

Seeded Emulsion Terpolymerization of Dimethyl Meta-Isopropenyl Benzyl Isocyanate (TMI®) with Acrylic Monomers

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ABSTRACT: Dimethyl meta-isopropenyl benzyl isocyanate (TMI®) is a novel bifunctional monomer. It has a double bond and an isocyanate group. The seeded emulsion terpolymerization of TMI with the acrylic monomers, methyl methacrylate and *n*-butyl acrylate, has been studied. A copolymer of methyl methacrylate and *n*-butyl acrylate was used as the seed latex. In order to minimize the risk of hydrolysis of TMI, polymerizations were carried out at 40°C using redox initiators. No additional surfactant was added during the second-stage polymerization in order to avoid the nucleation of secondary particles. TMI was found to retard the polymerization kinetics. The effect of variables, such as the total number of particles, initiator concentration, and the monomer feed rate on polymerization kinetics, was investigated. The composition of the second-stage polymer could be controlled by running the polymerization under monomer-starved conditions. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 685–694, 1998

Key words: seeded emulsion polymerization; dimethyl meta-isopropenyl benzyl isocyanate; kinetics

INTRODUCTION

The single-stage emulsion terpolymerization of dimethyl meta-isopropenyl benzyl isocyanate (TMI) with the acrylic monomers, methyl methacrylate (MMA) and *n*-butyl acrylate (BA), was discussed in a previous publication.¹ TMI was found to retard the polymerization kinetics and decrease the latex particle size. In this article, the seeded polymerization of MMA–BA–TMI is discussed. The interest in seeded polymerization was twofold. First, seeded polymerization is a useful technique for kinetic studies as it fixes the total number of polymerization sites (particles) if the nucleation of secondary particles is avoided in the second stage. Second, the locus of the NCO groups in the latex particles can be controlled by carrying

out the seeded polymerization of MMA–BA–TMI in the presence of a poly(MMA–BA) seed latex. It was felt that by adding TMI during the second-stage polymerization, the functional NCO groups could be concentrated at the surface of the latex particles. A preponderance of functional groups at the surface of polymer particles would result in interfacial crosslinking during film formation and curing. Interfacial crosslinking is known to significantly improve the mechanical properties of polymer films.²

The kinetics of seeded emulsion polymerization systems have been studied by many workers in recent years. Nomura et al.³ investigated the effect of various operating variables on the seeded copolymerization kinetics of styrene and acrylonitrile. The polymerization rate was found to increase with the total number of seed particles. However, at low particle numbers, the gel effect became dominant, as observed from a sharp increase in the slope of the conversion–time curves.

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Increases in the initiator concentration were found to increase the polymerization rate, with its influence deteriorating at higher concentrations. Unzueta and Forcada⁴ studied the effect of a mixed emulsifier (anionic and nonionic) system on the kinetics and particle size distribution in the seeded semicontinuous copolymerization of MMA and BA. Lee and coworkers^{5,6} carried out the two-stage emulsifier-free polymerization of styrene in the presence of a poly(methyl methacrylate) (PMMA) seed latex. A model was proposed to explain the kinetic data. Two-stage emulsifier-free polymerization of BA and MMA has also been reported.⁷ An increase in initiator concentration was found to decrease both the particle number and the polymer molecular weight. The effect of the core-to-shell ratio on the rate of polymerization and particle morphology was also discussed. Lepizzera and Hamielec⁸ investigated the seeded polymerization of vinyl acetate with and without poly(vinyl alcohol) (PVA). The absence of emulsifier in the second-stage polymerization resulted in particle growth without secondary nucleation. The addition of PVA, however, resulted in a bimodal particle size distribution. A theory was proposed to explain the effect of the polymeric emulsifier on the nucleation of particles in the second stage. Masa et al.⁹ carried out the seeded semicontinuous terpolymerization of styrene, 2-ethylhexyl acrylate, and methacrylic acid. Different types of anionic and nonionic surfactants were used, and the effect of the type and amount of surfactant on the polymerization was studied. The influence on latex properties, such as colloidal and freeze-thaw stability, chemical stability, and viscosity, was also reported. The emulsifier-free seeded polymerization of butadiene has also been studied in order to determine the propagation rate constant.⁹ Brooks and Wang¹⁰ compared the kinetics of the single-stage and seeded polymerizations of vinyl acetate. For the seeded systems, the polymerization rate was found to be independent of the monomer-to-polymer ratio and increased with initiator concentration. Chen and Chang¹¹ studied the particle growth mechanism of sulfonated polystyrene latexes by varying the size of the seed particles. The Smith–Ewart case II kinetics were found to be applicable only to small-sized (150–200 nm) particles. Urquiola et al.¹² studied the semicontinuous seed emulsion copolymerization of vinyl acetate and methyl acrylate. The effect of process variables on the overall conversion, the copolymer composition, and the particle size was investigated. A mathematical model

was proposed to describe the data. Seeded polymerizations of vinyl acetate that follow the Smith–Ewart case III behavior have also been reported.¹³

This article describes the seeded emulsion polymerization of MMA–BA–TMI in detail. The effect of process variables on the polymerization kinetics is discussed.

