Study of the Preparation and Mechanism of Formation of Hollow Monodisperse Polystyrene Microspheres by SPG (Shirasu Porous Glass) Emulsification Technique

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ABSTRACT: In a previous study, it was found that monodisperse polystyrene (PSt) hollow particles can be prepared under special conditions by combining a Shirasu Porous Glass (SPG) emulsification technique and subsequent suspension polymerization process. That is, a mixture of styrene (St), N,N-dimethylamino ethyl methacrylate (DMAEMA), hexadecane (HD), and initiator N, N'-azobis(2,4-dimethylvaleronitrile) (ADVN) was used as the dispersed phase in an aqueous phase containing poly(vinyl pyrrolidone) (PVP), sodium lauryl sulfate (SLS), and water-soluble inhibitor. The dispersed phase was created by pushing the oil phase through the uniform pores of an SPG membrane into the continuous phase to form uniform droplets. Then, the droplets were polymerized at 70°C. It has been puzzling that hollow microspheres were obtained only when sodium nitrite ($NaNO_2$) was used as a water-soluble inhibitor, while one-hole particles were formed when hydroquinone (HQ) or diaminophenylene (DAP) was used. In this study, the mechanism of formation of the hollow microspheres was verified by measuring the variation of diameter, molecular weight distribution, and monomer conversion, and by observing morphological changes during the polymerization, as well as by changing the type and amount of hydrophilic monomer, and initiator. It was found that the diameter of the oil droplets decreased, and a large amount of secondary new particles formed immediately after polymerization started in the case of $NaNO_2$. However, there was no such apparent behavior to be observed when HQ or DAP was used. It was determined that the hollow particles formed due to the rapid phase separation between PSt and HD, and as a consequence, a large amount of monomer diffused into the aqueous phase to form the secondary particles. Rapid phase separation confined the HD inside the droplets, a nonequilibrium morphology. On the other hand, one-hole particles, representing an equilibrium morphology, formed when the phase separation occurred slowly because a lot of monomer existed inside of the droplets to allow mobility of the PSt. The addition of DMAEMA allowed the hollow particles to be formed more easily by decreasing the interfacial tension between the copolymer and aqueous phase. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1530–1543, 2002

Key words: SPG membrane; membrane emulsification; suspension polymerization; hollow polystyrene microspheres; particle morphology

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INTRODUCTION

Hollow microspheres show many attractive characteristics, for example, thermal resistance, low density, thermal insulation, and optical opacity due to the small air void. They can be used in various fields such as paint, ink, paper industries, cosmetic foundations, floating materials for absorbing organic oils, and so forth. Monodisperse hollow particles have been prepared by utilizing phase separation in the presence of a crosslinking agent by seeded polymerization. Itou et al.[1] used submicron-size polystyrene (PSt) microspheres with a low molecular weight as a seed. The seed was obtained in the presence of a mercaptan (radical transfer agent) by emulsion polymerization. After the seed latex was swollen by a mixture of methyl methacrylate (MMA) and divinylbenzene (DVB) in an aqueous phase containing sodium dodecylbenzenesulfonate (SBS) emulsifier, then a hydrophilic initiator was added to carry out polymerization. Because the hydrophilic initiator and DVB crosslinking agent were used, a large part of the DVB was copolymerized with the MMA near the surface of particles, and the outer diameter was fixed in the initial stages of the polymerization. As the polymerization proceeded further, phase separation occurred between the seed polymer (PSt) and subsequently polymerized polymer (PMMA). Then complete phase separation occurred at the interface between the PSt and PMMA owing to the shrinkage of the latter, and water filled the separated part. The size of void became larger as the polymerization proceeded.

Okubo et al.[2,3] used their dynamic swelling technique to prepare hollow polymer microspheres with diameters of several microns. First, a PSt seed was dispersed in an ethanol/water (7/3, w/w) mixture where DVB, solvent (toluene, etc.), benzoyl peroxide (BPO), and poly(vinyl alcohol) (PVA) stabilizer were dissolved. Water was added continuously to the system to allow the DVB, solvent, and BPO to be absorbed by the seed, and then the polymerization was carried out. As the polymerization proceeded, the PSt moved towards the interior surface of the particles due to 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. The size of the void could be controlled by varying the degree of swelling, or using benzene and xylene as the solvent instead of toluene.

Both of the above techniques require two polymerization steps. We have developed a special method to prepare uniform PMMA hollow particles with diameters around 10 μm by a one-step polymerization, combining the SPG (Shirasu Porous Glass) membrane emulsion technique with a subsequent swelling and polymerization process.[4] SPG membranes are special porous glass membranes with very uniform pores. By applying a moderate pressure, an oil phase containing initiator permeates through the uniform pores of the membrane into the aqueous phase to form uniform droplets. The stabilizer and surfactant dissolved in the aqueous phase are adsorbed on the surface of the droplets to stabilize them. Then, by elevating the temperature to decompose the initiator, the suspension polymerization proceeds to form the uniform particles. During the polymerization, the monodispersity is maintained if the emulsification and polymerization conditions are adequate. With this method, we have successfully prepared monodisperse polystyrene (PSt),[5] PSt-PMMA,[6] polyurethane,[7] and polystyrene–polyimide[8] microspheres. The CV (coefficient of variation) value, which indicates the breadth of the size distribution of the particles, is typically about 10%. Although this value may not meet the strictest definition of monodispersity, this is the definition applied in this work. In the preparation of PMMA hollow particles, a special swelling method combined with the SPG emulsification technique was devised. The SPG emulsification method is not suitable for the direct emulsification of relatively hydrophilic monomers, such as MMA. Because the SPG membrane is composed of hydrophilic Al_2O_3–SiO_2, its pore walls are wetted easily by the hydrophilic monomer, generating a jet-like stream, which leads to nonuniform droplets. The process of preparation of hollow PMMA particles is as follows. Uniform droplets composed of hydrophobic heptane (HP), initiator, and sometimes, 2-ethylhexyl acrylate (2-EHA), were first prepared by the SPG technique. These were mixed with a fine secondary emulsion composed of hydrophilic MMA and ethylene glycol dimethacrylate (EGDMA), which was prepared using a homogenizer. The oil phase of the secondary emulsion diffuses through the aqueous phase being absorbed subsequently by the uniform seed droplets. Then, by the polymerization process, phase separation occurs with heptane localized in the center and a PMMA–EGDMA network as the shell of the particles, because PMMA is more hydrophilic than HP. After the HP was extracted,

hollow particles were obtained. Furthermore, it was found that incorporating a small amount of 2-EHA comonomer into the copolymer can enhance the elasticity of the wall and overcome the brittleness of PMMA.

