Preparation of Uniform Hollow Polystyrene Particles with Large Voids by a Glass-Membrane Emulsification Technique and a Subsequent Suspension Polymerization

Guang-Hui Ma,[1] Ai-Yi Chen,[2] Zhi-Guo Su,[1] Shinzo Omi[2]

[1] *National Key Laboratory of Chemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, No. 1 Bei-Er-Tiao, Zhong-Guan-Cun, Beijing 100080, China*
[2] *Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei, Tokyo 184-8588, Japan*

ABSTRACT: Hollow polymer particles with large voids were prepared with styrene (St) as the main component and in the presence of a small amount of *N,N'*-dimethylamino-ethyl methacrylate (DMAEMA) via a glass-membrane emulsification technique and a subsequent suspension polymerization. A mixture of the monomer, hexadecane (HD), and *N,N'*-azobis(2,4-dimethylvaleronitrile) as an initiator was used as a dispersed phase (oil phase). By the careful pushing of the dispersed phase through the pores of the glass membrane into the aqueous phase, an emulsion of fairly monodisperse monomer droplets was formed. Then, the polymerization was performed by temperature being elevated to 70°C. The aqueous phase (continuous phase) contained poly(*N*-vinyl pyrrolidone) as a stabilizer, sodium lauryl sulfate as a surfactant, Na_2SO_4 as an electrolyte, and sodium nitrite ($NaNO_2$) as a water-soluble inhibitor. Results related to the effects of the HD content, DMAEMA, and the composition of the comonomer, including the crosslinker and flexible segment, on the features of the hollow particles were investigated. When the content of DMAEMA was higher than 1.0 wt % based on the total monomer, small, secondary particles were generated in the aqueous phase, but the generation was effectively prevented when DMAEMA was limited to 0.5 wt %. Hollow particles, with an average diameter of around 7 μm, were obtained with an St–DMAEMA system. The void size of the hollow particles was controlled by the HD content. When the HD content was lower (<25 wt % based on the oil phase), unbroken hollow particles were easily obtained. However, they tended to break into halves after drying when the HD content was increased to 50 wt %. A soft segment, lauryl acrylate, and a crosslinker, ethylene glycol dimethacrylate, were added to overcome this problem. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 244–251, 2003

Key words: polystyrene; crosslinking; voids; particle size distribution; phase separation

INTRODUCTION

Hollow particles are considered valuable because of their high light scattering ability, light weight, thermal insulation, and so forth.[1] For example, hollow particles have been used in many applications such as paper coating, pigments, and cosmetic foundation powders through the utilization of their light scattering ability.[2] In addition, hollow, crosslinked, composite particles can be applied as carriers for the controlled release of drugs and as masking or pacifying agents for coating and molding materials.[3–6]

One preparation method for hollow particles is incorporating a component with a high coefficient of expansion into polymer particles. With the heating of the polymer particles, the material with its high coefficient of expansion will expand and form voids. By this method, however, particles with multivoids are often formed, and some of the voids exit on the surface. It is difficult to obtain real hollow particles, that is, with voids in the center, the polymer being a shell that engulfs each void completely.

Real hollow particles are usually prepared by the utilization of the phase separation between the polymer and solvent (porogen). The solvent is the core, and the polymer forms the shell. After the core is extracted or evaporated, hollow particles are easily obtained. Itou et al.[7] and Okubo et al.[4–6] prepared submicrometer-size and micrometer-size hollow particles, respectively, with a seeded polymerization method. Itou et al. used submicrometer-size polystyrene (PSt) particles with a low molecular weight as a seed and a mixture of methyl methacrylate (MMA) and divinylbenzene (DVB) as a second-stage monomer. After a hydrophilic initiator was added to initiate the polymerization, a large portion of the DVB was copolymerized with the MMA near the surfaces of the particles, and the outer diameter was fixed during the initial stages of the polymerization. As the polymerization proceeded further, complete phase separation

occurred at the interface between the PSt and poly-(methyl methacrylate) (PMMA) because of the shrinkage of the latter, and water filled the separated part. Okubo et al. used their dynamic swelling technique to prepare hollow polymer particles with diameters of several micrometers. After a PSt seed was swollen with a mixture of DVB, toluene, and benzoyl peroxide in an ethanol/water medium, the polymerization was carried out. As the polymerization proceeded, the PSt moved toward the interior surfaces of the particles because of the crosslinking reaction of DVB, allowing the hydrophobic toluene to separate in the center of the particles. As a result, hollow particles were obtained after the toluene was removed.