EXPERIMENTAL

Materials

MMA and BA (both from Aldrich [Milwaukee, WI]) were distilled under reduced pressure and stored at -2°C prior to use. All other reagents were used as received without further purification. TMI and sodium dihexyl sulfosuccinate (Aerosol MA 80) were received from Cytec Industries (Stamford, CT). Ammonium persulfate, potassium metabisulfite, and ammonium iron (II) sulfate hexahydrate (all from Aldrich) were stored in the dark before use. Distilled–deionized (DDI) water was used in all the experiments.

Polymerizations

Seed latex of poly(MMA–BA) (45 : 55) was prepared at 40°C following the same procedure as was used for the single-stage polymerization of MMA–BA–TMI described earlier.¹ It was shown that, at this temperature, the hydrolysis of the NCO group of TMI was minimal during the polymerization step. Therefore, the seeded polymerization of MMA–BA–TMI was also carried out at 40°C in order to minimize the risk of hydrolysis of TMI. The polymerizations were carried out in a 250-mL reactor equipped with a reflux condenser. Seed latex, second-stage monomer, DDI water, and the activator (ammonium iron (II) sulfate hexahydrate) were introduced into the reactor; and the contents were purged with nitrogen for 15 min while being stirred at 40°C . Then, 33% of the reductant (potassium metabisulfite) was added as an aqueous solution, and the mixture purged with nitrogen for another 15 min. At this time, 33% of the oxidant (ammonium persulfate) was added as an aqueous solution to start the polymerization. At the same instant, addition of the remaining initiator (10 g each of the oxidant and reductant aqueous solutions) was started; they were then added continuously over a period of 5 h. Additional surfactant was not used in order

to avoid the nucleation of secondary particles during the second-stage polymerization. One mL samples were withdrawn at regular intervals, and the reaction was short-stopped using a 1% aqueous solution of hydroquinone. In some cases, the monomer was added in a semicontinuous mode over a period of time. The feed policies are described in detail in the relevant portions of the Results and Discussion Section.

Determination of Percentage Conversion

The total monomer conversion was determined gravimetrically. Latex samples were dried in an oven at 75°C to constant weight. The percentage of solids was used to calculate the monomer conversion.

Particle Size Analysis

The particle size of diluted latex samples was determined using the capillary hydrodynamic fractionation (CHDF) technique.¹⁴ The total number of particles per cubic centimeter (cc) of water was calculated using the mean volume diameter D_v . The theoretical particle size was calculated from the seed particle diameter and the monomer conversion at a particular instant, using a mass balance.

RESULTS AND DISCUSSION

Batch Polymerization

In all of the seeded polymerizations that were studied, it was found that it was necessary to add the initiator in a semicontinuous mode in order to obtain appreciable conversions. Therefore, in the following discussion, batch polymerization refers exclusively to the mode of monomer addition and not the entire process.

Seeded emulsion polymerizations of MMA, BA, and TMI were carried out in the presence of a seed latex of poly(MMA-BA) (45 : 55). A sample recipe for the first- and second-stage polymerizations is shown in Table I. The solids content in this recipe was 20% for both stages. The final TMI concentration was 5%, and the core-to-shell ratio (C/S) was 1 : 2. The seed latex was prepared below the CMC of the Aerosol MA 80 surfactant (sodium dihexyl sulfosuccinate, Cytac Industries). The low surfactant concentration was expected to reduce or eliminate the secondary nucle-

ation of particles during the second-stage polymerization. The effect of several preparative variables on the polymerization kinetics will be discussed in the following sections. The particle diameter of the seed latex was 141 nm.

Effect of TMI Concentration

The effect of TMI concentration on the seeded polymerization kinetics was studied using the recipe shown in Table I. The TMI concentration was varied between 2 and 10 wt % based on the final polymer (seed polymer plus second-stage monomer). The TMI content was increased by decreasing the MMA concentration so as to maintain the solids content at 20%. The monomer was added in a batch mode, while the initiator was added semicontinuously, as explained in the experimental section. Batch addition of the initiator resulted in low conversions due to the depletion of the initiator before the completion of the polymerization. This result was similar to that obtained for the single-stage polymerization below the CMC.¹ The effect of TMI concentration on the conversion-time behavior is shown in Figure 1. Increased amounts of TMI were found to decrease the rate of polymerization. The polymerization at 2% TMI concentration proceeded rapidly and attained very high conversions within an hour. The runs at higher TMI concentrations were much slower in comparison until about 35–40% conversion. After this stage, the slopes of the curves increased significantly, indicating a rapid rate of polymerization, which continued until completion. The sudden increase in the polymerization rate was due to the gel effect, during which the polymerization becomes diffusion-controlled. The rate of termination of the propagating polymer chains decreases as a result of the high viscosity in the latex particle. As a result, the polymerization rate increases rapidly. The increase in viscosity is due to the depletion of monomer in the latex particles by polymerization. The gel effect also indicates the absence of monomer droplets in the reactor, which would otherwise have replenished the converted monomer in the polymer particles.

