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DISPERSED-PHASE POLYMERIZATION PROCESSES

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14.1 INTRODUCTION

In dispersed-phase polymerization processes, one or more of the ingredients may be partially or completely insoluble in the continuous phase. The continuous phase is typically water, but this is not always the case. Nowadays, supercritical carbon dioxide (scCO$_2$) or other compressed fluids can be used as continuous phase (Chapter 15). The polymerization usually takes place or proceeds at a faster rate in the dispersed phase. Dispersed-phase polymerization processes have the advantage of producing a reaction mass of low enough viscosity as to be carried out in reactors or equipments with conventional mixing. Another key advantage of these processes is the good heat release rate that allows for adequate temperature control. One major disadvantage is a reduced productivity, compared to bulk polymerization processes. Depending on the solubility of the ingredients (monomer and initiator, mainly) in the continuous phase and the droplet/particle size range of the dispersed droplets or particles, the processes are classified as dispersion, precipitation, suspension, or emulsion polymerizations (or variations of the latter). The differences and major issues associated with these processes are explained in the following subsections. An emphasis is placed on emulsion polymerization, given its complexity and commercial importance. In particular, this chapter provides the fundamentals of the emulsion polymerization process as well as an overview of related subjects such as particle morphology, control of particle size dispersity, characterization of latexes, micro- and miniemulsion polymerization, controlled free-radical polymerization (CRP) in aqueous systems, and applications of polymer latexes. A section on suspension polymerization is also included.

14.2 EMULSION POLYMERIZATION

14.2.1 Historical Developments

The word *latex* has become a generic term that applies to all kinds of polymer colloidal dispersions, including those found in nature and those obtained by emulsion polymerization. Latex obtained from the sap of certain trees was used around 1600 BC by the Mayas in the ancient Mesoamerica for medicines, paints, manufacturing of rubber balls, waterproof cloths, and other rubber artifacts [1]. At present, there are a vast number of applications of polymer latexes, some of which are mentioned below. The growing variety of applications and environmental concerns has constituted the driving force for the development of this field.

For a long time, natural rubber covered the demand of this kind of material; however, eventually the need for producing synthetic rubber arose (specifically during the Second World War) and the effort focused to mimic natural latex. It seems to be accepted [2–4] that the earliest reports regarding polymerization of monomers in the form of an aqueous emulsion are some patents by Farbenfabriken Bayer in 1909–1915. Toward the end of the 1940s, Harkins' theory was published [5], which is considered the most important qualitative theory of emulsion polymerization; for previous works, see References 2, 4, 6, and 7. Harkins' work was the precursor of the Smith and Ewart's quantitative theory [8]. These pioneering theories have been the starting point or the base of many studies for several decades, which reflect the difficulties and successes in advancing the understanding of this complex heterogeneous process. There are several reviews in the literature regarding the advances and controversial issues in

the field of emulsion polymerization [4, 9–16]. For the sake of clarity and given the colloidal nature of the latex, before starting with the analysis of the emulsion polymerization topic, some aspects of colloid science relevant to emulsion polymerization are treated in this chapter. For a deeper insight on this topic, readers can refer to colloid science textbooks [17–19], or chapters devoted to colloid stability in emulsion polymerization textbooks [20–22].

It is worth mentioning that it is not intended here to provide an exhaustive review of the area but to highlight only those references that can be useful as starting points for further reading.

14.2.2 Principles of Colloid Science

Colloid Science is the science of both large molecules and finely subdivided multiphase systems whose characteristic dimension is between ~1 nm and ~1 μm [18]. Such dimensions are large in comparison with atomic dimensions [23], and so we use the terms *continuous phase* and *dispersed phase* to refer to the medium and to the particles in the colloidal size range, respectively.

E*mulsions*, *suspensions*, and *dispersions* are examples of colloidal systems. It is important to mention that these terms are not always used consistently in the literature and that this situation may be confusing for students and nonpolymer scientists [24]. From the point of view of polymer science and engineering, these terms refer to heterogeneous polymerizations, particularly polymerizations in aqueous/alcoholic dispersed media. Thus, the aforementioned terms have connotations that have to do with the initiator, monomer, and polymer solubility in each phase as well as with particle size and the main locus of polymerization. These aspects are treated in detail later; for the moment, let us assume that there are no chemical reactions and that such terms are used in the context of colloid science.

14.2.2.1 Colloid Stability
In most cases, the fine dispersion of one phase into another is not a thermodynamically favored process, and hence interfacial area tends to be minimized. However, there are lyophobic colloids that notwithstanding they are thermodynamically unstable exhibit *kinetic* stability. Many two-phase mixtures do not undergo interfacial area changes over very long periods of time. The process by which the interfacial area is reduced is called *coagulation*, which refers to the fusion of two or more small particles to form a single larger particle. In the *aggregation* process, on the other hand, the small particles come together but they do not fuse, and they retain their identities instead; the aggregates look like a bunch of grapes. The greater the difficulty for the particles to coagulate or aggregate, the greater their kinetic stability. Unless

otherwise stated, in this chapter, the term *colloid stability* means kinetic stability, a usual practice in the literature.

Colloid stability comes from the interaction forces between neighbor particles. Such interactions are the result of repulsive (electrostatic and/or steric) and attractive (van der Waals) forces. The net potential energy is the sum of both kinds of interactions, and its height is analogous to the activation energy in ordinary reaction chemistry. This energy barrier serves as an obstacle along the path to coagulation. Quantitative description of such interaction forces constitutes what is known as the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory formulated in the 1940s. For more details about this theory, the reader is referred to textbooks [18, 19] and references cited therein.

14.2.2.2 Surfactants in Aqueous Solution
A very important component that is usually present in the lyophobic colloids is the surfactant. These molecules are amphiphilic, that is, a part of the molecule is much more polar than the other part. On the basis of the nature of the polar groups in the surfactant molecule, they are classified as ionic (anionic or cationic) and nonionic. When ionic-type surfactants are adsorbed onto polymer particles, they provide stabilization by electrostatic repulsion between them and when the nonionic type are adsorbed instead the mode of stabilization is by steric repulsion. Electrosteric stabilization is provided by polyelectrolyte chains that give place to both modes of repulsion: electrostatic and steric.

When a relatively small amount of surfactant is added to water, part of it is dissolved; the dissolved molecules move freely in the aqueous phase. The other part is reversibly adsorbed on the interfaces present. The free and adsorbed surfactant molecules are subject to an adsorption/desorption equilibrium. The greater their affinity to the substrate, the stronger their adsorption. The well-known Langmuir equation is often used to quantitatively describe the adsorption of surfactants, particularly in the case of anionic surfactants. For other types of surfactants or mixtures of them, other equations may apply; for details in this regard, the reader is referred to specialized textbooks [25, 26] and articles [27–29].

If more surfactant is added to water such that its concentration exceeds the *critical micelle concentration* (CMC), then solute molecules aggregate to form clusters, known as *micelles* [30], of roughly spherical shape and the interfacial concentration reaches its saturation value, which is equal to $1/a_s$, where a_s is the specific area of a given surfactant adsorbed onto a given substrate. Surfactant molecules aggregate with their hydrophobic tails pointing to the center of the sphere (the core of the micelle) and their hydrophilic part at the micelle surface, in contact with the water phase.

For the case of ionic surfactants, the attainment of the *CMC* is not the only necessary condition to form micelles; the *Kraft point* (T_k) of the surfactant has also to be taken into account. If the temperature is below T_k, a given surfactant is not soluble enough to reach the CMC and thus micelles are not formed. T_k values for several surfactants are reported in Reference 25 and in manufacturers' technical sheets.

For the case of nonionic surfactants, such as poly-oxyethylenated surfactants, their aqueous solutions become turbid if they are heated to a temperature known as *cloud point* [25].

14.2.2.3 Emulsions

When a relatively small amount of a hydrophobic liquid is added to a surfactant aqueous solution containing micelles, part of it is dissolved in the aqueous phase and the other part is solubilized inside the micelles, leading to an increment of the aggregation number and micelle size as well [31]. There is an upper limit to the amount of hydrophobic liquid that can be solubilized in a given surfactant solution. Below this limit, a microemulsion is obtained and beyond this limit a macroemulsion is formed if the mixture is subject to agitation. In the latter case, the excess solubilizate leads to the formation of droplets (diameter $\sim 1 - 10^3$ µm), which are much larger than micelles (diameter $\sim 10^4$ nm for ionic surfactants). In the absence of agitation phase-separation occurs forming what is known as a *Windsor I system*, where the lower layer is an oil in water microemulsion and the upper layer is formed by the hydrophobic liquid [19, 32, 33].

