

# Combining Process and Property Models: Development of Novel Reaction Strategies for High-Solids, Low-Viscosity Latices

Marcelo do Amaral,<sup>1</sup> Steven van Es,<sup>2</sup> José M. Asua<sup>1</sup>

<sup>1</sup>*Institute for Polymer Materials (POLYMAT) and Grupo de Ingeniería Química, Facultad de Ciencias Químicas, The University of the Basque Country, Apdo. 1072, 20080, Donostia-San Sebastián, Spain*

<sup>2</sup>*Surface Specialties UCB, Anderlecht Str. 33, Drogenbos, B-1620, Belgium*

Received 30 March 2004; accepted 6 May 2004

DOI 10.1002/app.21047

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Multiple strategies for the synthesis of high-solids, low-viscosity latices have been established in modern polymer industry. The basic principle supporting these strategies is the polydispersity of the particle size distribution. However, polymerization procedures are often based on experience, tacit knowledge acquired with time and repetitive trial-and-error procedures. Recently, a novel coupled polymerization–viscosity model has been proposed. The model aids screening of potential polymerization strategies. This work presents use of the model as a powerful tool

to design new strategies for obtaining highly concentrated aqueous polymer dispersions. By incorporating some simplifying assumptions into the coupled model, the feasibility for synthesizing high-solids latex with low viscosity using novel polymerization strategies was assessed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 733–744, 2005

**Key words:** polymerization–viscosity model; emulsion polymerization; dispersions; latices; synthesis

## INTRODUCTION

High-solids content, low-viscosity latices offer important potential advantages over conventional latices having lower polymer content. First, concentrated latices can be viewed as ecofriendly because their manufacturing energy consumption is proportionally lower, minimizing the contribution of the production process to the product life-cycle assessment. Second, drying rates are comparatively higher, favoring the application process.<sup>1</sup> Not surprisingly, commercial emulsion companies rushed to direct their research efforts toward gaining expertise for the synthesis of concentrated polymer dispersions.<sup>2–9</sup> New players risk entry into the uncertain and resource-consuming activity of fostering new polymerization formulations through trial-and-error approaches.

Recently, do Amaral et al.<sup>10</sup> proposed a simple coupled polymerization–viscosity model that could be used to aid in screening strategies for the synthesis of high-solids content (HSC), low-viscosity latices. Instead of focusing merely on the know-how, the authors proposed an alternative methodology to qualitatively and quantitatively judge the probability of success of a given formulation.

The aim of this work was to assess the applicability of the coupled polymerization–viscosity model as a screening tool for the development of alternative polymerization strategies for HSCs.

This article is organized as follows. First, a brief overview of the current state of the art for the polymerization of HSCs is given. Then, we focus on checking the possible application of the coupled polymerization–viscosity model as a screening and predictive tool for the synthesis of HSCs using alternative synthesis strategies. To the best of our knowledge, some of the polymerization strategies have not been previously attempted, either because of their novelty or because of the fact that they are usually viewed as too unpredictable. Some mechanistic assumptions were incorporated into the model to extend its applicability. The alternative strategies were simulated and then, based on the simulation results, experiments were carried out and analyzed.

## STATE OF THE ART FOR SYNTHESIZING HIGH-SOLIDS, LOW-VISCOSITY LATICES

A general trend can be found in polymerization procedures dealing with high-solids latices that constitutes, either implicitly or explicitly, ways of producing a polymer dispersion having a broad particle size distribution (PSD), usually depicted as the sum of a PSD of large particles with a PSD of small particles.<sup>2–9,12–27</sup> For ease of comparison, techniques may

Correspondence to: J. Asua (jmasua@sq.ehu.es).

be grouped according to the means used to manipulate the PSD, and by the mode of operation, either batch<sup>12,18</sup> or semibatch.<sup>2-9</sup> Within the semibatch group several subgroups are found. The basic framework is seed polymerization. Then, there are different ways of producing small particles, different seed composition, or different strategies to favor the growth of larger particles.

López de Arbina and Asua<sup>12</sup> tried to produce HSC latices with low viscosity, starting from concentrated miniemulsions. Although coarse coagulation was observed for polymerizations aiming to surpass the 60% solids content level, coagulum-free latices of 60% solids content were obtained. Under similar conditions, conventional emulsion polymerization could not lead to stable systems beyond 50% solids content. Becker et al.<sup>18</sup> used a blend of rather large ( $>1 \mu\text{m}$ ) and small particles, where particles were swollen with monomer and further polymerized. The authors remarked that, for the production of high-solids latices, one needs: first, a basic understanding of the main factors influencing the viscosity; second, the expertise for the creation of a desired PSD for a given monomer and stabilizer system; finally, the resulting product should possess required defined application properties.

Semibatch polymerization constitutes the core of examples dealing with high-solids, low-viscosity polymer dispersions. The use of polymer seeds is almost ubiquitous. On the other hand, the most striking feature is the selected procedure to affect the PSD. Various ways have been investigated to influence the PSD and thus the viscosity.

Monomer miniemulsions have been used to generate seeds with broad polydispersity.<sup>13-15</sup> Most often the monomer miniemulsion was used in the initial charge. BASF AG (Ludwigshafen, Germany) holds two patents where the use of miniemulsion is proposed.<sup>4,25</sup> According to the patents, the miniemulsion is not necessarily restricted to the initial charge. It can also be added throughout the polymerization to help control the PSD.

Systematic work covering the synthesis of high-solids, low-viscosity latex was performed by Chu et al.<sup>16,17</sup> Bimodal and trimodal latices were prepared. New particles were formed when the surfactant coverage was  $>70\%$ . It was observed that, the higher the amount of excess surfactant added, the greater was the proportion of small particles. Stable latices, with solids content of 64.5 wt % and viscosity of  $100 \text{ mPa s}^{-1}$ , were obtained. An important drawback of this technique is the amount of excess surfactant needed to generate new small particles, which is of the order of 7 wt % based on the total polymer mass. The alternative of generating new small particles by excess surfactant, for the synthesis of high-solids latices, is also covered in several patents.<sup>4,5,20,22,23</sup>

Chu et al.<sup>27</sup> also studied the synthesis of high-solids content latices using a blend of seeds having different particle sizes. The large seed was present from the beginning of the reaction, whereas the small seed was added shotwise at a given moment of the reaction. The exact point was selected to have an optimum relation between the final total mass of large and small particles. Tang and Chu<sup>28</sup> observed that it was very important, for obtaining latex having large particles, for it to be as concentrated as possible, and to have the lowest possible viscosity; otherwise, the unavoidable dilution, caused by the addition of the small-particle latex, would make the polymerization more susceptible to variations of stability because their addition could rebalance the surfactant distribution.

Several companies hold patents covering this strategy,<sup>2,3,7,29</sup> where the difference is focused on final product application.

Recently, Schneider et al.<sup>30,31</sup> proposed a new procedure to control the PSD and, consequently, master the final viscosity. The variation consisted of favoring the growth of larger particles over that of smaller, by the use of an organo-soluble initiator. The idea is to avoid the undesirable narrowing of the PSD, as explained by Vanderhoff et al.<sup>32</sup> The process consisted of swelling a large seed and adding an oil-soluble initiator. After reaching a solids content of about 60%, a monomer preemulsion and small seeds were added to the reaction medium. Schneider et al.<sup>31</sup> used a redox initiation system: the authors claimed that such a system would help to reduce the amount of hydrosoluble material by the end of the polymerization.

