Control of Pore Generation and Pore Size in Nanoparticles of Poly(styrene-methyl methacrylate-acrylic acid)

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ABSTRACT: Seeded emulsion polymerization of styrene-methyl methacrylate-acrylic acid onto seed latexes of monodisperse particles of poly(styrene-methyl methacrylate) was conducted with or without divinyl benzene as a crosslinking agent. Experiments revealed that almost no new particles were formed during the second stage of polymerization, and that the seeded latex particles obtained were almost monodisperse. An alkali-acid treatment was then applied to the seeded latex particles swollen in 2-butanone. Experimental results indicated that: (1) for uncrosslinked particles, an optimum volume expansion of >50% is reached for a ratio of the swelling agent, 2-butanone, to polymer (methyl-ethyl-ketone/polymer by weight) between 2.0 and 2.9; the volume expansion is much lower outside the above range. (2) For crosslinked particles, the particle volume expansion follows the same pattern, but with smaller values. (3) pH plays an important role in pore generation and volume expansion. Pore generation is optimized by decreasing pH to a value as low as 1.5 during acid treatment, and by keeping pH in the optimum range between 11.98 and 12.20 during alkali treatment. Based on the above observations, a discussion regarding the mechanism of pore generation and particle expansion is provided. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 419-426, 1999

Key words: poly(styrene-methyl methacrylate-acrylic acid); porous nanoparticles; control of pore generation; particle volume expansion

INTRODUCTION

Polymer colloidal particles have been used in research regarding colloids, as well as dispersable materials in a variety of applications. Numerous studies have been focused on latex preparation, including the control of particle size and surface properties.^{1,2} Since the 1970's, the research was directed toward the preparation of latex particles for specific applications and with various characteristics, such as reactive particles,^{3,4} core-shell particles,⁵ magnetic particles,⁶ fluorescent particles,⁶ and porous latex particles.^{7,8} Porous parti-

cles of micron size, particularly poly(styrene-codivinyl benzene) particles, have been extensively studied since the 1960's. They have been prepared *via* suspension polymerization⁹ or dynamic swelling polymerization.¹⁰ In the last decade, the emphasis was on nanoparticles, which can be used in drug delivery or as drug targeting systems.¹¹ Immobilization of biomolecules onto nanoparticles was conducted through either physical adsorption or chemical attachment. An alternative for immobilization of biomolecules is their encapsulation in polymers or their location into porous polymer nanoparticles. However, in contrast to porous particles of micron size, few studies regarding the porous nanoparticles have been reported.^{7,8,12} In this article, monodisperse coreshell latex particles containing a carboxylic acid are first prepared and then subjected to the al-

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kali-acid process suggested by Okubo and colleagues,¹³ to generate pores. The influence of experimental conditions upon pore generation is studied, and a mechanism of pore generation suggested.

EXPERIMENTAL

Materials

Styrene (St; Aldrich Chemical Co., Milwaukee, WI), stabilized with 4-tert-butylcatechol, methyl methacrylate (MMA; Aldrich), and acrylic acid (AA; Aldrich), stabilized with 4-methoxyphenol, were passed through an Inhibitor Removal Prepacked Column (Aldrich) to remove the inhibitors. Ammonium persulfate (APS; 99.99%; Aldrich) and sodium dodecylbenzene sulfonate (SDBS; Aldrich) were used as the initiator and the surfactant, respectively. A solution of 2 wt % of phosphotungstic acid (Sigma Chemical Co., St. Louis, MO) was used to increase the contrast of the particles for transmission electron microscopy (TEM) observations. Distilled and deionized water with a conductivity of 0.05 μ S cm⁻¹ was used. 2-Butanone [methyl-ethyl-ketone (MEK); Aldrich, >99%], the swelling agent of the polymer particles, and divinyl benzene (DVB; Fluka; 70-85% by gas chromatography) were used as received.

