HIGHLIGHT

Emulsion Polymerization: From Fundamental Mechanisms to Process Developments

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ABSTRACT: Emulsion polymers are "products by process" whose main properties are determined during polymerization. In this scenario of margins reduction, increasing competition, and public sensitivity to environmental issues, the challenge is to achieve an efficient production of high-quality materials in a consistent, safe, and environmentally friendly way. This highlight reviews the investigations carried out at The University of the Basque Country to develop a knowledge-based strategy to achieve these goals. First, the research in fundamental mechanisms is discussed. This includes studies in radical entry and exit, oil-soluble initiators, propagation-rate constants of acrylic monomers, processes involved in the formation of branched and crosslinked polymers, microstructure modification by postreaction operations, the formation of particle morphology, and reactive surfactants. The advanced mathematical models developed in the group are also reviewed. In the second part, the advances in process development (optimization, online monitoring and control, monomer removal, production of high-solids, low-viscosity latices, and process intensification) are presented. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 1025–1041, 2004

Keywords: emulsion polymerization; miniemulsion; mechanisms; modeling; online monitoring and control; structure-property relations

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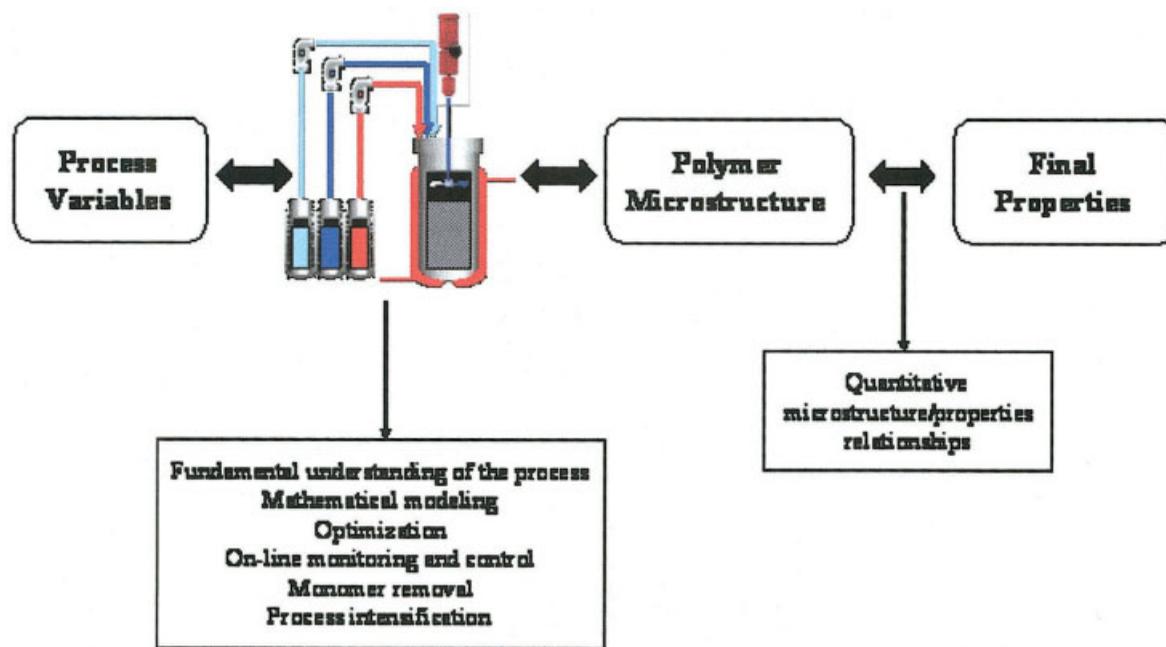*Correspondence to:* J. M. Asua (E-mail: jmasua@sq.ehu.es)

Figure 1. Knowledge-based strategy.

INTRODUCTION

Emulsion polymerization is used in the production of a wide range of specialty polymers including adhesives, paints, binders for nonwoven fabrics, additives for paper, textiles and construction materials, impact modifiers for plastic matrices, diagnostic tests, and drug-delivery systems.[1–4] The development of this industry has been due to both the possibility of producing polymers with unique properties and the environmental concerns and governmental regulations to substitute solvent-based systems by waterborne products.

The term *emulsion polymerization* encompasses several related processes: (1) conventional emulsion polymerization, (2) inverse emulsion polymerization, (3) miniemulsion polymerization,[5–7] (4) dispersion polymerization,[8–10] and microemulsion polymerization.[11,12] Conventional emulsion polymerization accounts for the majority of the world's production ($>20 \times 10^6$ tones/year).

In this scenario of margins reduction, increasing competition, and public sensitivity to environmental issues, emulsion polymer producers are forced to achieve an efficient production of high-quality materials in a consistent, safe, and environmentally friendly way. Emulsion polymers are "products by process" whose main properties are determined during polymerization. A critical point is to know how these process variables affect the final properties of the product. A possibility is to consider the reactor as a black box and to develop empirical relationships between process variables and product properties. Although this approach likely dominates current practice, this cannot be a long-term solution in a scenario of strong competition and margin reductions. Long-term success can only be guaranteed with knowledge-based strategies that use the polymer microstructure [here, the term microstructure is used in a broad sense including aspects such as copolymer composition, molecular weight distribution (MWD), branching, crosslinking, gel fraction, particle morphology, and particle size distribution (PSD) of the dispersion] as a link between the reactor variables and the final properties (Fig. 1).

The implementation of the approach illustrated in Figure 1 has important economic implications and is scientifically challenging. On the one hand, the needs/opportunities of the market, expressed as desired properties of the final product, should be translated in terms of the desired polymer microstructure. This requires quantitative microstructure/properties relationships. On the other hand, this polymer microstructure should be achieved in the reactor. This involves a deep understanding of the emulsion polymerization process, the highest level of understanding being the development of predictive mathematical models. In addition, an efficient, safe, and consistent production requires accurate online monitoring, optimization, and control. Last but not least, efficient methods for removal of residual monomer and volatile organic compounds (VOC) should be developed to produce environmentally friendly products.

