

Influences of the Polymerization Ingredients on the Porous Morphology of Soap-Free Poly(methyl methacrylate/ethyl acrylate/methacrylic acid) Seeded Latex Particles

Kai Kang, Cheng You Kan, Yi Du, De Shan Liu

Department of Chemical Engineering, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

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ABSTRACT: Monodispersed soap-free poly(methyl methacrylate/ethyl acrylate/methacrylic acid) latex particles were synthesized by the seeded emulsion polymerization of methyl methacrylate, ethyl acrylate, and methacrylic acid (MAA), and particles with a porous morphology were obtained after an alkali posttreatment. The effects of the unsaturated acid and crosslinking agent on the properties and morphology of the latex particles were investigated. The results showed that the particle size decreased and its distribution widened when the concentration of MAA was greater than 10.0 mol % or the concentration of ethylene glycol dimethacrylate (EGDMA) was greater than 1.5%. When more than 4.0 mol % MAA was used, a porous struc-

ture could be detected clearly under a transmission electron microscope, and the particle volume and pore size first gradually increased to a maximum and then decreased rapidly with an increase in the MAA concentration. The porous morphology disappeared completely as the MAA concentration reached 16.0 mol %. A multihollow morphology was generated when the EGDMA concentration exceeded 1.0%, and the particle volume decreased monotonously with the concentration of EGDMA increased. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1934–1939, 2006

Key words: emulsion polymerization; latices; morphology; TEM

INTRODUCTION

In the past 2 decades, porous polymeric materials have been widely used as catalyst supports, sorbents, ion-exchange resins, stationary phases for gas chromatography, membrane materials, plastic pigments, impact-resistance materials, and biomedical and pharmaceutical materials.^{1–6} Vanderhoff⁷ prepared porous particles simply by drying hydrophilic/hydrophobic composite latex particles with a soft alkali-swelling core and a hard shell. Okubo and coworkers^{8–12} invented a stepwise alkali/acid treatment method to prepare multihollow polymer latex particles of styrene (St), butyl acrylate, and methacrylic acid (MAA) and of St and MAA, and they also produced hollow polymer particles by the suspension polymerization of ethylene glycol dimethacrylate (EGDMA)/toluene droplets dissolving copolymers of St and methyl methacrylate (MMA). Frechet and coworkers^{13,14} established a multistage seeded polymerization for the synthesis of uniform macroporous poly(St-co-divinylbenzene) beads with a diameter of 7.4 μm , for which linear PSt was used as the component of the progenic

mixture. Ito et al.¹⁵ investigated crosslinked hollow polymer particles and found that these particles had excellent thermal stability and unique optical properties. The microporous glass membrane emulsification technique was another method developed for the synthesis of relatively uniform macroporous particles up to 10 μm in size.^{16,17} In our previous work,^{18–20} a series of monodispersed core/shell poly(styrene/methyl methacrylate/acrylic acid or methacrylic acid) latex particles were prepared via seeded emulsion copolymerization, and the influences of the polymerization recipe and alkali/acid posttreatment conditions on hollow formation inside the particles were investigated.

Until now, nearly all porous polymer latices were prepared by traditional emulsion polymerization, in which the emulsifier could potentially be a hindrance to their applications. Moreover, most of the investigations were mainly focused on the polymerization system of St. Compared with St, MMA is more hydrophilic, and carboxyl-containing poly(methyl methacrylate) particles with a porous morphology can be expected to have some promising applications in biomedical and biochemical fields. We have prepared monodispersed poly(methyl methacrylate/ethyl acrylate/acrylic acid) latex particles by batch soap-free emulsion polymerization for the first time, and the properties and morphology of these particles were

Correspondence to: C. Y. Kan (kancy@tsinghua.edu.cn).

TABLE I
Recipe of the Seeded Emulsion Polymerization

S (g)	MMA + EA + MAA (g)	MMA/EA (mass ratio)	MAA (mol %) ^a	APS (g)	EGDMA (wt %) ^b	H ₂ O (g)
20	20	19/1	0–16.0	0.20	0.0–3.0	113

^a MAA is expressed as the molar percentage of all monomers.

^b EGDMA is expressed as the weight percentage of all monomers.

well controlled via the adjustment of the polymerization and posttreatment conditions.^{21,22} In this study, poly(methyl methacrylate/ethyl acrylate/methacrylic acid) [P(MMA–EA–MAA)] particles with a narrow size distribution and with surface carboxyl groups were prepared by two-step soap-free seeded emulsion polymerization, and porous particles were obtained after an alkali posttreatment. The effects of the unsaturated acid and crosslinking agent on the polymerization and particle morphology were investigated.

