

## Agitation Effects in Emulsion Copolymerization of *n*-Butyl Methacrylate and N-Methylol Acrylamide

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### ABSTRACT

The effects of agitation in emulsion copolymerization have been studied using a semibatch emulsion copolymerization recipe that gave a latex with ca. 44 wt% solids. The two-stage polymerization process consisted of an in situ seed-formation step followed by copolymerization of the continuously added *n*-butyl methacrylate and N-methylol acrylamide monomers under monomer-starved conditions. A 2-dm<sup>3</sup> glass reactor and Rushton turbine agitators of different diameters (4, 6 and 8 cm) were used in the study. Agitation influenced the particle number at the end of the seed stage. This influenced properties like latex viscosity, the amount of water-soluble polymer, and the particle size in the final latex. Analysis

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of the water-soluble polymer using NMR spectroscopy showed that it was mostly a homopolymer of N-methylol acrylamide. With the 4 cm diameter agitator, the mixing of the pseudoplastic latex was poor during the feed stage. Formation of a zone of poor mixing could be observed on top of the fluid in the reactor, when the monodisperse particles in the latex formed an iridescent structure. Poor emulsification of the added *n*-butyl methacrylate monomer resulted in a greater amount of water-soluble polymer.

*Key Words:* Agitation; Semi-batch emulsion polymerization; Kinetics; Particle size distribution; Water-soluble polymer.

## INTRODUCTION

Industrial emulsion polymerization of vinyl monomers involves high-solids latexes. Frequently, water-soluble comonomers are used in small amounts, either to impart colloidal stability, surface functionality, or as crosslinking agents. The aqueous phase polymerization of these "functional" comonomers to form water-soluble polymer is a reaction that competes with the incorporation of the monomers in the polymer particles, and may not be desirable. The high viscosity, coupled with the difference in the mass transfer rates of the comonomers in the recipe (on account of different water-solubilities), makes the copolymer composition prone to the effects of agitation. This is especially true for the case of "monomer-starved" semibatch polymerization. By virtue of the small amounts of the functional monomers in the recipe, small differences in the degree of incorporation of these monomers could result in significant differences in the properties of the final latexes and polymer films. Hence, differences in the performance of the latexes synthesized in a lab-scale reactor and a large-scale reactor can be traced back to the differences in the incorporation of the functional monomers arising from different agitation conditions in the two reactors.

To minimize shear-induced coagulation of the latex particles, it is desirable to use relatively gentle agitation during the production of the latexes. Unless the agitator diameter and rotation speed are properly chosen, lowering the shear rate in the reactor, can also lower the mixing (liquid circulation) component of agitation. Although the monomer-starved semibatch process is widely used, reports on the mass transfer and mixing aspects of this process are relatively scarce in the literature.

We have studied the role of agitation in different aspects of semibatch emulsion copolymerization of a relatively water-insoluble *n*-butyl methacrylate (BMA) and a completely water-soluble monomer, N-methylol acrylamide (NMA). BMA gives uncrosslinked polymer when polymerized in emulsion,

using a thermal initiator like potassium persulfate. The function of NMA is to crosslink these polymer molecules after the latex is dried to form a film. Dave (1998) has studied the effects of agitation on coagulation during homopolymerization of BMA and its copolymerization with NMA using Newtonian latexes with viscosities of ca. 10 mPa-s (centipoise). The recipe used by Dave was sensitive to surface coagulation and shear induced aggregation. Coagulum as high as 4 pphm (parts per hundred parts monomer in the recipe) was formed even under relatively mild agitation conditions, if the reaction was not terminated at the end of the addition of the monomers. Consequently, the reaction was stopped along with the addition of the monomer feed streams, and the final latex contained a significant amount of residual monomer (ca. 10% of the total monomer). An objective of our work was to develop a more robust latex recipe which gave a high-solids, viscous latex, characteristic of industrial latexes. Monodisperse particles with diameters of ca. 200 nm were desired, the uniformity of particle size enabling easier characterization of the effect of agitation on particle nucleation and copolymer composition.

Two model latex recipes were developed to study the effects of mixing on copolymer composition. The final solids content in the first recipe was ca. 25% and the latex showed a Newtonian viscosity, the latex viscosity being independent of the shear rate. The effects of agitation in the emulsion copolymerization using this recipe will be reported in the following paper (Krishnan et al., 2003). The second recipe consisting of ca. 45% final solids content resulted in a viscous latex with shear-thinning or pseudoplastic behavior. These latexes were stable against shear-induced aggregation under a wide range of agitation conditions. The maximum coagulum at the end of the reaction was about 0.3 pphm.

## MATERIALS

*n*-Butyl methacrylate (BMA, 99%, CAS # 97-88-1, MW = 142.20 g/mol, Sigma-Aldrich) inhibited by 10 ppm monomethyl ether of hydroquinone (MEHQ, CAS # 150-76-5) was used as the monomer. The monomer was freed from the inhibitor by passing it through an inhibitor-removal column (Sigma-Aldrich). *N*-Methylol acrylamide (NMA, CAS # 924-42-5, MW = 101.11 g/mol, Sigma-Aldrich) was received as a 48 wt% solution in water and was inhibited with 30 ppm of MEHQ. Sodium dodecyl sulfate (SDS, CAS # 151-21-3, MW = 288.38 g/mol, Ultrapure Bioreagent, J. T. Baker) was used as the surfactant and potassium persulfate (KPS, CAS # 7727-21-1, 99+%, MW = 270.33 g/mol, ACS reagent, Sigma-Aldrich) was used as the initiator. Sodium bicarbonate (CAS # 144-55-8, MW = 84.01 g/mol, Mallinckrodt Baker, Inc.) was used as the buffer. The chain transfer



agent  $\text{CBr}_4$  (CAS # 558-13-4, 99%, MW = 331.65 g/mol) was obtained from Sigma-Aldrich. Deionized water (DI water) was boiled to remove dissolved oxygen, and cooled under nitrogen before use. The nitrogen gas (Zero Grade 0.5, minimum purity 99.998%, oxygen <0.5 ppm) was obtained from Airgas. Toluene (CAS #108-88-3, MW=92.14 g/mol, VWR Brand) was used as the solvent for the swelling measurements. All the chemicals except BMA were used as received.