This highlight discusses the work performed at the University of the Basque Country, placed within the
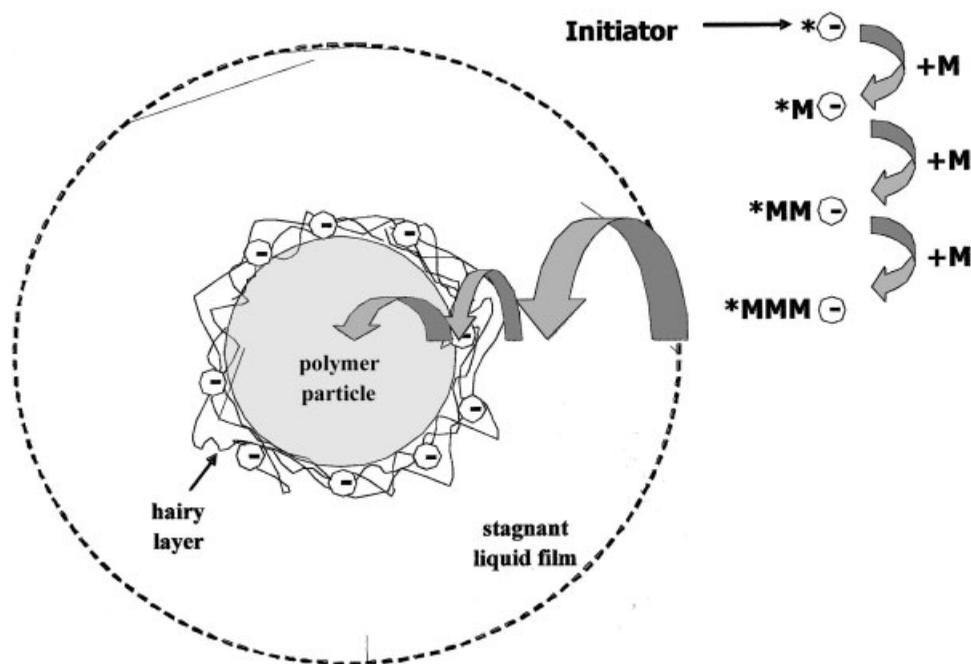
Figure 2. Mechanisms for radical entry.

context of the research published by other groups, in all these fields. This article is organized as follows. First, the research in fundamental mechanisms is discussed. Second, the advances in process development (optimization, online monitoring and control, monomer removal, the production of high-solids content low-viscosity latices, and process intensification) are presented. This article ends with a discussion on the prospects for emulsion polymerization.

INSIGHTS IN FUNDAMENTAL MECHANISMS

Radical Entry and Exit

From a mechanistic point of view, radical compartmentalization is likely the most distinctive feature of emulsion polymerization. This refers to the fact that the radicals are distributed among the different particles, and hence radicals in different particles cannot terminate between them. This allows the simultaneous achievement of high polymerization rates and high molecular weights. Both the polymerization rate and the molecular weights depend on the number of radicals per particle.

The average number of radicals per particle depends on the relative rates of radical entry from the aqueous phase, radical exit from the polymer particles, and bimolecular termination in the polymer particles. When water-soluble initiators are used, the radicals are generated in the aqueous phase, and often they are too hydrophilic to

be able to enter into the polymer particles. Therefore, they propagate in the aqueous phase, and once they become hydrophobic enough they enter into the polymer particles by diffusion through the stagnant liquid film, the surfactant hairy layer, and the polymer particle[13] (Fig. 2). In some cases, the growing oligoradical changes from being highly hydrophilic to becoming highly hydrophobic upon reaching a critical length z after the addition of one monomeric unit. Under these circumstances, in the so-called propagational entry model,[14] it is proposed that the entry of radicals of length z is instantaneous, and hence the rate of entry is the rate of formation of radicals of length z. Simulations show[15] that for systems in which the hydrophilicity of the oligoradical does not change abruptly upon addition of a single monomer unit, oligoradicals of lengths shorter and longer than z substantially contributed to the overall entry rate. Nevertheless, the propagational model represents a pragmatic approach to estimate the radical entry rate for emulsion homopolymerization.[15] However, in emulsion copolymerizations the choice of the critical length for entry may be difficult because the water solubility of the oligomers depends on the composition of the oligomer that for short-chain oligomers may vary significantly from chain to chain. In addition, the propagational model does not account for the decrease in entry rate caused by either electrostatic repulsion when highly charged latices are used[16] or thick layers of electrosteric stabilizer.[17,18]
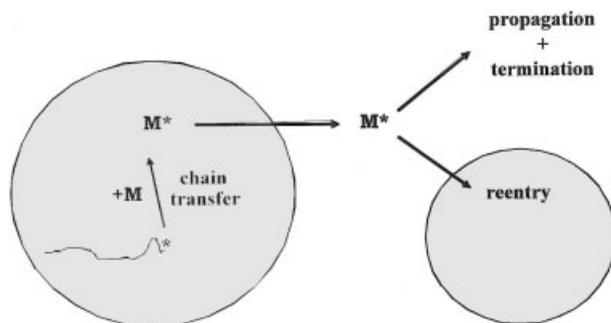
Figure 3. Mechanisms of radical exit.

Radical desorption occurs with the formation of single-unit radicals by chain transfer to monomer or to chain-transfer agents (CTAs) followed by diffusion of the newly formed radical to the aqueous phase. The desorbed radicals may either react in the aqueous phase by propagation and termination or reenter the polymer particles (Fig. 3). Radical desorption is commonly accounted for by the desorption-rate coefficient (k_d) such as the overall net rate of radical desorption for a population of (N_p) polymer particles with an average number of radicals per particle ($\bar{n}$,) as $R_{\text{exit}} = k_d\bar{n}N_P$(radicals/L s). Equations for the desorption-rate coefficient have been available for some time,[19] but it has been demonstrated[20] that they were erroneous, and a new equation has been proposed. The new model unveils the unexpected effects of several operational variables on k_d. In particular, k_d decreases with the number of polymer particles in the system (namely, with the solids content for a constant particle radius) because when N_p increases, it is more likely that the desorbed radicals re-enter the polymer particles, and hence the net exit rate decreases (Fig. 4). On the other hand, k_d increases as the concentration of radicals in the aqueous phase increases, namely, with an increasing initiator concentration or with redox systems. Another surprising result is that for a constant solids content, k_d was not significantly affected by the particle size because of the counteracting effect of the decreasing particle size and an increasing number of particles. Nevertheless, for a constant number of particles, k_d decreases as the particle size increases. This model also accounts for the reduction of the radical desorption-rate coefficient caused by dense hairy layers.[17,18]

Considerable effort has been devoted to estimate the radical entry- and exit-rate coefficients from the experimental data.[21–26] However, these investigations were not conclusive in terms of the elucidation of the mechanisms of radical exit because of the assumption that k_d was independent of operational variables such as the number of polymer particles and the initiator concentration. A practical consequence is that the desorption-rate coefficients determined under some given experimental con-

ditions cannot be directly used to predict the behavior of emulsion polymerization systems under different conditions.

