

# Emulsion Polymerization of Methyl Methacrylate Using Poly(Methyl Methacrylate-co-2-Hydroxypropyl Methacrylate)-Graft-Polyoxyethylene as the Stabilizer

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## SYNOPSIS

This study involved the use of an amphipathic graft copolymer, poly(methyl methacrylate-co-2-hydroxypropyl methacrylate)-graft-polyoxyethylene, as a stabilizer in the emulsion polymerization of methyl methacrylate. The stabilizing effectiveness of this graft copolymer was studied as a function of its chemical structure. It was found that the stabilizing effectiveness of the graft copolymer was independent of the molecular weight of the backbone within the investigated range of  $4 \times 10^3$  g/mol to  $2 \times 10^4$  g/mol. In all cases, stable emulsion polymerizations of methyl methacrylate were observed. Effective stabilization also occurred when the graft moieties possessed a molecular weight of either  $2 \times 10^3$  g/mol or  $5 \times 10^3$  g/mol. However, the stabilizing effectiveness was found to be dependent on the amount of polyoxyethylene (POE) contained in the graft copolymer. In this case, graft copolymers possessing 67% by weight POE were poor stabilizers, but ones with 85% POE were very good stabilizers. Moreover, the graft copolymers were found to be superior stabilizers as compared to POE homopolymers.

## INTRODUCTION

The use of amphipathic block and graft copolymers as stabilizers in colloidal dispersions has received significant attention in both the academic and the industrial arenas. However, few studies have focused on the effects of structural variations of the amphipathic materials on particle stabilization and polymerization kinetics.

Piirma and Chen<sup>1</sup> showed that adsorption of an ionic surfactant, potassium oleate, to colloidal particles is influenced by the chemical composition of the particles and the hydrophobic group of the surfactant. They found that maximum adsorption occurred when the chemical nature of the surfactant was similar to the chemical nature of the colloidal particles. In this case, larger amounts of potassium oleate were adsorbed to polystyrene particles than to particles composed of poly(methyl methacrylate-co-styrene), and the amount of adsorbed surfactant

decreased with increasing poly(methyl methacrylate) content. However, this phenomenon did not have a pronounced effect on the particle size. It was found that emulsion polymerization of methyl methacrylate yielded a similar particle size to the one obtained from a styrene emulsion polymerization. These results can be explained by the mode of stabilization of ionic surfactants. These surfactants impart stability through the mutual repulsion of the electrical double layers around colloidal particles. This repulsive force is not dependent on relatively small changes in concentration of the ions in the electrical double layer.

Adsorption of polymeric surfactants should also be dependent on the chemical nature of the colloidal particles and the hydrophobic group of the surfactant. Larger amounts of the polymeric surfactant are expected to be adsorbed when the chemical nature of the hydrophobic group of the surfactant is similar to the chemical nature of the particles. However, the stabilizing capability of the polymeric surfactant should be dependent on the amount of it attached to the colloidal particles. These results are anticipated because of the stabilization mode of

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nonionic polymeric surfactants. In this case, stability arises from the repulsive forces associated with free-energy changes when polymer segments are mixed together. This free energy of mixing,  $\Delta G_m$ , is dependent on the concentration of the polymeric segments or the stabilizing moieties.

Napper<sup>2</sup> and March and Napper<sup>3</sup> have illustrated that for maximum stabilizing effectiveness in colloidal dispersions the hydrophobic group or anchoring moiety must possess a high affinity for the dispersed phase and the hydrophilic group or stabilizing moiety must be highly soluble in the continuous phase.

The present study examines the stabilizing effectiveness of well-defined poly(methyl methacrylate-*co*-2-hydroxypropyl methacrylate)-graft-polyoxyethylene copolymers as a function of structural variation on the emulsion polymerization of methyl methacrylate. The structures were varied in the following manner: (i) changing the molecular weight of the backbone; (ii) altering the molecular weight of the graft units; and (iii) varying the amount of polyoxyethylene (POE) in the copolymer.