As we have described, hollow particles usually are prepared by a two-step polymerization. In a previous study, we found that uniform hollow particles could be prepared by a one-step polymerization combining the Shirasu porous glass (SPG) membrane emulsion technique and a subsequent suspension polymerization process.[8] The SPG membrane possesses a uniform pore size distribution with a free choice of nominal pore size, ranging from 0.1 to 18 μm. Therefore, quite uniform droplets of a desired size, composed of monomers mixed with an initiator and a solvent, can be obtained by the permeation of the monomer phase through the pores of the membrane into the aqueous phase under a controlled pressure. After polymerization, the droplets yield uniform polymer particles. The narrow size distribution of the monomer droplets usually can be maintained during polymerization. With this method, we have successfully prepared monodisperse PSt,[9] P(St-co-MMA),[10] polyurethane,[11] PSt–polyimide,[12] poly(lactic acid),[13] PSt/PMMA,[14,15] and magnetite polymer[16,17] microspheres. The coefficient of variation (CV), which indicates the breadth of the size distribution of the particles, is typically about 10%. The diameter of the particle is about 6 times the membrane pore size. In a previous study,[16] PMMA hollow particles were successfully prepared with MMA and ethylene glycol dimethacrylate (EGDMA) as monomers and with heptane (HP) as a solvent (porogen). Because PMMA is more hydrophilic than HP, phase separation occurred, with heptane localized in the center and with a PMMA–EGDMA network as the shell of the particles. After the HP evaporated or was extracted, hollow particles were obtained.

Because PSt is more hydrophobic than PMMA, it is difficult to prepare hollow PSt particles by the aforementioned one-step polymerization process used for the preparation of PMMA hollow particles. In a previous study with the purpose of synthesizing poly(St-co-DMAEMA) composite particles,[8] it was found that PSt hollow particles could be obtained with a mixture of St, N,N'-dimethylaminoethyl methacrylate (DMAEMA), hexadecane (HD), and N,N'-azobis(2,4-dimethylvaleronitrile) (ADVN) as an initiator as the dispersed phase and with an aqueous phase containing sodium lauryl sulfate (SLS), poly(N-vinyl pyrrolidone) (PVP), and sodium nitrite (NaNO$_2$; inhibitor) as the continuous phase. HD worked as a porogen. However, secondary nucleation often occurred because a portion of the DMAEMA and initiator diffused into the aqueous phase to generate secondary nucleation. In this study, the contents of HD and DMAEMA were varied to change the void size and minimize secondary nucleation. Furthermore, the EGDMA crosslinker and lauryl acrylate (LA) flexible component were added to the monomer phase to enhance the strength and elasticity of the polymer wall to prevent the breakage of the polymer wall.

EXPERIMENTAL

Materials

For emulsification, the dispersion phase consisted of commercial-grade styrene (St; Kinshid Chemical Co., Osaka, Japan), commercial-grade DMAEMA (Tokyo Chemical Industries Co., Ltd., Tokyo, Japan), commercial-grade LA (Aldrich Chemical Co., Inc., Milwaukee, WI), commercial-grade EGDMA as a crosslinker (Tokyo Chemical Industries, Tokyo, Japan), reagent-grade ADVN as an initiator (Wako Pure Chemical Industries, Ltd., Osaka, Japan), and reagent-grade HD (porogen) as a hydrophobic solvent (Tokyo Chemical Industries, Tokyo, Japan). St, DMAEMA, and LA were purified by distillation under reduced pressure. EGDMA was washed with a 3 wt % alkaline solution three times, was washed with distilled and deionized water five times, and then was dried with a 4-Å molecular sieve. HD and ADVN were used as received. The continuous phase was an aqueous solution containing reagent-grade PVP as a stabilizer (weight-average molecular weight = 40,000 g/mol; K30, Tokyo Chemical Industries), biochemical-grade SLS as a surfactant (Merck, Darmstadt, Germany), reagent-grade Na$_2$SO$_4$ as an electrolyte (Tokyo Chemical Co., Tokyo, Japan), and reagent-grade NaNO$_2$ as a water-soluble inhibitor (Kishida Chemical Co., Osaka, Japan). The solvents for the precipitation and purification of the polymer and for gel permeation chromatography (GPC) measurements were commercial-grade methanol and tetrahydrofuran (THF; Wako Pure Chemical Industries, Osaka, Japan), respectively. All of the reagents were used as received, unless otherwise specified.

Water was purified by distillation, which was followed by deionization with ion-exchange resins.

Apparatus

A miniature kit for emulsification with an MPG module (microporous glass, a brand name of SPG) installed was purchased from Ise Chemical Co. (Tokyo, Japan). A schematic diagram of this kit and the de-

TABLE I
Standard Recipe for Emulsification

Ingredient	Weight (g)
Continuous phase	
PVP	1.0
Inhibitor	
$(NaNO_2)$	0.1
Na_2SO_4	0.1
SLS	0.075
Water	225
Dispersion phase	20.0
ADVN	0.1
Total monomer	20.0–HD
HD	2.0, 5.0, 10.0

tailed emulsification process have been given else-where.[13,16] A membrane with a pore size of 1.42 μm was used in this study.

Preparation process

Emulsification

A standard recipe for emulsification in this study is shown in Table I. A mixture of the monomer and HD containing the dissolved initiator ADVN was used as the dispersed phase (oil phase), and water containing dissolved PVP, SLS, Na_2SO_4, and $NaNO_2$ was used as the continuous phase (aqueous phase). The emulsion was prepared by the dispersion phase being pressed into the aqueous phase through the glass membrane under a carefully controlled nitrogen pressure (always at 0.37 kgf/cm³).

