

Polymer Latex Containing Carboxylic Acid Functional Groups. I. Synthesis of Polymer Latex from MMA and AA

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Received 13 October 1998; accepted 5 March 1999

ABSTRACT: The polymer latex of poly(MMA-AA) was synthesized using two techniques: soapless seeded emulsion polymerization, and the soapless emulsion copolymerization technique. The reaction kinetics, morphology, composition, and size of latex particles, as well as the structure using thin-layer chromatographic separation techniques, glass transition temperature (T_g), and molecular weight of polymer products, were studied under different experimental conditions. The reaction of the hydrophilic AA monomer took place in two places—on or in the latex particles, and in the water phase. Therefore, the polymer latex, whose size is very small and uniform, dispersed uniformly all over the PAA continuous phase. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3111–3120, 1999

Key words: polymer latex; MMA/AA; thin-layer chromatographic separation; reaction kinetics

INTRODUCTION

Different hydrophilic monomers have different functional groups (i.e., hydroxyl, carboxyl, or amino). When latexes containing hydrophilic monomers copolymerized with hydrophobic monomers such as styrene, latex particles with functional groups on their surface are formed. Over the past few years, many scholars have studied latex particles with surface functional groups. These particles have a broad spectrum of applications, such as their use as high-tech and biomedical materials.

Shoaf et al.¹ reported that carboxylated copolymer latexes are widely used for the production of paper coatings, textile coatings, and adhesives. In 1987, Tsaur et al.² pointed out that latexes carrying sulfonate functional groups could favor

their stability toward hydrolysis, oxidation, and thermal degradation. Tuncel et al.³ produced monosize polystyrene particles carrying different functional groups (i.e., hydroxyl, carboxyl, or amino) in the micron-size range for diverse biomedical applications, such as latex diagnostics, chromatographic separation of biological macromolecules, scintigraphic imaging, cell labeling, and separation. In addition, several kinds of hydrophilic polymers with functional groups have been used as materials for humidity sensors.^{4–7}

A number of factors affect the properties of these latex particles. Reaction kinetics will be influenced by synthetic method, reaction temperature, the feed ratio of hydrophilic to hydrophobic monomers, and the concentration of the initiator, monomer, and crosslinking agent. Therefore, the number of surface functional groups is hence affected.

In our earlier work, we investigated the reaction kinetics and various important physical properties of poly(MMA-MAA) latex particles syn-

Correspondence to: W.-Y. Chiu.
Contract grant sponsor: National Science Council, Taiwan;
contract grant number: NSC-85-2216-E-002-003.

Journal of Applied Polymer Science, Vol. 74, 3111–3120 (1999)
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Table I Ingredients and Conditions for the Synthesis of Seed Latex (First Stage)

Methyl methacrylate (g)	120
Initiator (K ₂ S ₂ O ₈) (g)	0.892
Deionized water (g)	1100
Stirring rate (rpm)	300
Temperature (°C)	80
Reaction time (min)	60
Reaction method	Batch

thesized using two methods: either soapless seeded emulsion polymerization or soapless emulsion copolymerization, under different experimental conditions. In addition, we studied the humidity-related characteristics of the polymer film melted from the latex particles.⁸

Both MAA and AA are water-soluble monomers. However, they are quite different in reaction kinetics and mechanism. The MAA monomer reacted mainly on or in the latex particles. The reaction of the AA monomer took place in two places—on or in the latex particles to synthesize water-insoluble polymers through emulsion polymerization, as well as in the water phase to synthesize water-soluble polymers through solution polymerization. Moreover, the polymer latex, whose size is very small and uniform, dispersed uniformly all over the PAA continuous phase.

In this article, we report the reaction kinetics and some important physical properties of poly(MMA-AA) latex particles synthesized by both methods mentioned above.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and acrylic acid (AA) were distilled under nitrogen atmosphere

and reduced pressure prior to polymerization. The other materials were analytical grade, and used without further purification.

Ingredients and Conditions for Polymerization

In the seeded emulsion polymerization, PMMA seed latex was synthesized in the first stage via soapless emulsion polymerization.⁸ The ingredients and conditions for the synthesis of seed latex are given in Table I. In the second stage of the reaction, the seed latex and quantitative MMA and AA were then added into a 1-liter reactor. The ingredients and conditions for the synthesis of core-shell latex are given in Tables II and III. The reaction system was heated to the reaction temperature, with the addition of K₂S₂O₈, and the reaction of the second stage began.

In the emulsion copolymerization, the copolymer latex was synthesized via soapless emulsion polymerization. The ingredients and conditions for the synthesis of MMA-AA copolymer latex were given in Table IV.