### PROCEDURES

The latexes were prepared using the recipe shown in Table 1. The reactions were carried out at 70°C under a nitrogen atmosphere in a 2 dm<sup>3</sup> cylindrical glass reactor with a dish-shaped base shown in Figure 1. The reactor had an outer diameter of 14.0 cm (5.5 in) and an overall height of 18.1 cm (7.125 in). Attached to the custom-made stainless steel (SS) lid of the reactor were six 1.3 cm wide SS baffles. A water-cooled reflux condenser was also connected to the lid. The reactor was heated using a heating mantle (Glas-Col, No. 0576). The power-supply to the heating mantle was through a transformer (Powerstat variable autotransformer, 120 V & 50/60 Hz input, 0 to 140 V & 10 A output capacity; Superior Electric Co., Bristol, Connecticut). The temperature of the reaction fluid was measured using an iron-constantan thermocouple (Omega Engineering, Type J thermocouple), and was the input to a microprocessor based temperature controller (Omega Engineering, Model CN76000). The temperature controller maintained the temperature in the reactor at the set-point value (70°C) by regulating the output of the transformer. In addition, the heating mantle could be raised or lowered

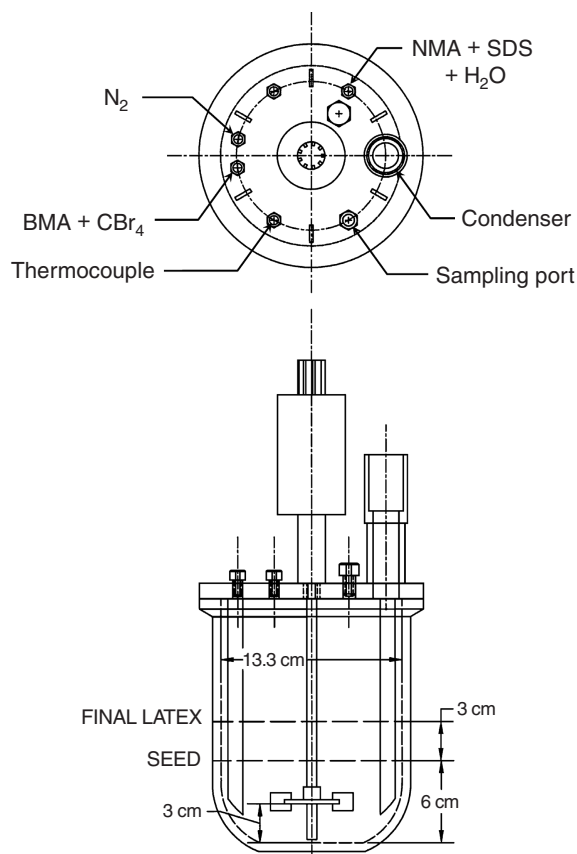
**Table 1.** Recipe for emulsion copolymerization of BMA and NMA.

Seed stage (70°C, 45 min)		Feed stage (70°C, 150 min) <sup>b</sup>	
Ingredient	Amount (g)	Ingredient	Amount (g)
DI water	510.00	DI water	90.0
BMA	60.00	BMA	402.3 (450 cm <sup>3</sup> )
SDS	0.735 (5 mM) <sup>a</sup>	NMA	12.0
KPS	0.414 (3 mM) <sup>a</sup>	SDS	3.5
NaHCO <sub>3</sub>	0.414 (9.7 mM) <sup>a</sup>	CBr <sub>4</sub>	0.81 <sup>c</sup>

<sup>a</sup>concentration in mmol per dm<sup>3</sup> water.

<sup>b</sup>final solids content of latex is ca. 44 wt %.

<sup>c</sup>0.2 wt % of the feed stage BMA monomer.



**Figure 1.** Reactor and experimental setup.

enabling temperature control within  $\pm 0.5^\circ\text{C}$ . A constant speed motor (Eurostar, IKA) with a speed range from 50 to 2000 rpm was used to provide the agitation. The motor has a microprocessor that maintains the speed constant with changes in viscosity. The speed and the torque were digitally displayed on the motor. Rushton turbine agitators with different diameters (4 cm, 6 cm, and 8 cm, cf. Figure 2) mounted on a 0.75 cm diameter SS shaft at ca. 3 cm from the reactor bottom were used to obtain a wide range of agitation power-input to the reactor. The dimensions of the agitators are given in Table 2.

The reactor contents were heated to the reaction temperature of  $70^\circ\text{C}$  in ca. 15 min. 20 g of the initiator solution consisting of KPS and  $\text{NaHCO}_3$  dissolved in DI water was injected after stirring of the emulsion for ca. 1 h.



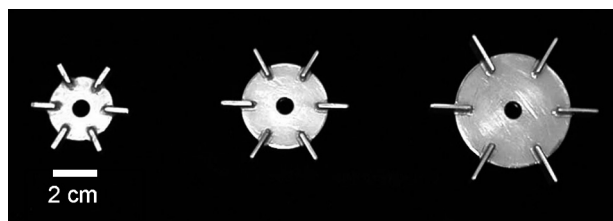


Figure 2. Rushton turbine agitators used to study the effects of agitation.

The droplet size distribution is expected to reach an equilibrium during this period. The seed stage consisting of homopolymerization of BMA was of 45 min duration. The BMA and NMA monomers were fed separately using stainless steel tubes during the feed stage. The feed tube for BMA had an inner diameter of 2.16 mm (3.175 mm O.D.), and the feed tube for NMA had an inner diameter of 0.76 mm (1.588 mm O.D.). The BMA was fed using a syringe pump of 500 cm<sup>3</sup> capacity (LC-5000 precision pump, Isco). The aqueous feed of composition 154/50/7 (parts by weight) of DI water/NMA solution/SDS was added using a smaller syringe pump (Harvard Apparatus, Model 22) at a rate of 0.690 cm<sup>3</sup>/min. CBr<sub>4</sub> was added continuously during the feed stage as a solution in the BMA monomer.

The reactor lid had a sampling port with a rubber septum so that samples could be withdrawn from the reactor using a SS needle inserted through the septum. This sampling port was also used to inject the initiator solution at the beginning of the reaction. Samples were withdrawn from near the agitator region. To quench the reaction, a few drops of 1% aqueous hydroquinone solution (inhibitor) were added to the sample vial, which was then placed in an ice-bath. Latex samples were withdrawn at the end of the seed stage (for particle size and conversion determination) and at 30 min intervals during the feed stage. The monomer conversion at the end of the seed stage was greater

Table 2. Dimensions of the Rushton turbine agitators.

