

Emulsion Terpolymerization of Dimethyl Meta-Isopropenyl Benzyl Isocyanate (TMI®) with Acrylic Monomers: Process Development and Kinetics

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SYNOPSIS

Dimethyl meta-isopropenyl benzyl isocyanate (TMI®) is a bifunctional monomer possessing a double bond and an isocyanate group. Emulsion terpolymerization of TMI with the acrylic monomers, methyl methacrylate and *n*-butyl acrylate, was studied. Polymerizations were carried out at 40°C using a redox initiator system in order to minimize the extent of hydrolysis of the isocyanate in the aqueous emulsion environment. The kinetics of the polymerization reaction were investigated. The polymerization rate was found to decrease with increasing TMI concentration. The effects of several preparative variables such as the monomer, surfactant, and initiator concentration on the polymerization kinetics was studied. Several semicontinuous polymerization processes were developed in order to enhance the incorporation of TMI at appreciable rates. These processes also allow us to control the polymer composition, latex particle size, and the locus of isocyanate groups in the latex particle. Process variables such as the mode of initiator addition (batch versus semicontinuous) were found to greatly influence the polymerization behavior. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polymer latexes capable of undergoing latent crosslinking after film formation are of paramount importance from the industrial point of view.¹ Such systems are designed by introducing functional groups which are capable of forming crosslinks upon thermal treatment or catalysis. Crosslinking improves the integrity of the polymer films and enhances desirable properties such as impact strength, tensile strength, peel strength, and water, alkali, and chemical resistance. Due to their improved properties, crosslinkable latexes have found many applications in areas such as fabric coatings and backings, textile finishes, fire-resistant coatings, ink binders, metal and wood adhesives, etc. Common functional monomers used for preparing thermally

crosslinkable latexes include *N*-methylol acrylamide and *N*-(isobutoxymethyl)acrylamide. Although many thermally curable systems have been commercialized, resins and polymer latexes capable of undergoing latent crosslinking at ambient temperatures are gaining significant practical interest. The increasingly stringent environmental stipulations for adhesives, inks, and coatings applications have added to their importance in industry. Such systems can be developed by incorporating functional monomers which can undergo crosslinking reactions at room temperature. One such functional monomer is dimethyl meta-isopropenyl benzyl isocyanate (TMI).

TMI is a novel bifunctional monomer possessing a reactive double bond and a tertiary aliphatic isocyanate (NCO) group. TMI can be incorporated into the polymer backbone via copolymerization with unsaturated monomers such as methyl methacrylate (MMA) and *n*-butyl acrylate (BA) in order to obtain polymers with pendant isocyanate groups. These isocyanate groups can be exploited to carry out latent

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curing at room temperature after film formation in the presence of moisture or other crosslinking agents. TMI can also be incorporated into polymeric systems via the isocyanate group. The reaction of the isocyanate group with polyols or polyamines provides polymers with unsaturation. These polymers can then be crosslinked using conventional crosslinkers such as divinylbenzene.

Ever since its introduction,^{2,3} many TMI-based formulations have been developed, as documented in the patent literature. The open literature also lists several novel applications of TMI. Brauer and Lee⁴ have copolymerized TMI with several methacrylates to synthesize oligomers with pendant isocyanate groups. These oligomers were used to develop tissue adhesives. TMI has been used to obtain siloxane-based aliphatic polyisocyanates⁵ which can be used as precursors for amphiphilic star polymers. Ekman and Nasman⁶ reacted the isocyanate group of TMI with an ethylene/vinyl alcohol copolymer to prepare radiation-curable polymers with pendant unsaturation. A blocked derivative of TMI was utilized by Parker and colleagues⁷ to develop reactively curable diene elastomers. Recently, Inaba and coworkers⁸ compared the film formation behavior of TMI latexes prepared via the conventional and miniemulsion polymerization routes. The performance of latex films containing TMI and a combination of TMI and methacrylic acid crosslinking system was investigated.

Despite the advantages of TMI copolymers, it is rather difficult to obtain significant conversions at high TMI concentrations, especially for bulk and solution polymerizations. This may be due to the structure of TMI (Fig. 1) which is similar to α -methyl styrene (AMS). AMS is known to exhibit rather slow polymerization rates. This behavior has been attributed to several factors such as steric restrictions,⁹ polymer depropagation,¹⁰ and kinetic factors.¹¹ The polymerization rate of AMS can be enhanced by utilizing emulsion polymerization. Kenney and Patel¹²⁻¹⁴ have studied the emulsion copolymerization of AMS with methacrylonitrile. Emulsion copolymerization of AMS with styrene has also been investigated.^{15,16}

This paper describes several emulsion polymerization processes which have been developed to incorporate high concentrations of TMI (up to 20 wt %, based on the oil phase) into the copolymer at appreciable polymerization rates. The emulsion terpolymerization of TMI with the acrylic monomers MMA and BA has been studied in detail. The effect of preparative variables such as the monomer, sur-

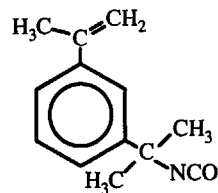


Figure 1 Chemical structure of TMI.

factant, and initiator concentration on the polymerization kinetics is discussed. Several semicontinuous polymerization processes are also described which enable us to control the terpolymer composition, latex particle size, and the locus of the NCO groups in the latex particle.

