Mechanism of Formation of Monodisperse Polystyrene Hollow Particles Prepared by Membrane Emulsification Technique. Effect of Hexadecane Amount on the Formation of Hollow Particles

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Summary: 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. The dispersed phase mainly containing St, hexadecane (HD), and initiator, was pressed through the uniform pores of a SPG membrane into the continuous phase to form uniform droplets. Then, the droplets were polymerized at 70°C. It was proposed that rapid phase separation between PSt and HD was a main reason responsible for the formation of hollow particle. Rapid phase separation confined the HD inside the droplets, it belonged to a non-equilibrium morphology. In this study, HD/St ratio was increased to a high value to confirm the above proposition by promoting rapid phase separation further between HD and PSt, to prevent monomer diffusion into aqueous phase, and to obtain hollow particle with a large hole.

Introduction

Recently hollow particle has attracted much attention, because it shows many attractive characteristics, for example, 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) particles with a low molecular weight as a seed. After the seed latex was swollen by a mixture of methyl methacrylate (MMA) and divinylbenzene (DVB) in an aqueous phase, then a hydrophilic initiator was added to carry out polymerization. As a large

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portion of the DVB was copolymerized with the MMA near the surface of particles, the outer diameter was fixed in the initial stages of polymerizations. As the polymerization proceeded further, phase separation occurred between the seed polymer (PSt) and subsequently polymerized polymer (PMMA). Finally, complete phase separation occurred at the interface between the PSt and PMMA owing to the shrinkage of PMMA, and water filled the separated part. Okubo et al. [2-3] used their dynamic swelling technique to prepare hollow polymer particles with the diameters of several micron. First, a PSt seed was dispersed in an ethanol/water (7/3, w/w) mixture where DVB, toluene, and benzoyl peroxide (BPO) were dissolved. After water was added into the system continuously to allow the DVB, toluene and BPO to be absorbed by the seed, 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.

As described above, hollow particles usually were prepared with two polymerization steps, and it is difficult to prepare hollow particles with the diameters more than 7 μm. In a previous study, it was found that PSt hollow particles with diameters around 10 μm can be synthesized by a one-step polymerization, combining the SPG (Shirasu Porous Glass) membrane emulsion technique with a subsequent polymerization process.[4] SPG membrane 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, 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 synthesized monodisperse polystyrene (PSt),[5] PSt-PMMA,[6] polyurethane,[7] and PSt-polyimide[8] microspheres. The CV (coefficient of variation) value which indicates the breadth of the size distribution of the particles is typically about 10%. Further more, by combining a SPG emulsification process of polymer solution and subsequent evaporation of solvent, we have prepared bio-degradable poly(lactic acid) particle[9] and PSt/PMMA composite particles.[10,11] The particle size can be controlled by the pore size of membrane, the resulting particle size is usually about 6 times as large as the pore size of the membrane.[5] In a previous study,[4] it was found that it is possible to prepare PSt hollow particles by using a mixture of St, N,N'-dimethyl amino ethyl methacrylate (DMAEMA), hexadecane (HD), and N, N'-azobis(2,4-dimethylvaleronitrile)

(ADVN) initiator as the dispersion phase, and a aqueous phase containing SLS, PVP, and $NaNO_2$ (inhibitor) as the continuous phase. However, it was puzzling that one-hole particles formed when HQ or DAP was used as an inhibitor instead of $NaNO_2$. Because a lot of secondary particles formed only when $NaNO_2$ was used, it was proposed that the hollow particle was formed due to the rapid phase separation between HD and PSt, as a large portion of monomer diffused into the aqueous phase to form the secondary particle at the initial stages of polymerization. It belongs to a non-equilibrium morphology. For the case of HQ or DAP, phase separation occurred gradually to form the equilibrium morphology because no secondary nucleation occurred and a large part of monomer presented inside of particle.

In this study, HD/monomer ratio was increased to a high value to confirm the above mechanism by promoting phase between HD and PSt, and to decrease the secondary nucleation by retarding monomer diffusion into the aqueous phase. It was found that hollow particle with a very large hole was formed when HD/monomer ratio was increased to 10/10 (g/g), even though no secondary nucleation occurred, because increase of HD promoted the rapid phase separation between HD and PSt. Further more, swelling and releasing experiment of hollow particle with toluene was carried out to confirm the above mechanism.

Experimental

Materials

Styrene (St) was commercial grade (Kishida Chemical Co.). N,N'-dimethyl amino ethyl methacrylate (DMAEMA) was reagent grade (Tokyo Chemical Industries, Co., Ltd.). Both of them were distilled under vacuum to remove the inhibitor.

2,2'-azobis(2,4-dimethylvaleronitrile) (V-65, ADVN) (Wako Pure Chemical Industries, Ltd.) was reagent grade. Hexadecane (HD) was reagent grade (Tokyo Chemical Industries, Co., Ltd.) and was used as a hydrophobic additive and porogen. Sodium nitrite ($NaNO_2$) and diaminophenylene (DAP) were reagent grade (Kishida Chemical Co.) and were used as inhibitors, to prevent the secondary nucleation in the aqueous phase. Sodium lauryl sulfate (SLS) was biochemical grade (Merck). Poly(N-vinyl pyrrolidone) (PVP, K30, M_w = 40000 g/mol) was reagent grade (Tokyo Chemical Co.). 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 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, a 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 paper.[9] A membrane with pore sizes of 1.42 μm was used in this study.

