

# Particle Features of a Poly(methyl methacrylate) Resin Prepared by a New Emulsion Polymerization Process

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**ABSTRACT:** A new emulsion polymerization process, in which water acted as the dispersed phase and a mixture of methyl methacrylate (MMA) and cyclohexane acted as the continuous phase, was applied to the preparation of a poly(methyl methacrylate) (PMMA) resin. The primary (latex) particles were formed in the early stage of polymerization and coagulated as the polymerization conversion increased. Scanning electron micrographs showed that the final PMMA particles were porous and composed of loosely aggregated primary particles. The porosity characterized by cold di(2-ethylhexyl) phthalate absorption increased as the water/oil and cyclohexane/MMA mass ratios increased. The PMMA primary particles were smaller than the primary particles in the PMMA resin prepared by suspension polymerization in the presence of cyclohexane. Because of the phase composi-

tion of the reaction system, the solubility of PMMA in a mixture of cyclohexane and MMA, and the particle morphology of PMMA, a particle formation mechanism, including the formation, growth, and coagulation of primary particles in dispersed water droplets, was proposed. The primary particles formed mainly through a homogeneous nucleation mechanism and increased in size as MMA diffused from the oil phase to the water phase to the primary particles. The coagulation of the primary particles occurred because of the lower colloidal stability and the space limitations of the primary particles. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1905–1911, 2004

**Key words:** emulsion polymerization; morphology; particle size distribution

## INTRODUCTION

Supramicrometer porous and hollow poly(methyl methacrylate) (PMMA) particles can be used as supports for medical assays, enzyme immobilization carriers, chromatographic packing, toners, inks, and coatings. Suspension polymerization in the presence of a porogen (or diluent),<sup>1,2</sup> an alkali swelling procedure (ASP),<sup>3,4</sup> a dynamic swelling method (DSM),<sup>5,6</sup> water-in-oil-in-water (W/O/W) emulsion polymerization,<sup>7–10</sup> and the aggregation of submicrometer emulsion particles<sup>11</sup> have been applied to the preparation of porous and hollow PMMA particles.

Because of the solubility of PMMA in its monomer, it is impossible to prepare porous PMMA by conventional suspension polymerization. Skovby and Kops<sup>1</sup> prepared porous PMMA beads by adding a porogen to the polymerization, and they used porous PMMA beads as the enzyme immobilization carrier. Kucük et al.<sup>2</sup> investigated the effects of diluents on the porous structure of crosslinked PMMA beads. Okubo and coworkers<sup>3–6</sup> prepared relatively monosized hollow

PMMA particles (<10  $\mu\text{m}$  in size) by ASP and DSM with the intension of substituting them for the expensive opacifier titanium dioxide and applying them to the field of medicine. However, these particles usually require a complex production process and take a very long time to produce. Kim et al.<sup>9,10</sup> prepared PMMA multihollow particles by a W/O/W emulsion polymerization technique; sorbitan monooleate was used as the primary surfactant, and sodium lauryl sulfate and a polypeptide derivative were used as the secondary surfactants. Shouldice et al.<sup>11</sup> prepared porous PMMA particles by a three-step synthetic route, including emulsifier-free latex preparation, aggregation and aggregation stabilization, and coalescence.

In this study, a new emulsion polymerization process was applied to the preparation of a porous PMMA resin, and the particle features of the resin and the particle formation mechanism were investigated.

## EXPERIMENTAL

### Materials

Industrial-grade methyl methacrylate (MMA; Dongfang Chemical Factory, Beijing, China) was distilled under reduced pressure before polymerization. Analytically-pure cyclohexane (Hangzhou Shuanglin Chemical Factory, Hangzhou, China) was used as a porogen. Analytically-pure potassium persulfate

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TABLE I  
Conditions for the MMA Emulsion Polymerizations