Agitator designation	D <sup>a</sup> (cm)	W <sup>b</sup> (cm)	H <sup>c</sup> (cm)
4 cm agitator	4.4	1.0	0.9
6 cm agitator	5.9	1.4	1.1
8 cm agitator	7.8	1.9	1.5

<sup>a</sup>D is the tip-to-tip distance of the agitator blades.

<sup>b</sup>W is the blade width measured parallel to the disc of the Rushton turbine.

<sup>c</sup>H is the blade height measured perpendicular to the agitator disc.

than 98%. An inert atmosphere of nitrogen was maintained in the reactor by flowing nitrogen throughout the reaction using a 3.175 mm O.D. tube. Nitrogen was bubbled through the emulsion during the seed stage, and passed through the reactor headspace during the feed stage. Because of continuous addition of SDS during the feed stage, excessive froth formation resulted if nitrogen was bubbled through the reaction fluid during this period.

At the end of the feed stage, the reaction was allowed to continue for an additional 30 min, after which ca. 5 cm<sup>3</sup> of the 1% aqueous hydroquinone solution was injected into the reactor. The amount of coagulum on the reactor inserts and in the latex was measured using a sieve with 55 μm pore size. The final latexes were iridescent indicating that narrow particle size distributions were obtained.

## RESULTS AND DISCUSSION

### Effect of Agitation on Particle Size in the Latex

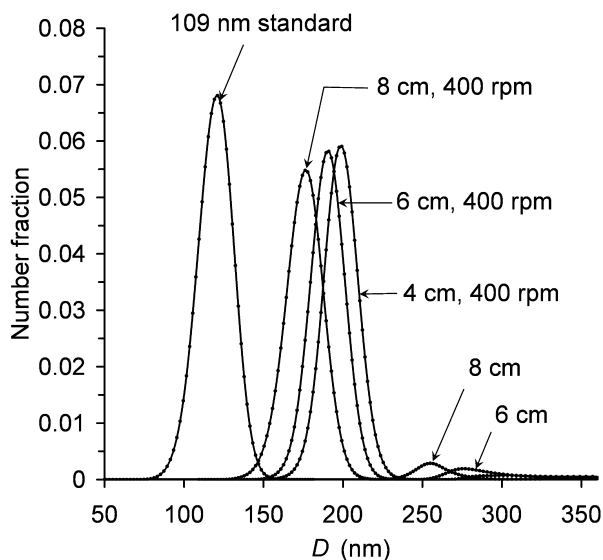
In the first set of experiments, the reactions were carried out using the three agitators at the same rotational speed of 400 rpm (rotations per minute). Figure 3 shows the number distribution of particles in the final latex determined using capillary hydrodynamic fractionation (CHDF 1100, Matec Applied Sciences). The distribution shows the number fraction of particles within a given range of particle diameters, each point representing the center of the range. The particles when observed under a transmission electron microscope or atomic force microscope appeared to be of uniform size. For monodisperse particles, the distribution should appear as a spike. The broadening of the distribution in CHDF chromatogram is because of axial dispersion (Silebi and DosRamos, 1989). The CHDF particle size distribution of a monodisperse 109 nm polystyrene standard (Dow Chemical Company; TEM standard deviation = 2.7 nm) is shown for reference. The mean particle diameter and the standard deviation, as determined by the CHDF, are 119.9 nm and 11.2 nm respectively.

The particle size was smaller for a higher degree of agitation (larger agitator diameter). In other words, the total particle number, given by Eq. 1, was greater for a higher degree of agitation.

$$N_{p,t} = \frac{6V_p}{\pi D_v^3} \quad (1)$$

where  $N_{p,t}$  is the total number of particles in the latex,  $V_p$  is the particle volume and  $D_v$  is the volume-average particle diameter. Determination of





**Figure 3.** Effect of agitation on particle size distribution in the final latex determined by capillary hydrodynamic fractionation.

the particle diameters in the samples from the seed latexes showed that the decrease in the particle size in the final latex was a consequence of the smaller particle diameters at higher agitation, in the seed latex itself. In Table 3 the seed latexes prepared under different agitation conditions are characterized. The volume-average diameter,  $D_v$ , is calculated using Eq. 2 where  $n_i$  is the number of particles with diameter  $D_i$

$$D_v = \left[ \frac{\sum n_i D_i^3}{\sum n_i} \right]^{1/3} \quad (2)$$

Thus, higher agitation intensity nucleates more particles. This observation is consistent with the interfacial nucleation mechanism recently proposed by

**Table 3.** Effect of agitation on particle size and concentration of the seed latexes.

Agitator	Agitator speed (rpm)	Monomer conversion (%)	$D_v$ (nm)	$N_p$ (particles/dm <sup>3</sup> water)
8 cm	400	98.2	89	$2.63 \times 10^{17}$
6 cm	400	98.0	99	$1.91 \times 10^{17}$
4 cm	400	99.5	105	$1.63 \times 10^{17}$



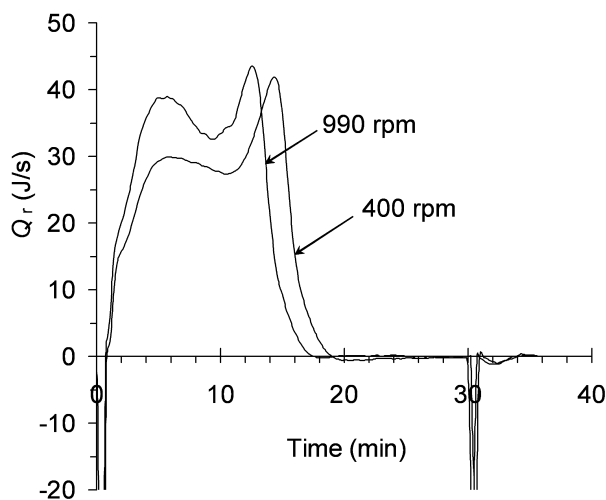
Ni et al. (2001). According to this mechanism, the minidroplets formed in the supersaturated region at the monomer-water interface act as particle nuclei. The droplet interfacial area is higher at a higher stirring speed, and a greater number of particle nuclei can be swept away from the droplet interface at a higher shear rate resulting in a higher number of particles. Oxygen impurity in the emulsion can also result in an increased nucleation of polymer particles (Nomura et al., 1972). The mass transfer rate of oxygen from the reactor headspace into the emulsion will increase with an increase in the agitation speed. The peaks in Figure 3 at higher particle diameters, especially with the 8 cm and 6 cm agitators are because of the second population of particles formed by shear-induced aggregation. The total number of such particles is, however, negligible compared to number of particles in the main population, as can be seen from the relative areas under the respective peaks.