Preparation of Microspheres

A standard recipe is shown in Table 1. 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 ($NaNO_2$ 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 continuously. 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 the monomer was always around 10 wt %, based on the aqueous phase. The detailed SPG membrane emulsification process was described elsewhere.[9]

Table 1. Standard recipe for SPG emulsification

Ingredients	Weight (g)
Continuous phase	
PVP	1.0
Inhibitor ($NaNO_2$, DAP)	0, 0.10
Na_2SO_4	0.10
SLS	0.075
Water	225
Dispersion phase	
ADVN	0.1
St +DMAEMA +HD	20.0
DMAEMA	0, 0.45
HD	2.0, 10.0

The emulsion obtained was transferred to a four-neck glass separatory flask equipped with a semicircular anchor-type blade, a condenser, and a nitrogen inlet nozzle. After the emulsion was purged with nitrogen gas for 1h, the nozzle was lifted above the surface of the emulsion and the temperature was elevated to 70°C gradually for the polymerization. The polymerization was carried out for 24 h under a nitrogen atmosphere.

Swelling of hollow particle

50 ml of the resulting dispersion of hollow particles (solids content 9.0 wt%, 4.5 g) were added to a 100mL beaker. The secondary emulsion was prepared by employing a homogenizer, where 9g of toluene was used as a 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). After the hollow particles were

swollen with toluene, the dispersion was stirred at room temperature for 24 h to allow the toluene to evaporate slowly.

Analyses

The diameters and morphologies of the dispersed phase before and after polymerization were observed with an optical microscope (OM) (Olympus BH-2 with a digital camera). The diameters of about 300 droplets or particles were measured to calculate the average diameters and size distribution. The surface features of polymer particles were observed using a JSM-5300 (JEOL) scanning electron microscope (SEM).

To check whether secondary particles formed or not quantitatively, 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 to 10^5-10^6 (g/mol). Bulk or solution polymerizations usually result in polymer with molecular weights of ~10^4 (g/mol). Therefore, two peaks should be detected by GPC measurements if secondary nucleation occurred to any significant extent. The fraction of the secondary particles was calculated from the areas of the two peaks.

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 from DMAEMA and the $-C_6H_5$ peak from St were used to calculate the DMAEMA fraction in the polymer.

The monomer conversion was determined gravimetrically. The polymer was precipitated by methyl alcohol, separated by centrifugation, dried in a vacuum, and weighed.

Results and Discussion

HD/monomer =2/18 (g/g)

The preparative results are reported in Table 2, OM and SEM micrographs with and without adding DMAEMA are shown in Figure 1 and 2, respectively, when 2g of HD was used based

Table 2. Effect of DMAEMA and inhibitor on the preparative results of polymer particles when HD/monomer ratio was 2/18 (g/g).[a]

	DMAEMA=0.45g (2.5wt %)		DMAEMA=0		
Run No. Inhibitor	253 DAP	254 $NaNO_2$	255 DAP	256 $NaNO_2$	319 No inhibitor
D_e (μm)[b]	7.83	8.10	7.66	8.53	8.58
CV of D_e (%)	9.54	10.00	9.27	9.39	9.17
D_p (μm)[b]	7.67	5.94	7.32	7.56	5.82
CV of D_p (%)	10.48	10.02	10.50	9.62	8.89
$(D_p/D_e)^3$	0.94	0.39	0.87	0.70	0.30
Conversion (%)	63.2	86.5	76.0	98.8	100.0
Morphology	One-hole	Hollow	Large-hole	One-hole	Nearly-hollow
PDMAEMA/Polymer (mol%)	0.26	0.32			
Fraction of secondary particle (wt%)	0.5	68.3	0	3.9	70.4

[a] ADVN=0.10 g, Inhibitor = 0.10 g

[b] D_e: number-average diameter of monomer droplet before polymerization; D_p: number-average diameter of polymer particle after

on 20g oil phase. The corresponding results of GPC measurement are shown in Figure 3.

By OM and SEM observations, it was evident that fairly monodisperse droplets were obtained. This monodispersity was maintained even after polymerization. The CV value of polymer particles was around 10%. It was found that hollow particles were obtained when $NaNO_2$ was used as an inhibitor in the presence of DMAEMA. However, one-hole particles formed when DAP was used as an inhibitor. From Table 2 and Figure 3(a), it was also found that a high fraction (68.3 wt%) of secondary particles formed and the conversion usually was high in the former case, and little secondary nucleation occurred and the conversion was relatively low in the later case. When $NaNO_2$ was used, further more, it was found by GPC measurement that the secondary particle formed rapidly and the diameter of the monomer droplet decreased dramatically within 1h after polymerization started, and the hollow particle already formed at 1h of polymerization. It was known from Table 2 that $(D_p/D_e)^3$ quantity showed a low value when $NaNO_2$ was used. That is, a large portion of the monomer diffused into the aqueous phase and contributed to the polymerization of the secondary particles. Therefore, we proposed that rapid phase separation between HD and polymer occurred as a large portion of monomer diffused rapidly into the aqueous phase to form the secondary particle in the initial stages of polymerization. By rapid diffusion of monomer into the aqueous phase, monomer inside the droplet decreased dramatically, inducing rapid phase separation. Although HD preferred to contact with the aqueous phase, it could not migrate to the surface and was confined inside the particle, due to high viscosity inside the droplet. Therefore, this morphology is a non-equilibrium morphology. By extracting HD in the purification process of particle, hollow particle can be obtained. When DAP was used, on the other hand, little monomer escaped into the aqueous phase because the secondary nucleation was prevented effectively. Therefore, monomer concentration inside the droplet was high, and the viscosity was lower in the initial stages of polymerization. As a result, HD can migrate to the surface of the droplet to form the hemisphere morphology. That is, phase separation occurred gradually to form an equilibrium morphology. After HD was extracted, one-hole particle was obtained. In order to confirm this mechanism proposed, the experiment was carried out further without adding DMAEMA, the results are also shown in Table 2. It was found that when DAP was added as water-soluble inhibitor, one-hole particle was obtained (Figure 2) as the case where

