

# Kinetic Study of Emulsion Copolymerization of Ethyl Methacrylate/Lauryl Methacrylate in Propylene Glycol, Stabilized with Poly(ethylene oxide)-*block*-Polystyrene-*block*-Poly(ethylene oxide) Triblock Copolymer

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Received 21 March 2000; accepted 8 February 2001

**ABSTRACT:** The kinetics of emulsion copolymerization of ethyl methacrylate (EMA)/lauryl methacrylate (LMA) in propylene glycol is very similar to the emulsion copolymerizations of water-soluble monomers in water because of the high solubility of EMA/LMA in propylene glycol. The initial rate of polymerization depends only on initiator concentration and is not affected by either monomer concentration or stabilizer concentration. The overall rate of polymerization is only slightly dependent on monomer concentration and stabilizer concentration and is independent of initiator concentration. The final particle number density increases with increasing amount of stabilizer and decreases with increasing monomer concentration. The total surface area increases with stabilizer concentration and is not governed by either initiator concentration or monomer concentration. Homogeneous nucleation is the dominant mechanism of particle nucleation, as shown by the kinetic data on seeded polymerization and monomer partition behavior. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1691–1704, 2001

**Key words:** PEO–PS–PEO triblock copolymer; kinetics; ethyl methacrylate; lauryl methacrylate; propylene glycol

## INTRODUCTION

The classical emulsion polymerization mechanism involves three intervals. After interval I, the particle formation is generally completed. At the end of interval II, the monomer droplets disappear from the continuous phase. During interval II, the particle volume increases as polymeriza-

tion proceeds and the particle number is kept constant. The monomer concentration in the particles remains constant. Interval III begins when the separate monomer phase disappears. The initial conversion of polymerization in interval I depends on the type of monomers. Generally, particle nucleation can involve three different mechanisms, which include micellar, homogeneous, and droplet nucleation. All these mechanisms may compete and coexist in the same system. However, one mechanism usually dominates in a given case.

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*Journal of Applied Polymer Science*, Vol. 82, 1691–1704 (2001)  
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In homogeneous nucleation the initiator radical propagates in the continuous phase to form an oligomer. These oligomers grow until they reach insolubility and then collapse and form the nucleus for the new particles. This theory was proposed by Fitch and coworkers.<sup>1</sup> Fitch and Tsai applied this theory to the emulsion polymerization of methyl methacrylate, for which homogeneous nucleation of particle formation is dominant. The experimental results had reasonably good correlation with theoretical predictions.

The homogeneous nucleation process can also be treated as a chain reaction, which was proposed by several researchers.<sup>2-6</sup> Each chain has its own probability for propagation, termination, and absorption. New particles are formed by the most probable mechanism. The course of emulsion polymerization depends on the solubility of monomers in the medium.<sup>7-46</sup> When the monomers have low solubility in the continuous phase, the polymerization rate can sometimes surpass the mass transfer rate of the monomer, which renders the polymerization diffusion controlled. The viscosity within the particles increases throughout the process of polymerization.

As described in a separate study,<sup>47</sup> 16 well-defined and narrow molecular weight distribution PEO-PS-PEO triblock copolymers were synthesized by an anionic polymerization process. The stabilizing efficiency of these 16 PEO-PS-PEO triblock copolymers was examined in the proposed model copolymerization system and is described elsewhere.<sup>47</sup>

Among the 16 PEO-PS-PEO triblock copolymers, only six of them gave stable latices. The rest of them could not generate a latex at all. For the purpose of fully understanding the mechanism of emulsion copolymerization of this system, the kinetics was studied.

The current system is analogous to emulsion polymerization using highly water soluble monomers. Ethyl methacrylate (EMA) and lauryl methacrylate (LMA) have relatively high solubility (5%) in propylene glycol. Homogeneous nucleation therefore could play an important role in this emulsion polymerization. It can be expected that the kinetic behavior of emulsion copolymerization of EMA/LMA in propylene glycol would deviate from the traditional Smith-Ewart theory, which was proposed based on low water soluble monomers.

The purpose for the present work was to study the kinetics of the batch emulsion copolymerization of EMA/LMA in propylene glycol. The effect

of stabilizer, initiator concentration, and monomer concentration on the particle size, rate of polymerization, and surface coverage were investigated. All of these studies focused on the mechanistic aspects of emulsion copolymerization.

## EXPERIMENTAL

### Materials

Ethyl methacrylate (EMA, 99%; Aldrich Chemical Co., Milwaukee, WI) and lauryl methacrylate (LMA, 96%; Aldrich) were used as monomers. They were purified by passing through inhibitor-removal columns (for HQ, or MEHQ; Aldrich).

All other materials were used as received, including propylene glycol (99.5+%, ACS reagent; Aldrich), 2,2'-azobis(isobutyronitrile) (AIBN, 98%; Aldrich), and hydroquinone (99%, Aldrich). PEO-PS-PEO triblock copolymers were synthesized according to the method described in a separate study.<sup>47</sup>

### Emulsion Copolymerization

Emulsion copolymerizations of EMA/LMA were carried out in propylene glycol at 60°C for a period of 24 h. A small glass vial (16 mL) was charged with the desired amount of propylene glycol, AIBN, PEO-PS-PEO triblock copolymer, and magnetic stir bar. EMA and LMA were well mixed in a separate beaker and poured into the small glass vial, which contained the mixture of propylene glycol, AIBN, PEO-PS-PEO triblock copolymer, and magnetic stir bar. The small glass vial was purged with nitrogen, capped, sealed, and placed in the 60°C constant water bath with continuous stirring.

### Effect of Initiator, Stabilizer, and Monomer Concentration

The recipe for studying the effect of initiator, stabilizer, and monomer concentration is given in Table I. The variables are the amount of the initiator, the stabilizer, or the monomer. The conversion-time curve was measured by both dilatometry and a gravimetric method. The dilatometer was filled with a mixture of monomers (EMA and LMA), initiator (AIBN), PEO-PS-PEO triblock copolymer, and propylene glycol to a point where part of the capillary was filled and the assembly was immersed in a 60°C constant temperature bath. After equilibration, the capillary height was

**Table I Recipe for Studying the Effect of Initiator, Stabilizer, and Monomer Concentration**

Ingredient	Amount (g)
Propylene glycol (g)	3.67; 3.41; 2.80
PEO-PS-PEO triblock copolymer xyd33 <sup>a</sup> (g)	0.10; 0.15; 0.20
Ethyl methacrylate (g)	0.57; 0.87; 1.15
Lauryl methacrylate (g)	0.41; 0.63; 0.85
AIBN <sup>b</sup> (g)	0.07; 0.055; 0.04

<sup>a</sup> Composition of triblock copolymer xyd33: 69PEO-29PS-69PEO.