Polymerization

After the emulsification was finished, the emulsion of the monomer droplets was immediately transferred to a glass separator flask equipped with a half-moon-blade stirrer, a nitrogen inlet, and an outlet through a condenser. A gentle bubbling of nitrogen from a noz-

TABLE II
Preparative Results of Monomer Droplets and Polymer Particles as a Function of HD Content

	Run No.		
	254	264	701
DMAEMA (g)	0.45	0.45	0.45
St (g)	17.55	14.55	9.55
HD (g)	2	5	10
Monomer droplets			
d_{drop} (μm)[a]	8.10	7.92	7.01
CV (%)	10.00	8.32	8.56
Polymer particles			
d_p (μm)[b]	5.94	5.49	6.85
CV (%)	10.02	8.78	8.18

[a] d_{drop} = number-average diameter of monomer droplets.
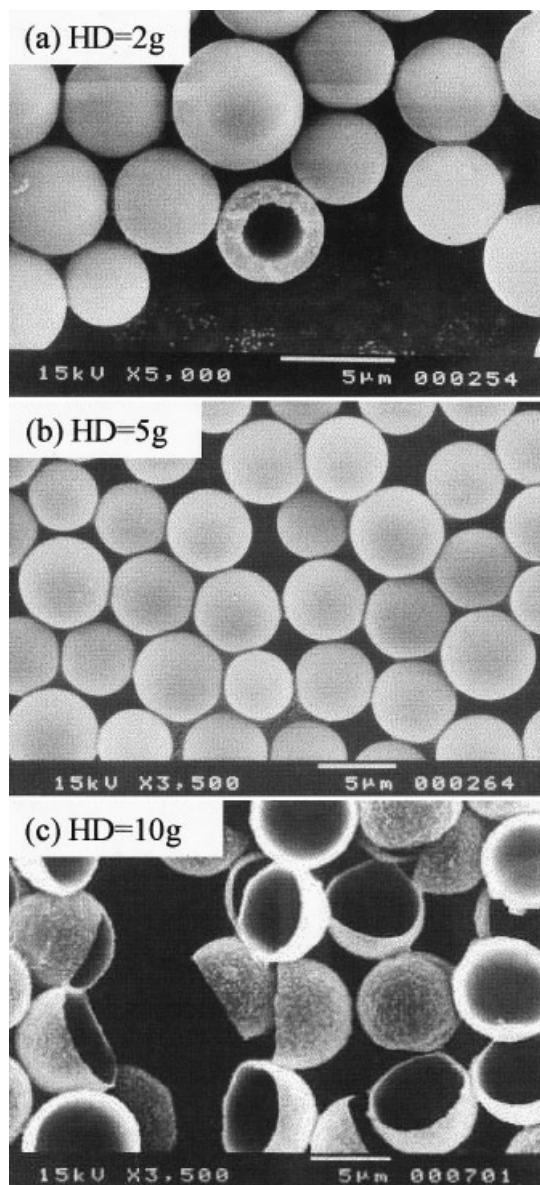[b] d_p = number-average diameter of polymer particles after polymerization.
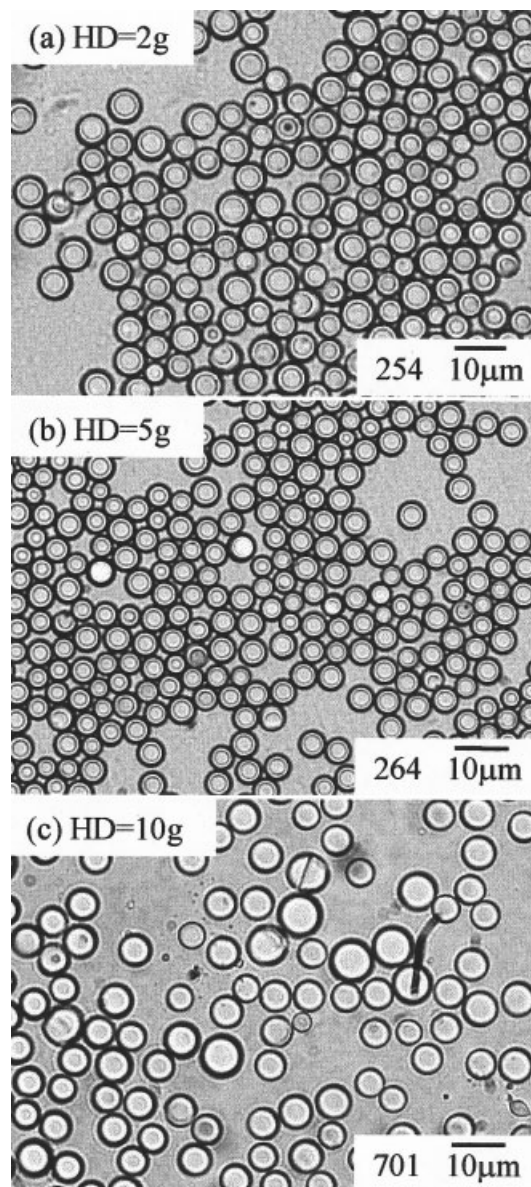
Figure 1 OM photographs of monodisperse polymer particles as a function of the HD content. The HD amount is based on a 20-g total oil phase: (a) 2.0, (b) 5.0, and (c) 10.0.

zle into the emulsion was continued for 1 h for the removal of the dissolved oxygen. The nitrogen nozzle was then lifted above the surface of the emulsion, and the temperature was raised to 70°C. The polymerization was carried out under a nitrogen atmosphere for 20 h at a stirring rate of 160 rpm. The monomer conversion was determined gravimetrically. The polymer in the weighed emulsion was precipitated by methanol, separated by centrifugation, dried in vacuo, and weighed.