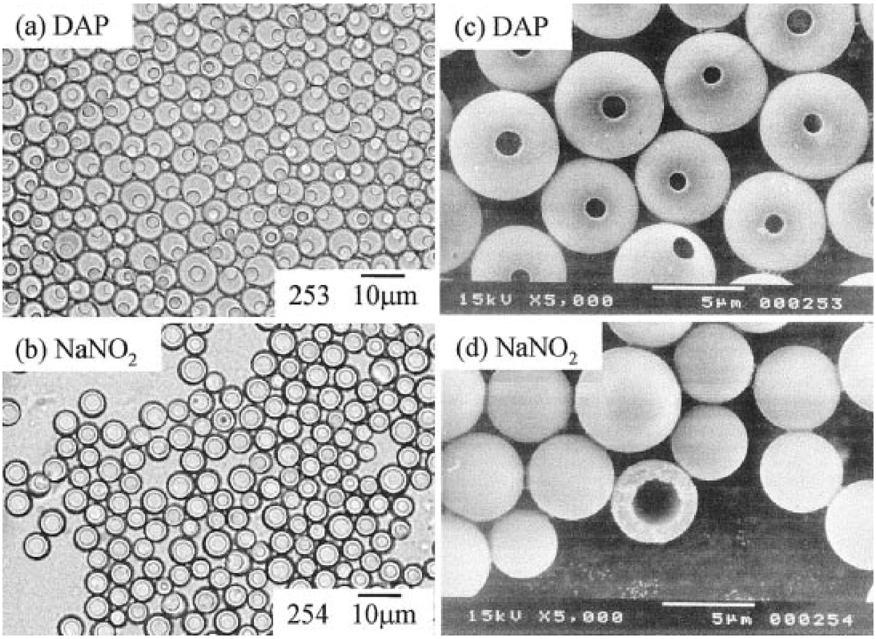


Figure 1. OM and SEM micrographs showing effects of water-soluble inhibitor when HD/monomer ratio was 2/18 (g/g) (with DMAEMA added); (a) (b) OM, (c)(d) SEM; Inhibitor: (a)(c) DAP, (b)(d) $NaNO_2$.

DMAEMA was used, but the hole was larger than the latter. This is because PSt polymer is more hydrophobic when DMAEMA was not added and can not engulf HD more inside of the particle. When $NaNO_2$ was used, however, one-hole particle was obtained, different from the case where DMAEMA was added. This is because that $NaNO_2$ was able to prevent the secondary nucleation when DMAEMA was not used (The reason was discussed in a previous study[4]). Little monomer diffused into the aqueous phase to form the secondary particles (the