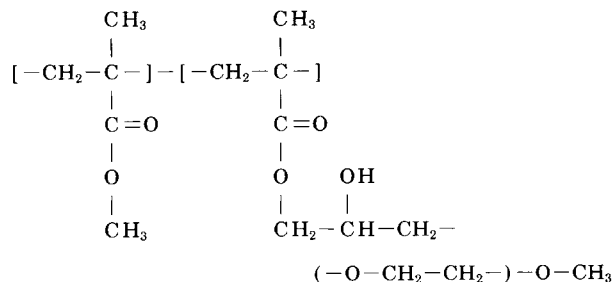
## EXPERIMENTAL

The recipes for the emulsion polymerization of methyl methacrylate are listed in Table I. The charge ratio of monomer to water was kept at 10 g/80 g so that the resultant latex would be dilute (max 12.5% solids). This concentration prevents interaction between the particles. The polymerization rates were determined gravimetrically. Particle size of the latex was determined at various conversions by dynamic light scattering using a Malvern Autosizer. The experimental procedures for the synthesis of the graft copolymer and for the emulsion polymerizations were described previously.<sup>4</sup>

## RESULTS AND DISCUSSION

A series of well-defined graft copolymers, poly(methyl methacrylate-*co*-2-hydroxypropyl meth-

acrylate)-graft-polyoxyethylene copolymers were prepared by a method described previously.<sup>4</sup> Their general structure is illustrated below:



These amphipathic graft copolymers were used as stabilizers in the emulsion polymerization of methyl methacrylate and styrene. Since it is widely accepted that the stabilizing effectiveness of a surfactant is related to the number of particles formed in the aqueous phase and to the polymerization kinetics, the work in this study used this basis for its evaluation. In other words, the stabilizing effectiveness of the graft copolymer was said to increase as the rate of polymerization and number of particles increased.

### Effect of the Graft Copolymer Concentration

Prior to studying the effect of structural variations, the graft copolymer (stabilizer) concentration was optimized first. Its concentration (stabilizer/monomer ratio) was varied from 10 g/100 g to 25 g/100 g. This graft copolymer possessed the following molecular parameters: (i) 86% by weight of the copolymer was POE; (ii) molecular weight,  $M_w$ , of the graft units was  $2 \times 10^3$  g/mol; and (iii) molecular weight,  $M_n$ , of the backbone was  $1 \times 10^4$  g/mol. This structure was selected for the evaluation because it was believed that it would function as one of the better stabilizers.

The kinetic and particle size data are listed in Table II. As the graft copolymer, the stabilizer, amount was increased from 10 to 20 g while keeping the amount of the rest of the ingredients listed in Table I constant, the particle size was found to decrease from 230 to 116 nm and the rate of polymerization was found to increase from  $2.3 \times 10^{-4}$  mol/L s to  $4.0 \times 10^{-4}$  mol/L s. Increasing the stabilizer amount from 20 to 25 g had only a slight effect on the kinetics of polymerization and the particle size. The rate of polymerization remained fairly constant at  $4.1 \times 10^{-4}$  mol/L s. The particle size did not change either and remained between 106 and 116 nm. Moreover, the number of particles increased

**Table I** Recipe for the Emulsion Polymerization of Methyl Methacrylate

Ingredient	Weight (g)
Methyl methacrylate	10.00
Water	80.0
Potassium persulfate	0.05
Graft copolymer	2.0

**Table II** Effect of Varying the Graft Copolymer Concentration in the Emulsion Polymerization of Methyl Methacrylate

g/100 g Monomer	$R_p \times 10^4$ (mol/L s)	$D_z$ (nm)	$N \times 10^{-14}$ ( $\text{cm}^{-3}$ aq phase)
10	2.3	230	0.13
20	4.0	116	1.0
25	4.1	106	1.3

POE in graft copolymer,  $M_w = 2 \times 10^3$  g/mol. Monomer/water = 1/8.

with increasing surfactant concentration from  $1.3 \times 10^{13}$  to  $1.3 \times 10^{14}$   $\text{cm}^{-3}$  aq phase. These results illustrate the fact that by increasing the amount of surfactant more surface area was stabilized. This resulted in a decrease in the particle size and an increase in the particle number. As a larger number of particles formed in the aqueous phase remained stable, this situation resulted in more sites for the polymerization of monomer, and, thus, the polymerization rate increased.

#### Effect of Varying the Molecular Weight of the Backbone

Structure-property relationships of the graft copolymers synthesized in this study were examined. The first structural variation that was studied was the effect of varying the molecular weight of the backbone of the graft copolymer on its characteristics as a stabilizer in the emulsion polymerization of methyl methacrylate. Three different molecular weight backbones were studied,  $M_n = 4,000, 10,000, 20,000$  g/mol, while keeping the molecular weight distribution very narrow. The weight of POE in the copolymer was kept fairly constant, ca. 81%–86% by weight, and POE graft units had a molecular weight of  $M_w = 2,000$  g/mol. The objective of this experiment was to study the effect of the backbone chain length when using a graft copolymer with a suitable anchor group and a suitable stabilizing group. In this case, a suitable anchor group was predicted to be one that possessed a chain length between adjacent graft units of 3 to 4 monomer units. This was the spacing between graft units when the copolymer was composed of 81%–86% POE by weight. A suitable stabilizing group was predicted to be one that has a molecular weight of  $M_w = 2,000$  g/mol. Under these conditions, it was possible to study only the effects of varying the backbone chain length.