Polymerization, Polymer, and Particle Characterizations

A seed latex was first prepared at 70°C, using 180 g of water, 28.5 g of St, 1.5 g of MMA, 0.15 g of SDBS, and 0.36 g of APS; this seed is denoted as S_1 . The subsequent seeded polymerization was conducted as follows: 165 g of water were mixed with 3 g of seed latex in a reactor, and the reactor,

stirred at 200 rpm, was located into a bath. After the temperature of 85°C was attained and an aqueous solution of the initiator (0.36 g in 15 mL of H_2O injected, a slow dropwise addition of the monomer mixture was completed within 5 h. In the second polymerization stage, the amounts of most of the ingredients (including water) introduced were the same as in the seed preparation; however, SDBS was no longer used, but AA (8 mol % of the monomers in the second stage, because, as noted previously,⁸ this value provides an optimum pore generation) and DVB (when the polymer was crosslinked) were added. The polymer crosslinking was investigated via Soxhlet extraction, using benzene as the solvent; the percentage of crosslinked polymer was obtained by determining the amount of unextracted polymer after 20 h of extraction. The monomer conversion was determined gravimetrically. Particle size (diameter in all cases) was obtained and particle morphology was examined by TEM (JEOL-2100).

Alkali-Acid Treatment

The seeded latex was diluted to a solid content of \sim 1 wt %, and 100 g of the diluted latex was introduced into a three-neck round-bottomed flask equipped with a stirrer; 0.1 g of SDBS was then added to ensure that the latex will remain stable upon the addition of NaOH and HCl. A selected amount of MEK was added to the flask while stirring, and this was followed by alkali and, subsequently, by acid treatment. In the alkali treatment, a selected pH was first achieved by the addition of a solution of sodium hydroxide (1 N). The flask, with the mixture in the flask stirred at 100 rpm, was then introduced into an oil bath at 90°C, where it was kept for 3 h. The flask was then taken out from the bath and cooled to room temperature. After the pH was changed

Table IProperties of Seeded Latex Particles of St-MMA-AA Polymerizedon Seed Latex of St-MMA and Polymer Crosslinking

Sample	DVB (wt %) ^a	D_n (nm)	$\stackrel{N_p}{_{(10^{15}\mathrm{L}^{-1})}}$	$\begin{array}{c} Crosslinking \\ (wt \ \%)^{b} \end{array}$	
S_{11}	0	450 (459) ^c	2.88 (2.69)	0	
S_{1X1}^{11}	0.5	451 (468)	3.04 (2.68)	33.5	
S_{1X2}	1.0	440 (455)	3.00(2.68)	67.2	

^a Wt % of all monomers.

^b Wt % of undissolved polymer by Soxhlet extraction with benzene.

^c Data in parentheses are calculated values obtained by assuming that all monomers were polymerized onto the seed particles.



Figure 1 Seeded latex particles of the uncrosslinked S_{11} and the crosslinked S_{1X2} (1 wt % DVB).

to a selected lower value with a solution of hydrochloric acid (1 N), the flask was reintroduced into the oil bath at 90°C for another 3 h.

RESULTS AND DISCUSSIONS

Crosslinking of Latex Particles

The diameter of the seed particles, S_1 , was ~ 108 nm, and the seeded emulsion polymerization of St-MMA-AA onto S_1 was conducted using various amounts of DVB. Table I, which summarizes the results, shows good agreement between the experimental and calculated values of the particle size and particle number. The calculated values were obtained by assuming that, in the second

polymerization stage, all the monomers were polymerized onto the seed particles. The micrographs of Figure 1 indicate that the particles are almost monodisperse, and suggest that no new particles were formed during the second polymerization stage. They also show that the crosslinked particles (S_{1X2}), prepared by using 1 wt % DVB (see Table I), possess a smoother surface than the uncrosslinked particles (S_{11}).

Effect of MEK on Pore Generation in Uncrosslinked Seeded Latex

As previously described, 2-butanone (MEK) was used as a swelling agent during the alkali-acid pore generation process. At a fixed amount of

Table IIEffect of 2-Butanone on Pore Generation and Particle Volume Expansion in the
Uncrosslinked Seeded Latex Particles (S_{11})

MEK/P ^a	0	0.58	2.03	2.70	2.90	4.05	5.39
$D_f (\mathrm{nm})^{\mathrm{b}}$	450	450	521	517	518	480	485
$\Delta V (\%)^{c}$	0	0	55.7	51.9	53.0	21.4	25.2
Pores	No	No	Yes	Yes	Yes	Yes	Yes

^a 2-Butanone/polymer ratio by weight.

^b Number average particle diameter after alkali-acid treatment.