Under certain circumstances the secondary nucleation process can be enhanced. Homogeneous nucleation, for instance, can be favored by the presence of ionic monomers or by the presence of other ionic species. The number of particles during polymerization can also be influenced by limited stability, causing a reduction in the number of particles attributed to coalescence among them. It is widely known that those processes are neither easy to control nor easy to model. Nevertheless, through experience one becomes acquainted with the general tendencies, and some processes explore this empirical knowledge.<sup>6,20,21</sup>

There are but a few examples where no preprepared polymer dispersions are used at some point in the processes where a highly concentrated preemulsion is fed semicontinuously and the final result is a suitably broad PSD, to enable the production of concentrated latices with low viscosity. Because the references are found only in patents, no clear explanation of the nucleation mechanism is given.<sup>19,24</sup>

Bimodality may also be achieved<sup>33</sup> by the use of a nonionic block copolymer surfactant. The mechanism is not given, but it is supposed to follow the one proposed by Piirma and Chang,<sup>34</sup> and observed by several other authors.<sup>34-37</sup> Accordingly, a second crop

of polymer particles is generated by micellar nucleation, ascribed to the nonionic surfactant being liberated from the monomer droplets, upon disappearance during the transition of Interval II to Interval III. The second particle mode appears only after a certain monomer conversion. The authors noted three disadvantages: (1) the intrinsic result of producing too large particles, which enhance the instability of the dispersion; (2) worse properties, which were supposed to be between the properties of large and small particle systems; and (3) a lower rate of polymerization.

In spite of the great interest that the subject generates, much of the work still relies on old rules-of-thumb, such as: the broader the PSD for a given polymer volume fraction, the lower the latex viscosity. The widespread use of empirical guidelines is easily demonstrated by the fact that none of the works seems to discuss the limits of viscosity and/or solids content for a given polymerization strategy. Several studies seek to perfect these rules, but do not seek fundamental knowledge: engineers often tend to accept these improved rules and sometimes avoid seeking in-depth understanding.<sup>38,39</sup>

### EXPLORING NEW STRATEGIES

The coupled polymerization–viscosity model<sup>10</sup> was used to explore four different strategies of polymerization. To ease the analysis of the simulations, a known seeded strategy was also simulated. The following polymerization strategies were simulated:

1. Starting with large and small polymer seeds, and carrying out a seeded semicontinuous polymerization.
2. Small seeds were swollen with oil-soluble inhibitor in an attempt to favor the volumetric growth of large particles.
3. Using polymer-stabilized miniemulsion, the possibility of using polymer beads as seeds for a small particle crop was investigated.
4. Starting with two miniemulsions, instead of beginning with premade polymer particles.
5. Late addition of acrylic acid (AA). Fixing the total amount of AA at 2% based on the total polymer mass and delaying its addition in an effort to favor second particle crop generation by homogeneous nucleation.

The first strategy represents a polymerization methodology established in the literature,<sup>2,3,6,7,9,27,31</sup> which complies with the basic assumptions initially built into the model. This strategy was used as a framework for the development of alternative polymerization procedures. Strategies 2 to 4, on the other hand, represent novel strategies, whereas Strategy 5 represents a meth-

odology codified in the patent literature, but most often viewed as too unpredictable.

In the process of developing alternative strategies, those working with polymerization in dispersed media must face the great complexity of the nucleation stage. Under conditions often found in industrial practice, the challenge is to master the factors that influence the generation and growth of polymer particles: the type and concentration of emulsifier, or emulsifier mixture, the rate of free-radical generation, the chemical nature of the initiator, the type and concentration of electrolyte, the reaction temperature profile, monomer type and amounts, procedure and schedules of addition of reagents, agitation type and intensity, ingredients that could act as swelling agents, and other factors that are not easily discernible, such as raw materials impurities, are characteristics that often have a great impact on the final properties of a latex.<sup>11</sup> Nevertheless, through experience, one usually knows how most factors act, and how to avoid the deleterious action of others. As a result, some mechanistic assumptions can be formulated that can be incorporated in the coupled polymerization–viscosity model to quickly develop alternative synthesis routes, avoiding the costly trial-and-error procedure.

Polymerizations were simulated, using the coupled polymerization–viscosity model developed by do Amaral et al.,<sup>10</sup> consisting of a means of computing the particles' competitive growth and then updating the PSD of the polymer dispersion [eq. (1)] to calculate the viscosity of the aqueous polymer dispersion [eq. (2)].

$$\frac{dv_i}{dt} = \sum_{j=A,B} k_{p_{Aj}} P_A^p + k_{p_{Bj}} P_B^p [M_j]_p \frac{\tilde{n}_i \bar{P}_M}{N_A \rho_p} \quad (1)$$

where  $v_i$  is the volume of the particles of class  $i$ ,  $k_{p_{Aj}}$  is the propagation rate constant of radical type  $A$  adding monomer  $j$ ,  $P_A^p$  is the relative frequency of radicals presenting monomeric unit of type  $A$  on its active end,  $[M_j]_p$  is the concentration of monomer type  $j$  within the polymer particles,  $\bar{P}_M$  is the average molecular weight of the monomer mixture,  $\rho_p$  is the polymer density,  $N_A$  is the Avogadro number, and  $\tilde{n}_i$  is the average number of radicals per particle.

$$\ln\left(\frac{\eta}{\eta_0}\right) = \left(\frac{[\eta]\varphi_n}{\sigma - 1}\right) \left[\left(\frac{\varphi_n - \varphi}{\varphi_n}\right)^{1-\sigma} - 1\right] \quad (2)$$

where  $\eta_0$  is the continuous medium viscosity,  $[\eta]$  is the intrinsic viscosity;  $\varphi_n$  is the maximum packing fraction;  $\varphi$  is the volume fraction; and  $\sigma$  is the particle interaction coefficient,<sup>40</sup> which is quantitatively related to physicochemical characteristics of the latex formulation and to the particle size distribution, as given by the following equation:

TABLE I  
Constants Used in the Simulations<sup>a</sup>

Parameter	Value	Parameter	Value	Parameter	Value
$[I_2]$	$5.9 \times 10^{-6}$ (mol/cm <sup>3</sup> )	$k_t$ [44]	$5.78 \times 10^{-5}$ (s <sup>-1</sup> )	$N_A$	$6.023 \times 10^{23}$
$k_a^*$ [42]	$7.0 \times 10^8$ (cm <sup>3</sup> /mol.s.nm)	$k_d^*$ [42]	$8.33 \times 10^{-5}$ (cm <sup>3</sup> /mol.s.nm)	$k_{tw}$ [43]	$7.0 \times 10^{10}$ (cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
$k_t$ [43]	$9.5 \times 10^4$ (cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	$\sigma_s$ [41]	1.3	$F$	0.04
$\sigma_{pc}$ [41]	8 (nm <sup>-1</sup> )	$\alpha$ [40]	0.247	$\varphi_m$ [40]	0.639
$\varphi_{n,ult}$ [40]	0.857				

<sup>a</sup> Reference numbers are indicated in brackets.

$$\sigma = \frac{\sigma_{pc}}{D_n} + \sigma_s \quad (3)$$

where  $\sigma_{pc}$  accounts for the influence of substances adsorbed on the particle surface, and  $\sigma_s$  reflects the contribution of the ionic species dissolved in the aqueous phase to the particle interaction coefficient  $\sigma$ .  $D_n$  is the number-average particle size.