As can be seen from the data in Table III, the molecular weight of the backbone did not affect the characteristics of the emulsion polymerization within the range studied. In each case, the rate of polymerization was unaffected by the change in the molecular weight of the backbone of the graft copolymer. The measured rates were  $4.0 \times 10^{-4}$  mol/L s and  $4.5 \times 10^{-4}$  mol/L s. The numerical values for the particle diameters and the number of particles were practically the same. The measured particle sizes were 110, 116, and 114 nm. Therefore, it was concluded that the molecular weight of the backbone of the graft copolymer did not influence its stabilizing capability in the emulsion polymerization of methyl methacrylate when the graft copolymers were compared on a weight basis. In all cases, highly stable latices were obtained possessing the same particle size and number.

Since the weight percent of POE in the graft copolymer was constant, it was possible to calculate theoretical molecular weights of the graft copolymers. These values for surfactant #1 and #3 in Table III were  $1.3 \times 10^5$  and  $2.1 \times 10^4$  g/mol, respectively. As can be ascertained from these values, one molecule possessing the highest molecular weight is just as efficient in stabilizing the emulsion polymerization as are six molecules possessing the lowest molecular weight.

#### Effect of Varying the Molecular Weight of the Graft Units

In this segment of the present study, the effect on the stabilizing capability of the graft copolymer in the emulsion polymerization was examined as a function of the molecular weight of the POE graft units. Three different molecular weights were examined:  $M_w = 750, 2,000, \text{ and } 5,000$  g/mol. The molecular weight of the backbone was approximately  $M_n = 10,000$  g/mol. To study the effect of the molecular weight of the graft units, the weight percent of POE in the copolymer was kept fairly constant. For the graft units possessing a molecular weight of 2,000 and 5,000 g/mol, this was accomplished easily. However, for the graft units with a molecular weight of 750 g/mol, it was a little more difficult to keep the weight percent constant while still maintaining a large enough anchor group (backbone) between grafts. In this case, a graft copolymer with 75% POE by weight was studied. This graft copolymer was used because it possessed a long enough anchor group, ca. 2.5 monomer units. Moreover, this copolymer was within the proper hydrophilic/hydrophobic balance as suggested by Napper.<sup>2</sup>

As listed in Table III for graft copolymer #4, #5 and #6, the rates of polymerization were approximately  $4.0 \times 10^{-4}$  mol/L s. Although the rate of polymerization was not influenced, the particle size and the number of particles were affected by the molecular weight change of the graft units. As the molecular weight of the grafts was reduced from 2,000 to 750 g/mol, the stabilizing effectiveness of the graft copolymer had decreased. This conclusion is supported by the change in the particle size and number of particles in the resulting latex as shown in Table III. The particle size increased from 116 to 164 nm, and the number of particles decreased from  $1.0 \times 10^{14}$  particles  $\text{cm}^{-3}$  aq phase to  $4.0 \times 10^{13}$  particles  $\text{cm}^{-3}$  aq phase. However, graft copolymers possessing graft units with a molecular weight of 2,000 and 5,000 g/mol exhibited similar stabilizing effectiveness. The particle size and number of particles were 105 to 116 nm and  $1.0 \times 10^{14}$  to  $1.4 \times 10^{14}$  particles  $\text{cm}^{-3}$  aq phase, respectively. In both cases, highly stable lattices were obtained with a similar particle size and number.

#### Effect of Varying the POE Content

Two graft copolymers were prepared with different amounts of POE grafted onto a methacrylate backbone with approximately the same molecular weight of  $2 \times 10^4$  g/mol. Since the molecular weight of the POE was  $2 \times 10^3$  g/mol, the amount of POE in the copolymer was altered by varying the number of grafts per molecule. The higher molecular weight backbone was used to enhance the hydrophilic/hydrophobic changes. In other words, for the backbone

with the higher molecular weight, more POE chains were needed to change the POE amount from 67 to 85% than for a copolymer with a lower molecular weight backbone.

