# Study on the Synthesis of Poly(methyl methacrylate)– Poly(methacrylic acid) Composite Latex and Their Humidity Sensitive Properties

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ABSTRACT: The composite latex particles of poly(methyl methacrylate)–poly-(methacrylic acid) [poly(MMA–MAA)] were synthesized through either soapless seeded emulsion polymerization or a soapless emulsion copolymerization technique. The reaction kinetics, morphology, and size of latex particles, composition, glass transition temperature ( $T_g$ ), and molecular weight of polymer products were studied under different experimental conditions. Moreover, this work also focused on the humiditysensitive properties of the polymer films fabricated by melting under the temperature of 200°C and followed by chemical modification with aqueous solution of NaOH. It is confirmed that there exists both an optimum ratio of hydrophilic to hydrophobic monomers and the initial structure of the latex particle to provide the humiditysensitive polyelectrolyte film with excellent water resistivity and good sensitivity to humidity. Besides, little hysteresis and quick response were observed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 47–57, 1999

**Key words:** soapless emulsion polymerization; latex; kinetics; hydrophilic monomer; humidity

# INTRODUCTION

There has been great attention to soapless emulsion polymerization for its high reaction rate, high conversion and product yield, low reaction system viscosity, uniform particle size, and prevention of contamination caused by emulsifier. Many factors related to this polymerization system, such as the kinetics, morphology, and molecular weight of polymer particles, surface tension, and compatibility of the polymers, have been thoroughly investigated.<sup>1-6</sup> In addition, it is well known that humidity sensor technologies amenable to widespread application in electronic control systems have become ever more important. Several kinds of hydrophilic polymers have been used as materials for humidity sensors. However, one of the problems to be solved is how to make the hydrophilic polymers insoluble in water.

In 1986, Sakai et al.<sup>7</sup> proposed that 3 methods should be used to give a hydrophilic polymer water resistivity. The first method is crosslinking the hydrophilic polymer. Miyoshi et al.<sup>8</sup> crosslinked polystyrenesulphonate in order to give it water resistivity. In 1988, Sakai et al.<sup>9</sup> reported that the simultaneously crosslinked with dibromobutane and quaternized poly-4-vinylpyridine showed excellent water resistivity as well as a sensitivity to humidity. The second

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method is copolymerization with a hydrophobic polymer. Sakai et al.<sup>9,10</sup> copolymerized 4-vinylpyridine with styrene, followed by quaternization of pyridyl group with alkyl halides. The third method is graft copolymerization. The hydrophilic polymer is grafted into a hydrophobic polymer. Hydrophilic polymers, such as polystyrenesulphonate,<sup>7</sup> quaternized poly-4-vinylpyridine,<sup>11</sup> and poly-2-hydroxy-3-methacryloyloxypropyl trimethylammonium chloride<sup>12</sup> were proved to be adequate for the branch polymers because of the high sensitivity of their electrical resistivity to humidity.

In 1993, Sakai et al.<sup>13</sup> reported the other method. They pointed out that an interpenetrating polymer network (IPN) film composed of crosslinked 2-hydroxy-3-methacryloxypropyl trimethyl-ammonium chloride (HMPTAC) polymer and crosslinked ethylene glycol dimethacrylate (EGDMA) polymer was used as a humidity sensor. The sensitivity to humidity of the IPN sensor is almost the same as that of an HMPTAC homopolymer sensor, and it has great durability against water, as well as sharp sensitivity to humidity.

In the present report, we combine these 2 important topics in polymer science. We investigate the reaction kinetics and some important physical properties of poly(MMA–MAA) latex particles synthesized by the method of either soapless seeded emulsion polymerization or soapless emulsion copolymerization under different experimental conditions. In addition, we study the humidity-related characteristics of the polymer film melted from latex particles prepared above.