EXPERIMENTAL

Materials

MMA, ethyl acrylate (EA), and MAA (all A.R.-grade; First Chemical Reagent Factory, Tianjin, China) and EGDMA (polymerization-grade; Beijing Eastern Acrylic Chemical Technology Co., Ltd., Beijing, China) were purified by distillation under reduced pressure and kept in a refrigerator. Ammonium persulfate (APS; A.R.-grade; Aijian Modern Reagent Factory, Shanghai, China) was purified by recrystallization twice in water before use. NH₄HCO₃, NaOH, HCl, and 2-butanone (all A.R.-grade; Beihua Fine Chemical Products Co., Ltd., Beijing, China) were used as received. Deionized and distilled water was employed.

Seeded emulsion polymerization

Seed latex (S) was prepared with 120 g of H₂O, 19 g of MMA, 1 g of EA, 0.24 g of APS, and 0.2 g of NH₄HCO₃ by batch emulsion copolymerization at 80°C for 6 h. The seeded emulsion copolymerization (the recipe is listed in Table I) was conducted by the dropwise addition of a mixture of MMA, EA, MAA, and EGDMA into diluted S (20 mL of S with 89 g of H₂O) under nitrogen atmosphere at 80°C. APS, dissolved in 24 g of H₂O, was introduced in two steps at different polymerization times: 2/3 at the beginning and 1/3 at 4 h. After the monomer addition was finished in 8 h, the polymerization was continued for an additional 3 h.

Alkali posttreatment

The original latex (10 mL) was diluted with 90 g of H₂O, and 5 mL of 2-butanone was then added to the diluted latex. After 15 min of stirring at the ambient tempera-

ture, the pH of the latex was adjusted to 11.0 with a 5% NaOH aqueous solution, and then the reactor was immersed in a water bath at 80°C with stirring at 450 rpm. After an alkali treatment for 90 min, the latex was cooled to the ambient temperature and neutralized to pH 7 with a 5% HCl aqueous solution.

The volume expansion of the particles (ΔV) was calculated as follows:

$$\Delta V = (D_e^3 - D_p^3) / D_p^3 \times 100\%$$

where D_p and D_e denote the mean diameters of the particles before and after the treatment, respectively.

Characterization

The size and morphology of the latex particles were observed on a Hitachi (Tokyo, Japan) H-800 transmission electron microscope with 2% aqueous phosphotungstic acid as a staining agent. The monomer conversion, particle diameter, crosslinking degree of the polymer, and computation of the particle polydispersity were characterized as described elsewhere.^{21,23}

RESULTS AND DISCUSSION

Preparation of soap-free P(MMA–EA–MAA) seeded latices

The seed particles were monodispersed and perfect spheres [Fig. 1(a)] with a diameter of 335 nm, and the monomer conversion of the polymerization was 97.74%. In the seeded emulsion polymerization, few secondary particles were generated when the monomer dropwise time was controlled at 8 h at an MAA concentration \leq 8.0 mol %. Monomer conversions of more than 94.0% were obtained in all the seeded emulsion polymerizations.

The influences of the MAA concentration on the particle size and its distribution were investigated. Figures 1(b,e) and 2 show that the particle size was almost unchanged when less than 8.0 mol % MAA was used; when more than 10.0% MAA was used, the particle diameter decreased and the particle size distribution widened with an increase in the MAA concentration. This was due to the solubility of MAA in