The droplet average size (DS) and droplet size distribution (DSD) of the macroemulsion so obtained depend on the volume fraction of the dispersed phase, the geometry of the vessel and impeller, stirring speed, as well as on physical properties of the continuous and dispersed phases, such as density and viscosity, and on interfacial properties [34–39].

The addition of co-stabilizers and the use of high efficient homogenization devices produce miniemulsions [40] where the droplet size (diameter $\sim 10^1 - 10^3$ nm) is intermediate between that of swollen micelles and the droplets present in a macroemulsion [41]. Besides the size of the droplets, another major distinction among macroemulsions, miniemulsions, and microemulsions is the stability that they exhibit.

In macroemulsions the DSD is determined by a droplet breakup-coalescence process. Breakup occurs only in the region very near the impeller, while coalescence occurs in the rest of the reactor, which is used to recirculate material back to the impeller [37]. Microemulsions, on the other hand, are thermodynamically (permanently) stable. Stability of miniemulsions lies in between those of macroemulsions and microemulsions.

14.2.2.4 Monomer Partitioning and Swelling in Polymer Colloids

Given the biphasic nature of the polymerization systems we are interested in, it is basic to know how their different components are distributed between the phases and the colloidal entities present in such systems. This distribution of components determines the contribution of the continuous phase and of the different colloidal entities to the overall rate of polymerization (R_p). For the case of copolymerizations, monomer partitioning defines the copolymer composition obtained because this depends on the concentration of monomers in the polymerization site, which can be different from the composition feed. Several models have been reported in the literature to quantitatively describe monomer partitioning in aqueous heterophase polymerizations. These approaches can be classified in two groups: those based on partition coefficient models [42–46] and those based on more fundamental thermodynamic considerations [47–52]. A simplified thermodynamic approach has been investigated by German and coworkers [53–58]. Dafniotis and Saldívar [52] and Gugliotta et al. [59] have compared the results of monomer partition models of different levels of complexity and have pointed out that selection of the model to be used is based on a good balance of simplicity, accuracy, and data availability.

Morton, Kaizerman, and Altier (MKA) [60] made the first contribution to the problem of describing the thermodynamics of partitioning and swelling. They obtained an equation for equilibrium swelling of polymer particles by a solvent. Such equation is commonly referred in the literature as *Morton* or *MKA equation*. According to this equation, when the polymer (subscript P) is in equilibrium with free solvent (subscript A), the following condition exists:

$$\left(\frac{\Delta G}{RT} \right)_A = \left[\ln \left(1 - \phi_P \right) + \left(1 - m_{AP} \right) \phi_P + \chi_{AP} \phi_P^2 \right] + \frac{2 \gamma \overline{V}_A}{r RT} \tag{14.1}$$

The terms between the brackets correspond to the osmotic contribution to the Gibbs free energy (ΔG), and they also constitute the standard expression for ΔG of the Flory–Huggins theory of polymer solutions [61], where ϕ_P is the volume fraction of polymer and m_{AP} the ratio of the equivalent number of molecular segments of solvent to polymer (usually expressed as the ratio of molar volumes of solvent and polymer). χ_{AP} is the Flory–Huggins interaction parameter of solvent and polymer and the last term of Equation 14.1 is the interfacial free energy contribution where γ is the interfacial tension, V_A the molar volume of solvent, and r the particle radius. T is temperature in Kelvin and R is the universal gas constant.

Modifications to the MKA equation have been proposed to take into account the swelling pressure and the dependence of the interfacial tension (γ) and the Flory–Huggins interaction parameter (χ) on particle size [62, 63] as well as the presence of adsorbed surfactant on particle swelling [64, 65]. These modifications have allowed to obtain better agreement between theory and experimental data for the swelling of polystyrene particles using reasonable parameter values.

14.2.3 Formulation Components in Emulsion Polymerization

There are several formulation components that can be present in an emulsion polymer (latex) formulation, which can be added before, during, or after the polymerization reaction. This section is intended to provide the reader with an overview on the role of each component, as well as their in impact the process and/or the product.

14.2.3.1 Monomers   The solid (essentially polymer) content of most of the commercial latexes is in the range of 45–55%, although for special applications and kinetic studies lower overall monomer concentrations are used.

One of the most important bulk property variables of polymers is the glass transition temperature T_g, which must be well below the use temperature to allow the interdiffusion and entanglement of polymer chains when the particles get in contact, once the aqueous phase has been evaporated. Thus, the monomer(s) used have to be selected such that the desired T_g is obtained. Useful tables showing T_g and other physical and chemical properties of homopolymers are available in the literature [66–68]. The well-known Fox equation [69] can be used to estimate the T_g of a copolymer as a function of monomer composition and T_gs of the component monomers. It is important to take into account that polar polymers tend to hydroplasticize, reducing the T_g in the film formation process [70]. Several commercial latexes are terpolymers that contain two of the monomers present in major amounts to grossly obtain the basic desired properties, with the third monomer present in a minor amount for fine tuning of a special property [71–73].

14.2.3.2 Water   Most modern emulsion polymerization processes use deionized water because the ionic species naturally present in water affect colloid stability. Ion exchange and inverse osmosis are the most common water deionization methods [74].

Oxygen content is important because this element is a free-radical scavenger that can act as an inhibitor or a retardant in emulsion polymerizations depending on the water solubility of the monomer(s) [75] and stirring [76–78].

14.2.3.3 Water-Soluble Initiator   There are two types of water-soluble initiator systems used in emulsion polymerization: dissociative and redox initiators [2, 79–89]. Inorganic persulfates are by far the most widely used class of dissociative initiators for emulsion polymerization reactions, in which the persulfate ion undergoes (thermal) homolytic dissociation into two sulfate radical anions. Redox initiators, on the other hand, are systems comprising a reducing agent and an oxidizing agent whose mutual interaction produces free radicals. Dissociative initiators are used in the temperature range of 50–90 °C, while redox initiators produce free radicals even at low temperatures, such as 5 °C. Low polymerization temperatures are used when crosslinking is to be avoided, as in the production of random styrene–butadiene rubber copolymer.

14.2.3.4 Surfactants   These substances are also known as *emulsifiers* or *soaps* and are typically used in the range 1–6% by weight with respect to monomer. Extensive practical testing is likely to be required to determine the least expensive emulsifying system that will give good performance during and after the polymerization process, as well as acceptable results in a given application.

Concerning performance during emulsion polymerizations, the surfactant should provide stability to the latex particles protecting them from mechanical coagulation, avoiding N (the number of particles per unit volume) to decrease [76] and minimizing the formation of macroscopic flocs or coagulum in the latex, or over the surfaces of the process equipment.

Nonionic surfactants enhance freeze-thaw, shear and electrolyte stability, but, on the other hand, they can reduce the free radical entry into particles [90–95] and R_p [96]. Thus, they are not normally used as the sole emulsifying agent in emulsion polymerization [96–101]. Sometimes the reaction is started in the presence of only an anionic surfactant, and a steric stabilizer is added at a higher conversion or as a poststabilizer.

A system named HLB (hydrophilic–lypophilic balance) constitutes a useful guide to the selection of a suitable surfactant for a given dispersed phase [2, 25, 97, 102].

14.2.3.5 Chain Transfer Agents   Chain transfer agents (CTAs) are used in free-radical emulsion polymerization to reduce the molecular weight of the produced polymer. For this purpose, mercaptans of high molecular weight are often used [103–107], which are alkyl compounds containing from 7 to 14 carbon atoms. A review of substances used as CTAs is provided in chapter 8 of Blackley's book [2]. The usage of surfactants with chain transfer agent properties ("transurfs") [108, 109] and catalytic CTAs [110] has also been studied.