The particle size and the number of particles are listed as a function of conversion in Table IV. When the graft copolymer with 67% POE was used as the stabilizer (#1), the emulsion polymerization exhibited larger particle size than did the system using the graft copolymer with 85% POE as the stabilizer (#2). The particle size formed with graft copolymer #1 was 87 nm at 7% conversion as compared to 62 nm at 6% conversion for graft copolymer #2. Furthermore, the number of particles in the aq phase for graft copolymer #2 ( $5.1 \times 10^{13}$  particles  $\text{cm}^{-3}$  aq phase) was 2.5 times the number of particles for graft copolymer #1 ( $2.1 \times 10^{13}$  particles  $\text{cm}^{-3}$  aq phase). This implies that even at the initial stages of the polymerization graft copolymer #2 is a superior stabilizer. As the polymerization proceeded, the difference in the particle size and number of particles decreased. At the coagulation point for the polymerization system containing graft copolymer #1, the particle size and number of particles were 103 nm and  $5.9 \times 10^{13}$  particles  $\text{cm}^{-3}$  aq phase, respectively. For the system containing graft copolymer #2, the particle size and the number of particles at 28% conversion were 91 nm and  $7.5 \times 10^{13}$  particles  $\text{cm}^{-3}$  aq phase, respectively. Furthermore, the graft copolymer containing the lower amount of POE, 67% POE, stabilized the emulsion polymerization only to 32% conversion, and the particle size was slightly larger than was the emulsion polymerization stabilized with a graft copolymer containing

**Table III** Effect of Varying the Molecular Weight of the Backbone and the Graft Units of the Graft Copolymer on the Emulsion Polymerization of Methyl Methacrylate

	Backbone	MWD <sup>a</sup>	Wt. % POE <sup>b</sup>	$R_p \times 10^4$ (mol/L s)	$D_z$ (nm)	$N \times 10^{-14}$ ( $\text{cm}^{-3}$ aq phase)
	$M_n^a \times 10^{-3}$ (g/mol)					
#1	4	1.1	81	4.0	110	1.2
#2	10	1.2	86	4.0	116	1.0
#3	20	1.2	85	4.5	114	1.1
	Graft Units POE	MWD <sup>a</sup>	Wt. % POE <sup>b</sup>	$R_p \times 10^4$ (mol/L s)	$D_z$ (nm)	$N \times 10^{-14}$ ( $\text{cm}^{-3}$ aq phase)
	$M_w$ (g/mol)					
#4	750		75	3.9	164	0.4
#5	2000		86	4.0	116	1.0
#6	5000		85	4.1	105	1.4

Emulsion pzn of methyl methacrylate at 45°C. Monomer/water = 1/8. Surface conc = 20 g/100 g monomer (2.5% aq phase).

<sup>a</sup> Data obtained by GPC.

<sup>b</sup> POE in the graft copolymer.

**Table IV** Effects of Varying Polyoxyethylene (POE) Content of the Graft Copolymer and of Equal Spacing between Grafts in the Surfactant on the Emulsion Polymerization of Methyl Methacrylate

Effect of POE Content of the Graft Copolymer						
	Backbone $M_n^c \times 10^{-4}$ (g/mol)	Wt. % POE <sup>b</sup>	$R_p \times 10^4$ (mol/L s)	$D_z$ (nm)	$N \times 10^{-13}$ (cm <sup>-3</sup> aq phase)	Conv (%)
#1	1.8	67	—	87	2.1	7
				99	3.9	19
				103	5.9	32 <sup>a</sup>
#2	2.0	85	4.5	62	5.1	6
				81	7.6	20
				91	7.5	28
				114	10.9	80
Effect of Equal Spacing between Grafts in the Surfactant						
	Graft copolymer $M_w$ of grafts	Wt. % POE	$R_p \times 10^4$ (mol/L s)	$D_z$ (nm)	$N \times 10^{-13}$ (cm <sup>-3</sup> aq phase)	Conv (%)
#3	2000	67	—	87	2.1	7
				99	3.9	19
				103	5.9	32 <sup>a</sup>
#4	5000	85	4.1	66	5.0	10
				78	6.7	21
				95	7.3	35
				105	14.0	75

Surface conc 20 g/100 g monomer (2.5% aq phase). Monomer/water = 1/8.

<sup>a</sup> Latex coagulated.

<sup>b</sup> POE in surfactant  $M_w = 2 \times 10^3$  g/mol.

<sup>c</sup> Results obtained by GPC.