The high rate of polymerization at 2% TMI concentration could be a result of secondary nucleation of particles during the second stage. This would result in an enhanced polymerization rate due to an increase in the total number of particles. However, the final particle diameters obtained (204 nm) in all three runs were close to the calculated value based on the seed latex particle diame-

Table I Recipe for the Batch Emulsion Polymerization of MMA-BA (45 : 55 w/w) and the Seeded Polymerization of MMA-BA-TMI (40 : 55 : 5)^a

Component	Stage I Amount (g)	Stage II Amount (g)
Seed latex (20% solids)	0	50.0
Methyl methacrylate	13.5	7.5
<i>n</i> -Butyl acrylate	16.5	11.0
TMI	0	1.5
Aerosol MA 80 ^b	0.90 (16.5 mM) ^c	0
Ammonium persulfate	0.1054 (3.85 mM) ^c	0.25
Potassium metabisulfite	0.1054 (3.95 mM) ^c	0.25
Ammonium iron (II) sulfate hexahydrate	0.0008	0.0025
Distilled-deionized (DDI) water	120.0	79.84

^a Polymerization temperature is 40°C.

^b 80% solids, sodium dihexyl sulfosuccinate, (Cytec).

^c Based on water.

ter (141 nm) and the amount of monomer added in the second stage. This indicates that the locus of polymerization during the second-stage polymerization was in the polymer particles, and the nucleation of secondary particles was minimal. To further confirm this hypothesis, the development of the particle size distribution was followed as a function of conversion using the CHDF technique. The particle size distributions of samples at different conversions are shown in Figure 2 for the run with 5% TMI. During the initial stages of the polymerization (7% conversion), a bimodal particle size distribution is observed, indicating the nucleation of secondary particles. However, as the conversion increased to 28%, the distribution tended

to become narrower, due to the limited aggregation of the small particles, which do not have sufficient amounts of surfactant available for stabilization. The shapes of the particle size distributions at 28 and 98% conversion are identical and merely shifted along the x-axis. This shows that the monomer was consumed by polymerization in the growing particles (without generation of new particles), or else the newly nucleated polymer particles were captured by the existing ones. In either case, the final number of particles remained almost the same as that in the seed latex, resulting in similar particle sizes in all three runs at different TMI contents. The difference in the polymerization rates can therefore be attributed to the sluggish polymerization behavior of TMI as a result of steric factors. TMI has a structure

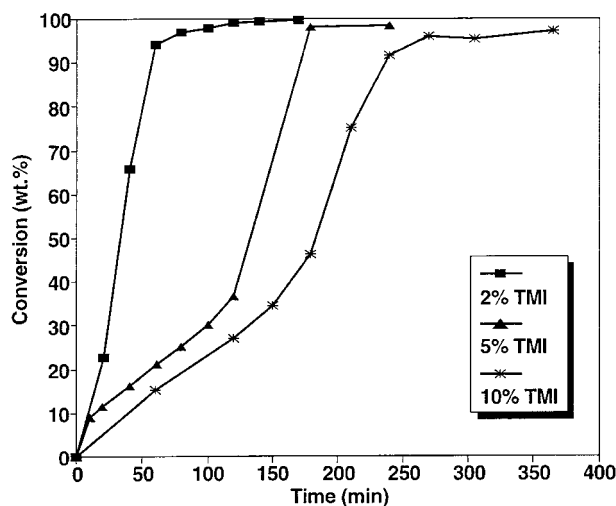


Figure 1 Effect of TMI concentration on the seeded emulsion terpolymerization of MMA-BA-TMI carried out at 40°C. The core-to-shell ratio is equal to 1 : 2.

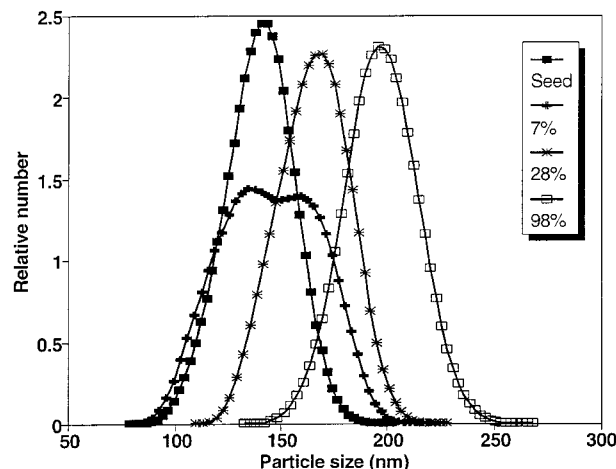


Figure 2 Particle size distributions for the run with 5% TMI concentration shown in Figure 1.