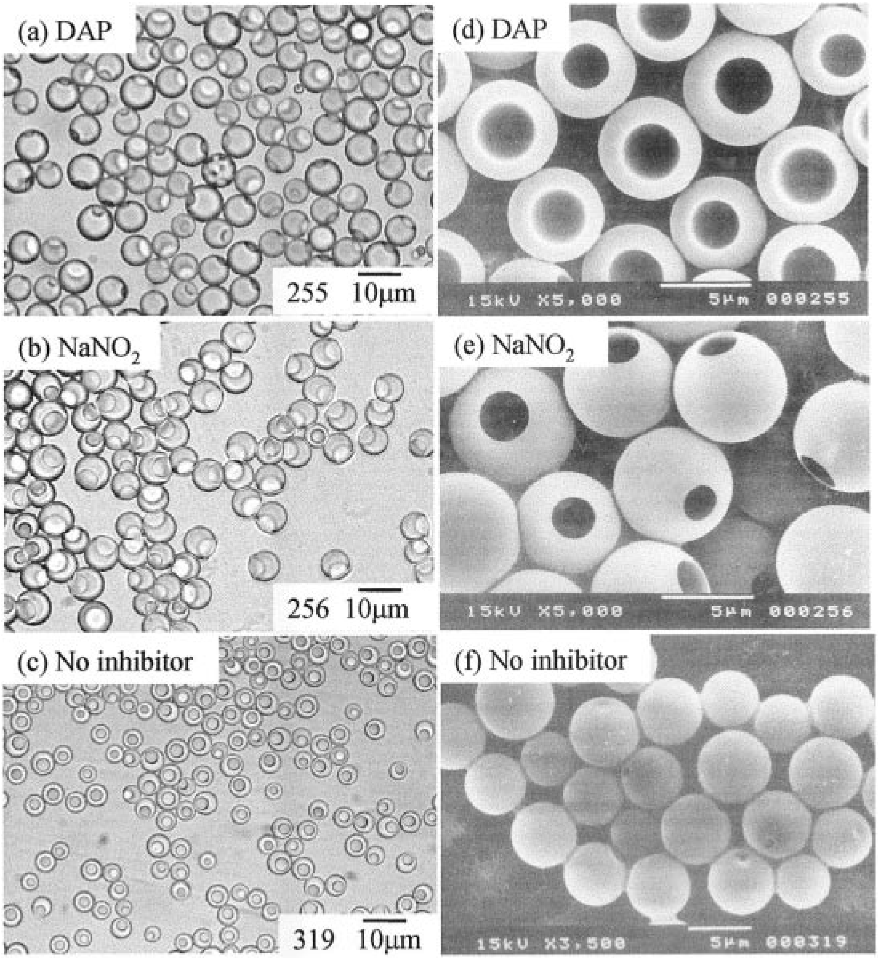


Figure 2. OM and SEM micrographs showing effects of water-soluble inhibitor when HD/monomer ratio was 2/18 (g/g) (without DMAEMA added); (a)-(c) OM, (d)-(f)SEM; Inhibitor: (a)(d) DAP, (b)(e) $NaNO_2$, (c)(f) no inhibitor.

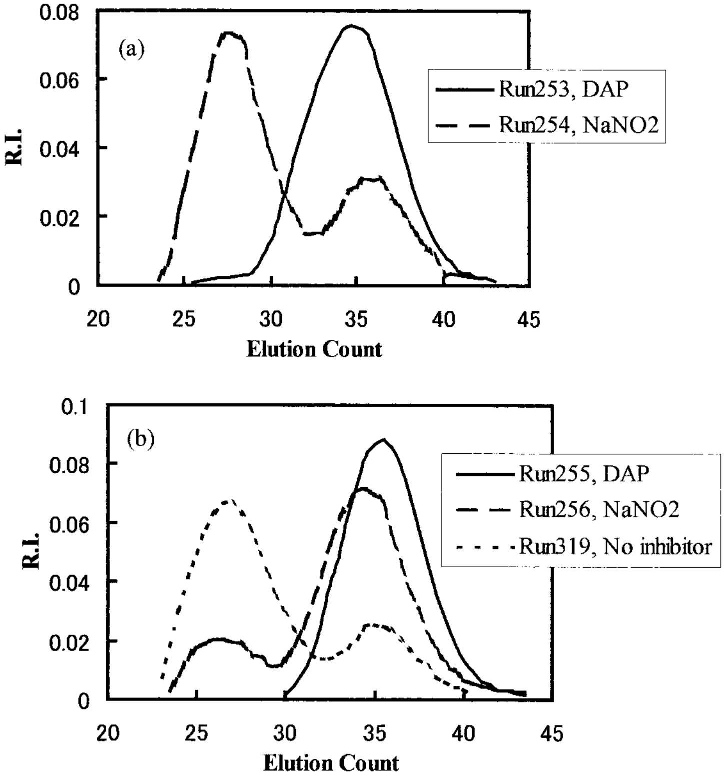


Figure 3. Normalized GPC chromatograms of polymer particles showing effects of water-soluble inhibitor when HD/monomer ratio was 2/18 (g/g); (a) with DMAEMA, (b) without DMAEMA.

fraction of the secondary particles was 3.9 wt%). Therefore, the viscosity inside the droplet was lower, phase separation occurred gradually to form hemisphere particle. Based on above results, the experiment was carried without adding inhibitor and DMAEMA in order to confirm the formation mechanism. It was found that nearly hollow particle was obtained even hydrophilic monomer DMAEMA was not added. Again, in this case, a higher fraction of secondary particles formed (70.4 wt%) and conversion was very high. This result confirmed again that the hollow particle formed mainly due to the rapid phase separation as a lot of monomer diffused into the aqueous phase. However, complete hollow morphology was not realized for this sample, some of the particles have small depressions on their surfaces. Because PSt was more hydrophobic when DMAEMA was not incorporated, it is more difficult to confine completely the HD in the center of the particle. Therefore, DMAEMA also contributed to the formation of the hollow particle.

HD/monomer =10/10 (g/g)

From above results, it was known that hollow particle can be prepared easily by utilizing rapid phase separation. The problem is that the secondary nucleation often accompanied to induce the rapid phase separation. In order to induce phase separation and prevent the secondary nucleation, other methods should be developed. Here, the HD/monomer ratio was increased to 10/10 (g/g) to promote rapid phase separation. Because HD is dissolved in St monomer, but PSt is insoluble in HD, it is expected that PSt will precipitate from HD more rapidly as HD/monomer ratio increases.

The results are concluded in Table 3 when HD/monomer ratio was 10/10 (g/g). The OM and SEM micrographs with and without adding DMAEMA are shown in Figure 4 and 5, and the corresponding GPC result are shown in Figure 6.