<sup>b</sup> AIBN: 2,2'-azobis(isobutyronitrile).

measured at regular time intervals during the polymerization.

A drop of solution was withdrawn from the mixture (a separate vial) at regular intervals and added to 1 mL of 1% hydroquinone/propylene glycol solution. The sample was placed in an ice bath, which was subsequently used for measuring the conversion by means of a gravimetric method and the particle size through a light-scattering method (Nicomp 370).

The particle number density was calculated based on the particle diameter, which was obtained via light scattering, the fractional conversion, and the density of the polymer, 1.19 g/cm<sup>3</sup>.

### Seeded Polymerization

Seed latex (1 mL) was made using the recipe in Table I. The stabilizer was xyd33 (69PEO-29PS-69PEO) and the amount used was 0.2 g. The emulsion copolymerizations of EMA/LMA were carried out in propylene glycol at 60°C for a period of 8 h. The recipe for the seeded polymerization is given in Table II. A small glass vial (16 mL) was charged with the desired amount of propylene glycol, AIBN, seed latex, PEO-PS-PEO triblock copolymers, and magnetic stir bar. EMA and LMA were well mixed in a separate beaker and poured into the small glass vial, which contained the mixture of propylene glycol, AIBN, seed latex, PEO-PS-PEO triblock copolymers, and magnetic stir bar. The small glass vial was purged with nitrogen, capped, sealed, and placed in the 60°C constant temperature water bath with continuous stirring.

The variable in this series of experiments was the amount of stabilizer (xyd33). Three emulsion copolymerizations were studied with the amount

of stabilizer varying at 0, 0.1, and 0.2 g. Samples were withdrawn every 2 h, and the reaction was terminated with 1 mL 1% of cold hydroquinone/propylene glycol solution. The particle size and distribution were measured through a light-scattering method. The experimental results are summarized in Table III.

### Monomer Partitioning Behavior in the Latex

A 1-g sample of latex, comprised of 29.96 wt % poly(ethyl methacrylate-co-lauryl methacrylate), 3.86 wt % PEO-PS-PEO triblock copolymer (xyd33), and 65.83 wt % propylene glycol, was mixed with 0.5 g of the monomer mixture (weight ratio of EMA to LMA was 0.87 : 0.63). The ratio of the two monomers is the same as that used before. The mixture was stirred for 24 h and then centrifuged. The top layer (supernatant) consisted of propylene glycol and monomers. The bottom layer consisted of swollen polymer. Both layers were separated and weighed, and the partitioning of the monomers in the two phases was calculated. The flow chart of this experimental process and the result obtained are illustrated in Figure 1.

## RESULTS AND DISCUSSION

### Effect of Stabilizer Concentration

The emulsion copolymerizations of EMA/LMA were carried out according to the recipe given in Table I. In the recipe, the variable is the amount of stabilizer, which was changed as follows: 0.10 g (1.97 wt %), 0.15 g (2.92 wt %), and 0.20 g (3.86 wt %), respectively. The conversion-time curve was measured by means of a dilatometer, which takes

**Table II Recipe for Seeded Polymerizations**

Ingredient	Amount (g)
Propylene glycol	3.41
PEO-PS-PEO triblock copolymer xyd33	0; 0.1; 0.2
Ethyl methacrylate (EMA)	0.87
Lauryl methacrylate (LMA)	0.63
Seed latex <sup>a</sup>	1 ml
AIBN <sup>b</sup>	0.07

<sup>a</sup> Seed latex was made using the recipe in Table I. The stabilizer was xyd33 (69PEO-29PS-69PEO) and the amount used was 0.2 g. The solid content is 30%.

<sup>b</sup> AIBN: 2,2'-azobis(isobutyronitrile).

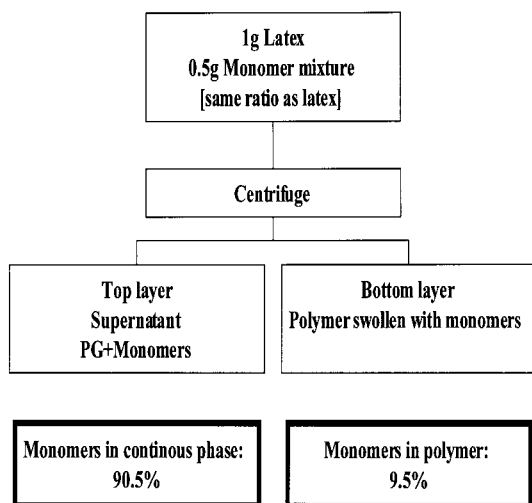
**Table III Experimental Results of Seeded Polymerizations**

Concentration of stabilizer (g)	0	0.1	0.2
Particle size (<2 h) (nm)		89 (peak 1), 149 (peak 2)	75 (peak 1), 153 (peak 2)
Particle size distribution (<2 h)	Coagulum	Bimodal	Bimodal
Particle size (>4 h) (nm)		158	151
Particle size distribution (>4 h)	Coagulum	Single peak	Single peak

advantage of the density differences between monomers and their polymers.

The effect of stabilizer concentration on conversion of emulsion polymerization is shown in Figure 2. It can be seen that the initial rate of polymerization is independent of stabilizer concentration initially (up to 8% conversion), but slightly dependent on stabilizer concentration at higher conversions.

The high solubility of EMA and LMA in propylene glycol suggests that homogeneous nucleation dominates. The loci of nucleation are in the medium instead of the monomer swollen micelles. At the beginning of the polymerization, free radicals initiate polymerization in the propylene glycol to form oligomeric radicals. These oligomers keep propagating until reaching their critical precipitation length. At that time, PEO-PS-PEO triblock copolymer adsorbs on the collapsed oligomeric chains to form the particles. Therefore, the rate of polymerization has zero dependence on PEO-PS-PEO triblock copolymer stabilizer concentration at the start of the polymerization.



**Figure 1** Flow chart of the experimental process for measuring monomer partitioning behavior.

Figure 3 displays the effect of PEO-PS-PEO triblock copolymer stabilizer concentration on particle number density. Three regions are observed. In region I, up to about 15% conversion, the particle density decreases sharply. Then, it declines gradually during region II. Finally, it reaches a steady state at about 80% conversion in region III. The effect of stabilizer concentration on final particle size and distribution is shown in Table IV.

