Kinetic Study on the Poly(methyl methacrylate) Seeded Soapless Emulsion Polymerization of Styrene. I. Experimental Investigation

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SYNOPSIS

In this work, methyl methacrylate (MMA) and styrene (ST) were used as monomers in the first stage and second stage of polymerization, respectively, and potassium persulfate ($K_2S_2O_8$) was used as the initiator to synthesize the poly(methyl methacrylate)-polystyrene (PMMA/PS) composite latex by the method of two-stage soapless emulsion polymerization, i.e., PMMA seeded soapless emulsion polymerization of styrene.

The morphology of the latex particles was observed by transmission electron microscopy (TEM). It showed that the composite latex particles had a core–shell structure. The particle-size distribution of the composite latex was very uniform.

The kinetic data of seeded soapless emulsion polymerization showed that the square root of polymer yield $(Wp)^{1/2}$ was proportional to the reaction time in the earlier period of the reaction. The slope of the line of $(Wp)^{1/2}$ vs. reaction time was independent of the content of the seed, but proportional to 0.5 power of the initiator concentration. The gel effect was apparent after monomer droplets disappeared. A glassy effect was found in the latter period of the reaction. The number-average molecular weight of the polymers increased but the weight-average molecular weight of the polymers decreased with decrease of the MMA/ST weight ratio. The number- and weight-average molecular weight increased with decreasing the temperature significantly. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, the seeded emulsion polymerization (or two-stage emulsion polymerization) was often used to synthesize core–shell polymer/polymer composites in industry. The core–shell structure could enhance the compatibility between the two phases of the polymer/polymer composite and could improve the interfacial adhesion between the two phases of the incompatible polymers. By the method of seeded emulsion polymerization, the core size could be easily controlled and the particle size was uniform. The core–shell polymer/polymer composites might include reinforced elastomers, high-impact plastics, toughened plastics, etc.

There were many factors to control the kinetics and morphology of polymer particles, such as the method of the monomer added into the system,[1,2] the sequence of monomers fed into the system, the monomer ratio in two stages, the hydrophilicity of the monomers, the surface tension, the molecular weight of the polymers,[2-4] the compatibility of the polymers,[5] and the properties of the initiators.[6]

Okubo et al. pointed out that the morphology of polymer particles could change with the molecular weight of the polymers, viscosity of polymerization loci, and hydrophilicity of the two polymers.[7-9] Lee and Ishikawa synthesized two kinds of hydrophilic seeds which had high molecular weight and low molecular weight, respectively, and the morphology of the particles changed with the molecular weight of the polymers. The effect of the monomer ratio in two stages on the particle morphology was also studied.[3] Muroi and Hosoi studied the structure of the core–shell latex particle. They pointed out that the polymer particle formed an inverted core–shell morphology when the hydrophobic monomer of the

Table I   Ingredients and Conditions for the Synthesis of Seed Latex (First Stage)

Methyl methacrylate (g)	120
Initiator ($K_2S_2O_8$) (g)	0.866
Deionized water (g)	1100
Temperature (°C)	70
Stirring rate (rpm)	300
Reaction method	Bath

second stage was polymerized in the presence of hydrophilic seeds.[10]

In this work, styrene was synthesized in the presence of poly(methyl methacrylate) (PMMA) seeds by the method of soapless emulsion polymerization, which formed the PMMA/polystyrene (PS) polymer/polymer composite latex. The purpose of this work was to investigate the morphology of the composite latex and to study the kinetics of the reaction.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and styrene (ST) were distilled under a nitrogen atmosphere and reduced pressure prior to polymerization. Water was redistilled and deionized. Other chemicals were of analytical grade and used without further purification.

Ingredients and Conditions for Polymerization Polymerization

As seen in Table I, in the first stage of the reaction, MMA was used to synthesize the PMMA seed latex. The synthesis of the seed latex was carried out at 70°C. The stirring rate was controlled at 300 rpm. Nitrogen was bubbled through the reaction mixture, and quantitative MMA and potassium persulfate were added into the reactor. The reaction went on for 1 h and the polymerization reaction of the first

Table II   Ingredients and Conditions for the Synthesis of Composite Latex in Seeded Polymerization (Second Stage)

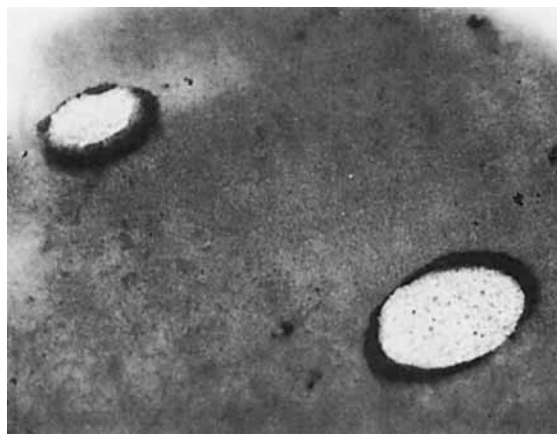|	
Seed latex (g)	300–750
Styrene (g)	73.77–98.36
Initiator ($K_2S_2O_8$) (g)	0.5–2
Deionized water (g)	85–490
Temperture (°C)	60, 70
Stirring rate (rpm)	300
Reaction method	Bath

Figure 1   TEM photograph (magnification = 75 K) of sectioned polymer particles at the end of the second-stage reaction; seed latex = 49.18 g; $K_2S_2O_8$ = 0.855 g; T = 70°C; ST = 73.77 g (MMA/ST = 1/1.5).

stage was complete; then, the seed latex was quenched to room temperature. In the second stage of the reaction, as seen in Table II, quantitative ST was added into the seed latex and the seeds were swollen for 24 h at room temperature. Then, the reaction system was heated in a water bath at the temperature of the reaction. The aqueous solution of $K_2S_2O_8$ was added into the reactor after the temperature of the system reached the temperature of the reaction and the reaction of the second stage began.

Conversion

At certain times during the second stage of polymerization, a sample of the emulsion latex was taken out of the reactor and poured into methanol with hydroquinone to stop the reaction. The precipitated polymers were washed with methanol and water several times and then dried in a vacuum oven.