#### Effect of Agitation on the Kinetics of Seed-Stage Polymerization Using Reaction Calorimetry

The Mettler RC1 reaction calorimeter was used to study the effect of agitation on the rate of emulsion polymerization of BMA using the seed-stage recipe of Table 1. The recipe consisted of 536.84 g of DI water, 63.16 g of BMA, 0.7741 g of SDS, 0.4354 g of KPS, and 0.4354 g of NaHCO<sub>3</sub>. A detailed investigation of the kinetics of emulsion polymerization of styrene using reaction calorimetry, and the interpretation of the calorimetric results has been presented by Varela de la Rosa et al. (1996, 1999a–c). A pitched blade turbine with 4 blades was used, and agitation speeds of 400 rpm and 990 rpm were employed. The tip-to-tip diameter of the agitator was 4.5 cm, and the blade width and blade height were 1.5 cm each. The rate of heat evolution,  $Q_r$ , which is proportional to the reaction rate, is shown in Figure 4 for two agitation speeds. It is seen that the reaction rate is higher at higher agitator speed. The reaction was terminated ca. 30 min after adding the initiator (time = 0). The negative spikes in  $Q_r$  at 0 and 30 min, respectively, correspond to the addition of the initiator and inhibitor solutions that were at room temperature, to the reaction fluid that was at 70°C. The monomer conversions in the final latexes prepared at 400 rpm and 990 rpm were, 98.4% and 98.2%, respectively, and the particle diameters (obtained by dynamic light scattering) in the final latexes were 104 nm and 96 nm, respectively. Thus, a greater number of particles were nucleated at 990 rpm, and the reaction rate given by Eq. 3 was higher:

$$R_p = \frac{k_p[M]_p \bar{n} N_p}{N_A} \quad (3)$$





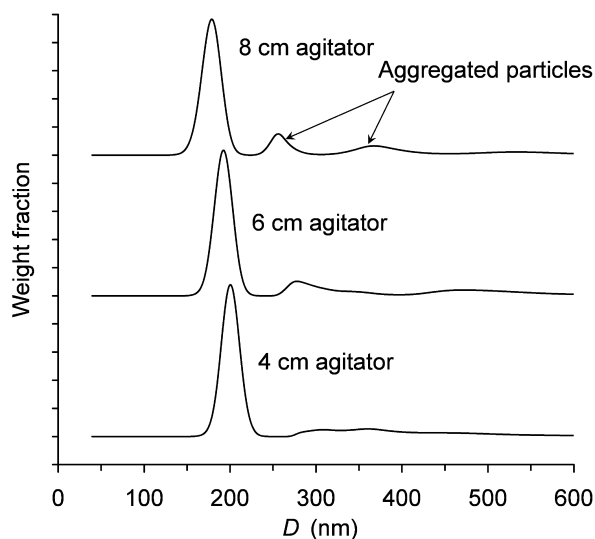
**Figure 4.** Effect of agitation on the kinetics of seed stage polymerization using the Mettler RC1 reaction calorimeter.

where  $R_p$  (mol/s per  $\text{dm}^3$  water) is the rate of polymerization,  $k_p$  ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) is the propagation rate constant of the monomer,  $[M]_p$  ( $\text{mol dm}^{-3}$ ) is the monomer concentration in the particles,  $\bar{n}$  is the average number of radicals per particle,  $N_p$  (number per  $\text{dm}^3$  water) is the particle concentration and  $N_A$ , Avogadro's number.

### Effect of Agitation on Particle Aggregation

Shear induced aggregation of particles is a well-known phenomenon in the field of emulsion polymers. A higher agitation increases the frequency of collisions, and also the intensity of collisions, between the sticky polymer particles. As expected, the amount of coagulum increased from ca. 0.09 ppm with the 6 cm agitator to ca. 0.25 ppm with the 8 cm agitator. Shear-induced particle aggregation in the final latexes can be clearly seen in the weight-distribution of particle diameter obtained from CHDF, and shown in Figure 5. The weight distribution shows the mass fraction of particles within a given range of particle diameters, and emphasizes the small number of particle aggregates that have a higher mass than the rest of the particle population. The mass fraction of larger size particles is seen to be higher with the 8 cm agitator.

The mass of coagulum at the end of the reaction was determined by scraping the solids sticking to the reactor inserts, and washing them with DI



**Figure 5.** Effect of agitation on relative amounts of particle aggregates in the final latexes determined by capillary hydrodynamic fractionation.

water using a 53  $\mu\text{m}$  sieve. The latex was also filtered through the sieve. However, most of the coagulum was on the reactor inserts, and almost no coagulum was in the latex. The coagulum was then dried in an aluminum pan, and weighed. Table 4 gives the total mass of coagulum under different agitation conditions. The experiments where the 4 cm agitator was used under different seed stage and feed stage agitation speeds will be described later.

### Effect of Agitation on the Latex Viscosity

Oprea and Dodita (2001) have given a comprehensive list of factors that affect the viscosity of a latex. They varied the agitation speed from 100 to 220 rpm during the synthesis of a 50% solids styrene-acrylic latex, in a 2-dm<sup>3</sup> reactor. Their final latexes showed a pseudoplastic behavior that could be described by the power law,

$$\tau = k \dot{\gamma}^n \quad (4)$$

where  $\tau$  is the shear stress, and  $\dot{\gamma}$  is the shear rate,  $k$  is the consistency index, and  $n$  the flow index. They found an increase in the particle diameter with an increase in the agitation speed because of particle coalescence during synthesis. They also found that the consistency index decreased, that