^c Particle volume increase after alkali-acid treatment.



Figure 2 Micrographs of S_{11} seeded latex particles after the alkali-acid treatment for different MEK/P weight ratios at pH 12.20 during alkali treatment and pH 2.20 during acid treatment.

latex, S_{11} , the amount of MEK was varied to investigate its effect on pore generation. Results are listed in Table II, which shows that there is an optimum MEK/Polymer (MEK/P) ratio by weight for pore generation. When the ratio was below unity, the particle volume remained unchanged after the alkali-acid treatment, and no pore could be detected by TEM. Once the MEK/P ratio increased to values between 2 and 3, pores could be easily identified, and the particle volume increased by >50% when compared with its value before alkali-acid treatment. For ratios larger

MEK/P (by wt)	0.58	1.16	2.03 (2.03) ^a	2.90 (2.90)	4.36	5.80
$D_{f}(\mathrm{nm})$	450	454	452 (440)	460 (480)	_	440
$\Delta V (\%)$	0	10	8.2 (≈0)	14.3 (20.6)	_	≈ 0
Pore	No	Yes	Yes (No)	Yes (Yes)	No	Yes

^a Data in parentheses were obtained for the latex S_{1X1} (33.5% crosslinked); all other data were obtained for S_{1X2} (67.2% crosslinked).

than 2.9, the diameter of the particles after treatment decreased with increasing MEK/P ratio.

Figure 2 presents the micrographs of S_{11} after alkali-acid treatment for MEK/P ratios of 0, 2.03, 4.05, and 5.39, respectively. One can see that, in the absence of MEK, the particles kept their morphology before treatment {i.e., a solid core surrounded by a loose outerlayer [compare Figures 1(A) and 2(A)}. For a MEK/P ratio of 2.03 [Figure 2(B)], numerous pores with sizes between 30 and 100 nm were formed, and a maximum volume increase of 55.7% reached. Although pores were also generated for higher MEK/P ratios [Figure 2(C,D)], their number and size decreased. A careful examination of the micrographs reveals a coreshell morphology, more clearly for the higher MEK/P ratios [Figure 2(D)].

This indicates a rearrangement of the polymer molecules during treatment. This rearrangement is probably caused by the tendency of the more hydrophilic polymer chains (those with a higher content of AA) to migrate toward the surface of the particles to form an AA-enriched outerlayer. As a result, the pores were formed mainly in the outerlayer. The smaller volume expansion in Figure 2(C,D) than in Figure 2(B) might be due to the collapse of the large pores when the MEK/P ratio is high.

Effect of MEK on Pore Generation in Crosslinked Latexes

Similar experiments were conducted with crosslinked latex particles prepared with two different amounts of DVB, and the results are listed in Table III. From these data, one can conclude that (1) as for the uncrosslinked latex particles, an MEK/P ratio between 2 and 3 favors pore generation, and a maximum particle expansion of $\sim 20\%$ is reached for a ratio of ~ 2.90 . (2) As for the uncrosslinked latex particles, a too large amount of swelling agent is not effective in increasing the particle volume expansion for S_{1X1} and S_{1X2} . For a MEK/P ratio of 5.80, the particle remained the same size as before treatment, and no pores were observed. For comparison purposes, Figure 3 presents the micrographs of the uncrosslinked particles, S_{11} , and the crosslinked particles, S_{1X1} . They clearly show that, as expected, the pore sizes are much smaller in the crosslinked particles. In addition, the small pores are homogeneously distributed inside the entire particle, owing to the limited migration of the polymer segments containing carboxylic groups. In contrast, in the uncrosslinked particles, the pores are mostly located near the surface of the particles.