14.2.3.6   Other Components   Other components of emulsion polymerization systems include electrolytes and sequestering agents. Sometimes electrolytes are added to act as buffers and to avoid the hydrolysis of monomers containing the ester group or the acceleration of persulfate initiators decomposition as well [79, 111]. It has to be kept in mind that the addition of electrolytes has an influence on the colloidal stability of the latex, CMC, micellar aggregation number, and adsorption of surfactant, as well as on other physicochemical phenomena [25].

It is common industrial practice to add very small amount of compounds such as ethylenediamine tetra-acetic acid to sequester traces of calcium and magnesium ions [2].

14.2.4   Overall Description of Emulsion Polymerization

As explained before, when surfactant, water, and monomer(s) are mixed, the colloidal system obtained consists of monomer-swollen micelles (if the surfactant concentration exceeds its CMC) and monomer droplets dispersed in an aqueous phase that contains dissolved molecules of surfactant and a small amount of the sparingly water-soluble monomer(s). When free radicals are generated in the aqueous phase by action of an initiator system, then the emulsion polymerization takes place. Its evolution is such that the colloidal entities initially present tend to disappear and new colloidal entities (polymer latex particles) are born by a process called *nucleation*. For convenience, we first focus on the particle nucleation mechanisms, a very important aspect of emulsion polymerization.

14.2.4.1   Nucleation Mechanisms   Particle formation can occur by homogeneous nucleation, micellar nucleation, or both mechanisms. In any case, the process begins with the generation and subsequent propagation and side reactions of free radicals in the aqueous phase [81, 112–114]. Most of these free radicals are amphiphilic in nature because they are formed by a hydrophobic propagating tail that has in its extreme a hydrophilic group that comes from the initiator. As the oligoradicals add more monomeric units in the aqueous phase, they become more hydrophobic until they reach a critical degree of polymerization, j_{cr}, at which these molecules are no longer water soluble and they separate from the solution forming a new particle called *primary* or *precursor particle*. This mechanism is known as *homogeneous nucleation* [115–117].

The initiator-derived radicals can undergo other events during their diffusion in the aqueous phase. If the surfactant concentration is above its CMC, they can penetrate into monomer-swollen micelles. If the time they remain in the micelles is long enough to propagate before they desorb back to the aqueous phase, then a primary particle is formed. This mechanism is known as *micellar nucleation* [5, 8].

The initiator-derived radicals can also undergo bimolecular termination in the aqueous phase or enter into a preexisting polymer particle, preventing the formation of a new particle. In other words, homogenous nucleation, micellar nucleation, termination of radicals in the aqueous phase, and free-radical capture in particles are competing processes.

Obviously, below the CMC of the surfactant, there are no micelles and hence in these conditions homogeneous nucleation is the only possible nucleation mechanism. Nowadays, it is widely accepted that well above the CMC, micellar nucleation is the dominant mechanism of primary particle formation. Experimental evidences, arguments, and theoretical results supporting this idea are reported elsewhere [46, 90, 118–126].

If the surfactant concentration is just slightly above the CMC, homogeneous nucleation could compete effectively with the micellar nucleation depending on the water solubility of the monomer. Homogeneous nucleation becomes more important as the surfactant concentration approaches the CMC. The experimental and theoretical results of Nomura et al. [127] on the emulsion polymerization of vinyl acetate (a partially water-soluble monomer) are also consistent with this idea.

A controversial issue related to the nucleation mechanism has been the colloidal stability of the primary particles when the surfactant concentration is above the CMC [10, 11, 128]. Below this value, there is no doubt that, to greater or lesser extent, limited coagulation occurs because of the low availability of surfactant. Coagulation of primary particles leads to particles with higher surface charge density because of the redistribution of the adsorbed surfactant onto a smaller surface. The interfacial area of a mature particle is smaller than the total interfacial area of the primary particles from which the former was formed; thus, surface charge density (and therefore stability) increases. Coagulation occurs, or it is limited to the moment at which polymer particles are stable and their growth is mainly propagative. This is called *limited coagulation*.

For the case of styrene emulsion polymerization above CMC, there are experimental results [129, 130] suggesting that if limited coagulation occurs, it is not as extensive as it was believed to be according to calculations based on the coagulative-nucleation mechanism [131]. It is by this mechanism that the primary particles formed either by homogeneous or micellar nucleation undergo limited coagulation to form mature particles.

Recently, the formation of a significant population of nanodroplets under conditions of a conventional emulsion polymerization has been reported; hence, it has been claimed that these nanodroplets might become the main locus of particle formation [16, 132]. This issue is still a subject of debate, but the generally accepted mechanism

of particle formation above the CMC continues to be the micellar nucleation.

Smith and Ewart [8] proposed the following equation to estimate the final value of the total number of polymer particles per unit volume, N, on the basis of micellar nucleation:

$$N = k \left(\frac{R_i}{\mu}\right)^{0.4} (a_s S)^{0.6} \qquad (14.2)$$

where μ is the (constant) rate of particle volume growth, R_i the rate of radical generation, a_s the specific area of the surfactant, and S the surfactant concentration. The constant k is 0.53 for the case in which all the generated radicals give place to new particles, and 0.37 for the case in which polymer particles compete with micelles for the capture of radicals. Deviations from Equation 14.2 observed for monomers with higher water solubility than styrene are ascribed to the higher probability of desorption of monomeric radicals that can contribute very significantly to micellar nucleation [125, 127, 133]. These monomeric radicals are produced within the particles by chain transfer to monomer. Desorption of these species has been recently studied by Brownian dynamic simulation [134, 135]. In the Smith and Ewart theory, nucleation by this kind of radicals and limited coagulation are not considered.

Those emulsion polymerizations for which initially polymer latex particles are not present, but in which particles are formed by some of the mechanisms described above, are known as *ab initio*. *Seeded* emulsion polymerizations are those in which at the beginning of the process there are preformed (and usually characterized) polymer latex particles; this kind of polymerizations are commonly used in industry to avoid the variability of the process associated with the nucleation stage.

14.2.4.2 Intervals of an Emulsion Polymerization

Taking as a reference the evolution of the colloidal entities present in an emulsion polymerization system, Gardon [136] proposed to distinguish three intervals in isothermal batch emulsion homopolymerization as follows:

Interval I. Nucleation takes place, and so N increases; monomer droplets are present.

Interval II. If coagulation of particles does not occur, then N is constant; monomer droplets are present.

Interval III. N is constant, but there are no monomer droplets present.

The evolution from interval I to interval II and from this to interval III are a consequence of the simultaneous and interrelated events associated with radical polymerization and the colloidal and physicochemical behavior of the species present in the system.

At the beginning of an emulsion polymerization performed above the CMC, the free radicals generated in the aqueous phase promote the nucleation of particles by the homogeneous and micellar mechanisms explained previously. The fact that the surface area of all monomer droplets is by far much smaller than that of all the other colloidal species makes it unlikely that the radicals existing in the aqueous phase enter and polymerize into monomer droplets. Thus, the droplets play the role of monomer reservoirs. The diffusion of this component through the aqueous phase provides the monomer needed to replace that consumed by reaction and to swell the polymer produced in the particles.

The growth of polymer particles constitutes the driving force not only for mass transport of monomer to the main reaction site, but also for adsorption of surfactant onto the growing surface of the particles. Hence, micelles (if present) disaggregate and their concentration diminishes with time until they eventually disappear, that is, when the surfactant concentration falls below CMC; at this point, micellar nucleation ceases. Only about 1/1000th of the micelles initially present act as nucleation sites, and the rest disaggregate to stabilize the growing particles.

Concerning homogeneous nucleation, strictly speaking, the formation of primary particles by this mechanism should not cease provided there is dissolved monomer and generation of radicals in the aqueous phase. However, eventually particle formation by this mechanism becomes nonsignificant because the number and size of particles is such that they capture most of the radicals produced in the aqueous phase. Interval I finishes when N does not increase anymore, independently of the mechanism(s) of nucleation involved.

During interval II, N is usually constant and the polymer particles are still growing at the expense of the monomer present in droplets. Eventually, monomer droplets disappear, marking the end of interval II. During this interval, the surface concentration of surfactant on the interfaces diminishes because this component has to be redistributed over a larger area as this interval proceeds (recall that there are not micelles anymore to keep the interfaces saturated).