Because PSt is more hydrophobic than PMMA, it is difficult to prepare PSt hollow particles by the above 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, it was found that PSt hollow particles could be obtained by using a mixture of St, *N,N′*-dimethylamino ethyl methacrylate (DMAEMA), hexadecane (HD), and *N,N′*-azobis(2,4-dimethylvaleronitrile) (ADVN) initiator as the dispersed phase, and an aqueous phase containing sodium lauryl sulfate (SLS), poly(*N*-vinyl pyrrolidone) (PVP), and $NaNO_2$ (inhibitor) as the continuous phase. However, it was quite mysterious that one-hole particles formed when hydroquinone (HQ) or diaminophenylene (DAP) was used as a water-soluble inhibitor instead of $NaNO_2$. In this study, the mechanism of formation of the hollow microspheres was verified by measuring the variation of diameter, molecular weight distribution, and monomer conversion, and by observing morphological changes during the polymerization, as well as by changing the types and amounts of the hydrophilic monomer and initiator.

EXPERIMENTAL

Materials

Styrene (St) was a commercial grade (Kishida Chemical Co.). *N,N′*-dimethylamino ethyl methacrylate (DMAEMA) and 2-hydroxyethyl methacrylate (HEMA) were reagent grades (Tokyo Chemical Industries, Co., Ltd.). All of the monomers were distilled under vacuum to remove the inhibitors.

2,2′-Azobis(2,4-dimethylvaleronitrile) (V-65, ADVN) (Wako Pure Chemical Industries, Ltd.) was reagent grade and was used as an initiator. Hexadecane (HD) was reagent grade (Tokyo Chemical Industries, Co., Ltd.) and was used as a hydrophobic additive and porogen. Sodium nitrite ($NaNO_2$), hydroquinone (HQ), and diaminophenylene (DAP) were reagent grade (Kishida Chemical Co.), and were used as water-soluble inhibitors, to prevent the secondary nucleation in the aqueous phase. Phenol and aniline were reagent grade (Wako Pure Chemical Industries, Ltd.), and

Table I   A Standard Recipe for SPG Emulsification

Ingredients	Weight (g)
Continuous phase	
PVP	1.0
Inhibitor (HQ, $NaNO_2$, DAP)	0.10
Na_2SO_4	0.10
SLS	0.075
Water	225
Dispersion phase	
ADVN	0.10
St	17.55
DMAEMA (or HEMA)	0.45
HD	2.0

were used for comparison with HQ and DAP. Sodium lauryl sulfate (SLS) was biochemical grade (Merck). Poly(*N*-vinyl pyrrolidone) (PVP, K30, MW = 40,000 g/mol) was reagent grade (Tokyo Chemical Co.), and was used as a stabilizer. Electrolyte Na_2SO_4 was reagent grade (Wako Pure Chemical Industries, Ltd.), and was used to adjust the electrolyte concentration of the aqueous phase. Methyl alcohol was a commercial grade (Kishida Chemical Co.), and was used to precipitate and wash the particles. All these reagents were used as received. Water was purified by distillation followed by deionization using ion-exchange resins.

Apparatus

A miniature kit for emulsification with an MPG module (microporous glass, brand name of SPG) installed was purchased from Ise Chemical Co. A schematic diagram of this kit and the detailed emulsification process were described in a previous article.[10] A membrane with pore sizes of 1.42 μm was used in this study. Usually, the resulting droplet size is about six times as large as the pore size of the membrane.[5]

Preparation of Microspheres

Emulsification

A standard recipe is shown in Table I. The monomer and HD mixture containing dissolved ADVN initiator was used as the dispersed phase (oil phase), and water containing dissolved PVP stabilizer, SLS surfactant, Na_2SO_4 electrolyte, and inhibitor (HQ, $NaNO_2$, or DAP), was used as the continuous phase (aqueous phase). The oil phase

was forced continuously by nitrogen gas pressure through the SPG membrane into the aqueous phase. Then, the stabilizer and SLS dissolved in the aqueous phase are adsorbed onto the surface of the droplets to stabilize them. The total amount of monomer was always around 10 wt % based on the aqueous phase. The detailed SPG membrane emulsification process was described elsewhere.[10]

Polymerization

The emulsion obtained was transferred to a four-neck glass separatory flask equipped with a semi-circular anchor-type blade, a condenser, and a nitrogen inlet nozzle. After the emulsion was purged with nitrogen gas for 1 h, the nozzle was lifted above the surface of the emulsion, and the temperature was elevated to 70°C for the polymerization. The polymerization was carried out for 24 h under a nitrogen atmosphere. When necessary, 5 mL of emulsion was sampled by using a syringe and a needle at a desired time interval, and used for morphological observation, measurement of monomer conversion, and molecular weight distribution.

Swelling of Hollow Particles

Swelling with St Monomer

Fifty grams of the resulting dispersion of hollow particles (run 254) (solids content 9.0 wt %, 4.5 g) were added to a 100-mL beaker. The secondary emulsion was prepared by employing a homogenizer, where St (1 g or 2.3 g) was used as the dispersed phase with 50 g of aqueous phase containing 0.05 g SLS as the continuous phase. Then, the secondary emulsion was mixed with the polymer dispersion under magnetic stirring (300 rpm) to allow the St monomer to be absorbed by the polymer particles. After 4 h, the dispersion was observed by optical microscopy.

Swelling with Toluene

The same procedure as described above was employed, but 9 g of toluene was used instead of St. After the hollow particles were swollen with toluene, the dispersion was stirred at room temperature for 1 week to allow the toluene to evaporate slowly, or at 70°C for 2 h to rapidly evaporate the toluene.

Analyses

Optical Microscope (OM) Observation

The diameters and morphologies of the dispersed phase before and after polymerization were ob-

served with an optical microscope (Olympus BHC with a Olympus DP10 digital camera). The diameters of about 300 droplets or particles were measured to calculate the average diameters and size distribution.

SEM Observation

The surface features of polymer particles were observed using a JSM-5300 (JEOL) scanning electron microscope (SEM). The specimens for SEM observations were prepared by coating a thin gold film (approx. 60 Å in thickness) on the sample under reduced pressure (below 8 Pa) with a JFC-1200 fine coater (JEOL).

GPC Measurement

To quantitatively check whether secondary particles formed or not, gel permeation chromatography (GPC) (HLC-801, Toso Co. Ltd.) measurements were carried out by employing tetrahydrofuran (THF) as an elution solvent. The polymerization in the droplets and the secondary nuclei follow different polymerization mechanisms, the former following homogeneous bulk or solution polymerization, and the latter proceeding by emulsion polymerization. It is well known that the molecular weight obtained in emulsion polymerization is higher than that obtained by bulk or solution polymerization, typically reaching 10^5–10^6 (g/mol). Bulk or solution polymerizations usually result in polymer with molecular weights of $\sim 10^4$ (g/mol). Therefore, two peaks should be detected by GPC measurements if secondary nucleation occurred to any significant extent. The weight ratio of the two kinds of polymers is calculated from the area ratio of the two peaks.

Measurement of DMAEMA Content in the Polymer

The DMAEMA content in the polymer was measured by ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectra were recorded using a 500 MHz spectrometer (JEOL α-500) at 40°C with trichloromethane-d$_3$ (CDCl$_3$) as the solvent and locking agent. Spectra were obtained after accumulating 200 scans, by using a sample concentration of 5 wt %. The areas of the —CH$_3$ peak for DMAEMA and the —C$_6$H$_5$ peak for St were used to calculate the DMAEMA content in the polymer.