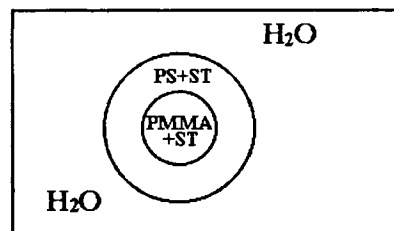The conversion of the seeded polymerization was calculated as follows:

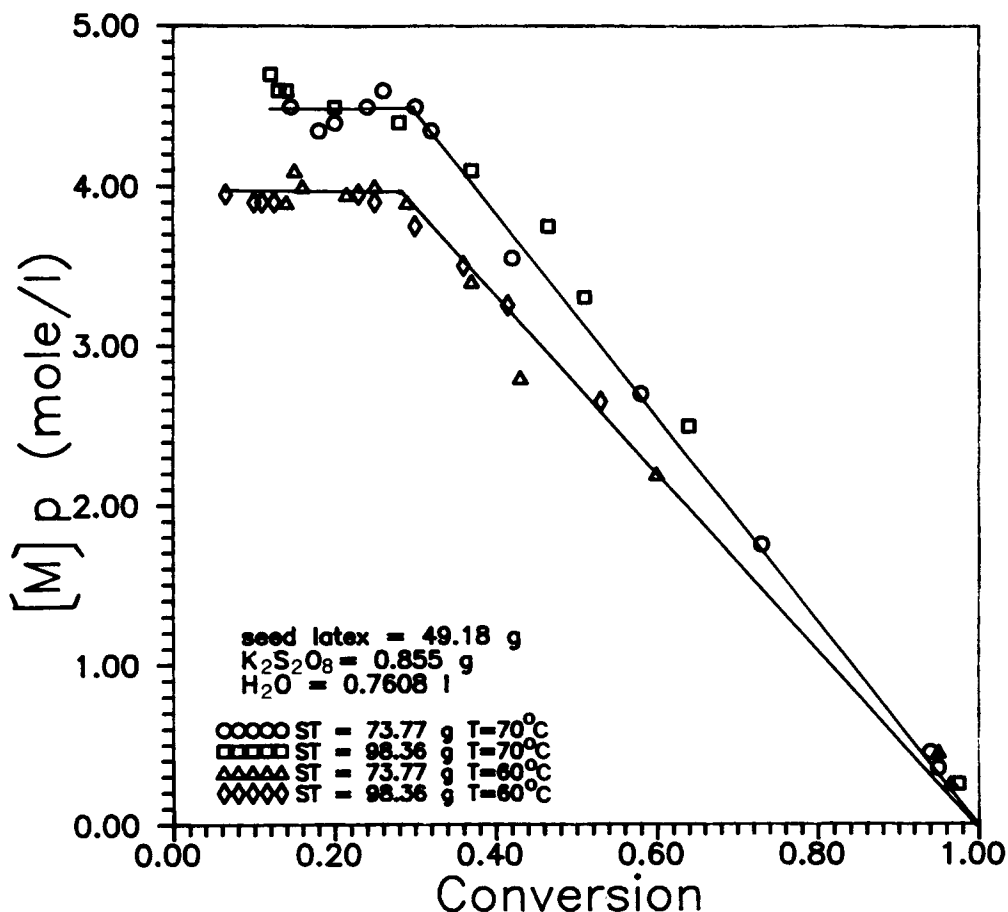**Figure 2**   The composite latex particle dispersed in water.

Figure 3   Concentration of monomer in polymer particles vs. conversion in the second-stage polymerization.

$$Conversion(x) = \frac{W_2 - W_1 \times B\%}{W_1 \times M_0(ST)\%}$$

where W_1 is the weight of the sample taken from the vessel; W_2, the weight of dry polymers obtained from the taken sample; $M_0(ST)\%$, the weight percentage of styrene monomer in the reaction mixture; and $B\%$, the weight percentage of PMMA in the reaction mixture.

Particle Size and Size Distribution

The samples taken from the reactor over the course of the seeded polymerization of ST would contain polymer particles and monomer droplets. The ST monomer droplets could be removed by centrifugation. The remaining samples then reacted at 90°C for 36 h with further addition of the initiator. The reaction was complete, and the size and size distribution of the polymer particles were determined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

Concentration of Monomer in Polymer Particles

A quantitative sample was taken out from the second stage of the reaction system, and the aqueous solution of hydroquinone was added into the sample to stop the reaction. The monomer droplets were removed away from the sample by the method of centrifugation. Then, the remaining sample was divided into two equal-weight parts.

Quantitative hydroquinone and methanol were added into one part and filtered and dried in oven at 80°C. The dry sample weight was designated as P. Quantitative $K_2S_2O_8$ was added into another part of the sample and reacted in a close system at 90°C for 36 h. After the reaction, the sample was dried in an oven at 80°C; the dry sample weight was designated as Q.

