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Synthesis and regular reflection property of cocoon-like poly(methyl methacrylate) particles by seeded suspension polymerization

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Abstract Synthesis and optical properties of cocoon-like poly(methyl methacrylate) (CPM) particles in the size range of $D_n = 3.0–6.5$ μm were studied. The synthesis of these anisotropic particles consists of two steps. The spherical poly(methyl methacrylate) (PMA) particles ($D_n = 2.2–5.5$ μm) cross-linked by 0.2–0.8 wt% ethylene glycol dimethacrylate (EGDMA) were prepared by dispersion polymerization, using a combination of poly(vinyl pyrrolidone) (PVP) and sodium di-(2-ethylhexyl) sulfosuccinate (NaEHS) as a stabilizer in 94:840 water–methanol. Then, a suspension polymerization of 9:1 methyl methacrylate (MMA)/EGDMA in the presence of the PMA particles as seed at 85 °C in water gave non-spherical, cocoon-like CPM particles, depending on the cross-linking densities of PMA particles. The cocoon-like CPM particles ($D_{n,c} = 4.0$ μm) showed the characteristic features of regular reflection, which can not be attained for conventional poly(methyl methacrylate) particles with a spherical shape. The effects of seed PMA particles with different properties on the formation of cocoon-like CPM particles and their regular reflection properties are described.

Keywords Seed suspension polymerization · Poly(methyl methacrylate) · Cocoon-like particles · Anisotropic particles · Regular reflection property

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Introduction

Micro-sized polymer particles with a narrow size distribution have attracted much attention in various areas, such as coatings, electronics, biomedical and information technology. To address the specialized requirements of this fast-growing technology, precise control of size, size distribution, and the morphologic features and properties of these particles have become more important [1–5]. One of the useful methods for producing micron-sized particles is dispersion polymerization, and in most cases polymer particles produced under favorable circumstances take on a spherical structure so as to minimize the interfacial free energy between the particles and the medium. So far, several approaches to preparing micron-sized monodisperse, non-spherical particles, such as snowman-like [5–9], confetti-like [8], egg-like [10], and disc-like particles [11] have been reported. The non-spherical particles can offer alternative benefits [12, 13]. These include the ability to show new optical and fluid properties which can not be achieved with spherical particles. Optimization of factors such as concentration of monomer, cross-linker, initiator, stabilizer, medium, and temperature is required for the preparation of these morphologically well controlled non-spherical particles.

In this work, the influences of the polymerization parameters on the synthesis of anisotropic, cocoon-like CPM particles from spherical PMA seed particles were investigated. Furthermore, the light-scattering properties of the anisotropic particles were examined and compared to those of spherical PMMA particles.

Experimental

Materials

Reagent grade methyl methacrylate (MMA, Mitsubishi Rayon Co. Ltd., 99%) and ethylene glycol dimethacrylate (EGDMA, Kyoeisha Chemical Co. Ltd.) were purified by conventional methods before use. Poly(vinyl pyrrolidone) (PVP, Dai-ichi Kogyo Seiyaku, Kyoto, Japan, $M_n = 360{,}000$), sodium di-(2-ethylhexyl) sulfosuccinate (NaEHS, Dai-ichi Kogyo Seiyaku) and ammonium polyoxyethylene alkyl sulfonate (APOS, $CH_3(CH_2)_{13-15}(OCH_2CH_2O)_{13}SO_3NH_4$, Dai-ichi Kogyo Seiyaku) were used as received. *t*-Butyl peroxypivalate (*t*-BPP, NOF Corporation, Tokyo, Japan), and benzoyl peroxide (BPO, NOF Corporation) were used as received. Deionized water was used in all experiments.