85% POE. These data clearly show that the graft copolymer with 85% POE (#2) is a superior stabilizer to the graft copolymer with 67% POE (#1). This conclusion is supported by the fact that coagulation occurred for the system using graft copolymer #1. It should be noted that both of the copolymers are completely water-soluble. Therefore, these results are not due to incomplete dissolution of the graft copolymer in water or the continuous phase. These results clearly show that for effective stabilization a critical amount of POE must be contained in the graft copolymer. So when designing a polymeric stabilizer for use in emulsion polymerization, water solubility or solubility in the continuous phase is not the only parameter that must be considered. The stabilizer must have a high enough hydrophilic/hydrophobic balance for the system. In this case, 85% by weight of the graft copolymer should be the hydrophilic portion.

### Equal Spacing between Grafts

The previous experiment illustrated the importance of the amount of POE in the graft copolymer. The question that must be answered is, What effect does equal spacing between grafts in the copolymer have on the emulsion polymerization as the molecular weight of the graft chains are varied? In this case, the effect of increasing the molecular weight of the POE graft chains from 2000 to 5000 g/mol while keeping the spacing between graft chains constant was examined. The average number of monomer units between grafts for the copolymer with 2000 g/mol graft chains and 5000 g/mol graft chains were 10 and 9, respectively. Since there were approximately 10 monomer units between graft chains on average, the increase in the molecular weight from 2000 to 5000 g/mol resulted in a change in the amount of POE from 67% to 85% by weight.

The effect on the particle size and particle number is illustrated in Table IV. As this table shows, there was a pronounced effect on the stabilizing capability of copolymer #3. Graft copolymer #4 stabilized the emulsion polymerization throughout conversion, but graft copolymer #3 did not. The emulsion polymerization using this copolymer as the stabilizer coagulated at 32% conversion.

The previous two experiments examined the effect of changing the POE chain length while keeping the weight percent or the spacing between grafts constant in the copolymer. When the molecular weight of the graft units was changed from 2000 to 5000 g/mol at a constant weight percent of POE, the graft copolymers were both very efficient stabilizers for the emulsion polymerization as reflected by the rate of polymerization, particle size, and particle number data. As is shown in Table III, the rate of polymerization, particle size, and number of particles for copolymer #5 and #6 were approximately  $4.0 \times 10^{-4}$  to  $4.1 \times 10^{-4}$  mol/L s, 116 to 105 nm, and  $1.0 \times 10^{14}$  to  $1.4 \times 10^{14}$  cm<sup>-3</sup> aq phase, respectively. These results indicate that the stabilizing effectiveness of the graft copolymers was not changed by altering the molecular weight of the POE graft units. However, for copolymers #3 and #4 in Table IV, the stabilizing capability was dependent on the POE chain length when the spacing between grafts was kept constant. In this case, the stabilizing effectiveness for these two graft copolymers was not equivalent. Graft copolymer #3, which possessed POE graft chains with a molecular weight of 2000 g/mol, was not as effective in stabilizing the emulsion polymerization of methyl methacrylate as was graft copolymer #4, which possessed POE graft chains with a molecular weight of 5000 g/mol, because the system containing copolymer #3 coagulated at 32% conversion. From these results, a constant weight percent of POE appears to be more important than does equal spacing between POE graft chains in the copolymer.

When determining whether an amphipathic polymeric material will stabilize a colloidal dispersion, the most important factor to consider is the amount of the stabilizing moieties anchored to the colloidal particles. A high concentration of polymeric chains or stabilizing moieties is required for effective stabilization because repulsive forces between the particles is related to this concentration. As was mentioned previously, this repulsive force is a result of unfavorable free-energy changes due to mixing of the polymeric chains as the colloidal particles approach each other, and these free-energy changes

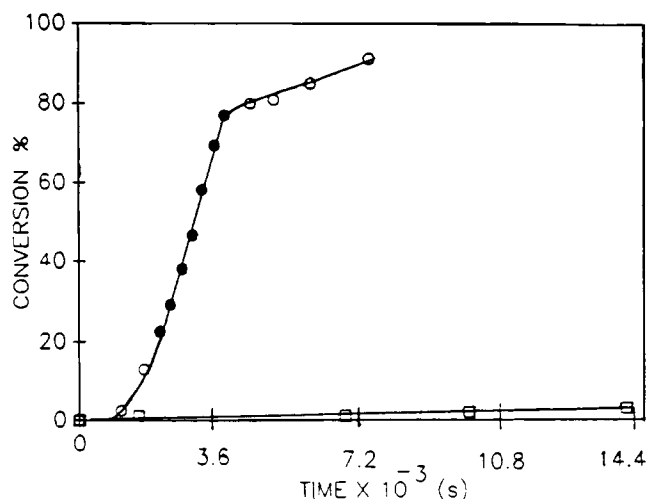
are proportional to the concentration of the stabilizing moieties.