Analyses

Observations by optical microscopy (OM)

OM (Olympus BHC with a Olympus DP10 digital camera, Tokyo, Japan), which simply but reliably identifies a

Figure 2 SEM photographs of monodisperse polymer particles as a function of the HD content. The HD amount is based on a 20-g total oil phase: (a) 2, (b) 5, and (c) 10.

particle's shape and morphology, was employed to observe the monomer droplets and resulting polymer particles. Two hundred monomer droplets on the OM photographs were measured to determine the number-average diameters of the monomer droplets.

Observations by scanning electron microscopy (SEM)

The latex was diluted with water about 10 times and dropped on an aluminum film attached to a specimen stub for SEM (JSM-5300, JEOL, Tokyo, Japan). After the specimen was dried, it was coated with a thin gold layer (ca. 60 Å thick) under a pressure reduced below 8 Pa with a fine coater (JFC-1200, JEOL, Tokyo, Japan) and then was observed with SEM for an examination

of the general features of the surface. Two hundred particles on the SEM photographs were measured to determine the number-average diameters of the polymer particles.

GPC measurements

GPC (HLC-801, Toso Co., Ltd., Tokyo, Japan) was used to measure the molecular weight and the molecular weight distribution. The number-average and weight-average molecular weights of the polymer were determined by GPC with the gel column system calibrated with standard PSt. THF was used as an elution solvent. Only the THF-soluble polymers were measured.

RESULTS AND DISCUSSION

Effect of the HD content

HD was used as a hydrophobic additive and porogen in this study. To change the void size and wall features, we changed the HD content from 2 to 10 g, that is, from 10 to 50 wt % based on the total oil phase. The DMAEMA content was fixed at 0.45 g. The amount of St was adjusted to maintain the total oil phase at 20 g.

The preparative results are concluded in Table II, and the OM and SEM photographs are shown in Figures 1 and 2. Normalized GPC chromatograms of polymer particles are shown in Figure 3. From OM and SEM photographs, it is evident that completely hollow particles with HD in the centers of the particles were obtained, regardless of the HD content. From Table II, it is known that the distribution of monomer droplets was maintained during polymerization, and the CV values of the monomer droplet and polymer particle were around 10%. The diameters of the droplets appeared larger than those of the polymer particles because of the difference in the densities of the monomer and polymer and the diffusion of the monomer into the aqueous phase. The void size could be controlled by the HD content. When the HD content
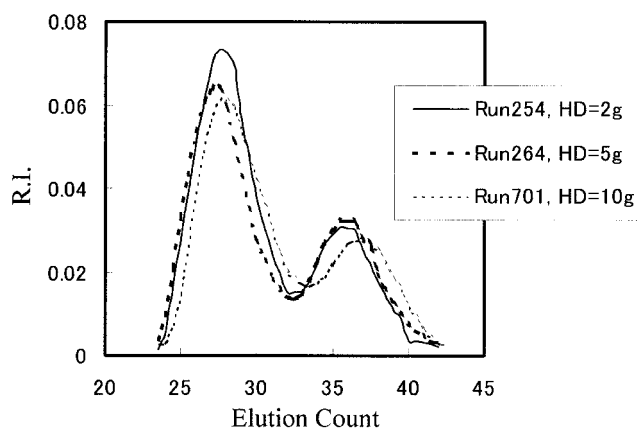
Figure 3 Normalized GPC chromatograms of polymer particles as a function of the HD content.
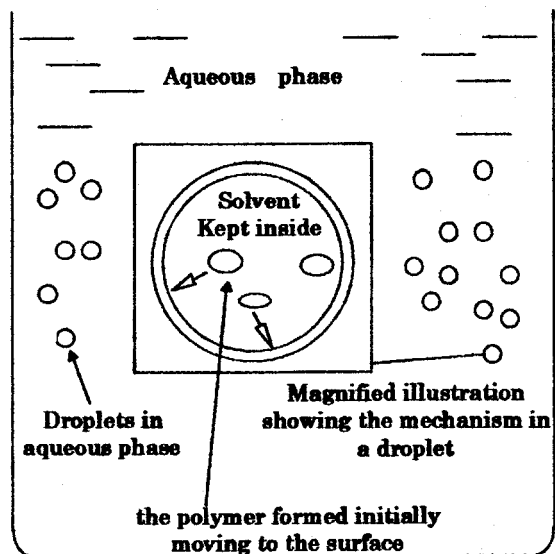
Figure 4 Schematic illustration showing the formation of hollow particles.

was lower than 5 g (25 wt % based on the oil phase), unbroken hollow particles were obtained even after the particles were dried for SEM observations. When the HD content was 10 g (50 wt %), hollow particles with large voids and thin walls were observed, but they broke into halves after being dried for SEM observations because the walls were thin and brittle.