Measurement of Monomer Conversion

The monomer conversion was determined gravimetrically. The polymer was precipitated by

Table II   Effect of DMAEMA and Inhibitor Type on the Morphology of the Particle

	DMAEMA = 0.45 g (2.5 wt %)			DMAEMA = 0			
Run No.	253	265	254	255	257	256	319
Inhibitor	DAP	HQ	NaNO$_2$	DAP	HQ	NaNO$_2$	No
D_e (μm)	7.83	8.34	8.10	7.66	8.65	8.53	8.58
CV of D_e (%)	9.54	8.54	10.00	9.27	8.39	9.39	9.17
D_p (μm)	7.67	7.80	5.94	7.32	6.40	7.56	5.82
CV of D_p (%)	10.48	6.68	10.02	10.50	10.98	9.62	8.89
$(D_p/D_e)^3$	0.94	0.83	0.39	0.87	0.41	0.70	0.30
Conversion (%)	63.2	48.8	86.5	76.0	100.0	98.8	100.0
Morphology	One-hole	One-hole	Hollow	One-hole	Nearly hollow	One-hole	Nearly hollow
PDMAEMA/Polymer (mol %)	0.26	0.22	0.32				
Secondary nucleation	No	No	A lot	No	A lot	A little	A lot

^{a}DMAEMA = 0.45 g (2.5 wt % based on total monomer), HD = 2.0 g (10 wt % based on oil phase), ADVN = 0.10 g, Inhibitor = 0.10 g.
^{b}D_e: diameter of monomer droplet before polymerization; D_p: diameter of monomer/polymer droplet after polymerization. Both were measured by optical microscopy.

methyl alcohol, separated by centrifugation, dried in a vacuum, and weighed.

RESULTS AND DISCUSSION

The preparative results, with and without the incorporation of DMAEMA, are reported in Table II. It was found that the morphology of particles was apparently affected by the presence of DMAEMA and the inhibitor type. These results are discussed in the following.

Effect of DMAEMA on the Morphology of the Particles

In a previous study, it was found that the morphology was affected by the incorporation of DMAEMA. The OM and SEM micrographs were shown in a previous article. In the presence of DMAEMA, hollow particles were obtained when NaNO$_2$ was used as the inhibitor. However, one-hole particles (an eccentric morphology where the void is formed at the surface of the particle) formed in the absence of DMAEMA. Therefore, it was initially assumed that the hollow particles were formed because of the incorporation of hydrophilic DMAEMA into the polymer. It has been accepted that the thermodynamically preferred equilibrium morphology of a particle will be one that has the minimum total free-energy change,[11–16] defined as follows:

$$\Delta G = \Sigma \gamma_{ij}A_{ij} - \gamma_0 A_0 \quad (1)$$

$$\Delta G = \gamma_{pw}A_{pw} + \gamma_{Hw}A_{Hw} + \gamma_{Hp}A_{Hp} - \gamma_0 A_0 \quad (2)$$

where A_{ij} is the interfacial area between components i and j for the final particle, γ_{ij} is the corresponding interfacial tension, A_0 and γ_0 are the interfacial area and corresponding interfacial tension of the initial state. Subscripts p, w, and H represent the polymer, water, and HD, respectively. When DMAEMA was incorporated into the polymer, γ_{pw} became lower because the hydrophilicity of PDMAEMA is much greater than PSt. Therefore, it was favorable for the minimization of ΔG that A_{pw} increased and A_{Hw} decreased. As a result, hollow particles were formed by making A_{Hw} equal to 0, that is, by allowing HD to locate in the center of particles. After the HD was extracted with methanol, hollow particles were obtained. On the other hand, γ_{pw} was close to γ_{Hw} when DMAEMA was not added. Both the polymer and HD can contact the aqueous phase. After the HD was removed, one-hole particles were obtained.

Effect of Inhibitor Type on the Morphology of the Particles

By changing the type of the inhibitor, it was found that hollow particles were not always obtained even when DMAEMA was incorporated into the

polymer. When DAP was used as the inhibitor, for example, particles with a large hole were obtained when DMAEMA was not added. After incorporating DMAEMA into the polymer, particles with a small hole had formed. This result implied that γ_{pw} became lower, and the copolymer tended to engulf the HD more inside resulting in a larger A_{pw} and a smaller A_{Hw}, compared with the case without adding DMAEMA. As a result, the hole that resulted from the extraction of HD became smaller. However, γ_{pw} was not small enough to allow the HD to be engulfed, and hollow particles were not obtained.

When HQ was used, a reverse phenomenon was observed. When DMAEMA was not used, most of particles showed a hollow morphology with a lot of new particles adsorbed on them. However, when DMAEMA was added, one-hole particles, similar to the case of DAP, were obtained.

Comparing the above three cases where DMAEMA was added and three kinds of inhibitors were used, respectively, it was shown that hollow particles were obtained only when NaNO$_2$ was used as the inhibitor. When DAP or HQ was used, one-hole particles were formed. From Table II, it was found that the DMAEMA content in the copolymer was not so different for the three cases. Even when a higher content of DMAEMA (2.21 mol %) was incorporated into the copolymer for the case of DAP, one-hole particles were obtained.[9] So this is not the reason for the morphological differences. Considering the molecular structures of the three kinds of inhibitors, a tentative explanation of the formation mechanism of hollow and one-hole particles is proposed as illustrated in the left side of Figure 1. When NaNO$_2$ was used, hollow particles formed easily because PDMAEMA, which located preferentially on the surface of the particles, decreased the interfacial tension between the polymer and the aqueous phase. When DAP or HQ was used, the inhibitor was adsorbed on the particle surface due to hydrogen bonding between the —OH or —NH$_2$ groups of the inhibitor and the amine group of PDMAEMA. As a result, γ_{pw} increased and became comparable to γ_{Hw}, allowing HD to come in contact with the aqueous phase, because of the presence of hydrophobic benzene rings on the particle surface. Therefore, the copolymer was not able to engulf the HD completely. To confirm this assumption, three experiments were run, as shown in the right side of Figure 1. The results are summarized in Table III. OM and SEM mi-
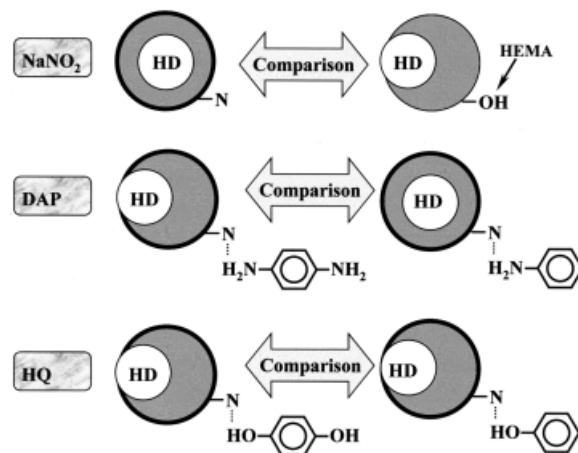