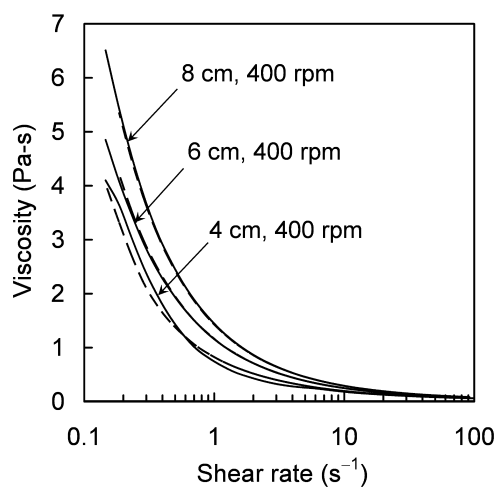


**Table 4.** Effect of agitation on the amount of coagulum on the reactor inserts.

Agitator	Agitation speed (rpm)		Coagulum	
	Seed stage	Feed stage	(g)	(%)*
8 cm	400	400	1.21	0.26
6 cm	400	400	0.44	0.09
4 cm	400	400	0.18	0.04
4 cm	400	500	0.26	0.05
4 cm	400	600	0.51	0.11

\*based on total monomer in the recipe (cf. Table 1).

is, the latex was less viscous, with an increase in the agitation intensity. However, an opposite trend was observed in this work. Figure 6 shows the viscosity as a function of shear rate for the latexes prepared using the 4 cm, 6 cm, and 8 cm agitators. The viscosities were measured using a Bohlin cup and cylinder rheometer at 25°C. Clearly, the latexes are pseudoplastic. The latex prepared using the 8 cm agitator has the highest viscosity at each shear rate. The latex viscosity was higher when the agitation intensity during the reaction was higher.



**Figure 6.** Viscosity vs. shear rate for the latexes prepared under different agitation conditions, measured with a Bohlin rheometer and a cup and cylinder arrangement at room temperature.

According to Einstein's equation, the viscosity of a dispersion,  $\eta_d$  is given by Eq. 5:

$$\eta_d = \eta_c(1 + 2.5\phi) \quad (5)$$

where  $\eta_c$  is the viscosity of the continuous phase, and  $\phi$  is the volume fraction of the solids in the dispersion. Thus, dispersions of spherical particles with equal solids content should have the same viscosity. Although Einstein's equation is valid only for very dilute suspensions, other equations for higher solids contents also predict that the viscosity should depend only on the volume fraction of the solids in the dispersion. However, as discussed by Schaller (1997), the particle size has a strong effect on latex viscosity, the viscosity being higher for smaller particles. The surface of the copolymer particles is expected to consist of a hydration layer not only because of the charged SDS molecules on the surface, but also due to the hydrophilic NMA units. The effective diameter of the particles and the effective volume fraction of the particles are higher because of this hydration layer. The relationship between the effective volume fraction,  $\phi_h$ , in the presence of a hydration layer of thickness,  $h$  (m), and volume fraction,  $\phi$ , of the solids based on the dry particle diameter can be easily derived, and is given in Eq. 6.

$$\frac{\phi_h}{\phi} = \left(1 + \frac{2h}{D}\right)^3 \quad (6)$$

where  $D$  (m) is the diameter of the particles. Thus for a hydration layer having a thickness that is 5% of the particle diameter, the effective volume fraction is expected to be ca. 33% higher. The volume fraction  $\phi$  can be determined from the mass fraction (solids content),  $m$ , of the particles in the latex using Eq. 7:

$$\phi = \frac{1}{1 + \left(\frac{\rho_p}{\rho_w}\right) \cdot \left(\frac{1}{m} - 1\right)} \quad (7)$$

where  $\rho_w$  is the density of water, and  $\rho_p$ , the density of polymer.

The smaller the size of the particles, the greater will be their surface area (for a given volume fraction of solids in the dispersion), and greater will be the amount of water immobilized in the hydration layer, giving a higher viscosity. This is also borne out by Eq. 5, where for a fixed  $\phi$  and  $h$ , the effective volume fraction,  $\phi_h$ , is higher for a smaller particle diameter,  $D$ .



In addition to the increased effective volume fraction, the interparticle distance is also smaller when the particle diameter is smaller (for the same solids content). The interparticle distance in the latex with uniform particle diameter can be calculated assuming a hexagonal close packed structure as shown in Eq. 8 (Schaller, 1997):

$$H = \left[ \left( \frac{0.74}{\phi} \right)^{1/3} - 1 \right] D \quad (8)$$

where  $H$  is the distance between the surface of the particles of diameter  $D$  in the latex. Thus, the particles are closer in the latex prepared using the 8 cm agitator. The interparticle distance in the latex is ca. 33 nm with the 8 cm agitator, and ca. 37 nm with the 4 cm agitator. The particles will be even closer, when the hydration layer is taken into account.

The solid curves in Figure 6 show the viscosity as the shear-rate is increased, and the dashed curves, the viscosity as the shear-rate is decreased. No hysteresis was observed for the 8 cm and 6 cm latexes. The viscosity values were the same on repeated increase and decrease of the shear-rate. On the other hand, the 4 cm latex showed a hysteresis at lower shear rates. This was not because of particle aggregation, because the plot retraced its path on increasing the shear rate again. The difference in the up and down values of viscosity could be due to the breaking and forming of the highly ordered arrangement of particles in the monodisperse latex.

The presence of water-soluble polymer in the aqueous phase of the latex is expected to increase the latex viscosity. Although, as will be shown in what follows, the amount of water-soluble polymer is higher with the 4 cm agitator, its viscosity is the lowest. Thus, the effect of particle size seems to have a stronger influence on the viscosity than the difference in the amount of water-soluble polymer in the latex serum.

### Effect of Agitation on Instantaneous Conversion

Instantaneous conversion in a semibatch polymerization is defined as the amount of polymer in the system at any instant divided by the total amount of monomer added up to that point (including the monomer in the seed stage). The instantaneous conversion of BMA can be calculated from the mass  $y$  of the solids obtained by drying mass  $x$  of the latex sample, and using Eq. 9 of Sajjadi and Brooks (2000):

$$x_i = \frac{\left( \frac{y}{x} \right) - f_a}{f_m} \quad (9)$$

where  $f_a$  is the ratio of total masses of non-volatile solids in the latex at any time during the feed stage to the total mass  $M_{\text{tot}}$  in the reactor at that time. The non-volatile solids include SDS, KPS,  $\text{NaHCO}_3$ ,  $\text{CBr}_4$  and reacted and unreacted NMA monomer. Similarly, the monomer fraction  $f_m$  is the ratio of the total mass of BMA added to the reactor at any point during the feed stage to  $M_{\text{tot}}$  at that time. Figure 7 shows the instantaneous conversion plotted as a function of time during the feed stage.