EXPERIMENTAL

Materials

MMA and BA (both from Aldrich) 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. Sodium lauryl sulfate (SLS) was obtained from FMC Corporation. 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 experiments.

Polymerizations

Polymerizations were carried out in either a 100-mL or 250-mL glass reactor equipped with a mechanical stirrer and a reflux condenser. The polymerizations were run at 40°C in order to minimize the hydrolysis of the isocyanate groups of TMI. Redox initiators comprising ammonium persulfate (oxidant), potassium metabisulfite (reductant), and ammonium iron(II) sulfate hexahydrate (activator) were used. Either SLS or Aerosol MA 80 was used as the surfactant. All of the surfactant was charged into the reactor along with most of the DDI water, and allowed to dissolve while being purged with nitrogen. Individual aqueous solutions of the oxidant, reductant, and activator were prepared with the remainder of the water charge. The activator solution and the monomers were added to the aqueous surfactant solution in the reactor, which was maintained at 40°C in a thermostated water bath. The

Table I Recipe for Batch Emulsion Terpolymerization of MMA/BA/TMI (43/55/2 w/w) using Sodium Lauryl Sulfate as the Surfactant

Component	Amount (g)
Methyl methacrylate	6.02
<i>n</i> -Butyl acrylate	7.70
TMI	0.28
Sodium lauryl sulfate	0.0996 (6.2 mM) ^a
Ammonium persulfate	0.0715 (5.6 mM) ^a
Potassium metabisulfite	0.0715 (5.8 mM) ^a
Ammonium iron(II) sulfate hydrate	0.0076
DDI water	55.84

Polymerization temperature = 40°C.

^a Based on water.

contents of the reactor were allowed to reach equilibrium temperature while being stirred and purged with nitrogen. This took approximately 15 min. The reductant solution was then added, and the emulsion purged for an additional 15 min. The oxidant solution was then introduced and the polymerization carried out under a blanket of nitrogen. The beginning of the polymerization period was taken to be the time of the oxidant addition. One-milliliter samples were withdrawn from the reactor at appropriate intervals using a Teflon tube connected to a syringe. Samples were emptied into glass vials containing a few drops of a 1% aqueous hydroquinone solution in order to short-stop the polymerization. For semicontinuous polymerizations, several initiator and monomer feed policies were followed. These are discussed in detail in the relevant portions of the Results and Discussion section.

Determination of Percentage Monomer Conversion

The overall monomer conversion was determined gravimetrically, while the individual monomer conversions were obtained using gas chromatography. For the gravimetric method, samples were weighed into tared aluminum pans and dried to a constant weight at 75°C. The percentage conversion was obtained from the ratio of the experimental and theoretical polymeric solids. An HP 5890 gas chromatograph was used for the determination of the individual monomer conversions. Peak areas were compared with previously generated calibration curves in order to determine the residual monomer in the latex samples and the percentage conversion.

Particle Size Analysis

The particle size of diluted latex samples was determined using the capillary hydrodynamic fractionation (CHDF) technique.¹⁷ The total number of particles per milliliter of water was calculated using the mean volume diameter.

Determination of Isocyanate Content

The amount of isocyanate in the freeze-dried latex polymer was determined using the dibutylamine titration method.¹⁸ Approximately 0.1 g of polymer was dissolved in 30 g toluene, and 25 mL of a 0.1N dibutylamine solution in toluene was pipetted into it. The mixture was stirred for about 15 min, after which 50 g of isopropyl alcohol was added. The contents were then titrated against 0.1N HCl solution. Potentiometry was used to determine the end point. The procedure was repeated without the polymer sample. The difference between the two readings was used to determine the amount of isocyanate present in the polymer.

RESULTS AND DISCUSSION

Batch Polymerization

The recipe for the batch emulsion terpolymerization of TMI with MMA and BA, carried out in a 100-mL glass reactor, is shown in Table I. Figure 2 shows the conversion-time curve for the different monomers. It can be observed that the monomers become incorporated into the terpolymer in the order MMA > TMI > BA. Although MMA is consumed the earliest, TMI is converted at a faster rate than BA. A favorable outcome of this result is that any monomer remaining at the end of the polymerization would be BA and not the isocyanate. Although TMI was consumed completely in the above polymerization, it may well have been due to hydrolysis rather than polymerization. In order to study the extent of hydrolysis of the NCO group of TMI during emulsion polymerization, a control experiment was designed using the same recipe. In this experiment, all of the ingredients of the recipe shown in Table I, except for the initiator, were charged into the reactor and maintained at 40°C for 5 h with constant stirring. Samples were withdrawn at regular intervals, and the amount of TMI remaining in the emulsion was determined using gas chromatography. The results are compared with an actual polymerization run in Figure 3. It is clear that during polymerization, TMI

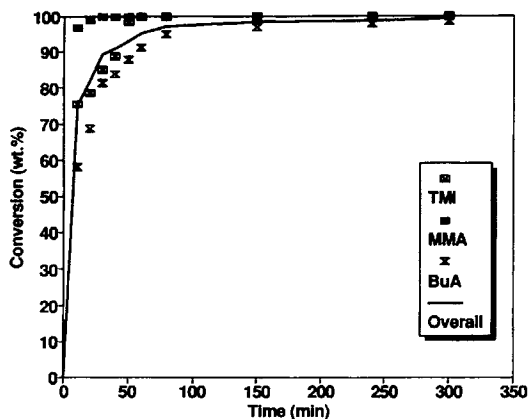


Figure 2 Conversion-time behavior for the batch emulsion terpolymerization of MMA/BA/TMI (43/55/2 w/w) carried out at 40°C using SLS as the surfactant.