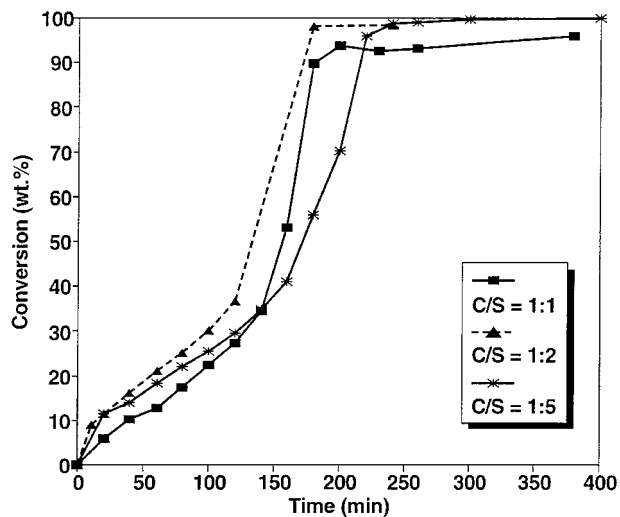


Figure 3 Effect of the core-to-shell ratio (C/S) on the seeded polymerization kinetics of MMA-BA-TMI (40 : 55 : 5). Final solids equal 20%; T equals 40°C.

similar to α -methyl styrene, which is known to retard polymerizations. The decrease in the rate of polymerization with increasing TMI concentrations was also observed in single-stage polymerizations, as reported earlier.¹

Effect of Core-to-Shell Ratio

In the absence of nucleation of secondary particles during the second-stage polymerization, the amount of feed latex (and, hence, the C/S ratio) in the recipe fixes the number of polymer particles in the reactor. This is very important as the seed latex particle is the sole locus of polymerization in such cases. Therefore, the effect of C/S ratio on the seeded polymerization was studied. Polymerizations were carried out at different C/S ratios, keeping the TMI concentration constant at 5%, based on the oil phase. The final solids content was fixed at 20%. Three different C/S ratios (i.e., 1 : 1, 1 : 2, and 1 : 5) were studied as shown in Figure 3. Since the amount of monomer added in the second stage was different in the three runs, the initiator concentration was varied accordingly. The initiator concentration was 1.25% based on the amount of monomer added in the second stage. The conversion-time plots indicate a change in slope after approximately 10% conversion, after which the lines are linear until 30% conversion. The initial high slope could be due to the nucleation of secondary particles, which increases the polymerization rate. The linear region between 10–30% conversion indicates that the po-

lymerization proceeded without further generation of new particles at a constant rate. The particle sizes obtained in the three runs were found to be quite close to the theoretically calculated values, as shown in Table II. This again indicates that the generation of new particles was not significant, and polymerization resulted in the growth of the existing seed latex particles. The absence of secondary particles was confirmed by following the development of particle number as a function of conversion. The plot for the highest C/S ratio (C/S equal to 1 : 5) is shown in Figure 4. It can be observed that the number of particles remained almost constant throughout the course of the polymerization.

The conversion-time plots exhibit a sharp increase in slope after 30% conversion, which can be attributed to the gel effect. The gel effect was most pronounced at the lowest core-to-shell ratio (C/S equal to 1 : 1) when the amount of monomer added in the second stage was the least. Moreover, the run with C/S equal to 1 : 5 exhibited the gel effect later than the experiment with C/S equal to 1 : 1, despite being faster (during the initial stages) than the latter. This can be attributed to more monomer being added in the second stage in the run with C/S equal to 1 : 5. Table II also compares the rates of polymerization for the three core-to-shell ratios. The rates were determined from the slopes of the conversion-time curves between 10–30% conversion. It can be observed that the run with the highest number of particles (N_p/cc) exhibited the slowest polymerization rate. Usually, in seeded polymerizations, the rate of polymerization increases with the number of particles due to an increase in the number of polymerization sites. The anomalous behavior in our case can be explained as follows. The total amounts of second-stage monomer added in the three runs were (1) 15 g for C/S equal to 1 : 1; (2) 20 g for C/S equal to 1 : 2; and (3) 25 g for C/S equal to 1 : 5. All of the TMI (1.5 g) was added in the second stage. Therefore, the percentage of TMI added in the second-stage monomer feed was the highest for C/S equal to 1 : 1. As a result, this run exhibited the slowest rate of polymerization (since TMI is known to retard the polymerization kinetics). Following the same logic, the run with C/S equal to 1 : 5 was expected to be the fastest since it had the lowest percentage of TMI in the second-stage monomer feed. However, this run was found to be slower than that obtained with C/S equal to 1 : 2. Since the final solids content of all the runs was 20%, the amount of seed latex

Table II Particle Size Data and Rates of Polymerization at Different Core to Shell Ratios^a

Core to Shell Ratio	D_v (theor) (nm)	D_v (exp) (nm)	N_p cc $\times 10^{-12}$	Rate of Polym $\times 10^4$ (g cc s ⁻¹)
1 : 1	181	176	76.0	4.35
1 : 2	204	202	50.5	6.40
1 : 5	256	245	25.3	6.20

^a D_v = volume average particle diameter; N_p = total number of particles.

used in the experiment with C/S equal to 1 : 5 was the lowest. Hence, there were a lower number of polymerization sites (latex particles) in this run. The polymerization was found to proceed in the existing seed particles without any significant fresh nucleation of a secondary crop of particles. Since the rate of polymerization depends on the number of particles, it was found to be lower for the run with C/S equal to 1 : 5 as compared to the run with C/S equal to 1 : 2.