Run	$M_{CH}/M_{MMA}$	$M_{H_2O}/M_{oil}$	Concentration of KPS (mmol/L of H <sub>2</sub> O)	Concentration of Tween 20 (mmol/L of H <sub>2</sub> O)	Polymerization temperature (°C)
E1	1.20	0.35	8.89	—	70
E2	1.20	0.35	8.89	4.76	70
E3	1.20	0.15	8.89	4.76	70
E4	1.20	0.25	8.89	4.76	70
E5	1.20	0.45	8.89	4.76	70
E6	1.20	0.55	8.89	4.76	70
E7	1.20	0.65	8.89	4.76	70
E8	1.20	0.75	8.89	4.76	70
E9	0.845	0.35	8.89	4.76	70
E10	1.00	0.35	8.89	4.76	70
E11	1.40	0.35	8.89	4.76	70
E12	1.60	0.35	8.89	4.76	70

(KPS) was used as an initiator in MMA emulsion polymerization. Benzoyl peroxide was used as an initiator in MMA suspension polymerization. Poly(ethylene oxide) sorbitan monolaurate (Tween 20; Wenzhou Qingming Chemical Factory, Wenzhou, China) was chemically pure. Hydropropyl methylcellulose (HPMC; 90SH100), used as a suspending agent in the suspension polymerization, was supplied by Japanese Synthetic Chemical Co.

### Polymerization

MMA emulsion polymerization was carried out in a 500-mL reactor equipped with a helix-belt agitator, a thermometer, a nitrogen inlet, and a reflux condenser. First, the reactor was charged with deionized water, a mixture of MMA and cyclohexane, and the Tween 20 emulsifier (if Tween 20 was included in the reaction recipe). Then, nitrogen was purged, and agitation was started. After 15 min of dispersion at room temperature, the reactor temperature was brought to 70°C, and the reaction was initiated by the addition of a KPS solution. The conditions for the MMA emulsion polymerizations are shown in Table I.

Samples of the reaction mixture were taken at various reaction times with a glass syringe for the characterization of the particle size distribution and morphology. The polymerization conversion of MMA to PMMA was determined with the weighing method. The final polymerization conversion of MMA was around 90%.

MMA suspension polymerization in the presence of cyclohexane was also carried out at 70°C in the same reactor, but the reactor was equipped with a two-bladed flat turbine agitator. The recipe for the MMA suspension polymerization was as follows: 100 mL of H<sub>2</sub>O, 22 g of MMA, 26 g of cyclohexane, 0.10 g of benzoyl peroxide, and 0.2 g of HPMC. The final polymerization conversion of MMA was 85.0%.

### Characterization of PMMA

The particle size distribution of PMMA was characterized with a Coulter LS-230 laser particle size analyzer (Coulter Co., Miami, Florida). PMMA latex particles obtained during the early stage of polymerization were observed with a JEM 1200EX transmission electron microscope (JEOL, Ltd. Tokyo, Japan). Final PMMA particles were sectioned under a microscopy directly and gold-coated *in vacuo*. The morphology of the PMMA particles was observed with an XL30ESEM scanning electron microscope (Philips Electric Co. Eindhoven, Netherlands). The porosity of the PMMA resin was characterized by cold plasticizer absorption. A weighed amount of the PMMA resin was placed in a sand-core tube and allowed to absorb di(2-ethylhexyl) phthalate (DOP) at room temperature (20 ± 2°C) for 30 min. The unabsorbed DOP was removed by centrifugal separation (at 3000 rpm for 60 min).