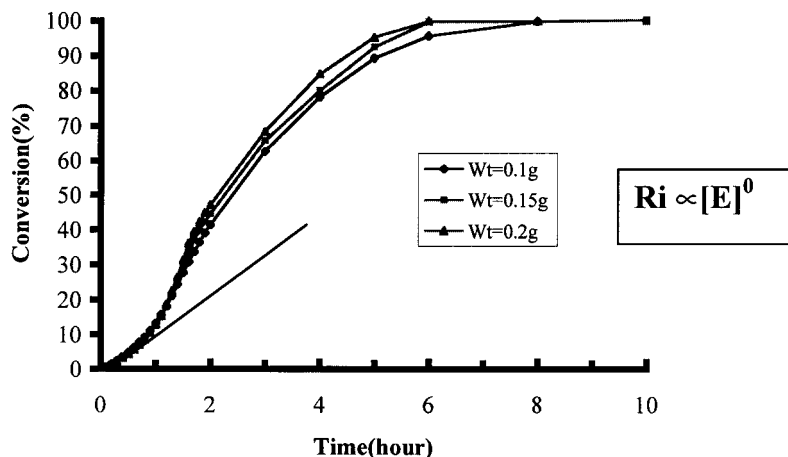
In region I the initial high particle number density must be attributed to the high rate of primary particle generation by homogeneous nucleation. The rapid decline in the particle number density is most likely adsorption rate dependent. The rate at which new particle surface is created is greater than the adsorption rate. During polymerization, more stabilizers generate more particles (Fig. 3) and more surface area (shown later in Fig. 5).

In region II the particle volume increases as polymerization proceeds. Additional PEO-PS-PEO triblock copolymer stabilizer is required for stabilization. This can be accommodated by a rearrangement of the PEO-PS-PEO triblock copolymer stabilizers on the surface and of further adsorption. The rate of adsorption, however, still cannot keep up with the rate of increasing particle surface area. This leads to further flocculation.

In region III, finally, the adsorption rate is sufficiently fast to keep the particle stabilized.

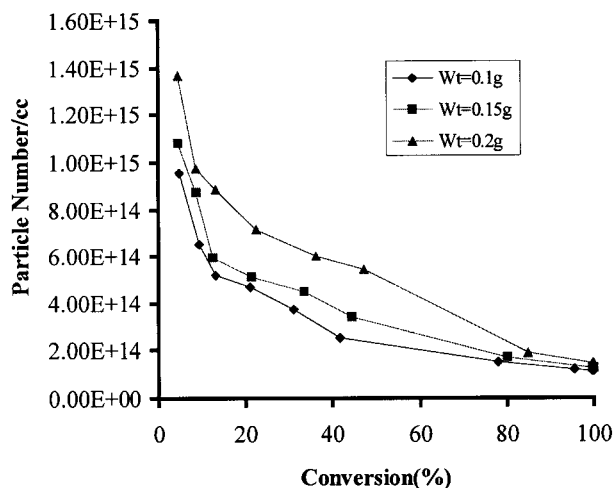
With higher concentration of PEO-PS-PEO triblock copolymer stabilizer, more particles can be stabilized. The particle number density increases with the concentration of PEO-PS-PEO triblock copolymer stabilizer. This is shown in Figure 4 by the power dependence on stabilizer concentration.

The effect of the concentration of PEO-PS-PEO triblock copolymer stabilizer on the total surface area is illustrated in Figure 5. The total surface area is determined from the particle diameter and particle density.



**Figure 2** Conversion versus time curves for the model EMA/LMA nonaqueous emulsion copolymerization system showing the effect of the variation in the concentration of PEO-PS-PEO triblock copolymer stabilizer at 60°C.

The experimental results indicate that the total particle surface area increases until it reaches full conversion, despite the decreasing particle number density. This is because the particle growth rate is faster than the limited rate of flocculation. Thus more stabilizer molecules are required to provide steric stabilization on the particles, while the separate monomer phase is present. Once the separate monomer phase disappears, the particles should shrink in volume and decrease in area, which should increase the adsorbed stabilizer concentration at the particle



**Figure 3** Particle density versus conversion curves for the model EMA/LMA nonaqueous emulsion polymerization system showing the effect of the variation in the concentration of PEO-PS-PEO triblock copolymer stabilizer at 60°C.

interface and hence increase particle stability. Higher stabilizer concentration yields slightly larger total surface area. The 0.13 power dependence of the total surface area on the concentration of PEO-PS-PEO triblock copolymer is suggested in Figure 6.

As expected, the particle size decreases with higher concentration of PEO-PS-PEO triblock copolymers. This is shown as the power dependence on the stabilizer concentration in Figure 7.

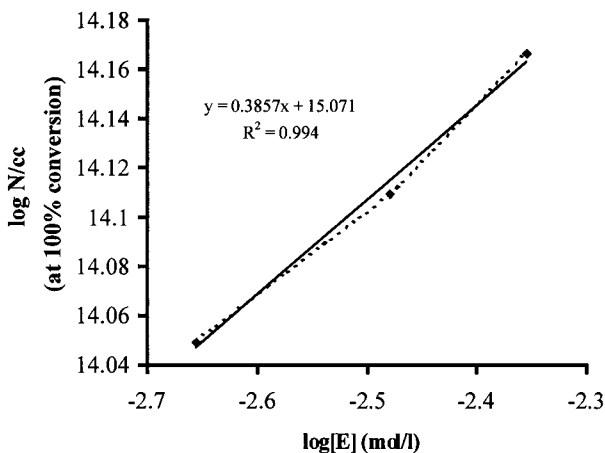
The solubility of monomers in propylene glycol is relatively high (5%), and homogeneous nucleation is the suspected mechanism at the beginning. At high stabilizer concentration, more particles are stabilized at the start, which accelerates the polymerization. As particles grow bigger, more stabilizer is required for each particle. However, the limited stabilizer amount at the particle surface is not enough to stabilize all the particles. Therefore, some will flocculate and the surface

**Table IV** Effect of Stabilizer Concentration on Particle Size and Distribution

Stabilizer Concentration (g)	$D_n^a$ (nm)	$D_w^b$ (nm)	Polydispersity
0.10	163	171	1.05
0.15	156	161	1.03
0.20	149	156	1.05

<sup>a</sup>  $D_n$ : number-average particle size (light-scattering Nicomp).

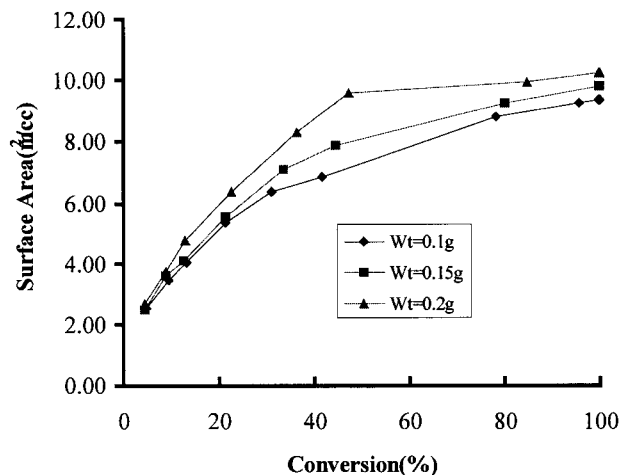
<sup>b</sup>  $D_w$ : weight-average particle size (light-scattering Nicomp).