Figure 1 Proposed inhibitor adsorption mechanism and its possible influence on the formation of hollow particles.

crographs are shown in Figure 2. In the first experiment, the same amount of HEMA monomer was added to the oil phase instead of DMAEMA. From Figure 2(a), it was found that one-hole particles instead of hollow particles were obtained even though HEMA is more hydrophilic than DMAEMA. This result implied that hollow particles cannot always be obtained even when a hydrophilic monomer unit is incorporated into the copolymer. Next, phenol or aniline, which contain mono-hydroxyl groups or mono-amino groups, respectively, was added into the aqueous phase together with NaNO$_2$. The amount added was the same as HQ or DAP. If the adsorption of HQ or DAP inhibitor was responsible for the one-hole particles, particles with the same morphology should be obtained when phenol or aniline was added to the oil phase. As shown in Figure 2(b) and (c), however, hollow particles were obtained when aniline was used, and the particles showed a one-hole morphology when phenol was added. This result contrasted with the prediction, suggesting that the adsorption of the inhibitor was not the reason for the formation of the one-hole particles.

Variation of Monomer/Polymer Droplet During the Polymerization

To understand the real reasons for the formation of hollow particles, the variation in the morphology, conversion, diameter, and molecular weight distribution of the particles during the polymerization was investigated. OM micrographs as a

Table III   Effect of Aniline, Phenol, and Hydrophilic Monomer Type on the Morphology of Particle When NaNO$_2$ was Used

Run No.	254	304	288	326
Inhibitor	NaNO$_2$ Only	NaNO$_2$ Only	NaNO$_2$ with Aniline	NaNO$_2$ with Phenol
Monomer	DMAEMA	HEMA	DMAEMA	DMAEMA
D_e (μm)	8.10	7.95	7.27	8.07
CV of D_e (%)	10.02	7.87	9.50	10.34
D_p (μm)	5.94	6.81	5.59	6.97
CV of D_p (%)	10.00	8.51	8.67	8.50
$(D_p/D_e)^3$	0.39	0.63	0.45	0.64
Conversion (%)	86.5	43.5	97.4	64.1
Morphology	Hollow	One-hole	Hollow	One-hole
PDMAEMA/Polymer (mol %)	0.32	0.27	0.33	0.36
Secondary nucleation	A lot	No	A lot	A little

^{a}DMAEMA = 0.45 g (2.5 wt % based on total monomer), HD = 2.0 g (10 wt % based on oil phase), ADVN = 0.10 g, NaNO$_2$ = 0.1 g, phenol or aniline = 0.10 g.
^{b}D_e: diameter of monomer droplet before polymerization; D_p: diameter of monomer/polymer droplet after polymerization. Both were measured by optical microscopy.

function of polymerization time are shown in Figures 3 and 4, where NaNO$_2$ and DAP were used as the inhibitor, respectively. From Figure 3, it can be seen that when NaNO$_2$ was used, the diameter decreased immediately after the poly-

merization started, and apparently phase separation had occurred and hollow particles had already formed after 1 h of polymerization. On the other hand, when DAP was used, the diameter did not decrease, and phase separation was not observed until 3 h of polymerization. The varia-
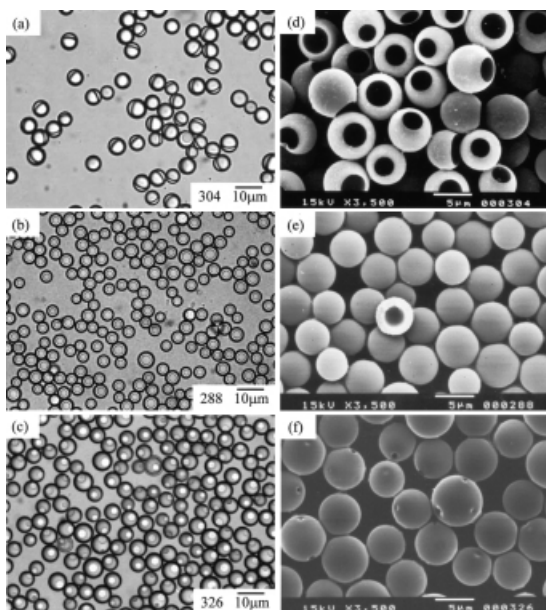

Figure 2 SEM micrographs of polymer particles formed by an SPG/polymerization process. Effect of various parameters based on run 254. (a–c): OM; (d–f) SEM. (a,d) HEMA instead of DMAEMA (run 304); (b,e) addition of Aniline (0.10 g) with NaNO$_2$ (run 288); (c,f) addition of phenol (0.10 g) with NaNO$_2$ (run 326).
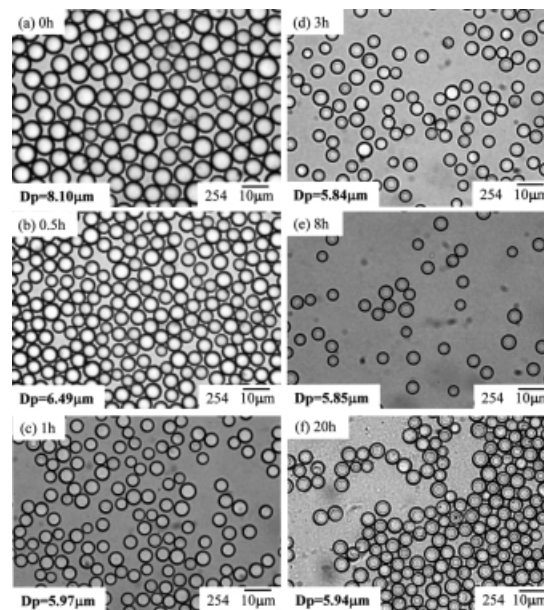

Figure 3 OM micrographs of monomer droplets and polymer particles as a function of polymerization time when NaNO$_2$ was used as the inhibitor. Polymerization time: (a) 0; (b) 0.5; (c) 1; (d) 3; (e) 8; (f) 20 h. D_e, D_p: diameters of monomer droplets and polymer particles.

tion of diameter and monomer conversion as a function of polymerization time are summarized in Figure 5. The quantity $(D_p/D_e)^3$ was calculated and is included in Table II, where D_e and D_p are the diameters of the droplets and particles before and after polymerization (20 h). It was shown in Table II that the volume of the polymer particles decreased to about 39 vol % of the initial droplet volume after polymerization when $NaNO_2$ was used, while a high value resulted (94 vol %) in the case of DAP. This meant that a lot of monomer diffused into the aqueous phase to form secondary particles when $NaNO_2$ was used. The corresponding GPC results as a function of polymerization time are shown in Figure 6(a) and (b), respectively. It is evident that a lot of secondary particles already formed after 30 min of polymerization when $NaNO_2$ was used. As the polymerization proceeded, the polymer fraction due to the secondary particles increased further. After the polymerization time exceeded 1 h, the relative amount of polymer in the new particles and the original large particles apparently did not vary any further. When DAP was used, on the other hand, a peak at the lower elution times was not detected, that is, only the polymer of the original large particles was observed.