Conversion

During the second stage of seeded emulsion polymerization, a sample of the emulsion latex was periodically taken out of the reactor, immediately poured into a chilled hydroquinone methanol solution, and immersed in an ice bath to quench the reaction. The precipitated polymers were dried in an oven at 40°C overnight, and then in a vacuum oven at 40°C until the loss of weight did not change.

The conversion of the seeded polymerization was calculated as followed:

$$\text{Conversion} = \frac{W_2 - W_1 \times B\%}{W_1 \times M_0\%} \quad (1)$$

Table II Ingredients and Conditions for the Synthesis of Core-Shell Latex in Seeded Emulsion Polymerization (Second Stage)

Seed latex (g)	500 (polymer + unreacted monomer + K ₂ S ₂ O ₈ = 50, deionized water = 450)
Monomers (g)	73.716
Deionized water (g)	310
Initiator (K ₂ S ₂ O ₈) (g)	0.251
Stirring rate (rpm)	300
Temperature (°C)	80, 70 or 60
Ratio of MMA to AA monomers	9 : 1 or 8 : 2
Reaction method	batch

Table III Ingredients and Conditions for the Synthesis of the Crosslinked Core-Shell Latex in Seeded Emulsion Polymerization (Second Stage)

Seed latex (g)	500 (polymer + unreacted monomer + $K_2S_2O_8$ = 50, deionized water = 450)
Monomers (g)	73.716
Deionized water (g)	310
Crosslinked agent EGDMA (g)	1.853
Initiator ($K_2S_2O_8$) (g)	0.251
Stirring rate (rpm)	300
Temperature ($^{\circ}C$)	80
Ratio of MMA to AA monomers	8 : 2
Reaction method	batch

where W_1 is the weight of sample taken from vessel; W_2 is the weight of dry polymers obtained from the taken sample; $M_0\%$ is the weight percentage of monomers (MMA and AA) initially in the reaction mixture; $B\%$ is the weight percentage of PMMA initially in the reaction mixture.

The conversion of soapless emulsion copolymerization was determined using the same method and calculated as follows:

$$\text{Conversion} = \frac{P}{W \times M\%} \quad (2)$$

where P is the weight of dry polymer obtained from the taken sample; W is the weight of the taken sample; $M\%$ is the weight percentage of total monomers initially in the reaction mixture.

Morphology and Particle Size

The morphology of latex particles was observed under transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The particle size was measured from TEM photos by taking the average of 50 latex particles.

Table IV Ingredients and Conditions for the Synthesis of Copolymer Latex in Emulsion Copolymerization

Monomers (g)	122.86
Percentage of hydrophilic monomer (wt %)	13 or 6
Initiator ($K_2S_2O_8$) (g)	0.617 or 0.411
Deionized water (g)	760
Stirring rate (rpm)	300
Temperature ($^{\circ}C$)	70 or 80
Reaction method	batch

Measurement of Acid in Water Phase

The acid concentration in the water phase that was centrifuged from the latex emulsion was titrated with 1 N NaOH solution. The acid concentration in the water phase was measured by the method of titration. In the method of titration, the phenolphthalein of ethanol solution was used as the indicator.

- Copolymer, 6%AA, 70 $^{\circ}C$
- Core-Shell, 6%AA, 70 $^{\circ}C$
- ▲ Core-Shell, 13%AA, 70 $^{\circ}C$
- △ Core-Crosslink Shell, 13%AA, 70 $^{\circ}C$
- + Copolymer, 13%AA, 70 $^{\circ}C$

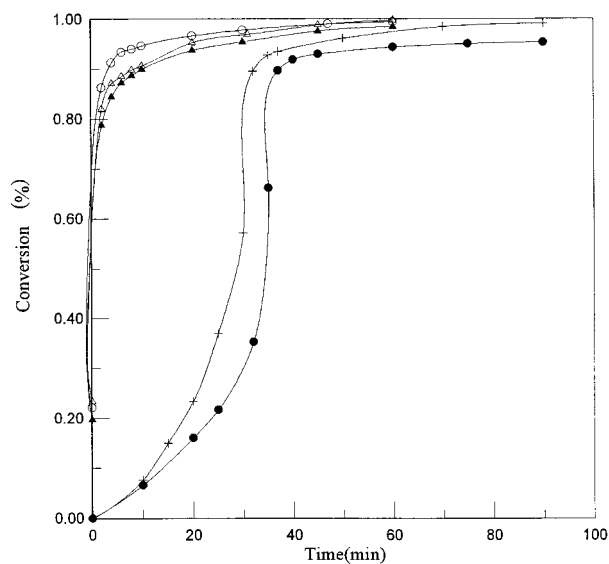


Figure 1 Conversion versus time of the emulsion polymerization reaction using different synthesis techniques and ratios of hydrophobic to hydrophilic monomers.