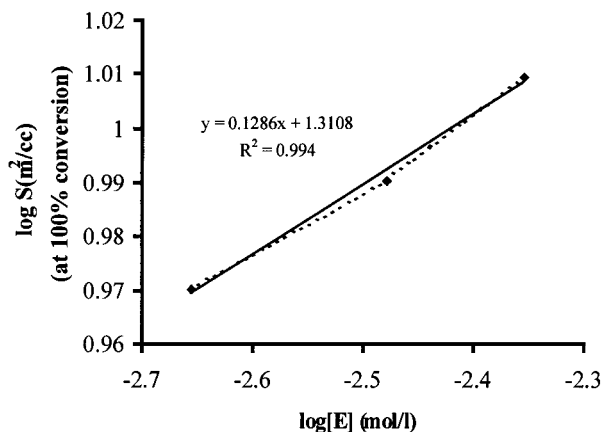
$$N_p - [E]^{0.39}$$

**Figure 4** Dependence of final particle number density versus the concentration of PEO-PS-PEO triblock copolymer stabilizer for the model EMA/LMA nonaqueous emulsion polymerization system at 60°C.

coverage dynamically reequilibrates. More surface coverage is achieved at the sacrifice of particle number density. A faster polymerization rate in region II and smaller particle size were obtained at higher stabilizer concentrations. The particle number density was proportional to the 0.39 power of the stabilizer concentration. The



**Figure 5** Total surface area versus conversion curves for the model EMA/LMA nonaqueous emulsion polymerization system showing the effect of the variation in the concentration of PEO-PS-PEO triblock copolymer stabilizer at 60°C.



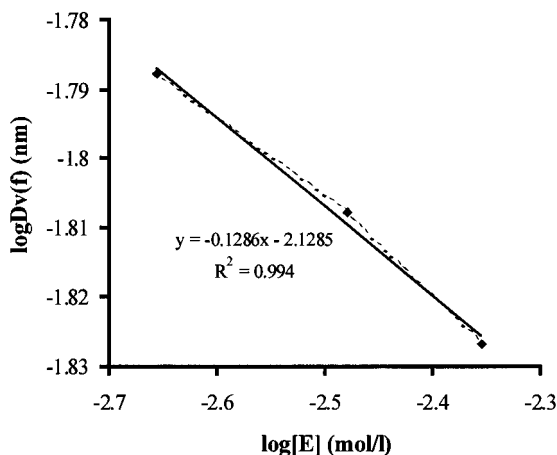
$$S - [E]^{0.13}$$

**Figure 6** Dependence of the total surface area versus the concentration of PEO-PS-PEO triblock copolymer stabilizer for the model EMA/LMA nonaqueous emulsion polymerization system at 60°C.

particle surface area was proportional to the 0.13 power of the stabilizer concentration. The final particle size was inversely proportional to the 0.13 power of the stabilizer concentration. According to Sutterlin's study,<sup>20</sup> the kinetic dependence on stabilizer concentration depends on the monomer solubility. For the monomers that have 5% solubility in water, the particle number density has 0.40 power dependence on the concentration of surfactant. Therefore, the kinetic dependence on stabilizer concentration, which was obtained in this study, is in the range of the reported values<sup>20</sup> for emulsion polymerization of water-soluble monomers in aqueous medium. This further implies the similarity between this model system with aqueous emulsion polymerization for water-soluble monomers.

#### Effect of Initiator Concentration

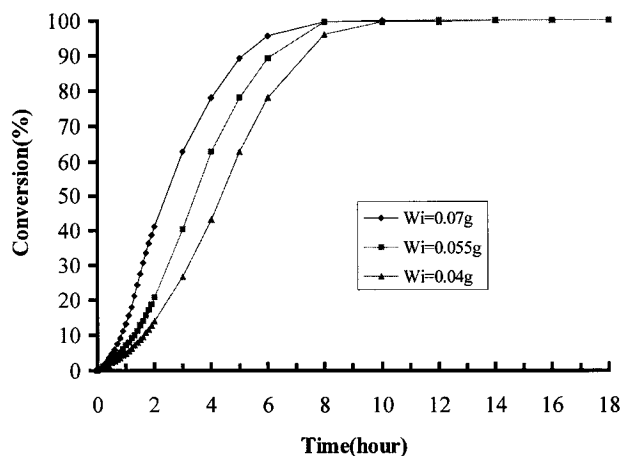
Emulsion copolymerizations of EMA/LMA were carried out based on the recipe described in Table I, using PEO-PS-PEO triblock copolymer as stabilizer and EMA/LMA as comonomers. The amount of initiator was varied as follows: 0.04 g (1.35 wt %), 0.055 g (1.36 wt %), and 0.07 g (1.38 wt %), respectively. Figure 8 shows the effect of initiator on conversion. The rate of



$$Dv - [E]^{-0.13}$$

**Figure 7** Dependence of the particle size versus the concentration of PEO-PS-PEO triblock copolymer stabilizer for the model EMA/LMA nonaqueous emulsion polymerization system at 60°C.

polymerization increases with increasing initiator concentration at low conversion. It is independent of the initiator concentration at higher conversions. The initial rate of polymerization is proportional to the 0.5 power of the initiator concentration, as shown in Figure 9. Particle number density increases with increasing initi-



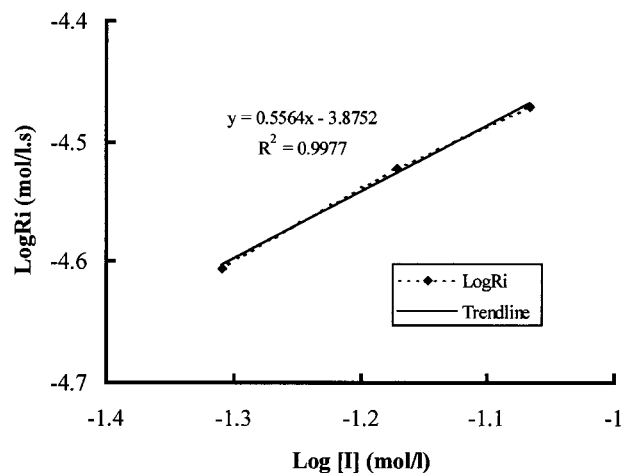
**Figure 8** Conversion versus time curves for the model EMA/LMA nonaqueous emulsion polymerization system showing the effect of the variation in the concentration of initiator (AIBN) at 60°C.

ator concentration at the beginning of the polymerization. However, it is independent of the initiator concentration toward high conversion of polymerization, which is illustrated in Figure 10. Accordingly, there is small increase in total surface area with increasing initiator concentration below 60% conversion. The total surface area after 60% conversion reaches the same value regardless of the initiator concentration used, as shown in Figure 11. The effect of initiator concentration on final particle size and distribution is shown in Table V. As expected, the final particle size is independent of initiator concentration.