From Figure 3, it is known that two peaks were detected in each case. The one at the higher elution count (lower molecular weight) resulted from the polymer of the original droplet (hollow particle), and the other that appeared at the lower elution count (higher molecular weight) originated from the polymer of the secondary nucleation, which was generated in the aqueous phase, because a portion of the monomer diffused into the aqueous phase from the monomer droplet. The polymerizations in the original droplets and the secondary nuclei followed different polymerization mechanisms, the former following homogeneous bulk or solution polymerization, and the latter proceeding by emulsion polymerization. It is well known that a molecular weight obtained through an emulsion polymerization is higher than that obtained by bulk or solution polymerization, typically reaching 10^5 to 10^6 g/mol. Bulk or solution polymer-

izations usually result in polymers with molecular weights of approximately 10^4 g/mol. From a comparison of the two peaks in Figure 3, it is evident that the area of the polymer that resulted from the secondary particles was larger than that which originated from hollow particles. This implies that a large number of secondary particles were generated. Furthermore, the HD clearly showed a slight effect on the prevention of the formation of the secondary particles.

In this work, the formation of a hollow particle was considered essentially a phase separation of a hydrophobic solvent from a wall polymer. The proposed mechanism is illustrated in Figure 4. In the illustration, a droplet is magnified to explain the mechanism. In brief, hydrophilic DMAEMA incorporated into the polymer chains was thought to play the role of promoting the movement of the polymer to the surface. The polymer was aggregated at the surface and formed a shell layer; at the same time, the hydrophobic solvent, immiscible with the copolymer, was separated in the core of the droplet. The particles with clear hollow structures were confirmed by SEM observations after the solvent was extracted and the particles were dried.

Effect of the monomer composition

As mentioned previously, the void size was varied easily through changes in the HD content. However, there were many secondary particles because DMAEMA and ADVN diffused into the aqueous phase to generate secondary nucleation on account of their hydrophilicity. Furthermore, the hollow particles broke into halves when the HD content was higher. Therefore, the effect of monomer composition was investigated to overcome these problems. The formulations are given in Table III. The monomer formulations are classified as A–D. The HD content was maintained at 10 g. St was the main monomer component, and DMAEMA was present in a small amount in all of the formulations. For type A, only St and DMAEMA were used. For B and C, EGDMA or LA was added, in addition to St and DMAEMA. For type D, both EGDMA and LA were added, and their ratio was varied. EGDMA and LA were expected to improve the strength and elasticity of the polymer wall, preventing the breakage of the hollow particles.

TABLE III
Type of Monomer Formulation Classified as A–D

Dispersion phase	Type			
	A	B	C	D
Total monomer (g)	10.0	10.0	10.0	10.0
DMAEMA (g)	Varied (0.05–0.45)	0.05	0.05	0.05
EGDMA (g)	0	Varied (0.10–0.20)	0	Varied (0.10–0.20)
LA (g)	0	0	Varied (0.10–0.20)	Varied (0.10–0.20)
HD (g)	10.0	10.0	10.0	10.0

TABLE IV
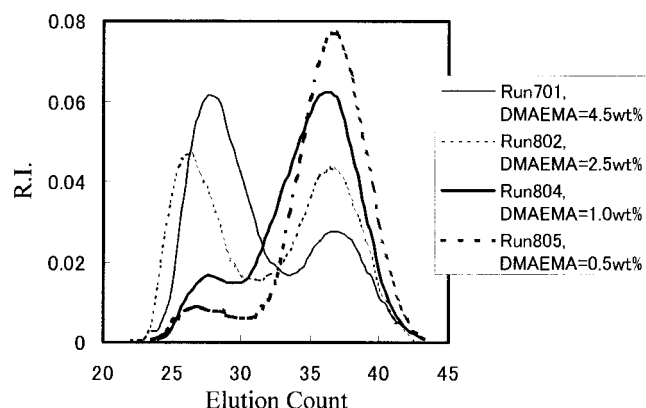**Preparative Results of Monomer Droplets and Polymer Particles as a Function of DMAEMA Content**

	Run No.			
	701	802	804	805
DMAEMA (g)	0.45	0.25	0.10	0.05
St (g)	9.55	9.75	9.90	9.95
Emulsion droplets				
d_{drop} (μm)[a]	7.01	6.79	7.68	7.23
CV (%)	8.56	9.23	8.60	9.14
Polymer particles				
d_p (μm)[b]	6.85	6.02	6.48	7.02
CV (%)	8.18	8.75	7.27	12.97

