Monodisperse Core/Shell Latex Particles Containing Carboxylic Acid Groups and Their Optimum Acid Content for Pore Generation

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ABSTRACT: Monodisperse seeded latex particles with a core-shell morphology were prepared by copolymerizing, via dropwise addition, styrene (St)-methyl methacrylate (MMA)-acrylic acid (AA) or St-MMA-methacrylic acid (MAA) onto monodisperse seed latex particles of P(St-MMA). The seeded particles thus prepared were subjected to an alkali/acid treatment in order to generate pores in the particles. For the same carboxylic acid content, the volume expansion of the particles due to pore generation was higher in the particles containing AA than in those containing MAA. The size of the pores increased with increasing AA content. However, a maximum particle volume expansion of about 50% was observed for the particles containing 8 mol % AA in the monomer mixture employed in the second stage, and an explanation for this optimum is suggested. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1455–1460, 1999

Key words: seeded core/shell particles; styrene; methyl methacrylate; acrylic acid; pore generation

INTRODUCTION

The interest in porous polymer particles has continuously increased since the 1960s. According to their sizes, they are commonly classified as micron-sized porous particles (i.e., porous microbeads) and submicron-sized porous particles. The former are mainly based on poly(styrene divinylbenzene) and have been widely employed as catalyst supports, ion exchangers,¹ as well as biomedical and pharmaceutical materials.² The porous microbeads are mostly prepared via suspension polymerization,^{3,4} and their sizes vary from a few to several hundred microns. In spite of the growing usefulness of the submicron-sized porous particles, few studies^{5–7} have been reported. Vanderhoff et al.⁷ synthesized, via the seeded polymerization method, composite latex particles with a hydrophilic core and a hydrophobic shell and generated microvoids in the core through simple drying. In the porous core/shell particles obtained by Vanderhoff et al., a bimodal size distribution was observed. Okubo et al.^{8,9} applied an alkali/acid treatment to carboxylic acid-containing copolymer latexes based on styrene (St)–butyl acrylate (BA)–methacrylic acid (MAA) or St–MAA to generate pores.

The goal of the present article was to prepare, via the seeded polymerization method, monodisperse latex particles with a core/shell morphology. The seeds consisted of St and MMA, and the mixture of monomers used in the second stage contained, in addition, either acrylic acid (AA) or MAA. The alkali/acid treatment was used to generate pores in the particles. It is shown that the total volume of the pores passes through a maximum with increas-

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Samples	$D_n \; ({ m nm})$	D_v (nm)	D_v/D_n	
S_1	74.0	74.2	1.002	
S_2	107.8	108.0	1.002	
$\bar{S_1A_2}$	298.0	298.3	1.001	
$S_{2}A_{2}$	463.9	464.2	1.001	
$\tilde{S_1MA_2}$	293.0	294.0	1.003	

Table IParticle Sizes and Dispersities of theP(St-MMA)Seed Latexes and theCorrespondingSeeded Latexes

ing AA content in the monomer mixture employed in the second stage.

EXPERIMENTAL

Materials

St (stabilized with 4-*tert*-butylcatechol, TBC), MMA, MAA, and AA (all three stabilized with 4methoxyphenol, MEHQ) were purchased from Aldrich. The inhibitors were removed, prior to polymerization, by passing the monomers through an Inhibitor Removal Prepacked Column (Aldrich). Ammonium persulfate (APS, 99.99%, Aldrich) and sodium dodecylbenzene sulfonate (SDBS, Aldrich) were used as an initiator and a surfactant, respectively. The phosphotungstic acid (PTA, Sigma) was used as a staining agent for the transmission electron microscope (TEM) observations. Distilled and deionized water with a conductivity of 0.05 μ S/cm was employed.

Polymerization and Particle Characterization

The polymerization was carried out via seeded emulsion polymerization. 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, 0.36 g of $NaHCO_3$, and 0.36 g of APS. This seed latex is denoted hereafter as S₁. Another seed latex, denoted S_2 , was prepared in the absence of NaHCO₃. The subsequent seeded polymerization was carried out as follows: Water, 165 g, was mixed in a reactor with 3 g of one of the above seed latexes. After the temperature of 85°C was attained, an aqueous solution of the initiator $(0.36 \text{ g/}15 \text{ mL H}_2\text{O})$ was injected while the mixture in the reactor was stirred at 200 rpm. Then, a mixture of monomers was added dropwise into the reactor within 5 h with stirring. Except for SDBS, which was no longer used, and AA or MAA, which was added, the amounts of the other ingredients (including water) were as in the seed preparation step. The conversion was determined gravimetrically and the particle size and morphology were examined by TEM (Model JEOL-2010) using PTA as a staining agent. The arithmetic average size (D_n) and volume average size (D_n) were obtained from TEM, and the ratio D_v/D_n was used as a measure of the particle dispersity. The number of particles per unit volume (N_p) was obtained from the particle size (D_n) ,



Figure 1 Micrographs of the P(St–MMA) seed latex particles (A) S_1 , (B) S_2 , and (C) the seeded latex particles S_2A_2 .