The influence of initiator concentration on the kinetics of EMA/LMA emulsion polymerization in the nonaqueous propylene glycol medium can be explained by the general eq. (1) for heterogeneous polymerization kinetics (Smith-Ewart case I kinetics):

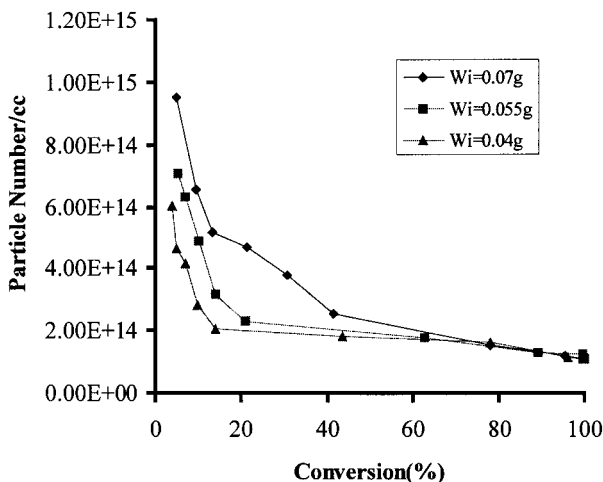
$$R_p = k_p [M_p] \{ (\rho_A V_p) / 2kt \}^{0.5} \quad (1)$$

where  $R_p$  is the rate of polymerization;  $M_p$  is the monomer concentration in the particle;  $\rho_A$  is the rate of adsorption of oligomeric radicals by polymer particles;  $V_p$  is the volume fraction of poly-



$$Ri - [I]^{0.5}$$

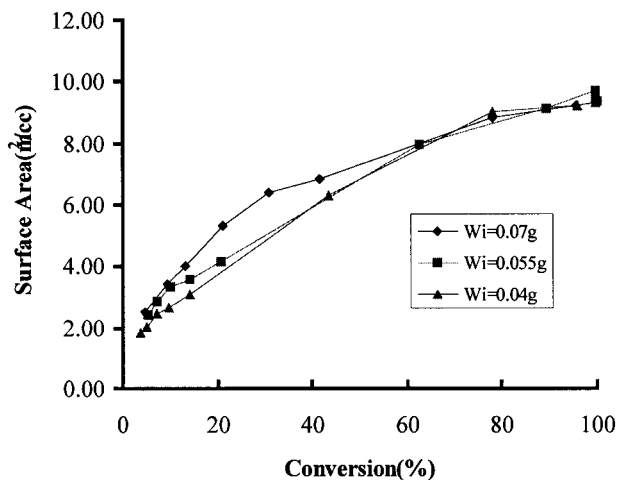
**Figure 9** Dependence of the initial rate of polymerization versus the concentration of initiator (AIBN) for the model EMA/LMA nonaqueous emulsion polymerization system at 60°C.



$$N_p \text{ (at 100\% Conversion) } - [I]^{-0}$$

**Figure 10** Particle density versus conversion curves for the model EMA/LMA nonaqueous emulsion polymerization system showing the effect of the variation in the concentration of initiator (AIBN) at 60°C.

mer particles in the system;  $k_p$  is the rate constant for propagation; and  $k_t$  is the rate constant for termination.



$$S \text{ (at 100\% Conversion) } - [I]^{-0}$$

**Figure 11** Total surface area versus conversion curves for the model EMA/LMA nonaqueous emulsion polymerization system showing the effect of the variation in the concentration of initiator (AIBN) at 60°C.

**Table V** Effect of Initiator Concentration on Particle Size and Distribution

Initiator Concentration (g)	$D_n^a$ (nm)	$D_w^b$ (nm)	Polydispersity
0.07	163	171	1.05
0.055	163	173	1.06
0.04	163	171	1.05

<sup>a</sup>  $D_n$ : number-average particle size (light-scattering Nicomp).

<sup>b</sup>  $D_w$ : weight-average particle size (light-scattering Nicomp).

The rate of adsorption of oligomeric radicals by the particles  $\rho_A$  can be given by diffusion theory:

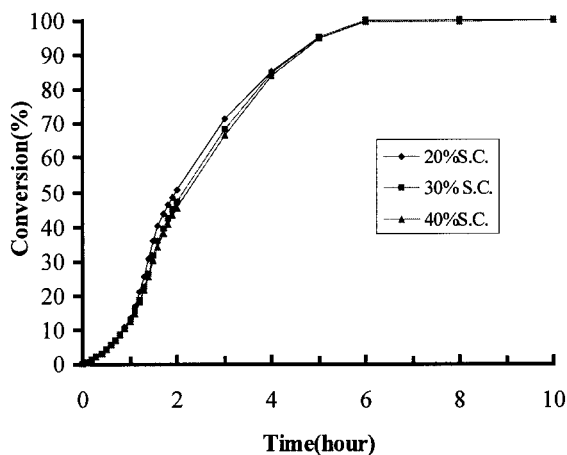
$$\rho_A = 4\pi r N_p \sum_{j=1}^{j_{cr}-1} D_j P_j^* \quad (2)$$

where  $r$  is the radius of monomer-swollen polymer particles;  $N_p$  is the particle number density;  $D_j$  is the diffusion coefficient;  $P_j^*$  is the concentration of oligomeric radicals of chain length  $j$  in the continuous phase; and  $j_{cr}$  is the critical length for oligomers to precipitate from the continuous phase.

At the same high conversion, the monomer concentrations in the polymer particles were identical when different initiator concentrations were used. The final particle size was independent of initiator concentration; thus,  $\rho_A$  is independent of initiator concentration. Consequently, the rate of polymerization is independent of initiator concentration at high conversion, implying diffusion control of oligomer radical adsorption by particles.

The particle number density and the final surface coverage were governed by limited coalescence, so they were independent of initiator concentration. Specifically, at low conversion, homogeneous nucleation dominates because monomers have high solubility in propylene glycol. The rate of polymerization, particle density, and total surface area are independent of initiator level. At high conversion, the heterogeneous polymerization mechanism becomes dominant. The rate of polymerization is the same because of the identical monomer concentration in each particle. The particle size, particle density, and total surface area are governed by the inherent stabilizing capacity of the PEO-PS-PEO triblock copolymer; thus these factors are not affected by the initiator concentration.