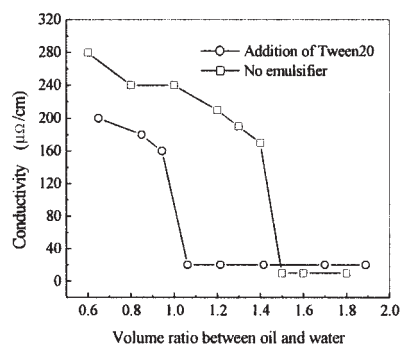
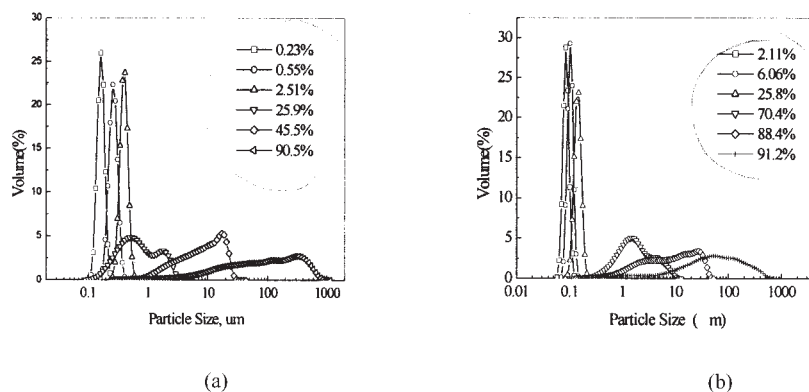


Figure 1 Influence of the oil/water volume ratio on the conductivity of the reaction system without the emulsifier and with the addition of the Tween 20 emulsifier.



**Figure 2** Variations of the particle size distribution with the polymerization conversion for (a) polymerization E1 and (b) polymerization E2.

## RESULTS AND DISCUSSION

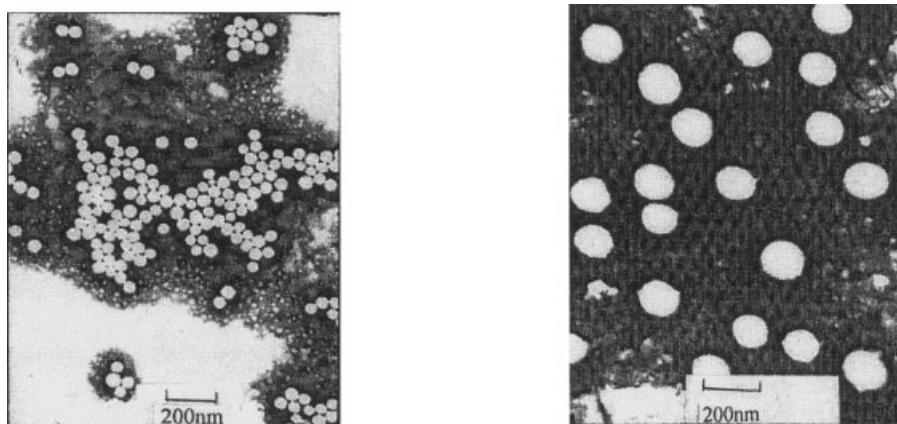
### Variation of the particle size distribution and morphology of the PMMA particles with the polymerization time

The initial experiments showed that a certain amount of a porogen, such as cyclohexane, should be added to the reaction system to obtain porous PMMA particles. To clarify the phase composition of the reaction system, we measured the conductivity of the agitated oil/water mixture. The oil phase was composed of MMA and cyclohexane, and the mass ratio of cyclohexane to MMA was 1.2/1.0. NaCl (1.5 g/L H<sub>2</sub>O) was added to the water phase to increase the conductivity of the water phase. The influence of the oil/water volume ratio on the conductivity is shown in Figure 1 for the system without the emulsifier and with the addition of the Tween 20 emulsifier (4.76 mmol/L of H<sub>2</sub>O).

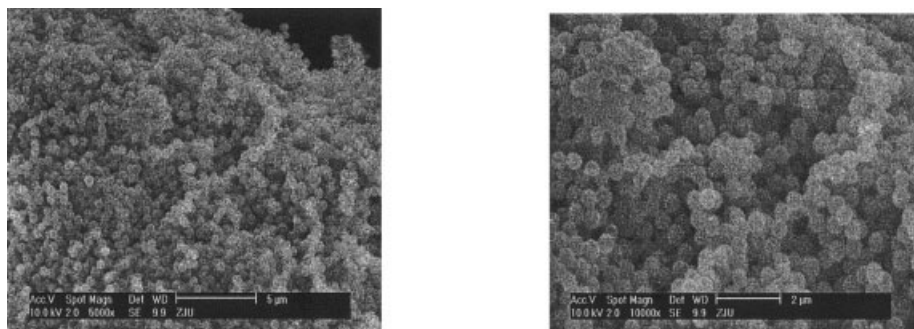
Figure 1 shows that the conductivity of the system was greater when the oil/water ratio was lower, and this indicates that water acted as the continuous

