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SHORT COMMUNICATION

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Preparation of nonspherical polymer particles by spraying aqueous dispersions of hydrophobic solvent droplets into methanol

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Abstract Nonspherical polymer particles were prepared by spraying an aqueous dispersion of hydrophobic solvent droplets (containing dissolved polymers) into methanol. Nonspherical particles were prepared for polystyrene and poly(methyl methacrylate), and spherical particles were prepared for poly(ethyl methacrylate) and poly(*i*-butyl methacrylate). It is concluded that condensation of the polymer molecules at the interface of the droplet is a key factor for the formation of nonspherical polymer particles.

Keywords Nonspherical shape · Particle · Solvent · Interfacial tension

Introduction

In general, polymer particles produced by emulsion, dispersion, and suspension polymerizations are spherical because they minimize the interfacial free energy between the particle and medium. However, during series of our investigations on the production of the submicron-sized composite polymer particles by seeded emulsion polymerization, various nonspherical particles have been produced [1, 2, 3, 4, 5, 6, 7, 8, 9].

Recently, micron-sized, monodisperse, nonspherical polymer particles with rugby ball-like and red blood corpuscle-like shapes were produced by seeded polymerization for highly monomer swollen particles prepared by the dynamic swelling method (DSM) [10, 11].

Moreover, we have succeeded in preparing about 2 μm-sized, monodisperse polystyrene (PS) particles with large surfaces dents by spraying an aqueous dispersion of highly toluene swollen PS particles [12], which were prepared by mixing toluene and the PS dispersion based on an idea obtained from the thermodynamic treatment of the DSM [13, 14, 15], into a methanol bath. The size of dents was controllable, and a postulated formation mechanism was suggested.

In this paper, we aim to clarify the formation mechanism in detail. In particular, the affects of polymer identity and solvent on the preparation of nonspherical particles will be examined.

Experimental

Materials

Used monomers were purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent-grade 2,2'-azobis(isobutyronitrile) (AIBN) was purified by recrystallization. Poly(vinyl alcohol) (PVA) (Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%) was supplied by Nippon Synthetic Chemical, Osaka, Japan. Deionized water was distilled with a Pyrex distillator. Reagent-grade toluene and cyclohexane were used as received.

Preparation and Characterization

Various homopolymers were prepared by solution polymerizations in sealed glass tubes under the conditions listed in Table 1. The tubes were horizontally shaken at 60 cycles min^{-1}. Crude polymers were purified by reprecipitation, washed with methanol and dried under reduced pressure. Weight-average molecular weight (Mw) was measured by gel permeation chromatography with calibration against PS standards with tetrahydrofuran as the eluent.

Preparation of nonspherical polymer particles

Toluene (1 g) and the dissolving polymer (0.1 g) were mixed with a 0.33 wt% aqueous solution of PVA (30 g). The mixture was stirred by a Nissei ABM-2 homogenizer at 1000 rpm for 2 min in a glass cylindrical reactor. The o/w dispersion (about 10 g) was sprayed into an excess amount of methanol (200 ml) in a bath, whilst stirring at 500 rpm with a nebulizer with a nozzle diameter of 0.39 mm, equipped with an air pump (pressure, 0.12 kg f cm^{-2}; flow, 32 l min^{-1}) to rapidly release the toluene from the droplet-dissolving polymer. The droplets and particles obtained were observed with a Nikon MICROPHOT-FXA optical microscope and a Hitachi S-2500 scanning electron microscope (SEM).

Table 1. Preparations of different kinds of homopolymers by solution polymerizations

Ingredients		PS[a]	PMMA[b]	PEMA[b]	P*i*-BMA[b]
Monomer	(g)	18	10	15	20
Toluene	(g)	12	22	15	13
AIBN	(mg)	54	30	30	60
Mw[c]	($\times10^5$)	2.0	1.2	2.9	1.6

[a] N_2, 50 °C, 48 h
[b] N_2, 70 °C, 24 h
[c] Weight-average molecular weight measured by gel permeation chromatography
Abbreviations: PS, polystyrene; PMMA, poly(methy1 methacrylate); PEMA, poly(ethyl methacrylate); P*i*-BMA, poly(*i*-butyl methacrylate); AIBN, 2,2'-azobis(isobutyronitrile)

Turbidity measurement

Nonsolvent (methanol) was slowly added stepwise to a 0.5 wt% solution of polymer in toluene. The transmittance at 470 nm was continuously measured as a function of methanol content at room temperature with a photoelectric photometer (Tokyo Koden, Model 7).