Assuming that the volumes of the polymer and monomer in the polymer particles were additive, then the monomer concentration in the polymer particles was calculated as
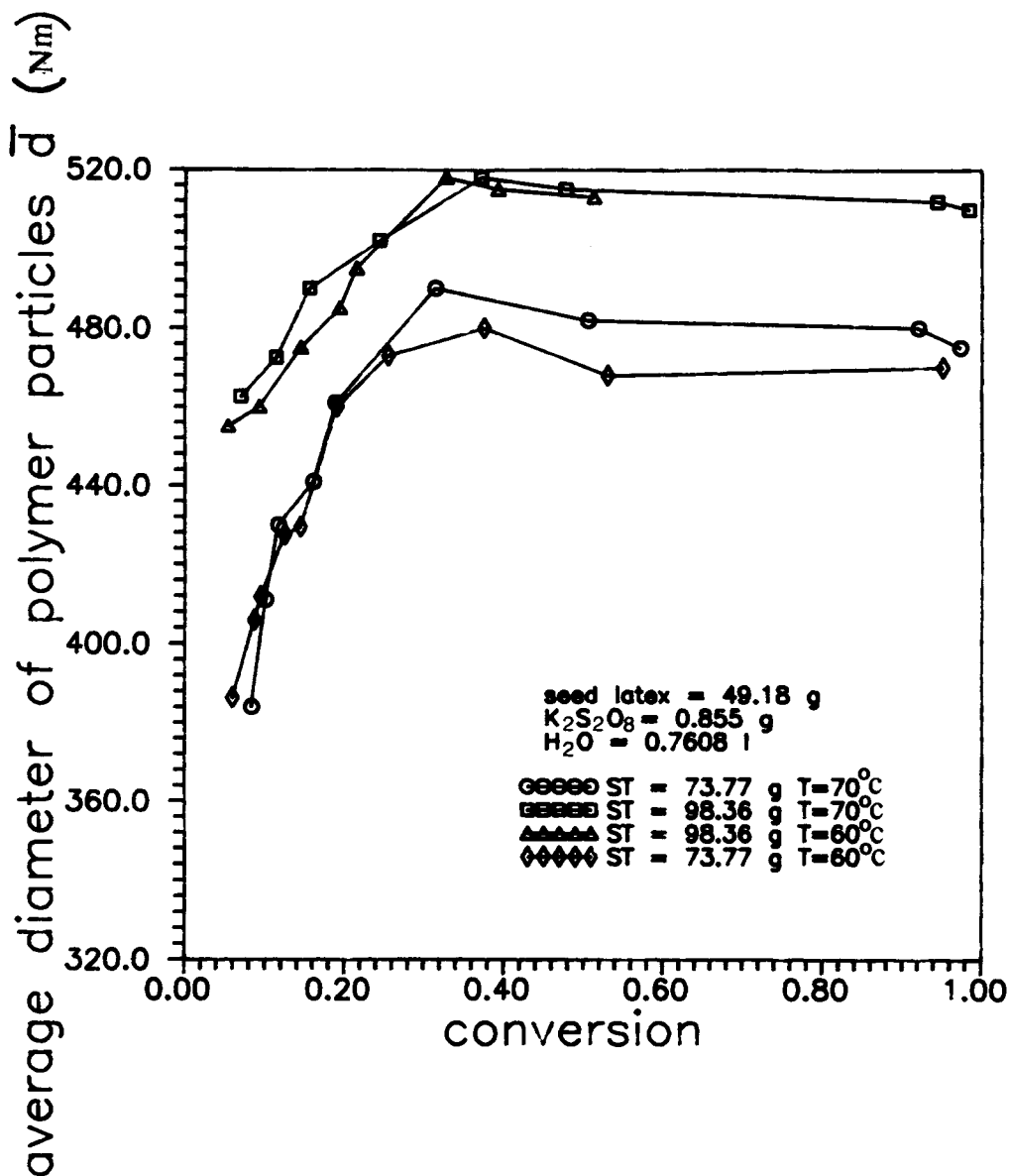
Figure 4 Average diameter of polymer particles from TEM measurement vs. conversion in the second-stage polymerization.

$$[M]_P = \frac{(Q - P)}{\dfrac{P}{\bar{\rho}_P} + \dfrac{(Q - P)}{\rho_M}} \times \frac{1}{104}$$

where $\bar{\rho}_P$ is the average density of PMMA and PS (1120.5 g/L); ρ_M, the density of ST (905 g/L)[11]; 104, the molecular weight of ST; and $[M]_P$, the monomer concentration in the polymer particles.

Molecular Weight Determination

The average molecular weight of the polymers was determined with a Shodex RI gel permeation chro-

matograph (GPC Model SE-61) on dry samples dissolved in tetrahydrofuran. In the seeded polymerization, the polymer that we obtained contained both PMMA and PS, so a mixed Q factor used in our calculation of the GPC curve was required:

$$\frac{1}{Q_{mix}} = \frac{W_{PMMA}}{Q_{PMMA}} + \frac{W_{PS}}{Q_{PS}}$$

where Q_{mix} is the mixed Q factor of PMMA and PS; Q_{PMMA}, the Q factor of PMMA ($Q = 23$); Q_{PS}, the Q factor of PS ($Q = 41$); W_{PMMA}, the weight fraction
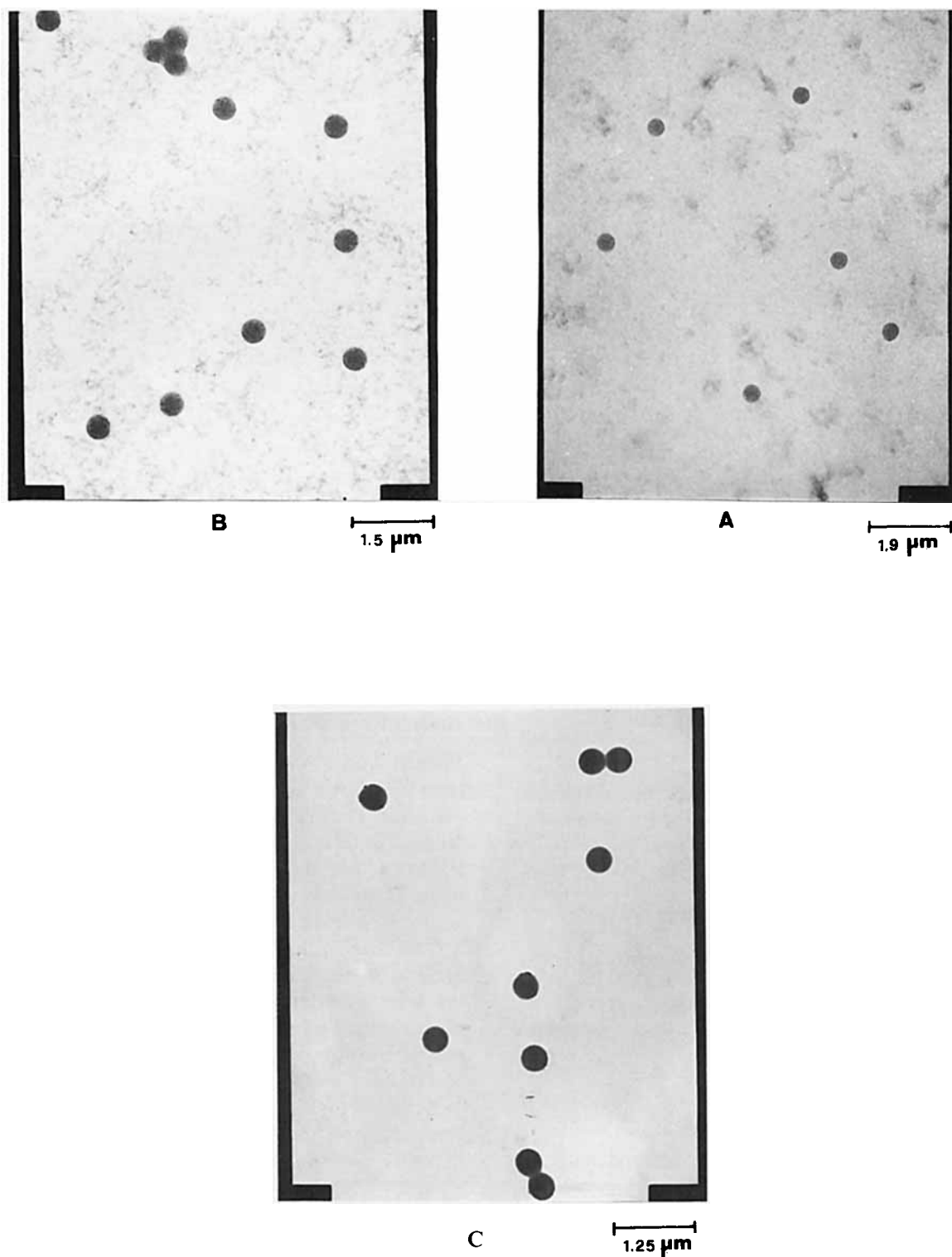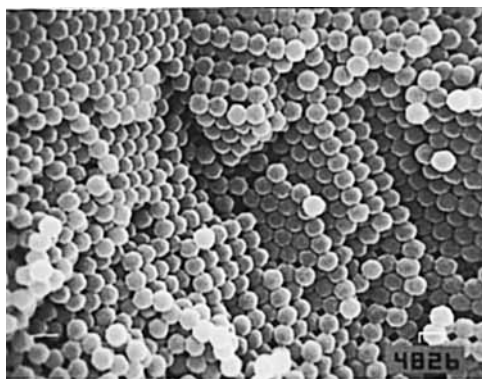
Figure 5   TEM photographs of PMMA/PS composite polymer particles at different reaction times in the second-stage polymerization at 70°C: with seed latex = 49.18 g; $K_2S_2O_8$ = 0.855 g; H_2O = 0.7608 L; ST = 73.77 g (MMA/ST = 1/1.5): (A) t = 4 min, $\bar{d}$ = 412.5 nm; (B) t = 8 min, $\bar{d}$ = 420 nm; (C) t = 20 min, $\bar{d}$ = 433 nm.