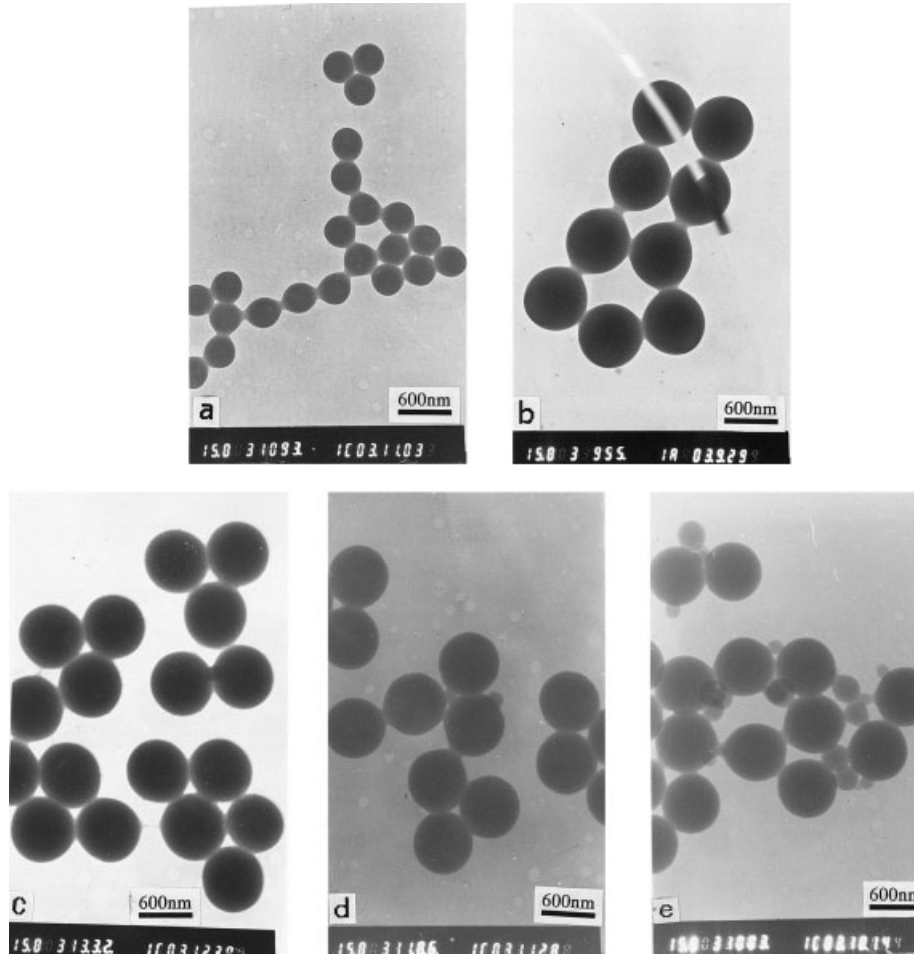


Figure 1 Transmission electron photographs of latex: (a) poly(methyl methacrylate/ethyl acrylate) seed particles and P(MMA-EA-MAA) latex particles with (b) 8.0 mol % MAA and 0.0% EGDMA, (c) 8.0 mol % MAA and 1.0% EGDMA, (d) 8.0 mol % MAA and 3.0% EGDMA, and (e) 16.0 mol % MAA and 0.0% EGDMA.

water: the more it was used, the severer the homogeneous nucleation was, and therefore the more new particles were produced.

The properties of particles with different concentrations of EGDMA are given in Figures 1(c,d) and 3. The particle size decreased slowly as the concentration of

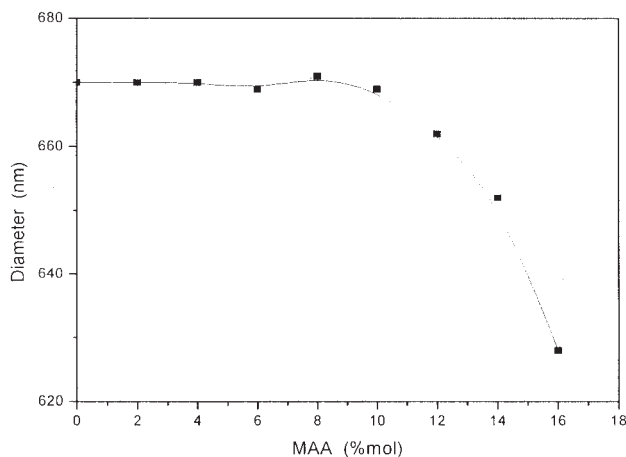


Figure 2 Influences of the MAA concentration (without EGDMA) on the size of the latex particles.

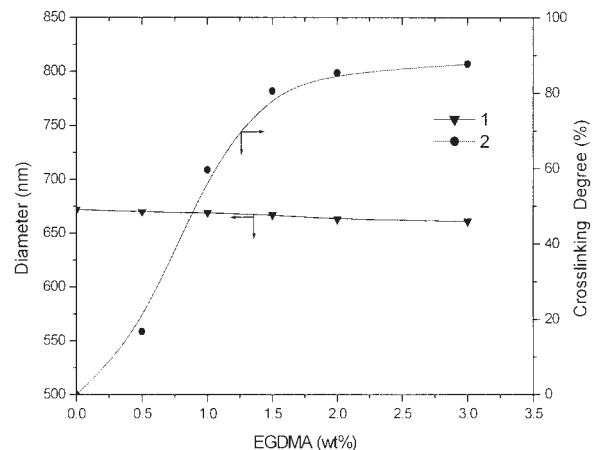


Figure 3 Influences of the EGDMA concentration (8.0 mol % MAA): (1) EGDMA and the size of the latex particles and (2) EGDMA and the crosslinking degree of the polymer.