Measurement of the solubility of cyclohexane in methanol (the releasing bath)

Cyclohexane (8 g) was added to methanol (10 g) in a glass tube and then left at 30 °C for several hours. The amount of the cyclohexane dissolving in the methanol was measured by gas chromatography (Shimadzu, GC-18APFsc).

Interfacial tension measurement

Toluene solution (40 g) with 0.01 wt% of each homopolymer was gently poured into water (50 g). After 3 h, the interfacial tension between water and the toluene solution was measured by the du Noüy ring method at room temperature with a Shimadzu DN surface tensiometer.

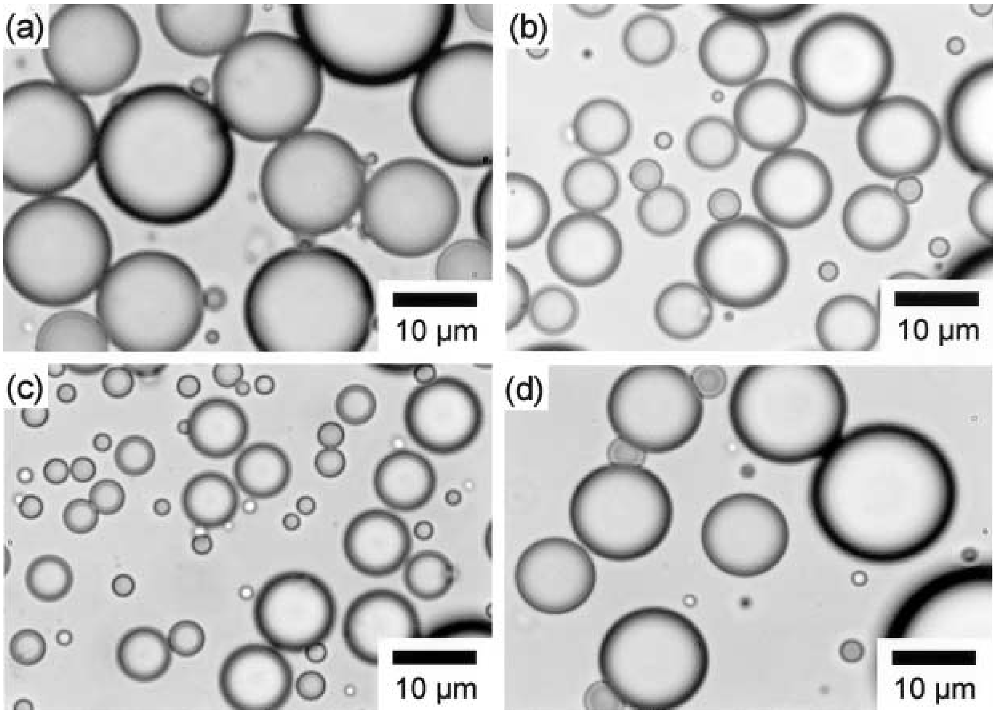

Fig. 1a–d. Optical micrographs of the toluene droplets dissolving various homopolymers (polymer/toluene: 1/10, w/w) under the conditions listed in Table 2: **a** polystyrene (PS), **b** poly(methyl methacrylate) (PMMA), **c** poly(ethyl methacrylate) (PEMA), **d** poly(*i*-butyl methacrylate) (P*i*-BMA)

Results and discussion

Figure 1 shows optical micrographs of toluene droplets dissolving various homopolymers (polymer/toluene: 1/10, w/w): (a) PS; (b) poly(methyl methacrylate) (PMMA); (c) poly(ethyl methacrylate) (PEMA); (d) poly(*i*-butyl methacrylate) (P*i*-BMA). These dispersions were prepared under the conditions listed in Table 2. All droplets were spherical, homogeneous and had broad size distributions.

Figure 2 shows optical micrographs of polymer particles after the toluene was rapidly released from the droplets by spraying their aqueous dispersions with a nebulizer into a methanol bath. Nonspherical shapes were observed for PS and PMMA (Figs. 2a, b), whereas spherical ones were observed for PEMA and P*i*-BMA (Figs. 2c, d).

Table 2. Preparations of toluene droplets[a] dissolving various homopolymers

Ingredients		
Polymer[b]	(g)	0.1
Toluene	(g)	1.0
Poly(vinyl alcohol)	(g)	0.1
Water	(g)	30.0

[a] Dispersion of toluene droplets was prepared with a homogenizer at 1000 rpm for 2 minutes

[b] Prepared by solution polymerization under the conditions listed in Table 1

Figure 3 shows SEM photographs of the polymer particles shown in Fig. 2. In photographs Fig. 3a, b, the PS and PMMA particles have large dents at the surfaces, whereas the PEMA and P*i*-BMA (Fig. 3c, d) have smooth surfaces. The nonspherical shapes were similar to those obtained in the previous article [12].