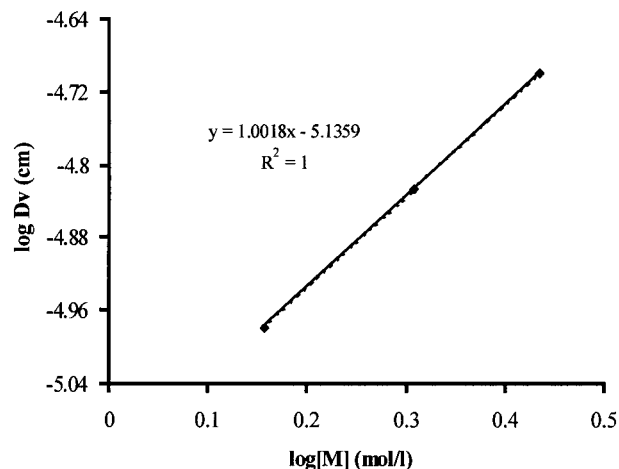


$$R_i - [M]^0$$

**Figure 12** Conversion versus time curves for the model EMA/LMA nonaqueous emulsion polymerization system showing the effect of the variation in monomer concentration at 60°C.

#### Effect of Monomer Concentration

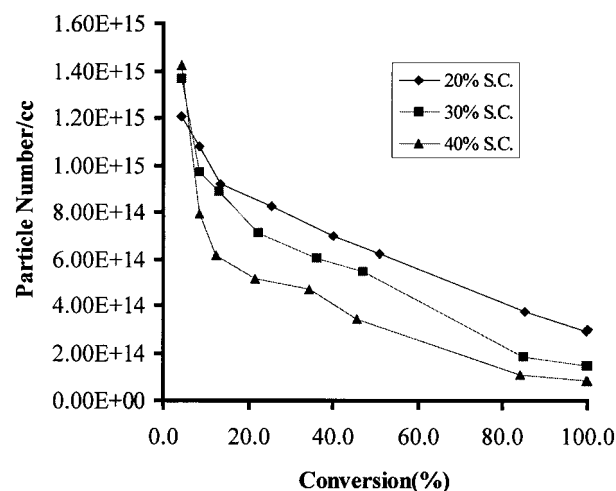
The same procedure was followed as before for the emulsion copolymerizations of EMA/LMA. The amount of EMA monomer concentration was varied as follows: 0.57 g (11.59 wt %), 0.87 g (16.80 wt %), and 1.15 g (22.68 wt %), respectively. The corresponding changes in the amount of LMA monomer were 0.41 g (8.33 wt %), 0.63 g (12.16 wt %), and 0.85 g (16.77 wt %). Figure 12 displays the effect of monomer concentration on conversion of emulsion copolymerization. The initial rate of polymerization is independent of monomer concentration. The rate of polymerization increases slightly with increasing monomer concentration in the higher conversion region. The dependence of final particle size on monomer concentration is illustrated in Figure 13. The volume-average particle diameter increases proportionally with monomer concentration. The particle number density decreases with increasing monomer concentration (see Fig. 14) and is inversely proportional to the 2 power of the monomer concentration (see Fig. 15). At the beginning of the polymerization, the total surface area decreases with increasing monomer concentration. At high conversion, it becomes independent of the monomer concentration. These phenomena are represented in Figure 16.



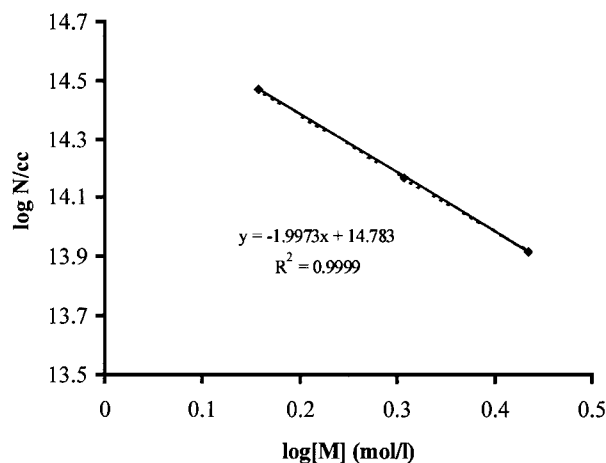
$$Dv_{\infty} [M]$$

**Figure 13** Dependence of the particle size versus monomer concentration for the model EMA/LMA nonaqueous emulsion polymerization system at 60°C.

Because the nucleation starts in the propylene glycol medium, the initial rate of polymerization is determined by both the monomer concentration in the propylene glycol and the initiator concentration in the medium. At the start of the polymerization, because the monomers (EMA and LMA) have limited solubility in propylene glycol,



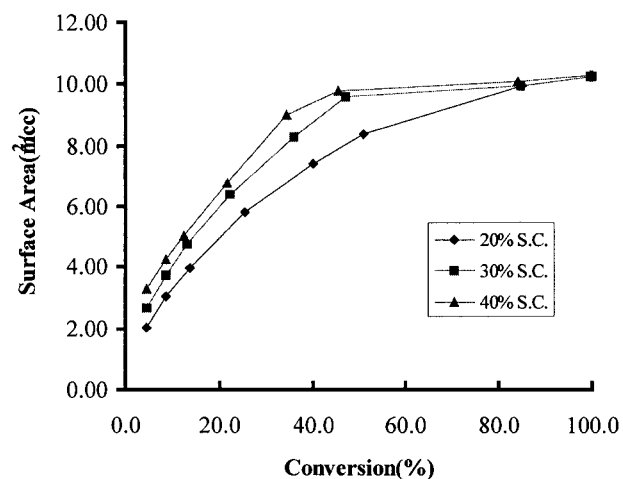
**Figure 14** Particle number density versus conversion curves for the model EMA/LMA nonaqueous emulsion polymerization system showing the effect of the variation in monomer concentration at 60°C.



$$N_p \text{ (at 100\% conversion) } \propto [M]^{-2}$$

**Figure 15** Dependence of the particle number density versus the monomer concentration for the model EMA/LMA nonaqueous emulsion polymerization system at 60°C.

the actual monomer concentration in propylene glycol is the same, regardless of the amount of monomers added to the reactor. The initial rate of polymerization is the same because the same amount of initiator was used (see Fig. 12). The effect of monomer concentration on final particle size and distribution is shown in Table VI. With



**Figure 16** Total surface area versus conversion curves for the model EMA/LMA nonaqueous emulsion polymerization system showing the effect of the variation in monomer concentration at 60°C.

**Table VI** Effect of Monomer Concentration on Particle Size and Distribution

Monomer Concentration (g)	$D_n^a$ (nm)	$D_w^b$ (nm)	Polydispersity
20	105	108	1.03
30	149	158	1.06
40	199	205	1.03

<sup>a</sup>  $D_n$ : number-average particle size (light-scattering Nicomp).