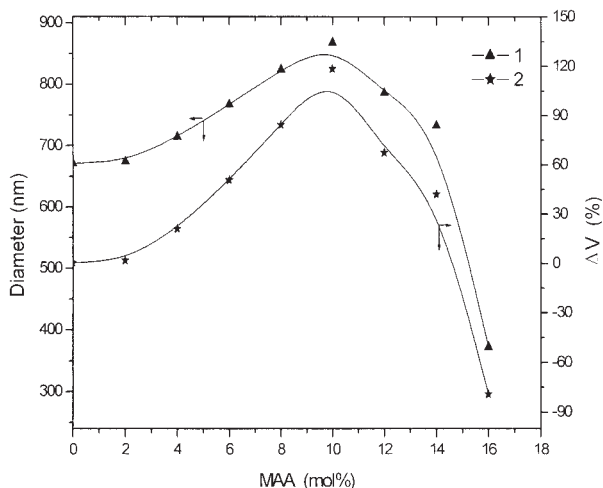


Figure 4 Influences of the MAA concentration (without EGDMA): (1) MAA and the size of the latex particles after alkali treatment and (2) MAA and ΔV .

EGDMA increased, and the particle size distribution broadened at a high EGDMA concentration of 3.0%. This may be attributed to the limited growth of particles as a result of the reduced swellability of the crosslinked polymers to monomers.²⁴ The crosslinking degree of the polymers increased significantly from 0 to 80.53% when the concentration of EGDMA varied from 0.0 to 1.5%, and this increase slowed when the EGDMA concentration was more than 1.5%.

Influence of MAA on the morphology of the particles

The polymer composition plays an important role in particle morphology by affecting the particle size, molecular weight, and polarity of polymer segments.^{25,26} Here, a series of latices with different concentrations of MAA were treated under the same conditions to investigate the influence of MAA on the morphology of the uncrosslinked particles. The results are shown in Figures 4 and 5, which indicate the following. First, at an MAA concentration below 2.0 mol %, the particle