During interval III, N is usually constant as well and the monomer concentration in particles diminishes because there are no remaining droplets to replace the monomer consumed in the polymerization. Nearly total monomer conversion is reached.

In emulsion polymerizations performed below CMC, limited coagulation of mature particles might occur so that the transition from interval I to interval II might not be obvious. The end of interval II is the same as in polymerizations above CMC.

14.2.4.3 Rate of Polymerization R_p

The rate of polymerization is important not only because it determines the

productivity of the process but also because it is a macroscopic manifestation of phenomena occurring at the microscopic and submicroscopic levels. Gardon's description of the intervals in emulsion polymerization has been complemented with the behavior of the rate of polymerization (R_p). On the basis of the idea that $R_p \propto N$, several authors have considered that R_p increases, remains constant, and diminishes in intervals I, II, and III, respectively. The notion that R_p is constant during interval II is also supported by the fact that at intermediate conversions statistical analysis of gravimetric data leads to conclude that monomer conversion varies linearly with time. However, Gardon [137] has questioned this concept on the basis that the nonlinear nature of the conversion–time curve can be hidden if the conversion range studied is too narrow. The nonconstant behavior of R_p during interval II in emulsion polymerization above the CMC has been confirmed by quasicontinuous calorimetric measurements [138–141]. These results also show that R_p does not necessarily decrease during interval III but often exhibits a maximum as a consequence of the autoacceleration effect [142–145]. R_p is given by

$$R_p = \frac{K_p C_{Mp} \bar{n} N}{N_A} \qquad (14.3)$$

where K_p, C_{Mp}, and $\bar{n}$, are the propagation kinetic rate coefficient, the monomer concentration in particles, and the average number of radicals per particle, respectively. N_A is Avogadro's number. The effect of each one of these parameters on R_p is discussed next.

K_p is constant during most of the polymerization, but it may diminish toward the end of interval III, at high monomer conversions, due to diffusion limitations.

C_{Mp} maintains its saturation value during intervals I and II provided that the interfacial area of monomer droplets is high enough to allow the monomer transport to the growing particles where it replaces the monomer consumed swelling the polymer formed [146]. However, on the basis of Monte–Carlo simulations, Tauer and Hernandez [147] have claimed that latex particles in emulsion polymerization never experience either a period of saturation with monomer or a constant monomer concentration during interval II, as frequently assumed.

C_{Mp} evolution is affected to certain extent by the evolution of γ. As explained before, during intervals I, II, and III in an emulsion polymerization above CMC, γ is constant, increasing, and practically constant, respectively. During interval II, the increases in γ and in r approximately compensate each other in such a way that the average C_{Mp} in all the particles tends to be constant [118] or slightly decreases [148, 149].

During interval III, C_{Mp} monotonically diminishes according to the conversion of monomer to polymer.

Concerning $\bar{n}$, three scenarios can exist, which are known as the Smith–Ewart (S–E) cases [8]:

- Case 1: $\bar{n} < 0.5$. In this scenario, the radicals produced by chain transfer to monomer inside the particles have high probability of being desorbed to the aqueous phase. Small particle sizes and low rates of free-radical capture in particles favor this scenario.
- Case 2: $\bar{n} \cong 0.5$. If the rate of chain transfer-desorption of radicals is negligible compared to the rate of free-radical capture in particles, and the mutual termination rate of two radicals is so high that only particles with zero and one radicals can exist, then approximately one-half of the particles contain a single free radical. Small particle sizes and high rates of free-radical capture in particles favor this scenario.
- Case 3: $\bar{n} > 0.5$. In this scenario, there is not instantaneous termination as in cases 1 and 2; thus, two or more radicals can coexist in a particle. Large particle sizes, high rates of free-radical capture in particles, and the Trommsdorff effect (Chapter 4) favor this scenario.

S-E cases 1 and 2 correspond to what is known as zero–one systems, in which the radicals grow in isolated compartments, reaching very high molecular weights; hence, this characteristic feature of emulsion polymerization is known as *compartmentalization*. In case 3, this characteristic is relaxed so that radicals in a given particle grow in the presence of other radicals. As more radicals coexist within the particles, the system approaches the behavior of a bulk polymerization (or pseudobulk system).

Regarding $N,$ it has been reported [116] that this parameter reaches a maximum during the nucleation stage if the polymerization is performed below the CMC, because the low availability of surfactant causes limited coagulation. On the other hand, N tends to increase in this stage when the surfactant concentration is above the CMC. During interval II, N is typically assumed to be constant, but some authors have reported that this parameter increases in this period [138, 150–152]. The subject is still a matter of debate due to the limitations of certain particle sizing techniques [125, 129, 130].

Next, the effect of the simultaneous evolution of the parameters involved in Equation 14.3 on R_p is discussed.

In intervals I and II, R_p is mainly determined by the products $\bar{n} C_{Mp} N$ and $\bar{n} C_{Mp}$, respectively.

According to theoretical results [125], $\bar{n}$ exhibits a minimum at early times of emulsion polymerizations above CMC. This minimum is explained in terms of the competition between micelles and particles for the capture of radicals and has been characterized as an

evolution from case 1 toward case 2 during the early stages of the polymerization. $\bar{n}$, C_{Mp}, and N increase, and consequently R_{p} does so. N rises from zero to typically 10^{12}–10^{13} and 10^{14} particles/cm^3 water, for emulsion polymerizations performed below and above the CMC, respectively. Therefore, any decrease of other parameter(s) can be overcompensated and consequently R_{p} increases in interval I. In interval II, N is usually constant; hence, R_{p} depends on the product $\bar{n}C_{\mathrm{Mp}}$. As it was explained before, C_{Mp} tends to be constant or to slightly diminish in this interval. Therefore, the R_{p} evolution depends on how $\bar{n}$ counterbalances the C_{Mp} evolution. In interval III, N is also usually constant and K_{p} eventually becomes diffusion-controlled; hence, R_{p} depends on the product $K_{\mathrm{p}}\bar{n}C_{\mathrm{Mp}}$. The maximum of the R_{p} evolution curve, characteristic of the autoacceleration (Trommsdorff) effect in free-radical polymerization systems, can also be observed in emulsion polymerization. Considering that the parameters defining R_{p} can evolve in different ways in different polymerization systems, it is not plausible to establish a general R_{p} profile.

14.2.4.4 Molecular Weight Molecular weight determines many end-use properties of polymers. Thus, it is very important to know the events that control it. The relative importance of such events is highly system dependent; hence, the molecular weight obtained in heterogeneous systems like emulsion polymerization can be very different from that obtained in homogeneous systems like bulk and solution polymerizations. In homogeneous systems, the generation, propagation, and termination of free-radicals occur in the same phase so that any radical has access to any other. However, in an emulsion polymerization, the generation of radicals takes place in the aqueous phase and their propagation and termination occur predominantly within the polymer particles. In this way, a radical in one particle does not have direct access to radicals in another particle so that they grow isolated in their own compartments. Termination events occur when another radical enters a particle that previously contains a growing chain or when this latter undergoes a chain transfer reaction. Bimolecular termination occurs instantaneously for relatively small particle sizes, as those present during interval I of emulsion polymerization above the CMC, so that only particles containing zero or one radicals exist (i.e. a 0–1 system). As particles become bigger, the probability that two or more radicals can coexist in the same particle is higher, that is, the system tends to behave like a bulk polymerization from the point of view of molecular weight. Compartmentalization has a profound effect on the kinetics of emulsion polymerization. Polymerization rates and molecular weights are usually higher than in the corresponding bulk or pseudobulk systems because the termination rate is reduced [153–155].

14.2.5 Batch, Semibatch, and Continuous Processes

In *batch processes*, all the formulation components are completely added to a stirred-tank reactor (STR) at the start of the polymerization, while in *semibatch* operation only certain part is initially added and the rest is continuously fed over some period of time. *Continuous* reactors are operated with continuous input flow of components and output flows of products.

Most polymers produced by emulsion polymerization are copolymers; therefore, it is important to consider the effect of the reactor operation mode on copolymer composition. Moreover, because of the heterogeneous nature of the system, partition of the monomers between the phases during the polymerization as well as monomer reactivities have to be taken into account.