phase. When the oil/water ratio reached a critical value (the critical values were 1.5 and 1.06 for the systems without the emulsifier and with the addition of Tween 20, respectively), the conductivity decreased rapidly, and this indicated phase inversion. As the oil/water ratio increased again, the conductivity remained at a smaller value. This indicated that the water phase acted as the dispersed phase and the oil phase acted as the continuous phase. The water phase was expected to act as the dispersed phase in the real polymerization system because the applied oil/water ratio was much greater than the critical oil/water ratio for the phase inversion.

MMA emulsion polymerizations without the emulsifier and with the addition of Tween 20 were first carried out with the water/oil mass ratio ( $M_{H_2O}/M_{oil}$ ) kept at 0.35/1.0 and the cyclohexane/MMA mass ratio ( $M_{CH}/M_{MMA}$ ) kept at 1.2/1.0 (runs E1 and E2 in Table I). Samples of the reaction mixture were taken at various polymerization times, and the polymerization conversions of MMA were measured. The reaction



**Figure 3** Transmission electron micrographs of PMMA particles obtained during the early stages of E1 polymerization (for the left image, the polymerization conversion was 0.10%; for the right image, the polymerization conversion was 0.23%).



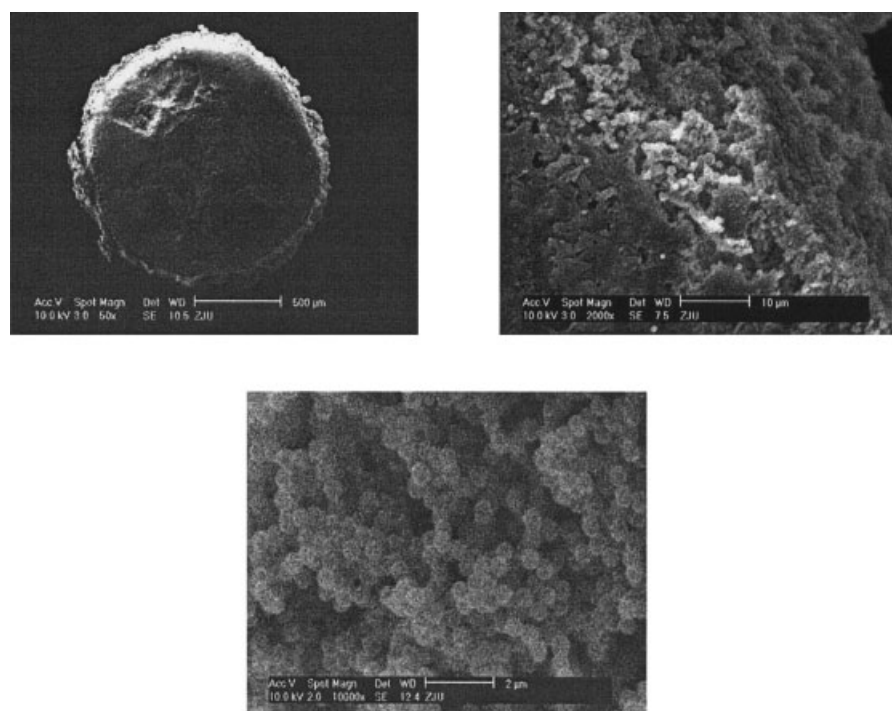
**Figure 4** SEM micrographs of the final PMMA particle prepared by polymerization E1 (the left image shows the surface layer of the particle, and the right image shows the interior of the particle).

mixture gradually changed from an initially clear dispersion to a stable latex to a mixture of the latex and precipitating particles to a suspension of the precipitating particles.