Table 3. Effect of DMAEMA and inhibitor on the preparative results of polymer particles when HD/monomer ratio was 10/10 (g/g).[a]

	DMAEMA=0.45g (2.5wt %)		DMAEMA=0		
Run No.	299	701	316	297	332
Inhibitor	DAP	$NaNO_2$	DAP	$NaNO_2$	No inhibitor
D_e (μm)[b]	7.68	7.01	8.19	7.64	7.63
CV of D_e (%)	8.81	6.99	9.30	9.99	8.22
D_p (μm)[b]	7.07	7.01	7.56	7.13	7.38
CV of D_p (%)	8.85	8.56	9.83	9.50	7.07
$(D_p/D_e)^3$	0.78	0.99	0.78	0.81	0.90
Conversion (%)	53.9	-	83.4	76.3	98.2
Morphology	Half-moon	Hollow	Hollow	Hollow	Hollow
PDMAEMA/Polymer (mol%)	0.15	0.39			
Fraction of secondary Particle (wt%)	12.2	67.2	0	0	26.0

[a] ADVN=0.10 g, Inhibitor = 0.10 g

[b] D_c: number-average diameter of monomer droplet before polymerization; D_p: number-average diameter of polymer particle after polymerization.

From OM and SEM micrographs, it was known that monodisperse particles were also obtained when HD/monomer ratio was increased to 10/10 (g/g). When DMAEMA was added, the similar result was obtained with the case of HD/monomer ratio = 2/18 (g/g). It was known from OM micrographs of Figure 4 that hemisphere particle was obtained when DAP was used as the water-soluble inhibitor. After HD was extracted, half-moon particle was observed from SEM micrograph. Again, for this sample, only a little secondary occurred and the monomer conversion was very low (Table 3, Figure 6). When $NaNO_2$ was used as the water-soluble inhibitor, hollow particle was obtained. From OM micrographs of Figure 4, it was evident that spherical microsphere was obtained. However, the hollow particle was broken in two halves after it dried. This is because the PSt wall was thin and brittle when HD/monomer ratio was high, it was broken easily when it was dried. It is necessary to incorporate other flexible components to avoid this phenomenon. For this sample, a lot of new particle formed (67.2wt%) as shown in GPC chromatogram of Figure 6(a), similar with the case where HD/monomer ratio was 2/18 (g/g). Unfortunately, the droplet of this sample was not so stable during polymerization, hollow particle suspended on the surface of the dispersion and a lot of polymer precipitate on the wall of glass flask. Therefore, the monomer

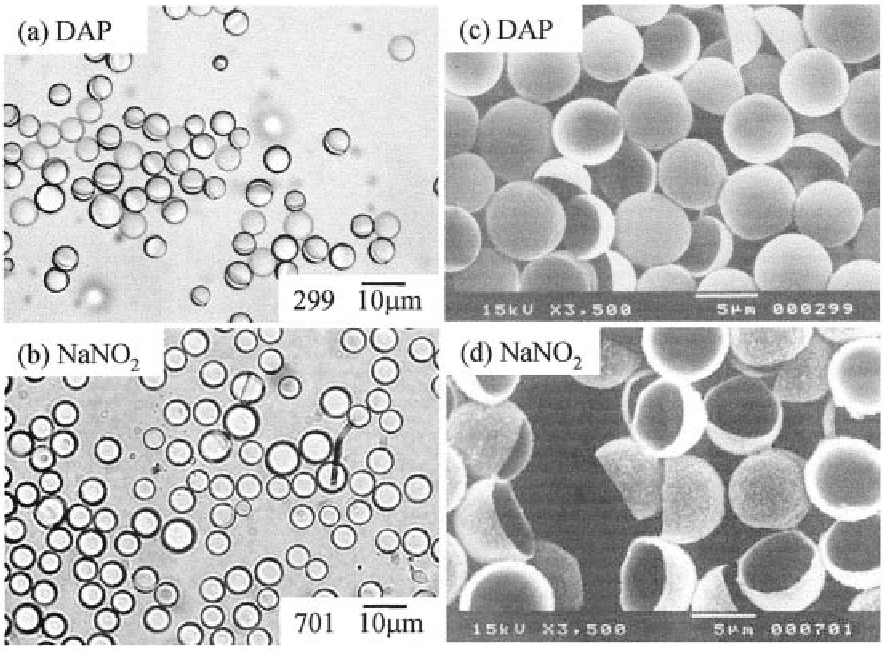


Figure 4. OM and SEM micrographs showing effects of water-soluble inhibitor when HD/monomer ratio was 10/10 (g/g) (with DMAEMA added); (a) (b) OM, (c)(d) SEM; Inhibitor: (a)(c) DAP, (b)(d) $NaNO_2$.