is completely consumed in about 140 min. However, for the uninitiated control experiment, almost all of the TMI remains unreacted even after 5 h. This indicates that the consumption of TMI in an initiated system is indeed due to polymerization and not hydrolysis. It should be pointed out that the addition of the redox initiator system may change the pH of the emulsion, which might have an effect on the hydrolysis reaction. In order to obtain more conclusive proof that TMI does not hydrolyze during emulsion polymerization, the amount of NCO groups remaining intact after polymerization was determined using the dibutylamine titration technique. We found that the amount of isocyanate present in the polymer was approximately equal to the amount initially present in the recipe (2 wt %). This confirmed the previous result that the consumption of TMI during polymerization was due to its incorporation in the terpolymer, and not by hydrolysis.

Figure 4 shows the effect of TMI concentration on the polymerization kinetics. As expected, TMI was found to retard the polymerization process. The structure of TMI is similar to AMS, which is known to polymerize rather inefficiently. At 5 wt % TMI concentration (based on the oil phase), a limiting conversion of roughly 45% was observed. It should be noted that the SLS concentration in this run was below its critical micelle concentration (CMC = 7 mM). Similar results were obtained at 5% TMI concentration while using Aerosol MA 80 below its CMC (24.5 mM), as shown in Figure 5. The recipe for the emulsion polymerization using Aerosol MA 80 as the surfactant is shown in Table II. The polymerizations presented in Figure 5 were carried out in a 100-ml glass reactor. The figure indicates that ap-

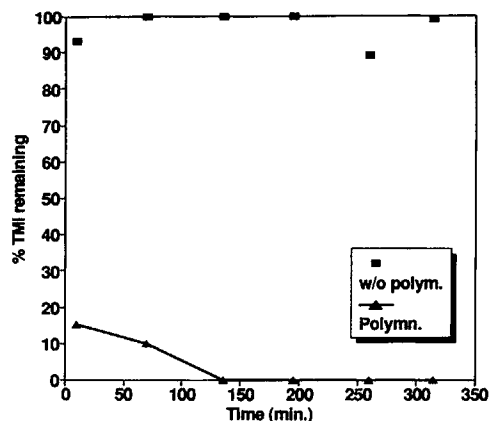


Figure 3 Consumption of TMI in the presence/absence of polymerization; $T = 40^{\circ}\text{C}$.

preciable conversions were obtained when the Aerosol MA 80 concentration was above its CMC.

The effect of TMI concentration on emulsion polymerizations carried out above the CMC of Aerosol MA 80 was studied. These polymerizations were run in a 250-mL glass reactor using the recipe shown in Table III. The amount of TMI was varied between 5 and 20 wt %, based on the oil phase, as shown in Figure 6. The total amount of monomer in the recipe was maintained constant by adjusting the MMA content between 25 and 40%. Although the rate of polymerization was found to decrease with increasing TMI concentrations, almost complete conversions were obtained even at 20% TMI content. The particle size data for these runs are compared in Table IV. The latex particle size decreased with increasing TMI concentration, while the particle size distribution become broader. In order to understand

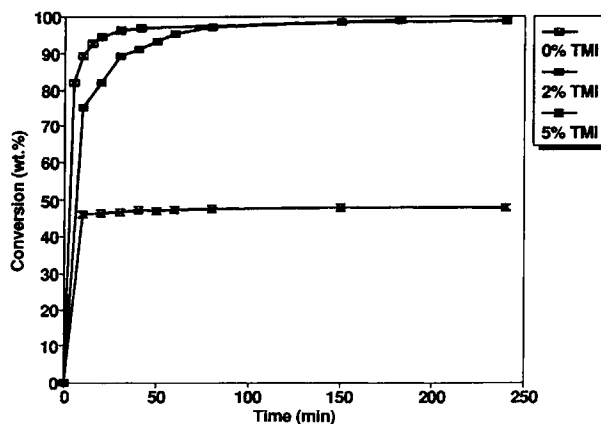


Figure 4 Effect of TMI concentration on the batch emulsion polymerization kinetics of MMA/BA/TMI; $T = 40^{\circ}\text{C}$.

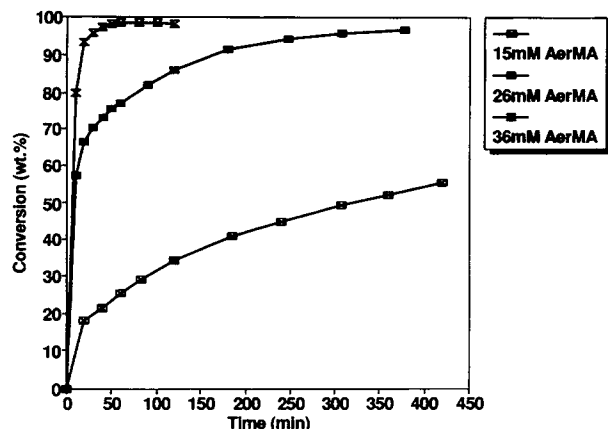


Figure 5 Effect of Aerosol MA 80 concentration on the batch emulsion polymerization kinetics of MMA/BA/TMI (40/55/5 w/w); $T = 40^{\circ}\text{C}$.