It is seen that the instantaneous conversion is lower with the 4 cm agitator. Also, it takes a longer time to reach the plateau value of  $x_i$ . There is a drop in the instantaneous conversion value after ca. 120 min of feed with the 4 cm agitator. The liquid level in the reactor rises continuously during the feed stage, and the latex progressively becomes more viscous with the increase in the solids content. With the 4 cm agitator, a zone of poor mixing could be observed in the reactor from the iridescent nature of the latex.

Figure 8 shows the mixing in the reactor at different stages of the reaction. Before the addition of the initiator solution, the emulsion appears translucent [Figure 8(a)]. Within ca. 5 min, the emulsion becomes opaque. Good mixing can be observed at the surface of the liquid in Figure 8(b) at this stage. Movement of the fluid at the top of the reactor can be still seen in Figure 8(c), at ca. 26 min of the feed stage. Figure 8(d) (ca. 88 min of the feed stage) shows the increased liquid height in the reactor and ripples at the liquid surface. In Figure 8(e), which shows the emulsion at ca. 112

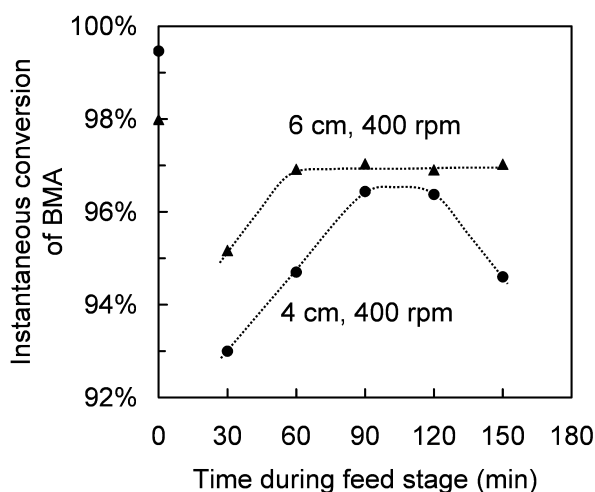
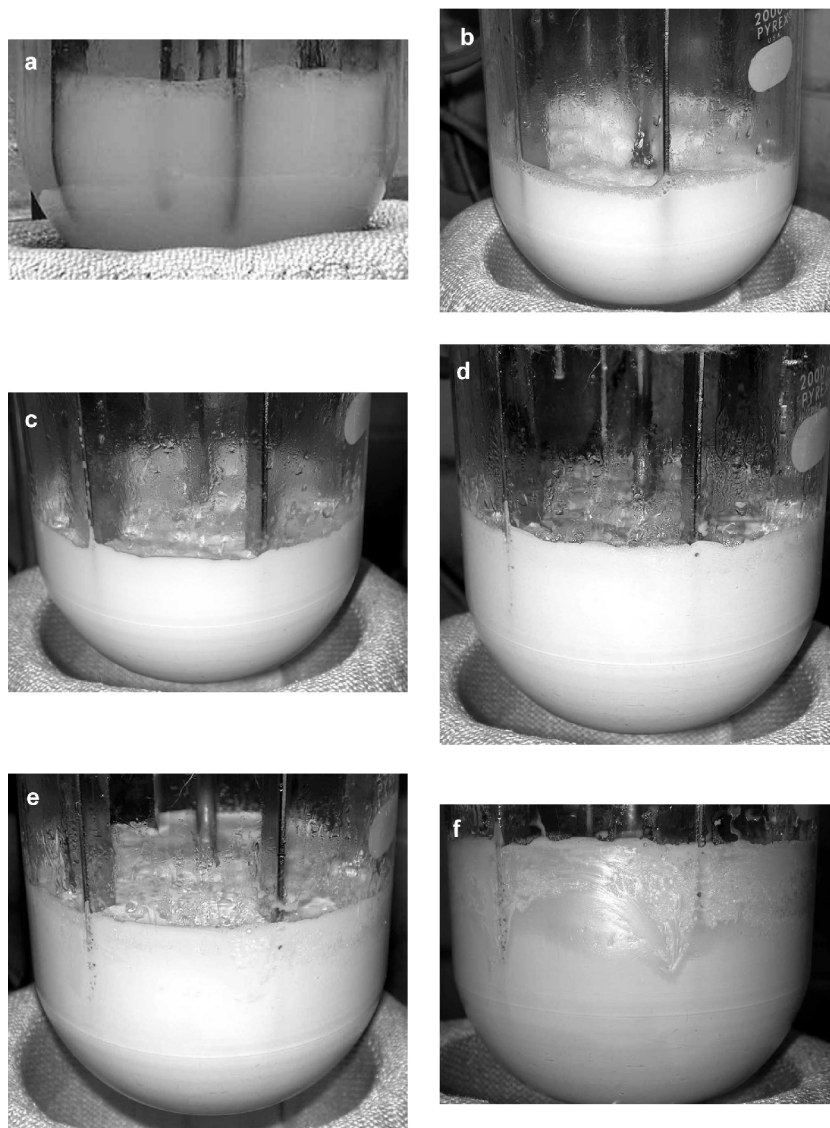


Figure 7. Effect of agitation on instantaneous conversion.





**Figure 8.** Appearance of the latex at different stages of the semibatch emulsion copolymerization reaction using the 4 cm agitator at 400 rpm; (a) emulsion before the addition of initiator solution; (b)  $t = 5$  min after adding the initiator (seed stage); (c)  $t = 26$  min after starting feed (feed stage); (d) 88 min, feed stage; (e) 112 min, feed stage; and (f) 144 min, feed stage.



min of the feed stage, the formation of an iridescent segregation zone at the top of the reactor can be seen. The liquid is almost stagnant at the top of the reactor. Figure 8(f) clearly shows the top-to-bottom non-uniformity in the reactor due to poor bulk mixing. The picture was taken at ca. 144 min during the feed stage. Because of the small size of the agitator, the shear rate in the reactor is lower in the top part of the reactor. The latex is more viscous in this region due to the low shear rate. This results in poor mixing and almost stagnant latex at the top part of the reactor.

The breaking of the added BMA monomer into droplets occurs in the agitator region. If the shear rate in the agitator region is low, large droplets are formed which rise because of buoyancy to the top of the fluid, coalesce and form a pool of monomer. If the circulation in the reactor is good, the monomer pool will be drawn into the agitator region and will be emulsified. Thus, a monomer pool will be formed when the shear rate in the agitator region is low and when there is poor circulation. When monomer pooling occurs, the instantaneous conversion drops because of the low rate of monomer transfer to the polymer particles associated with the low monomer-water interfacial area.