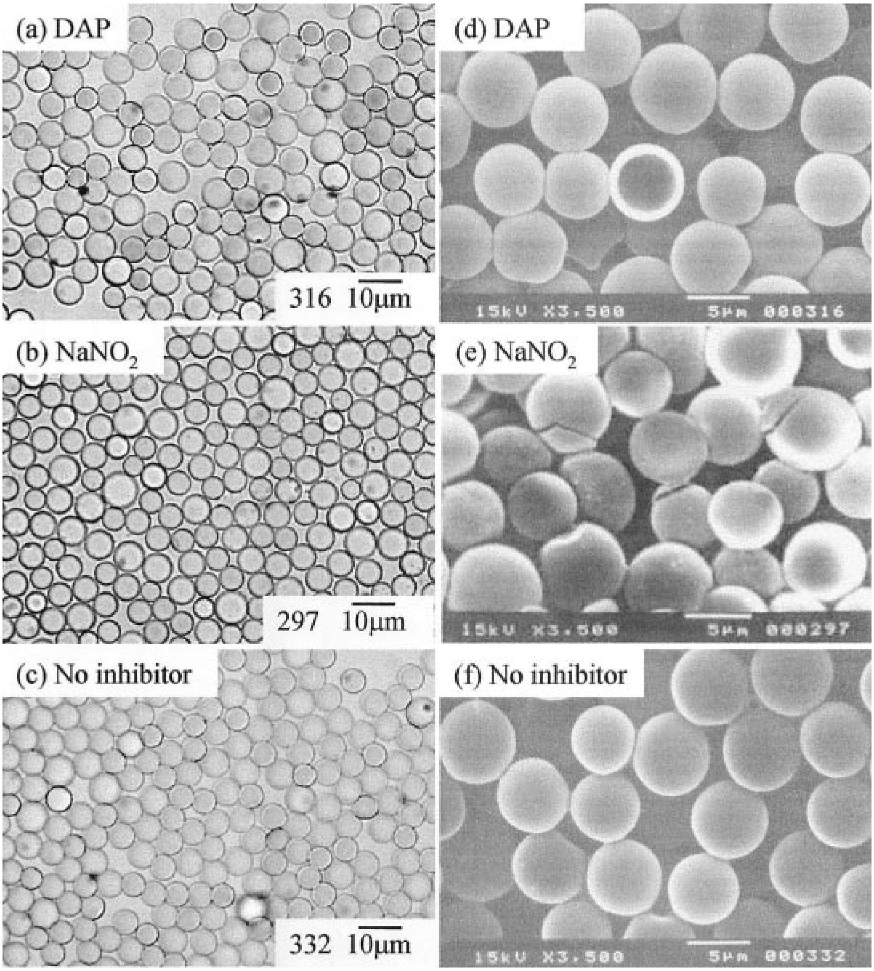
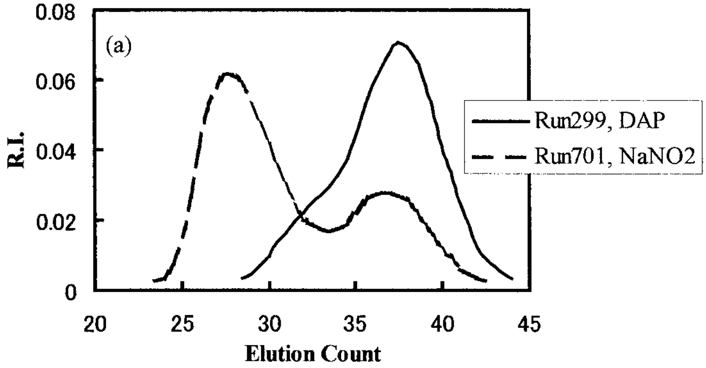


Figure 5. OM and SEM micrographs showing effects of water-soluble inhibitor when HD/monomer ratio was 10/10 (g/g) (without DMAEMA added); (a)-(c) OM, (d)-(f)SEM; Inhibitor: (a)(d) DAP, (b)(e) $NaNO_2$, (c)(f) no inhibitor.

conversion was not measured correctly. However, it was believed that the monomer conversion was fairly high because a high fraction of secondary particles formed. It was well known that emulsion polymerization usually resulted in high monomer conversion. When DMAEMA was not added, quite different results were obtained. The hollow particle was obtained, irrespective of type of inhibitor, although polymer was more hydrophobic compared with the case where DMAEMA was added. This is because higher conversion was attained



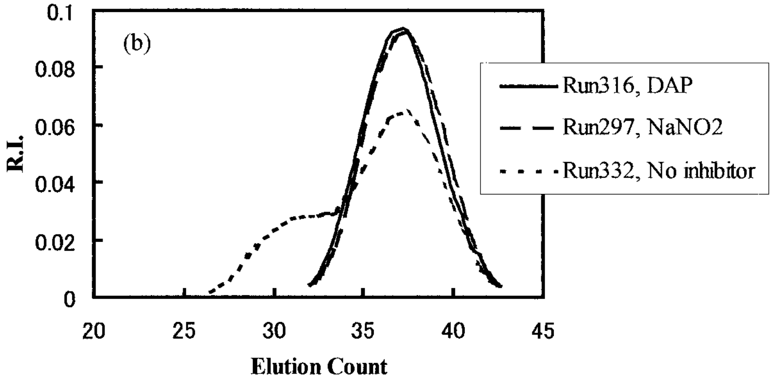


Figure 6. Normalized GPC chromatograms of polymer particles showing effects of water-soluble inhibitor when HD/monomer ratio was 10/10 (g/g); (a) with DMAEMA, (b) without DMAEMA.