Figure 4 shows turbidimetric titration curves at 470 nm with the addition of methanol as nonsolvent into toluene solutions containing 0.5 wt% of various homopolymers. The PS began to precipitate at about 30 wt% of methanol content, whereas the three kinds of methacrylate polymers precipitated at 70~90 wt%. According to the formation mechanism of nonspherical particle by fast release of solvent from droplet of polymer solution proposed in the previous article [12], fast precipitation of polymer at the interface of the droplets is needed to prepare nonspherical particles. Therefore, such precipitation behaviors suggest that PS can give the nonspherical particles, but the methacrylate polymers cannot.

Figure 5 shows turbidimetric titration curves at 470 nm with the addition of methanol as nonsolvent into two P*i*-BMA solutions (cyclohexane, toluene). The methanol content required to begin phase separation was much smaller for cyclohexane than for toluene. In the case of cyclohexane, since it was almost the same as that without P*i*-BMA, the behavior does not seem to be based on the precipitation of P*i*-BMA. As shown in Table 3, in the two layers that appeared after the addition of methanol into the solution of P*i*-BMA in cyclohexane, P*i*-BMA existed only in the lower layer. The

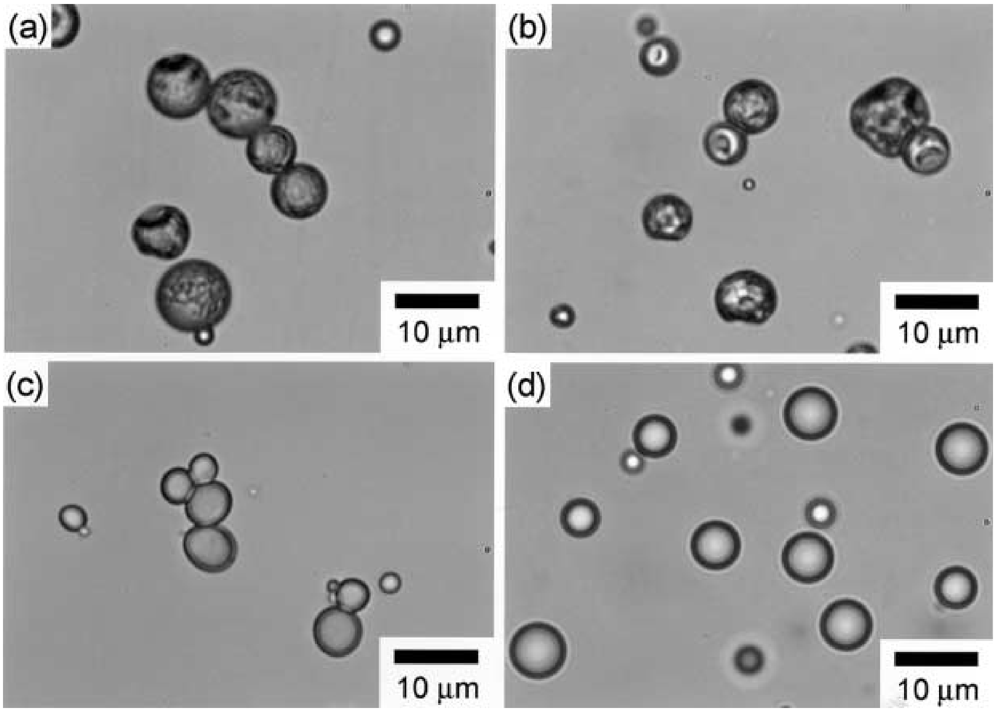

Fig. 2a–d. Optical micrographs of polymer particles from which the toluene (polymer/toluene: 1/10, w/w) was rapidly released into a methanol bath by spraying the dispersions with a nebulizer: **a** PS, **b** PMMA, **c** PEMA, **d** P*i*-BMA

P*i*-BMA content in the lower layer was higher than that of the original solution (P*i*-BMA/cyclohexane: 1/10, w/w). On the other hand, since the solubility of cyclohexane in methanol is 60.2 g $(100\ \mathrm{g})^{-1}$ methanol at 30 °C, we might expect cyclohexane to dissolve into the methanol bath quickly. Indeed, the droplets of cyclohexane (50 mg) disappeared into methanol (50 g) within about 10 seconds. This suggests that cyclohexane must be quickly released from the droplets dissolving P*i*-BMA into the methanol bath after the dispersion of the droplets was sprayed and methanol penetrated into the droplets. Since mutual diffusion of the solvents occurs quickly through the interface of the droplet, the phase separation followed by condensation of P*i*-BMA