Figure 2 Micrographs of the S_1A_1 sample before the alkali/acid treatment.

polymer density, and the solid content of the latex. In addition, for comparison purposes, the size of the seeded particles was calculated assuming that the numbers of seeds and seeded particles are equal.

Alkali/Acid Treatment

Ten grams of the core/shell polymer latex was diluted in a flask to a solid content of about 1 wt % and 0.1 g of SDBS added to ensure the stability of the dispersion during the treatment. Then, 5 mL of 2-butanone (MEK, Aldrich) was introduced as a swelling agent of the polymer particles. After the pH of the mixture, about 3 initially, was adjusted to 12.2 using a 1N NaOH solution, the flask was immersed in an oil bath of 90°C for 3 h while the mixture in the flask was stirred at 100 rpm. The flask was then taken out and cooled to 20°C in 5 min with tap water. The pH was again adjusted to 2.2 at 20°C using a 1N HCl solution and the flask reintroduced into the bath for another 3 h. The latex was then cooled, neutralized with a NaOH solution, and the MEK steam-stripped under reduced pressure. The volume change of the particles after this treatment was calculated by comparing the particle sizes before and after the treatment.

RESULTS AND DISCUSSION

Monodispersity of the Seed and the Seeded Core/Shell Particles

The samples prepared by polymerizing St-MMA-AA on the S_1 seed particles are denoted S_1A_x , and those prepared by polymerizing St-MMA-MAA on the S_1 particles are denoted



Figure 3 Micrographs of MAA-containing core/shell particles before and after the alkali/acid treatment: $(A,B) S_1MA_1$ before and after; $(C,D) S_1MA_2$ before and after the treatment, respectively.

Samplag	AA or MAA ^a	D (nm)	$M_{(10^{15}/T)}$
Samples	(70)	D_n (IIIII)	$N_p (10 / L)$
S_1A_0	AA, 4.1	$296 (301)^{b}$	8.86 (8.41) ^c
S_1A_1	AA, 6.0	298 (306)	9.01 (8.38)
S_1A_2	AA, 8.0	308 (311)	8.57 (8.38)
$S_2 A_2^d$	AA, 8.0	464(459)	2.63(2.69)
S_1MA_1	MAA, 6.0	310 (318)	8.99 (8.36)
S_1MA_2	MAA, 8.0	293(307)	9.84(8.36)

Table II Properties of Latexes Prepared by Copolymerizing St-MMA-AA (S₁A_x) or St-MMA-MAA (S₁MA_x) onto P(St-MMA) Seed Latex

^a AA or MAA content by mol %.

^b Nos. in parentheses are calculated values.

^c Particle nos. after the seeded polymerization (the nos. in parentheses are the particle nos. of the seed latexes).

 d S₂ seed, $D_n = 107.8$ nm; S₁ seed, $D_n = 74$ nm.

 S_1MA_x (see Table I). Figure 1 presents the micrographs of the seed latexes S_1 and S_2 and of the seeded latex S₂A₂ of Table I. The micrographs of the other samples are not included because they are similar to those in Figure 1. The data in Table I and the micrographs reveal that the particles are almost monodisperse. This indicates that the seeded copolymerization with a slow monomer addition rate prevents the generation of new particles.

Figure 2 shows that the particles of the sample S_1A_1 have a core/shell morphology before the alkali/acid treatment. The size of the core (about 150 nm) is, however, larger than that of the seed particles (74 nm). It is likely that most of the St-MMA copolymerizes inside the growing particles and most of the AA or MAA copolymerizes in the aqueous medium and is captured by the growing particles. The latter polymer chains segregate near the water-particle interface because of their higher hydrophilicity. This may explain why the diameter of the core of the seeded particles is larger than that of the seed and why the shell/core interface is so sharp. A similar observation can be made regarding the micrographs of the samples prepared with MAA [Fig. 3(A,C)].