A difference in monomer reactivity causes that the more reactive monomer is consumed preferentially leading to a drift in copolymer composition. In batch polymerization, the copolymer may exhibit a broad composition distribution because all the monomers are added at the beginning, and so there is no chance to control the concentration of monomers in the polymerization sites that, together with the reactivity ratios, determine the copolymer composition. In contrast, in the semibatch mode, the polymerization can be performed under monomer-starved conditions. Under these conditions, the copolymer formed has the same overall composition as that of the comonomer mixture added. Thus, in the latter process, if a comonomer mixture of constant composition is fed, copolymers of uniform composition are produced. Otherwise, if the monomer feed is such that polymer latex particles are swollen at their equilibrium value, then monomer-flooded conditions are present and the semibatch polymerization is essentially indistinguishable from the equivalent batch reaction. To ensure colloidal stability as particles grow, it is usually necessary to feed more surfactant during the period of monomer addition. This is done by adding the monomer mixed with water and surfactant (as an emulsion) or by adding the surfactant as a separate input stream. It is also possible to feed the monomers in a calculated manner, such that the drift in composition is compensated by the composition of the monomer feed (time dependent). A number of works have been published in the literature regarding composition control in semibatch emulsion polymerizations [156–160]. Continuous stirred-tank reactors (CSTRs) are economically advantageous when high production rates are required or when product grades differ slightly [161–163]. Monomer conversion in CSTRs might exhibit sustained oscillations [164] leading to product quality problems. These oscillations have been ascribed to on–off nucleation phenomena coupled with particle growth; thus, the use of seed significantly enhances reactor stability. Another alternative is the use of tubular reactors that exhibit stable

operation [165]. Wall fouling and plugging are potential disadvantages of this kind of reactors; however, these can be avoided by using a pulsation source [165].

Free-radical polymerizations are exothermic, and so the heat produced during polymerization must be removed. This is not a significant problem in a laboratory scale; however, heat transfer problems constitute a restriction for batch processes in an industrial scale. In the case of semibatch and CSTR, the cold monomer and water feed are beneficial for heat removal so that much higher production rates are feasible than for a batch reactor of the same volume. For tubular reactors, their large heat transfer area is advantageous for the strongly exothermic polymerizations.

The reactor type and operation mode also influence the particle size distribution (PSD). This aspect is treated next in the context of PSD control.

14.2.6   Control of Number and Size Distribution of Particles

PSD is one of the most important characteristics of latexes. For some applications, a very low particle size dispersity is required [166], while in others [167, 168] a multimodal PSD is necessary.

Latex particles are not strictly monodisperse. The reason is that particles are not born at the same time, but they are formed during a period of time (i.e., the nucleation stage) in which they simultaneously grow. Thus, particles formed toward the end of the nucleation stage will be smaller than those formed at early times of the polymerization. Therefore, the longer the nucleation stage, the wider the PSD. In general, polymerizations carried out at or below the CMC will lead to the formation of bigger particles with more uniform sizes. Occurrence of limited coagulation during the nucleation stage tends to homogenize by itself the particle sizes.

The reason why some kind of anionic surfactants leads to lower particle size dispersities was studied recently by Farias et al. [65].

If polydisperse latexes are desired in batch emulsion polymerizations above CMC, high S_0 values and low initial initiator concentrations (I_0) prolong interval I enhancing the formation of negatively skewed [169] or even bimodal PSDs [127].

Secondary nucleation can also be used to produce bimodal or multimodal PSDs. This can be done in several ways by means of seeded [170] or *ab initio* polymerizations [171–178]. Miniemulsion polymerization can also be used to produce broad PSDs [179, 180].

14.2.7   Particle Morphology

Composite latexes, that is, those with particles containing different phases, are used for many applications such as adhesives and coatings [181], impact modifiers [182], and other high value-added products [73]. They are prepared by a series of consecutive emulsion polymerizations with different monomer types where the monomer(s) is/are added under conditions such that polymerization occurs in the pre-existing particles. As the concentration of newly formed polymer chains increase, phase separation occurs, leading to the formation of clusters that migrate in such a way that the interfacial energy of the system tends to be minimized. The final morphology strongly depends on the kinetics of such cluster migration whose driving force comes from the balance between van der Waals and viscous forces [183–185]. Equilibrium morphologies such as core–shell or inverted core–shell may be attained if the internal viscosity of the particle is low, and the polymers are very incompatible. If the morphology is kinetically controlled, then the different phases are not fully consolidated and nonequilibrium-type structures such as salami-, raspberry-, and octopus like are obtained [186–188].

14.2.8   Latex Characterization

Characterization of polymer latexes can be performed by techniques available for polymers in general and by other techniques specific for emulsions.

Monomer Conversion. Off-line methods such as gravimetric analysis and gas chromatography as well as several online methods can be used to determine monomer conversion throughout polymerization [116, 138, 149, 189–195].

Particle Size and PSD. According to the basic principles that they are based on, the techniques for measuring these important characteristics of the latexes are classified into four major groups [196]: (i) microscopy, (ii) light scattering, (iii) particle movement (e.g., capillary hydrodynamic chromatography and field flow fractionation methods), and (iv) acoustics.

The choice of the method depends on several factors, such as the size range of interest, the accuracy desired, and the time required for a measurement. Availability, cost, and method limitations of the instrument have to be considered as well. Useful guidelines to instrument selection are given by Collins [196] and Schoenmakers [197].

Particle Morphology. It can be observed by means of transmission electron microscopy, scanning electron microscopy, and atomic force microscopy. Useful information about particle morphology can also be obtained by means of other techniques [198–203].

14.3   MICROEMULSION POLYMERIZATION

As mentioned above, micelles have a limited capability to solubilize hydrocarbons within them; thus, *swollen micelles*

is another term for microemulsions [18]. Microemulsions are thermodynamically stable and transparent dispersions containing oil, water, and surfactant(s). A useful guide to their formulation is given by Candau [204].

The term *microemulsion polymerization*, as is the case with some other polymerization processes in aqueous dispersed media, refers to the initial state of the system before polymerization.

When a water-soluble initiator is added to a microemulsion, polymer particles are nucleated mainly by the micellar mechanism. The role of the monomer-swollen micelles in microemulsion polymerization is not only to act as nucleation loci and surfactant reservoir but also as monomer reservoir. The fast nucleation rate leads to the initial increment of R_p. As the monomer is polymerized, its concentration in micelles diminishes and eventually monomer concentration within polymer particles decreases as well [205]. As a consequence, the nucleation and polymerization rates tend to decrease, explaining in this way the maximum in the R_p evolution curve experimentally observed. The final latex consists of surfactant-stabilized polymer particles that typically contain only polymer and empty micelles formed by excess surfactant.

The utility of microemulsion polymerization comes from its capability of producing smaller particles than those obtained by emulsion polymerization and of forming porous solid materials (by inverse microemulsion polymerization). This process has also been found to be suitable for performing CRP [206]. More particularities on microemulsion polymerization can be found in References 188, 204, 207, and 208.

14.4 MINIEMULSION POLYMERIZATION

The size of the colloidal entities and their stability in *mini*emulsions lies between those of *macro*emulsions and *micro*emulsions. The diameter of miniemulsion droplets ranges from 50 to 500 nm and their stability vary from days to months [41]. A typical formulation consists of water, monomer(s), surfactant, initiator system, and co-stabilizer. The main function of the latter is to retard the Ostwald ripening effect. Hexadecane and cetyl alcohol are typically used as co-stabilizers. Miniemulsions are formed by subjecting the mixture to high shear and/or cavitation to break the oil phase into submicron size droplets [209]. This can be done by means of devices such as high pressure homogenizers, rotor stators, and ultrahigh sonifiers [210–212].

The droplet size distribution, DSD, and the presence of swollen micelles in miniemulsions depend on the formulation, homogenization procedure, and storage time [40]. Assuming that a water-soluble initiator is used, a key difference between miniemulsion and conventional

emulsion polymerizations is that, in the former, monomer (mini) droplets compete with monomer-swollen micelles for capturing the oligoradicals generated in the aqueous phase. The goal in this regard is to maximize the fraction of particles generated by minidroplet nucleation, by adjusting the amount of surfactant and the homogenization procedure. Nucleation in minidroplets can be enhanced by pre-dissolving 1% polymer into the monomer before homogenization [213, 214]. Other hydrophobic species such as oil-soluble initiators [215, 216], CTA [217], and other reactive species [218] have been evaluated as co-stabilizers.