Effect of Initiator Concentration

The effect of initiator concentration on the seeded polymerization kinetics was studied by carrying out the polymerization at two different initiator levels (1.0 and 1.25 wt %, based on the oil phase). The core-to-shell ratio was 1 : 5, and the TMI concentration was 5 wt %. The conversion–time plots are shown in Figure 5. It is seen that there is a decrease in the slope of the curves after the initial stages (less than 10% conversion) of the reaction, after which the rate remains almost constant until the gel effect occurs. The high initial

slope in the initial stages of polymerization is assumed to be due to some fresh nucleation of secondary particles. The figure shows that this slope is almost the same in both the runs, thereby indicating that the initiator concentration does not affect the extent of secondary nucleation in the concentration range studied. The constant rate period (constant slope regions between 10–30% conversion) for the two runs, however, indicates different slopes, with the higher one being for the experiment with the higher initiator concentration. This is the period during which polymerization takes place in the latex particles without fresh nucleation. As expected, the rate of polymerization increases with initiator concentration. The final particle diameters for the two runs were compared and found to be approximately the same (245 nm) in both cases; i.e., the particle size was independent of the initiator concentration. This suggested that the fresh nucleation of particles

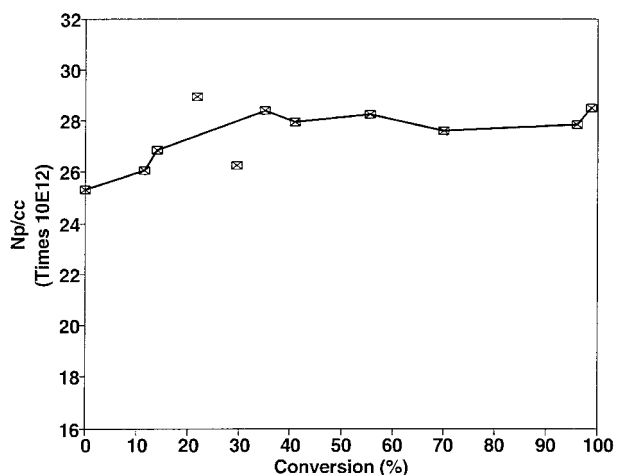


Figure 4 Development of particle number as a function of monomer conversion. TMI equals 5%; core-to-shell ratio is equal to 1 : 5.

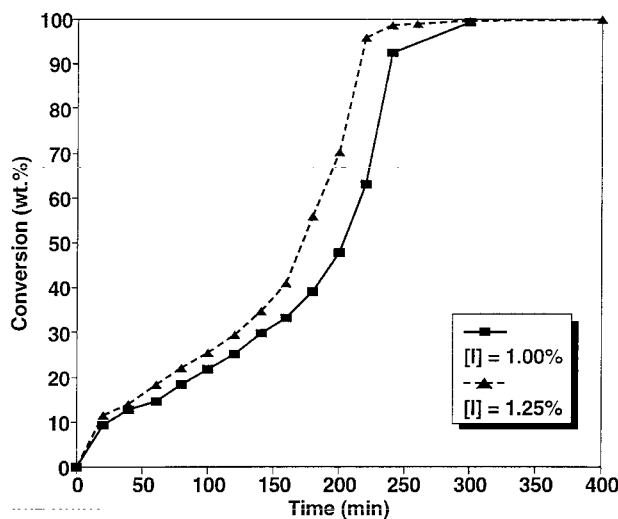


Figure 5 Effect of initiator concentration on the seeded polymerization kinetics of MMA–BA–TMI (40 : 55 : 5). 33% of the initiator was added in a batch mode and the remainder was added continuously over 5 h. T equals 40°C.

Table III Recipe for the Semicontinuous Seeded Emulsion Polymerization of MMA-BA-TMI (40 : 55 : 5 w/w)^a

Component	Amount
Seed latex (20% solids)	25.0
Methyl methacrylate	9.75
<i>n</i> -Butyl acrylate	13.75
TMI	1.50
Ammonium persulfate	0.08 (2.9 mM) ^b
Potassium metabisulfite	0.08 (3.0 mM) ^b
Ammonium iron (II) sulfate hexahydrate	0.0008
Distilled-deionized (DDI) water	99.84

^a Polymerization temperature = 40°C.

^b Based on water.

was minimal and that polymerization took place in the existing seed latex particles. The rates of polymerizations were calculated from the slopes of the conversion–time plots and determined to be 4.93×10^{-4} and 6.20×10^{-4} g cc s⁻¹, respectively.

Semicontinuous Polymerization

Batch seeded polymerization was successfully employed in order to introduce the NCO groups of TMI in the shell layer of the polymer particles. However, due to the different reactivity ratios of TMI, MMA, and BA, the composition of the shell terpolymer could not be controlled. Semicontinuous polymerization, if run under monomer-starved conditions, is a convenient means of controlling the terpolymer composition. Under monomer-starved conditions, the monomer is fed into the reactor at a rate less than the polymerization rate. Therefore, the rate of polymerization is controlled by the monomer feed rate. As a result, the terpolymer composition is essentially the same as that of the monomer feed composition.