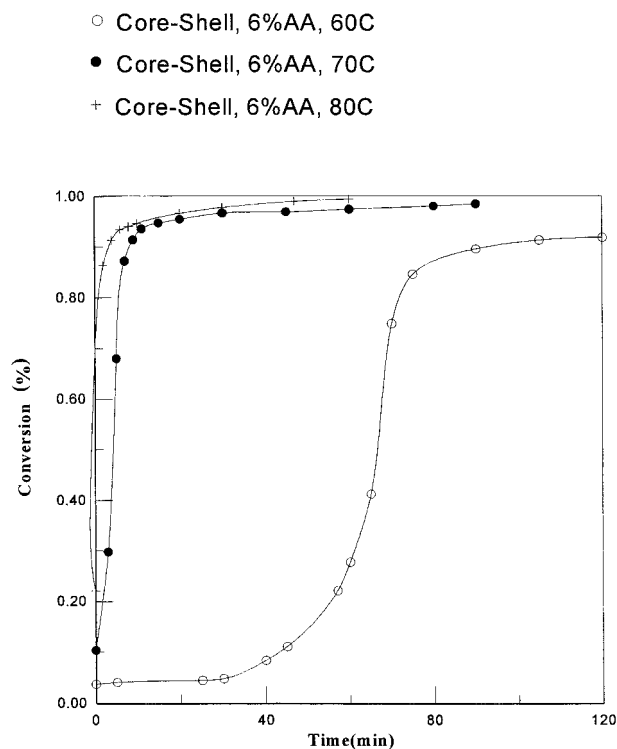


Figure 2 Conversion versus time of the seeded emulsion polymerization reaction with 6% hydrophilic monomers at different temperatures.

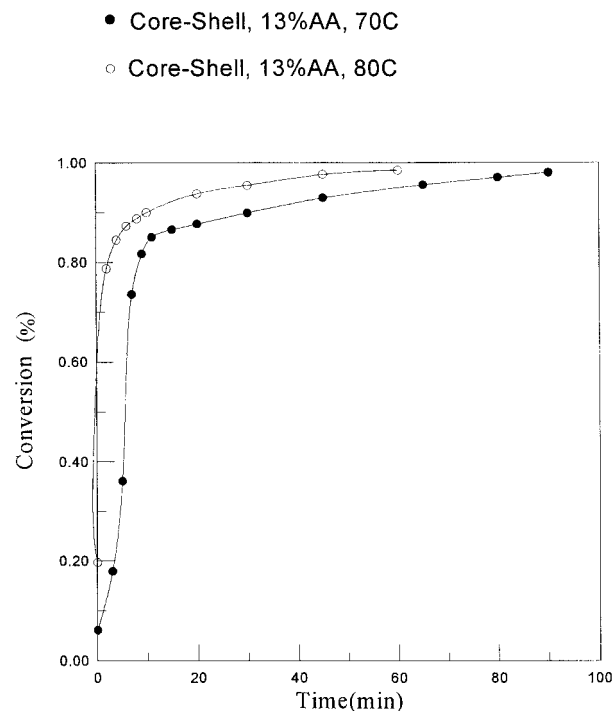


Figure 3 Conversion versus time of the seeded emulsion polymerization reaction with 13% hydrophilic monomers at different temperatures.

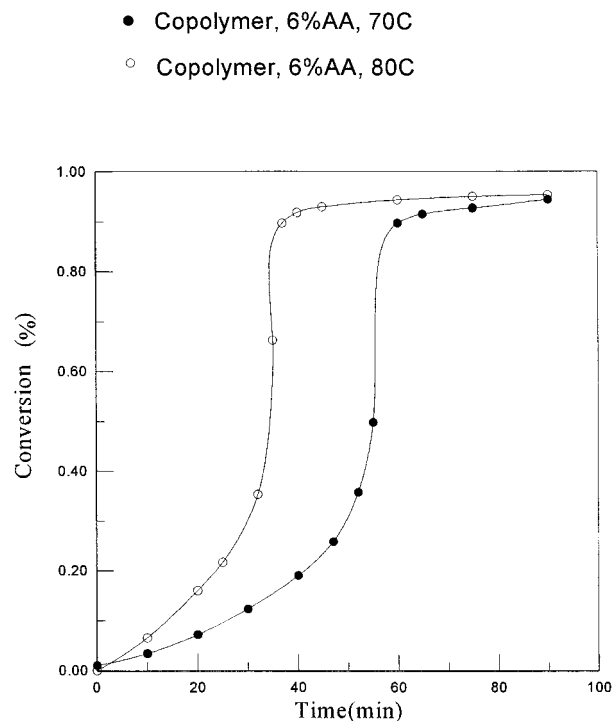


Figure 4 Conversion versus time of emulsion copolymerization reaction with 6% hydrophilic monomers at different temperatures.