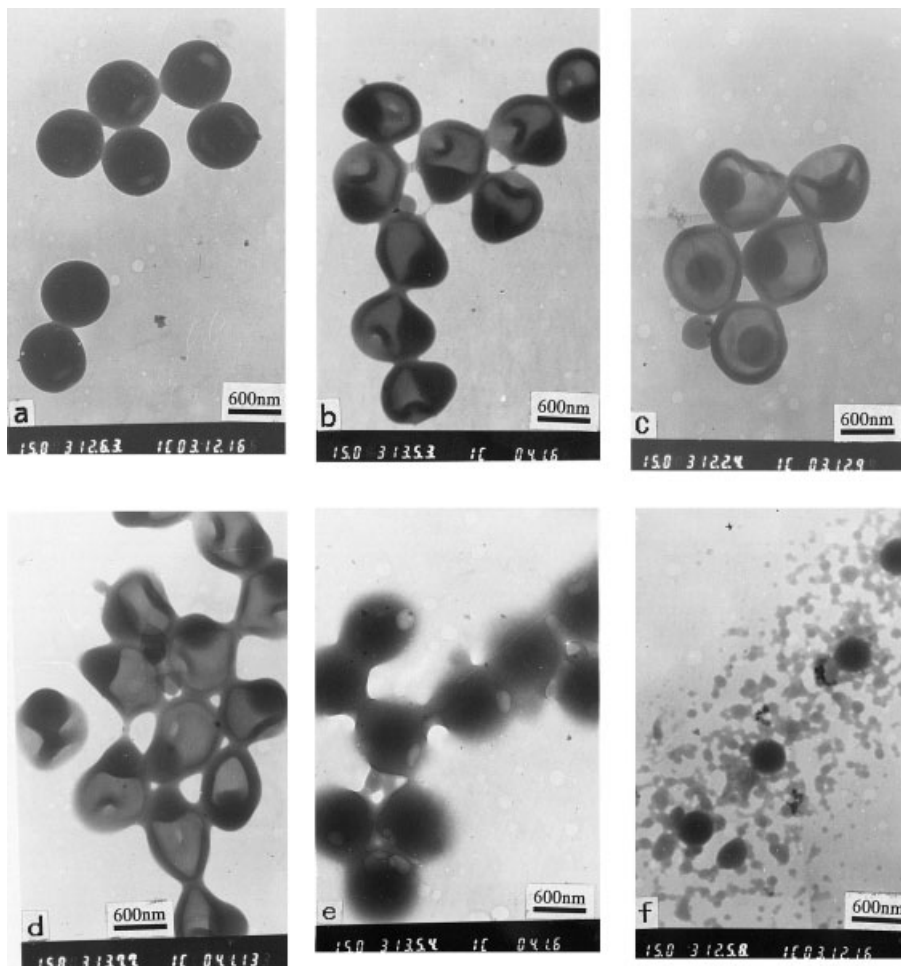


Figure 5 Transmission electron photographs of uncrosslinked P(MMA-EA-MAA) latex particles with different concentrations of MAA (mol %) after alkali treatment: (a) 4.0, (b) 6.0, (c) 10.0, (d) 12.0, (e) 14.0, and (f) 16.0.

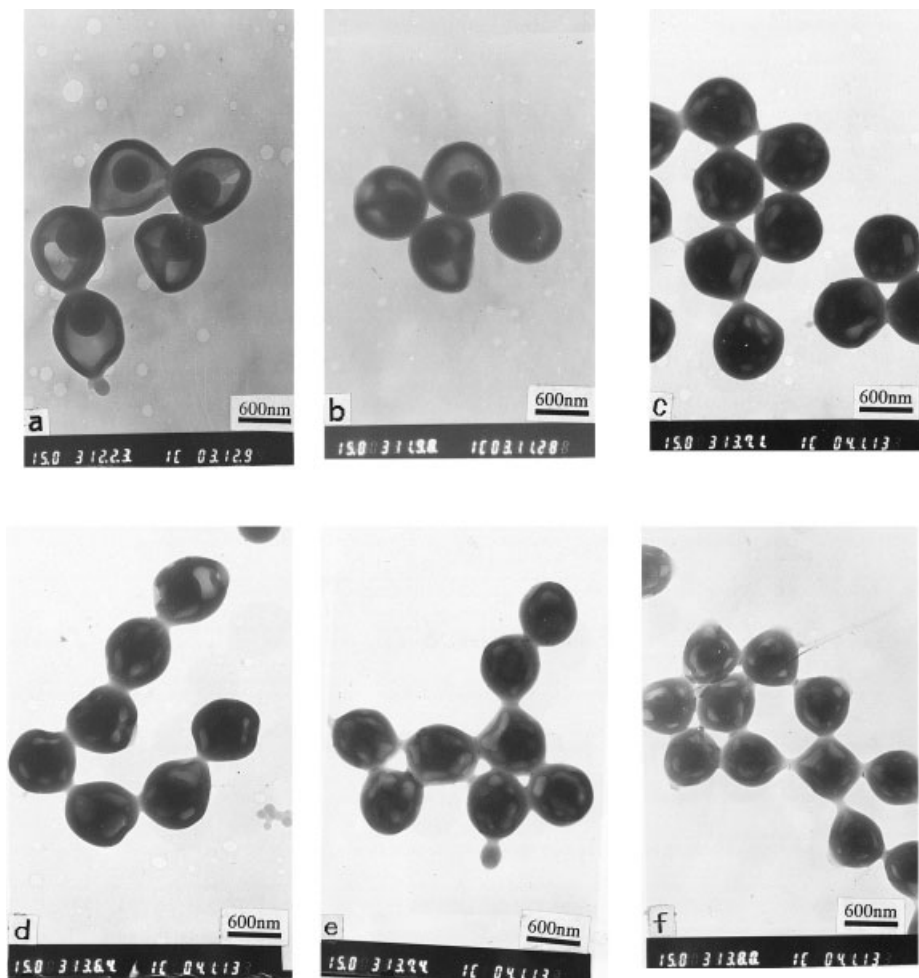


Figure 6 Transmission electron photographs of P(MMA-EA-MAA) latex particles (8.0 mol % MAA) with different concentrations of EGDMA (wt %) after alkali treatment: (a) 0.0, (b) 0.5, (c) 1.0, (d) 1.5, (e) 2.0, and (f) 3.0.

size and morphology remained almost unchanged after the alkali treatment. Second, when the MAA concentration was between 4.0 and 14.0%, a porous structure appeared; both the particle volume and the pore size increased gradually to a maximum at 10.0% MAA and then decreased rapidly, and relatively small pores inside most of the particles combined with each other to form a large one when the MAA concentration reached more than 10.0%. Third, as the concentration of MAA was further increased to 16.0%, the porous structure disappeared completely, the whole shell layer of the particles dissolved into the aqueous phase, and only the original seed particles used in the seeded emulsion polymerization were left.