Seeded Polymerization with Core-to-Shell Ratio Equal to 1 : 5

An initial recipe developed for the seeded semicontinuous polymerization of MMA-BA-TMI with a core-to-shell ratio of 1 : 5 is shown in Table III. A seed latex of poly(MMA-BA) (45 : 55) with a particle size of 151 nm was used. Seed latex, DDI water, and the activator (ammonium iron (II) sulfate hexahydrate) were introduced into the reactor and heated to 40°C. The contents were

purged with nitrogen for 15 min. Then, 33% of the reductant (potassium metabisulfite) was added, and the mixture purged with nitrogen for an additional 15 min. At this time, 33% of the oxidant (ammonium persulfate) was added as an aqueous solution. At the same instant, the addition of three streams to the reactor was started, using a syringe pump. The first stream consisted of the neat monomer mixture comprising MMA, BA, and TMI. The second and third streams comprised the remaining oxidant and reductant solutions (10 g each). The three streams were added over a period of 5 h, after which the polymerization was run for an additional hour. No additional surfactant was added during the second-stage polymerization.

Figure 6 shows the conversion–time history for the semicontinuous seeded polymerization of MMA-BA-TMI. The instantaneous conversion shown in the figure refers to the conversion of monomer, which has been added up to a particular stage of the polymerization. This depends on the rate of polymerization and the monomer feed rate and may therefore either increase or decrease accordingly. The overall conversion is calculated on the basis of the total monomer in the recipe and always increases with time, as the monomer is being fed continuously into the reactor. The two conversions converge when the monomer feed is complete. The overall conversion was found to increase so long as the initiator was fed into the reactor (5 h), after which a limiting conversion of

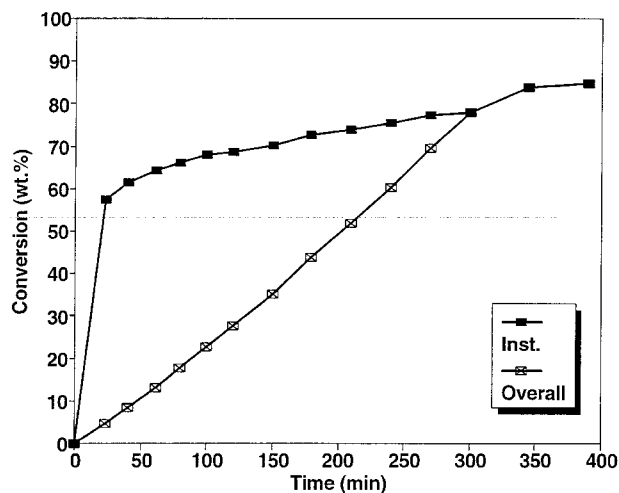


Figure 6 Conversion–time plot for the semicontinuous seeded polymerization of MMA-BA-TMI (40 : 55 : 5). The monomer was added over 5 h. 33% of the initiator was added in a batch mode; the remainder was added over 5 h; T equals 40%.

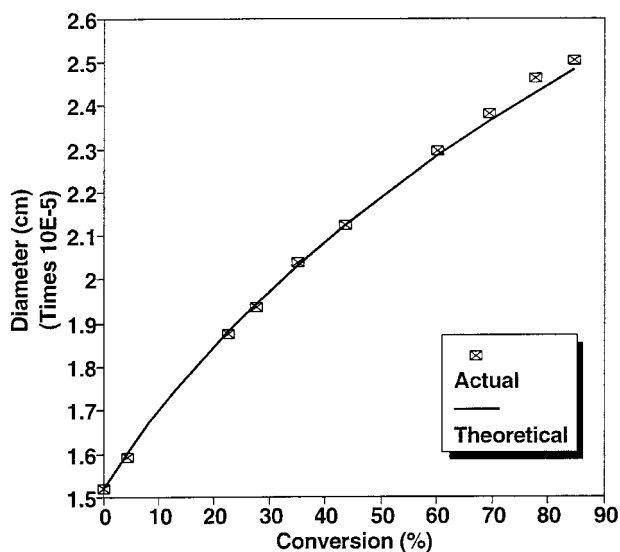


Figure 7 Evolution of particle size as a function of conversion for the experiment shown in Figure 6.

approximately 85% was obtained. The instantaneous conversion was found to be in the vicinity of 70%. This indicated that monomer-starved conditions, which are necessary in order to obtain a homogeneous polymer composition, were not attained. Due to the low instantaneous conversion, monomer accumulated in the reactor; and the incorporation of the different components of the monomer mixture was dictated by the reactivity ratios. The evolution of particle size was followed as a function of conversion in order to determine if the secondary nucleation of particles had occurred during the second-stage polymerization. Figure 7 compares the experimental data with the theoretically predicted values. A very close match was obtained, indicating that no fresh nucleation of particles occurred; and the second stage polymerization proceeded in the seed latex particles. A slight deviation was observed at higher conversions. This could be due to limited aggregation of particles, resulting in a lower number of particles with a larger diameter.