Seeded Copolymerization with AA and MAA

For comparison purposes, seeded copolymerizations were carried out with AA and MAA. The results, summarized in Table II, show that the seed particle number and the final core/shell particle number are close in both cases. Except for S_2A_2 , for which a slightly lower core/shell particle number than the seed particle number was observed, for all the other samples, the core/shell particles number was slightly higher, in particular for the latexes prepared with MAA. This implies that a small number of new particles were formed during the second copolymerization step. The higher difference between the number of core/shell and seed particles for MAA than for AA may be explained in the following two ways: (1)Let us first ignore the presence of St and MMA whose solubilities in water are very small in comparison to those of AA or MAA. The persulfate radicals induce the polymerization of AA or MAA in the aqueous phase, generating water-soluble oligomers. If captured by an existing seed particle, these oligomers will contribute to its growth. They will form new particles only if they attain a critical length,¹⁰ at which they become insoluble in water, before being captured. This critical length is expected to be larger for the more hydrophilic AA than for MAA,¹¹ and, therefore, the

Samples	AA or MAA $(\%)^{\rm a}$	$D_n \; ({\rm nm})$	D_{nf}^{b} (nm)	$\Delta V^{ m c}$ (%)	Pores Observed
$S_1 A_0^{d}$	0	296	296	0	No
S_1A_1	AA, 6.0	298	328	33.3	Yes
S_1A_2	AA, 8.0	308	355	53.1	Yes
$S_1 A_3$	AA, 11.5	293	301	8.4	Yes
S_1A_4	AA, 14.8	310	300	-10	No
S_1MA_1	MAA, 6.0	310	309	≈ 0	Yes
S_1MA_2	MAA, 8.0	293	305	12.6	Yes

Table III Particle Size and Volume Increases After Alkali/Acid Treatment

AA or MAA content by mol %.

^b D_{nf} , arithmetic average diameter after alkali/acid treatment. ^c ΔV , volume increase of the particles after alkali/acid treatment.

^d Sample prepared without AA and MAA in the second polymerization stage.



likelihood of new particle formation may be lower for AA than for MAA. (2) If the presence of St is taken into account (the amount of MMA is much smaller than that of St and can be neglected), a larger number of St molecules will copolymerize with AA than with MAA because of their reactivity ratios ($\mathbf{r}_{\text{St}} = 0.15$, $\mathbf{r}_{\text{MAA}} = 0.49$ in the copolymerization of St with MAA¹²; $\mathbf{r}_{\text{St}} = 0.15$, $\mathbf{r}_{\text{AA}} = 0.25$ in the copolymerization with AA¹³). The affinity of the P(St–MMA) seed particles for the AA-containing oligomers will therefore be higher than for the MAA-containing oligomers. The AAcontaining oligomers are therefore more likely to be captured by the seed particles, and the probability to generate new particles will be smaller. The latter explanation appears to be more plausible than does the former.

Pore-formation Capability of Particles Containing AA or MAA

To compare the capabilities for pore generation, the samples S_1A_1 , S_1A_2 , S_1MA_1 , and S_1MA_2 were subjected to the alkali/acid treatment, and the results are listed in Table III. One can see that for the same carboxylic content the AA-containing particles expanded much more than did those containing MAA. For an AA content of 6 mol % in the monomer mixture introduced in the second step, the particle volume increased by 33.3% after the treatment and attained 53.1% when the AA content was increased to 8 mol %. In contrast, for the MAA-containing particles, the volume expansion was hardly observed at 6 mol % MAA, and the increase in volume was only 12.6% for 8 mol % MAA. This clearly indicates that it is easier to achieve a higher pore volume in the AA- than in the MAA-containing particles. This occurs because AA is more hydrophilic, and the glass transition temperature of the AA-containing copolymer is lower than that of the MAA-containing copolymer.¹⁴ This means that the segments of the AA-containing copolymer are more flexible and their affinity for the alkali solution is higher. Figure 3 presents the micrographs of the S_1MA_1 and S₁MA₂ samples before [Fig. 3(A,C)] and after [Fig. 3(B,D)] the treatment. The micrographs of the

Figure 4 Micrographs of P(St-MMA-AA) seeded particles of different AA content (mol %) after alkali/ acid treatment: (A) 6.0%; (B): 8.0%; (C) 11.5%; (D) 14.8%.