1.8μm

Figure 6 SEM photograph of PMMA/PS composite polymer particles at the end of the second-stage polymerization at 70°C with seed latex = 49.18 g, $K_2S_2O_8$ = 0.855 g, H_2O = 0.7608 L, ST = 73.77 g (MMA/ST = 1/1.5).

of PMMA in the polymers; and W_{PS}, the weight fraction of PS in the polymers.

Then, the number (or weight)-average molecular weight of the polymers containing both PMMA and PS was calculated as

$$\bar{M}_{n(mix)}(\text{or } \bar{M}_{w(mix)}) = G \times \frac{Q_{mix}}{Q_{PS}}$$

where G is the number (or weight)-average molecular weight measured by GPC based on PS standards, and Q_{PS}, the Q factor of PS.

Observation of Particle Morphology

The latex particles from the seeded polymerization were ultramicrotomed and stained with RuO_4. The stained sections of the latex particles were observed under the TEM.

RESULTS AND DISCUSSION

Morphology

The PMMA seeds were synthesized under the conditions listed in Table I. The average size of PMMA seeds was about 314 nm and the size distribution was very uniform. The concentration of the polymer particles in the seed emulsion was about 5.71×10^{15} L/L-H_2O. Then, the seeded emulsion polymerization of ST was carried out under the conditions listed in Table II and the morphology of PMMA/PS com-

posite latex particles was observed under TEM. It showed a core–shell structure as seen in Figure 1. In this figure, the dark zone is PS and the bright zone is PMMA. A core–shell kinetic model was proposed in our following work[12] to describe the mechanism and kinetics of the synthesis of the core–shell latex particle. Actually, the morphology of the polymer particle could vary with different kinds of initiators. For example, if azobisiobutyronitrile (AIBN) was used as the initiator instead of to synthesize the PMMA/PS composite latex, the PMMA/PS composite latex particle was found to be of a homogeneous morphology.[12] In fact, the core–shell morphology of the latex particle formed in this work by using $K_2S_2O_8$ as the initiator could be explained from both kinetic and thermodynamic factors.

Kinetic Factor

In our reaction system, $K_2S_2O_8$ was used as the initiator. The SO_4^- group, which decomposed from $K_2S_2O_8$, anchored on the surface of the latex particle, so the polymerization proceeded on the shell region of the latex particle. In the first stage of the reaction, the PMMA core was formed and was followed by the formation of the PS shell in the second stage of the reaction.

Thermodynamic Factor

PMMA and PS were incompatible polymers, but both could dissolve in ST very well. During soapless emulsion polymerization of ST with PMMA as seeds, the latex particle included the region of PMMA + ST and the region of PS + ST, and the latex particle was surrounded by water in the reaction system as seen in Figure 2.

The interfacial tension would control the morphology of the composite latex particle. Although the interfacial tension of PS to water was slightly higher than that of PMMA to water,[6] in emulsion polymerization, the latex particle was surrounded by the ionic groups (SO_4^-), which decreased the interfacial tension of the PS shell to water significantly.[6] Therefore, the core–shell structure of the particle was rather stable in the emulsion.

Concentration of Monomer in Polymer Particles ($[M]_p$)

