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ORIGINAL CONTRIBUTION

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Monodisperse polystyrene particles crosslinked with poly(dimethyl siloxane) diacrylate using dispersion polymerization and their monomer swelling capability

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Abstract A flexible poly(dimethyl siloxane) diacrylate (PDMSDA) crosslinker was synthesized using different molecular weights of poly(dimethyl siloxane) (PDMS, $M_n = 550$, 1,700, 4,000 g/mol). The monodisperse polystyrene (PS) particles crosslinked with various contents of PDMSDA were prepared by dispersion polymerization, and applied as seed particles in the seeded polymerization. The crosslinking density of the PS particles was determined from the rate of transport of the monomer molecules to the crosslinked seed particles. It was confirmed that the monomer swelling capacity of seed particles and final morphological changes of polymer beads were determined significantly by the crosslinking density of the seed particles. In addition, the morphological change was not observed without the oligomer swelling step in the seeded polymerization due to the hydrophobic property of PDMS. When highly crosslinked seed particles were used in the seeded polymerization, peculiar morphology (doublet structure) of polymer beads appeared.

Keywords Poly(dimethyl siloxane) diacrylate · Flexible crosslinker · Monodisperse crosslinked PS particles · Crosslinking density · Morphology

Introduction

Monodisperse micron-sized polymer beads are useful materials for a wide range of industrial fields such as standard calibration kits, medical diagnostics, solid-phase catalysts, and ball type spacers in the liquid crystal display (LCD) [1, 2]. High monodispersity of the beads plays an important role in meeting their original requirements and in obtaining better efficiency in the applications. In general, dispersion polymerization has been widely used to produce monodisperse polymer particles in the size range of 1–15 μm [3–6]. The colloidal polymer particles are formed in a continuous medium during polymerization in the presence of a stabilizer. Although the dispersion polymerization has a great advantage in the direct preparation of monodisperse polymer particles, it has restricted application due to the limitation of monomer applicable to this technique [7]. In addition, it is very sensitive to many variables including medium solvency, temperature, concentration, and types of initiator or stabilizer [8, 9], especially, the incorporation of a small amount of crosslinker results in broad size distribution, odd shape, and coagulum [10–13]. Step-wise seeded polymerization technique containing monomer swelling stage can be proposed as an alternative to overcome the drawbacks of dispersion polymerization. Vanderhoff et al. [2, 14, 15] developed a successive seeded polymerization method in a gravity-free condition. Also, Ugelstad et al. [1, 16, 17] proposed an activated swelling process for the preparation of various monodisperse polymer particles. This method is featured by utilizing an effective monomer-swelling agent having low solubility in water (oligomer). Okubo et al. [18, 19]

suggested a dynamic swelling method, which makes the seed particles absorb a large amount of the second monomer by adding water in the medium slowly and continuously. Some other techniques were also reported [20, 21]. These methods usually employed linear polymer as seed particles because a crosslinked structure was difficult to prepare as mentioned earlier.

In the seeded polymerization, the monomer swelling capacity of seed particles and the morphology of final beads are important characteristics for the production of monodisperse polymer beads. From our previous works [22–24], it has been found that these factors were determined by the crosslinking density of seed particles. In case of high crosslinking density, incomplete monomer swelling or the phase separation was observed. While the hydrophobic oligomer swelling or other treatments was needed for an efficient monomer swelling and the prevention of de-swelling of monomer during the polymerization when linear polymer was used as seed particles. Slightly crosslinked seed particles using flexible crosslinker, such as urethane acrylate (UA) [22] or polypropylene diacrylate (PPGDA) [23], provide a sufficient monomer swelling without morphological changes. However, an appropriate content of these crosslinkers for the slight crosslinking was too small to trap the swollen monomer when the hydrophobic oligomer swelling step was omitted. Based on the results, it is expected that de-swelling of swollen monomer would be prevented by incorporating large amount of crosslinker for sufficient crosslinking network. Simultaneously, efficient monomer swelling would be achieved by introducing hydrophobic moiety in the crosslinker without oligomer swelling stage.

In the present study, a new poly(dimethyl siloxane) diacrylate (PDMSDA) crosslinker was synthesized to eliminate the oligomer swelling step in the seeded polymerization without morphological change and de-swelling of monomer emulsion. Different molecular weights of poly(dimethyl siloxane) (PDMS) were used in the synthesis of PDMSDA, and various contents of PDMSDA were incorporated in the dispersion polymerization. The kinetic of polymerization and the morphology of crosslinked polystyrene (PS) particles were examined. The effect of crosslinking density of PS particles on the monomer swelling capacity in the seeded polymerization and final morphology were investigated.