The magnitude of the parameters used in the simulations is given in Table I.<sup>41–44</sup>

To simulate the alternative strategies, some coarse mechanistic simplifications were taken into account. For Strategy 2, small particles swollen with oil-soluble inhibitor, it was considered that the addition of the inhibitor would lead to a lag time in the polymerization within the small seeds. Particles smaller than 90 nm, and consisting of about 20 wt % of the initial charge mass, were considered. Accordingly, small particles were in the reaction media, but could not grow in size until the end of the first 0.5 h of the semicontinuous polymerization. For Strategy 3, it was considered that, because of the poor swelling capacity of high molar mass compounds,<sup>45,46</sup> the small monomer droplets would lose monomer to other particles present in the system. After monomer diffusion, the resultant small monomer droplets would act as polymer seeds. In the simulation, an average droplet size of 120 nm was considered, and the volume fraction of the small monomer droplets accounted for about 65% of the initial total organic mass. In the simulation of Strategy 4 it was considered that no significant Ostwald ripening<sup>46,47</sup> would occur and that monomer droplets of different sizes would behave in a manner similar to that of polymer seeds. Here, small monomer droplets of 80 nm, about 8 times smaller than the large monomer droplets, were considered, and corresponded to 10% of the initial total monomer charge. Finally, Strategy 5 used no small seeds in the initial charge, and it was regarded that small particles, initially smaller than 15 nm, were generated by homogeneous polymerization as a result of late addition of acrylic acid into the reaction medium. The values of initial monomer droplet size, initial latex particle size, and the mass proportion between large and small species reflect reasonable values often found in practice.

Admittedly, some of the assumptions incorporated into the coupled model are oversimplifications. However, as discussed later, the model still applies for the screening purposes of this work.

Figure 1 shows the simulated evolution of the viscosity of the proposed strategies. Strategy 1, taken as the reference because it represents a procedure commonly used to produce concentrated latices, could produce a 65% solids content latex with a low shear viscosity of 372 mPa s<sup>-1</sup>. By swelling small particles with oil-soluble inhibitors, the procedure used for Strategy 2, an attempt was made to hinder the volumetric growth of small particles. As discussed by do Amaral et al.,<sup>10</sup> with the progress of the polymerization the PSD tends to narrow,<sup>32</sup> which is unfavorable for obtaining a low viscosity at high-solids content.<sup>40</sup> Applying this hypothesis to the coupled polymerization–viscosity model, considering that small particles present a lag time in the polymerization, a lower value of viscosity (115 mPa s<sup>-1</sup>) at an equivalent solids content could be obtained. Strategy 3, which uses miniemulsion stabilized with a high molar mass compound to generate small particles, gave a final viscosity higher than that obtained in the reference case. Nevertheless, according to the simulation, the strategy could still be used to obtain a latex with about 65 wt % with a viscosity < 3 Pa s<sup>-1</sup>. The final viscosity simulated for Strategy 4, where two miniemulsions of different droplet size were used, was also found to be

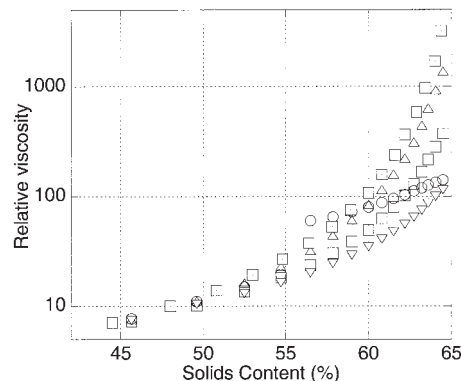


Figure 1 Simulation of the viscosity evolution with solids content: Strategy 1 ( $\square$ ); Strategy 2 ( $\nabla$ ); Strategy 3 ( $\square$ ), Strategy 4 ( $\triangle$ ); Strategy 5 ( $\circ$ ).



higher than the viscosity obtained for Strategy 1. Finally, comparing Strategy 5 with the reference case, at the beginning of the polymerization large seeds would not be competing with smaller particles for radical capture. By the time small particles would be available in the reaction medium, the large particles would have a relatively larger diameter. Furthermore, small particles generated by homogeneous nucleation would probably have an initial diameter smaller than the diameter of the small seed used in the reference reaction. Taking into account these two aspects, a lower viscosity would be expected, as found in the result of the simulation of Strategy 5. In summary, according to the simulation results all the proposed alternative Strategies 2 to 5 are devised to obtain a high-solids latex with low to moderate viscosity.

## EXPERIMENTAL

### Materials

Technical-grade monomers, 2-ethylhexyl acrylate and methyl methacrylate containing 10–20 ppm of hydroquinone monomethyl ether (MEHQ) and with minimum purity of 99%, were purchased from Quimiroga S.A. (Barcelona, Spain), and used as supplied. Technical-grade acrylic acid (AA), with purity  $\geq 99\%$ , was purchased from Fluka Chemika (Buchs, Switzerland). Dowfax 2A1 and Disponil A 3065, supplied by Dow Chemical (Midland, MI) and Cognis GmbH (Düsseldorf, Germany), respectively, were used as received. Reagent-grade  $\text{NaHCO}_3$  (Panreac Química S.A., Barcelona, Spain),  $\text{Na}_2\text{S}_2\text{O}_5$  (Aldrich, Milwaukee, WI),  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $\text{Na}_2\text{S}_2\text{O}_8$  (Fluka), sodium formaldehyde sulfoxylate (Fluka), ascorbic acid (Fluka), *tert*-butyl hydroperoxide, acetone (Sigma, St. Louis, MO), and hexadecane (Aldrich), were also used as received. Methoquinone, 2,5-di-*tert*-butylhydroquinone, and phenothiazine were purchased from Aldrich and used as received. Doubly deionized water (DDI) was used throughout the work.

Polymerizations were carried out in a 500-mL reactor equipped with a reflux condenser, stainless stirrer with pitched blades, sampling device, nitrogen inlet, and feed inlet tubes when appropriate. Control of the reaction temperature and inlet flows of the semicontinuous feeds was carried out by means of Camile TG software (Sagian, Inc., Indianapolis, IN).

Conversion was measured by gravimetry. Latex samples of about 1-mL were withdrawn during the polymerization, placed in a preweighed aluminum capsule, and immediately thereafter shortstopped with about 0.2 mL of an aqueous 1% hydroquinone solution. The capsule was dried to a constant weight at 50°C. A monomer miniemulsion was prepared by means of ultrasonication or a high-pressure homogenizer. The sonic dismembrator model Branson 450

(Branson Ultrasonics Corp., Danbury, CT) or the Manton-Gaulin (UK) Lab 60 TBS homogenizer was used.