Oil-Soluble Initiators

In some cases, for example, when polymerization in the aqueous phase needs to be minimized, the use of oil-soluble initiators is advantageous. Highly water-insoluble initiators can also be used to limit diffusional degradation of the monomer droplets in miniemulsion polymerization.[27] Although oil-soluble initiators are mainly located in the polymer particles, they exhibit some water solubility (e.g., the partition coefficient of azobisisobutyronitrile between polymer particles and the aqueous phase is 115). Therefore, radicals are formed in both polymer particles and the aqueous phase. There has been a debate about which phase is the main source of effective radicals. For some researchers, the two radicals formed by decomposition of the initiator in the polymer particles will suffer from instantaneous termination because they are restricted to a very small volume. Consequently, only the radicals generated in the aqueous phase would be effective for initiating the polymerization. For others, the rate of diffusion out of the particle of the newly formed radicals is greater than the rate of termination, and hence they do not immediately terminate in the polymer particles being the main source for effective radicals. Simulations carried out by Asua et al.[28] suggested that radicals formed in the polymer particles are the main source of effective radicals. Opposite results also were obtained by simulation by Nomura and Fujita[29] with a model in which the type of radical was not accounted for properly. Seeded emulsion polymerizations carried out at varying organic-phase/aqueous-phase
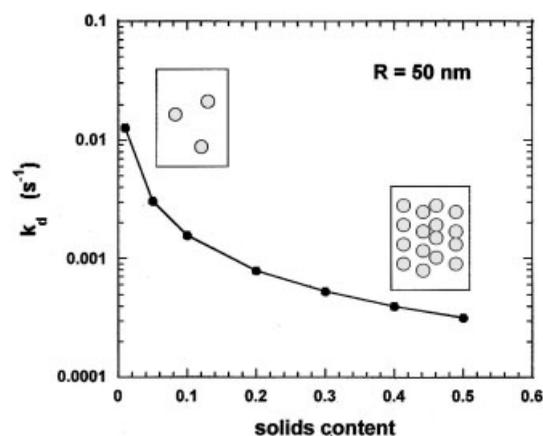

Figure 4. Effect of the number of polymer particles (solids content at constant particle size) on the exit-rate coefficient.

volume ratios showed that for the rest of the conditions constant, the polymerization rate per polymer particle increased when the organic/aqueous volume ratio increased, namely, when the amount of initiator dissolved in the aqueous phase per polymer particle decreased.[30] This is evidence against a dominant formation of radicals in the aqueous phase. However, these results are consistent with a mechanism in which the radicals are mainly produced in the oil phase. More recently, Suzuki and Nomura[31] failed to explain their experimental results with a model in which the initiator dissolved in the aqueous phase was the main source of effective radicals, and they attributed the failure to the preferential formation of radicals in the polymer particles. Asua[32] with a first-principles model concluded by simulation that radicals formed in the polymer particles are responsible for particle growth. In addition, in conventional emulsion polymerization, nucleation of polymer particles is due to the radicals generated in the aqueous phase because the probability of bimolecular termination in micelles is very high, and the rate of desorption of initiator radicals from monomer droplets is very low. However, in miniemulsion polymerization nucleation of polymer particles is due to radicals generated in the monomer droplets.

Propagation-Rate Constant of Acrylic Monomers

The polymerization rate is proportional to the propagation-rate constant (k_p). Pulsed-laser polymerization (PLP) has been adopted as the method of choice for the determination of the k_p's, and benchmark values have been provided for some monomers.[33,34] However, the method has encountered difficulties for determining k_p values of alkyl acrylates at temperatures higher than 30 °C.

Alkyl acrylates are prone to suffer both intra- and intermolecular chain transfer to polymer[35–41] yielding branched polymers. Evidence of the formation of branches in PLP of butyl acrylate (BA) has been provided.[42] It has been demonstrated[43] that the formation of tertiary radicals by intramolecular chain transfer (back-biting) is responsible for the difficulties encountered in determining k_p by means of PLP experiments. In these reactions, tertiary radicals, which are significantly less reactive than the secondary radicals formed by propagation, are produced. Therefore, in a PLP experiment the chains that suffer back-biting will reach a shorter length than those that did not undergo any back-biting. In addition, the length of each chain depends on the number of back-biting reactions that the chain suffered. This leads to featureless molecular weight distributions (MWDs) from which no consistent value of the k_p can be obtained. This problem is more evident at high temperatures because the activation energy of the back-biting is higher than that of the propagation, and hence the fraction of tertiary
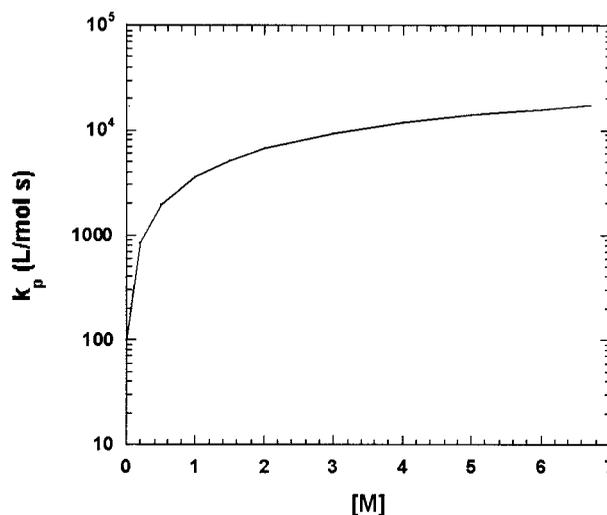
Figure 5. Influence of the monomer concentration on the effective propagation-rate constant of butyl acrylate ($T = 75$ °C).

radicals sharply increases with temperature.[42] Simulations carried out by Nikitin et al.[44] further support the idea that back-biting is responsible for the problems encountered in the determination of k_p in acrylic systems. These researchers discussed the conditions in which successful PLPs of acrylic monomers could be performed. In addition, they found[45] that the value of the k_p determined from those experiments depends on the frequency of the pulsed laser. For very high frequencies, the measured k_p corresponds to that of the secondary radicals. The measured k_p decreases as the pulse frequency decreases, and at low frequencies the value of the effective k_p defined by Plessis et al.[37] is reached.

The existence of tertiary radicals has important practical implications. The effective k_p is the average between the k_p's of secondary and tertiary radicals. Therefore, it depends on the relative concentrations of these radicals, which depend on the monomer concentration in the polymer particles, and to a lesser extent on the polymer concentration. Consequently, the effective k_p depends not only on temperature but also on monomer and polymer concentrations in the polymer particle.[37,46] Figure 5 shows that the effective k_p sharply decreases when the emulsion polymerization is performed under starved conditions.

Branched and Crosslinked Emulsion Polymers

As illustrated in Table 1, the application properties of branched and crosslinked polymers substantially depend on the polymer architecture. Consequently, there is strong interest in understanding the processes involved in the formation of the polymer architecture. There are two

Table 1. Effect of Polymer Microstructure on the Adhesive Properties of Poly(Butyl Acrylate)

| Gel Fraction (%)	M_w	Tack (cm)	Shear (s)	Peel (N/100 mm)
1	340,000	0 ± 0	45 ± 12	11 ± 1.1
32	430,000	0 ± 0	1820 ± 210	23.4 ± 3.6
55	523,000	0.5 ± 0.2	40 ± 10	16.9 ± 1.6

different situations. In emulsion polymerization of monomers containing a single double bond, branching occurs by chain transfer to polymer and to a lesser extent through propagation to terminal double bonds. Polymer networks (gel) can be formed in these systems if termination by combination is predominant. When monomers containing two or more double bonds are included in the formulation, the network formation is mainly due to propagation to pendant double bonds.