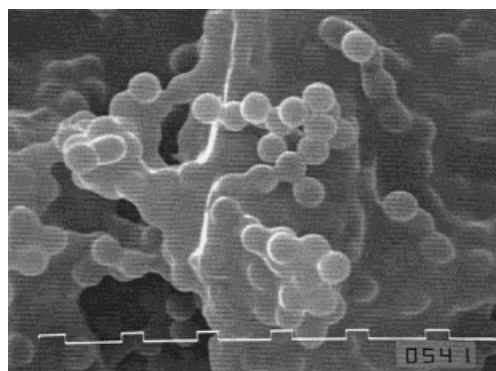
Content Analysis of Water-Soluble and Water-Insoluble Polymers

The contents of water-soluble and water-insoluble polymers were measured by weight percentage analysis of the dried polymers in the water phase and in the cake individually after centrifugation of the latex.

Thin-Layer Chromatographic Separation Techniques

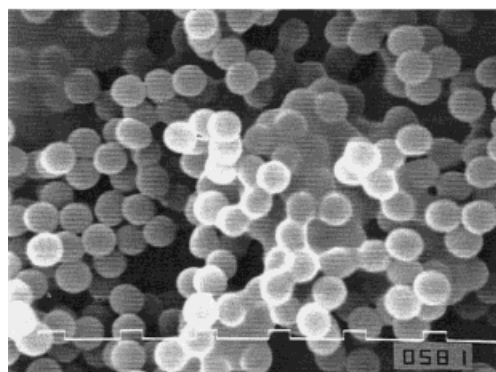
Polymer solutions were prepared by dissolving the polymers in tetrahydrofuran (THF) at a concentration of 5 g/L, and applying them to the TLC plates. The sample size ranged from 10 to 20 μg .

The TLC separation was made in a two-stage development: THF was used as the initial developer, and the solvent front was set at 5.5 cm above the starting level. This development was repeated more than three times. After the primary development had been completed, the plate was subjected to secondary development with THF-ethyl acetate mixture (5 : 1) as developer. The secondary development was also repeated more than three times. The solvent front was set at 2 cm in this development. After drying, the plates were



1 μm

a)



1 μm

b)

Figure 5 (a) SEM photograph of poly(MMA-AA) polymer latex particles synthesized through the seeded emulsion polymerization technique. (b) SEM photograph of poly(MMA-AA) polymer latex particles synthesized through the emulsion copolymerization technique.

put into a glass bottle containing I_2 for 10 s and taken out to observe the separation results.

Analysis of Glass Transition Temperature

Glass transition temperature (T_g) was measured with the differential scanning calorimetry (DSC), using a heating rate of 10°C/min.

Analysis of Molecular Weight

The weight-average and number-average molecular weight of polymers were measured with gel permeation chromatography (GPC Model SE-61).

Table V Particle Size

Structure of Latex Particles, Weight Fraction of AA in Total Monomers, Reaction Temperature	Particle Size (nm)
Core	235
Core-Shell, 6%AA, 60°C	309
Core-Shell, 13%AA, 70°C	307
Core-Shell, 6%AA, 70°C	308
Core-Shell, 13%AA, 80°C	310
Core-Shell, 6%AA, 80°C	312
Copolymer, 6%AA, 70°C	337
Copolymer, 6%AA, 80°C	297

RESULTS AND DISCUSSION

Conversion

Conversion versus time for different experimental conditions are shown in Figures 1–4. Figure 1 shows that in the seeded emulsion polymerization, the reaction rate would be higher with more MMA. This is because the second-stage reaction took place primarily on or in the PMMA seed latex; therefore, with more hydrophobic monomers of MMA, the reaction rate increases. As for copolymerization system, the nucleation reaction proceeded primarily by hydrophilic monomer AA at the early stage of the reaction, so the reaction rate increased proportionally with AA concentration. In addition, the reaction rate of the seeded emulsion polymerization at the second stage was higher than that of copolymerization; the propagation reaction took place immediately, because seed latex had been synthesized at the first stage. However, in the copolymerization system, the nucleation reaction should take place prior to the

Table VI Analysis of Acid Content in the Water Phase by Titration

Structure of Latex Particles, Weight Fraction of AA in Total Monomers, Reaction Temperature	Acid in the Water Phase/ Total Fed Acid (wt %)
Core-crosslinked shell, 6%AA, 80°C	32.21
Core-shell, 13%AA, 70°C	33.43
Core-shell, 6%AA, 70°C	34.49
Core-shell, 6%AA, 60°C	33.30
Copolymer, 6%AA, 70°C	25.24

Table VII Weight Percentage Analysis of Water-Soluble Polymers

Structure of Latex Particles, Weight Fraction of AA in Total Monomers, Reaction Temperature	Content of Water-Soluble Polymers (wt %)
Core-shell, 6%AA, 80°C	3.33
Core-shell, 6%AA, 70°C	1.96
Core-shell, 6%AA, 60°C	0.81
Copolymer-crosslinked, 6%AA, 80°C	1.21
Copolymer, 6%AA, 70°C	1.63
Copolymer, 6%AA, 80°C	2.85

propagation reaction. The addition of crosslinking agent would also increase the reaction rate.