the particle nucleation mechanism, the evolution of particle number was followed as a function of monomer conversion. The data for two separate runs (5 and 20% TMI) are compared in Figures 7 and 8, respectively. In both cases, we found that the particle number increased until the end of the polymerization, indicating that particle nucleation continued until the very end of the reaction. Another interesting result seen in these runs is that although the number of particles increased with an increase in TMI concentration, the rate of polymerization decreased. This anomalous behavior is due to the decrease in the overall propagation rate constant with increasing TMI concentration. As mentioned above, TMI, being similar in structure to AMS, displays polymerization-retarding characteristics. The decrease in particle size (or increase in particle number) at higher TMI concentrations may be explained as follows: Initially, particle nucleation occurs as a result of the capture of initiator radicals by micelles swollen with monomer. As the polymerization progresses, the surface area of the polymer particles increases while the number and total surface area of the micelles decrease. As a result, the polymer particles begin to compete with the micelles for radicals. This can be observed in Figures 7 and 8, in which the particle generation rate (slope) decreases with increasing conversion. At 5% TMI concentration the rate of polymerization is higher, and therefore the particles grow at a faster rate compared to the run at 20% TMI. As a consequence, the total particle surface area available for radical capture is greater in the former case. Therefore, the ratio of the number of radicals captured by polymer particles to that captured by micelles is greater at 5% TMI

concentration. Hence, the final number of particles is lower, and the final particle size is higher at lower TMI concentrations. Due to the continuous particle generation, particles nucleated at different times grow simultaneously. As a result, the particle size distribution widens with increasing conversion. At higher TMI concentrations, the number of particles nucleated is greater, and therefore the particle size distribution is broader (Table IV).

Semicontinuous Polymerizations Below the CMC

The disadvantage of using a batch process above the CMC for our system is that it poses a constraint on the final particle size. As shown in Table IV, particles with diameters in the size range of 45–65 nm could be obtained using this technique. For certain applications, larger particle sizes are desirable; hence, an attempt was made to increase the particle size by decreasing the initiator concentration from 5.9 to 2.9 mM. However, a significant increase in the particle size was not observed. Further reduction in the initiator concentration resulted in incomplete conversions. The other alternative for obtaining a larger particle size is to decrease the surfactant concentration. Results discussed in the previous section indicated that appreciable conversions could not be obtained while working below the CMC. Therefore, in order to obtain a larger particle size, several semicontinuous processes were designed. All of the semicontinuous polymerizations were carried out in a 250-mL glass reactor using the recipe shown in Table III, except for the surfactant concentration which was reduced to 15.6 mM (below the CMC).

Semicontinuous Addition of Initiator

In this process, the surfactant and the activator were first dissolved in a portion of the total amount of DDI water in the recipe. The monomers were added in a batch mode to the reactor and purged with nitrogen at 40°C . Now, in order to obtain a larger particle size, only 33% of the total amount of initiator (oxidant + reductant) was added initially (at time $t = 0$). The rest (separate aqueous solutions of the oxidant and reductant) was dissolved in the remaining DDI water feed and added continuously over a period of 4 h.

The conversion–time histories for four different TMI concentrations are shown in Figure 9 and the particle size data are collected in Table V. While the low surfactant concentration (below the CMC) resulted in a larger particle size (90 to 116 nm com-

Table II Recipe for Batch Emulsion Terpolymerization of MMA/BA/TMI (40/55/5 w/w) using Aerosol MA 80 as the Surfactant below the CMC

Component	Amount (g)
Methyl methacrylate	6.02
<i>n</i> -Butyl acrylate	7.70
TMI	0.28
Aerosol MA 80 ^a	0.42 (15.6 mM) ^b
Ammonium persulfate	0.1288 (10.1 mM) ^b
Potassium metabisulfite	0.1288 (10.4 mM) ^b
Ammonium iron(II) sulfate hydrate	0.0076
DDI water	55.84

Polymerization temperature = 40°C.

^a 80% solids.

^b Based on water.

pared to 47 to 61 nm obtained using batch polymerization above the CMC), the constant addition of initiator ensured almost complete conversion. It should also be mentioned that except for the run with 20% TMI, the polymerizations reached completion even before all of the initiator could be added (4 h). In order to understand the particle growth mechanism, the development of particle number was followed as a function of conversion using the CHDF. The data for two different TMI concentrations are shown in Figures 10 and 11. From the particle size data in Table V and Figures 10 and 11, three trends could be identified with an increase in TMI concentration: (1) the particle size decreased, (2) the particle size distribution was broadened at the highest TMI concentration, and (3) the period of particle nucleation became shorter. Since the polymerization was carried out below the CMC, the generation of particles was via a homogeneous nucleation mechanism, which depends on the solubility of the freshly nucleated oligomeric chains in water. The TMI concentration was increased at the expense of the hydrophilic MMA. Therefore, the critical chain length at which water-soluble oligomers precipitate to form polymer particles decreased with increasing TMI concentration. As a consequence, an increased number of polymer particles were nucleated, resulting in a smaller final particle size at low TMI concentrations. The increased hydrophobicity of the oil phase also resulted in a shorter (in terms of conversion) period of nucleation at the high TMI concentrations. Another interesting feature of these polymerizations is the narrow particle size distribution observed at low TMI concentrations

despite the long nucleation period. This may be due to the limited aggregation of smaller particles resulting in a comparatively narrow distribution. The aggregation is due to insufficient surfactant being present for stabilization (surfactant concentration was below the CMC). It may be recalled that such aggregation behavior and the resulting narrow particle size distributions were not observed for the polymerizations carried out above the CMC (Table IV).