Emulsion polymerization of acrylic monomers is representative of the first situation because these monomers are prone to suffer chain transfer to polymer, and termination is mainly due to combination, although disproportionation may also be operative.[47] In the semicontinuous emulsion polymerization of BA, Plessis et al.[38,39,46] found that the higher the initiator concentration and the longer the process time the higher the level of branches, but the same gel fraction was obtained independently of the process conditions. This means that gel and branching were not correlated. The reason is that most of the branches were produced by intramolecular chain transfer (back-biting). This reaction yields short branches that do not contribute to the formation of gel. The occurrence of back-biting is inversely proportional to the concentration of free monomer in the polymer particles. Under starved conditions, relatively modest variations of the instantaneous conversion lead to substantial changes in monomer concentration, and hence higher initiator concentrations and longer process times led to a higher number of branches. The predominance of the intramolecular mechanism has been further supported by Farcet et al.[48] with end-group analysis of polymers obtained in nitroxide-mediated, controlled radical polymerization.

The formation of long-chain branches (followed by termination by combination) is required for gel formation. Long branches are formed by intermolecular chain transfer to polymer. The rate of this process is proportional to the concentration of polymer in the polymer particles, which do not vary significantly under starved conditions. Therefore, the gel fraction was not affected by the initiator concentration and the process time. This is technologically significant because the gel content should be tuned to achieve the desired final properties.

Plessis et al.[41] demonstrated that the efficient control of both the gel content and the sol MWD can be achieved with chain-transfer agents (CTAs). They also found that the level of branches was not affected by the CTA concentration, which is consistent with a polymer architecture in which most branches were short. In emulsion polymerization of acrylic monomers, the polymer architecture is strongly modified by the presence of relatively small fractions of styrene in the formulation. In the copolymerization of BA and styrene,[39] the fraction of gel decreased from 55% to almost nil, and the level of branches decreased from 14 to 5 branches per 1000 carbons in the backbone when the amount of styrene increased from 0 to 10 wt %. However, the gel content and the sol MWD of the seed had no influence on the architecture of the final polymer.[49] Some limited work on the emulsion polymerization of 2-ethyl hexyl acrylate (2EHA) indicated that the reaction scheme proposed for BA was also operative for 2EHA.[40] In addition, both monomers seem to follow the same correlation between branching level and monomer concentration (Fig. 6). The results in Figure 6 are in conflict with those reported by Heatley et al.[50] who found that 2EHA tends to give higher levels of branches than BA.

In studies involving the use of crosslinking agents of different reactivity [allyl methacrylate (AMA) and butanediol diacrylate (BDA)] in the emulsion polymerization of BA, it was found[51] that at the beginning of the process the more reactive crosslinker (BDA) gave a polymer more crosslinked than the less reactive one (AMA). However, at the end of the process, the crosslinking density of the polymer containing AMA was greater. This trend was accelerated during the cooking period in which the crosslinking density of the polymer containing AMA substantially increased, whereas
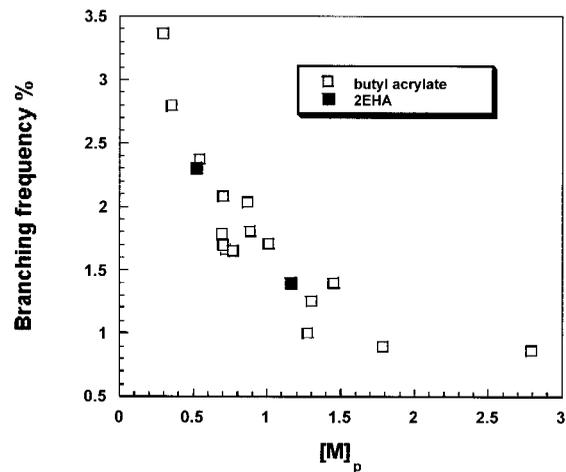
Figure 6. Effect of monomer concentration on branching level in the polymerization of acrylic monomers.
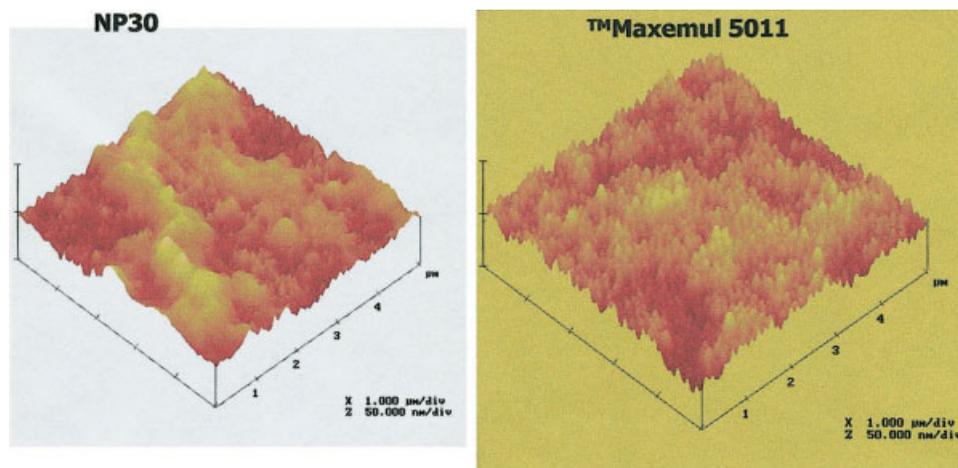
Figure 7. Evidence of exudation of a conventional surfactant (NP30) as compared with a non-migratory surfmer (™ Maxemul 5011).

for BDA there was no additional change of the crosslinking density.

Microstructure Modification

Emulsion polymers are considered to be "products by process"; hence, their characteristics are determined by the process variables used during polymerization. Although this is so for many emulsion systems, in some cases, the emulsion polymers may be modified either accidentally or on purpose in postreaction operations. An example of accidental modification of the microstructure (MWD, branching, and gel fraction) of the emulsion polymers may occur during postpolymerization of residual monomer with initiators able to generate free radicals in the polymer backbone, which may induce chain scission leading to shorter polymer chains and/or termination by combination yielding longer polymer chains. This may result in undesired modification of the polymer microstructure and consequently of the product properties. However, this may be an opportunity to extend the range of properties achievable with a given base emulsion polymer.