Either in seeded emulsion polymerization or emulsion copolymerization, raising reaction temperature increases the reaction rate, as shown in Figures 2–4.

Morphology

SEM

The SEM photographs of the morphology of polymer latex particles synthesized through either soapless seeded emulsion polymerization or soapless emulsion copolymerization were shown in Figure 5(a) and 5(b). We found that the latex particles were all uniform in size, and no apparent secondary nucleation appeared.

Thin films were observed among latex particles in both photos, due to the water-soluble polymers generated in the water phase. This indicated that the polymerization reaction took place in two places: the first was on the latex particles to synthesize water-insoluble polymers through emulsion polymerization; the second was in the water phase to synthesize water-soluble polymers through solution polymerization. Moreover, the

polymer latex, whose size is very small and uniform, dispersed uniformly all over the PAA continuous phase.

Particle Size

The average size of the latex particles is listed in Table V. This shows that the effect of reaction temperature and the ratio of hydrophilic to hydrophobic monomers on the particle sizes was insignificant in seeded emulsion polymerization.

In this work, uniform seed particles were first obtained from the first-stage reaction. In the second stage of the reaction, we added the same amount of monomers, and the conversions were higher than 90% for all runs of the reaction under different experimental conditions. Thus, the shell thickness of particles due to the second-stage reaction did not vary much.

In emulsion copolymerization, however, we found that particle size decreased with increasing reaction temperature. This can be explained by the fact that in emulsion copolymerization system, the mechanism of nucleation is greatly influenced by temperature. When the reaction temperature was higher, the initiator $K_2S_2O_8$ would dissociate to release more free radicals, and increased particle numbers would be generated. Therefore, under the same monomer concentration, the particle size would be smaller.

Contents of Acid in Water Solution

The contents of acid measured in water solution that was centrifuged from latex under different experimental conditions by titration are listed in Table VI. The acid came mostly from water-soluble PAA, and partly from unreacted hydrophilic AA monomers. The acid content in water phase of emulsion copolymerization was even less than that of seeded polymerization, because in the emulsion copolymerization reaction, nucleation reaction was primarily proceeded by monomers

Table VIII The Total Conversion of Monomers and the Conversions of AA and MMA Monomers

Structure of Latex Particles, Weight Fraction of AA in Total Monomers, Reaction Temperature	Total Conversion of Monomers (%)	Conversion of AA Monomers (%)	Conversion of MAA Monomers (%)
Core-shell, 6%AA, 70°C	98.6	97.7	98.7
Core-shell, 6%AA, 60°C	91.9	79.1	93.3
Copolymer, 6%AA, 70°C	94.5	100	94.1

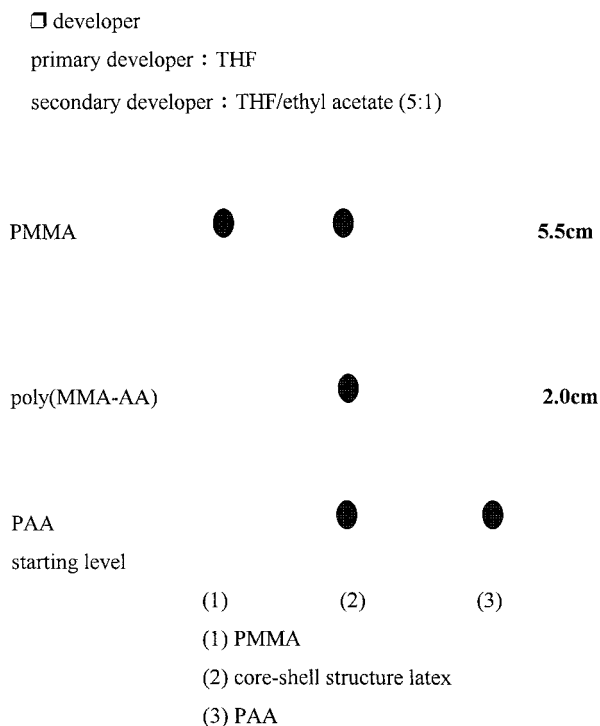


Figure 6 TLC chromatograms obtained for poly(MMA-AA) polymer synthesized through the seeded emulsion polymerization, and reference samples PMMA and PAA.