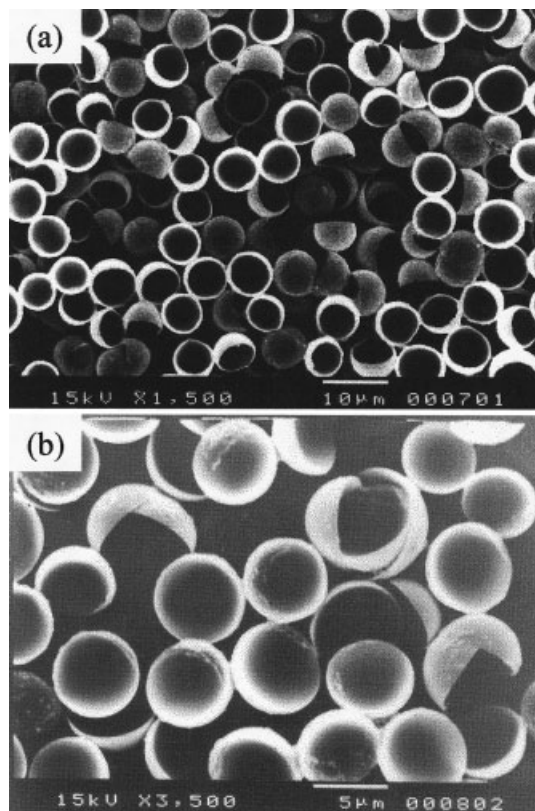[a] d_{drop} = number-average diameter of monomer droplets.
[b] d_p = number-average diameter of polymer particles after polymerization.

Type A

In a previous study,[8] it was clarified that PSt could not engulf HD completely if DMAEMA was not added. However, when a substantial amount of hydrophilic DMAEMA was present, it led to secondary nucleation in the aqueous phase, as described previously. One reason was that considerable DMAEMA diffused into the aqueous phase to generate the secondary particles. Therefore, DMAEMA was reduced from 0.45 (4.5 wt %) to 0.05 g (0.5 wt %), based on 10 g of total monomer. The results are reported in Table IV. The normalized GPC chromatographs are shown in Figure 5. From the curve corresponding to 4.5 wt % DMAEMA, the area of the peak assigned to the secondary particles is larger than that of the peak assigned to the hollow particles, indicating that many secondary particles formed. In parallel with the reduction of DMAEMA, the generation of secondary particles decreased, as seen from the curve for 2.5 wt % DMAEMA. For the purpose of further restraining the secondary nucleation, the amount of hydrophilic DMAEMA was reduced further. When the amount of
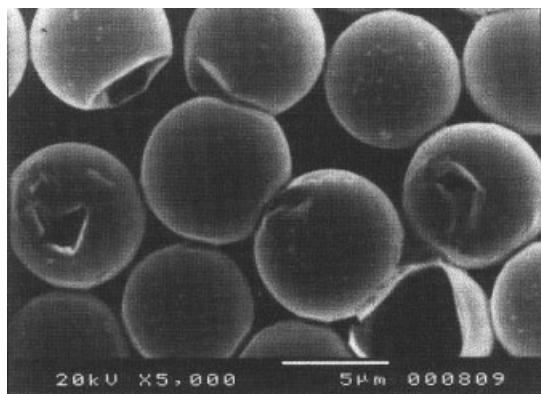

Figure 6 SEM photographs of polymer particles obtained from the type A formulation when 10.0 g of HD was used: (a) run 701 and (b) run 802.

DMAEMA was 1.0 wt %, the peak at the lower elution count, which showed the generation of secondary particles, obviously decreased. When only 0.5 wt % DMAEMA was added, the peak assigned to the suspension polymerization of the hollow particles was dominant, and only a few secondary particles were detected. The SEM photographs are shown in Figure 6. It is evident from the SEM photographs that the hollow structure of the polymer particles was retained, although it broke after drying. These results suggest that approximately 0.5 wt % DMAEMA was sufficient for the purpose of hollow structure formation and that the generation of secondary particles was effectively prevented through the control of the amount of DMAEMA at a lower level. Therefore, the DMAEMA content was maintained at 0.5 wt % in the subsequent experiments.

Type B

Although the amount of secondary particles was reduced to a low level through a decrease in the DMAEMA content, the particles broke into halves after they were dried for SEM observations. Because the particles showed complete spherical shapes in the emulsion state as observed by OM but a broken shape as observed by SEM, it was concluded that the hollow

Figure 5 Normalized GPC chromatograms of polymer particles as a function of the DMAEMA content. The weight percentages of DMAEMA (based on the total monomer) were 4.5, 2.5, 1.0, and 0.5.