Emulsion Terpolymerization under Semi-starved Conditions

Semicontinuous polymerization processes are an effective means of controlling the polymer composition of multicomponent monomer systems. Monomers of different reactivities can be made to become incorporated at the same rate into the polymer backbone by feeding them into the reactor at a rate lower than the rate of batch polymerization.¹⁹⁻²¹ In our system, TMI is being used as a functional monomer in order to obtain latexes capable of undergoing latent curing at ambient temperatures. Semicontinuous processes can also be used to control the locus of the functional (NCO) groups in the latex by feeding TMI into the reactor at different stages of the polymerization. The locus of functional groups determines the type of crosslinking in latex films, viz., homogeneous, interfacial, or interstitial. Several semicontinuous processes have been designed for this purpose. The recipe used was the same as shown in Table III except for the surfactant concentration, which was reduced to 15.6 mM (below the CMC),

Table III Recipe for Studying the Effect of TMI on the Batch Emulsion Terpolymerization of MMA/BA/TMI using Aerosol MA 80 as the Surfactant

Component	Amount (g)
Methyl methacrylate	12.00
<i>n</i> -Butyl acrylate	16.50
TMI	Variable ^b
Aerosol MA 80 ^a	1.80 (31.2 mM) ^c
Ammonium persulfate	0.1575 (5.9 mM) ^c
Potassium metabisulfite	0.1575 (5.8 mM) ^c
Ammonium iron(II) sulfate hydrate	0.0015
DDI water	117.58

Polymerization temperature = 40°C.

^a 80% solids.

^b 2-20% based on total monomer.

^c Based on water.

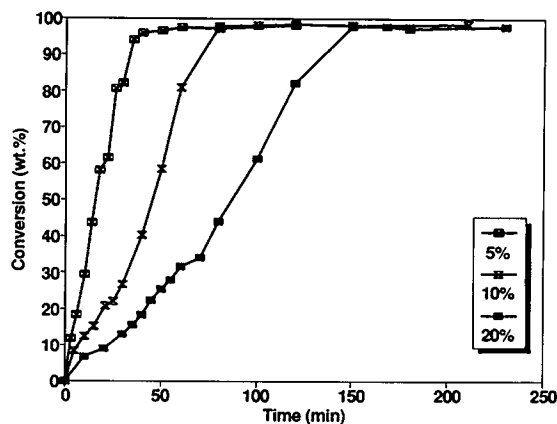


Figure 6 Effect of TMI concentration on the batch emulsion polymerization kinetics of MMA/BA/TMI; Aerosol MA 80 concentration = 31.2 mM; $T = 40^{\circ}\text{C}$.

and the initiator concentration, which was increased to 8 mM.

Figure 12 shows the conversion–time data for a semicontinuous polymerization run in which the surfactant, initiator, DDI water, and 50% of the acrylic monomers (MMA and BA) were added initially at $t = 0$. The remaining acrylic monomers were mixed with TMI and fed continuously from $t = 5$ min for a period of 4 h as a neat monomer feed. The “instantaneous conversion” shown in the figure is the conversion of monomer which has been added up to a particular time and may either increase or decrease depending on the polymerization and monomer feed rates. The “overall conversion” is based on the total amount of monomer in the recipe. The overall conversion always increases with time because the monomer is continuously being fed into the reactor. The two conversions converge when the monomer feed is complete. The overall conversion was found to reach a limiting value of approximately 70% after 3 h. In order to improve the final conversion, the initiator concentration was doubled to 16 mM in the next run (Fig. 13). The first data point

Table IV CHDF Particle Size Data for Experiments Shown in Figure 6

TMI (wt %)	D_n^a (nm)	D_w^b (nm)	PDI ^c
5	61.2	66.6	1.09
10	52.3	62.7	1.19
20	47.2	58.5	1.24

^a D_n = number-average diameter.

^b D_w = weight-average diameter.

^c PDI = polydispersity index, D_w/D_n .

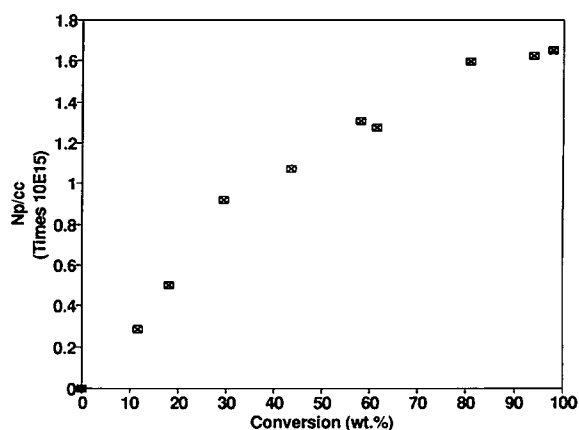


Figure 7 Evolution of the particle number as a function of conversion for the experiment shown in Figure 6; [TMI] = 5% of oil phase.

in the figure obtained before the monomer feed was started represents the batch copolymerization of MMA and BA. A large discrepancy is observed between the individual conversions of MMA and BA. This is due to the much higher reactivity ratio of MMA (1.8) as compared to BA (0.37).²² However, after the monomer feed is started, monomer-starved conditions are reached, as indicated by the linear portion of the overall conversion curve. Under such conditions, the monomer feed rate is less than the batch polymerization rate. As a result, the three monomers become incorporated into the polymer chain at almost the same ratio as they were fed into the reactor; thus the terpolymer composition approximates that of the monomer feed. This can be observed from the similar instantaneous conversion values for the three monomers. The instantaneous