AA. Thus, the amount of AA left in the water phase to form PAA would be lessened.

Content Analysis of Water-Soluble and Water-Insoluble Polymers

In our system, polymer latex synthesized by seeded polymerization method without a crosslinking agent were composed of three parts. The

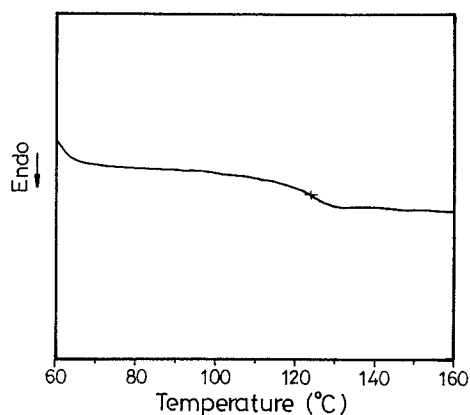


Figure 7 DSC result of the seed region of PMMA.

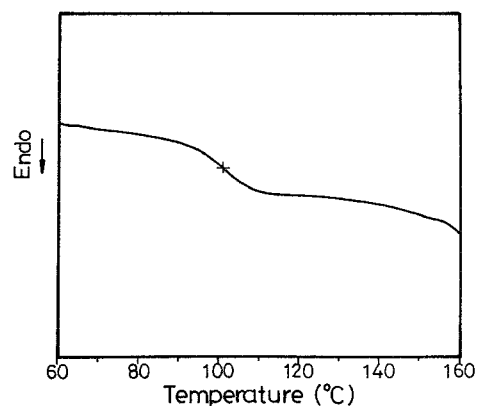


Figure 8 DSC result of PAA.

first part was the seed region of PMMA homopolymer. The second part included not only the graft copolymers between seed and shell regions, but the poly(MMA-AA) copolymer in the shell region. The third part was the PAA homopolymer in the water solution. Using the same method, latex prepared with the addition of a crosslinking agent would also be comprised of three parts: the seed section of PMMA homopolymer; the crosslinked poly(MMA-AA) copolymer in shell region, and graft copolymers between seed and shell section; and finally, the PAA homopolymer. However, by the method of emulsion copolymerization, only poly(MMA-AA) copolymer and the water-soluble polymer PAA formed in the synthesized products.

By the method of weight fraction analysis, we are able to evaluate the amount of water-soluble polymers. Table VII shows that the contents of water-soluble polymers via emulsion copolymerization were less than that via seeded emulsion polymer-

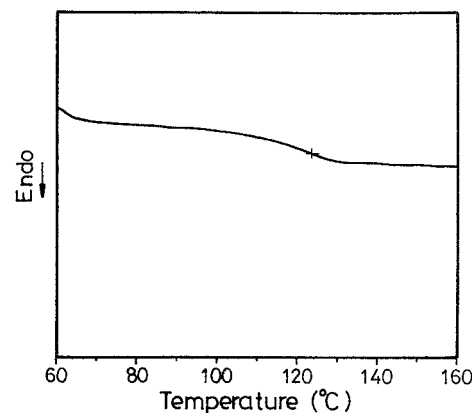


Figure 9 DSC result of latex polymers synthesized through seeded emulsion polymerization with 6% AA at 70°C.

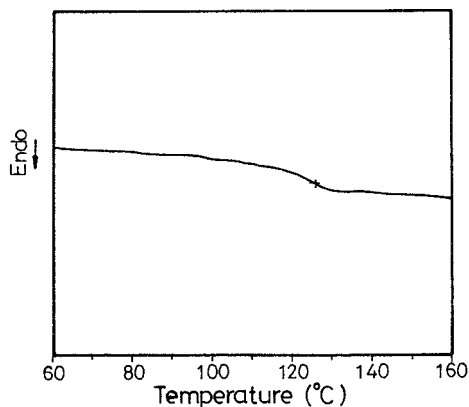


Figure 10 DSC result of latex polymers synthesized through seeded emulsion polymerization with 6% AA at 80°C.

ization, due to the fact that in emulsion copolymerization reaction, nucleation reaction was primarily proceeded by monomer AA. Thus, the amount of AA left in the water phase to form PAA would decrease. With the addition of a crosslinking agent, the amount of AA involved in the nucleation and propagation reactions increased, and hence, the amount of water-soluble polymers decreased.

From Table VI we are able to obtain the contents of acid in the water solution. The contents of water-soluble polymers can also be obtained from Table VII, and the difference of the two contents is exactly the amount of unreacted AA monomers. Moreover, from the total conversion and the mass balance of monomers, we can get the amount of unreacted MMA monomers. The total conversion of monomers and the conversions of MMA and AA monomers are shown in Table VIII.