In the present study, when the spacing between grafts was kept constant, the concentration of the stabilizing moieties was reduced by decreasing their molecular weight. However, when the weight percentage of the POE graft units was kept constant, the concentration did not change by altering the molecular weight. Therefore, in this experiment, the reduction in the stabilizing effectiveness by lowering the molecular weight of the POE graft units was caused by decreasing the concentration of the graft units and was not caused by decreasing the molecular weight.

### Comparison of Polyoxyethylene to Poly(Methyl Methacrylate-co-2-Hydroxypropyl Methacrylate)-Graft-Polyoxyethylene

In this segment of the study, the stabilizing effectiveness of the graft copolymer, poly(methyl methacrylate-co-2-hydroxypropyl methacrylate)-graft-polyoxyethylene was compared to POE in the emulsion polymerization of methyl methacrylate. The graft copolymer with graft chains of  $M_w = 2,000$  g/mol and with graft chains of  $M_w = 5,000$  g/mol was compared to POE of  $M_w = 2,000$  and 5,000 g/mol. The purpose of this segment of the study was to evaluate importance of the hydrophobic methacrylate portion of this amphipathic graft copolymer. Since the hydrophobic portion of the surfactant functions by anchoring the stabilizing moieties to the particles, the results of these experiments illustrated the importance of anchoring. Conversion vs. time plots are shown in Figures 1 and 2. The emulsion polymerization of MMA using the graft copolymer as the stabilizer is represented by the circles, and the emulsion polymerization of MMA using POE as the stabilizer is represented by the squares. As can be seen from both figures, when using the graft copolymer as the stabilizer, rapid polymerization and high conversion were obtained in about 2 hr. However, conversion as a function of time was very slow, and coagulation occurred at very low conversion when POE was the sole stabilizer.

Particle size data are listed in Table V. As the data show, oxyethylene homopolymers with molecular weights of 2,000 and 5,000 g/mol were very inefficient stabilizers for this system. The particle sizes were quite large, 279 and 780 nm at 2% and 3% conversions, and the latex coagulated at very low conversions, ca. 3% conversion. The number of particles decreased from  $1.9 \times 10^{11}$  particles cm<sup>-3</sup> aq



**Figure 1** Conversion vs. time plot for the emulsion polymerization of methyl methacrylate using polyoxyethylene or the graft copolymer as the stabilizer. ○: PMMA-g-POE, where  $M_w = 2,000$  g/mol for the POE grafted chains; □: POE -  $M_w = 2,000$  g/mol.

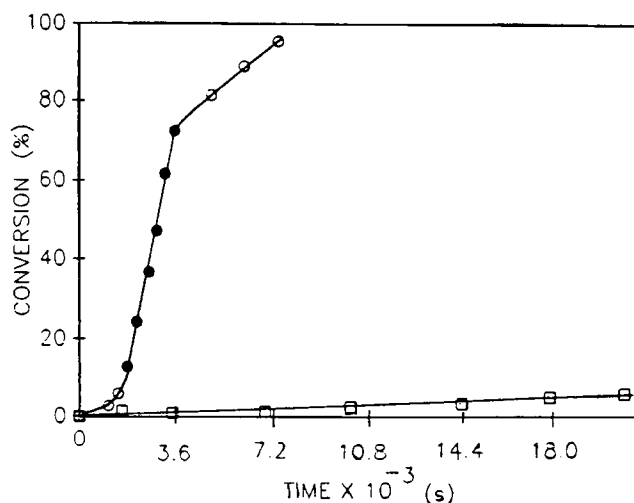
phase to  $1.3 \times 10^{10}$  particles  $\text{cm}^{-3}$  aq phase. This indicates that coagulation occurred from the onset of polymerization. However, for the graft copolymer with the grafted chains of POE (molecular weight = 2,000 g/mol), the particle sizes were much smaller (110 nm) at a higher percent conversion. Moreover, there was a larger number of particles in the aqueous phase and the latex was stable throughout the conversion. Similarly, the graft copolymer with grafted chains of POE (molecular weight 5,000 g/mol) was a very efficient stabilizer. Again, when used in the emulsion polymerization of methyl methacrylate, small particle size (105 nm) and a large number of particles were observed even at high conversion and the latex was stable throughout conversion. However, POE with a molecular weight of 5000 g/mol was a very inefficient stabilizer as reflected in the particle size and number. These results illustrate unequivocally that the hydrophobic group of the amphipathic graft copolymer (stabilizer) is required for effective stabilization. When the hydrophilic chains (POE chains) were used alone, the stability of the emulsion polymerization was extremely poor. These experiments demonstrate the anchoring effect of the surfactant. In order to observe highly stable systems, the stabilizer must be firmly anchored to the colloidal particles.