Figure 7 SEM photograph of polymer particles obtained from run 809 of the type B formulation. The EGDMA content was 1.0 wt % based on the total monomer.

particles broke when they were dried. The SEM observations and gold coating were carried out in vacuo; HD would evaporate in vacuo. Once a weak point formed on a wall of a hollow particle during the evaporation of HD, the weak point extended along the periphery of the hollow particle. As a result, the hollow particle broke into halves. To improve the strength of the polymer wall, we added EGDMA as a crosslinker to type B: 1.0–2.0 wt % EGDMA was added, based on the total monomer. DMAEMA was maintained at 0.5 wt % for the prevention of secondary nucleation, and St was adjusted so the total weight of the monomer would remain unchanged. When EGDMA was added, a different broken state was observed. A typical SEM photograph is shown in Figure 7 for a case in which 1.0 wt % EGDMA was added. It is clear that some of the hollow particles were broken from bursting voids of the polymer walls, although these polymer particles appeared unbroken in the emulsion state, which was confirmed by OM. The difference in the breakage between types A and B demonstrated that the crosslinker EGDMA improved the strength of the polymer walls, that is, the resistance against breakage into halves. Because the strength of the wall was enhanced, a weak point could not extend to a wide area but just extended within a small area. Probably because the flexibility of the PSt wall was not sufficient, a bursting void formed from a weak point when the evaporation rate of HD was abrupt. Therefore, a flexible component was added to the monomer phase.
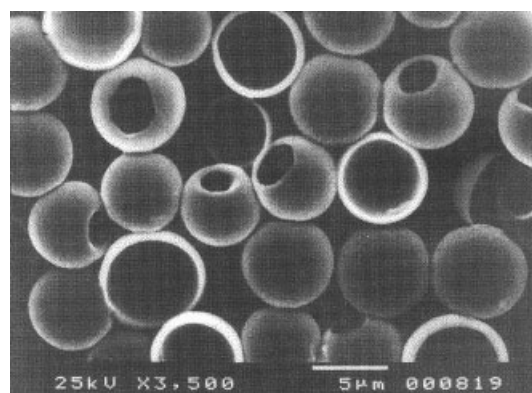
Type C

Because the lack of flexibility probably was a reason for the breakage, the acrylic monomer LA, with its long, linear alkyl side chain, was used to resolve the problem of breakage in the type C series. An acrylic monomer with a long, linear alkyl chain has been incorporated for lowering the glass-transition temper-

ature (T_g) and for other purposes, such as providing insight into the heterogeneity and roughness of polymer surfaces.[18] Because poly(lauryl acrylate) showed a lower T_g, incorporating the LA monomer into the polymer wall was expected to provide rubbery flexibility to the polymer wall. As a result, the polymer particles showed broken states different from those of type B. A typical SEM photograph is shown in Figure 8. Some of the particles broke into halves, and some of them formed small voids. These results suggested that only improving the flexibility of the polymer wall was not sufficient to avoid breakage of the polymer wall. Both the strength and flexibility of the polymer wall should probably be considered.

Type D

On the basis of these results, EGDMA and LA were added together in type D, and their amounts were varied. The SEM photographs are shown in Figure 9. The resulting particles revealed different surface features, which strongly depended on their added amounts. The weight percentages of LA and EGDMA were varied as 2.0 and 1.5 wt % (run 822), 1.0 and 1.0 wt % (run 826), and 2.0 and 1.0 wt % (run 823) based on the total monomer. From a comparison of the different appearances of the hollow particle surfaces, it seemed that the formulation of 2.0 wt % LA and 1.0 wt % EGDMA was most effective for preventing the breakage of hollow particles, as shown in Figure 9(c) (run 823). It is surprising that a slight variation of LA and EGDMA resulted in quite different surface features of the hollow particles. When LA was lower [run 826, Fig. 9(b)], the flexibility was not enough to avoid the breakage of particles during the evaporation of HD. However, when EGDMA was higher [run 822, Fig. 9(a)], although the strength of the polymer wall was enhanced, its flexibility was spoiled because of the crosslinking of the polymer wall. It is a well-known phenomenon that a crosslinker will decrease T_g of a polymer.

Figure 8 SEM photograph of polymer particles obtained from run 819 of the type C formulation. The LA content was 2.0 wt % based on the total monomer.
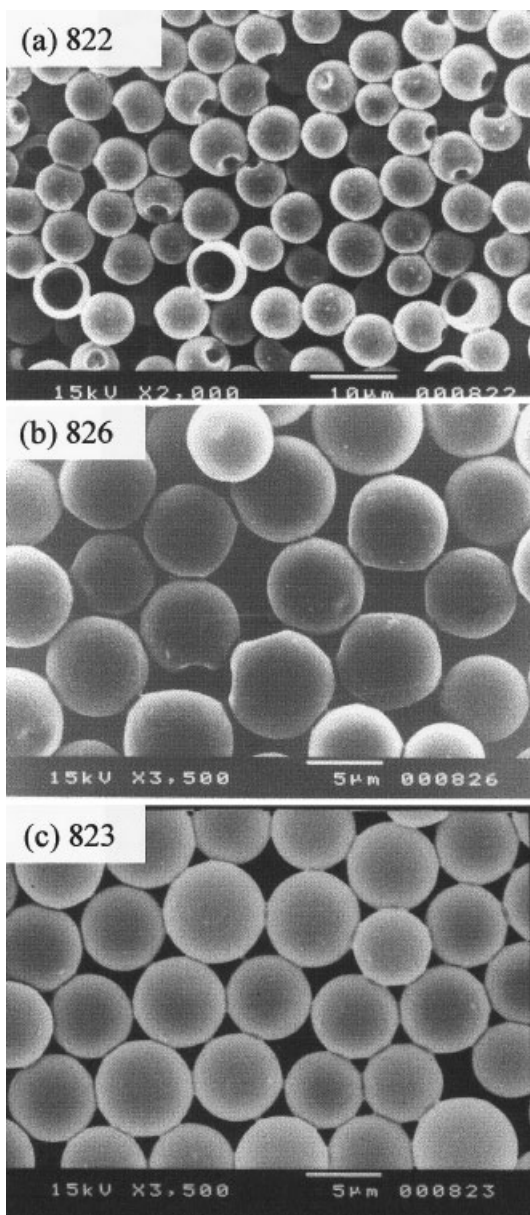
Figure 9 SEM photographs of polymer particles obtained from the type D formulation: (a) run 822, 2.0 wt % LA and 1.5 wt % EGDMA; (b) run 826, 1.0 wt % LA and 1.0 wt % EGDMA; and (c) run 823, 2.0 wt % LA and 1.0 wt % EGDMA.