Preparation of poly(methyl methacrylate) (PMA) particles

A typical preparation of seed particles was as follows. A solution of PVP (23.3 g) and NaEHS (6.7 g) in a mixture of methanol (840 g) and water (94 g) was placed in a 2 L four-necked round-bottom flask, and was warmed at 50 °C under a nitrogen atmosphere. Then, a mixture of MMA (100 g), EGDMA (0.4 g) and *t*-BPP (2.4 g) was added into the solution. The mixture was stirred at 100 rpm for 20 h at 50–51 °C. The particles were separated by using a centrifugal dehydrator, washed

Table 1 Preparation of seed PMA particles by dispersion polymerization

Run	Stabilizer		BPP (g)	Monomer	Medium	Temp. (°C)	D_n (μm)	C_v[a]	Symbol
	PVP (g)	NaEHS (g)		MMA/EGDMA (g/g)	H_2O/CH_3OH				
1	23.3	–	2.4	100/0.4	94/840	50–51	0.6, 2.7	–	PMA-1
2	32.6	–	2.4	100/0.4	94/840	50–51	Coagulum		PMA-2
3	14.0	6.7	2.4	100/0.4	94/840	50–51	3.0	11.2	PMA-3
4	23.3	6.7	2.4	100/0.4	94/840	50–51	3.0	14.8	PMA-4
5	32.6	6.7	2.4	100/0.4	94/840	50–51	2.2	7.6	PMA-5
6	23.3	6.7	2.4	100/0	94/840	50–51	2.3	14.0	PMA-6
7	23.3	6.7	2.4	100/0.2	94/840	50–51	4.9	22.9	PMA-7
8	23.3	6.7	2.4	100/0.8	94/840	50–51	1.5	60.9	PMA-8
9	23.3	6.7	2.4	100/0.4	280/654	50–51	1.1	13.0	PMA-9
10	23.3	6.7	2.4	100/0.4	0/934	50–51	3.0	10.2	PMA-10
11	23.3	8.0	1.6	100/0.4	94/840	50–51	2.5	11.4	PMA-11
12	23.3	6.7	2.4	100/0.4	98/840	55–56	Coagulum		PMA-12
13	23.3	6.7	1.6	100/0.4	94/840	55–56	3.8	17.1	PMA-13
14	23.3	5.2	1.6	100/0.4	94:840	55–56	5.5	25.2	PMA-14

[a] Coefficient of variation

with water, and then dried. Cross-linked spherical PMMA (PMA) particles as seeds were obtained in an 85% yield (85 g). Recipes for the preparation of the seed PMA particles, the number average diameter (D_n) and coefficient of variation (C_v) of the PMA particles are shown in Table 1.

Preparation of cocoon-like poly(methyl methacrylate) (CPM) particles

The preparation of cocoon-like CPM particles was carried out as follows. Micron-size PMA particles (120 g) were added into a solution of APOS (1.8 g) in deionized water (1,200 mL), and dispersed by using a Nihonseiki ultrasonic disperser US-600T. A monomer-suspension solution containing MMA (216 g), EGDMA (24 g), BPO (4.8 g) and APOS (3.6 g) in deionized water was added all at once into the suspension solution of PMA particles. The mixture was stirred at 80 rpm for 30 min at room temperature under a nitrogen atmosphere, and then warmed at 85 °C for 4 h with a stirring speed of 50 rpm. Cocoon-like CPM particles were separated by using a centrifugal separator and washed repeatedly with hot water (70 °C). The cocoon-like CPM particles [$D_{n,c} = 4.0$ μm ($D_{n,c}$: average major axis of a particle) and $C_v = 20.3\%$] were obtained in a 95% yield (317 g).

Measurements

Microscopic observation was monitored with a Nikon AFX-DX OPTPHOT-2 optical microscope. The particles were observed by a Hitachi S-1250 scanning electron microscope (SEM). The number average diameter (D_n) and coefficient of variation (C_v) of the particles were determined by a Coulter Electronics Multisizer II particle distribution counter. The light-scattering property of cocoon-like CPM particles was measured with a Murakami Color Research Laboratory Gonino Photometer GP-200.