The R_p curves of miniemulsion and conventional emulsion polymerization obtained by calorimetry show the same general behavior [219]. In contrast to conventional emulsion polymerization, in miniemulsion polymerization, the monomer concentration in polymer particles diminishes throughout the polymerization. At the beginning, the nucleation rate overcompensates the decrease of monomer concentration leading to the first rise in the R_p. The number of droplets decreases and the remaining droplets shrink in size due to monomer loss by molecular diffusion to the polymer particles. As a consequence, the nucleation rate diminishes and eventually it may not be fast enough to compensate the decrease of the monomer concentration. Thus, R_p may reach a maximum and decrease before the end of the nucleation period [219]. In conventional emulsion polymerization, the nucleation period ends before the first maximum in R_p, which is ascribed to the disappearance of monomer droplets [125].

Applications of miniemulsion polymerization come from taking advantage of the droplet nucleation mechanism. Some examples are production of high solid content latexes [179], encapsulation of inorganic solids [220], encapsulation of fragrances [221], production of hybrid polymer particles [222–224], step polymerization [225–228], CRP [229–233], and so on.

14.5 APPLICATIONS OF POLYMER LATEXES

Emulsion polymers have been used in a broad range of applications because of their environment-friendly nature and the versatility of the process for adjusting both macromolecular and colloidal properties of the latex. Out of the worldwide demand of emulsion polymers, 23% is used for surface sizing and coating of paper and paper board, 20% for paints and coatings, 25% for adhesives and sealants, and 9% for carpet backing [234]. References 234 and 235 and several chapters of the book edited by Lovell and El-Aasser are devoted to the major industrial uses of emulsion polymerization and polymer latexes.

Besides these large-volume applications of latexes, there are specialty applications, such as some in the

optoelectronics and biotechnology fields, for which high added-value latexes are produced at a smaller scale. This kind of products requires fine control of composition, particle size, PSD, morphology, surface chemistry, and functionalities [236].

14.6 DISPERSION AND PRECIPITATION POLYMERIZATIONS

A free-radical dispersion polymerization is a heterogeneous process where particles are formed in the presence of an adequate stabilizer, with a reaction mixture homogeneous at the beginning of the polymerization. This process can be described as proceeding in three stages [237–239]. In "Stage 1," primary radicals are formed from thermally promoted fragmentation of the initiator. These primary radicals rapidly react with monomer molecules to produce polymer chains that upon fast growth become insoluble in the continuous phase. The aggregation of polymer chains results in the formation of unstable polymer microdomains. The reaction mixture consists primarily of pure monomers, initiator, primary radicals, and oligomer radicals, since the polymer concentration is lower than its solubility limit. Therefore, in this stage, the polymerization can be described as a solution polymerization process. In "Stage 2," because of the very limited stability of the microdomains, they rapidly aggregate to form primary polymer particles, also called *domains*. From this point on, the polymerization proceeds in two phases, namely, the polymer-rich phase and the continuous, monomer-rich phase. This stage goes from the time of appearance of the dispersed polymer phase to a fractional overall monomer conversion, x_c, at which the monomer concentration in the continuous phase is negligible and eventually disappears. The overall polymerization rate is given by the sum of the polymerization rates in each phase. Finally, in "Stage 3," at higher overall monomer conversions ($x_c < x \le 1$), the polymerization proceeds mainly in the polymer-rich phase. The polymer particles are swollen with monomer and solvent; thus, the monomer mass fraction in the polymer phase decreases as the total monomer conversion approaches a final limiting value.

The mathematical modeling of the polymerization kinetics and molecular weight development in dispersion polymerization processes (using scCO$_2$ as continuous phase), using the approach described above, has been reported in the literature [237–239]. Besides the kinetics and molecular weight development equations that describe the polymerization in each phase (similar to those described in Chapter 12), it is necessary to account for species partitioning among the phases. The equations for species partitioning can go from simple partition coefficients [237–239] to elaborate thermodynamic equations for polymer solutions

(e.g., the Sanchez–Lacombe equation of state) [240, 241] (Section 14.2.2.4).

Representing the dispersion polymerization process as proceeding in three stages has some implications regarding its mathematical treatment. If the system is modeled as starting as a single-phase polymerization, the rigorous modeling of the formation of the second phase will not be an easy issue to handle, since fulfillment of the initial conditions may lead to numerical difficulties. Moreover, the three-stage representation suggests imposing a second discontinuity (when going from stage 2 to 3), which may not be necessary, since a continuous model should be able to capture the behavior of the system when monomer in the continuous phase has been fully consumed. Although Kiparissides et al. [237] first proposed and used this three-stage approach, which implied using two discontinuous transitions, a later contribution from the same group [240] and the model approach used by Mueller et al. [241] treat the system as consisting of a two-phase polymerization from the very beginning, which is reasonable due to the very fast formation of high molecular weight polymer, which will phase-separate.

Precipitation polymerization is similar to dispersion polymerization. They both start as a solution polymerization (homogeneous phase). However, in the case of precipitation polymerization, there is no colloidal stabilizer present, and so the polymer formed precipitates as a completely separate phase, while in dispersion polymerization, the polymer particles are stabilized by a colloidal stabilizer.

14.7 SUSPENSION POLYMERIZATION

14.7.1 Generalities[1]

The topic of suspension polymerization has been reviewed by several authors at different times, with different emphases [24, 242–248]. In a suspension polymerization process, the monomer (or monomers in the case of a copolymerization), which is relatively insoluble in water, is (are) dispersed as liquid droplets. Dispersion stability is maintained with the help of a stabilizer and vigorous stirring. The final product, once the continuous (usually aqueous) phase has been removed, consists of solid polymer particles (beads). The initiators used in this process are usually soluble in the liquid monomer. The terms *pearl* and *bead polymerization* are also used for the suspension polymerization process when particle porosity is not required. The major aim in suspension polymerization is the formation of an, as uniform as possible, dispersion of monomer droplets in the aqueous phase, with controlled

coalescence of these droplets during the polymerization process. The interfacial tension, the degree of agitation, the design of the stirrer/reactor system, the amount of dispersed phase, and the evolution of the polymer molecular weight distribution govern the dispersion of monomer droplets, typically with diameters in the range of 10 μm–5 mm. The presence of suspending agents (e.g., stabilizers) hinder the coalescence of monomer droplets and the adhesion of partially polymerized particles during the course of the polymerization, so that the solid beads may be produced in the same spherical form in which the monomer was dispersed in the aqueous phase. Many important commercial suspension polymers yield bead sizes above 10 μm, and so these relatively large particles (compared to emulsion particles) are simply isolated by centrifugation, filtration, and/or sedimentation [244].

Nonaqueous suspension agents such as paraffin oils have been developed to polymerize polar monomers, such as acrylic acid. The so-called water-in-oil (W/O) suspension polymerization (reversed phase suspension polymerization) comprises an aqueous solution containing the hydrophilic monomer(s) and initiator(s), which are dispersed in a liquid paraffin oil or other nonpolar hydrocarbon media and polymerized. The use of perfluorocarbon fluids has extended the scope of the suspension polymerization method to monomers and initiators that cannot be used, due to their high solubility and reactivity, in conventional suspension media [249].

The reactor vessel is usually a stirred tank. The monomer phase is subjected either to turbulent pressure fluctuations or to viscous shear forces, which break it into small droplets that assume a spherical shape under the influence of interfacial tension. These droplets undergo constant collisions (collision rate ≥ 1 s^{-1}), with some of the collisions resulting in coalescence. Eventually, a dynamic equilibrium is established, leading to a stationary mean particle size. Individual drops do not retain their unique identity, but undergo continuous breakup and coalescence instead. In some cases, an appropriate dispersant can be used to induce the formation of a protective film on the droplet surface. As a result, pairs of clusters of drops that tend to coalesce are broken up by the action of the stirrer before the critical coalescence period elapses. A stable state is ultimately reached in which individual drops maintain their identities over prolonged periods of time [247].