AA-containing latex particles after treatment are given in Figure 4. One can see that for both the AA- and MAA-containing particles the pores are of a comparable size at the same carboxylic acid content; the number of pores is, however, larger for the AA-containing particles.

Effect of the AA Content on Pore Formation

Latex particles with different AA contents $(S_1A_1,$ S_1A_2 , S_1A_3 , S_1A_4 in Table III) were subjected to the alkali/acid treatment. Figure 4 presents micrographs of the corresponding porous particles. Table III shows that the volume expansion of the particles first increases with increasing AA content, reaches a maximum of 53.1% at 8 mol % AA, and then decreases. The volume of the particles even shrunk by 10% for the particles containing 14.8 mol % AA and no pores were observed. For the latex particles with a volume expansion lower than 34%, it seems that the pores are mostly located in the shell [Fig. 3(B,D) and Fig. 4(A)], where the density of the carboxylic groups is expected to be higher. A possible explanation for the optimum porosity at 8 mol % AA is as follows: While the mechanism of the pore formation is not yet well understood, it is clear that the carboxylic groups are responsible for the pore generation. One or perhaps several such groups constitute a nucleation site for the generation of one pore. If the number of the nuclei is sufficiently small, the porosity of the particles is expected to be proportional to the number of nuclei. When the number of nuclei becomes sufficiently large, the pores generated overlap in part with one another, and while the total volume of the pores still increases with an increasing number of nuclei, the increase is less than proportional. When the crowding of the nuclei is large enough, the overlaps of the pores become so large that the volume of the pores starts to decrease with increasing carboxylic content. When the crowding of the carboxylic groups becomes so large that the distance between them is of the order of the range of hydrogen-bonding interactions, a restructuring takes place, which will lead to a lower volume of the particles than before treatment. The treatment is still essential because it stimulates the restructuring of the polymer in the particles.

CONCLUSIONS

1. Monodisperse core/shell latex particles can be prepared, via the seeded polymer-

ization, by the slow dropwise addition of the monomers in the second stage. Particles were obtained by copolymerizing St-MMA-AA (orMMA) onto monodisperse seed particles of poly(St-MMA). The core/ shell particles had a dispersity of 1.001-1.003.

2. Pores have been generated in the core/shell particles by the alkali/acid treatment, and it was found that the total volume of the pores passes through a maximum with increasing AA content. This maximum was attributed to the crowding of the sites on which the pores are generated.

REFERENCES

- Guyot, A.; Revillon, A.; Yuan, Q. Polym Bull 1989, 21, 577.
- Pichot, C.; Delair, T.; Elaissari, A. In Polymeric Dispersions: Principles and Applications; Asua, J. M., Ed.; Kluwer: The Netherlands, 1997; p 515.
- Lewandowski, K; Svec, F.; Frechet, J. M. J. J Appl Polym Sci 1998, 67, 597.
- Coutinho, F. M. B.; Teixeira, V. G.; Barbosa, C. C. R. J Appl Polym Sci 1998, 67, 781.
- Kowalski, A.; Vogel, M.; Blakenship, J. Eur. Patent 22 633, 1980.
- Hook, J. W.; Harren, R. E. In Organic Coating Technology; Partitt, G. D.; Patsis, A. V., Eds.; Marcel Dekker: New York, 1984; p 299.
- Vanderhoff, J. W.; Park, J. M.; El-Aasser, M. S. In Polymer Latexes: Preparation, Characterization & Applications; Daniel, E. S.; Sudol, E. D.; El-Aasser, M. S., Eds.; American Chemical Society: Washington, DC, 1992; p 272.
- Okubo, M.; Ichikawa, K. Colloid Polym Sci 1994, 272, 933.
- Okubo, M.; Ito, A.; Hashiba, A. Colloid Polym Sci 1996, 274, 428.
- Ugelstad, J.; Hansen, F. K. Rubb Chem Techn 1976, 49, 536.
- Kricheldorf, H. R., Ed.; Handbook of Polymer Syntheses; Marcel Dekker: New York, 1991; p 271.
- Ryabov, A. V.; Semchicov, Y. D.; Sivannitskaya, N. N. Vyskomol Soedin A 1970, 12, 533.
- Chapman, C. B.; Valentine, L. J Polym Sci 1959, 34, 319.
- Brandrup, J.; Immergut, E. H., Eds.; Polymer Handbook, 3rd ed.; Wiley: New York, 1989; p VI-215.