Results and discussion

Preparation of PMA particles

Homopolymers such as PVP [6, 14] and poly(acrylic acid) [15] have been applied as steric stabilizers in a dispersion polymerization. It has been widely accepted that the particles can be stabilized by the absorption of the polymer stabilizers onto the surface of the particles and/or the anchoring of grafted stabilizers formed during the polymerization into the resulting particles [4]. The addition of cross-linking agents in a dispersion polymerization system usually makes it difficult to control particle shape, size and size distribution [16]. The formation of uniformly sized particles depends strongly on the type and quantity of stabilizers. So, we first examined the effectiveness of PVP as a stabilizer to prepare cross-linked poly(methyl methacrylate) (PMA) particles having the desired sizes (2.0–5.0 μm) with a narrow size distribution, which will be used as seeds for subsequent suspension polymerization. The fixed and varied factors used for the preparation of the PMA particles are summarized in Table 1. When PVP = 23.3 g was used as a stabilizer, the polymerization of 100:0.4 MMA/EGDMA gave particles with a bimodal distribution ($D_n = 0.6$ and 2.7 μm). Further addition of PVP (32.6 g) resulted in the formation of individual particles within aggregates, but they could not be broken up. It is well known that co-stabilizers with low molecular weights such as surfactants and alcohols with long alkyl chains are effective to control particle size and size distribution [17, 18]. In this study we used sodium di-(2-ethylhexyl) sulfosuccinate (NaEHS) as a co-stabilizer. As shown in Figs. 1b and 2a, monodispersed spherical particles (PMA-4, $D_n = 3.0$ μm) were formed for the dispersion polymerization of 100:0.4 MMA/EGDMA in the presence of PVP (23.3 g) and NaEHS (6.7 g), although their surface was not so smooth. No significant change in spherical particle size (PMA-3) was observed when PVP = 14.0 g was used, but rather small particles (PMA-5) were obtained by an increase in PVP (32.6 g). Thus, the combination of PVP and NaEHS function well as stabilizers for the preparation of seed PMA particles.

Particle size is also governed by the concentration of initiator and polymerization temperature, i.e., in a system of higher concentrations of radicals, growing polymer chains are liable to undergo termination to give soluble oligomers in the medium before reaching enough chain length to form nuclei. Therefore, concentrations of polymers with high molecular weights capable of forming nuclei become relatively low in a dispersion medium. In the following growth step, the fewer particles which existed in the polymerization system had a chance to grow larger due to the incorporation of a sufficient amount of monomers and the flocculation of oligomers

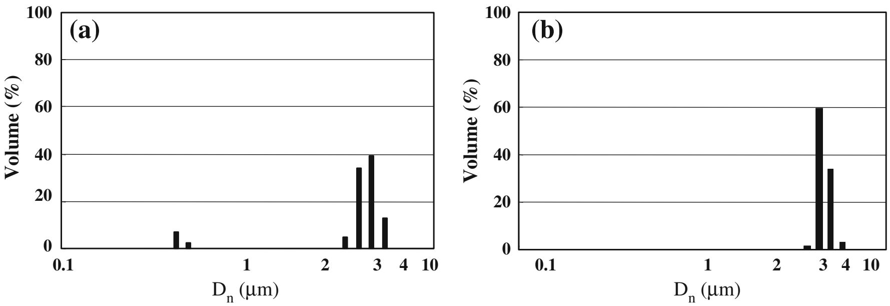

Fig. 1 Size distribution curves of PMA particles obtained by dispersion polymerization in the presence of **a** PVP and **b** PVP and NaEHS

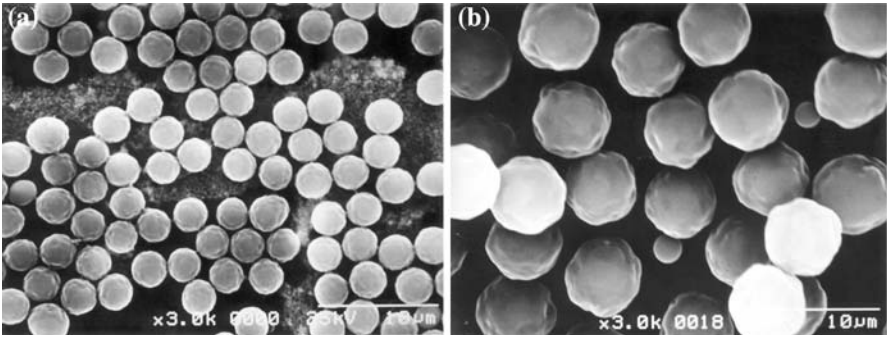

Fig. 2 Scanning electron microscope (SEM) photographs of **a** PMA-4 and **b** PMA-14 particles produced under the conditions listed in Table 1