In the previous experiment, the overall conversion increased only so long as the initiator was fed into the reactor; and a limited conversion of roughly 85% was obtained. In order to enhance the conversion in the next run, the initiator was fed over 6 h (instead of 5). The monomer was, however, fed over 5 h. Again, it was observed (Fig. 8) that the polymerization stopped after the initiator feed was complete (6 h). This could be due to the depletion of initiator in the reactor. The final conversion was again close to 85%. The insta-

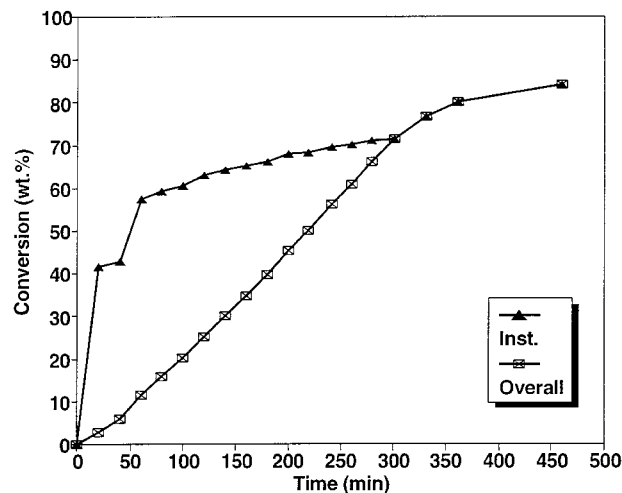


Figure 8 Conversion-time plot for the semicontinuous seeded polymerization of MMA-BA-TMI (40 : 55 : 5). The monomer was added over 5 h; 33% of the initiator was added in a batch mode; the remainder was added over 6 h. T equals 40%.

neous conversion in this case, however, was lower (between 60–70%). This was due to the lower amount of initiator added up to any given time during the initial 5 h, as compared to the previous run in which the rate of addition of the initiator was faster (initiator added over 5 h instead of 6). No fresh particles were nucleated in this experiment either, and the number of particles remained constant until the final stages of the polymerization (Fig. 9).

Semicontinuous Polymerization under Monomer-Starved Conditions

The semicontinuous polymerizations discussed in the previous section exhibited low instantaneous

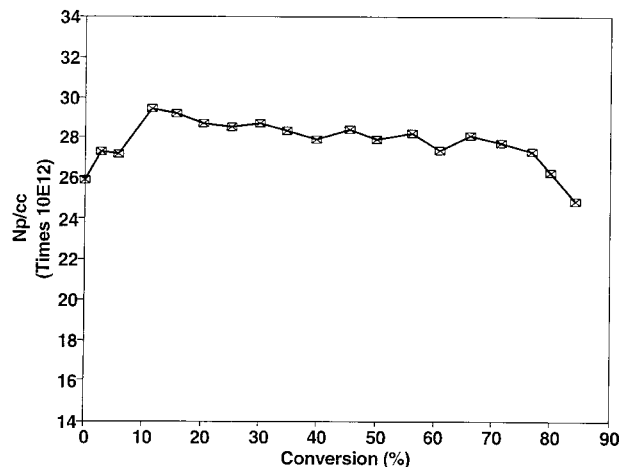


Figure 9 Evolution of particle number as a function of conversion for the experiment shown in Figure 8.

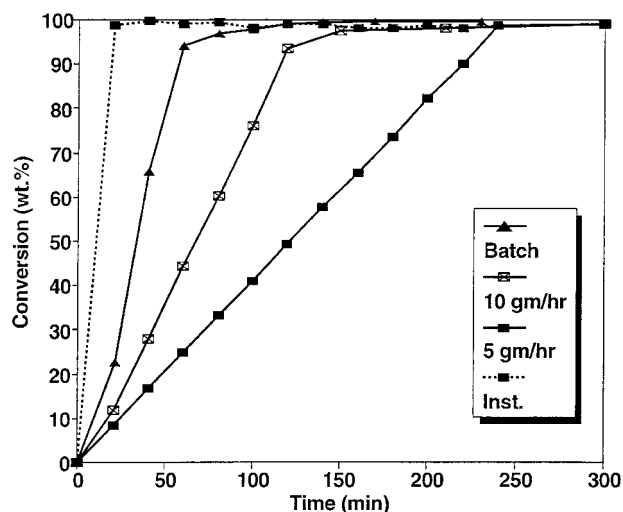


Figure 10 Effect of monomer feed rate on the seeded polymerization of MMA-BA-TMI (43 : 55 : 2). The core-to-shell ratio is equal to 1 : 2; T equals 40°C. The dashed curve represents the instantaneous conversion for the run conducted at 5 gm/h.