### Particle size characterization

Latex particle size distribution (PSD) was measured by capillary hydrodynamic fractionation, using the Matec CHDF 2000 apparatus (Matec Applied Sciences, Northborough, MA). This technique is based on the fractionation of dispersed colloidal particles that are carried through a capillary tube by a carrier fluid,<sup>48</sup> and has been shown to be capable of providing reliable information regarding the PSD of polydisperse systems.<sup>49</sup> Carrier fluid 1X, supplied by Matec, was used as received. To minimize the probability of clogging, the C-202 column was used. The accuracy of the measurement was frequently assessed by checking the calibration of the apparatus. The light-scattering technique (Coulter N4 Plus; Coulter, Fullerton, CA) was also used to determine the droplet size of monomer miniemulsions and of the particle size of particles swollen with oil-soluble inhibitor. In both cases the colloidal dispersion was diluted with DDI water.

### Latex viscosity

The viscosity of the high-solids content latices was measured by means of a viscometer (Model ELV-8; Viscometers UK). All measurements were carried out at room temperature and, whenever possible, the viscosity was assessed at a constant shear rate (60 rpm) and using spindle number 4.

### Synthesis of the small-seed latex

The small-seed latex was obtained by a semicontinuous emulsion polymerization. The reactor was initially charged with 230 g of DDI water, 0.375 g of  $\text{NaHCO}_3$ , 1.25 g of  $\text{Na}_2\text{S}_2\text{O}_8$ , 2.78 g of Dowfax 2A1, and 3.85 g of Disponil A 3065. The reactor was kept under a nitrogen atmosphere throughout the polymerization. The polymerization temperature was set at 80°C, and the stirring rate was 250 rpm. The monomer mixture was semicontinuously fed at a rate of 2.125 g/min.  $\text{Na}_2\text{S}_2\text{O}_8$  (5.9 wt % solution in water) was added at a feeding rate of 0.177 g/min. The addition of the semicontinuous streams was carried out by means of computer-controlled feeding pumps for 2 h. After the end of the feeding period, the reactor was maintained at 80°C for 1 h. The reactor was then cooled and the latex was collected. No coagulum was found.

### Synthesis of the large-seed latex

The large-seed latex was synthesized by miniemulsion polymerization. The aqueous solution of surfactant (230 g of DDI water, 0.37 g of  $\text{NaHCO}_3$ , and 3.85 g of

**TABLE II**  
Formulation of Strategy 1

Reactions	Strategy 1
Temperature	70°C
Initial charge	
DDI water, g	30
Large-seed latex, g ( $D_n$ : 590 nm)	53
Small-seed latex, g ( $D_n$ : 34 nm)	13
Additional streams	Feeding time: 240 min
Initiator	
DDI water, g	30
(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , g	2.9
Preemulsion	
DDI water, g	77
Disponil A3065, g	1.1
Dowfax 2A1, g	4.9
NaHCO <sub>3</sub> , g	0.22
Monomer, <sup>a</sup> (g)	292.5
Final total solids content (%)	64.2

<sup>a</sup> Monomer composition: 2-EHA/MMA/AA: 88/10/2 wt %.

Disponil A 3065) was mixed with the solution of monomers and hexadecane (250.6 g of a monomer mixture composed of 88/10/2 wt % of 2-EHA/MMA/AA and 5 g of hexadecane) by means of a magnetic stirrer for 10 min. Immediately thereafter, the coarse dispersion was fed into the Manton-Gaulin high-pressure homogenizer, whose first valve was set at 2000 psi, and its second at 400 psi. Five cycles were used to homogenize the dispersion. The miniemulsion was immediately charged to the reactor, set at 50°C, and then an aqueous solution of 1.25 g of ammonium persulfate and 1.25 g of Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> in 15.5 g of DDI water was added to the reactor. The polymerization was carried out for 4 h.

### Strategies for the synthesis of high-solids latices

A similar semicontinuous addition time, varied from 240 to 360 min, was used in all five strategies. The feeding period was determined to mimic process conditions often found in industrial practice, where process optimization seeks to reduce process time.

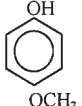
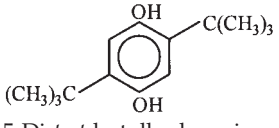
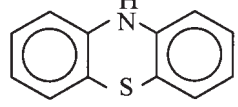
Strategy 1: starting with large and small polymer seeds

Strategy 1 consisted of a seeded polymerization, where large and small seeds were used in the initial charge. Monomer preemulsion and initiator were added for a period of 4 h. The formulation is given in Table II.

Strategy 2: small particles swollen with oil-soluble inhibitor

The inhibitors were first dissolved in reagent-grade acetone. This solution was added dropwise to the latex

**TABLE III**  
Oil-Soluble Inhibitors Used to Swell the Small Polymer Seeds

Inhibitor	Concentration
	0.01 phm S2_A
Methoquinone	
	0.1 phm S2_B
2,5-Di- <i>tert</i> -butylhydroquinone	
	0.045 phm S2_A
Phenotiazine	

of small seed particles. The latex was kept under mild agitation at room temperature until all the acetone evaporated. The inhibitor-swollen particles were later used in the initial charge. Table III details the inhibitor used for each polymerization. Inhibitors of differing water solubilities were used, ranging from phenotiazine and 2,5-di-*tert*-butylhydroquinone, considered as water insoluble, to methoquinone, which possesses a water solubility of 4.1 g/100 g. The concentration is given as parts per hundred of the total polymer mass obtained at the end of the polymerization, considering complete monomer conversion and the formation of no coagulum. The formulations used for the polymerizations are given in Table IV.

**TABLE IV**  
Formulations of Strategy 2

Reaction	S2_A	S2_B
Temperature	80°C	80°C
Initial charge		
DDI water, g	20	20
Large seed, g ( $D_n$ : 590 nm)	53.06	53.06
Small seed, g	23 (87 ± 32 nm)	23 (77 ± 21 nm)
Disponil A3065, g	0.5	0.5
Feed 1	Feeding time: 360 min	
DDI water, g	30	30
Initiator, g	2.925	2.925
Feed 2	Feeding time: 360 min	
DDI water, g	78	78
Surfactant		
Dowfax 2A1, g	4.78	4.78
Disponil A3065, g	2.206	2.206
NaHCO <sub>3</sub> , g	0.215	0.215
Monomer, <sup>a</sup> g	292.5	292.5

<sup>a</sup> Monomer composition: 2-EHA/MMA/AA: 88/10/2 wt %.

**TABLE V**  
**Formulation of Strategy 3**

Reaction	S3_A
Temperature	80°C
Initial charge	
Large seed, g ( $D_n$ : 590 nm)	48.2
Miniemulsion, g (Droplet size: 120 nm)	98.2, from which Organic Phase 2-EHA: 40.9; MMA: 4.54; AA: 0.91; poly(styrene): 5.91 Aqueous Phase DDI water: 45.45; Dowfax 2A1: 0.75; Disponil A3065: 0.17
Disponil A3065, g	0.468
Feed 1	Feeding time: 240 min
DDI water, g	27.3
Initiator (APS), g	2.66
Feed 2	Addition time: 240 min
DDI water, g	71
Surfactant	
Dowfax 2A1, g	4.34
Disponil A3065, g	2.00
NaHCO <sub>3</sub> , g	0.219
Monomer, <sup>a</sup> g	266

<sup>a</sup> Monomer composition: 2-EHA/MMA/AA: 88/10/2 wt %.