Our previous study of the poly(styrene/methyl methacrylate/acrylic acid) latex system¹⁹ indicated that a critical minimum of 6.1 mol % acrylic acid was necessary in the second step of the polymerization to generate multihollow latex particles. For a soap-free P(MMA-EA-MAA) latex system, a similar critical minimum of MAA (ca. 4.0 mol %) was needed to form porous particles [Fig. 5(a)]. At a higher MAA concentration, the immigration

of polymer chains containing carboxyl groups led to an increase in the particle size and pore number [Fig. 5(b)], and therefore ΔV increased with an increase in the MAA concentration. Once the size of each pore became large enough, they overlapped in part with one another; along with this, the combination of these pores occurred, and finally only one large pore was generated in each particle [Fig. 5(c)]. As the MAA concentration was further increased, some polymer chains that bonded more carboxyl groups were separated from the particle surface because of their higher hydrophilicity, so ΔV and the pore size decreased significantly as the MAA concentration increased [Fig. 5(d,e)]. Finally, the porous structure disappeared, and the very polar polymers in the shell of the particles dissolved completely into the aqueous phase [Fig. 5(f)].

Influence of EGDMA on the morphology of the particles

The flexibility of polymer chains is essential for the formation of pores inside the particles. The mobility of

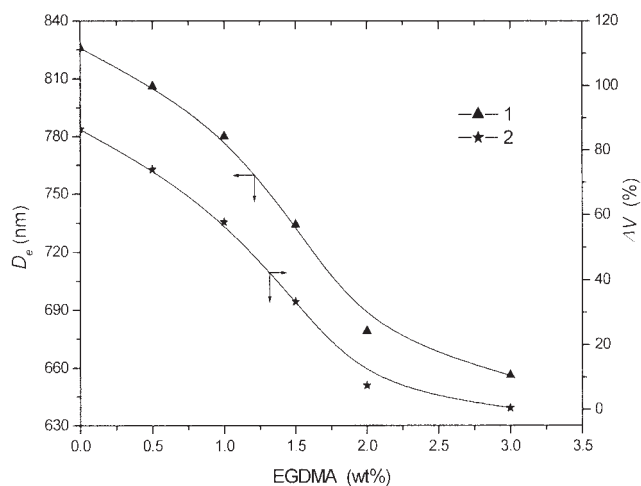


Figure 7 Influences of the EGDMA concentration (8.0 mol % MAA): (1) EGDMA and the size of the latex particles after alkali treatment and (2) EGDMA and ΔV .

polymer chains with abundant carboxyl groups, which will be dragged out from inside the particles in the alkali treatment, can be expected to be limited if the particles are crosslinked. Figures 6 and 7 show that crosslinking caused both an obvious increase in the pore number and a reduction of ΔV and the pore size when 8.0% MAA was employed. For the uncrosslinked particles, the number of pores was less than three and ΔV was as high as 86.5%. At a low concentration of EGDMA (0.5%), ΔV decreased to 74.1%, although no obvious change in the particle morphology could be observed. When the concentration of EGDMA was more than 1.0%, a multihollow structure was obtained, and ΔV declined to only about 0.5% and, on average, eight pores in each particle existed when 3.0% EGDMA was used [Fig. 6(f)]. This indicated that the mobility of the polymer chains decreased significantly even when a small concentration of the crosslinking agent was introduced into the polymerization process.

CONCLUSIONS

Soap-free P(MMA-*EA*-MAA) latex particles with a narrow size distribution and a porous morphology were prepared via seeded emulsion polymerization followed by an alkali posttreatment. Polymerization ingredients such as MAA and crosslinking agent

(EGDMA) had significant influences on the formation of this special structure. The porous structure inside the latex particles was identified under a transmission electron microscope when the content of MAA was 4.0–14.0 mol %. As the EGDMA concentration was increased to more than 1.0%, multihollow particles with about eight pores on average were observed.

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