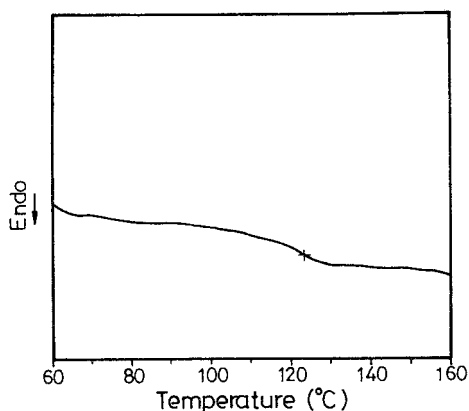


Figure 11 DSC result of latex polymers synthesized through emulsion copolymerization with 6% AA at 70°C.

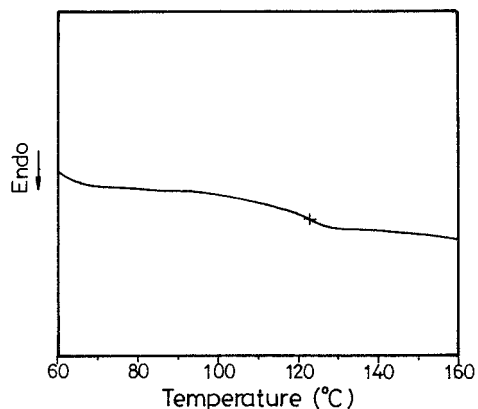


Figure 12 DSC result of latex polymers synthesized through emulsion copolymerization with 13% AA at 80°C.

Thin-Layer Chromatographic Separation Techniques

The primary developer was chosen so that the seed region of the PMMA homopolymer migrated up to the solvent front set at 5.5 cm, whereas the poly(MMA-AA) copolymer and the PAA homopolymer remained immobile on the starting level. With the secondary development, the poly(MMA-AA) migrated up to the solvent front set at 2 cm, and the PAA homopolymer remained on the starting level.

Figure 6 shows the chromatogram obtained by the core-shell structure latex where the sample (2) was separated into three spots. The two spots located at 0 and 5.5 cm were attributed respectively to PAA and PMMA by a simultaneous development of the reference samples. Therefore, our suggestion that there were three components that were

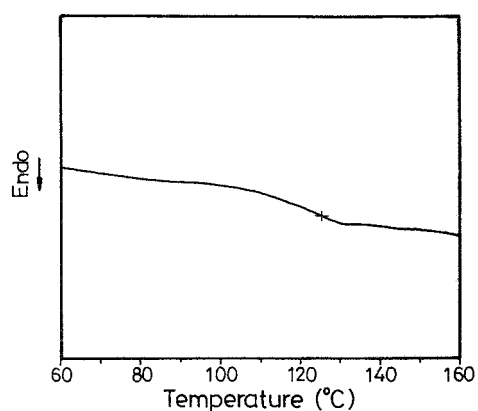


Figure 13 DSC result of latex polymers synthesized through seeded emulsion polymerization with 13% AA at 70°C.

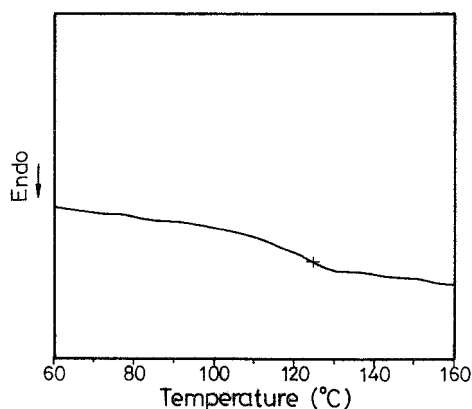


Figure 14 DSC result of water-insoluble polymers synthesized through seeded emulsion polymerization with 13% AA at 70°C.

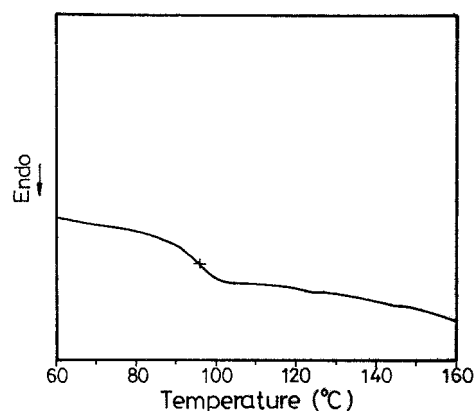


Figure 15 DSC result of water-soluble polymers synthesized through seeded emulsion polymerization with 13% AA at 70°C.

PMMA, poly(MMA-AA) and PAA formed by seeded emulsion polymerization was justified.