In obtaining Eq. 9 it was assumed that the latex dispersion is uniform throughout the reactor, and that the sample withdrawn has the same overall composition as that of the latex in the reactor. When monomer pooling occurs, the sample withdrawn from the bottom part of the reactor will not have the average composition of the material in the reactor. Using mass balance, Eq. 9 can be modified to take into account the effect of BMA pooling on the instantaneous conversion.

$$x_i = \frac{\left(\frac{y}{x}\right) \left(1 - \frac{p}{M_{\text{tot}}}\right) - f_a}{f_m} \quad (10)$$

where  $p$  is the mass of monomer that forms the pool at the top of the reactor at a given time. Thus, the value of  $x_i$  calculated using Eq. 9 would be higher than the actual value.

### Effect of Agitation on Crosslinking of the Copolymer Films

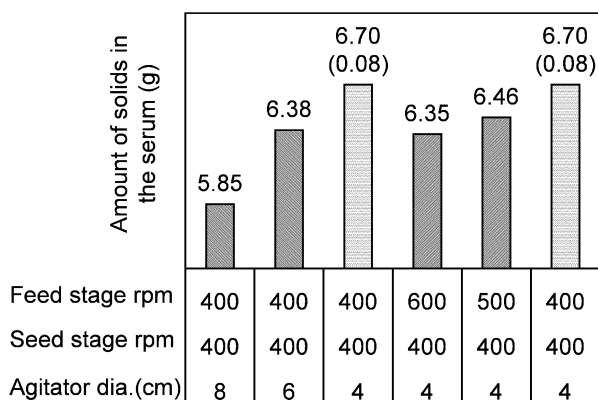
The latexes were dried at room temperature in a fume-hood for 2 to 3 weeks, and then cured in an oven at ca. 150°C for 30 min. About 1 g of the cured polymer (ca. 2 mm thick) was soaked in ca. 100 g of toluene for a week, with intermittent shaking. The swollen gel was separated from the solvent by filtering using a pre-weighed stainless steel wire mesh filter. The



mass of the swollen gel was determined, and the dry gel was also weighed after evaporating the solvent. The gel fraction of the cured polymer sample was determined by dividing the mass of the dry gel by that of the original sample of uncured polymer. Gravimetric determination of the soluble fraction in the sol gave values consistent with the measured gel fraction. The swelling index was calculated as the ratio of the mass of the swollen gel to the mass of the dry gel. The measurements were made in duplicate, and the standard deviations were usually less than 2% of mean values. The fraction of the cured polymer that was insoluble in toluene (gel fraction) had values of 81%, 71%, and 68%, respectively, for latexes prepared using the 8 cm, 6 cm, and 4 cm agitators. As expected, the swelling index values of 10.0, 11.0, and 11.4 showed the reverse trend, increasing with a decrease in the agitation power-input. Thus, the latexes prepared using higher agitation power-inputs showed a higher density of crosslinking in the resulting films. This can be attributed to greater extent of NMA incorporation in the polymer particles, as will be shown below.

#### Effect of Agitation on NMA Incorporation and Water-Soluble Polymer Formation

The amount of water-soluble polymer in the serum (aqueous phase of the latex) was determined by ultracentrifugation and gravimetry. The



**Figure 9.** Amount of water-soluble species in the aqueous phase of the latex depending on the agitator diameter and the agitation speed during the seed and the feed stages. The number in the brackets is the standard deviation from the mean value, of the amount of solids in the sera of latexes from two different syntheses under identical conditions.

latexes were diluted to ca. 11% solids (10 g latex + 30 g DI water) and centrifuged at 4°C and 37000 rpm for 6 hrs (Beckman, L8-M Ultracentrifuge) to separate the polymer particles from the aqueous phase. About 15 g of serum was dried to constant weight in an oven at 75°C, cooled to room temperature in a desiccator, and weighed to determine the amount of water-soluble species in the latex. Figure 9 shows the amount of water-soluble species in the latex sera as a function of the agitation conditions. Columns 3 and 6 show the reproducibility of the data for two different experiments carried out under identical conditions (the standard deviation enclosed in the parenthesis). The water-soluble species in the serum are water-soluble copolymer, NMA homopolymer, SDS, NaHCO<sub>3</sub>, KPS, and any unreacted NMA monomer. The variation in the mass of water-soluble species with agitation is mainly because of different amounts of water-soluble polymer. A <sup>1</sup>H-NMR spectrum of the serum species shows that the water-soluble polymer contains negligible BMA units, and is to a large extent the homopolymer of NMA. Also, the amount of SDS in the serum is small compared to the amount of polymer. The <sup>1</sup>H-NMR spectrum of the serum solids in D<sub>2</sub>O shown in Figure 10 is similar to that for poly(NMA) reported by Bonardi et al. (1991). The greater the amount of water-soluble polymer in the serum, the lower is the incorporation of NMA in the polymer particles. With the 4 cm, 6 cm, and 8 cm agitators, the amount of water-soluble polymer is the least with the 8 cm agitator.

It would be expected that only the feed stage agitation should have any effect on copolymerization because, the copolymerization reaction is carried out only during the feed stage. However, the experiments carried out with

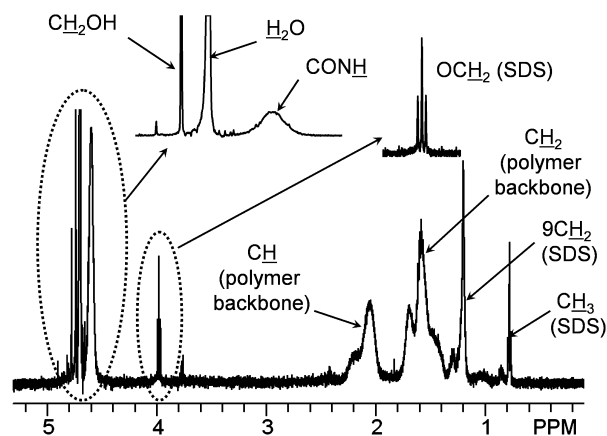


Figure 10. <sup>1</sup>H-NMR spectrum of the serum solids dissolved in D<sub>2</sub>O.