into the nuclei. As described above, for the dispersion polymerization of MMA and EGDMA with *t*-butyl peroxypivalate (*t*-BPP, $t_{1/2} = 19$ h at 50 °C) at 50–51 °C, spherical particles with $D_n = 3.0$ μm can be obtained. Attempts to prepare particles with a relatively large size were carried out at a higher temperature. Polymerization with *t*-BPP = 2.4 g at 55–56 °C, however, led to the formation of ill controlled aggregated precipitates, suggesting that the radical concentration was too high to control the particle formation processes. By using a low concentration of *t*-BPP (1.6 g) and NaEHS (5.2 g), particle sizes with $D_n = 5.2$ μm (PMA-14) can be obtained, although their surface was somewhat rough, as shown in Fig. 2b.

Seed PMA particles with different cross-linking densities were prepared as described in Table 1 (run 4 and run 6–run 8). As EGDMA increased from 0.2 to 0.8 wt% (on the basis of MMA), the average particle diameter decreased from 4.9 μm (PMA-7) to 1.5 μm (PMA-8). The PMA-8 particles, however, have ill controlled and broader size distributions, suggesting that higher cross-linking density hinders uniform growth by the flocculation of primary particles [4].

Particle sizes and size distribution are also affected by media solvency. The particle size increased from $D_n = 1.1$ μm (PMA-9) in 280:654 water/methanol to $D_n = 3.0$ μm (PMA-10) in methanol. The results can be simply explained in terms of the critical polymer chain length in a given media for the nucleation process. In the water/methanol dispersion media, nucleation is favorable for PMMA with lower molecular weights due to the decreasing solubility of those with increasing water content. This results in the generation of more nuclei in the early stage of polymerization, which finally leads to the formation of smaller particles. As will be described later, the medium used for the preparation of the PMA particle is unexpectedly important, i.e., particles formed by seeded suspension polymerization of MMA and EGDMA take different shapes, depending on the medium of the seed particle polymerization.

Synthesis of cocoon-like CPM particles

Sheu et al. [5] showed that for a monomer-swollen cross-linked particle in the seed polymerization system, the elevation of temperature causes monomer phase-separation from the particles, which leads to forming a monomer bulge out of each particle. It is believed that the extent of such monomer-transfer through a polymer network giving rise to anisotropic particles depends strongly upon the interfacial tensions of the particle and the aqueous phase, the particle and the monomer, and the monomer and the aqueous phase [9, 19].

Although there are many parameters which affect seed suspension polymerization, in this study, except for seed particles with a different degree of cross-linking and concentration of the emulsifying agent (APOS), all parameters such as concentrations of MMA, EGDMA, BPO, polymerization temperature, polymerization time, and agitation rate were fixed, as described in the Experimental section. The PMA seeds were allowed to stand for 30 min at room temperature until the monomer and additives were absorbed by the seed PMA particles, and then the mixture was warmed to a temperature of 85 °C. Figure 3 shows SEM photographs of the polymer particles (CPM) obtained from the suspension polymerization. Non-spherical, cocoon-like PMMA particles (CPM-I), which resemble snowman-like particles in shape, were formed when the seed particles, PMA-4, were used. Similarly, the cocoon-like particles, CPM-VI and CPM-VII were obtained by using the PMA-13 and PMA-14 seed particles, respectively (Table 2). The surface of the CPM particles was smooth and their size (average major axis of the particle, $D_{n,c}$)

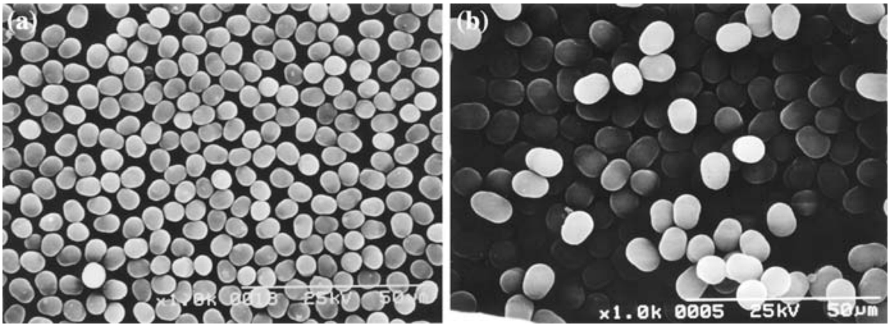

Fig. 3 Scanning electron microscope (SEM) photographs of **a** cocoon-like CPM-I and **b** CPM-VII