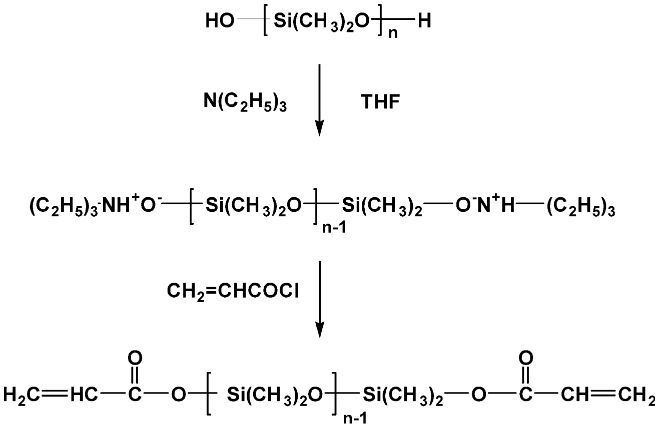
Experimental

Materials

Hydroxyl terminated PDMS ($M_n = 550$, 1,700, 4,000 g/mol, Aldrich), triethylamine (TEA, Junsei), acryloyl chloride (AC, Sigma Chemicals), and tetrahydrofuran (THF, Mallinckrodt) were used for the synthesis of PDMSDA crosslinker. Styrene (St, Kanto), polyvinylpyrrolidone (PVP, $M_w = 40{,}000$ g/mol, Sigma), polyvinylalcohol (PVA, $M_w = 88{,}000–92{,}000$ g/mol, 87–89% hydrolyzed, Kuraray), sodium lauryl sulphate (SLS, Wako), and aerosol-OT (AOT, Wako) were all reagent grades. 1-Butanol (Aldrich) and ethanol (Carlo) were used as received. Azobis(isobutylronitrile) (AIBN, Junsei) and benzoyl peroxide (BPO, Junsei) were recrystallized from methanol and THF.

Synthesis of PDMSDA

PDMSDA was synthesized by the reaction of a hydroxyl-terminated PDMS with AC. Three different molecular weights ($M_n = 550$, 1,700, 4,000 g/mol) of PDMS were selected. PDMS (1 mol) and TEA (2 mol) dissolved in THF (75 g) were poured into a 250 ml round-bottomed flask and cooled to 5°C. After 5 h of stirring (200 rpm), AC (2 mol) was slowly added into the reactor and then reacted at 50°C for 5 h. Then, the reaction mixture was filtered to remove the salt, triethanolamine hydrochloride, and was evaporated completely. Continuously, the crude PDMSDA was dissolved in methylene chloride (MC) and washed repeatedly with water to remove remnant salts and non-reactants. After trapping the moisture in the solution with anhydrous $MgCl_2$, the reaction mixture was filtered again. The filtrate was evaporated to remove the MC, until a viscous PDMSDA was recovered. The reaction procedure and molecular structure of PDMSDA are presented in Scheme 1.



Scheme 1 Reaction procedure and schematic molecular structure of PDMSDA crosslinker

PS particles crosslinked with PDMSDA

The crosslinked PS particles were produced by dispersion polymerization. PVP, AOT, and butanol were weighed into a 250-ml four-necked round flask equipped with a reflux condenser, a nitrogen inlet apparatus, and a mechanical stirrer. Then St, PDMSDA, and AIBN mixture was poured into the reactor at room temperature. After 30 min of vigorous stirring, the homogeneous mixture was reacted at 70°C for 24 h with 40 rpm of stirring. The product was purified three times through centrifugation at 2,500 rpm for 10 min, and washed with ethanol to remove the surface-anchored PVP molecules. Final particles were dried at room temperature. The standard recipe of the dispersion polymerization is shown in Table 1.

Monomer swelling and polymerization

Monomer swelling and polymerization was carried out in a 250-ml four-necked glass flask equipped with a reflux condenser, a nitrogen inlet apparatus, and a mechanical stirrer.