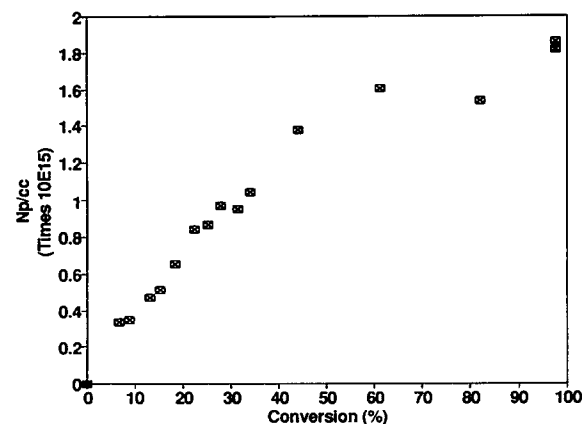


Figure 8 Evolution of the particle number as a function of conversion for the experiment shown in Figure 6; [TMI] = 20% of oil phase.

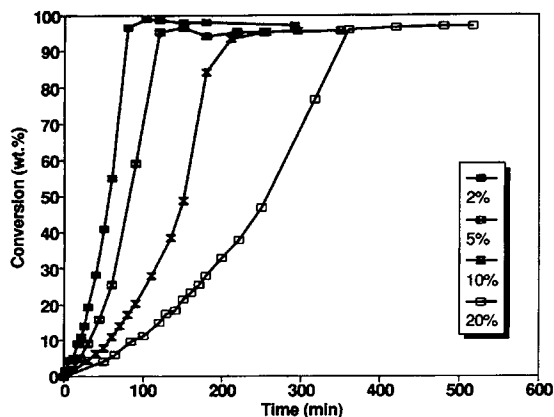


Figure 9 Emulsion terpolymerization of MMA/BA/TMI below the CMC of Aerosol MA 80; Aerosol MA 80 concentration = 15.6 mM; monomer added in a batch mode; initiator added semicontinuously over 4 h; [TMI] varied from 2–20%, based on total monomer; $T = 40^{\circ}\text{C}$.

conversions are less than 100% due to mass transfer limitations.^{23,24} There are three physical factors which limit the polymerization rate in a particle: (1) diffusion of monomer through the aqueous phase, (2) diffusion of monomer within the particle, and (3) an interfacial resistance. When the monomer is fed into the reactor, it has to diffuse through the aqueous phase, cross the water–particle interface, and diffuse into the monomer–polymer particle. The diffusion rate through the aqueous phase to the particle is greater than the diffusion rate of the monomer entering the particle and reacting with the growing polymer chains. Therefore, the diffusion rate through the aqueous phase is greater than the rate of polymerization. Since the former is a measure of the monomer feed rate, the polymerization rate is less than the feed rate. As a result, the instantaneous conversion is less than 100%.

Although the final conversion in the above run was found to increase with initiator concentration, it still tended to level off at 85%. We speculated that this was due to consumption of the initiator, which has a low half-life period, before the completion of

Table V CHDF Particle Size Data for Experiments Shown in Figure 9

TMI (wt %)	D_n (nm)	D_w (nm)	PDI
2	116.6	117.5	1.01
5	105.9	106.1	1.00
10	101.2	102.5	1.01
20	90.6	99.8	1.10

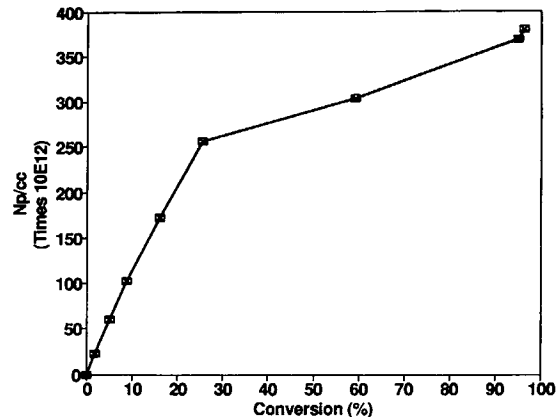


Figure 10 Evolution of the particle number as a function of conversion for the experiment shown in Figure 9; [TMI] = 5% based on total monomer.

the monomer feed. Hence, in the next experiment, the initiator was added in two shots. Fifty percent of the initiator (reductant and oxidant) was added at $t = 0$, and the remainder was added as a second shot (two separate aqueous solutions of the reductant and oxidant) at a later time, as shown in Figure 14 for the two initiator concentrations. It can be seen from the figure that during the initial stages, the polymerization with the higher initiator concentration is faster. However, after the second shot of initiator is added, monomer-starved conditions are attained. The polymerization rate is now controlled by the monomer feed rate and therefore, the conversion–time curve is linear in nature. Since the monomer feed rates are equal in both runs, the two curves overlap.