The relation between the conversion and concentration of the monomer in polymer particles during the seeded polymerization was observed from experiments. The result is shown in Figure 3. In the earlier period of the reaction, ST monomer droplets
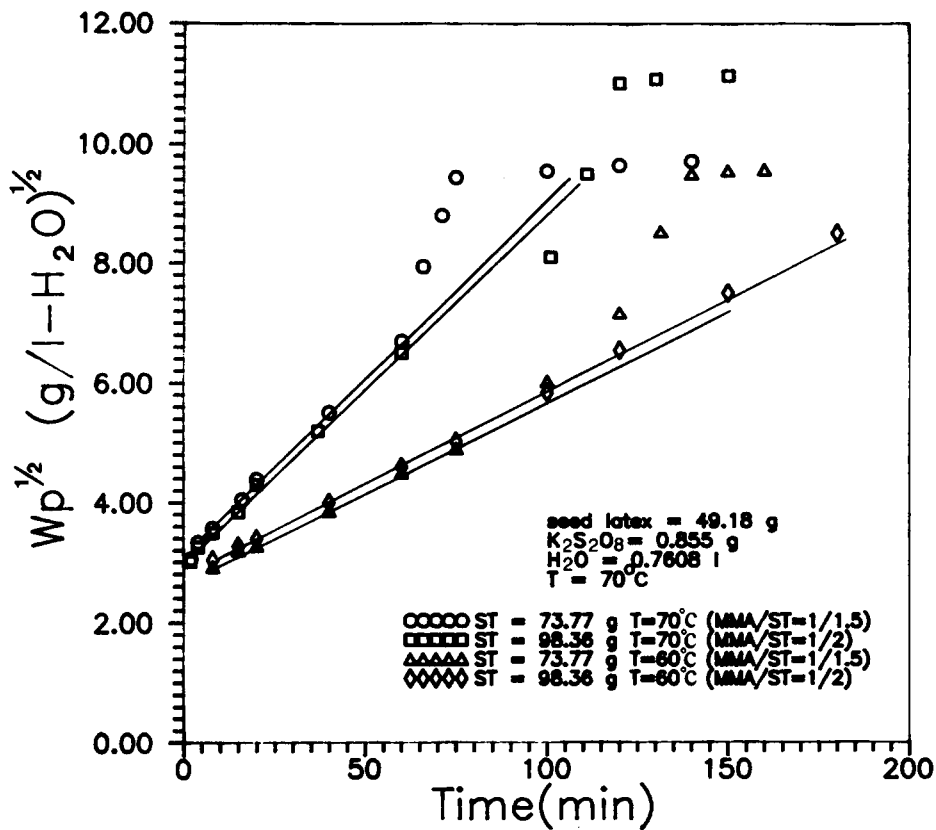
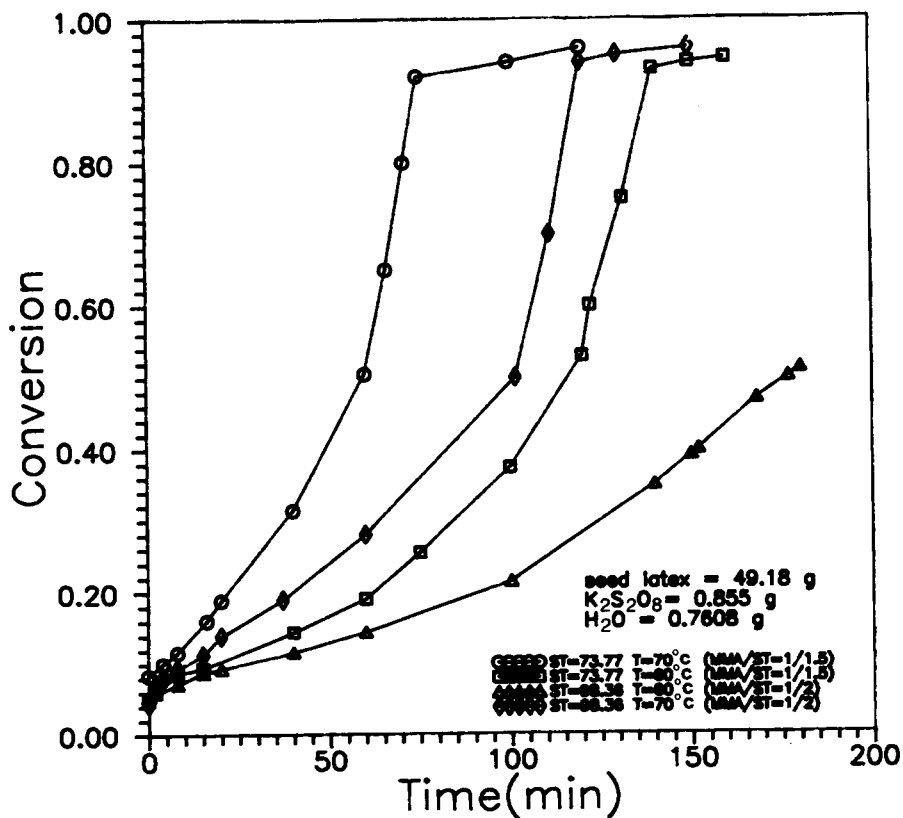**Figure 7** $(Wp)^{1/2}$ vs. reaction time in the second-stage polymerization.