conversions. As a result, monomer accumulated in the reactor, leading to heterogeneous polymer composition. True monomer-starved conditions facilitate control over the polymer composition. In such cases, the instantaneous conversion is close to 100%, and the rate of polymerization is controlled by the monomer feed rate. In the previous runs, incomplete conversions (85%) were obtained. A convenient means of improving conversions in emulsion polymerization is by increasing the number of particles. In seeded systems, this can be done by decreasing the core-to-shell ratio. Therefore, in the following experiments, the core-to-shell ratio was changed to 1 : 2, and semicontinuous polymerizations were carried out using the recipe shown in Table I. The TMI concentration was reduced to 2%. The effect of the monomer feed rate on the polymerization kinetics was studied. Two different monomer feed rates, 5 and 10 g/h were used; and the results compared with the batch process, as shown in Figure 10. It can be observed that the batch process exhibited the highest polymerization rate, with the rate of polymerization decreasing with decreasing monomer feed rate. This result was expected, as the batch process can be considered to be a semicontinuous run at an infinite monomer feed rate. The abundance of monomer in the batch process ensures a constant supply to the polymerization sites, i.e., the polymer particles. However, when the polymerization is run in a semicontinuous mode, the

supply of monomer to the polymerization sites is controlled by the rate of monomer feed. Hence, the slower the rate of monomer feed, the slower is the polymerization rate. Monomer-starved conditions were achieved at the slower feed rate of 5 g/h. Under these conditions, the maximum possible polymerization rate was faster than the rate at which the monomer was fed into the reactor. Hence, the polymerization rate was essentially the same as the rate of monomer feed, as indicated by the linear relationship between the conversion and time. The instantaneous conversion, shown in the figure for this monomer feed rate, was almost 100% throughout the polymerization. This shows that there was no accumulation of monomer in the reactor during the entire process. On the other hand, the instantaneous conversion for the polymerization with a monomer feed rate of 10 g/h (not shown in the figure for the sake of clarity) was found to vary between 70 and 90%. This indicated that fully monomer-starved conditions were not reached in this case. As a result, monomer accumulated in the reactor during the course of the polymerization, leading to a rate of polymerization that is not completely dependent on the monomer feed rate. However, the polymerization rate is slower than that obtained in the batch process since it is partially controlled by the monomer feed rate. In the latter case, excess monomer is always available in the reactor until the droplets disappear.

All three polymerization processes resulted in the formation of particles with approximately the same particle size (around 200 nm), which was close to the theoretically predicted value. The final particle size distributions of the seed latex and the latex obtained via semicontinuous polymerization at a monomer feed rate of 5 g/h are compared in Figure 11. The shape of the two-stage latex distribution is similar to that of the seed latex, although shifted along the x-axis. This confirms the absence of any secondary nucleation of particles during the second-stage polymerization. The final latex particle size distribution is narrower as a result of limited aggregation of small particles.

CONCLUSIONS

Processes were developed for the seeded polymerization of MMA-BA-TMI. A copolymer of MMA and BA (45 : 55) was used as the seed latex. These processes allowed us to obtain NCO-function-

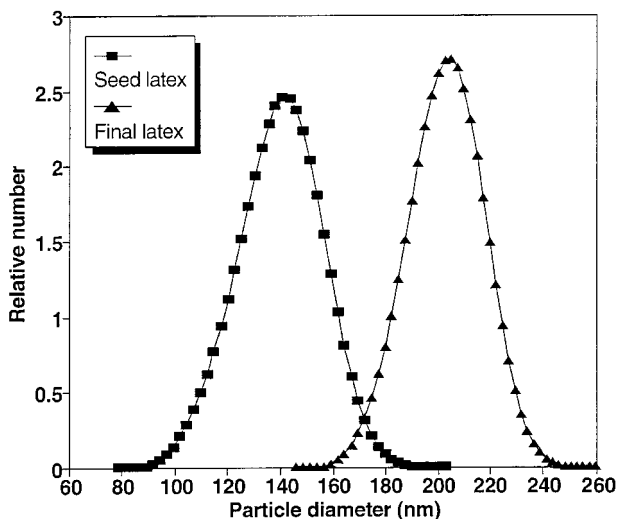


Figure 11 Final particle size distribution for the experiment with a feed rate of 5 g/h shown in Figure 10.

alized latexes with larger particle sizes (200–250 nm), as compared to the ones prepared using single-stage emulsion polymerization (40–120 nm). Moreover, the locus of the NCO groups could be controlled using these processes by preferentially localizing them in the shell polymer. The NCO groups were concentrated at the surface of the latex particles by adding TMI in the second stage. The presence of functional groups at the surface of the particles should enhance interfacial cross-linking and, thereby, the mechanical properties of the polymer films. The composition of the second-stage polymer could be controlled by running the polymerizations semicontinuously under monomer-starved conditions.

The kinetics of the seeded polymerization were investigated. TMI was found to retard the polymerizations on account of steric barriers presented by its molecular structure. The seed latex was prepared below the CMC of the surfactant in order to minimize or eliminate the nucleation of secondary particles during the seeded polymerization. No additional surfactant was added in the second stage. As a result, the nucleation of a fresh crop of particles was minimal. The effect of the

number of particles (core-to-shell ratio) on the kinetics was also studied. When the number of particles was increased (this enhances the polymerization rate), the amount of TMI added in the second stage was also increased (this retards the polymerization kinetics). As a result of these two opposing factors, no trend was observed in the effect of the number of particles on the rate of polymerization. The rate of polymerization was found to increase with increasing initiator concentration and monomer feed rates. Complete conversions could not be obtained in semicontinuous polymerizations run at high core-to-shell ratios (1 : 5), at 5% TMI concentration.

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