<sup>b</sup>  $D_w$ : weight-average particle size (light-scattering Nicomp).

higher monomer concentration, the particles are larger for the same role of nucleation. The monomer concentration increases with increasing particle size, provided the interfacial tension remain a constant. As a result, the rate of polymerization is faster. This explains why the rate of polymerization is not affected by the monomer concentration at the beginning, and increases slightly toward high conversion.

As a result of the fixed amount of stabilizer in the reactor, the total surface area that can be stabilized in the system is a constant. Because larger size particles have less surface area, a lesser amount of the stabilizer is needed to provide steric stability; and because the particle density is inversely proportional to the 3 power of the particle diameter, the particle number density decreases with increasing monomer concentration. The total surface area has power 2 dependency on particle diameter. It increases with monomer concentration in the early stage of the polymerization. However, the intrinsic properties of PEO-PS-PEO triblock copolymer determine the maximum surface area, which can be stabilized. Once the maximum surface area is reached, no more new particles can be stabilized. The PEO-PS-PEO triblock copolymers on the existing particles have to rearrange by means of reducing the particle number density and increasing particle diameter. Therefore, the total surface area is not controlled by monomer concentration at the end of the polymerization.

### Seeded Polymerization

This set of experiments was designed to provide experimental evidence to support the proposed homogeneous nucleation mechanism. The emulsion copolymerizations of EMA/LMA were carried out according to the recipe given in Table II. The

amount of PEO-PS-PEO triblock copolymers was varied as follows: 0, 0.1, and 0.2 g. The amount of seed was kept constant for all the experiments. The experimental results presented in Table III show that no stable latex can be generated without the participation of a PEO-PS-PEO triblock copolymer. With the addition of a certain amount of the PEO-PS-PEO triblock copolymer, a stable latex can be made. A bimodal particle size distribution was observed and could come from two possible sources: (1) existing seed particles; (2) new particles. Earlier in the polymerization, the sizes of the newly generated particles are small when compared to that of the seed particles and two peaks are detected. This indicates that new particles are formed from the beginning of polymerization. Although monomer swollen particles will capture some of the radicals, new particles form by a homogeneous nucleation process.

#### Monomer Partitioning Behavior in the Latex

Experimental results showed that, during the polymerization, most of the monomers (90.5 wt %) reside in the propylene glycol continuous phase. This further implies that homogeneous nucleation occurs.

#### Mechanism of Particle Nucleation

Emulsion polymerization can be divided into three intervals: (1) particle formation; (2) particle growth in the presence of monomer droplets; and (3) polymerization of the monomer remaining in the monomer-swollen polymer particles.

In interval I, given that EMA and LMA have relatively high solubility (5%) in propylene glycol, free radicals react with the monomers to form oligomeric chains. When these oligomeric chains grow to the critical precipitation length, they will aggregate to form particles. PEO-PS-PEO triblock copolymers adsorbed on the surface of these particles impart steric stabilization (homogeneous nucleation). The locus of particle nucleation is in propylene glycol solution instead of in the monomer-swollen micelles. Bimodal distribution observed in seeded polymerization (see Table III) confirmed this hypothesis.

Interval II involves the growth of the polymer particles. As the particles grow, more PEO-PS-PEO triblock copolymers are required to offer stability. However, either a limited amount of PEO-PS-PEO triblock copolymers exist in the solution or the adsorption rate is slow with respect to the

rate of surface area generation. Therefore, limited coalescence is unavoidable.

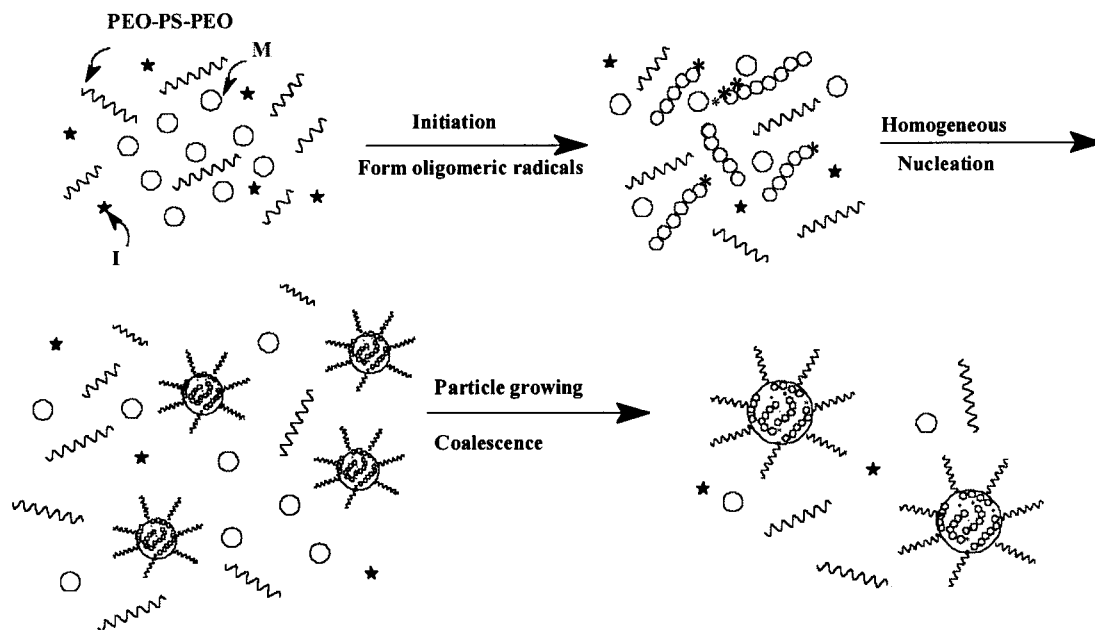
During interval III, the maximum surface coverage of PEO-PS-PEO triblock copolymers is reached. The polymer particles become more viscous as the monomer concentration falls; thus diffusion-controlled termination and diffusion-controlled propagation occur.

A mechanism based on the preceding discussions is proposed for particle nucleation and growth in this system. Schematic representations of these two processes are given in Figure 17.