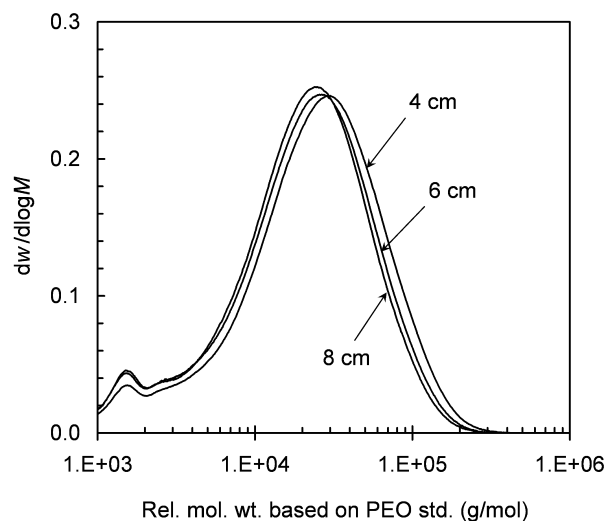


the 4 cm, 6 cm, and 8 cm agitators show an effect of agitation on the total number of particles in the latex. The seed stage agitation plays an indirect role in the incorporation of NMA, through its effect on particle nucleation. NMA incorporation will be greater when the total number of particles in the latex is higher. With the 4 cm agitator, the BMA monomer entering the reactor experiences a lower shear and is emulsified to give a small number of larger droplets. On the contrary, the 8 cm agitator results in better emulsification of the monomer, producing a greater number of monomer droplets that are smaller in size. Thus, under monomer-starved conditions, the 4 cm agitator results in a lower concentration of BMA in the water and the polymer particles. Its copolymerization with NMA occurs to a lower extent, and more water-soluble polymer (predominantly NMA homopolymer) is formed.

To isolate the effect of feed stage agitation, a set of experiments was performed with the 4 cm agitator where the seed stage agitation speed of 400 rpm was the same in all cases, while the feed stage agitation was chosen to be 400 rpm, 500 rpm, and 600 rpm. Because the seed stage agitation was the same in all the three experiments, the total number of particles was the same. (There was no evidence of secondary nucleation during the feed stage). However, the amount of water-soluble polymer was lower when the agitation speed during the feed stage was 600 rpm. This effect is solely because of the effect of agitation on the mechanism of copolymerization, and is expected to increase in importance with the scale of the synthesis. As discussed before, the pseudoplastic nature of the latex seems to be an important factor in the manifestation of the mixing effect (cf. Figure 8). The flow may be turbulent in the agitator region owing to the higher shear-rate and lower viscosity. However, in the remaining part of the reactor, the shear-rate will be lower, and the viscosity, higher. A higher feed stage agitation speed causes a higher shear rate in all parts of the reactor, favorable for emulsification of the BMA feed stream, and better circulation, for top-to-bottom uniformity in the reactor.

### Molecular Weight of Serum Polymer

Figure 11 shows the molecular weight distributions (MWDs) of the water-soluble polymer for the latexes prepared using the 4 cm, 6 cm, and 8 cm agitators at 400 rpm. The distributions were determined by gel permeation chromatography using Waters 515 HPLC Pump, Tosoh Biosep TSK-GEL columns PWXL and GMPWXL, Waters 410 Differential Refractometer detector, and poly(ethylene oxide) standards with narrow molecular weight distributions (obtained from Polymer Laboratories). The MWDs reported are not absolute, but based on a calibration using the



**Figure 11.** Effect of agitation on the molecular weight of the water-soluble polymer.

poly(ethylene oxide) standards. Unlike the polymer chains in the particles, the serum polymer has low molecular weight (a number-average molecular weight,  $M_n$ , of ca. 10000 g/mol, and a weight average molecular weight,  $M_w$ , of ca. 30000 g/mol). This is expected, because the locus of formation of this polymer is the aqueous phase where more frequent termination of the growing polymer chains is possible.

The molecular weight decreases with an increase in the agitation power ( $M_w$ 's are ca. 35000 g/mol, 31000 g/mol, and 29000 g/mol, for the 4 cm, 6 cm, and 8 cm agitators, respectively). If oxygen impurity remained in the reactor headspace in spite of the continuous flow of nitrogen, this decrease in molecular weight can be attributed to the faster transfer of oxygen from the reactor headspace into the aqueous phase, followed by the termination of the free radicals in the water. However, it seems more likely that the decrease in the molecular weight is due to the  $CBr_4$  chain transfer agent used in the recipe.  $CBr_4$  added during the feed stage as a solution in the BMA monomer, will be consumed in the aqueous phase and the polymer particles. The aqueous phase concentration of  $CBr_4$  will be higher at higher agitation intensity because of a faster supply of  $CBr_4$  from the monomer droplets into the aqueous phase. The greater droplet-water interfacial area at higher agitation power is mainly responsible for this faster supply. Therefore, the molecular weight of the polymer formed in the aqueous phase will be lower.



## CONCLUSIONS

The effects of agitation in semibatch emulsion copolymerization of *n*-butyl methacrylate and N-methylol acrylamide were investigated in a 2-liter reactor using a model recipe with ca. 44% solids content. The reaction consisted of two stages: the seed stage which was homopolymerization of BMA, and the feed stage during which BMA and NMA monomers were continuously added to the reactor. Agitation affected different properties of the latex. The main effect was on the particle nucleation. The concentration of the sodium dodecyl sulfate surfactant in the seed stage recipe was 5 mmol/dm<sup>3</sup>, below its cmc. Higher agitation (larger agitator diameter and/or greater agitation speed) resulted in the nucleation of a greater number of particles. The final latexes showed a decrease in viscosity with an increase in the shear-rate. At any given shear-rate, the latex prepared using the 8 cm agitator had a greater viscosity than that prepared using the 4 cm agitator. This is because of the larger number of particles in the former, although the final solids content was the same in both. The amount of coagulum increased with the agitation power (agitator diameter and/or agitation speed). The amount of water-soluble species decreased at higher agitation. This is a combined effect of two factors: the effect of seed stage agitation on particle number; and the effect of feed stage agitation on emulsification of the BMA feed stream, and bulk uniformity in the reactor. Formation of a region of poor mixing could be visually seen when the 4 cm agitator was used at 400 rpm. Thus, even on a 2-liter scale, the effects of agitation on copolymerization could be characterized by careful experiments. The experimental results offer an insight into the mechanism of semibatch copolymerization, and the effects of agitation.

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