# **EXPERIMENTAL**

# **Materials**

Methyl methacrylate (MMA) and methacrylic acid (MAA) were distilled under nitrogen atmo-

Table IIngredients and Conditions for theSynthesis of Seed Latex (First Stage)

| Methyl methacrylate (g)     | 120   |
|-----------------------------|-------|
| Initiator $(K_2S_2O_8)$ (g) | 0.892 |
| Deionized water (g)         | 1100  |
| Stirring rate (rpm)         | 300   |
| Temperature (°C)            | 80    |
| Reaction method             | batch |

Table IIIngredients and Conditions for theSynthesis of Composite Latex in SeededEmulsion Polymerization (Second Stage)

| Seed latex (g)                | 500           |
|-------------------------------|---------------|
| Monomers (g)                  | 98.288        |
| Initiator $(K_2S_2O_8)$ (g)   | 0.251         |
| Deionized water (g)           | 310           |
| Stirring rate (rpm)           | 300           |
| Temperature (°C)              | 80, 70, or 60 |
| Ratio of MMA and MAA monomers | 7:3  or  8:2  |
| Reaction method               | batch         |
|                               |               |

sphere and reduced pressure prior to polymerization. The other materials were of analytical grade and used without further purification. Distilled and deionized water was used throughout the work.

# Ingredients and Conditions for Polymerization

In the seeded emulsion polymerization, poly(methyl methacrylate) (PMMA) seed latex was synthesized via soapless emulsion polymerization. The ingredients and conditions for the synthesis of seed latex are given in Table I. In the first stage, the reaction was carried out at 80°C for 1 h, and the stirring rate was controlled at 300 rpm. After the first stage was completed, the seed latex was quenched to room temperature. In the second stage of the reaction, the seed latex was swollen with quantitative MMA and MAA for 24 hours at room temperature. The ingredients and conditions for the synthesis of composite latex are given in Table II. The reaction system was heated to the reaction temperature, with the addition of  $K_2S_2O_8$ , and the reaction of the second stage began.

In the emulsion copolymerization, the copolymer latex particles were synthesized via soapless emulsion polymerization. The ingredients and conditions for the synthesis of MMA–MAA copolymer latex particles are given in Table III.

# Table IIIIngredients and Conditions for theSynthesis of Composite Latex in EmulsionCopolymerization

| Monomers (g)                             | 147.432  |
|--|----------|
| Percentage of hydrophilic monomer (wt %) | 20 or 13 |
| Initiator $(K_2S_2O_8)$ (g)              | 0.617    |
| Deionized water (g)                      | 760      |
| Stirring rate (rpm)                      | 300      |
| Temperature (°C)                         | 70 or 80 |
| Reaction method                          | batch    |

# Conversion

At certain times during the second stage of seeded emulsion 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 dried in an oven at 40°C overnight and then in a vacuum oven at 40°C until the loss of weight didn't change.

The conversion of the seeded polymerization was calculated, as follows:

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

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 MAA) 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

$$Conversion = \frac{P}{W \times M_0 \%}$$
(2)

where P is the weight of dry polymer obtained from the taken sample, W is the weight of the taken sample, and  $M_0\%$  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.

# Measurement of Acid in Water Phase

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

# 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 water phase and in the cake individually after centrifugation of the latex.

#### Analysis of Glass Transition Temperature

Glass transition temperature  $(T_g)$  was measured with the differential scanning calorimetry (DSC), with the 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).

# **Humidity Sensitive Properties**

The latex was dip-coated on the sintered alumina substrate with a pair of interdigitated silver-palladium (Ag-Pd) electrodes. It was then melted at 200°C for 3 hours, followed by cooling at 50°C for 1 h, and then chemical modification with 1 N NaOH, followed by repeated water rinsing; finally, it was dried at 50°C for 24 hours. The impedance of the sensor at various humidities was measured with a LCZ meter (GenRad 1689M) at a frequency of 1 kHz.

# **RESULTS AND DISCUSSION**

#### Conversion

Either in seeded emulsion polymerization or emulsion copolymerization, raising the reaction temperature, initiator concentration, or MAA monomer ratio would increase the reaction rate, as shown in Figures 1 and 2.

At the early stage of emulsion copolymerization, it was hydrophilic monomer MAA that proceeded the nucleation reaction. Thus, the reaction rate increased with more MAA concentration.

# Morphology

#### SEM

The morphology of composite latex particles synthesized through either soapless seeded emulsion polymerization or soapless emulsion copolymerization was observed under SEM. The latex par-



**Figure 1** Conversion versus time of seeded emulsion polymerization reaction at different temperatures, ratios of hydrophobic to hydrophilic monomers, and initiator concentrations.

ticles were all uniform in size, and no apparent secondary nucleation appeared. See Figure 3(a) and (b).

# Particle Size

The average size of the latex particles is listed in column 2 of Table IV. It shows that the effect of



**Figure 2** Conversion versus time of emulsion copolymerization reaction at different temperatures, ratios of hydrophobic to hydrophilic monomers, and initiator concentrations.