The effect of different initiator systems (*tert*-butyl hydroperoxide, *tert*-amyl hydroperoxide, *tert*-butyl perbenzoate, hydrogen peroxide, and potassium persulfate, all of them combined with ascorbic acid) on the polymer microstructure (MWD and gel content) of different emulsion polymers (vinylic, acrylic, and styrene-acrylic) was investigated, finding that only the initiator systems producing highly reactive *tert*-butoxyl radicals were able to cause polymer modification.[52] The effect of the *tert*-butoxyl radicals depends on the copolymer composition. In vinyl acetate (VAc)-rich copolymers, the *tert*-butoxyl radicals led to a decrease of the molecular weight. In

BA-rich polymers, the *tert*-butoxyl radicals caused an increase of the gel content. However, the microstructure of styrene–acrylic latices was not affected by treatment with *tert*-butoxyl radicals.

Particle Morphology

The performance of composite latex particles is strongly affected by their morphology. Early attempts to model this process have considered only limiting situations in which either the polymer chains do not move from the point in which they were formed[53,54] or the polymer chains and the clusters are completely mobile and the equilibrium morphology is instantaneously reached.[55] However, there is experimental evidence that incompatible polymer chains move from the point in which they were formed and that nonequilibrium morphologies are formed.[56] Gonzalez-Ortiz and Asua[57–59] developed a model able to describe the dynamics of the formation of particle morphology. The model, which agrees with the experimental findings, showed that the final particle morphology heavily depends on kinetic factors, such as the polymerization rate and the internal viscosity of the polymer particles. Although composite latex particles are almost entirely prepared in semicontinuous reactors, the feasibility of producing them in continuous stirred tank reactors has been explored.[60]

Reactive Surfactants

Surfactants play a crucial role in the production and applications of the dispersed polymers. However, they can also have adverse effects because of the possibility of desorption from the latex particle surface, which reduces mechanical stability under high shear and the

migration of the film that affects water sensitivity, adhesion, and gloss. The use of polymerizable surfactants (surfmers) is a promising way to overcome the drawbacks associated with the use of conventional emulsifiers. The use of surfmers in heterophase polymerization has been reviewed in terms of the mechanisms relevant to the process.[61] Improvements in water resistance[62] and adhesion[63] have been reported with surfmers instead conventional emulsifiers. Water and vapor permeability were also reduced with surfmers.[64] Atomic force microscopy[65,66] measurements determined that these improvements are likely due to the fact that the use of surfmers is an effective way of eliminating unwanted surfactant exudation (Fig. 7). This has been further checked by Rutherford backscattering spectrometry.[66]

The reactivity of the surfmer and its adsorption characteristics are critical in surfmer performance. Relatively water-soluble surfmers of high reactivity tend to polymerize in the aqueous phase causing premature latex instability.[62,67]

To be effective, the surfmers must react in such a way that for the main part of the process, the surfmer conversion should be low (to avoid surfmer burying and hence maximize the amount of surfmer present at the surface of the polymer particles), and toward the end of the reaction, high surfmer conversion should be achieved (to avoid surfmer migration during film formation).[68] These requirements are the main drawback of surfmers because the optimal surfmer structure (reactive group) and feed strategy depend on the monomer system and the way in which the monomers are fed into the reactor. Strategies based on optimal surfmer addition profiles calculated with a mathematical model for the process[69] have been implemented. Thus, in the emulsion copolymerization of methyl methacrylate (MMA)/BA/acrylic acid, stabilized with a commercial surfmer (Maxemul 5011, Uniqema), despite the low reactivity of the surfmer, with the optimal policy it was possible to increase the surfmer conversion from 58 to 72% maintaining the latex stability and reducing substantially the process time.[70]

One may expect that the use of surfmers will affect the nucleation process. However, for the emulsion homopolymerizations of styrene, MMA, and VAc, the substitution of a conventional surfactant for a maleate surfmer had no effect on the nucleation mechanism (which was micellar for styrene and homogeneous for both MMA and VAc).[71] In addition, the type of surfactant [reactive vs sodium dodecyl sulfate (SDS)] did not affect the dependence of the number of particles upon the surfactant concentration for styrene, but the dependence for the surfmer was lower than that for SDS in the cases of MMA and VAc. Similar conclusions were reached in the emulsion polymerization of styrene with an allyl surfmer.[72]

Advanced Mathematical Modeling

As stated above, the highest level of process understanding is the development of predictive mathematical models. Therefore, considerable effort has been dedicated to the organization of the fundamental understanding in terms of mathematical models. Models for radical desorption;[20] the distribution of radicals in the polymer particles;[53] MWD of linear,[73] branched,[39,74] and crosslinked[46,75] polymers; PSD;[76] the development of nonequilibrium particle morphology;[57–59] polymerization of multimonomer (vinylic, divinylic, and acidic) systems;[77] surfmer polymerization;[69] systems affected by diffusional limitations;[78] dispersion polymerization;[79] microemulsion polymerization;[80] and postpolymerization of residual monomers[81] have been developed.

PROCESS DEVELOPMENTS

To implement the strategy outlined in Figure 1, it is necessary to translate the ultimate product performance in terms of polymer microstructure by means of quantitative polymer micro-structure–property relationships. Although examples of quantitative micro-structure–property relationships are available (e.g., for the effect of copolymer composition profile[82] and MWD[83,84] on adhesive properties and for the effect of PSD on latex rheology[85]), much work is needed in this area.

Optimization

Once the desired microstructure of the polymer is known, an optimal trajectory should be computed. When a mathematical model is available, the optimal trajectory can be calculated with standard optimization algorithms.[86–90] The first-principles mathematical models for emulsion polymerization are often complex and neural networks[91–93] have been used to reduce the complexity of the problem. In some cases, a good understanding of the process allows the simplification of the optimization problem. Thus, for the production of copolymers with a given composition (Y_A), it is sufficient to maintain the ratio of monomer concentrations at the value calculated from the Mayo–Lewis equation[94–96]

$$\frac{[A]_P}{[B]_P} = \frac{(K_1 - 1) + [(K_1 - 1)^2 + 4r_A r_B K_1]}{2r_A} \quad (1)$$

where $[i]_p$ is the concentration of monomer i in the polymer particles, $K_1 = Y_A (1 - Y_A)$, and r_i are the reactivity ratios. To correlate the concentrations of the monomers in the polymer particles with the total amount of monomers in the reactor, the partitioning of the mono-

mers among the different phases should be calculated. This can be done with models of different complexity. The models have been reviewed by Gugliotta et al.,[97] who on the basis of using the simplest but sufficiently accurate model, recommended constant partition coefficients for monomers of low and moderate water solubility (<5/100 g of water) and the Morton model[98] for highly water-soluble monomers (e.g., acrylic acid). The reactivity ratios used in eq 1 are based on the ultimate model, which has been reported[99] to accurately describe the evolution of the copolymer composition. Methods to estimate the reactivity ratios from emulsion polymerization experiments with the whole range of monomer conversions have been reported.[100]

In addition, maximum production in emulsion polymerization reactors is limited by the heat-removal capacity of the reactor. Therefore, the optimal process is a process in which the rate of heat generation by polymerization is equal to the safe, maximum heat-removal rate of the reactor. In this context, the safe, maximum heat-removal rate means that some additional cooling power is available as a safety margin. When the heat-removal capacity of the reactor is known, the optimal trajectory is readily available and has been used in both open-loop[101] and closed-loop[102] control strategies. In addition, the heuristic knowledge of the plant operators can be used to build a fuzzy system to determine online the optimal trajectory.[103]

Online Monitoring

To follow the optimal polymerization trajectory, both open-loop and closed-loop control may be used. Early strategies were based on open-loop strategies,[94–96,101,104] but the run-to-run irreproducibility forced the development of closed-loop control. A successful closed-loop control strategy needs robust and accurate online monitoring devices.