In the case of a polymer that is miscible in all proportions with its monomer (e.g., styrene and methyl methacrylate), a very large variation of the range of the dispersed-phase viscosity is observed during the course of polymerization. The initially low viscosity liquid monomer is transformed gradually into an increasingly viscous polymer in monomer solution and, as conversion increases, the dispersed phase acquires the characteristics of a solid particle. Rapid polymerization during the sticky stage minimizes the

number of effective collisions among polymer particles and thus should reduce coagulation [247] (which may lead to catastrophic coagulation with reaction runaway and loss of the batch). The most important issue in the practical operation of suspension polymerization is the control of the final PSD. The size of the particles will depend on the monomer type, the viscosity change of the dispersed phase with time, the type and concentration of stabilizer, and the agitation conditions in the reactor. The particle morphology is an important characteristic for the application of the polymer product, particularly in the cases of expandable polystyrene (EPS), ion-exchange resins, and poly(vinyl chloride) [246]. The polymerization kinetics and the mechanism of primary particle aggregation in the polymerization of vinyl chloride are rather different to the ones present in bead polymerization. The differences are mainly due to the insolubility of polyvinyl chloride in vinyl chloride. Modeling of the polymerization kinetics and PSD (using a population balance equation) in vinyl chloride polymerization has been addressed by the group of Kiparissides [250].

Suspension polymerization has the following advantages compared to the other polymerization processes (bulk, solution, and emulsion): easy heat removal and temperature control; low dispersion viscosity; low levels of impurities in the polymer product (compared to emulsion); low separation costs if the polymer is to be used as a solid (compared to emulsion); and final product in particle form. On the other hand, among the disadvantages of suspension polymerization one may refer to the following: lower productivity for the same reactor capacity (compared to bulk); wastewater problems (contamination); polymer build-up on the reactor wall, baffles, agitators, and other surfaces; no commercial continuous process operable yet; and difficulty to produce homogeneous copolymer composition during batch suspension polymerization [246]. Semibatch operation is more difficult with suspension versus emulsion polymerization because of the lower interfacial area (particle/water).

A number of important commercial resins are manufactured by suspension polymerization, including poly(vinyl chloride) and copolymers, styrene resins [general purpose polystyrene, EPS, high impact polystyrene (HIPS), poly(styrene-acrylonitrile) (SAN), poly(acrylonitrile-butadiene-styrene) (ABS), styrenic ion-exchange resins], poly(methyl methacrylate) and copolymers, and poly(vinyl acetate). However, some of these polymers rather use a mass-suspension process, in which the polymerization starts as a bulk one and, at certain conversion, water and suspending agents are added to the reactor to form a suspension and continue the polymerization in this way up to high conversions. No continuous suspension polymerization process is known to be employed on a

commercial scale, but such processes have been carried out in the laboratory and on pilot-plant scale [246].

The step of scaling up a reactor from pilot plant to industrial scale is an issue where much empiricism is still used and where expensive and time-consuming experimental programs are usually required. Complete geometric, kinematic, dynamic, chemical, and thermal similarity cannot be simultaneously achieved in a scale up procedure, and so some differences should be allowed at some point [251].

14.7.2 Some Issues about the Modeling of PSD in Suspension Polymerization

Although the suspension polymerization process has been widely studied over more than 60 years, the present situation is that its understanding is still limited and a lot of experimental effort and empirical knowledge are still used to design new resins and to scale their production up from a pilot scale reactor to an industrial level one. The least developed issues in the suspension polymerization process are related to the changing rheological behavior of the reacting mass during polymerization, the nonhomogeneous flow and rate of energy dissipation field distributions within the tank reactor, and the relationship among them and the polymerization kinetics with the breakage/coalescence phenomena that ultimately determine the PSD [248]. The PSD in suspension polymerization is affected by many factors. There have been many studies related to the study of the effects of these parameters on the PSD, although few of them have been complete and systematic. These factors, listed in the first column of Table 14.1, can be classified into four categories: polymerization kinetics, surface phenomena, intensity of mixing, and dispersion concentration.

Some of the responses that can be related to the PSD in suspension polymerization are listed in the second column of Table 14.1. The values of some of these factors can be fixed *a priori*. It is known that the kinetics of polymerization strongly affects the PSD, but this dependence goes in only one direction (namely, the PSD does not affect the kinetics of polymerization in bead suspension polymerization). The link between the polymerization kinetics and the PSD is the zero shear viscosity of the disperse phase, which depends on the molecular weight of the polymer. The effects of the kinetic factors on molecular weight development are reasonably well understood and can be studied independently. This means that by changing the values of the kinetic factors it is possible to generate different molecular weight evolution profiles (thus, different viscosity evolution profiles). A known and adequate evolution profile can be obtained by choosing adequate values for crosslinker concentration, temperature, initiator concentration, and concentration of CTA.

TABLE 14.1 Important Factors and Responses in Suspension Polymerization

Factors	Responses
Polymerization Kinetics	*Main Responses*
Monomer type	Mean diameter
Monomer concentration	Particle size distribution
Crosslinker concentration (comonomer concentration)	Identity point
Temperature	*Secondary Responses*
Initiator type (mono- or bifunctional)	Conversion
Initiator concentration	Dispersed-phase viscosity
Presence or absence of chain transfer agent (CTA)	Viscoelasticity
CTA concentration	Molecular weight averages
Inhibitor type	Interfacial tension
Inhibitor concentration	
Intensity of Mixing	
Gravity effect (Froude number)	
Agitator design	
Impeller diameter	
Agitation speed	
Agitation time	
Off-bottom clearance	
Distance of separation between impellers	
Presence or absence of baffles	
Vessel configuration (geometry of the tank)	
Reactor volume	
Surface Phenomena	
Stabilizer type (protective colloid or inorganic powder)	
Stabilizer concentration	
Dispersion Concentration	
Disperse phase holdup	

Although many studies on PSD in suspension polymerization have been published in the last few decades, the understanding of the influence and importance that the known key factors have on the shape and spread of the PSD is still unclear and incomplete. In the critical review on suspension polymerization presented by Vivaldo-Lima et al. [248], a systematic approach to the study of PSD in suspension polymerization was proposed, which was aimed at providing an adequate framework for the development of an effective mathematical model for the calculation of the PSD. Some of the stages of that approach included the selection of the polymerization conditions using a mechanistic model-based experimental design technique [252], and the development of a preliminary mathematical model for the PSD using a compartment-mixing (CM) model approach to

account for the nonhomogeneous mixing in the tank reactor [253]. The original idea of using a CM modeling approach for the calculation of the PSD in suspension polymerization, calculating the intensity of mixing for each compartment from rigorous computational fluid dynamics (CFD) simulations of the actual tank reactor, first proposed [248] and used [253] by the group of Hamielec, has also been used by others since then [254–257]. The homogeneous mixing approach (single CM model) is still used in the context of proposal or evaluation of different variations of the breakage-coalescence models, or evaluation of numerical techniques to solve the population balance equations [258–260].

A Bayesian experimental design technique has been used to determine the relative importance that the different factors of the process have on the PSD [261]. The information obtained served as a measure of how much greater a degree of complexity is needed about the different phenomena that affect the PSD to improve the mathematical model.

14.8   CONTROLLED RADICAL POLYMERIZATION (CRP) IN AQUEOUS DISPERSIONS

Once the basic synthesis techniques and mechanisms of CRP were established (around 2000), a significant part of the research effort in this field has been focused on the development of processes in aqueous dispersions (mostly emulsion and miniemulsion), given the industrial advantages of these processes. In spite of these efforts, there are still important challenges to overcome. The most successful results fall in the category of miniemulsion processes [262–265], but true emulsion processes, which are preferable from the industrial point of view, are still in the development stages.

The basic CRP techniques and mechanisms are discussed in Chapter 4; here only those issues associated with the presence of water in the system are dealt with. The subject has been reviewed by several authors [206, 266, 267]. Perhaps the most important challenge in this field is the development of a robust and general *ab initio* emulsion process (without using a seed). An essential problem in this endeavor is to avoid the nucleation in monomer droplets, which causes colloidal instability.