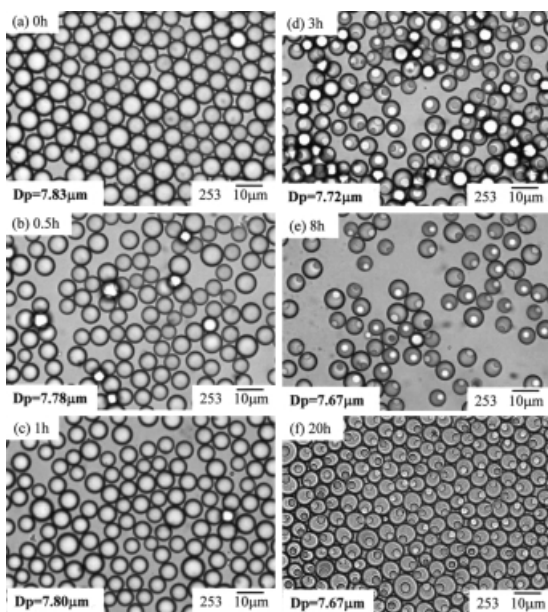The conversion as a function of polymerization time is summarized in Figure 5(b). Furthermore,

Figure 5 Variation of diameter (a) and conversion (b) during polymerizations.

Figure 4 OM micrographs of monomer droplets and polymer particles as a function of polymerization time when DAP was used as the inhibitor. Polymerization time: (a) 0; (b) 0.5; (c) 1; (d) 3; (e) 8; (f) 20 h. D_e, D_p: diameters of monomer droplets and polymer particles.
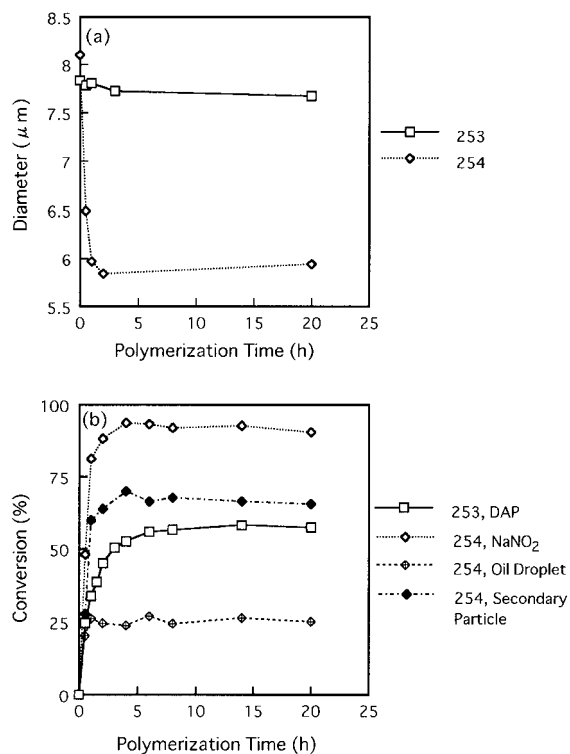
the conversion in the case of $NaNO_2$ was divided between the original large particles and the secondary particles, which were calculated from the total conversion and the areas of the two peaks in the GPC chromatograms, as shown in the same figure. From Figure 5(b), it is seen that the conversion increased more gradually in the case of DAP, and it slows to a low value (63 wt %) even after polymerizing for 20 h. On the other hand, the conversion increased rapidly when $NaNO_2$ was used. And, it was confirmed again that the conversion of the original large particles did not change apparently after 1 h of polymerization. This implied that a large part of the monomer diffused into the aqueous phase in the initial stages of the polymerization, and the polymerization inside the large particles did not proceed further after 1 h.

Based on the above results, the formation mechanism of P(St-DMAEMA) hollow particles is schematically represented in Figure 7. Because $NaNO_2$ is not effective for the inhibition of polymerization in the aqueous phase when DMAEMA was used, a large portion of the monomer diffused into the aqueous phase to form the secondary particles immediately after polymerization started.

As a result, the polymer polymerized inside the original large droplets phase separated from the HD. Because a large amount of monomer diffused into the aqueous phase, less St monomer existed inside the droplets. Therefore, the polymer was not able to dissolve in the HD-rich monomer any more, and rapid phase separation occurred. This rapid phase separation probably resulted in a nonequilibrium morphology. Although HD preferred to contact the aqueous phase, rapid phase separation prevented it from migrating to the surface of the particles (a kinetic controlled morphology). That is, HD was confined inside the particles by rapid phase separation due to rapid diffusion of monomer into the aqueous phase. When DAP or HQ was used, on the other hand, a fraction of each partitioned into the droplets (both have a hydrophobic character), and therefore, the polymerization rate was slowed, secondary nucleation was effectively prevented, and little monomer diffused into the aqueous phase. Because most of the monomer was present inside the particles until relatively high monomer conversions, phase separation occurred more slowly. As a result, HD could migrate to the surface of particles, and an equilibrium morphology was obtained. Further-
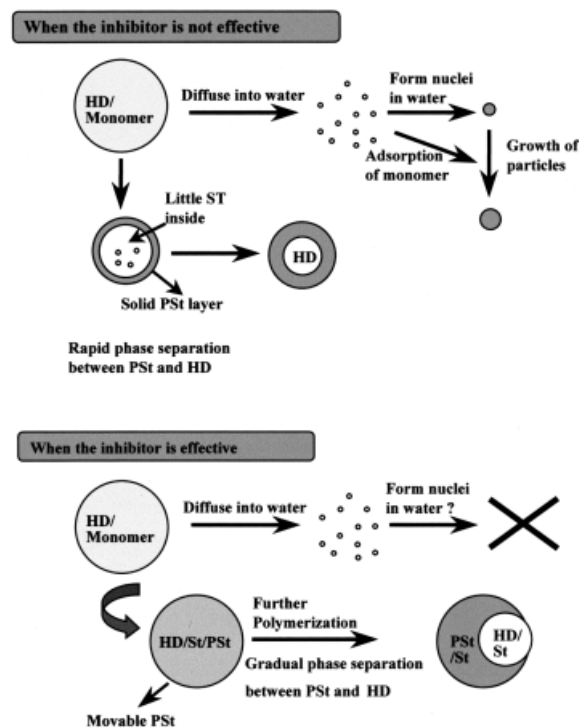

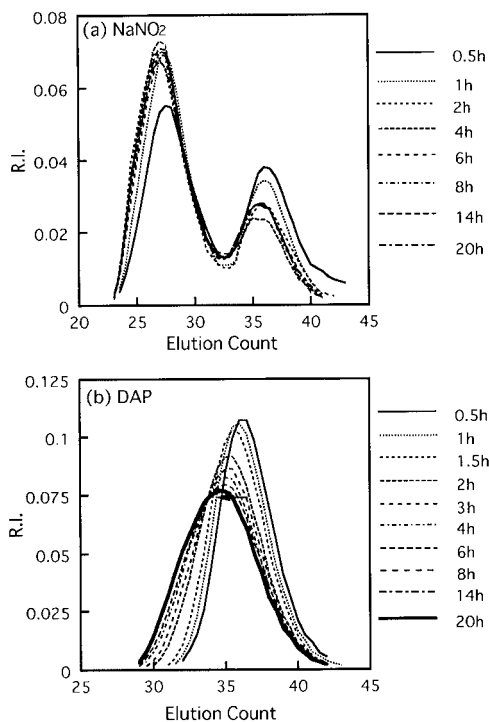**Figure 7** Proposed mechanism of formation of hollow particles and one-hole particles.

more, because a lot of the monomer retained inside of the particles was partitioned into the HD phase, the interfacial tension between the HD phase and aqueous phase decreased. As a result, the HD phase was allowed to contact the aqueous phase, and one-hole particles were easily formed.