Table 2 Preparation of cocoon-like CPM particles by suspension polymerization using selected PMA particles

Seed PMA particle	$D_{n,c}$ (μm)	C_v [a]	Particle shape	Symbol
PMA-4	4.0	20.3	Cocoon-like	CPM-I
PMA-6	2.8	12.1	Sphere	CPM-II
PMA-7	2.8	10.5	Sphere	CPM-III
PMA-8	1.7	67.4	Disordered	CPM-IV
PMA-10	4.2	13.8	Sphere	CPM-V
PMA-13	4.8	22.7	Cocoon-like	CPM-VI
PMA-14	6.5	29.3	Cocoon-like	CPM-VII

[a] Coefficient of variation

increased with increasing the seed's size. The particle shape is expected to be affected by media [7]. In fact, the cocoon-like particles could not be obtained for the PMA-4-seeded suspension polymerization in 94:840 or 280:654 H_2O–EtOH, indicating that the increase of media solvency imposes an unfavorable influence.

The decrease in the total concentration of the emulsifying agent (APOS = 2.7 g) for seed suspension polymerization resulted in the formation of anisotropic particles but with ill controlled shapes, whereas its increase (APOS = 8.1 g) brought about the formation of undesired small particles, probably due to the involvement of emulsion polymerization.

As expected, spherical particles were obtained for the polymerization of MMA and EGDMA when noncross-linked PMA-6 particles were used. Similarly, spherical particles were obtained for the seed suspension polymerization using 0.2 wt% cross-linked PMA-7 particles. Meanwhile, when PMA-8 particles with 0.8 wt% EGDMA were used, non-spherical particles (CPM-IV) were produced but some aggregates and by-product particles were formed. These results indicate that the degree of cross-linking of seed particles definitely affects the formation of cocoon-like particles.

For the formation of anisotropic particles, it has been shown that cross-linked seed particles first overswell and then shrink, leaving a monomer droplet on the surface of the particle. The shape of the monomer droplets will be primarily governed by the seed particle/monomer wetting properties and the kinetics of the swelling and contraction of seed [7, 18]. Figure 4 showed optical micrographs of PMA-4 and PMA-8 in a suspension solution of MMA and EGDMA at 35 °C. For the PMA-4 particles, a new bulb on the seed particles was formed (Fig. 4a). The shape observed was physically similar to that of final cocoon-like particles, and the boundary between the particle and the monomer bulb was not observed, suggesting that the surface of the seed particles is compatible with the monomers. Contrary to this, for the PMA-8 particles the swelling caused shape deformation, which was again similar to the final particles with disordered shape (Fig. 4b).

For the snowman-like particles prepared from cross-linked seed particles swollen by a different monomer, the polymer chains formed by the seeded polymerization is immiscible with the cross-linked seed polymer [6, 8]. When the seed particles are

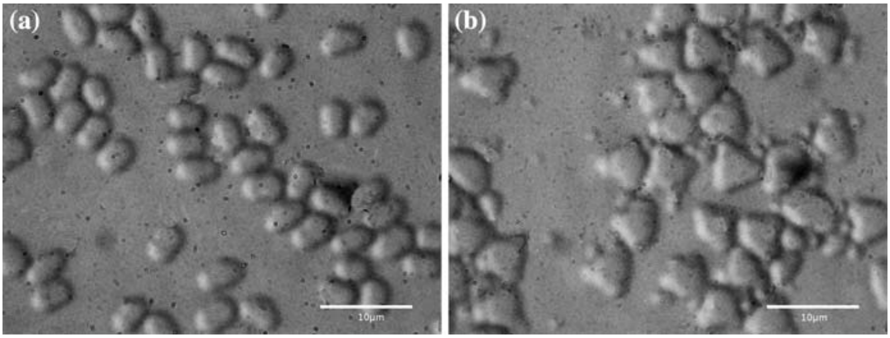

Fig. 4 Optical micrographs of **a** PMA-4 and **b** PMA-8 particles in the suspension solution of MMA and EGDMA at 35 °C