Two phenomena are behind the complex interaction between the controlled/living character of the polymerization, the particle nucleation phenomenon and the latex stability. One is the superswelling [206] of polymer particles with low molecular weight species. This phenomenon was reported by Ugelstad et al. [268], who revealed that, in the presence of strong hydrophobes, oligomers can swell the polymer particles in a volume ratio as high as 100. In the initial stages of CRP, because of the controlled nature of the

process, only oligomers are generated; these favor the superswelling, which provokes unusual growth of the polymer particles and latex destabilization due to increasing buoyant forces acting on the particles, altering also the partitioning of controlling agent among the phases and reducing the living/controlled character of the polymerization. The second phenomenon, *Ostwald ripening* [206], described above, also promotes excessive growth of particles leading to latex instability and/or bimodalities in the PSD.

In miniemulsion polymerization, the presence of a cosurfactant (highly hydrophobic) inhibits the Ostwald ripening and favors the latex (kinetic) stability; however, this process has the drawback of requiring intense stirring to disperse the monomer droplets in the aqueous phase, consuming high energy, and demanding the use of special mechanical devices.

14.8.1   Nitroxide Mediated Radical Polymerization (NMRP) in Aqueous Dispersions

In general, it is possible to perform stable and reproducible NMRP processes in miniemulsion [262–264]; however, *ab initio* emulsion processes usually exhibit either colloidal stability problems or poor living/controlled character [269–271]. An additional technical requirement is to achieve sufficiently high concentration of the nitroxide in the particle phase. Two or the most successful techniques that can be considered *ab initio* are described next. In the nanoprecipitation process [270], seed particles are generated dispersing an acetone solution of polymeric (polystyrene) macroinitiator containing alkoxyamine groups in a surfactant aqueous solution. Then the acetone is evaporated, and the particles are swelled with more monomer to continue with the polymerization. Good colloidal stability and controlled character have been demonstrated. Self-assembly is a second successful group of techniques [272]. In general, they use a water-soluble alkoxyamine that avoids the nucleation in monomer droplets by different strategies. In a variation of this technique, which is the closest one to an *ab initio* process, a water-soluble SG1 macroalkoxyamine, together with monomer and surfactant-free water, are heated to form block copolymers that self-assemble into nanoparticles dispersed in the aqueous phase. After a slightly unstable period, the latex becomes more stable as the reaction progresses. On the other hand, seeded emulsion polymerizations are simpler due to their lack of a nucleation period with its inherent instability [269, 271, 273, 274].

14.8.2   Atom Transfer Radical Polymerization (ATRP) in Aqueous Dispersions

The subject has been reviewed in the literature [275, 276]. There are some literature reports on successful miniemulsion ATRP reactions; [277] however, side reactions owing

to the presence of water tend to hinder the controlled character. The Cu^{2+} deactivator complex can be dissociated in the presence of protic substances, losing effectiveness and resulting in an excess of the active species, which leads to poor control. Ligand selection is important in order to keep the Cu complexes mostly in the organic phase. In addition, Cu^{1+} is easily oxidized during the emulsification stage due to the presence of oxygen, and therefore some variations of ATRP (e.g., Activators Generated by Electron Transfer (AGET) ATRP), less sensitive to oxygen, are preferred in this case [278]. The surfactant should be nonionic or cationic, since anionic surfactants can deactivate the copper complexes. Truly emulsion ATRP systems usually fail because the initiator tends to migrate to the organic phase leading to excessive nucleation and colloidal instability.

14.8.3 Reversible Addition Fragmentation chain-Transfer (RAFT) in Aqueous Dispersions

RAFT chemistry is probably the most versatile and robust one for polymerization in aqueous dispersions amongst the different CRP techniques. The RAFT agent is bonded to the polymeric chains and therefore does not tend to partition back to the aqueous phase. However, this type of systems also exhibits problems of colloidal stability. In miniemulsion systems, these are attributed to nucleation in monomer droplets and superswelling and can be minimized by adding more cosurfactant and using oligo- or polymeric RAFT agents. A number of homopolymers have been synthesized by miniemulsion RAFT polymerization: styrene, acrylates, methacrylates, vinyl acetate, acrylic acid, as well as block and gradient copolymers using several of these monomers [279]. Some of these systems show the rate retardation phenomenon, which is also observed in solution or bulk RAFT polymerizations using some CTAs (dithiobenzoates) [280]. In addition to the possible causes of rate retardation reported for bulk and solution systems (slow fragmentation of the adduct and intermediate radical cross-termination with live polymer), it is likely that in aqueous systems the leaving R group desorbs from the particles reinforcing the retardation phenomenon [281, 282].

As for other CRP systems, *ab initio* RAFT emulsion polymerization is difficult to perform due to colloidal stability problems. The use of xanthates (Macromolecular Design via Inter-exchange of Xanthate (MADIX) process) [283] as transfer agents diminishes this problem due to the low transfer constant of these species, leading to relatively high molecular weights at low conversions and reducing the superswelling phenomenon. A drawback of these systems is that they result in relatively large polydispersities.

14.8.4 Controlled Radical Suspension Polymerization

The first CRP carried out in suspension was reported by Georges et al. [284]. They copolymerized styrene and

TABLE 14.2 Controlled Radical Suspension Polymerizations (in chronological order)

Type of CRP	Monomers	Controller	Initiator	Comments	References
NMRP	STY/Butadiene	TEMPO	BPO	$M_w/M_n = 1.35$	[284]
	MMA/DVB	TMTD and p-XDC		Narrow PSD microspheres	[285]
NMRP	STY	TEMPO	BPO & DCP	$M_n > 100,000$ and $M_w/M_n < 1.5$	[286]
ATRP	MMA	$RuCl_2(PPh3)3$	B	High $M_n (\sim10^5)$ and $M_w/M_n = 1.1$	[287]
NMRP	STY/AN/BMA	TEMPO	BPO & DCP	Block copolymers with $M_w/M_n \sim 1.5$	[288]
ATRP	MMA	dNbpy	EBiB	$M_w/M_n = 1.18 - 1.33$ at high conversions, using different stabilizers	[289]
ATRP	BA/STY	$Fe(Cp)I(CO)_2$	A	$M_w/M_n = 1.25$ for poly(n-BA) and 1.2 for Polystyrene	[290]
NMRP	VC	TEMPO	C	$M_w/M_n = 1.9$	[291]
ATRP	VAc	$Co(acac)_2$	V-70	Satisfactory particles of P(VAc) with $M_w/M_n = 1.35$	[292]
ATRP	BMA	Cu(I)Br and Cu(I)Cl	EBiB	M_n and M_w/M_n depend on ligands	[293]
NMRP	STY/BA	TEMPO	BPO	$M_n = 4793$ and $M_w/M_n = 1.14$ for PSTY	[294]
RAFT	MMA	2-Cyane-2-propyl dithiobenzoate	AIBN	$M_w/M_n \sim 1.25$	[295]
RAFT	VND/EGDMA	Xhantates		Similar microsphere distributions as in RP for poly(VND-EGDMA)	[296]
RAFT	MMA	2-Cyane-2-propyl dithiobenzoate		$M_w/M_n \sim 1.25$	[266]

dNbpy, copper halide/4,4′-di(5-nonyl)-2,2′-bipiridine; EBiB, ethyl-2-bromoisobutirate; VND, vinyl neodecanoate; EGDMA, ethylen-glycol-dimethacrylate; V-70, 2,2′-azobis(4-methoxy-2,4-dimethyl valeronitrile); Fe(Cp)I $(CO)_2$ dicarbonylcyclopentadienyliodoiron(II) $Co(acac)_2$, copper acetylacetonate; A, $(CH_3)_2C(CO_2-Et)I$; B, dichloroacetophenone; C, 1,1-dimethyl-2-ethylhexanperoxoate; TMTD, tetramethylthiuram disulfide; p-XDC, dimethyldithiocarbamate-p-xylene; DCP, dicumyl peroxide; and AIBN, 2,2′-azobisisobutyronitrile; DVB, divinyl benzene; STY, styrene; MMA, methyl methacrylate; AN, acrylonitrile; BMA, butyl methacrylate; BA, butyl acrylate; VC, vinyl chloride; VAc, vinyl acetate.

butadiene in the presence of BPO (benzoyl peroxyde) as initiator and TEMPO (2,2,6,6, tetramethylpiperidin-1-yl)oxyl) as controller. They obtained reasonably low molecular weight dispersities (~1.35). Other CRP cases carried out in suspension are listed in Table 14.2.

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