butadiene in solution and in emulsion, it can be shown that the emulsion polymerization progresses two magnitudes faster and yields polymers of considerably higher molar mass (Echte 1993).

16.5.5 Quantitative Theory of Smith and Ewart

The first satisfactory quantitative description of an emulsion polymerization was achieved by Smith and Ewart (1948). It is based on the following assumptions.

Starting with the basic kinetics of radical polymerization:

$$v_{br} \cong v_p \tag{16.6}$$

$$-\frac{d[M]}{dt} = k_p [M]\left[P^{\bullet}\right] \tag{9.4}$$

$$\left[P^{\bullet}\right] = \bar{n} \cdot \frac{N_{Mic}}{N_L} \tag{16.3}$$

$$-\frac{d[M]}{dt} = k_p [M] \cdot \frac{N_{Mic}}{N_L} \cdot \bar{n} \tag{16.4}$$

The radicals are formed in the water phase and enter *a single* latex particle with a rate ρ (number of radicals/(s · cm^3)):

$$\frac{dn}{dt} = \frac{\mathbf{r}}{N_{Mic}} \tag{16.7}$$

n Number of radicals in the latex particle

The radicals can also exit the latex particle again (desorb):

$$-\frac{dn}{dt} = k_0 \cdot S \cdot \left(\frac{n}{\upsilon}\right) \tag{16.8}$$

S Surface of the latex particle

υ Volume of the latex particle

k_0 Desorption rate constant

Two radicals in one latex particle can combine and terminate chain growth:

$$-\frac{dn}{dt} = 2k_t \cdot \frac{n(n-1)}{\upsilon} \tag{16.9}$$

Each radical can now only react with $(n-1)$ radicals—it cannot react with itself.

If we look at the dispersion at the point in time t, it thus contains

N_0 Latex particles without radicals

N_1 Latex particles with one radical

N_2 Latex particles with two radicals

⋮

N_n Latex particles with n radicals

The sum of all micelles (N_{Mic}) is then given by equation (16.10):

$$\sum_{n=0}^{n} N_n = N_{Mic} \tag{16.10}$$

Resulting from this, the average number of radicals equals

$$\bar{n} = \frac{0 \cdot N_0 + 1 \cdot N_1 + 2 \cdot N_2 + \cdots + n \cdot N_n}{N_0 + N_1 + N_2 + \cdots + N_n} = \frac{\sum_{n=0}^{n} n \cdot N_n}{\sum_{n=0}^{n} N_n} \tag{16.11}$$

How are the latex particles N_n formed that are filled with n radicals?

1. When each radical enters a latex particle N_{n-1} with $(n-1)$ radicals
2. When each radical exits a latex particle with $(n+1)$ radicals
3. At each termination between two radicals and a latex particle N_{n+2} with $(n+2)$ radicals

For the stationary state, the formation of N_n equals the decrease of N_n, so that

$$\begin{aligned} &N_{n-1} \cdot \frac{\rho}{N} + N_{n+1} \cdot \frac{k_0 \cdot S}{\upsilon} \cdot (n+1) + 2N_{n+2} \cdot \frac{k_t}{\upsilon} \cdot (n+2)(n+1) = \\ &N_n \cdot \frac{\rho}{N} + N_n \cdot \frac{k_0 \cdot S}{\upsilon} \cdot n + 2N_n \cdot \frac{k_t}{\upsilon} \cdot n(n-1) \end{aligned} \tag{16.12}$$

With the condition that radicals do not exit latex particles, i.e., $k_0 = 0$ and that two radicals combine very rapidly, i.e., $\rho/N \ll k_t/\upsilon$, it holds that

$$\begin{aligned} &N_0 \cdot \frac{\rho}{N} + \underbrace{N_2 \cdot \frac{k_0 \cdot S}{\upsilon} \cdot 2}_{=0,\text{since } k_0=0} + \underbrace{2 \cdot N_3 \cdot \frac{k_t}{\upsilon} \cdot 3 \cdot 2}_{=0,\text{since } N_3=0} = \\ &N_1 \cdot \frac{\rho}{N} + \underbrace{N_1 \cdot \frac{k_0 \cdot S}{\upsilon} \cdot 1}_{=0,\text{since } k_0=0} + \underbrace{2 \cdot N_1 \cdot \frac{k_t}{\upsilon} \cdot 1 \cdot 0}_{=0,\text{since one factor is } 0} \end{aligned} \tag{16.13}$$

If a desorption doesn't occur and the radicals combine rapidly, N_3 equals zero.

Thus

$$N_0 \cdot \frac{\rho}{N} = N_1 \cdot \frac{\rho}{N} \tag{16.14}$$

$$N_0 = N_1 \tag{16.15}$$

$$\bar{n} = \frac{0 \cdot N_0 + 1 \cdot N_1}{N_0 + N_1} = \frac{N_1}{N_1 + N_2} = \frac{1}{2} \tag{16.16}$$

Equation (16.16) implies that a polymerization only takes place in every second micelle. A radical that now enters a micelle either terminates the growing chain or starts a new one. If the above requirements are not met, deviations from this simple result can be expected. A comprehensive solution of (16.12) was achieved by Stockmayer and O'Toole (Stockmayer 1957; O'Toole 1965).

16.5.6 Applications, Advantages, and Disadvantages of Emulsion Polymerization

Industrially, this polymerization method is of great importance; for example, polyvinyl chloride, polystyrene, polyacrylates, and polyvinyl acetate are produced with this method, among others. In many cases polymers are not used as such, but as dispersions (e.g., as emulsion paints, paper coatings, and glues). The polymers can also be separated from the water phase with spray driers, roller driers, or by coagulation, filtering, and drying. However, in most cases the emulsifier remains in the polymer and affects its properties.

The advantages of emulsion polymerization are (1) the process management in water is conducted without organic solvents and (2) the viscosity of the system remains low up to high solid contents so that, as with suspension polymerization, the heat of reaction can be removed without problems. The polymerized emulsion is, in many cases, ready for use. However, all the additives remain in the polymer.

16.6 Gas Phase Polymerization

Gas phase polymerization is most relevant in the catalytic polymerization of olefins such as ethylene and propene and is discussed in ► Sect. 11.5.

References

Echte A (1993) Handbuch der Technischen Polymerchemie. Chemie Weinheim, S 326
Henrici-Olivé G, Olivé S (1958) Kinetic measurements regarding Trommsdorff effect in polystyrene. Kunststoffe—Plastics 5:315–320
O'Toole JT (1965) Kinetics of emulsion polymerization. Appl Polym Sci 9:1291–1297
Smith WV, Ewart EH (1948) Kinetics of emulsion polymerization. J Phys Chem 16:592–599
Stockmayer WH (1957) The kinetics of emulsion polymerization. J Polym Sci 24:314–317