 $1\mu m$ 



(b)

**Figure 3** SEM photograph of poly(MMA–MAA) composite latex particles synthesized through (a) the seeded emulsion polymerization technique and (b) the emulsion copolymerization technique.

reaction temperature and the ratio of hydrophilic to hydrophobic monomers on the particle sizes were insignificant in seeded emulsion polymerization.

In this work, uniform seed particles were firstly obtained from the first-stage reaction. In the second stage of 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 didn't vary much.

But in emulsion copolymerization, we found that particle sizes decreased with an increasing reaction temperature. This was because in the emulsion copolymerization system, the mecha-

| Structure of Latex Particles,<br>Polymer Composition, and<br>Reaction Temperature | Particle Size<br>(nm) | Acid in Water<br>Phase/Total Fed<br>Acid (wt %) | Water-Soluble<br>Polymers/all<br>Polymers (wt %) |
|---|-----------------------|---|--|
| Core  | 229                   | _   | _  |
| Core–Shell, 13% MAA, 70°C   | 324                   | 1.29  | 0.51   |
| Core–Shell, 20% MAA, 70°C   | 325                   | 1.39  | 0.82   |
| Core–Shell, 13% MAA, 80°C   | 322                   | 2.76  | _  |
| Core–Shell, 20% MAA, 80°C   | 326                   | 2.61  | _  |
| Copolymer, 13% MAA, 70°C  | 414                   | _   | _  |
| Copolymer, 20% MAA, 70°C  | 440                   | _   | _  |
| Copolymer, 13% MAA, 80°C  | 321                   | 0.49  | 0.21   |
| Copolymer, 20% MAA, 80°C  | 329                   | 0.58  | 0.33   |

 Table IV
 Particle Size, Acid Content in Water Phase, and Weight Percentage

 of Water-Soluble Polymers

nism of nucleation was greatly influenced by temperature. When the reaction temperature was higher, the initiator  $K_2S_2O_8$  would dissociate more free radicals, and more particle numbers would be generated. Under the same monomer concentration, the particle size would, hence, be smaller.

# Contents of Acid in Water Solution

The contents of acid measured in water solution centrifuged from latex under different experimental conditions by titration are listed in column 3 of Table IV. It showed that the contents of acid in the centrifuged water solutions were very small. The acid content in water phase of emulsion copolymerization was even less than that of seeded polymerization. It was because, in emulsion copolymerization reaction, nucleation reaction was primarily proceeded by both MMA and MAA. Thus, the amount of MAA left in the water phase to form PMAA would be lessened. Through the analysis of acid content in water solution centrifuged from latex, we also found that hydrophilic monomers MAA could be polymerized mostly into the latex particles through both polymerization methods.

# Content Analysis of Water-Soluble and Water-Insoluble Polymers

In our system, latex particles synthesized by seeded polymerization method without crosslinking agent were composed of 3 parts, as follows: the first part was the seed region of PMMA homopolymer; the second part was the graft copolymers between seed and shell regions; the third part was the poly(MMA–MAA) copolymer in shell region. However, by the method of emulsion copolymerization, only the poly(MMA–MAA) copolymer would be synthesized.

Besides, by the method of weight fraction analysis, we could evaluate the amount of water-soluble polymers. In column 4 of Table IV shows that the amount of water-soluble polymers was very small, and it proved that hydrophilic monomers MAA would be polymerized with hydrophobic monomer MAA onto latex particles during polymerization process.

# Analysis of Glass Transition Temperature

The glass transition temperatures of polymers are listed in column 2 of Table V. Polymers synthesized through the seeded polymerization method had 2  $T_g$ s. The lower one was the  $T_g$  of PMMA from seed region, and the other one was the  $T_g$  of poly(MMA–MAA) copolymer from shell region. It also showed that with more MAA, the  $T_g$  of the shell region was higher; however, reaction temperature had no effect on it.

On the other hand, polymer synthesized through copolymerization method had only 1  $T_g$ , poly(MMA–MAA) copolymer. The  $T_g$  was also higher with more MAA content and was still not influenced by reaction temperature.