Analysis of Glass Transition Temperature

The T_g of polymer products are shown in Figures 7–15. The T_g of the PMMA was only about 22°C higher than that of PAA, as shown in Figures 7 and 8. According to our suggestion, there should be three components generated by seeded emulsion polymerization. However, only one T_g corresponding to PMMA was clearly found in our polymer products, as seen in Figures 9, 10, and 13. Because the content of AA was low, the other two T_g s corresponding to the copolymer and PAA phase were not easy to identify. As for the copolymerization reaction, two components were generated, but the content of water-soluble polymers was even smaller, and there was also only one T_g observable on the DSC chart, as shown in Figures 11 and 12. Figures 14 and 15 show the T_g s of

water-soluble and water-insoluble polymers that were separated from the core-shell polymer product, with its DSC result in Figure 13. With the success of getting water-soluble polymers and their DSC results, our suggestion of their existence was justified. The above DSC results were listed in Table IX.

Analysis of Molecular Weight

The analysis of molecular weight by GPC is listed in Table X. In general, the average molecular weight was lower with a higher reaction temperature. However, we observed that the average molecular weight of polymers synthesized through seeded emulsion polymerization with 6% AA at 60°C was smaller than that at 70 and 80°C. This is because the conversion of the former was only 91.88%, while that of the latter was more than 98.5%. Table IX also shows a relatively larger ratio of \bar{M}_w to \bar{M}_n from 5.88 to 7.14. This is be-

Table IX Glass Transition Temperature of Polymers

Structure of Latex Particles, Weight Fraction of AA in Total Monomers, Reaction Temperature	Glass Transition Temperature (°C)	T_g of Water-Soluble and Water-Insoluble Polymers	
		Water-Soluble	Water-Insoluble
PMMA	123.89	—	—
PAA	101.01	—	—
Core-shell, 6%AA, 70°C	123.55	—	—
Core-shell, 6%AA, 80°C	123.89	—	—
Copolymer, 6%AA, 70°C	123.33	—	—
Copolymer, 13%AA, 80°C	122.79	—	—
Core-shell, 13%AA, 70°C	125.25	95.87	124.66

Table X Molecular Weight of Polymers

Structure of Latex Particles, Weight Fraction of AA in Total Monomers, Reaction Temperature	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
Core	545559	74760	7.30
Core-shell, 13%AA, 70°C	813501	132527	6.14
Core-shell, 13%AA, 80°C	739021	125615	5.88
Core-shell, 6%AA, 60°C	652833	109297	5.97
Core-shell, 6%AA, 70°C	756069	118069	6.40
Core-shell, 6%AA, 80°C	748270	95711	7.82
Copolymer, 6%AA, 70°C	944869	143066	6.60
Copolymer, 13%AA, 80°C	572047	87212	6.56

cause in the soapless emulsion polymerization system, particles with a larger size will be obtained. The gel effect is more apparent, and further, leads to a broader distribution of molecular weight.

CONCLUSION

In the seeded emulsion polymerization of MMA and AA, the reaction rate increased with MMA concentration. As for the copolymerization system, the reaction rate increased with AA concentration. In addition, the reaction rate of the seeded emulsion polymerization at the second stage was higher than that of copolymerization. In both the seeded emulsion polymerization and emulsion copolymerization, raising the reaction temperature increased the reaction rate. In emulsion copolymerization, the average particle size was smaller at a higher temperature, while in seeded emulsion polymerization, the ratio of hydrophilic to hydrophobic monomers and the temperature had no significant effect on particle size.

The latex particles synthesized through either technique are of uniform size, with no occurrence of secondary nucleation. It was suggested that the polymerization reactions took place via two routes: one is on or in the latex particles, the other is in the water phase. Moreover, the polymer latex, whose size is very small and uniform, dispersed uniformly all over the PAA continuous phase. By the method of titration and weight percentage analysis, it was found that the acid content in the water phase of emulsion copolymerization was less than that of seeded polymerization. Polymer latex synthesized by the seeded polymerization method without a crosslinking agent were composed of three parts: first, the seed region of PMMA homopolymer; second, not only the graft

copolymers between seed and shell regions, but the poly(MMA-AA) copolymer in the shell region; and finally, the PAA homopolymer in the water phase. Using the same method, polymer latex prepared with the addition of a crosslinking agent was also comprised of three parts: first, the seed section of PMMA homopolymer; second, the crosslinked poly(MMA-AA) copolymer in shell region and graft copolymers between the seed and shell section; and third, the PAA homopolymer. However, using the method of emulsion copolymerization only the poly(MMA-AA) copolymer and water-soluble polymer PAA formed in the synthesized products.

The authors acknowledge with gratitude financial support from the National Science Council, Taiwan, R.O.C., through Grant No. NSC-85-2216-E-002-003. They are also grateful to Professor K. S. Chen of the Tatung Institute of Technology, Taiwan, R.O.C., for his helpful comments.

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