#### Strategy 3: using polymer-stabilized miniemulsion

A miniemulsion was prepared with high molar mass polystyrene as hydrophobe: its formulation is given in Table V. The aqueous phase was mixed with the organic phase for 10 min at 1000 rpm by means of a magnetic stirrer. Afterward, the coarse monomer dispersion was sonicated for 5 min at 80% duty cycle and 8 output. This miniemulsion was added to the initial charge, as detailed in Table V. The initial charge also contained the large seed latex: the initial charge was kept at 80°C for 1 h before starting the polymerization. Therefore, monomer from the miniemulsion droplets

could migrate to the polymer particles, given the limited swelling capacity of the polymer.<sup>45,46</sup>

#### Strategy 4: starting with monomer miniemulsions of different droplet sizes

Two monomer miniemulsions were initially charged in the reactor under this strategy. The monomer miniemulsion with small droplet size was obtained according to the formulation given in Table VI. The aqueous phase was mixed with the organic phase for 10 min at 1000 rpm by means of a magnetic stirrer. Afterward,

**TABLE VI**  
**Polymerization Formulation of Strategy 4**

Reaction	S4_A
Temperature	80°C
Initial charge	
Large droplet miniemulsion, g (Droplet size: 620 nm)	100
Small droplet miniemulsion (g) (Droplet size: 80 nm)	20, from which Organic phase MMA: 6; hexadecane: 15 mmol (based on water) Aqueous phase DDI water: 14; Dowfax 2A1: 5 mmol (based on water)
Feed 1	Feeding time: 240 min
DDI water, g	30
Initiator, g	2.7
Feed 2	Feeding time: 240 min
DDI water, g	107
Dowfax 2A1, g	1.35
Disponil A3065, g	2.025
NaHCO <sub>3</sub> , g	0.2
Monomer, <sup>a</sup> g	270

<sup>a</sup> Monomer composition: 2-EHA/MMA/AA: 88/10/2 wt %.

TABLE VII  
Polymerization Formulation of Strategy 5

Reaction	S5_A
Temperature	80°C
Initial charge	
DDI water, g	30
Large seed, g ( $D_n$ : 590 nm)	65
Disponil A3065, g	0.5
Feed 1	Feeding time: 240 min
DDI water, g	30
Initiator, g	2.925
Feed 2	Feeding time: 240 min
DDI water, g	77
Dowfax 2A1, g	4.87
Disponil A3065, g	1.125
NaHCO <sub>3</sub> , g	0.219
2-EHA, g	232.3
MMA, g	25.8
Feed 3	Lag and feeding time: 75, 165 min
2-EHA, g	25.8
MMA, g	2.58
AA, g	5.735

the coarse monomer dispersion was sonicated for 5 min at 80% duty cycle and 8 output. The large droplet size miniemulsion was generated according to the procedure previously described for the synthesis of the large-seed latex. Table VI gives the high-solids polymerization formulation, with all quantities expressed in grams. The polymerization was carried out at 80°C, and the semicontinuous streams were added within 4 h.

#### Strategy 5: late addition of acrylic acid

The late addition of AA strategy consisted of manipulating the mode of feeding the acrylic acid into the reactor. Monomers were added in two separate streams. A preemulsion was prepared without acrylic acid. A second stream of neat monomer was prepared with the entire amount of acrylic acid (to achieve 2 wt % in the final polymer composition). The neat monomer stream was fed to the reactor only after 75 min from the beginning of the reaction. Consequently, the instantaneous concentration of AA in the polymerization loci was increased, without changing the overall monomeric composition. Table VII further describes the experiments, with all quantities expressed in grams.

## RESULTS AND DISCUSSION

### Strategy 1: starting with large and small polymer seeds

A coagulum-free latex was obtained: after the polymerization, the stirrer and reactor walls were free from lumps of polymer. The time evolution of the total

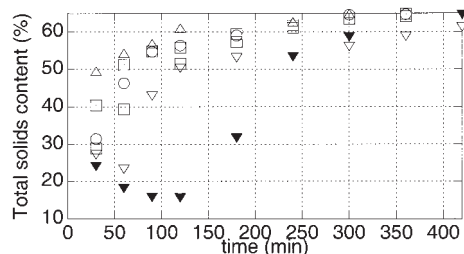


Figure 2 Time evolution of the total solids content: Strategy 1 (□); Strategy 2: S2\_A (▽), S2\_B (▼); Strategy 3 (□), Strategy 4 (△); Strategy 5 (○).

solids content is given in Figure 2. During the polymerization of the bimodal latex, samples were taken to analyze the PSD. Figure 3 shows the progress of the latex PSD: the bars in the figure represent the predictions of the model for the final size of the large and small seeds. The discrete values of the final size of the seeds, calculated with the model, are also illustrated in the figure. The predicted final average diameter of both large and small seeds gave values smaller than those observed experimentally. This indicated, most probably, the occurrence of coalescence among particles. An alternative explanation could be the number of small particles used in the simulation, obtained from the number-average particle size of the small seed latex, which had a higher polydispersity. Using this number-average particle size could have led to the calculated number of particles in the reactor being greater than that under the experimental conditions. It is worth mentioning that the PSD data indicated that the formation of a new population crop was negligible for the bimodal strategy. This is consistent with many industrial processes, in which the number of particles is controlled by the seed and a judicious addition of surfactants, and consistent with the assumption made in the model that no new particles are generated.

The final solids content and the latex viscosity data are given in Table VIII. The value of the viscosity

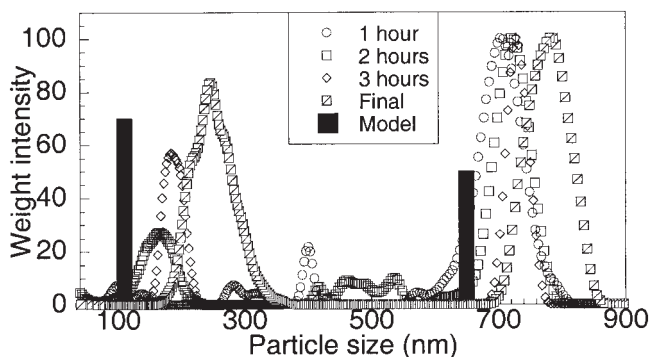


Figure 3 Latex final PSD: experimental and predicted PSD of Strategy 1.



**TABLE VIII**  
**Results Obtained in the Synthesis of High Solids Latices Using Different Polymerization Strategies**

Strategy	Reaction	Total solids content (%)	Measured viscosity (mPa s <sup>-1</sup> )	Viscosity equation + model PSD <sup>a</sup> (mPa s <sup>-1</sup> )	Viscosity equation + experimental PSD <sup>b</sup> (mPa s <sup>-1</sup> )
1	S1	64.2	370		366
2	S2_A	61.3	6830		140
2	S2_B	64.7	24,900		100
			(Spindle 2 at 30 rpm)		
3	S3_A	65.5	4360	3200	3600
4	S4_A	64.7	220	1375	330
5	S5_A	64.7	51		140

<sup>a</sup> Viscosity calculated with the final particle size predicted by the coupled model.