Considering the reproducibility, we carried out the same experiment with the same recipe of run 823. Unbroken polymer particles were observed again by SEM observations.

On the basis of these results, we concluded that unbroken hollow particles with small voids were easily obtained when the HD content was lower. However, hollow particles with large voids broke into halves when the HD content was higher. This problem was solved by the addition of a 1.0 wt % EGDMA crosslinker and a 2.0 wt % LA flexible component. Adding a crosslinker has another advantage: the hol-

low morphology can be maintained even though it is used in a good solvent for PSt. A drawback is that the formulation for obtaining unbroken hollow particles with large voids is quite strict. Further investigations will be carried out through changes in the porogen, crosslinker type, and so forth.

CONCLUSIONS

By employing an SPG emulsification technique followed by a suspension polymerization process, we prepared monodisperse PSt particles. We proposed that DMAEMA enhanced the formation of the polymer wall, engulfing HD inside of the particles, and eventually formed hollow PSt particles. However, hydrophilic DMAEMA led to secondary nucleation in the aqueous phase. By controlling the content of DMAEMA at 0.5 wt % of the total monomer, we prevented secondary nucleation. When the HD content was lower, unbroken hollow particles were easily obtained because of the thick wall. When the HD content was higher, however, hollow particles with large voids and thin voids broke when they were dried for SEM observations. This was overcome by the addition of 2.0 wt % LA and 1.0 wt % EGDMA.

References

1. Tamai, H.; Sumi, T.; Yasuda, H. J Colloid Interface Sci 1996, 177, 325.
2. Beppu, M. M.; de Oliveira Lima, E. C.; Galembeck, F. J Colloid Interface Sci 1996, 178, 93.
3. Kowalski, A. U.S. Patent 4,427,836, 1984.
4. Okubo, M.; Kanaida, K.; Fujimura, M. Chem Express 1990, 5, 797.
5. Okubo, M.; Ichikawa, K.; Fujimura, M. Colloid Polym Sci 1991, 269, 1257.
6. Okubo, M.; Ichikawa, K.; Fujimura, M. In Polymer Latexes—Preparation, Characterization, and Applications; Daniels, E. S.; Sudol, E. D.; El-Aasser, M. S., Eds.; ACS Symposium Series No. 492; American Chemical Society: Washington, DC, 1992; Chapter 18, p 492.
7. Itou, N.; Masukawa, T.; Ozaki, I.; Hattori, M.; Kasai, K. Colloids Surf A 1991, 153, 311.
8. Ma, G.-H.; Nagai, M.; Omi, S. J Appl Polym Sci 2001, 79, 2408.
9. Omi, S.; Katami, K.; Yamamoto, A.; Iso, M. J Appl Polym Sci 1994, 51, 1.
10. Nuisin, R.; Ma, G.-H.; Omi, S.; Kiatkamjornnwong, S. J Appl Polym Sci 2000, 77, 1013.
11. Yuyama, H.; Yamamoto, K.; Shirafuji, K.; Ma, G.-H.; Nagai, M.; Omi, S. J Appl Polym Sci 2000, 77, 2237.
12. Omi, S.; Matsuda, A.; Imamura, K.; Nagai, M.; Ma, G.-H. Colloids Surf A 1999, 153, 373.
13. Ma, G.-H.; Nagai, M.; Omi, S. Colloids Surf A 1999, 153, 383.
14. Ma, G.-H.; Nagai, M.; Omi, S. J Colloid Interface Sci 1999, 214, 264.
15. Ma, G.-H.; Nagai, M.; Omi, S. J Colloid Interface Sci 1999, 219, 110.
16. Omi, S.; Ma, G.-H.; Nagai, M. Macromol Symp 2000, 151, 319.
17. Omi, S.; Kanetaka, A.; Shimamori, Y.; Supsakulchai, A.; Nagai, M.; Ma, G.-H. J Encapsul 2001, 18, 749.
18. Bongiovanni, R.; Malucelli, G.; Priola, A. J Colloid Interface Sci 1995, 171, 283.