The development of accurate and robust online monitoring devices is the limiting factor for the implementation of control strategies in emulsion polymerization reactors. Excellent reviews on online monitoring of (emulsion) polymerizations are available.[105–108] There are three main reasons for these limitations. First, latices are thermodynamically unstable multiphase systems prone to suffer coagulation. Second, emulsion polymers are complex materials with multiple characteristics (copolymer composition, chemical composition distribution, MWD, branching, gel, PSD, particle morphology, etc.), whose determination requires the use of a variety of experimental techniques. Third, some of the analysis requires long times (sometimes longer than the polymerization time), the equipments are expensive, and are not adapted for online purposes.

In practice, only a few characteristics are observable online. Here, the term observable is used in a somehow loose way and includes the characteristics that can either be directly measured online or that can be estimated in a relatively precise way from online measurements. Monomer concentration, the polymerization rate, and copolymer composition are the characteristics most often measured online. The three magnitudes are related through the material balance.

Online analysis of unreacted monomers in high solids (55 wt %) emulsion polymerization was achieved with gas chromatography (GC).[109] The setup was used to monitor emulsion copolymerizations[110] and terpolymerizations[111] as well as the consumption of CTAs.[87] However, online GC is prone to suffer mechanical problems.

The polymerization rate is best measured with either heat-flow or heat-balance reaction calorimetry.[112] Heat-flow reaction calorimetry is best adapted for small lab reactors. The main limitation of this technique is that the value of the overall heat-transfer coefficient must be known. This limitation may be overcome with oscillatory heat-flow calorimetry that allows the online estimation of the overall heat-transfer coefficient.[113] The usefulness of oscillatory calorimetry is limited to small reactors.[114,115] Heat-balance calorimetry is best suited for large-scale commercial reactors. Reaction calorimetry allows the online determination of the rate of heat generation by polymerization, which is proportional to the polymerization rate. Integration of the polymerization rate over time allows the estimation of monomer conversion and copolymer composition. This was first demonstrated by Urretabizkaia et at.,[116] and since then both open-loop[117–121] and closed-loop[122,123] estimators have been proposed.

Under starved conditions, which are commonly used in emulsion polymerization, the accuracy of reaction calorimetry for the estimation of the amount of unreacted monomer is limited. This can be illustrated by the following example. If an emulsion polymerization is conducted in such a way that the instantaneous conversion is 0.9 and applying reaction calorimetry the estimated conversion is 0.94, the error in monomer conversion is about 4%, which for most applications would be acceptable. However, the estimated fraction of unreacted monomer would be 0.06 instead of 0.1, which represents a 40% error. This may have severe consequences in process control because the polymerization rate and polymer characteristics depend on the amount of unreacted monomer in the reactor.

Spectroscopic techniques are in principle able to provide a direct measurement of the unreacted monomer. An excellent discussion of the strengths and weaknesses of the different spectroscopic techniques has been published by Hergeth.[107,124] The recent development of fiber-optic probes suitable for remotely collecting spectra

via optical fibers has given rise to the possibility of making *in situ* measurements in remote and harsh environments[125] (high temperatures, pressures, toxic environments, etc.). The spectroscopic techniques coupled with fiber optics have a high potential for online monitoring and can provide important information about the state and nature of the samples under analysis. An additional advantage is that a fiber-optic probe can be installed in an existing reactor without time-consuming and expensive modifications.

Raman spectroscopy is well suited for online monitoring in emulsion polymerization because water has a very weak Raman response, and double and triple bonds in monomers and polymers are very strong Raman scatterers. Styrene/butadiene,[126,127] styrene/*n*-BA,[128] and Veova 9/BA[129] emulsion copolymerizations have been monitored by means of Raman spectroscopy. For systems containing styrene, usually the peak associated with the ring-breathing mode of styrene at 1000 cm^{-1} is used to normalize the spectral intensity, and the calibration stage does not present any difficulties.[125] All acrylic copolymerizations are much more complex because the bands of the main functional groups of the different acrylic monomers of the formulation overlap because of the similarity in the chemical structure. Therefore, univariate calibration methods are not appropriate, and multivariate calibration techniques such as partial least-squares regression[130] are required. An online monitoring technique based on Fourier transform Raman for all acrylics high-solids-content (50 wt %) emulsion copolymerizations has been developed.[131] The method was applied to a system containing *n*-BA and MMA. Unreacted monomer amounts, solids content, and cumulative copolymer compositions were the variables monitored.

Particle size and PSD strongly affect the emulsion polymerization process as well as the application properties of the latex. The accurate offline determination of the latex PSD is still an unsolved issue,[132] and the advances in online monitoring of this variable are modest.[133–136] Artificial neural networks were evaluated as soft sensors to monitor particle size online during the 55 wt % emulsion polymerization of VAc and Veova 10 carried out in a continuous loop reactor.[137]

Online Control

The ultimate goal of the control strategies is to achieve maximum production of emulsion polymers of consistent quality under safe and environmentally friendly conditions. Because emulsion polymerization is prone to suffer run-to-run irreproducibility, only feedback control may ensure the consistency of the product quality. In addition, product quality depends on many microstructural characteristics of the latex including copolymer composition, MWD, branching, crosslinking, gel content, particle morphology, and PSD. However, no attempts to simultaneously control all of these properties have been reported. Reviews on this subject are available.[138,139]

Polymer composition is the characteristic more frequently controlled. Control schemes based on GC monitoring were developed,[140] and although in some cases the composition of copolymers[110] and terpolymers[111] of relatively high solids content (55 wt %) was controlled, online GC was prone to suffer mechanical problems. Successful strategies for copolymer[118,119,141] and terpolymer[120,142] composition control based on reaction calorimetry have been reported. The problem of the maximum production of latices of well-defined composition was addressed by Saenz de Buruaga et al.[102] The control scheme developed by these researchers was also able to avoid monomer accumulation in the reactor that may lead to potentially dangerous thermal runaways.