Figure 8   Conversion vs. reaction time at different MMA/ST weight ratios and different temperatures in the second-stage polymerization.
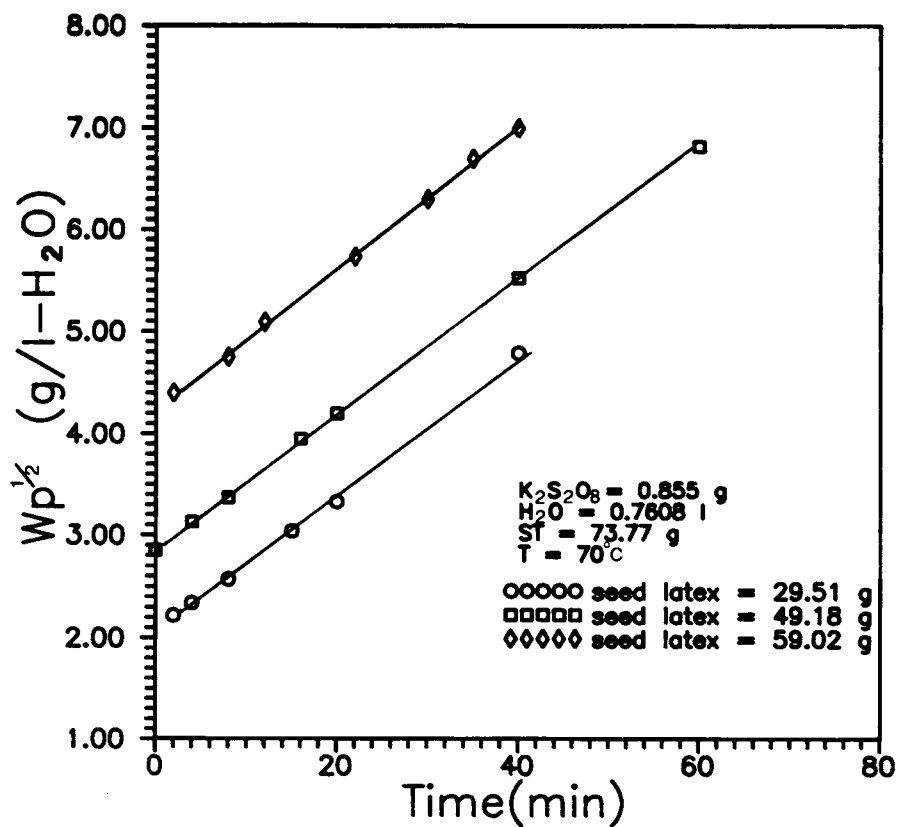
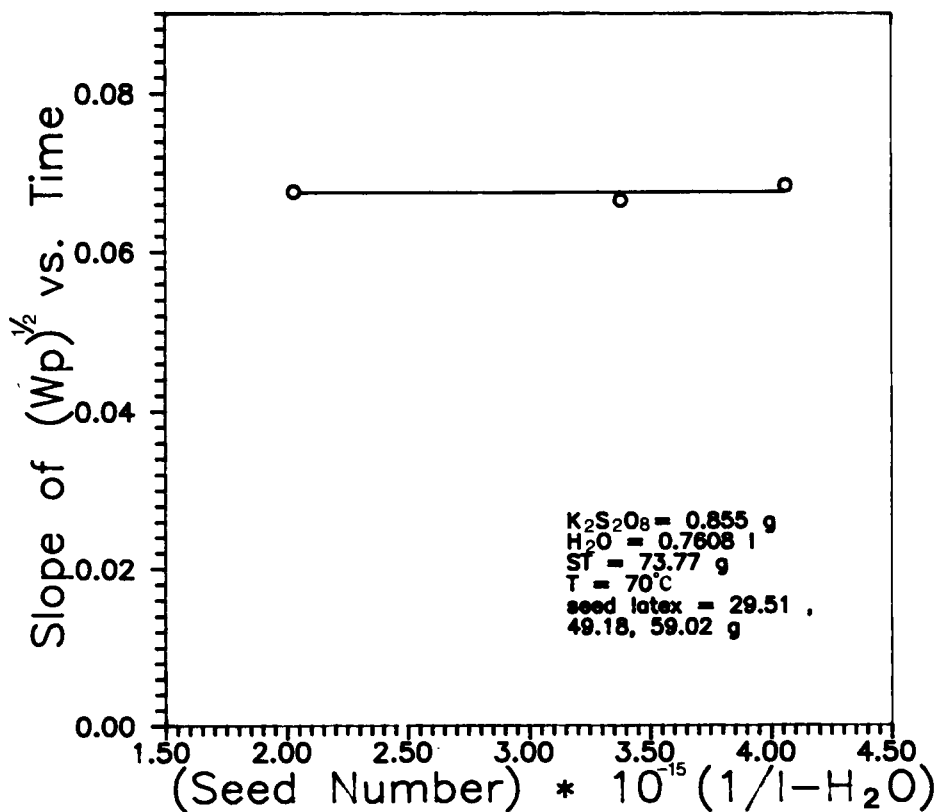**Figure 9** $(Wp)^{1/2}$ vs. reaction time at different seed contents in the second-stage polymerization.

Figure 10   The slope of the line of $(Wp)^{1/2}$ vs. time in Figure 9 for different contents of seeds.
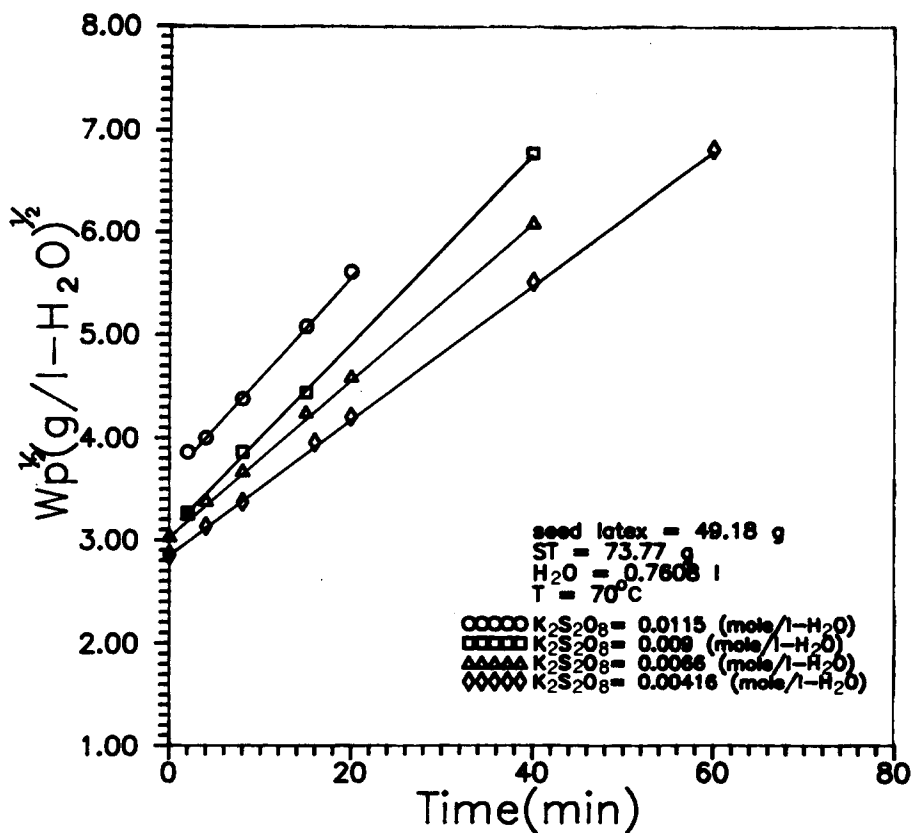
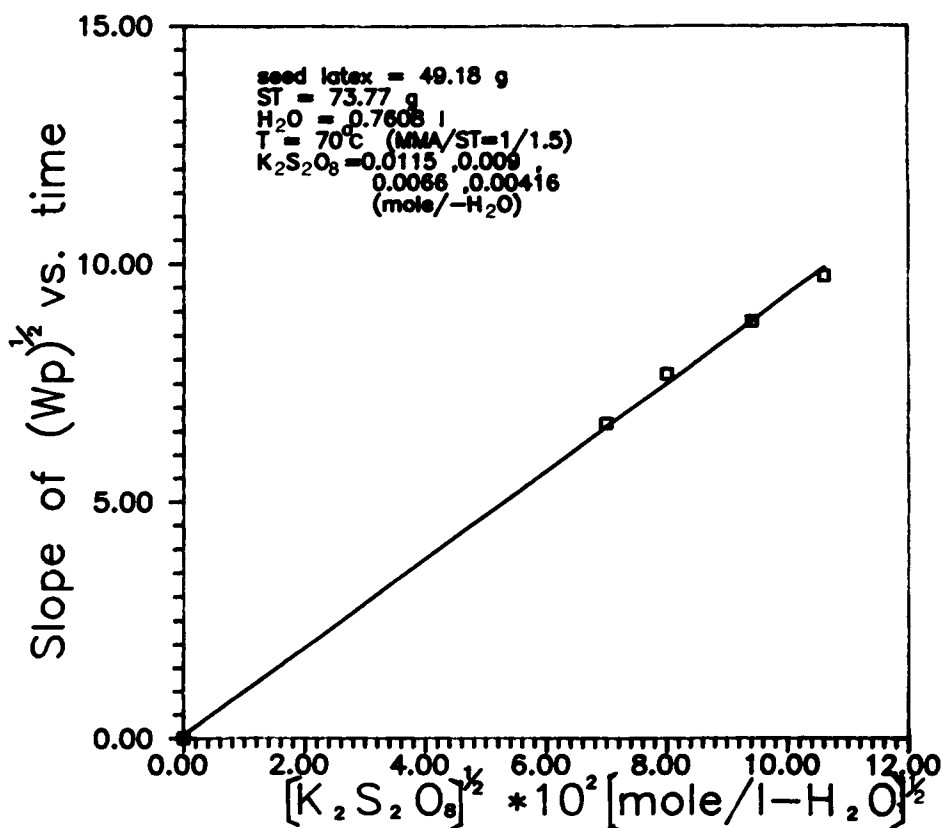**Figure 11** $(Wp)^{1/2}$ vs. reaction time at different initiator concentrations in the second-stage polymerization.