<sup>b</sup> Viscosity calculated with the viscosity equation using the measured PSD.

calculated with the viscosity equation [eq. (2)] for the experimental PSD is also given in the table. The viscosity obtained from the model was not taken into account because of the difference of the simulated and real PSD values. Good agreement between the predicted and the measured viscosity for both latices was obtained, indicating that the parameter of the viscosity could reflect rather well the physicochemical characteristics of the latex.

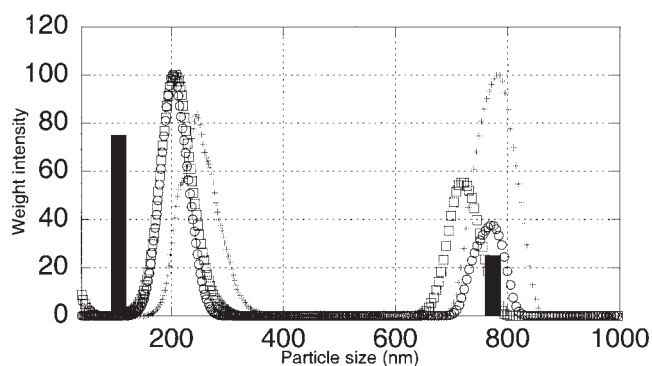
### Strategy 2: small particles swollen with oil-soluble inhibitor

This polymerization strategy consisted of trying to maximize the size difference between large and small particles. Taking the reaction with two seeds as a reference, by enhancing the pace of growth of the large seeds, with respect to the small seeds, the coupled polymerization–viscosity model predicts a lower viscosity. To a certain extent, the central idea of this strategy is similar to that proposed in a recent patent issued to Atofina,<sup>9</sup> based on the study by Schneider et al.,<sup>31</sup> in which the growth of large seeds is favored by swelling large seeds with oil-soluble initiators. However, in this study the way of favoring the growth of larger seeds was attempted by avoiding the growth of smaller ones.

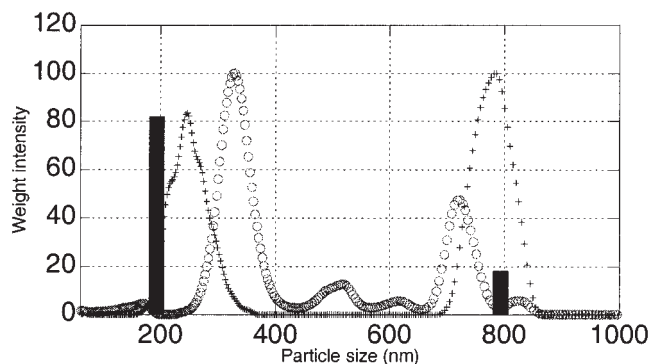
Table III shows the particle size of the small seeds swollen with oil-soluble inhibitor. The addition of the oil-soluble inhibitor led to an increase of the particle size from its initial value ( $68 \pm 18$  nm), which could not be explained by the small amount of inhibitor added to the latex. Some limited coalescence likely occurred in the process. Other factors being equal, starting with a larger size of the small seed would lead to a comparatively higher final viscosity with respect to the reference reaction. The kinetics of the total solids content is shown in Figure 2. The final PSD values, obtained in S2\_A and S2\_B, are given in Figure 4. The PSD of the reference case (Strategy 1), and the predictions of the coupled model, are also included in the

figure. The PSD obtained in Strategy 2 was close to the PSD of the reference case, except for a lower intensity of the large particles. The final solids contents of S2\_A and S2\_B are given in Table VIII.

Table VIII also presents the experimental viscosity of the latices, as well as the viscosity that was calculated using the experimental PSD data, and the values of the parameters of the viscosity equation used in the model calculations (Table I), which were considered to be representative for the formulations studied. It can be seen that very high viscosities were measured and that they were significantly different from those calculated using the viscosity equation, indicating that the parameters chosen to represent the system were not accurate. Higher rates of interaction among the polymer particles could increase the particle interaction coefficient,<sup>41</sup> thus increasing the latex viscosity; however, under the experimental conditions, it was not possible to infer the phenomenon leading to a higher particle interaction. This result indicated that, for substantial changes in the system composition (in the present case the change was not expected *a priori*), it is mandatory to determine the correct value or magnitude of the parameters of the viscosity equation; otherwise, this powerful tool might become useless.



**Figure 4** Latex final PSD: S2\_A ( $\square$ ), S2\_B ( $\circ$ ); Reference case Strategy 1 (+). Bars represent the model predictions for Strategy 2.



**Figure 5** Latex final PSD: S3\_A (○), Strategy 1 (+). Bars represent the model predictions for Strategy 3.

Although it was possible to produce high-solids content latices, the supposition that, under the experimental conditions proposed, the growth of the small particles would be reduced and that the large particles would grow more with respect to the reference formulation did not hold. By comparing the PSD values of S2\_A and S2\_B with the reference case, it could be seen that both reactions presented a higher weight intensity relative to that of the small particles. The fact that the starting size was larger, for the reactions using small seeds swollen with inhibitor, might have some influence, but the results strongly suggest that the inhibitor did not preferentially hinder the growth of the small particles.

In the investigation of the transport phenomenon during miniemulsion polymerization it was demonstrated that the water-insoluble 2,5-di-*tert*-butylhydroquinone could be transferred to other particles or droplets through reciprocal collision<sup>50</sup>: such a process might also happen under the experimental conditions chosen for the strategy using small particles swollen with inhibitors.

### Strategy 3: using polymer-stabilized miniemulsion

The droplet size of the small sized miniemulsion was measured by light scattering immediately after its preparation, and was found to have a value  $120 \pm 15$  nm. No inhibition was noticed, and the reaction progressed steadily. A coagulum-free latex was obtained at the end of the reaction. The kinetics of reaction S3\_A is given in Figure 2, whereas the final PSD is given in Figure 5, which includes the PSD of the reference case, and the simulated final value of the polymer particles. The final PSD was found to have some relevant differences with respect to the reference case. First, several particle modes were observed for S3\_A. Furthermore, the small particles showed a larger value in Strategy 3. A comparison of experimental results with the simulation showed reasonable agreement. It is important to remember that some major simplifica-

tions were made to use the coupled model to provide a quantitative orientation with respect to the proposed alternative for synthesizing a high-solids, low-viscosity latex.

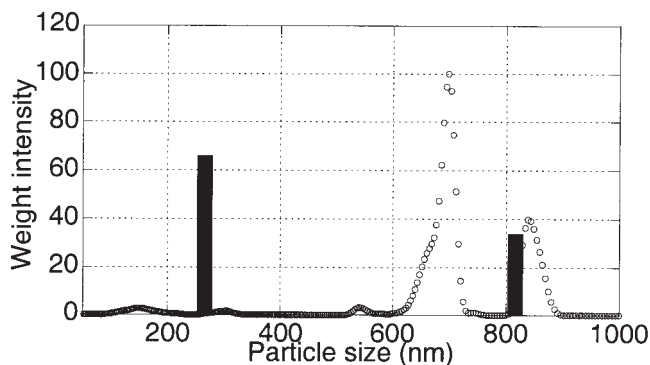
The final solids content and the latex viscosity are given in Table VIII. A final high-solids content was obtained at a moderately high viscosity. The result obtained from the model, and the viscosity calculated with the viscosity equation using the latex final PSD, are also included in Table VIII.