Influence of pH in the Alkali-Acid Treatment on Pore Generation

Using the uncrosslinked latex, S_{11} , the pH was varied during alkali treatment at a constant MEK/P ratio of 2.90, followed by acid treatment at pH 2.20. In another group of experiments, the pH during acid treatment was varied, while that during the preceding alkali treatment was kept at 12.20. Results are presented in Table IV, which shows that the pH in the alkali-acid treatment has an important effect on the pore generation and particle volume expansion. Volume expansions of >50% are reached by changing the pH during the alkali treatment between 11.98 and 12.20. The expansion sharply decreases for a pH larger than 12.20 or smaller than 11.98. The effect of pH during the acid treatment on the particle volume expansion is even more pronounced. An expansion of the particle volume of 53.1% is observed at pH 2.20, and a much larger expansion of 82.6% is noted for pH 1.50. However, by increasing pH from 2.2 to 2.9, the particle expansion is reduced to 25.2%. Figure 4 presents the micrographs of the corresponding latex particles. The number of pores in the particles treated at



Figure 3 Comparison of the micrographs of the uncrosslinked latex particles S_{11} (left) and the crosslinked latex particles S_{1X1} (right) (MEK/P = 2.9, pH 12.20 in alkali and pH 2.20 in acid treatment).

pH 1.50, as well as their size, are obviously larger. A core-shell structure with a more porous shell can be noted in Figure 4(A) (particles treated at pH 2.90); this is probably due to the lower acidity in this case than in those presented in Figure 4(B,C).

Mechanism of Pore Generation and Particle Volume Expansion

Our experimental results have clearly indicated that swelling of the particles plays an essential role in pore generation and particle volume expansion during alkali-acid treatment. Indeed, in the absence of MEK, no pores could be generated, and no volume expansion observed. This swelling agent is very soluble in water¹⁴ and is also a solvent for polystyrene.¹⁵ As a result, it can swell the copolymer and even entrain some water during swelling. The swelling allows the penetration of the sodium hydroxide molecules inside the particles, where they react with the carboxylic groups, amplifying their ionization. The charges thus generated lead, because of electrostatic repulsion, to more extended configurations of the copolymer chains. Because of the particle swelling and the more extended configurations of the polymer chains, the volume of the particles is expanded. The swelling also stimulates the rearrangement of the polymer chains, which have the tendency to expose as

Table IV pH Effect on Pore Generation and Particle Volume Expansion in Alkali-Acid Treatment

Acid Treatment ^a					Alkali/Treatment ^b					
pH	1.50	2.20	2.90	10.50	11.50	11.98	12.10	12.20	12.35	
$D_f(\mathrm{nm})$	550	518	485	458	455	521	523	519	486	
ΔV (%)	82.6	53.1	25.2	5.6	3.7	55.3	56.7	53.1	25.6	
Pores	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	

^a pH was kept at 12.20 in the preceding alkali treatment.

^b pH was kept at 2.20 in the subsequent acid treatment.



Figure 4 Particle morphologies of latex S_{11} alkalitreated at pH 12.20 and acid-treated at different pH values. (A, pH 2.90; B, pH 2.20; and C, pH 1.50).

much as possible their hydrophilic segments to the water solution. When the acid (HCl) is added, the degree of ionization of the carboxylic groups is decreased and the electrostatic repulsion diminished. As a result, the chains become more flexible. Because the molecules have the tendency to expose their more hydrophilic segments to the swelling solution, a rearrangement, stimulated by their higher flexibility, occurs, that generates the pores.

Experiment indicates the existence of an optimum pH in the alkali treatment as well as of an optimum amount of swelling agent. The optimum pH probably occurs because a too low concentration of NaOH does not sufficiently ionize the carboxylic groups, whereas a too high pH generates a too high ionic strength, which decreases the electrostatic repulsion among the charges present on the polymer chains. The optimum amount of swelling agent is probably due to a too low dielectric constant of the swelling solution (MEK and water) when the MEK/P ratio is above 2.90, and this decreases the degree of dissociation of the carboxylic groups.

CONCLUSIONS

Seeded emulsion polymerization of St-MMA-AA onto seed latexes of poly(St-MMA) was conducted, and the latex particles obtained were subjected to an alkali-acid treatment to generate pores. The experiments lead to the following conclusions:

- 1. A swelling agent (2-butanone, MEK) is needed to generate pores, and there is an optimum amount of MEK for which the particle volume expansion is maximum. In the present case, the optimum volume expansion in the particles was reached when the weight ratio of MEK to the polymer was between 2.03 and 2.90.
- 2. Optimum pore generation and particle expansion are obtained for pH values between 11.98 and 12.20 during alkali treatment, followed by an acid treatment at pH 2.20. The volume expansion is even higher when the pH during acid treatment is lower.
- 3. A mechanism of pore generation is suggested, on the basis of which the above experimental results are explained.

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