Figure 12   The slope of the line in Figure 11 vs. 0.5 power of initiator concentration.
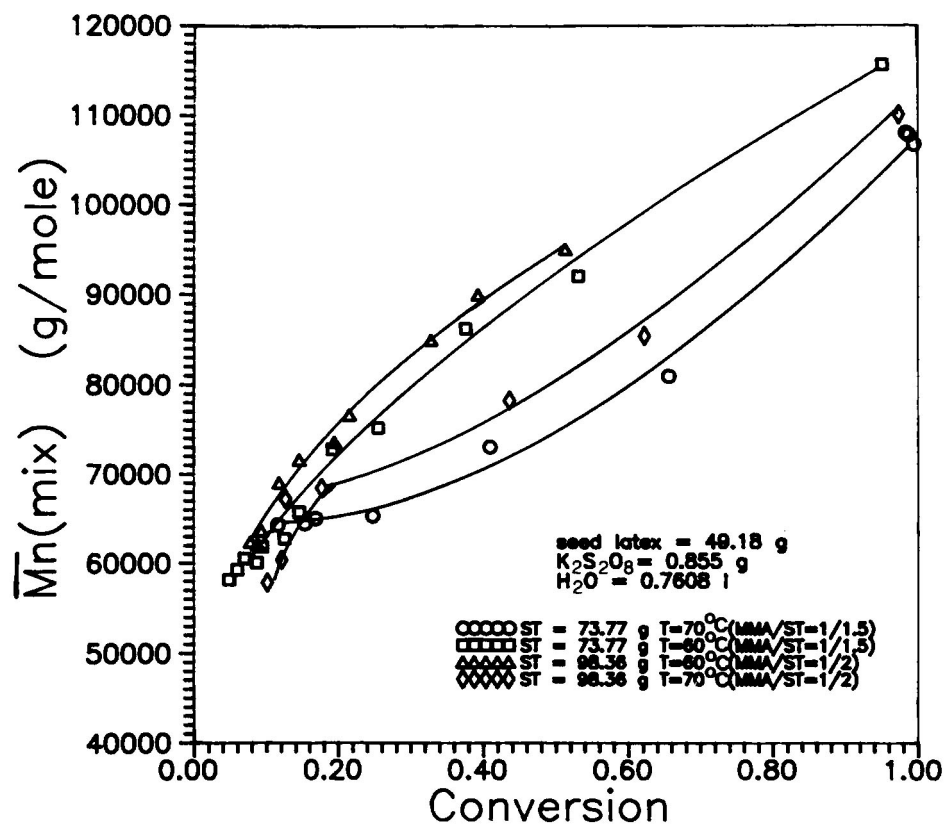
Figure 13   Number-average molecular weight of polymer composites [$\overline{M}_{n(\text{mix})}$] vs. conversion in the second-stage polymerization.
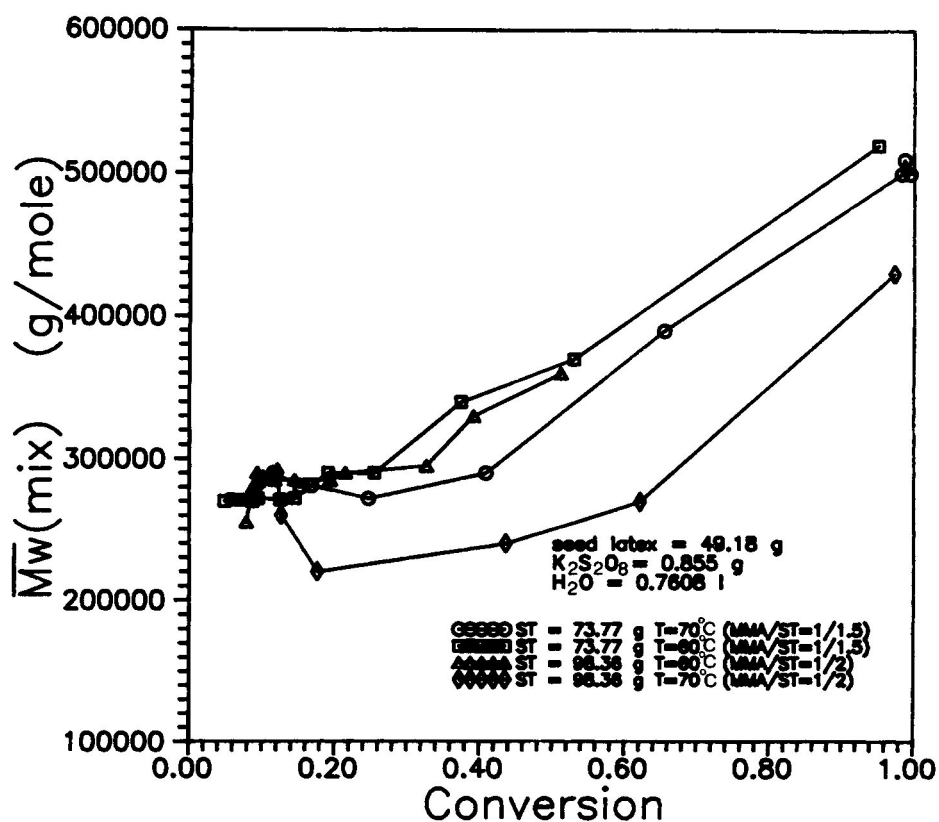