when DMAEMA was not added. It has been clarified that polymerization rate and monomer conversion were higher when DMAEMA was not added.[4] Therefore, rapid phase separation was more easy to realize, and HD was certainly confined inside of the particles. Compare Table 2 and Table 3, it was clear that the hollow particles was not obtained in the case of HD/monomer ratio = 2/18 (g/g), when DMAEMA was not added and DAP or $NaNO_2$ was used as water-soluble inhibitor, although the monomer conversion was high. This result suggested that increase of HD/monomer ratio promoted rapid phase separation. When no inhibitor was used, hollow particle was also obtained, which resulted from two reasons, high HD/monomer ratio and formation of secondary particles. However, the fraction of the secondary particle was much lower than the case of HD/monomer ratio = 2/18 (g/g). For these three samples where DMAEMA was not added, the hollow particles were obtained and conversions were relatively high although no or only a little secondary particles formed. This result suggested that HD prevented the monomer from diffusing into the aqueous to form the secondary particle. However, even no secondary or only a little secondary particle generated,

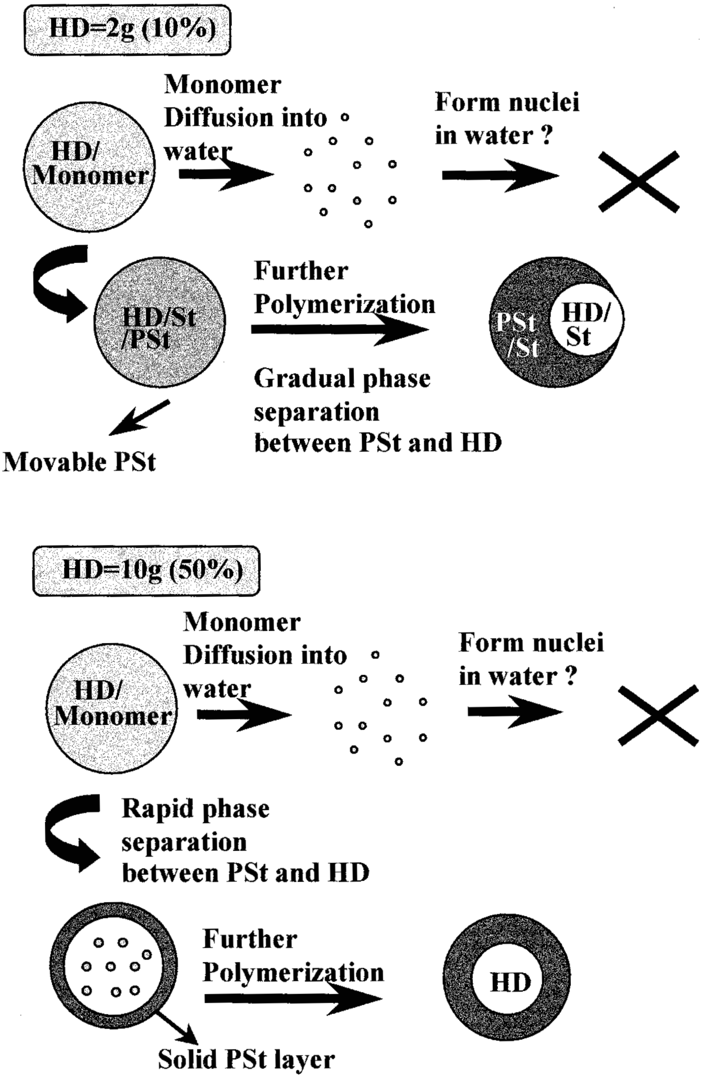


Figure 7. Illustration showing schematically effect of HD on formation of hollow particles.

hollow particles were obtained. This result confirmed that the HD can induce the rapid phase separation due to the immiscibility between HD and PSt. As presented schematically in Figure 7, when HD/monomer ratio and the conversion were lower, a large portion of St monomer existed inside the particle to allow PSt movable, so the phase separation occurred slowly, and equilibrium morphology realized. However, when HD/monomer ratio was high, phase separation should occur in the initial stages of polymerization as St monomer converted to PSt, because PSt is insoluble in HD. Therefore, the HD was confined inside the particle in the initial stages of polymerization.

A complementary experiment was carried as follows. Three different of HD/St (2/18, 5/15, and 10/10, g/g) mixtures (50g) were prepared in 100 mL beakers. A 30 wt% PSt in St solution was added drop wise into the HD/St mixturse, 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 HD concentration inside the particle is high.

The morphology of the polymer microspheres have been studied experimentally and theoretically.[12-17] The Lehigh group[12] has reported that the morphology can change with monomer conversion. 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 of polymerization. They investigated the morphological variation as a function of conversion, 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 non-equilibrium morphology would be fixed.

Swelling and releasing of hollow particles with toluene

In order to prove that the hollow particle morphology obtained in this study represented a non-equilibrium 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 re-construct the morphology of the hollow particles. The hollow particle was swollen by toluene for 2 hours, then the toluene was evaporated at room temperature for 24 hours. The OM and SEM micrographs before swelling, and after swelling and releasing of toluene are shown in Figure 8 and 9, respectively for Run 316 and 332. By swelling of hollow particle with toluene, the polymer became movable. During the evaporation of toluene, it was expected that non-equilibrium morphology would change to equilibrium one. It was evident that Run 316 changed to a one-hole morphology and Run 332 changed to half-moon morphology after swelling and releasing of toluene. This implied that both of the hollow morphology of Run 316 and Run 332 were non-equilibrium morphology.