#### Effect of Varying the Chemical Nature of the Monomer

The present study evaluated the effect of polymerizing different monomers in the presence of the

MMA-OE graft copolymer. The results of this experiment were in accordance with expectations based on the work of Piirma and Chen.<sup>1</sup> They found that adsorption of a potassium oleate, a low molecular weight surfactant, to colloidal particles can be considerably different when the particles are composed of different polymers. In their study, they found that there was larger quantities of the surfactant on the colloidal particles when the particles were composed of polystyrene than when the particles were composed of poly(methyl methacrylate-co-styrene).

The results of the present study showed that the stabilizing effectiveness of a polymeric surfactant, poly(methyl methacrylate-co-2-hydroxypropyl methacrylate)-graft-polyoxyethylene, was dependent on the chemical nature of the colloidal particles. The chemical nature of colloidal particles was altered by changing the type of monomer in the emulsion polymerization. In this case, styrene and methyl methacrylate were independently evaluated. The recipes for the emulsion polymerizations were identical in both cases, and this recipe is listed in Table I. The conversion vs. time plots are shown in Figure 3. As shown by this figure, the emulsion polymerization of methyl methacrylate exhibited typical emulsion polymerization characteristics when using the graft copolymer as the stabilizer. These characteristics were rapid polymerization and high stability throughout the polymerization process. As



**Figure 2** Rate plot for the emulsion polymerization of methyl methacrylate using polyoxyethylene or the graft copolymer as the stabilizer. ○: PMMA-g-POE where  $M_w = 5,000$  g/mol for the POE grafted chains; □: POE -  $M_w = 5,000$  g/mol.

**Table V Particle Size Comparison of Emulsion Polymerizations Stabilized with Polyoxyethylene (POE) or the Graft Copolymer (from Ref. 5)**

POE $M_w$ (g/mol)	Wt. % PMMA in Graft	$D_z$ (nm)	$N \times 10^{-11}$ ( $\text{cm}^{-3}$ aq phase)	Conv. (%)
2000	None	279	1.9	2
2000	None	780	0.13	3 <sup>a</sup>
2000	19	110	1210	80
5000	15	105	1440	75
5000	None	287	2.2	2.6
5000	None	1200	0.07	6 <sup>a</sup>

Emulsion pzn of methyl methacrylate at 45°C. Stabilizer conc = 20 g/100 g monomer (2.5% aq phase). Monomer/water = 1/8.

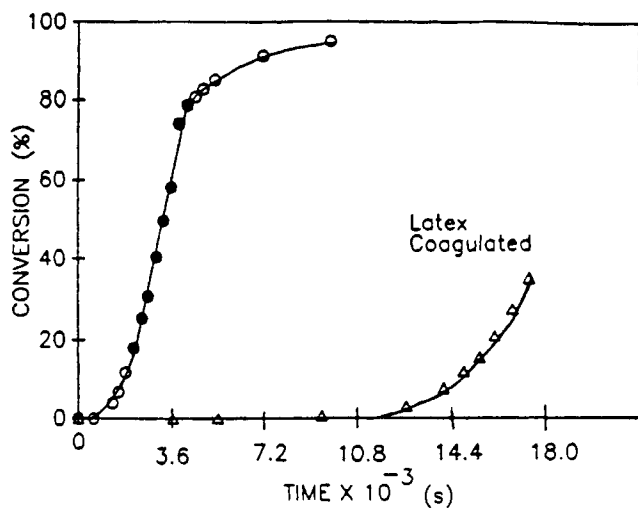
<sup>a</sup> Latex coagulated.

previously discussed, these results proved that the graft copolymer was a very efficient stabilizer for this emulsion polymerization. Moreover, the chemical nature of the hydrophobic group of the surfactant and the monomer used in the emulsion polymerization were similar so that association occurred between them. This association induced complete coverage of the colloidal particles with the graft copolymer during the emulsion polymerization. Thus, the colloidal system exhibited excellent stability.