Reviewing Table II again, it was found that most of particles also show hollow or nearly hollow morphologies even in the absence of DMAEMA when HQ or no inhibitor was used (runs 255 and 319). For these two cases, a large amount of secondary particles were detected by the GPC measurements, which implies that a rapid phase separation also occurred. This result confirmed again that the formation of hollow particles in run 254 was related to the rapid phase separation, and the hollow particles were possibly formed once rapid phase separation had occurred. In these two samples, a small fraction of the particles also showed a one-hole morphology. Because PSt is more hydrophobic than P(St-DMAEMA), it is more difficult to form hollow particles than in the case where DMAEMA was added. Furthermore, from Table III, it was found that hollow particles were obtained when aniline was added together with NaNO$_2$, where a lot of the secondary particles were also formed and the

Figure 6 Normalized GPC chromatograms of polymer particles as a function of polymerization time. Inhibitor: (a) NaNO$_2$; (b) DAP.

conversion was high. When phenol was used, however, because only a limited amount of secondary particles were formed and the conversion was low, a lot of monomer remained inside of the particles, and the resulting particles had a one-hole morphology. This result implied that phenol also played some role in the inhibition of the DMAEMA/St system.

The Lehigh group[12] has reported that the morphology can change with monomer conversion, when the interfacial tension between the polymer/monomer phase and the aqueous phase increases as the polymer/monomer ratio increases. For example, they synthesized PSt/PMMA composite particles by using a PSt latex as a seed with MMA monomer, and 2,2′-azobis(isobutyronitrile) (AIBN) initiator in the second stage polymerization. They investigated the morphological variation as a function of conversion experimentally and theoretically, and found that the inverted core-shell (PMMA core, and PSt shell) was the thermodynamically preferred morphology when the monomer conversion was relatively low (<40%), while a hemisphere morphology was preferred when the conversion was higher. If the viscosity inside the polymer particles was very high (slow polymer diffusion), the morphology at the lower conversion should be maintained until high conversions. That is, a nonequilibrium morphology would be fixed. We also studied the morphological variation as a function of the PMMA/PSt ratio, by emulsifying mixtures of PMMA and PSt dissolved in dichloromethane into an aqueous phase by the SPG emulsification method, followed by evaporation of the dichloromethane.[17,18] It was found that the occluded morphology was fixed when the PMMA/PSt ratio was relatively high, although the core-shell morphology was preferred thermodynamically. Because PMMA/dichloromethane solutions showed a much higher viscosity than PSt/dichloromethane solutions, small PSt domains cannot grow to one single domain due to the high viscosity of the PMMA matrix as the dichloromethane is evaporated.

To confirm the proposed mechanism of formation of the hollow particles, some complementary experiments were carried out.

Complementary Experiments to Prove the Formation Mechanism of Hollow Particles

Precipitation of PSt in HD/St Mixture

Three different HD/St (2/18, 5/15, and 10/10, g/g) mixtures (50 g) were prepared in 100-mL beakers.

A 30 wt % PSt in St solution was added drop wise into the HD/St mixtures, and observed for any change in turbidity. By changing the HD/St ratio, it was found that only the 10/10 (g/g) HD/St mixture became turbid. This implied that the PSt precipitated in the HD/St mixture, when the HD/St ratio was large. This result confirmed that rapid phase separation should occur if the St concentration inside the particles is low. In the case of the hollow particles (run 254), from the conversion of the original large particles shown in Figure 5(b), the amount of monomer becoming polymer in the original droplets was about 25.0% × 18 (g) = 4.5 (g). Therefore, the HD/polymer ratio was 2/4.5 (g/g). This value is between the 10/10 and 5/15 (g/g) ratios. The HD/monomer ratio in the polymer particles should be much larger than 5/10 (g/g) in the initial stages of the polymerization, after a large amount of the monomer had diffused into the aqueous phase to nucleate and grow the secondary particles, while a part of the polymer formed inside of the droplets. Therefore, rapid phase separation occurred in the initial stages of the polymerization.

Swelling of the Hollow Particles

To prove that the hollow particle morphology obtained in this study represented a nonequilibrium morphology, that is, the hollow particles formed due to the rapid separation of P(St-DMAEMA) and HD in the particles as described above, a swelling technique was used to reconstruct the morphology of the hollow particles.

First, the hollow particles were swollen with St monomer. When 1 g of St (about 20 wt % of the copolymer) was used, no apparent morphological change was observed by optical microscopy, that is, the reconstruction of morphology did not occur because the mobility of the PSt was still very low. When 2.3 g of St (about 50 wt % of the copolymer) was added, reconstruction of the morphology of the hollow particles was observed. The SEM micrographs are shown in Figure 8(a). It is evident that the original hollow particles changed to one-hole particles. Because the copolymer became mobile owing to the existence of a large amount of monomer inside the particles, the equilibrium one-hole morphology could be reconstructed. This phenomenon confirmed that hollow particles would not be obtained if a large amount of monomer did not diffuse into the aqueous phase early in the polymerization.

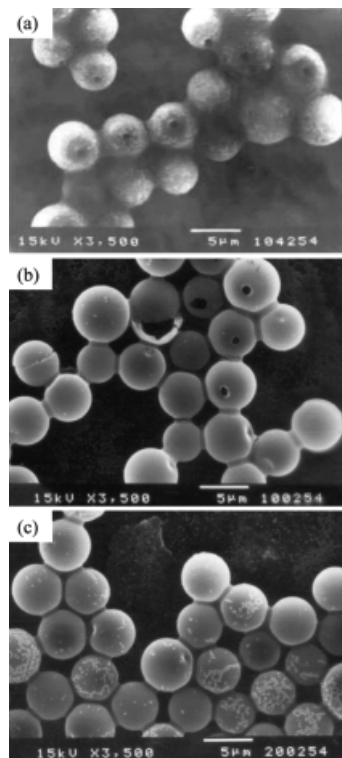The hollow particles were also swollen with toluene, and then the toluene was evaporated at

Figure 8 SEM micrographs of hollow polymer particles (run 254) swollen with St monomer and toluene, respectively: (a) swollen with St; (b) swollen with toluene followed by its evaporation at room temperature for 1 week; (c) swollen with toluene followed by its evaporation at 70°C for 2 h.