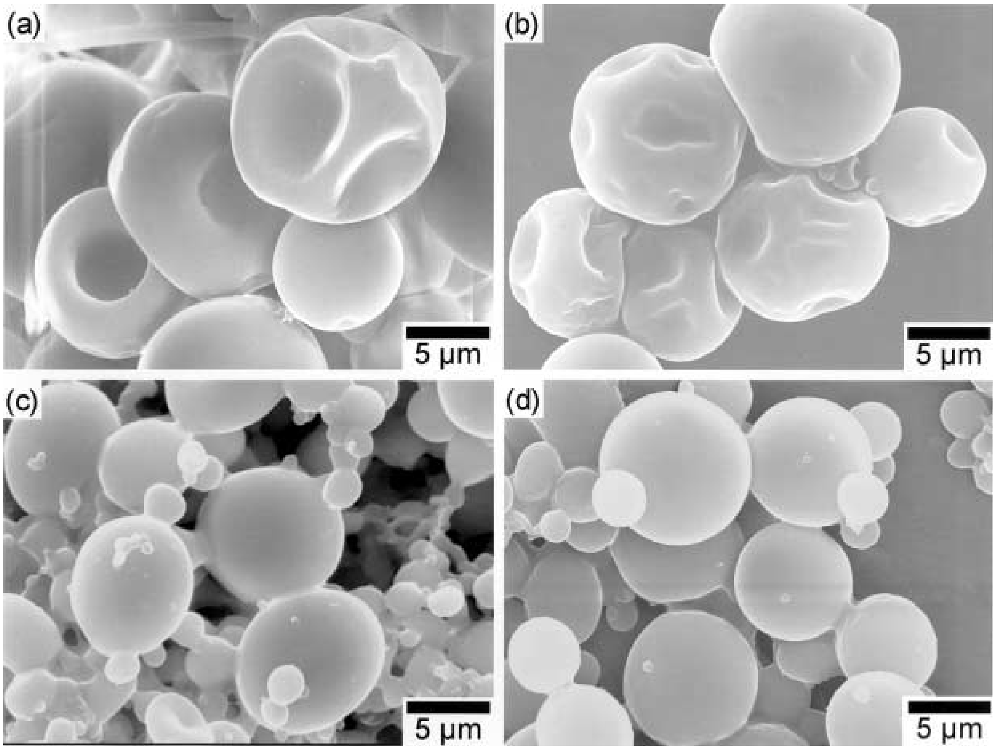

Fig. 3a–d. Scanning electron microscope (SEM) photographs of the polymer particles from which the toluene (polymer/toluene: 1/10, w/w) was rapidly released into the methanol bath by spraying the dispersions with a nebulizer: **a** PS, **b** PMMA, **c** PEMA, **d** P*i*-BMA

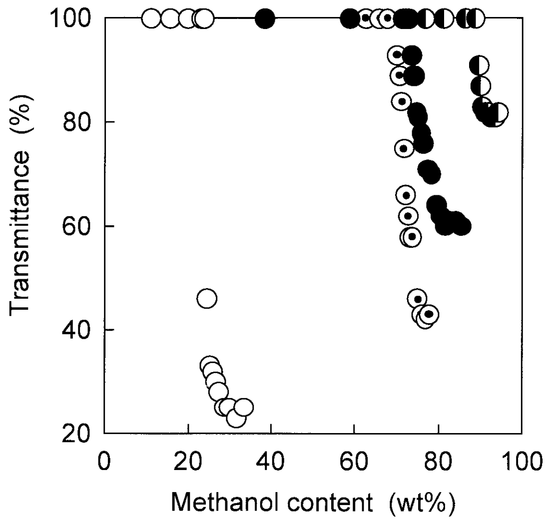

Fig. 4. Turbidimetric titration curves at 470 nm with the addition of methanol as nonsolvent into toluene solutions with 0.5 wt% of various homopolymers: *open circles*, PS; *circles with dots*, PMMA; *half-filled circles*, PEMA; *filled circles*, P*i*-BMA