Emulsion linear homopolymers of well-defined MWD were obtained by means of control strategies based on online GC measurements of both unreacted monomer and CTA[87] and on reaction calorimetry.[143] The simultaneous online control of copolymer composition and MWD of linear copolymers based on reaction calorimetry has also been reported.[144] The strategy for MWD control, which is summarized in Figure 8, was based on the fact that for linear polymers produced by free-radical polymerization, the polymer chains do not suffer modifications once they are formed. This opens the possibility of decomposing the desired final MWD in a series of instantaneous MWDs to be produced at different stages of the process. Each of the instantaneous MWDs is characterized by a single parameter, the number-average molecular weight (X_n), which depends on the monomer/CTA ratio

$$X_n = \frac{k_P[M]_P}{k_{fCTA}[CTA]_P} \qquad (2)$$

where k_{fCTA} is the CTA constant. When combining the two pieces of information, the evolution of the monomer/CTA ratio required to achieve the desired MWD is calculated (Fig. 8).

The formation of nonlinear polymers involves processes such as chain transfer to polymer and propagation to terminal and pendant double bonds, which imply that the inactive chains may reenter in the polymerization modifying their molecular weight. This makes the online control of the MWD of nonlinear polymers more challenging.[145,146] Although open-loop control strategies have been developed,[89] the closed-loop control of the MWD of these polymers is still a pending issue.

$$\overline{X}_{n,i} = \frac{R_p}{R_t} = \frac{k_p [M]_p}{k_{fCTA} [CTA]_p}$$
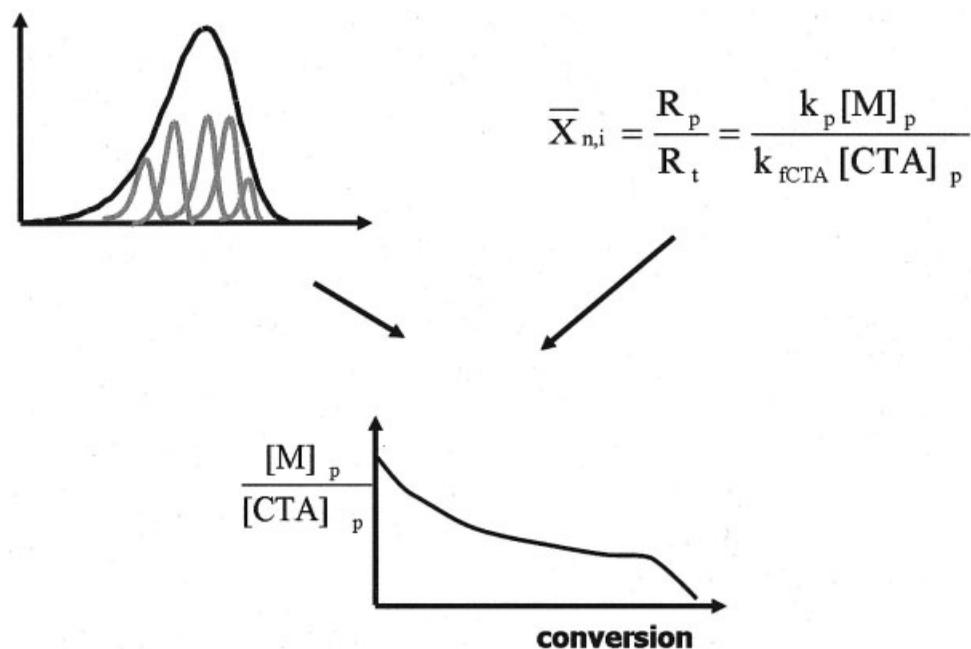
Figure 8. Strategy for MWD control of linear polymers.

Monomer Removal

In emulsion polymerization the reaction rarely proceeds to completion and inevitably some amount of unreacted monomer remains in the polymer. Because of environmental regulations and market preferences, it is necessary to remove unreacted monomers and other organic compounds (VOCs) from the latex.

Both postpolymerization and devolatilization are used to reduce the residual monomer content in latices.[147] Postpolymerization consists of adding, after the end of the main polymerization process, initiators to polymerize the residual monomer. This is the preferred method for monomer removal because it may be carried out in the polymerization reactor or in the storage tank, and no additional equipment is needed. Water-soluble redox initiators yielding hydrophobic radicals present advantages for monomer removal by postpolymerization, independently of the water solubility of the monomers.[148] The main reason is that hydrophobic radicals can enter into the polymer particles, where most of the residual monomer is, much easier than the hydrophilic radicals, which must undergo a number of propagation steps before becoming hydrophobic to be able to enter into the polymer particles. However, some of these redox systems (e.g., those containing *tert*-butyl hydroperoxide) may suffer secondary reactions that would give VOCs as byproducts.[149] Model-based optimal postpolymerization strategies minimizing the amounts of both the residual monomers and VOCs have been developed.[150]

Postpolymerization cannot be applied to the removal of nonpolymerizable VOCs. These compounds may be impurities contained in the raw materials as well as products of side reactions occurring during the polymerization and/or postpolymerization. When nonpolymerizable VOCs are present, devolatilization must be used. In the devolatilization, the latex is stripped with either steam or inert gas *in vacuo* conditions until acceptable low concentrations of residual monomer and VOCs are reached. The main advantage of this process is that both monomer and nonpolymerizable VOCs can be removed. However, devolatilization is highly energy-consuming and requires additional investments in equipment. In addition, under some conditions, foaming and coagulation may occur. Devolatilization experiments carried out with VAc/BA/acrylic acid latices of different particle sizes and under different agitation and sparger geometries showed that the mass transfer from the aqueous phase to the gas phase was the controlling step.[151] This implies that the process variables involved in the mass transfer between the aqueous phase and the gas phase, such as agitation, geometry of the sparger or gas-flow rate would improve devolatilization.

High-Solids, Low-Viscosity Latices

The synthesis of high-solids, low-viscosity latices has raised great interest from both industry and academia.[152] Possible advantages of highly concentrated emulsions,
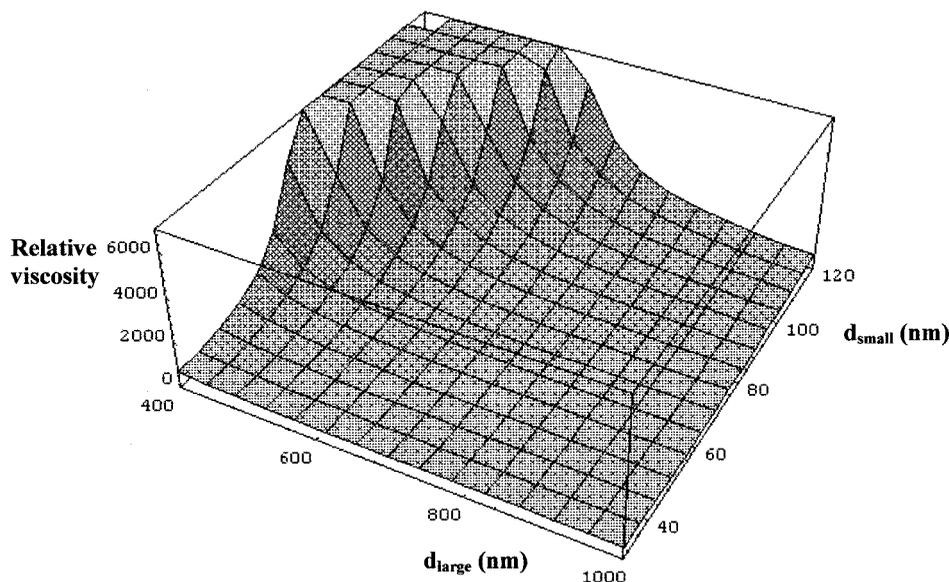
Figure 9.   Effect of the sizes of the small and large particles on the viscosity latex with a trimodal PSD [solids content: 70 vol %, weight proportion of particles: 80/10/10 (large/medium/small), medium particle size equal to 1.5 d_{small}.