Good agreement between the experimental viscosity, and the value calculated with the viscosity equation using the experimental PSD, was found, indicating that the assumption—that the viscosity parameters were representative for the system under study—was correct. The results show the feasibility of Strategy 3 for obtaining high-solids latex. In spite of the major assumptions incorporated into the model it was shown that the model could still guide the development of this alternative strategy for the synthesis of high-solids content latices, whose nucleation mechanism is admittedly complex.

### Strategy 4: starting with monomer miniemulsions of different droplet size

The droplet size of the small-size miniemulsion was measured by light scattering immediately after its preparation, resulting in a value of  $80 \pm 7$  nm. The large-sized miniemulsion was also characterized by light scattering, and the droplet size was  $620 \pm 250$  nm. The latex obtained was free from coagulum. The time evolution of the total solids content is represented in Figure 2. The final PSD, together with the final size of the large and small particles obtained by simulation, is given in Figure 6.

The results, given in Figure 6, show that it was quite difficult to predict the possible shape of the latex final PSD. S4\_A presented a PSD of complex shape, with multiple particle modes. Some important facts need to be taken into account. First is that the oversimplification, that no droplet degradation would happen under



**Figure 6** Latex final PSD: S4\_A and model predictions.

the experimental conditions, did not hold. Second, the model used the discrete value of the droplet size obtained by light scattering, but the result indicated by the standard deviation that both miniemulsions possibly had a broad distribution of droplet size. Moreover, as already discussed, coalescence among particles could make the simulation results differ quite significantly from the experimental results.

The final solids content and the latex viscosity are given in Table VIII. The results obtained from the polymerization simulation and from the low shear viscosity equation, using the latex PSD data and the same viscosity parameters used in the model, are also given in the table.

The viscosity obtained from the simulation differed significantly from the experimental result. Most probably, the discrepancy resulted from the difference of PSD values. On the other hand, using the viscosity equation and the experimental PSD, good agreement could be found, indicating that the viscosity parameters were substantially representative for the interaction among particles in the formulation used. The low viscosity, obtained for this strategy, resulted from the PSD, which favored larger particle size modes, and could be correctly predicted by the viscosity equation.

Most of the processes, for making use of miniemulsion in high-solids, low-viscosity formulations, advocate its use for the generation of a polymer seed of broad PSD.<sup>5,8</sup> However, usually just one miniemulsion is present that usually represents only a small proportion of the final polymer mass.<sup>5</sup> Furthermore, starting from monomer miniemulsion can be viewed as a process simplification because it is no longer necessary to store the latex to be used as seed.<sup>51</sup> However, it presents the disadvantage of having to produce two miniemulsions at once.

### Strategy 5: late addition of acrylic acid

The kinetics of reaction S5\_A is given in Figure 2, whereas the final PSD of Strategy 5 is represented in Figure 7, together with the PSD of the reference case, Strategy 1. The PSD of S5\_A supports the hypothesis that is underlined in the strategy of late addition of acrylic acid. Considering the reference PSD, it can be seen that a lower weight intensity and a smaller size were obtained for the small particles. This result favored a lower viscosity of S5\_A with respect to the reference case, as discussed below.

The final solids content and latex viscosity are given in Table VIII. The predicted viscosity is also included in Table VIII: it was calculated from the experimental PSD data, using the viscosity parameters previously experimentally determined by do Amaral<sup>41</sup> that were considered to be representative for the reactions carried out.

The result obtained in reaction S5\_A agreed with the previous qualitative analysis carried out using the cou-

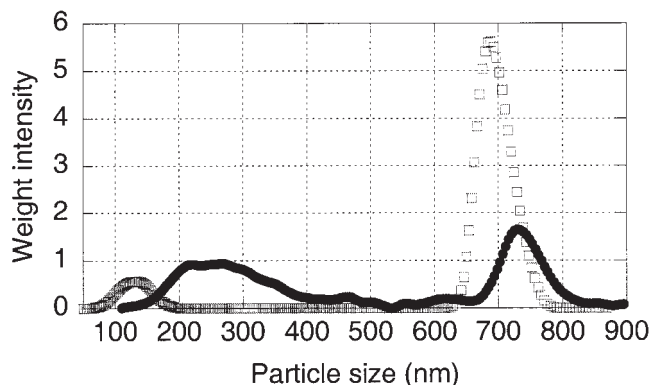


Figure 7 Latex final PSD: S5\_A (□) and Strategy 1 (●).

pled polymerization–viscosity model. Furthermore, using the viscosity equation, it was possible to determine—with limited accuracy—the magnitude of the viscosity. The slight difference in the results indicated that the values of the parameters of the viscosity equation were reasonably representative for the interaction among particles. However, a more precise estimation of the parameters of the viscosity equation would probably enable the correct estimation of the latex viscosity. From the final PSD it is clear that it was possible to generate a second crop of small particles. However, it is important to note that, for this strategy, some slight coagulation was observed, lower than 2 wt %. The lack of stability was likely attributable to the absence of acrylic acid during the early period of the polymerization. The fact is that the role that monomer plays on the generation of new particles cannot be disassociated from its role on the particle stabilization.<sup>52</sup>

As a general remark, it was difficult, in the analysis of all strategies, to dissociate the multiple aspects influencing particle nucleation and coalescence from the general assumptions and simplifications concerning particle nucleation proposed for each strategy. For instance, new small particles could always be generated by homogeneous nucleation, which was not taken into account in the model. However, to counteract their stabilizing ability and favor a coalescing process, a very small amount of surfactant was used in all polymerizations. Particle coagulation could also have an important impact on the accuracy of the model predictions because it was not taken into account therein. The PSD could to a large extent be modified by the coagulation of particles. As a consequence, the latex final viscosity would also be altered.

Manipulating probability can be risky under some circumstances. In fact, by favoring a nucleation process over others, one is just changing the probability of each of the possible mechanisms. Because the strategies represent systems that could hardly be phenomenologically described, one relies on experience and general knowledge to expect a certain level of particle

coalescence and new particle generation. On the other hand, because the coupled polymerization–viscosity model enables one to precisely know how a given PSD affects the final viscosity it is possible to guess within which borderlines one is traveling. Therefore, the process of devising new formulation alternatives is safer than merely relying on trial-and-error. This potential application may be considerably extended by incorporating into the polymerization process model a more comprehensive phenomenological description of the particles' nucleation and growth.<sup>53–56</sup>

## CONCLUSION

It has been shown that the coupled polymerization–viscosity model is a powerful tool to supplement the practice of educated guesses. By coupling the new insight into the phenomena influencing the viscosity of concentrated aqueous polymer dispersion with experience on emulsion polymerization, it is rather straightforward to formulate new polymerization routes. The miniemulsion polymerization technique was incorporated into two new strategies for the synthesis of high-solids latices, which were experimentally assessed: a rather low viscosity at moderate to high solids was obtained.