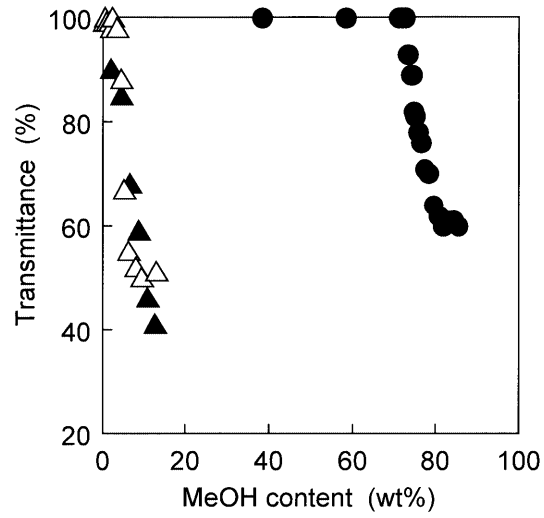

Fig. 5. Turbidimetric titration curves at 470 nm with the addition of methanol as nonsolvent into 0.5 wt% of P*i*-BMA solutions (*filled triangles*, cyclohexane; *filled circles*, toluene) and cyclohexane without P*i*-BMA (*open triangles*)

Table 3. Compositions of each layer after phase separation at 30 °C by addition of methanol[a] into cyclohexane solution dissolving P*i*-BMA

Composition (wt%)	P*i*-BMA[b]	Cyclohexane[c]	Methanol[c]
Upper layer	0	44.5	55.5
Lower layer	11.3	79.5	9.2

[a] Total composition after addition of methanol: P*i*-BMA/cyclohexane/methanol: 1/10/5, weight ratio

[b] Measured by gravimetry

[c] Measured by gas chromatography

proceeds at the interface of the droplet during the solvent-releasing process, which results in vitrification of the condensed P*i*-BMA phase at the interface [16]. This may allow the formation of the P*i*-BMA shell. When release of the solvent proceeds more, the shell becomes thicker, and methanol should penetrate into the droplet through the shell because the inside of the droplet is evacuated. However, since the shell is hydrophobic, the penetration rate of methanol into the droplet is much slower than the releasing rate of cyclohexane from the droplet. As a result, part of the shell is dented because the strength of the shell is not enough to withstand the pressure [11, 12]. As shown in Fig. 6, significant nonspherical particles were prepared using cyclohexane. This indicates that condensation of polymer molecules at the interface is important for the formation of nonspherical particles.

However, it is unclear the reason why the nonspherical particles were prepared from toluene droplets dissolving PMMA, because PMMA precipitated at high methanol content as shown in Fig. 4.

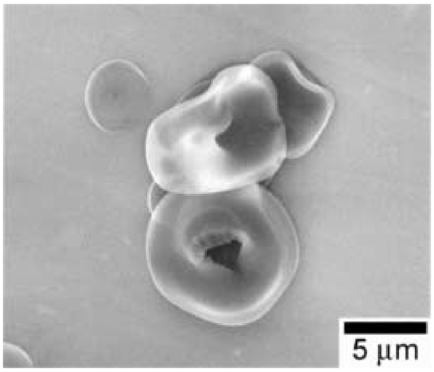

Fig. 6. A SEM photograph of P*i*-BMA particles produced when cyclohexane (P*i*-BMA/cyclohexane: 1/10, w/w) was rapidly released into a methanol bath by spraying the dispersion with a nebulizer

Table 4. Interfacial tensions[a] between water and toluene solutions with 0.01 wt% of various homopolymers obtained by solution polymerizations

		None	PS	PMMA	PEMA	P*i*-BMA
Mw	($\times 10^5$)	–	2.0	1.2	2.9	1.6
Interfacial tension	(mN m^{-1})	31.5	29.7	21.1	25.4	28.6

[a] Measured by the du Noüy ring method at 23 ± 1 °C

Table 4 indicates the interfacial tension between water and toluene solutions with 0.01 wt% of the various homopolymers. The interfacial tensions for the methacrylate polymers were in the range of 21.1~28.6 mN m^{-1}. The values for the P*i*-BMA and PS were slightly less than that of pure solvent, and were lowest for the PMMA. These results indicate that, since the PMMA is relatively more polar than the P*i*-BMA and PS, the PMMA concentration at the interface of the droplets with water was higher than those of the other polymers before the solvent-releasing process. This seems to be the reason why PMMA precipitated at the interface in the solvent-releasing process, resulting in the PMMA shell, even though high methanol content is needed to precipitate as described in Fig. 4. If the polymer shell is formed by the precipitation, the formation of nonspherical particle proceeds according to the formation mechanism proposed in a previous paper [12].

From the above results, we conclude that the condensation of the polymer molecules at the interface of the droplet is a key factor for the preparation of nonspherical particles.

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