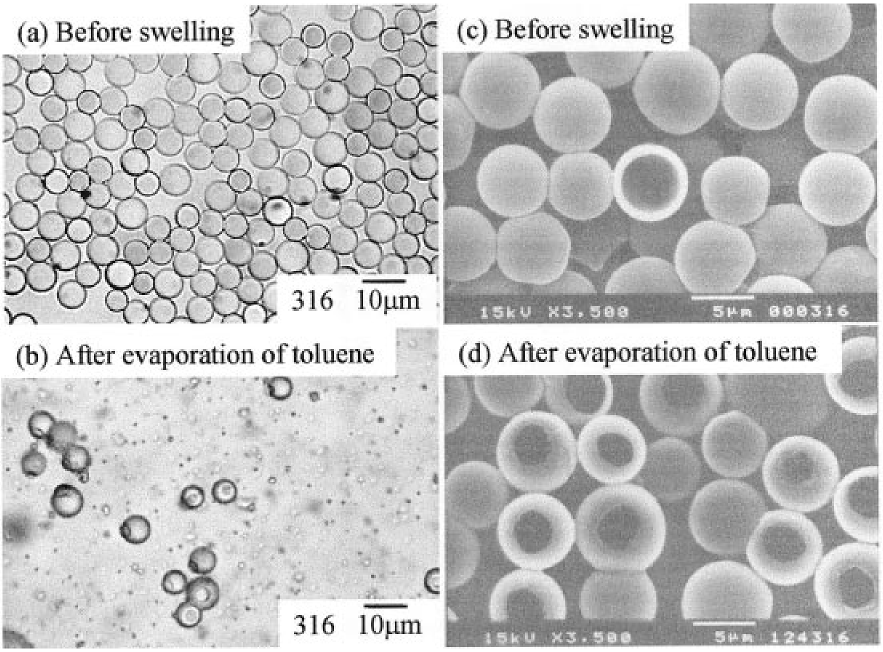


Figure 8. OM and SEM micrographs of hollow polymer particles (Run 316) swollen with toluene; (a)(b) OM, (c)(d) SEM; (a)(c) before swelling, (b)(d) swollen with toluene followed by its evaporation at room temperature for 24h.

As described above, increasing HD/monomer ratio has some advantages. (1) It can promote rapid phase separation, phase separation was induced even though little monomer diffused into the aqueous phase. On the other hand, when HD content was lower, diffusion of monomer into aqueous phase was necessary to induce rapid phase separation. (2) It retarded the diffusion of monomer into the aqueous phase, as a result, the secondary nucleation in the aqueous phase decreased. (3) The hollow particles with a large hole and a thin wall can be easily obtained. However, the wall was brittle and broken easily, it is necessary to incorporate

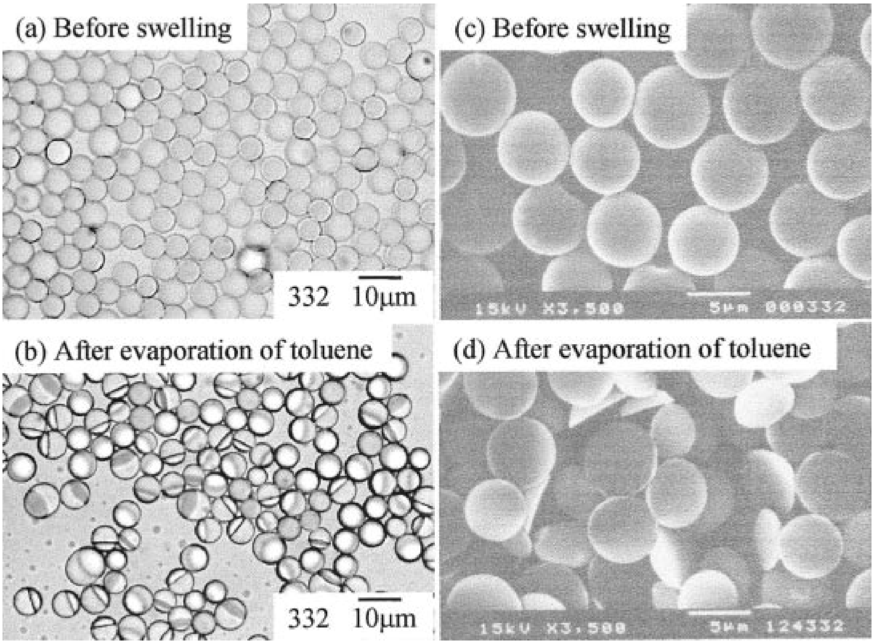


Figure 9. OM and SEM micrographs of hollow polymer particles (Run 332) swollen with toluene; (a)(b) OM, (c)(d) SEM; (a)(c) before swelling, (b)(d) swollen with toluene followed by its evaporation at room temperature for 24h.

flexible component to improve the strength of the thin wall.

Conclusion

The monodisperse PSt hollow particles can be prepared by employing a SPG emulsification technique followed by a suspension polymerization process. The hollow particle was obtained by utilizing rapid phase separation between PSt and HD. When HD/monomer ratio was lower, rapid phase separation was induced by diffusion of monomer into the aqueous phase. Increasing HD/monomer ratio can promote phase separation even though little monomer diffused into the aqueous phase, hollow particles with a large hole were obtained without formation of the secondary particles. Further investigation should be carried out to improve the strength of the thin wall.

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