#### Comparison of Kinetic Behavior of Different PEO-PS-PEO Triblock Copolymers

As mentioned earlier, only six synthesized PEO-PS-PEO triblock copolymers (xyd33, xyd34, xyd37, xyd38, xyd42, and xyd43) could form stable latices. The compositions of these six PEO-PS-PEO triblock copolymers are detailed in Table VII. All the latices, which were stabilized with the above-mentioned six PEO-PS-PEO triblock copolymers, gave similar particle diameters when the amount of stabilizer, initiator, and monomers were the same. Under the experimental conditions of 0.1 g of PEO-PS-PEO triblock copolymer, 0.07 g (or 0.04 g) initiator (AIBN), and 30% solid contents in the reactor, the particle diameter was about 163 nm, as seen in Table IV. The corresponding particle density was  $1.12 \times 10^{14}$  particles/cm<sup>3</sup>, and the resulting total surface area was 9.34 m<sup>2</sup>/g. When the reactor was charged with 0.2 g of PEO-PS-PEO triblock copolymer, 0.07 g initiator (AIBN), and 30% solid contents, the particle size lowered to 149 nm, the particle density increased to  $1.46 \times 10^{14}$  particles/cm<sup>3</sup>, and the total surface area increased to 10.21 m<sup>2</sup>/g; whereas using 0.2 g of PEO-PS-PEO triblock copolymer, 0.07 g initiator (AIBN), and 40% solid contents gave a particle size of 199 nm. The corresponding particle density reduced to  $8.26 \times 10^{13}$  particles/cm<sup>3</sup> and the total surface area was 10.27 m<sup>2</sup>/g.

The difference between the components of these six PEO-PS-PEO triblock copolymers is reflected in the rate of polymerization. For PEO-PS-PEO triblock copolymers xyd33 and xyd34, 40% of the monomers were converted into polymer within 2 h, whereas in the case of PEO-PS-PEO triblock copolymers xyd37 and xyd38, only 20% conversion was reached at 2 h of polymerization. With PEO-PS-PEO triblock copolymers xyd42 and xyd43, the polymerization rate was



**Figure 17** Schematic representation of the mechanism of the particle growth process (as well as particle formation).

even lower and approximately 10% of the monomers were reacted within 2 h. Although all the latices achieve 100% conversion over a 24-h period, the rate of polymerization has significant differences at the early stages of the polymerization.

As discussed in a separate study,<sup>47</sup> the adsorption behavior of these six PEO-PS-PEO triblock

copolymers varies. Each PEO-PS-PEO triblock copolymer partitions differently in the latex system. With xyd33 (or xyd34) as the stabilizer, the polymer particles require less PEO-PS-PEO triblock copolymers on the surface (including those physically adsorbed and anchored on each particle). This is true regardless of the latices that were made with different initiator concentra-

**Table VII** Characteristics of Synthesized PEO-PS-PEO Triblock Copolymers

Sample	MW <sup>a</sup> (Total)	MW <sup>b</sup> (PS)	PS Block	MW <sup>b</sup> (PEO)	PEO Block	Composition
xyd32	6.7E+03	3.1E+03	30	3.6E+03	82	41-30-41
xyd33	9.1E+03	3.0E+03	29	6.1E+03	138	69-29-69
xyd34	1.04E+04	2.9E+03	28	7.5E+03	170	85-28-85
xyd35	1.21E+04	3.2E+03	31	8.9E+03	202	101-31-101
xyd36	5.5E+03	1.9E+03	18	3.6E+03	82	41-18-41
xyd37	7.4E+03	2.0E+03	19	5.5E+03	124	62-19-62
xyd38	9.7E+03	2.0E+03	19	7.8E+03	176	88-19-88
xyd39	1.14E+04	2.1E+03	20	9.3E+03	212	106-20-106
xyd41	7.9E+03	4.3E+03	41	3.6E+03	82	41-41-41
xyd42	9.5E+03	4.1E+03	39	5.5E+03	124	62-39-62
xyd43	1.14E+04	4.2E+03	40	7.2E+03	164	82-40-82
xyd44	1.33E+04	4.3E+03	41	9.0E+03	204	102-41-102
xyd45	5.1E+03	1.5E+03	14	3.6E+03	82	41-14-41
xyd46	7.0E+03	1.6E+03	15	5.5E+03	124	62-15-62
xyd47	8.6E+03	1.5E+03	14	7.1E+03	162	81-14-81
xyd48	1.03E+04	1.4E+03	13	8.9E+03	202	101-13-101

<sup>a</sup> GPC data.

<sup>b</sup> Calculated data.

tions, stabilizer concentrations, and monomer concentrations. The amount of stabilizer needed increased with PEO-PS-PEO triblock copolymers xyd37 and xyd38. A further increase in the amount needed for stability was observed for PEO-PS-PEO triblock copolymers xyd42 and xyd43. This implies that it takes longer for some molecules to achieve the same coverage, and represents the reduced stabilizing efficiency in the order of xyd33 (or xyd34), xyd37 (or xyd38), and xyd42 (or xyd43). As a result, more PEO-PS-PEO triblock copolymers were needed for stabilization of the same particle surface area. At the same stabilizer concentrations for xyd37 to xyd43, fewer particles were generated and hence the rate of polymerization was lower. This accounts for the difference in monomer conversion during polymerization.

## CONCLUSIONS

The kinetics of emulsion copolymerization of ethyl methacrylate/lauryl methacrylate in propylene glycol demonstrates many similarities to the kinetics of emulsion polymerization of water-soluble monomers in water. The experimental results show the initial rate of polymerization is dependent on the 0.5 power of the initiator concentration. However, it is independent of both stabilizer concentration and monomer concentration. Because of the high solubility of EMA/LMA in propylene glycol, particles are generated in the solution. Homogeneous nucleation is the dominant mechanism. This is supported by all the experimental kinetic data, seeded polymerization, and monomer partitioning behavior.

Particle number density increases with increasing stabilizer concentration and decreases with increasing monomer concentration. Initiator concentration has no effect on particle number density at the end of polymerization. Generally speaking, the particle number density versus conversion curve can be divided into three regions. Interval I corresponds to the particle nucleation stage, in which the PEO-PS-PEO triblock copolymers adsorb on the particles without rearrangement. In interval II particle number density is reduced gradually because of limited coalescence. The hallmark of this region is emulsifier adsorption with rearrangement on newly created primary particles. Interval III is characterized by saturation coverage of the PEO-PS-PEO triblock copolymer stabilizer. Dynamic equilibrium of

PEO-PS-PEO triblock copolymer chains on the particle surface is established along with slow rearrangement.

Total surface coverage increases with increasing stabilizer concentration. Notwithstanding, it is independent of both monomer concentration and initiator concentration.

Variations in the kinetic profiles between individual PEO-PS-PEO triblock copolymers result from their adsorption differences. Among the six PEO-PS-PEO triblock copolymers that were able to generate stable latices, the number of PEO-PS-PEO triblock copolymer chains needed for contributing to the stabilization increases in the sequence of xyd33, xyd34, xyd38, xyd37, xyd43, and xyd42. The rate of polymerization decreases in that order. This is because more time is required in the nucleation stage for establishing the dynamic equilibrium on the surface if more PEO-PS-PEO triblock copolymer chains are needed.

Taken together these kinetic data offer a general guideline for controlling the emulsion polymerization of EMA/LMA in propylene glycol.

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