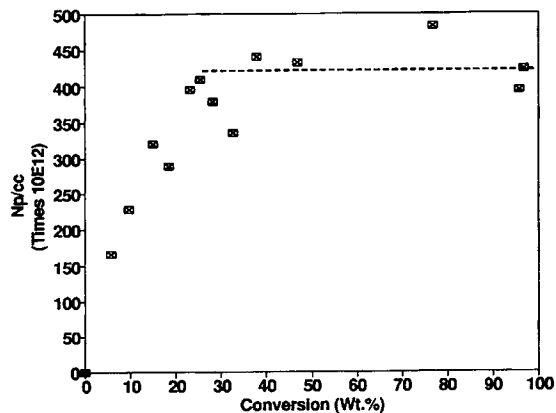


Figure 11 Evolution of the particle number as a function of conversion for the experiment shown in Figure 9; [TMI] = 20% based on total monomer.

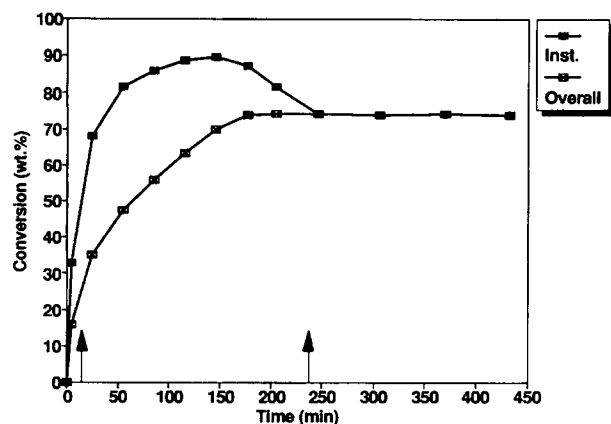


Figure 12 Semicontinuous emulsion terpolymerization of MMA/BA/TMI (40/55/5 w/w). Monomer feed added between $t = 5$ to 245 min; $[I] = 8$ mM; $T = 40^\circ\text{C}$.

A possible disadvantage of the above technique is that the addition of the second shot of initiator in the later stages of polymerization might lead to polymer chains with low molecular weight, which may affect the final film properties. Moreover, this may also result in the fresh nucleation of particles, thereby leading to a bimodal particle size distribution. Hence, the semicontinuous process was modified to overcome this problem. Instead of adding the initiator in two shots, one-third of it was added at $t = 0$ and the rest was added continuously as two different streams of the oxidant and reductant over a period of 4 h. The monomer was also added semicontinuously over this time period as a separate stream. The conversion-time data for a polymerization using the recipe in Table III (with the surfactant concentration decreased to 15.6 mM) is shown in Figure 15. It can be observed that the overall conversion increases steadily, and almost complete conversion is obtained after about 5 h; hence, this process is as efficient in obtaining high conversions as the two-step initiator addition technique. In order to examine whether the continuous initiator feed resulted in an extended period of particle nucleation, the particle number was followed as a function of conversion (Fig. 16). The particle number was found to increase until approximately 40% conversion, after which it remained constant. This indicates that particle nucleation ended at 40% conversion, after which particle growth occurred without the generation of new particles. The particle size distribution was found to be fairly narrow (polydispersity index = 1.02).

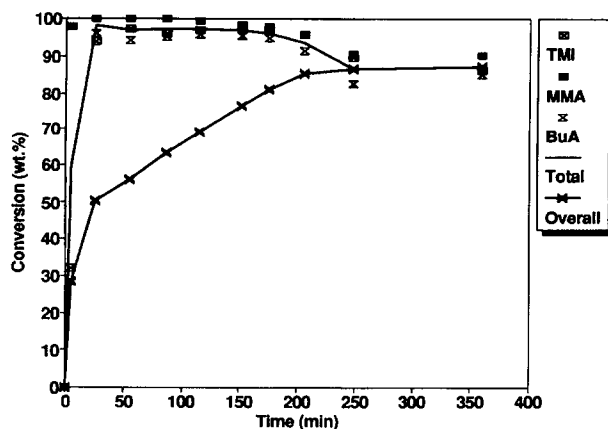


Figure 13 Semicontinuous emulsion terpolymerization of MMA/BA/TMI (40/55/5 w/w). Monomer feed added between $t = 5$ to 245 min; $[I] = 16$ mM; $T = 40^\circ\text{C}$. "Total" refers to the total instantaneous conversion. "Overall" conversion is based on the total monomer in the recipe.

Effect of TMI Concentration and Monomer Feed Rate

Figure 17 illustrates the effect of TMI concentration on the semicontinuous polymerization kinetics. During the initial stages, the process with the higher TMI concentration exhibited a slower polymerization rate (smaller slope) which is consistent with the results discussed in the previous section for batch polymerization. However, after a certain period of time, monomer-starved conditions were reached and the polymerization rate was controlled by the monomer feed rate. As a result, the two curves show identical slopes. Figure 18 compares the kinetics of polymerization processes carried out at two different

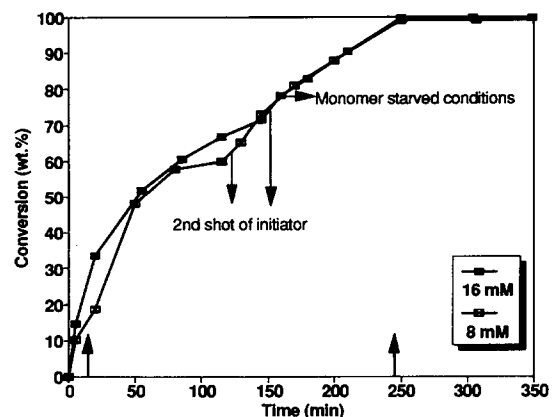


Figure 14 Semicontinuous emulsion terpolymerization of MMA/BA/TMI (40/55/5 w/w). Monomer feed added between $t = 5$ to 245 min; $[I] = 8$ and 16 mM; initiator added in two shots; $T = 40^\circ\text{C}$.