Variations of the particle size distribution of the PMMA particles with the polymerization conversion of MMA are shown in Figure 2. The PMMA particles were small and the particle size distributions were narrow when the polymerization conversions of MMA were relatively low, whereas the PMMA particles increased in size and the particle size distribution became wide when the conversion of MMA increased. The increase in the particle size was probably caused by the coagulation of latex particles in these cases. The

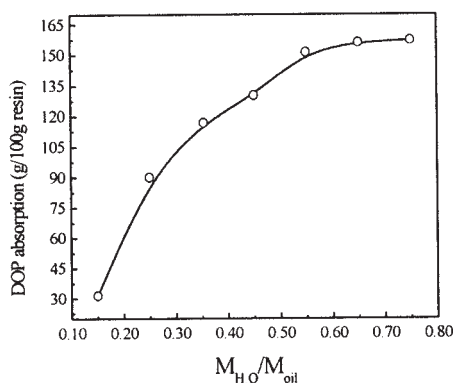
coagulation of latex particles occurred at an earlier polymerization conversion for E1 than for E2. This was caused by the increased colloidal stability toward latex particles in polymerization E2 as Tween 20 was added.

Transmission electron micrographs of PMMA particles prepared in polymerization E1 with conversions of 0.10 and 0.23% are shown in Figure 3. The PMMA latex particles with narrow particle size distributions, similar to conventional emulsion polymerization PMMA latex particles, were formed during the early stage of polymerization. Because the water-soluble KPS initiator was used and MMA was a relatively water-soluble monomer, the emulsion polymerization



**Figure 5** SEM micrographs of the final PMMA particle prepared by polymerization E2 (the top left image shows the sectioned particle, the top right image shows the surface layer of the particle, and the bottom image shows the interior of the particle).





**Figure 6** Influence of  $M_{H_2O}/M_{oil}$  on the DOP absorption of the PMMA resin.

started at the dispersed water droplets. The PMMA latex (primary) particles formed through a homogeneous nucleation mechanism.

Scanning electron microscopy (SEM) micrographs of the final PMMA particles prepared in polymerizations E1 and E2 are shown in Figures 4 and 5, respectively. The final PMMA particles were composed of aggregated primary particles. The size of the primary particles was approximately  $0.5 \mu\text{m}$ . Because polymerization mainly proceeded in the dispersed water droplets, more space was occupied by the particles as the polymerization conversion and particles size increased. On the other hand, no emulsifier or a small amount of the emulsifier was added to the polymerization system, and the colloidal protection for the primary particle was weak. As a result, the aggregation of the primary particles occurred at a certain polymerization conversion, and PMMA particles composed of aggregated primary particles formed.

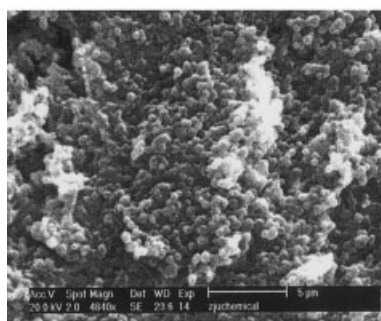
#### Influence of $M_{H_2O}/M_{oil}$ and $M_{CH}/M_{MMA}$ on the particle morphology of the PMMA resin

MMA emulsion polymerizations in the presence of Tween 20 were carried out with different  $M_{H_2O}/M_{oil}$

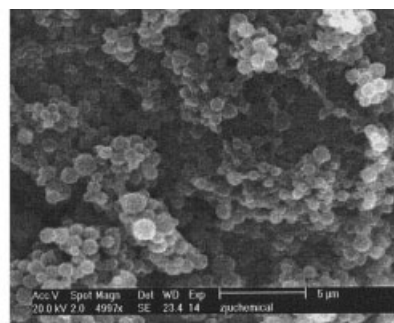
and  $M_{CH}/M_{MMA}$  values. In the first series of polymerizations,  $M_{CH}/M_{MMA}$  was fixed at 1.2/1.0, and  $M_{H_2O}/M_{oil}$  was varied from 0.15 to 0.75 (E2–E8). The variation of the DOP absorption of the PMMA resin with  $M_{H_2O}/M_{oil}$  is shown in Figure 6. The DOP absorption of the PMMA resin prepared by conventional MMA suspension polymerization was about 10 g/100 g of resin. Figure 6 shows that the DOP absorption of the PMMA resin prepared by the new polymerization process was greater than 30 g/100 g of resin, and the DOP absorption increased as  $M_{H_2O}/M_{oil}$  increased.