swollen by monomers having the same components, it appears that the growth of monomer droplets on the seed particles is favorable and the compatibility between seed particles and monomers containing growing polymer chains is mild favorable, depending on the degree of cross-linking of the seed particles and media solvency. Thus, the formation of the cocoon-like particles seems to be based on similar formation mechanism of anisotropic particles.

Interestingly, the seed suspension polymerization of MMA and EGDMA using PMA-10 particles, which were prepared from 100:0.4 MMA/EGDMA in methanol, gave spherical particles (CPM-V) but not cocoon-like particles. This result may be explained in terms of the cross-linking density of seed particles. In methanol a number of PMMA polymer chains with relatively high molecular weights can participate in the nucleation process during dispersion polymerization. This may bring about an increase in PMMA chain length between branching monomer EGDMA units in the particles, i.e., the formation of particles with low cross-linking density. For these seed particles with relatively loose structures it seems that the homogeneous growth of the seed is preferred rather than anisotropic growth on the surface, suggesting that the medium for the preparation of the seed particles is also an important key for the preparation of cocoon-like CPM particles. Thus, anisotropic PMMA particles can be obtained from cross-linked spherical PMMA particles under specific sets of conditions.

Light-scattering properties of cocoon-like CPM particles

PMMA is well known to show intrinsically excellent optical properties. It is highly interesting to examine how particles with anisotropic structures affect optical properties. A preliminary examination of the light-scattering properties of CPM-I was examined. The intensity distribution of reflected and diffused light by illuminating CPM-I is shown in Fig. 5. For conventional PMMA particles with spherical structures ($D_n = 4.0$ μm), the particles diffuse incident light at a 10° ($\Theta = 10°$). The same result was obtained at $\Theta = 45°$. Compared to this behavior, CPM-I ($D_n = 4.0$ μm) showed regular reflection with relatively strong intensity,

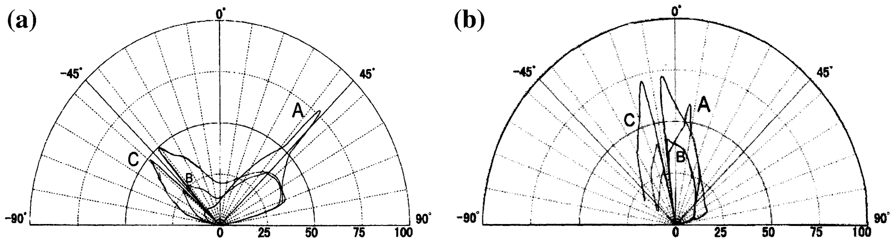

Fig. 5 Regular reflection properties of cocoon-like CPM-I particles (*left*) at $\Theta = 10°$ and (*right*) $\Theta = 45°$. **a** Cocoon-like CPM-I particles with $D_n = 4.0$ μm, **b** spherical PMMA particles with $D_n = 4.0$ μm, **c** spherical PMMA particles with $D_n = 6.0$ μm

together with very weak diffused light. The regular reflection of the particles became marked at $\Theta = 45°$. Thus, cocoon-like CPM-I particles have features characteristic of regular reflection properties.

Conclusions

For the dispersion polymerization of MMA and cross-linker EGDMA using a combination of PVP and NaEHS as the stabilizer, the effects of the polymerization parameters, i.e., initiator and EGDMA concentrations, temperature, and medium on the cross-linked particle size and size distribution were investigated. Spherical cross-linked PMA particles in the size range of 1.1–5.5 μm were obtained under favorable circumstances, which can be used for subsequent seed suspension polymerization of MMA and EGDMA. The seed suspension polymerization of PMA particles cross-linked by 0.4 wt% EGDMA prepared in a water/methanol medium gave non-spherical, cocoon-like CPM particles with a size range of $D_{n,c} = 4.0$–6.5 μm. However, particles with higher (8 wt%) or lower (2 wt%) wt% of cross-linker than 4 wt% did not give cocoon-like particles. Thus, cocoon-like particles can be obtained only under specific conditions. As expected, the cocoon-like CPM particles showed characteristic regular reflection, reflecting their anisotropic shapes.