As shown in Figure 3, the emulsion polymerization of styrene exhibited a different behavior than the one for the emulsion polymerization of methyl methacrylate. There was a more pronounced induction time than for the emulsion polymerization of MMA. This observation could be attributed to low

association between the surfactant and the growing oligomeric radicals in the aqueous phase.

Once the polymerization began, the course of the emulsion polymerization of styrene was very much the same as in the other system. However, at approximately 36% conversion, coagulation occurred. This event is a result of poor anchoring of the poly(methyl methacrylate) backbone onto the polystyrene particles. Since PMMA is more polar than is polystyrene, the polymeric surfactant preferred to remain in the aqueous phase rather than be adsorbed by the polystyrene particles. This event dramatically reduced the amount of surfactant on the particles. Moreover, the small amount of surfactant that was adsorbed by the particles was not firmly anchored to the particles and desorption occurred quite readily. Thus, instability resulted at a very low percent conversion.



**Figure 3** Comparison of the emulsion polymerizations of different monomers using the graft copolymer as the stabilizer. O: methyl methacrylate; Δ: styrene.

## CONCLUSIONS

The effect of structural variations of the poly-(methyl methacrylate-co-2-hydroxypropyl methacrylate)-graft-polyoxyethylene was studied in the emulsion polymerization of methyl methacrylate. It was found that the molecular weight of the backbone of the graft copolymer in the range of  $M_n = 4,000$  to 20,000 g/mol did not influence the emulsion polymerization kinetics, the latex particle size, and number of particles. In all cases, highly stable latices were obtained possessing the same particle size and number.

A parameter that influenced the stabilizing effectiveness of the graft copolymer was the chain length of the polyoxyethylene (POE). It was found that low molecular weight graft moieties, ca. 750 g/



mol, influenced the stabilizing effectiveness of the graft copolymer as reflected in the particle size and number. As the molecular weight of the grafts was reduced from 2,000 to 750 g/mol, the particle size of the resulting lattices had increased substantially and the number of particles had decreased, indicating a reduction in the stabilizing capability of the graft copolymer. However, graft copolymers possessing graft units with a molecular weight of 2,000 and 5,000 g/mol exhibited similar stabilizing effectiveness when the weight percent of POE was kept constant. In both cases, highly stable lattices were obtained with a similar particle size and number. It was found that the stabilizing capability of the graft copolymer was not the same if the molecular weight of the graft units was varied from 2,000 to 5,000 g/mol while keeping the spacing between them constant. The copolymer with graft units possessing a molecular weight of 5000 g/mol was a more efficient stabilizer than was the copolymer with graft units possessing a molecular weight of 2000 g/mol. The previous two experiments illustrate that the weight percent of POE in the copolymer is the important factor when altering the molecular weight of the stabilizing (POE) moieties.

Another parameter that influences the stabilizing effectiveness is the amount of POE. Graft copolymers with a high POE content (85% by weight) functioned quite effectively as stabilizers, but graft copolymers with a low POE content (67% by weight) were not effective stabilizers in the emulsion polymerization of methyl methacrylate. It was believed that copolymers with a high POE content possessed enough POE to provide an effective repulsive barrier on the surface of the particles (proper hydrophilic/hydrophobic balance), but ones with a low POE content did not provide an effective barrier.

One excellent experiment to test the effect of attachment (anchoring) of the POE grafted chains to

the colloidal particles is to compare the stabilizing effectiveness of the graft copolymer to POE. The results of this study clearly demonstrated that anchoring of the stabilizing moieties (POE graft chains) to the colloidal particles is crucial. Excellent stability was observed when the stabilizing moieties (POE) were firmly anchored to the colloidal particles by the methacrylate portion of the graft copolymer. However, polymeric macromolecules that were free in solution (free POE) were very inefficient stabilizers. These systems coagulated at very low conversions.

The chemical nature of the monomer used in the emulsion polymerization affected the stability of the resulting latex. It was found that the graft copolymer did not stabilize the emulsion polymerization of styrene. This system coagulated at low conversion. The instability of the styrene emulsion polymerization was attributed to the inability of the graft copolymer to anchor to the nonpolar particles. As a result, a lower amount of the graft copolymer was attached to the colloidal particles, which caused a reduction in the stability of the emulsion polymerization.

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*Received March 8, 1990*

*Accepted May 17, 1990*