room temperature for 1 week, or at 70°C for 2 h. The SEM micrographs after evaporation of the toluene are shown in Figures 8(b) and (c), respectively. From Figure 8(b), it is evident that the particles changed to one-hole particles after adsorbing and then releasing the toluene at room temperature. By absorbing the toluene, the inside of the droplets became homogeneous and then a slow phase separation developed as the toluene evaporated. As a result, the equilibrium one-hole morphology formed. On the other hand, when the toluene was evaporated at high temperature (70°C), only a depression on the particle surface was observed. This result suggested that the copolymer can confine the HD inside more easily when the toluene was removed rapidly. This condition corresponds to the rapid diffusion of the monomer into the aqueous phase during the polymerization. The above result confirmed again that the hollow particles obtained in this study resulted from the rapid phase separation between the copolymer and the HD.
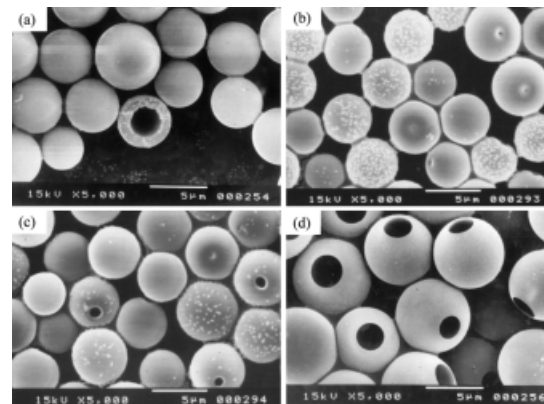

Figure 9 SEM micrographs of polymer particles showing effects of the amount of DMAEMA (g): (a) 0.45; (b) 0.09; (c) 0.06; (d) 0.

Effect of Amount of DMAEMA

Because the amount of DMAEMA in the oil phase also affected the conversion, as well as the DMAEMA content in the copolymer, its effect on the formation of hollow particles was investigated to verify the above proposed mechanism of formation of hollow particles. The DMAEMA amount was varied from 0.45 to 0 g. SEM micrographs and GPC results are shown in Figures 9 and 10, respectively. The detailed recipe and results are shown in Table IV. By decreasing the DMAEMA to 0.09 g, a depression on the particles was observed, although the $(D_p/D_e)^3$ were almost the same in each case. This result implied that the hollow particles were more easily formed by incorporating an adequate amount of the hydrophilic DMAEMA monomer into the copolymer. By decreasing the DMAEMA amount further to 0.06 g, some of the particles showed a one-hole
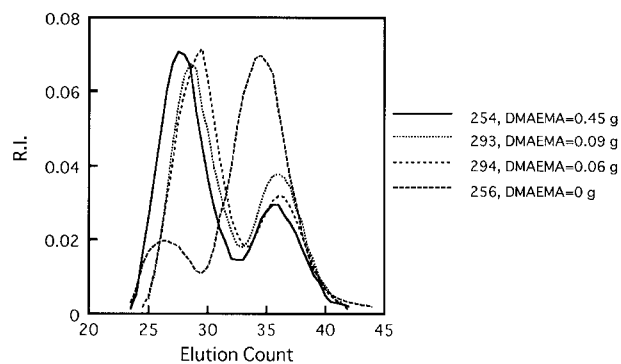

Figure 10 Normalized GPC chromatograms of polymer particles showing effects of the amount of DMAEMA (Inhibitor: NaNO$_2$).

Table IV   Effect of DMAEMA Amount on Morphology of Particle

Run No.	254	293	294	256
DMAEMA (g)	0.45	0.09	0.06	0
D_e	8.10	7.25	7.85	8.53
CV of D_e (%)	10.02	7.94	10.06	9.39
D_p (μm)	5.94	5.28	6.00	7.56
CV of D_p (%)	10.00	8.82	8.56	9.62
$(D_e/D_p)^3$	0.39	0.39	0.44	0.70
Conversion (%)	86.5	92.2	66.5	98.8
Morphology	Hollow	Depression	Partially one-hole	One-hole
PDMAEMA/polymer (mol %)	0.32	0.08	0.06	0
Secondary Nucleation	A lot	A lot	A lot	A little

[a] HD = 2.0 g (10 wt % based on oil phase), ADVN = 0.10 g, $NaNO_2$ = 0.10 g.
[b] D_e: diameter of monomer droplet before polymerization; D_p: diameter of monomer/polymer after polymerization. Both were measured by optical microscopy.

morphology, and $(D_e/D_p)^3$ increased from 0.39 to 0.44. This result suggested that the monomer diffusion to the aqueous phase was weakened by decreasing the amount of DMAEMA. A slower phase separation occurred compared with the case of a higher amount of DMAEMA; therefore, some of the particles showed a one-hole morphology. When DMAEMA was not used, the amount of new particles decreased significantly, and all of the particles showed a one-hole morphology.

Effect of Amount of NaNO₂

The monomer conversion was certainly affected by the water-soluble inhibitor. Thus, its effect on the formation of hollow particles was also investigated. The amount of $NaNO_2$ was varied from 0.10 to 1.0 g. The SEM micrographs and GPC results are shown in Figures 11 and 12, respectively. The detailed recipe and results are shown in Table V. By increasing the $NaNO_2$ from 0.10 g to 0.30 g, a depression on the particles was observed, although $(D_p/D_e)^3$ was almost the same as the case where 0.10 g $NaNO_2$ was used. By increasing the $NaNO_2$ amount further to 1.0 g, some of the particles showed a one-hole morphology, and $(D_p/D_e)^3$ increased from 0.39 to 0.49. Because the effect of monomer diffusion to the aqueous phase was weakened and a large amount of monomer was retained inside of the particles by increasing the amount of $NaNO_2$, a slower phase separation occurred compared to the cases using the lower amounts of $NaNO_2$. Therefore, some particles showed a one-hole morphology.

The relationship between the total conversion and $(D_p/D_e)^3$ for all of samples in this study is summarized in Figure 13. The particles with a depression are described as nearly hollow, and the partial one-hole particles are classified as one-hole particles. It is evident that the hollow and nearly hollow particles showed higher conversions and lower $(D_p/D_e)^3$. On the other hand, the
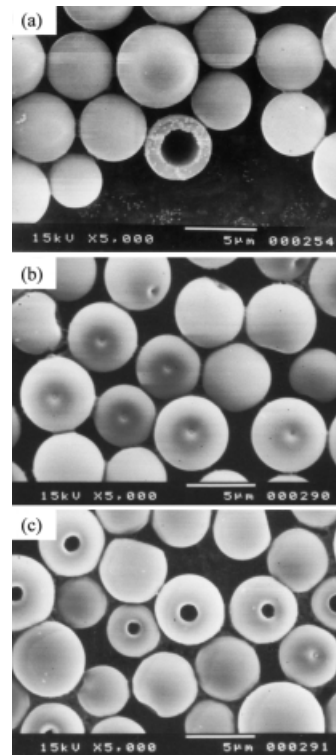

Figure 11   SEM micrographs of polymer particles showing effects of the amount of $NaNO_2$ inhibitor (g): (a) 0.10; (b) 0.30; (c) 1.0.
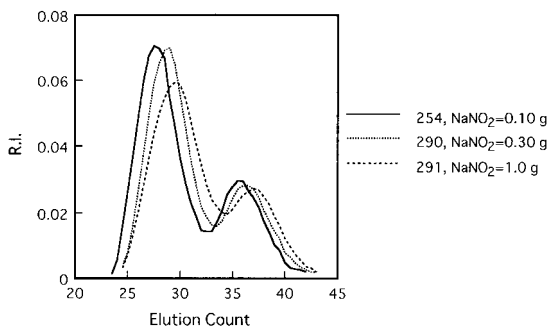
Figure 12 Normalized GPC chromatograms of polymer particles showing effects of the amount of $NaNO_2$ inhibitor.