The PS particles (0.1 g) were redispersed in a 0.25 wt% SLS of ethanol aqueous solution (SE solution, EtOH/water = 1/5, g/g; 40 g) by sonification. Various amounts of the monomer (St) and initiator (BPO, 1 wt% to the St) emulsion in the SE solution (21 g) were poured into the reactor. The swelling was continued until emulsion droplets disappeared completely at 30°C. Then the swollen particles were stabilized with 5% PVA aqueous solution (50 g), and polymerized at 80°C for 10 h. The particles were washed repeatedly with water and dried in a vacuum oven.

Table 1 Standard recipe of dispersion polymerization

Ingredient	Quantity (g)
St	Variable[a]
PDMSDA	Variable[b]
AIBN[c]	0.125
PVP[d]	2.0
Aerosol OT[e]	0.4
Butanol	85.0

[a] 100, 97, 95, 90, and 80% based on the total monomer weight
[b] 0, 3, 5, 10, and 20% based on the total monomer weight with different molecular weights of PDMSDA (M_n = 550, 1,700, 4,000 g/mol)
[c] Initiator: 1 wt% based on total monomer
[d] Stabilizer: 2 wt% based on the total weight
[e] Co-stabilizer: di-2-ethylhexyl ester of sodium sulphosuccinic acid

Characterization

The chemical structure of PDMSDA was confirmed by ^{1}H-NMR (Gemini 300 spectrometer) using $CDCl_3$, and Fourier transform-infrared (FT-IR) spectroscopy (Mahgna IR-550, Nicolet). Monomer swelling procedure, and morphology of crosslinked PS seed particles and polymer beads were monitored by optical microscope (OM, Olympus BH-2) and scanning electron microscope (SEM, JSM-6330F JEOL), respectively. About 100 individual particle sizes were measured from SEM photographs, the average was taken to the diameter of the particle, and their particle size distribution (PSD) was obtained. The conversions were determined with a conventional gravimetric method [23].

Results and discussion

PDMSDA crosslinker

The PDMSDA synthesized was characterized by utilizing FT-IR and ^{1}H-NMR. In FT-IR measurement, a broad OH peak of PDMS around 3,600–3,100 cm^{-1} disappeared (Fig. 1a), and a new carbonyl bond at 1,720 cm^{-1} and carbon double bond at 1,645 cm^{-1} emerged after PDMSDA synthesis as shown in Fig. 1b. Figure 2 shows the ^{1}H-NMR spectra of PDMSDA (M_n = 1,700 g/mol). The signals recorded are as follows: $\delta = 0$ ppm (H_{ii}) for the methyl groups in PDMS back-

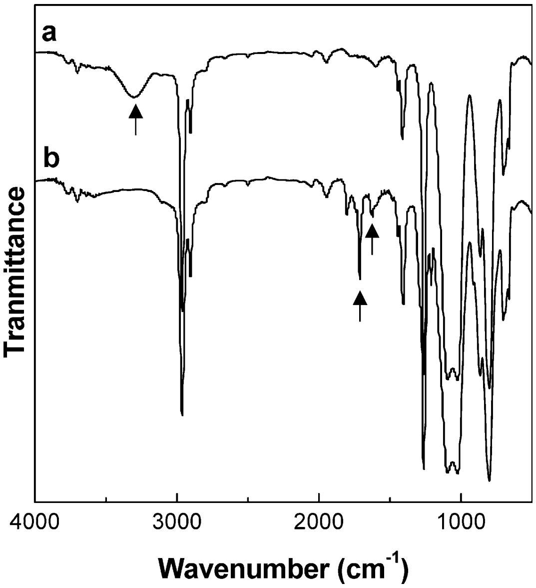


Fig. 1 FT-IR spectra of hydroxyl-terminated PDMS (**a**) and PDMSDA (**b**)