#### Analysis of Molecular Weight

The average molecular weight of polymers  $(M_w \text{ or } \bar{M}_n)$  prepared by the seeded polymerization method was much higher than that of PMMA in seed region, as seen in columns 3 and 4 of Table VIII. This was due to the gel effect during the

| Structure of Latex Particles, Polymer<br>Composition, and Reaction Temperature | Glass Transition<br>Temperature (°C) | ${ar M}_w$ | $ar{M}_n$ |
|--|--------------------------------------|------------|-----------|
| РММА   | 123.19                               | 497,985    | 77.322    |
| Core–Shell, 13% MAA, 70°C  | 122.22                               | 1.100.303  | 129.462   |
|  | 144.03                               | _,,        |           |
| Core–Shell, 20% MAA, 70°C  | 122.65                               | 983,060    | 142,888   |
|  | 150.80                               |            |           |
| Core–Shell, 13% MAA, 80°C  | 123.12                               | 1,159,713  | 156,425   |
|  | 143.34                               |            |           |
| Core–Shell, 20% MAA, 80°C  | 123.88                               | 1,086,606  | 151,900   |
|  | 150.61                               |            |           |
| Copolymer, 13% MAA, 70°C   | 139.52                               | —          | —         |
| Copolymer, 20% MAA, 70°C   | 145.37                               | _          | _         |
| Copolymer, 13% MAA, 80°C   | 138.04                               | 833,477    | 133,872   |
| Copolymer, 20% MAA, 80°C   | 145.13                               | 877,318    | 128,823   |
| PMMA   | 175.58                               | _          |           |

second stage reaction. The high viscosity in polymer particles caused the termination of polymer radicals to be more difficult and, hence, increased the average molecular weight of polymers.

#### **Humidity-Sensitive Properties**

In our work, if the latex with functional group —COOH reacted with NaOH solution, an acid– base neutralization reaction would occur. In this reaction, Na<sup>+</sup> would replace  $H^+$  on the original COOH group to make the polymer much more dissociable alkali form. The reaction was as follows:

$$-COOH + NaOH \rightarrow -COO^{-}Na^{+} + H_2O$$

Through this chemical modification process, the Na<sup>+</sup> ion serving as the charge transport carrier would equip the polymer with a highly humidity-sensitive property. Using the fact that their ionic conductivity increased with an increase in water absorption, we evaluated their response characteristics by the use of reading the impedance versus relative humidity plot.

# Length of Time for Chemical Modification

Figure 4 shows different response curves with different time lengths for chemical modification. The impedance of the film without being processed with chemical modification didn't change with humidity. The film processed for 1 min was not sufficiently modified, and only a small fraction of the  $H^+$  was replaced by Na<sup>+</sup>, so the impedance

was higher than that of the film chemically processed for 5 or 10 min. It was noticeable that due to the long reaction with the strong base solution of NaOH, the film appearance with modification for 10 min was partially damaged. Therefore, the modification time of 5 min was selected in our experiments.

# Ratio of Hydrophilic to Hydrophobic Monomers

The polymer without hydrophilic functional group, such as pure PMMA, was not capable of



**Figure 4** Comparison of response curves with different modification time lengths.



**Figure 5** Influence of the hydrophilic monomer concentration on the response curve.

absorbing water molecules and couldn't acquire strong alkali ion through chemical modification process so that it had no sensitivity to humidity changes. Judging from the above, it was for certain that undesirable NaOH crystals could be completely removed by repeated water rinsing. And so the possibility of the involvement with conductivity mechanism by undesirable NaOH was excepted. All these could be seen in Figure 5. In this figure, it was found that the more the hydrophilic functional group, the lower the impedance. This result suggested that with a higher hydrophilic functional group ratio, the dissociation of ions became much more possible, and the ionic mobility (for example, Na<sup>+</sup>) increased due to the absorption of a lot more water vapor molecules at a higher relative humidity.

However, the response curve (that is, impedance as a function of humidity) of the film composed of 100% hydrophilic polymer, that is, the PMAA polymer film, didn't have an ideal virtue of being linear, and the impedance was higher than that of polymer film melted from either the coreshell structure latex or copolymer latex. It was ascribed to their poor durability against water. It was found that the water-soluble PMAA polymer film without any incorporation of hydrophobic structure would be seriously destroyed during chemical modification process and lost part of its sensitivity to humidity.

Hence, we found that there exists an optimum ratio of hydrophilic to hydrophobic monomers, where the polymer should be given good water resistivity as well as sharp humidity sensitivity. Y. Sakai and Y. Sadaoka et al.<sup>14</sup> did some research on the best degree of grafting ratio and had a similar conclusion.