understood by a highly concentrated latex with a solids content above 60 wt %, are numerous, including the higher unitary usage of industrial installations and the faster drying rates during application. Low viscosity is required for a higher heat-removal rate and a better mixing during the polymerization process that allows improvements in safety, production capacity, and product quality. For a given solids content, the latex viscosity decreases with the broadness of the PSD. In addition, bimodal PSDs containing about 20 wt % of small particles and 80 wt % of large particles yield low-viscosity latices. The viscosity of these bimodal PSDs is further reduced by increasing the size of the large particles. This heuristic knowledge has prompted a number of polymerization strategies. Masa et al.[153] and Unzué and Asua[154] used semicontinuous processes in which both the initial charge and the feed were monomer miniemulsions. The continuous nucleation of the miniemulsion droplets resulted in a broad PSD that allowed obtaining a 65 wt % solids constant latex of low viscosity. Leiza et al.[155] obtained a 61 wt % solids content latex by preparing by miniemulsion polymerization a latex with a rather broad PSD as initial charge and using this latex as seed in a conventional, semicontinuous emulsion polymerization. Bimodal PSDs have been prepared in semicontinuous emulsion polymerizations by generating a second crop of particles through the addition of a shot of emulsifier.[156] The use of several seeds is a popular way of producing bimodal latices. Chu and Guyot[157] used a large particle size seed in the initial charge, and a small one was added as a shot during the process. Schneider et al.[158,159] fa-

vored the growth of the large particles with an oil-soluble initiator.

To a great extent, the strategies for the production of high-solids-content, low-viscosity latices outlined above were developed based on heuristic knowledge through trial-and-error approaches. To implement the strategy outlined in Figure 1 to the production of high-solids, low-viscosity latices, a quantitative relationship for the effect of PSD on latex rheology should be available. Recently, do Amaral et al.[85] experimentally assessed the capability of Sudduth's[160] viscosity equation to account for the influence of both the PSD and the physicochemical characteristics of the dispersion. Combining the viscosity equation with a polymerization model, do Amaral et al.[161] developed a knowledge-based approach, which was used to explore possible polymerization scenarios (Fig. 9) in such a way that the most promising reaction conditions were identified and experimentally checked.[162,163] In this way, high-solids-content latices with fine-tuned viscosity were obtained[164] (Table 2).

Table 2.   High-Solids Content Latices with Fine-Tuned Viscosity

Solids Content (wt %)	Viscosity (mPa · s)
65.5	4300
67.7	150
70.4	2850

Process Intensification

Process intensification refers to technologies that replace large, expensive, energy-intensive equipment or processes with ones that are smaller, less costly, and more efficient. The development of the continuous loop reactor[165] (CLR) is an example of process intensification in emulsion polymerization. This reactor consists of a tubular loop that connects the inlet and the outlet of a recycle pump. Reactants are continuously fed into the reactor, and the product is continuously withdrawn from the reactor. Because of its large heat-transfer area/reactor volume ratio, high conversions in short residence times can be achieved. This results in a substantial reduction of the reactor volume.[166] Because of the small volume and the short residence time, the CLR can be used with great flexibility and minimum losses in the manufacture of different emulsion polymers. The small volume and the absence of head space make the process intrinsically safe. Likely, the main drawback is that because of the presence of the recycle pump, formulations with high mechanical stability are required to prevent shear-induced coagulation.

Abad et al.[167] compared the performance of a CLR with that of a continuous stirred tank reactor (CSTR), finding that the behavior of both reactors is almost the same at low heat-generation rates; otherwise, thermal runaway occurred in the CSTR while the temperature of the CLR was easily controlled. It has been reported[168] that the startup procedure did not affect the steady-state values of the monomer conversion, number of polymer particles, and MWD, but the smoothness of the operation could be substantially improved if the reactor was initially filled with previously formed latex. Araujo et al.[169] examined the effect of temperature, residence time distribution, and initiator concentration on the performance of a CLR in the redox-initiated emulsion copolymerization of VAc and Veova 10 under industrial-like conditions. For these latices, the technological goal is to achieve high conversions in short residence times (maximizing production rate) of a high-molecular-weight (maximum wet-scrub resistance of the paint formulated with this latex) and water-resistant polymer. However, it was found that to achieve high conversion at long residence times, high temperatures (that reduce the molecular weight) or high initiator concentrations (that reduce both the molecular weight and the water resistance of the polymer) should be used. Nevertheless, it has been demonstrated[170] that it is possible to take advantage of the particular reactor dynamics and conduct the polymerization in such a way that a pseudosteady state is reached in which high monomer conversions at short residence times, low temperatures, and low initiator concentrations are obtained. Basically, this strategy consists of starting the process at relatively high values of the residence time, temperature, and initiator concentration and later reducing them to the desired values. If these final conditions were implemented from the beginning of the process, low conversions, and sometimes coagulation, would be obtained.

PROSPECTS

In the near future, many new emulsion polymers will join the existing wide range of these materials available in the market. Nanocomposite nanoparticles (both polymer–polymer and polymer–inorganic), polymers with finely controlled architecture (block, graft, star, and hyperbranched), and linear and polar-functionalized polyolefins will likely be in the list of new waterborne polymers. This will require further developments in miniemulsion polymerization, controlled radical polymerization, and waterborne catalytic polymerization.

For both the existing and the new emulsion polymers, knowledge-based production strategies are advantageous. For the implementation of these strategies, substantial efforts should be devoted to gain fundamental understanding of miniemulsion polymerization, particle morphology formation and stabilization, polymer network formation, controlled radical polymerization, and waterborne catalytic polymerization, among other processes. Both hardware and software sensors for PSD, MWD, and particle morphology will be needed to address to problem of the control of the complete polymer microstructure. Last but not least, quantitative microstructure–property relationships including *ab initio* modeling should be developed.

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