SEM micrographs of the PMMA resin prepared with  $M_{H_2O}/M_{oil}$  ratios of 0.15 and 0.55 are shown in Figure 7. SEM micrographs of the PMMA resin prepared at  $M_{H_2O}/M_{oil} = 0.35$  are shown in Figure 5. Comparing these SEM micrographs, we find more pores in the PMMA particles prepared with a greater  $M_{H_2O}/M_{oil}$  ratio. The increase in  $M_{H_2O}/M_{oil}$  produced more volume for the aggregation of primary particles, and the average occupied space of each primary particle increased when the total amount of the polymer or primary particles was fixed. As a result, more pores were formed, and the DOP absorption increased.

A series of polymerizations with different  $M_{CH}/M_{MMA}$  ratios (E2 and E9–12) were carried out. The influence of the  $M_{CH}/M_{MMA}$  ratio on the DOP absorption of the PMMA resin is shown in Figure 8. The DOP absorption increased as the  $M_{CH}/M_{MMA}$  ratio increased. The function of adding cyclohexane was to reduce the solubility of PMMA in the oil phase. The solubility of PMMA in the cyclohexane/MMA mixture decreased significantly when  $M_{CH}/M_{MMA}$  was greater than 0.67, and PMMA became insoluble when  $M_{CH}/M_{MMA}$  was greater than 1.50.  $M_{CH}/M_{MMA}$  was greater than 0.67 in polymerizations, and the solubility of PMMA in the oil phase was lower, so PMMA that formed in the water phase stably existed in the particle form. Cyclohexane was absorbed by PMMA particles during the polymerization process. After cyclohexane was removed in the drying process, pores formed.

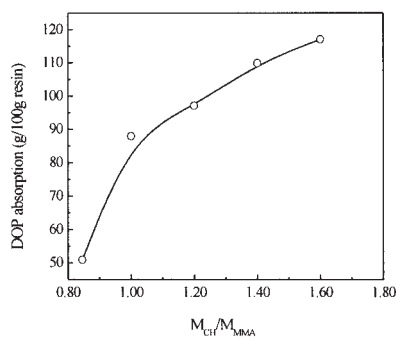


(a)



(b)

**Figure 7** SEM micrographs of PMMA resins prepared with  $M_{H_2O}/M_{oil}$  ratios of (a) 0.15 and (b) 0.55.



**Figure 8** Influence of  $M_{CH}/M_{MMA}$  on the DOP absorption of the PMMA resin.

More cyclohexane was absorbed, and more pores were formed, as  $M_{CH}/M_{MMA}$  increased.

### Mechanism of particle formation

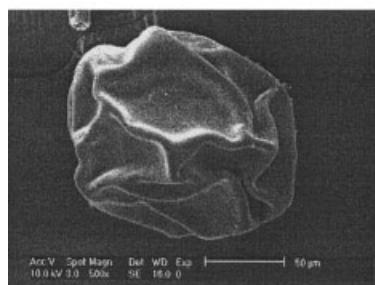
MMA suspension polymerization in the presence of cyclohexane was also carried out for the preparation of porous PMMA particles. The typical morphology of the obtained PMMA particles is shown in Figure 9. The PMMA particles collapsed and had a thick surface layer (membrane). The porous particles were also composed of primary particles, but the size of the primary particles was much greater than that of the primary particles in the PMMA resin prepared by the new emulsion polymerization process. The formation of primary particles in suspension polymerizations was caused by the insolubility of PMMA in the oil phase. From the primary particle size difference between the two kinds of porous PMMA particles, we further concluded that the formation of primary particles occurred in the water phase in the new MMA emulsion polymerization.