Most of the alternative routes lie within a region that is usually pictured as too dangerous to be experimentally assessed through trial-and-error approaches. Nonetheless, the quantitative and qualitative analysis provided by the developed model can contribute to develop safer and novel strategies for obtaining high-solids, low-viscosity systems.<sup>57</sup>

## References

- Guyot, A.; Chu, F.; Schneider, M.; Graillat, C.; McKenna, T. F. *Prog Polym Sci* 2002, 27, 573.
- Hoy, K. L.; Peterson, R. H. U.S. Pat. 4,130,523 (1978).
- Siol, W.; Fink, H.; Klesse, W.; Rauch, H.; Suetterlin, N. U.S. Pat. 4,456,726 (1984).
- Bauer, G.; Aydin, O.; Neutzner, J.; Mächtle, W. U.S. Pat. 5,349,858 (1994).
- Portugall, M.; Aydin, O.; Mächtle, W.; Neutzner, J. U.S. Pat. 5,350,787 (1994).
- Hayes, P. C.; Triantafillouopoulos, N. U.S. Pat. 5,726,259 (1995).
- Peters, A. C. I. A.; Overbeek, G. C. EP 0799278 (1996).
- Dames, B.; Mathauer, K.; Mächtle, W. U.S. Pat. 5,990,221 (1999).
- Betremieux, I.; Luyen, K.; Meeschaert, N.; Noguez, P. WO 01/48026A1 2001.
- do Amaral, M.; Van Es, S.; Asua, J. M. *Macromol Theory Simul* 2004, 13, 107.
- Schaller, E. J. *Advances in Emulsion Polymerization and Latex Technology*; Davos Short Course, Lecture 14, Davos, Switzerland, 1998.
- López de Arbina, L.; Asua, J. M. *Polymer* 1992, 33, 4832.
- Masa, J. A.; López de Arbina, L.; Asua, J. M. *J Appl Polym Sci* 1993, 48, 205.
- Unzué, M. J.; Asua, J. M. *J Appl Polym Sci* 1993, 49, 81.
- Leiza, J. R.; Sudol, E. D.; Adams, M.; El-Aasser, M. S. *J Appl Polym Sci* 1997, 64, 1797.
- Chu, F.; Graillat, C.; Guyot, A. *J Appl Polym Sci* 1998, 70, 2667.
- Chu, F.; Graillat, C.; Guyot, A. *J Polym Adv Technol* 1998, 9, 844.
- Becker, R.; Hashemzadeh, A.; Zecha, H. *Macromol Symp* 2000, 151, 567.
- Celanese Corp. Brit. Pat. GB 1203524, 1971.
- Portugall, M.; Aydin, O.; Mächtle, W.; Neutzner, J. U.S. Pat. 5,350,787 (1994).
- Häberle, K.; Bauer, G.; Mämpel, L. U.S. Pat. 5,350,823, 1994.
- Dittrich, U.; Stanger, B.; Neutzner, J.; Pföhler, P.; Müller, H.; Türk, J. U.S. Pat. 5,405,693 (1995).
- Aydin, O.; Portugall, M.; Neutzner, J.; Mächtle, W. U.S. Pat. 5,426,146 (1995).
- Bukhardt, D. DE 2762 A 1964, 1 1998.
- Mathauer, K.; Mächtle, W.; McKee, G. E.; Kröner, H. U.S. Pat. 6,160,049 (2002).
- Rehmer, G.; Stanger, B.; Aucter, G.; Türk, J.; Aydin, O.; Füssl, R. U.S. Pat. 6,225,401 (2002).
- Chu, F.; Guyot, A. *Colloid Polym Sci* 2001, 279, 361.
- Tang, C.; Chu, F. *J Appl Polym Sci* 2001, 82, 2352.
- Adler, H. J.; Jahny, K.; Vogt Birndrich, B.; *Prog Org Coat* 2001, 43, 251.
- Schneider, M.; Graillat, C.; Guyot, A.; McKenna, T. F. *J Appl Polym Sci* 2002, 84, 1916.
- Schneider, M.; Graillat, C.; Guyot, A.; McKenna, T. F. *J Appl Polym Sci* 2002, 84, 1935.
- Vanderhoff, J. W.; Vitaske, J. F.; Bradford, E. B.; Alfrey, T., Jr. *J Polym Sci* 1956, 20, 225.
- Herget, W. D.; Bloss, P.; Schmoltzler, K. D.; von Ehrenstein, J.; Döring, E. DD 274229 A1, 1989.
- Piirma, I.; Chang, M. *J Polym Sci Polym Chem Ed* 1982, 20, 489.
- Emelie, B.; Pichot, C.; Guillot, J. *Makromol Chem Suppl* 1985, 10/11, 43.
- Unzueta, E.; Forcada, J. *Polymer* 1995, 36, 1045.
- Özdeger, E.; Sudol, E. D.; El-Aasser, M. S.; Klein, A. *J Polym Sci Part A: Polym Chem* 1997, 35, 3827.
- Anderson, C. J.; Glassman, M.; McAfee, R. C.; Pinelli, T. *J Eng Technol Manag* 2001, 18, 131.
- Koskinen, K. U.; Vanharanta, H. *Int J Prod Econ* 2002, 80, 57.
- Sudduth, R. D. *J Appl Polym Sci* 1993, 48, 37.
- do Amaral, M. Ph.D. Dissertation, The University of the Basque Country, Spain, 2003.
- Asua, J. M.; de la Cal, J. C. *J Appl Polym Sci* 1991, 42, 1869.
- Matheson, M. S.; Am, E. E.; Bevilacqua, E. B.; Hart, E. J. *J Am Chem Soc* 1951, 73, 1700.
- Masson, J. C. In: *Polymer Handbook*; Brandrup, J.; Immergut, E. H., Eds.; Wiley-Interscience: New York, 1975.
- Ugelstad, J.; Mørk, P. C.; Kaggerud, K. H.; Ellingsen, T.; Berge, A. *Adv Colloid Interface Sci* 1980, 13, 101.
- Asua, J. M. *Prog Polym Sci* 2002, 27, 1283.
- Higuchi, W. I.; Misra, J. *J Pharm Sci* 1962, 51, 459.
- Selebi, C. A.; dos Ramos, J. G. *J Colloid Interface Sci* 1989, 130, 14.
- Elizalde, O.; Leal, P. G. W.; Leiza, J. R. *Part Part Syst Char* 2000, 17, 236.
- Asua, J. M.; Rodriguez, V. S.; Silebi, C. A.; El-Aasser, M. S. *Makromol Chem Macromol Symp* 1990, 35/36, 59.
- Bouti, S.; Graillat, C.; McKenna, T. F. *Polymer Colloids: Preparation and Properties of Aqueous Polymer Dispersions*; Kluwer Academic/Plenum: Irsee, Germany, 2002.
- Urrutabizkaia, A.; Asua, J. M. *J Polym Sci Part A Polym Chem* 1994, 32, 1761.
- Min, K. W.; Ray, W. H. *J Appl Polym Sci* 1978, 22, 89.
- Rawlings, J.; Ray, W. *Polym Eng Sci* 1988, 28, 237.
- Araujo, P. H. H.; de la Cal, J. C.; Asua, J. M.; Pinto, J. C. *Macromol Theory Simul* 2001, 10, 769.
- Immanuel, C. D.; Doyle, F. J., III *Chem Eng Sci* 2003, 58, 3681.
- do Amaral, M.; Asua, J. M. ES 200300334, 2003.