Figure 14   Weight-average molecular weight of polymer composites ($\overline{M}_{w(\text{mix})}$) vs. conversion in the second-stage polymerization.

still existed in the system and the concentration of monomer in polymer particles was kept at a constant value ($[M]g$). This meant that the monomers diffused from monomer droplets into the polymer particles very quickly during the reaction whenever monomer droplets existed in the reaction system, so the concentration of the monomer in the polymer particles remained at a saturated concentration. After monomer droplets disappeared, at which the conversion was about 0.3, the concentration of the monomer in the polymer particles was unable to retain the saturated concentration; it would decrease linearly with increasing the conversion, as in Figure 3. The value of $[M]g$ was about 4.5 mol/L at 70°C and 4 mol/L at 60°C.

Size of Polymer Particles

Figure 4 shows the plot of the average diameter of the polymer particles vs. the conversion at different monomer weight ratios of MMA/ST and different temperatures in the second stage of polymerization. An increase of conversion (or reaction time) would increase the size of the polymer particles, as expected. The decrease of the MMA/ST weight ratio would increase the shell (PS) layer, so the size of the polymer particles would be larger at the end. However, the influence of temperature on particles size in the second-stage reaction was insignificant.

Figure 5 shows the TEM photographs of the PMMA/PS composite polymer particles at MMA/ST = 1/1.5 and a temperature of 70°C. It shows that the size distribution of the polymer particles was very uniform over the course of the seeded polymerization. Figure 6 shows the SEM photograph of PMMA/PS composite polymer particles at MMA/ST = 1/1.5 and a temperature of 70°C at the end of the reaction. The size distribution of the polymer particles was very uniform.

Polymer Yield

Figure 7 shows the data of 0.5 power of the PS yield $(Wp)^{1/2}$ vs. reaction time at different MMA/ST monomer weight ratios and different temperatures in seeded polymerization. It shows that the reaction time was proportional to the 0.5 power of the PS yield in the earlier period of the reaction. The slope of the line of $(Wp)^{1/2}$ vs. time was higher at higher temperature, but it was independent of the content of ST fed into the reaction system. Figure 8 shows the plot of conversion vs. the reaction time during the entire course of the seeded polymerization at different weight ratios of MMA/ST and different

temperatures. It appears that the increases in temperature and MMA/ST weight ratio would increase the rate of polymerization. The rate of polymerization increased abruptly around a conversion of 0.3, at which monomer droplets disappeared and the gel effect became significant. In the latter period of the reaction, the rate of polymerization was very small and the reaction could not reach 100% conversion due to the glassy effect.

Influence of Seed Content

Figure 9 shows the data of the 0.5 power of the PS yield vs. the reaction time at different contents of seeds in the earlier period of the reaction. The figure shows that the reaction time was proportional to the 0.5 power of the PS yield before the gel effect took place. The PS yield increased with increasing content of the seeds, but the slope of the line of $(Wp)^{1/2}$ vs. time was independent of the content of the seeds. Figure 10 shows the slope of the line of $(Wp)^{1/2}$ vs. the time in Figure 9 for different contents of the seeds.

Influence of Initiator Concentration

Figure 11 shows the data of the 0.5 power of the PS yield vs. reaction time at different initiator concentrations in the earlier period of the reaction. The reaction time was proportional to the 0.5 power of the PS yield before the gel effect took place, as mentioned above. The slope of the line of $(Wp)^{1/2}$ vs. time increased with increasing the initiator concentration. Here, the concentration of the initiator included both $K_2S_2O_8$, retained in the seed latex, and new $K_2S_2O_8$ added to the seeded polymerization.

Figure 12 shows the plot of the slopes of the lines in Figure 10 vs. the 0.5 power of the initiator concentration. It appears that the slope is proportional to the 0.5 power of the initiator concentration.

Average Molecular Weight of Polymers

Figure 13 shows the number-average molecular weight of the polymers vs. conversion in the seeded polymerization. The result shows that the average molecular weight of the polymers increased gradually with increasing conversion; the decrease in the MMA/ST weight ratio or decrease in temperature would all increase the number-average molecular weight of the polymers. The temperature effect seemed to be more significant.

The weight-average molecular weight of the polymers vs. conversion is shown in Figure 14. It

appears that the decrease in temperature would increase the weight-average molecular weight of the polymer and the increase in MMA/ST weight ratio would increase the weight-average molecular weight of the polymer, due to that when the reaction system contained less ST monomer (i.e., higher MMA/ST ratio) the gel effect was more significant, so the weight-average molecular weight of polymer increased.

CONCLUSION

The morphology of PMMA/PS composite latex particles synthesized by two-stage soapless emulsion polymerization (i.e., seeded polymerization) in this work was of a core–shell structure. The concentration of the monomer in the polymer particles was 4.5 and 4 mol/L, respectively, at 70 and 60°C before the monomer droplets disappeared. After the monomer droplets disappeared, the concentration of the monomer in the polymer particles would decrease linearly with increasing conversion.

Before the gel effect took place, the 0.5 power of the PS yield was proportional to the reaction time. The slope of the line of (PS yield)$^{1/2}$ vs. time at different initiator concentrations was proportional to the 0.5 power of the initiator concentration. But the slope of the line was independent of the content of the seeds in the reaction mixture.

The average size of the polymer particles increased with increasing the reaction time. A decrease in the MMA/ST weight ratio would increase the shell layer, and the size of polymer particles would be larger at the end. The size distribution of the polymer particles was very uniform. The number-average molecular weight of the polymers increased but the weight-average molecular weight of the polymers decreased with decrease of the MMA/ST weight ratio.

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