On the basis of the phase composition of the reaction system, the solubility of PMMA in a mixture of cyclohexane and MMA, and the particle features of the PMMA resin prepared by the new emulsion polymer-

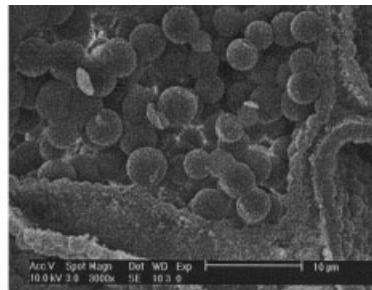
ization process, the following particle formation mechanism, including the formation of primary particles, the growth of latex particles, and the coagulation of primary particles to form secondary particles in dispersed water droplets, is proposed. The formation of primary particles mainly occurs through a homogeneous nucleation mechanism, in which free radicals generated in water become insoluble when a critical chain length is achieved. The water-insoluble oligomeric radicals coil and form particle nuclei. This is followed by the formation of stable primary particles via limited flocculation among unstable particle nuclei. PMMA primary particles increase in size as more and more monomer diffuses into them and polymerizes within them. The monomer in the water is replenished by the oil phase. PMMA particles are converted from water droplets as more and more primary particles coagulate in the droplets. PMMA chains exhibit a lipophilic nature when they achieve a certain length, and persulfate residues are hydrophilic. Therefore, PMMA chains and primary particles tend to stay at the boundary of the water droplets. At the same time, a some PMMA is formed in the monomer phase as lipophilic free radicals diffuse into the oil phase. They also tend to be located at the boundary of the water droplets and coagulate with existing PMMA particles. As the conversion increases, PMMA particles with more coagulated primary particles and with higher coagulation strength are formed.

### CONCLUSIONS

A porous PMMA resin was prepared with a new emulsion polymerization process, in which cyclohexane acted as a porogen. The conductivity measurements showed that water acted as the dispersed phase and a mixture of cyclohexane and MMA acted as the continuous phase at the beginning of the polymerization. Primary (latex) particles were formed during the early stage of the polymerization and coagulated as the polymerization conversion increased. The final



whole particle



sectioned particle

**Figure 9** SEM micrographs of the PMMA particle prepared by MMA suspension polymerization in the presence of cyclohexane (the left image shows the whole particle, and the right image shows the sectioned particle).

PMMA particles were composed of loosely coagulated primary particles, and the porosity of the PMMA resin increased with an increase in  $M_{H_2O}/M_{oil}$  and  $M_{CH}/M_{MMA}$ . The morphology of the PMMA resin prepared by the new polymerization process was quite different from that of the PMMA resin prepared by suspension polymerization in the presence of cyclohexane, and this indicated different particle formation mechanisms for the two polymerization methods. The particle formation process in the new polymerization process included the formation, growth, and coagulation of primary particles in dispersed water droplets.

## References

1. Skovby, M. H. B.; Kops, J. *J Appl Polym Sci* 1990, 39, 169.
2. Küçük, H.; Kuyulu, A.; Okay, O. *Polym Bull* 1995, 35, 511.
3. Okubo, M.; Ito, A.; Hashiba, A. *Colloid Polym Sci* 1996, 274, 428.
4. Okubo, M.; Mori, H. *Colloid Polym Sci* 1997, 275, 634.
5. Okubo, M.; Minami, H. *Colloid Polym Sci* 1996, 274, 433.
6. Okubo, M.; Minami, H. *Colloid Polym Sci* 1997, 275, 992.
7. Florence, A. T.; Whitehill, D. *J Colloid Interface Sci* 1981, 79, 243.
8. Florence, A. T.; Whitehill, D. *Int J Pharm* 1982, 11, 277.
9. Kim, B. S.; Kim, J. W.; Suh, K. D. *J Appl Polym Sci* 2000, 76, 38.
10. Kim, B. S.; Kim, J. W.; Suh, K. D. *Colloid Polym Sci* 1999, 277, 252.
11. Shouldice, G. T. D.; Rudin, A.; Paine, A. J. *J Polym Sci Part A: Polym Chem* 1996, 34, 3061.