# Effect of Method of Synthesis

As shown in Figure 6, polymer film melted from the core-shell structure latex had lower impedance than polymer film melted from copolymer latex, and its humidity sensitivity was also better. The reason for that was because functional groups of the polymer produced by copolymerization method were often buried inside the latex particle due to twisting and coiling of polymer chains, while functional groups of the polymers by the seeded polymerization method were mostly located on the surface of latex particles.

Moreover, core-shell latex particles prepared in our system had the structure where poly (MMA-MAA) copolymer was partially grafted onto PMMA seed. It was said<sup>7,14</sup> that the durability against water, together with their sensitivity



**Figure 6** Influence of different synthesis techniques on the response curve.



**Figure 7** Hysteresis behavior of humidity-sensitive polymer film formed from melted latex particles with 20% MAA.

to humidity, of hydrophobic polymer grafted with hydrophilic polymer was by far better than that of the cross-linked hydrophilic homopolymer or of the linear copolymer formed by both hydrophilic and hydrophobic monomers. The above statement also corresponded with our result.

# Hysteresis

Little hysteresis was observed for each of the humidity-sensitive polymer films, as shown in



**Figure 8** Hysteresis behavior of humidity-sensitive polymer film formed from melted latex particles with 13% MAA.



**Figure 9** Temperature effect on the response curve of the humidity-sensitive polymer film formed from melted latex particles synthesized through emulsion copolymerization with 20% MAA at 80°C.

Figures 7 and 8. The impedance for desorption processes was always lower than that for sorption processes. This was due to the fact that during desorption processes, water molecules permeating through during the entire sorption process had accumulated inside the humidity-sensitive



**Figure 10** Temperature effect on the response curve of the humidity-sensitive polymer film formed from melted latex particles synthesized through seeded emulsion polymerization with 20% MAA at 80°C.

# **Response Curve of Desorption :**

- core-shell, 20%MAA, 70C
- core-shell, 13%MAA, 70C
- core-shell, 20%MAA, 80C
- core-shell, 13%MAA, 80C
- copolymer, 20%MAA, 80C
- □ copolymer, 13%MAA, 80C



**Figure 11** Impedance variation upon humidity change with time for different humidity-sensitive polymer films during desorption process.

polymer film, and they were not easy for quick removal, so that it was expected that lower impedance would be observed.

# **Temperature Effect**

As shown in Figures 9 and 10, the impedance would decrease with an increase in temperature, and the difference between the highest and lowest impedance increased; that is, the sensitivity to humidity got better. This was due to the mobility of charge carrier (for example,  $Na^+$ ) became higher at a higher temperature.

# **Response Time**

The variation of impedance under humidity change was plotted against time for both the sorption and desorption process, as shown in Figures 11 and 12, respectively. We found that the impedance changed immediately upon any delicate variation of ambient humidity; that is, it was remarkable that the ambient humidity changed and the response of the polymer film to it occurred simultaneously.

# CONCLUSION

It was found that raising the reaction temperature, the initiator concentration, and the content of hydrophilic monomer MAA would increase the reaction rate. In emulsion copolymerization, the average particle size was smaller at higher temperature, while in seeded emulsion polymerization, the ratio of hydrophilic to hydrophobic monomers and the temperature had no significant

# **Response Curve of Sorption :**

- core-shell, 20%MAA, 70C
- core-shell, 13%MAA, 70C
- core-shell, 20%MAA, 80C
- ◊ core-shell, 13%MAA, 80C
- copolymer, 20%MAA, 80C

□ copolymer, 13%MAA, 80C



**Figure 12** Impedance variation upon humidity change with time for different humidity-sensitive polymer films during the sorption process.

effect on particle size. The latex particles synthesized through either technique were of uniform size, and there was no occurrence of secondary nucleation. By the method of titration and weight percentage analysis, only a little acid coming from PMAA or MAA was detected in the water phase. Latex particles synthesized by seeded polymerization method without crosslinking agent were composed of the following 3 parts: PMMA homopolymer, graft copolymer, and poly(MMA-MAA) copolymer. Polymers synthesized through seeded polymerization method had 2  $T_{\sigma}$ s. On the other hand, polymer synthesized through copolymerization method had only 1  $T_g$ . Humidity-sensitive polymer films formed from melted latex particles with a core-shell structure had lower impedance and better sensitivity than those with simply a copolymer particle structure. All our humidity-sensitive polymer films had rather quick response, high sensitivity, and little hysteresis. The impedance lowered, and the sensitivity sharpened with increasing temperature.

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