References

1. Fudouz H, Xia Y (2003) Photonic papers and inks: color writing with colorless materials. Adv Mater 15:892–896
2. Min K, Matyjaszewski K (2007) Atom transfer radical dispersion polymerization of styrene in ethanol. Macromolecules 40:7217–7222
3. Song J-S, Winnik MA (2006) Monodisperse, micron-sized reactive low molar mass polymer microspheres by two-stage living radical dispersion polymerization of styrene. Macromolecules 39:8318–8325
4. Kawaguchi S, Ito K (2005) Dispersion polymerization. Adv Polym Sci 175:299–328
5. Sheu HR, El-Aasser MS, Vanderhoff JW (1990) Phase separation in polystyrene latex interpenetrating polymer networks. J Polym Sci Part A Polym Chem 28:629–651

6. Wang D, Dimonie VL, Sudol ED, El-Aassser MS (2001) Effect of PVP in dispersion and seeded dispersion polymerizations. J Appl Polym Sci 84:2721–2732
7. Okubo M, Wang Z, Ise E, Minami H (2001) Adsorption of styrene on micron-sized, monodisperse, cross-linked polymer particles in a snowman-shaped state by utilizing the dynamic swelling method. Colloid Polym Sci 279:976–982
8. Okubo M, Fujibayashi T, Yamada M, Minami H (2005) Micron-sized, monodisperse, snowman/confetti-shaped polymer particles by seeded dispersion polymerization. Colloid Polym Sci 283:1041–1045
9. Kim J-W, Larsen RJ, Weitz DA (2006) Synthesis of nonspherical colloidal particles with anisotropic properties. J Am Chem Soc 128:14374–14377
10. Okubo M, Miya T, Minami H, Takekoh R (2002) Morphology of micron-sized, monodisperse, nonspherical polystyrene/poly(*n*-butyl methacrylate) composite particles produced by seeded dispersion polymerization. J Appl Polym Sci 83:2013–2021
11. Fujibayashi T, Okubo M (2007) Preparation and thermodynamic stability of micron-sized, monodisperse composite polymer particles of disc-like shapes by seeded dispersion polymerization. Langmuir 23:7958–7962
12. Manoharan VN, Elsesser MT, Pine DJ (2003) Dense packing and symmetry in small clusters of microspheres. Science 301:483–487
13. Xu S, Nie Z, Seo M, Lewis P, Kumacheva E, Stone HA, Garstecki P, Weibel DB, Gitlin I, Whitesides GM (2005) Generation of monodisperse particles by using microfluidics: control over size, shape, and composition. Angew Chem Int Ed 44:724–728
14. Jiang S, Sudol ED, Dimonie VL, EL-Aasser MS (2008) Dispersion polymerization of methyl methacrylate: effect of stabilizer concentration. J Appl Polym Sci 107:2453–2458
15. Ober CK, Lok KD (1987) Formation of large monodisperse copolymer particles by dispersion polymerization. Macromolecules 20:268–273
16. Choi J, Kwak S-Y, Kang S, Lee S-S, Park M, Lim S, Kim J, Choe CR, Hong SI (2002) Synthesis of highly crosslinked monodisperse polymer particles: effect of reaction parameters on the size and size distribution. J Polym Sci Part A Polym Chem 40:4368–4377
17. Tseng CM, Lu YY, El-Aasser MS, Vanderhoff JW (1986) Uniform polymer particles by dispersion polymerization in alcohol. J Polym Sci Part A Polym Chem 24:2995–3007
18. Jayachandran KNN, Chatterji RR (2001) Preparation of linear and crosslinked polymer microspheres by dispersion polymerization. J Macromol Sci Polym Rev C41:79–94
19. Mock EB, De Bruyn H, Hawkett BS, Gilbert RG, Zukoski CF (2006) Synthesis of anisotropic nanoparticles by seeded emulsion polymerization. Langmuir 22:4037–4043