Figure 13 Relationship between total monomer conversion and $(D_p/D_e)^3$.

one-hole particles showed lower conversions and higher $(D_p/D_e)^3$. Only one sample (run 256) showed a high conversion. Because there was only a small amount of secondary particles formed in this sample, the rapid phase separation was not able to be realized. Furthermore, DMAEMA was not present in this sample, and as a result, hollow particles were difficult to produce.

From the above results, it can be concluded that the hollow particles can be prepared easily by incorporating DMAEMA into the polymer to decrease the interfacial tension between the polymer and the aqueous phase, and by utilizing the rapid phase separation between the polymer and the HD in the initial stages of the polymerization. The problem is that secondary nucleation will occur to promote this rapid phase separation, because a lot of monomer should diffuse into the aqueous phase to lead to the rapid phase separation between HD and the polymer and high mono-
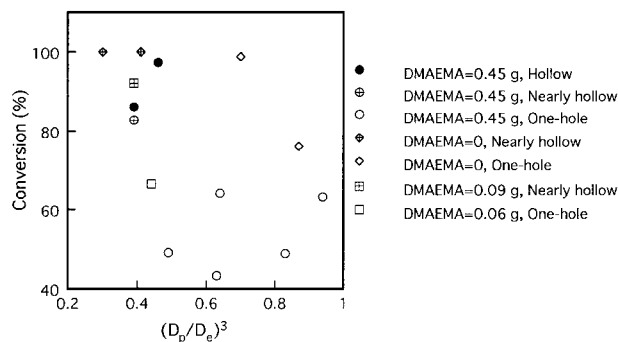
mer conversion. Two methods are expected to solve this problem. One is to increase the HD/monomer ratio to accelerate the rapid phase separation between HD and the polymer in the initial stages of the polymerization, and to prevent monomer from diffusing into the aqueous phase. Another method is to utilize a very hydrophobic initiator with a rapid decomposition rate to increase the polymerization rate inside the droplets and lead to a rapid phase separation, avoiding the secondary nucleation. These two methods are currently being investigated.

CONCLUSIONS

Monodisperse large hollow P(St-*co*-DMAEMA) particles can be prepared by employing the SPG emulsification technique followed by a polymerization process. Hollow particles were obtained

Table V   Effect of NaNO₂ Amount of Morphology of Particle

Run	254	290	291
$NaNO_2$ (g)	0.10	0.30	1.0
D_e (μm)	8.10	8.04	7.01
CV of D_e (%)	10.02	11.63	7.76
D_p (μm)	5.94	5.89	5.51
CV of D_p (%)	10.00	10.48	9.34
$(D_e/D_p)^3$	0.39	0.39	0.49
Conversion (%)	86.5	82.8	49.0
Morphology	Hollow	Depression	Partially one-hole
PDMAEMA/polymer (mol %)	0.32	0.40	0.51
Secondary Nucleation	A lot	A lot	A lot

[a] DMAEMA = 0.45 g (2.5 wt % based on total monomer), HD = 2.0 g (10 wt % based on total oil phase), ADVN = 0.10 g.
[b] D_e: diameter of monomer droplet before polymerization; D_p: diameter of monomer/polymer after polymerization. Both were measured by optical microscopy.

only when $NaNO_2$ was used as the water-soluble inhibitor. When DAP and HQ was used instead of $NaNO_2$, one-hole particles were always observed. The mechanism of formation was clarified by measuring the variation of the particles with the polymerization time and other complementary experiments. It was found that the formation of the hollow particles was controlled by kinetic factors to a large extent. Rapid phase separation between HD and copolymer due to the diffusion of a lot of the monomer into the aqueous phase, was responsible for the formation of the hollow particles, which belong to a nonequilibrium morphology. When DMAEMA was added, the hollow particles were more easily formed than without DMAEMA, because its incorporation decreases the interfacial tension between copolymer and the aqueous phase.

REFERENCES

1. Itou, N.; Masukawa, T.; Ozaki, I.; Hattori, M.; Kasai, K. Colloids Surf A Physiochem Eng Aspects 1999, 153, 311.
2. Okubo, M.; Minami, H.; Yamashita, T. Macromol Symp 1996, 101, 509.
3. Okubo, M.; Minami, H. Colloid Polym Sci 1996, 274, 433.
4. Omi, S.; Ma, G.-H.; Nagai, M. Macromol Symp 2000, 151, 319.
5. Omi, S.; Katami, K.; Yamamoto, A.; Iso, M. J Appl Polym Sci 1994, 51, 1.
6. Nuisin, R.; Ma, G.-H.; Omi, S., Kiatkamjornwong, S. J Appl Polym Sci 2000, 77, 1013.
7. Yuyama, H.; Yamamoto, K.; Shirafuji, K.; Ma, G.-H.; Nagai, M.; Omi, S. J Appl Polym Sci 2000, 77, 2237.
8. Omi, S.; Matsuda, A.; Imamura, K.; Nagai, M.; Ma, G.-H. Colloids Surf A Physicochem Eng Aspects 1999, 153, 373.
9. Ma, G.-H.; Nagai, M.; Omi, S. J Appl Polym Sci, 2001, 79, 2408.
10. Ma, G.-H.; Nagai, M.; Omi, S. Colloids Surf A Physicochem Eng Aspects 1999, 153, 383.
11. Chen, Y.-C.; Dimonie, V. L.; El-Aasser, M. S. J Appl Polym Sci 1991, 42, 1049.
12. Chen, Y.-C.; Dimonie, V. L.; El-Aasser, M. S. Macromolecules 1991, 24, 3779.
13. Chen, Y.-C.; Dimonie, V. L.; El-Aasser, M. S. J Appl Polym Sci 1991, 46, 691.
14. Sundberg, D. C.; Casassa, A. P.; Pantazopoulos, J.; Muscato, M. R. J Appl Polym Sci 1990, 41, 1425.
15. Winzor, C. L.; Sundberg, D. C. Polymer 1992, 33, 4269.
16. Durant, Y. G.; Sundberg, D. C. J Appl Polym Sci 1995, 58, 1607.
17. Ma, G.-H.; Nagai, M.; Omi, S. J Colloid Interf Sci 1999, 214, 264.
18. Ma, G.-H.; Nagai, M.; Omi, S. J Colloid Interf Sci 1999, 219, 110.