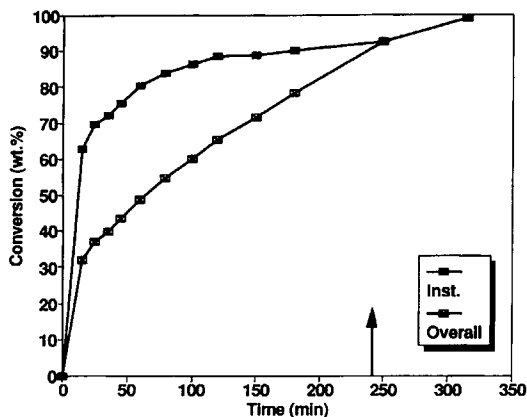


Figure 15 Semicontinuous emulsion terpolymerization of MMA/BA/TMI (40/55/5 w/w). Monomer and initiator added semicontinuously between $t = 0$ to 240 min; $[I] = 5.9 \text{ mM}$; $T = 40^\circ\text{C}$.

monomer feed rates. In the beginning, the two runs showed similar rates of polymerization. However, as the polymerization proceeded, monomer-starved conditions were reached and the monomer feed rate controlled the rate of polymerization. Hence, the process with the faster monomer feed rate underwent polymerization at a more rapid rate than the other run. This is reflected by the slightly higher slope of the linear portion of the conversion-time curve. It should also be mentioned that the initiator feed rate was also higher (proportional to the monomer feed rate) in the second run. This may explain the crossover of the two curves at 40% conversion.

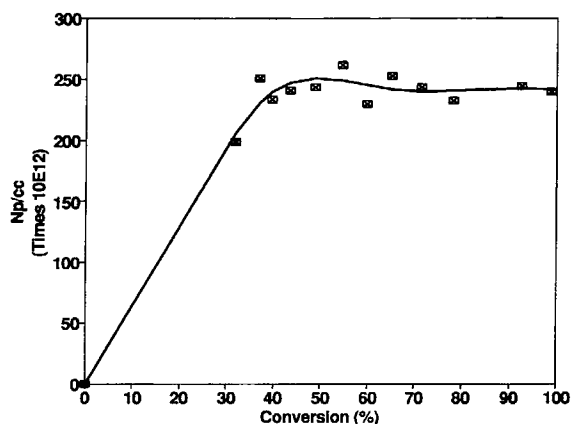


Figure 16 Development of particle number for the experiment shown in Figure 15.

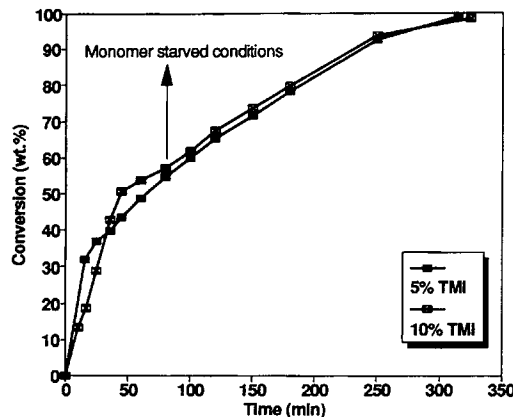


Figure 17 Effect of TMI concentration on the semicontinuous emulsion terpolymerization of MMA/BA/TMI; monomer and initiator added semicontinuously between $t = 0$ to 240 min; $[I] = 5.9 \text{ mM}$; $T = 40^\circ\text{C}$.

CONCLUSIONS

The emulsion terpolymerization of TMI with the acrylic monomers, MMA and BA was studied in detail. The NCO group was found to be quite stable towards hydrolysis under the polymerization conditions used in this study. TMI was found to retard the batch polymerization kinetics. The rates of consumption of the monomers were found to be in the order $\text{MMA} > \text{TMI} > \text{BA}$. Efforts to accelerate the batch polymerization by increasing the surfactant concentration resulted in the formation of latexes with small particle sizes. Several semi-

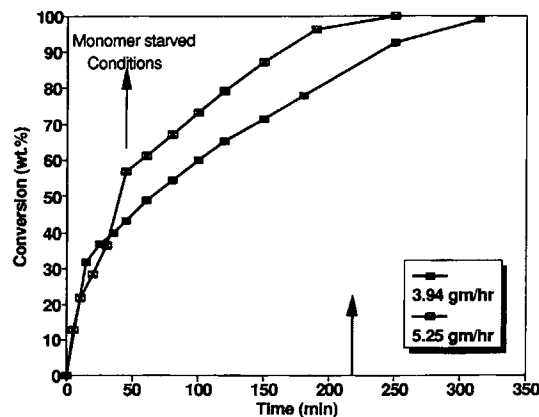


Figure 18 Effect of monomer feed rate on the semicontinuous emulsion terpolymerization of MMA/BA/TMI; monomer and initiator added semicontinuously between $t = 0$ to 240 min; $[I] = 5.9 \text{ mM}$; $T = 40^\circ\text{C}$.

continuous polymerization processes were developed in order to obtain terpolymers with controlled polymer composition and particle size. The particle size was found to decrease with increasing TMI concentration. It was necessary to feed the initiator over a period of time to obtain appreciable conversions for polymerizations carried out below the CMC.

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