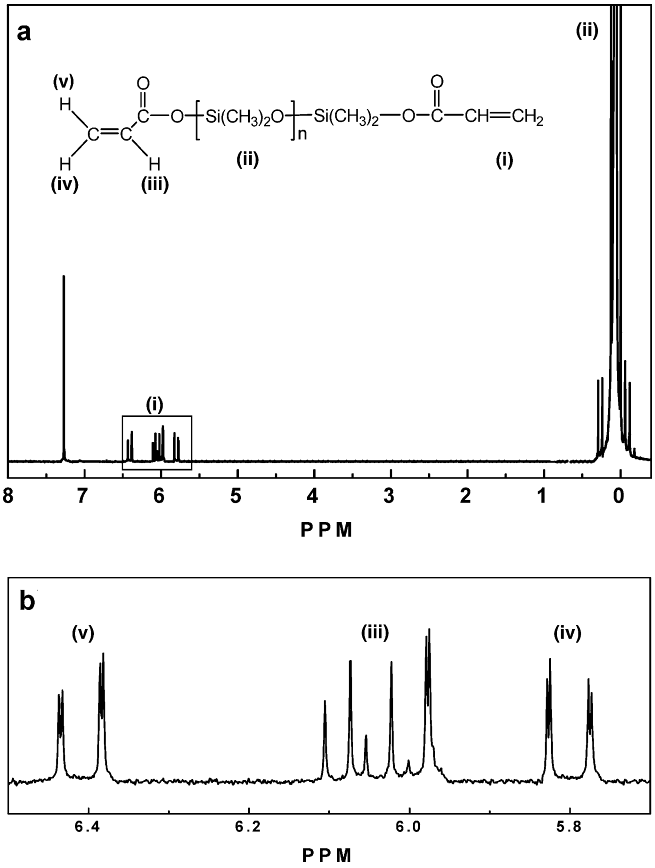


Fig. 2 ^{1}H-NMR spectra of PDMSDA (**a**) and the magnification of square box (**b**)

bone (Fig. 2a), and in detail, $\delta = 5.8$ ppm (H_{iv}), $\delta = 6.0$ ppm (H_{iii}), and $\delta = 6.4$ ppm (H_v) for the acryl groups at both ends of molecules as shown in Fig. 2b, which is the high magnification of a square box in Fig. 2a. In addition, we confirmed the same results in the different molecular weights of PDMSDA ($M_n = 550$, 4,000 g/mol). Consequently, it was reasonable that all the PDMSDA crosslinkers designed were synthesized successfully.

The monomer swelling capacity of seed particles was controlled by using the flexible crosslinkers, UA and PPGDA, without any morphological change [22–24]. But the proper content of these crosslinkers for slightly crosslinked particles was about 3 wt% based on the monomer, which supplies an insufficient crosslinking network in the seed particles to prevent de-swelling of swollen monomer during polymerization. The flexible crosslinker, PDMSDA, was synthesized to incorporate the hydrophobic moiety in the seed particles without swelling the hydrophobic oligomer into the seed particles before the second monomer swelling. It is generally known that the silicone resins are more hydrophobic than organic polymers, and thus are superior in moisture resistance and water repellency [25]. Besides, the amount of PDMSDA can be controlled by changing the molecular weight of PDMS.

Monodisperse crosslinked PS particles

Figure 3 and Table 2 show the SEM photographs and the characteristics of PS particles crosslinked with varying concentrations and different molecular weights of PDMSDA after the dispersion polymerization. Polydisperse size distribution and odd shapes were observed in case of PS5-550 (Fig. 3b) and PS20-1700 (Table 2) since the second particles and coagulants were generated during the dispersion polymerization by means of the high-crosslinking density [23]. However, monodisperse and clear surface were obtained when 20 wt% of PDMSDA was used by increasing the molecular weight of PDMSDA as shown in Fig. 3f and Table 2 (PS20-4000). From these results, to prepare slightly crosslinked particles, a suitable content of PDMSDA was 3 wt% at 550 g/mol, 10 wt% at 1,700 g/mol, and 20 wt% at 4,000 g/mol of PDMSDA.

Figure 4a shows the conversion (C_v) curves of the PS particles crosslinked with various contents of PDMSDA ($M_n = 1{,}700$ g/mol) through the dispersion polymerization as a function of polymerization time. The polymerization rate (R_p) of linear PS particles is relatively slower than those of typical dispersion polymerization because butanol was used as a medium. The PDMSDA crosslinker did not dissolve in ethanol completely, but was solubilized in butanol due to the hydrophobicity of PDMS. Although the R_p was influenced by the medium, morphological changes were not observed as shown in Fig. 3. In the C_v curves, it was of interest to note that as the PDMSDA content increased, the R_p became faster. For a more precise explanation, the R_p was obtained from the time–conversion curve at each conversion and replotted against the fractional conversion as shown in Fig. 4b. R_p became faster with increasing PDMSDA content at the low conversion region. In contrast, in the high conversion region, R_p is independent of the PDMSDA contents. This can be illustrated by a crosslinked network structure of the primary particles readily absorbing the monomer from the medium [23, 26]. Moreover, as shown in Fig. 3 and Table 2, the particle sizes were reduced with the increase in the PDMSDA concentration, which means total surface was enlarged. Therefore, the equilibrium distribution of monomer

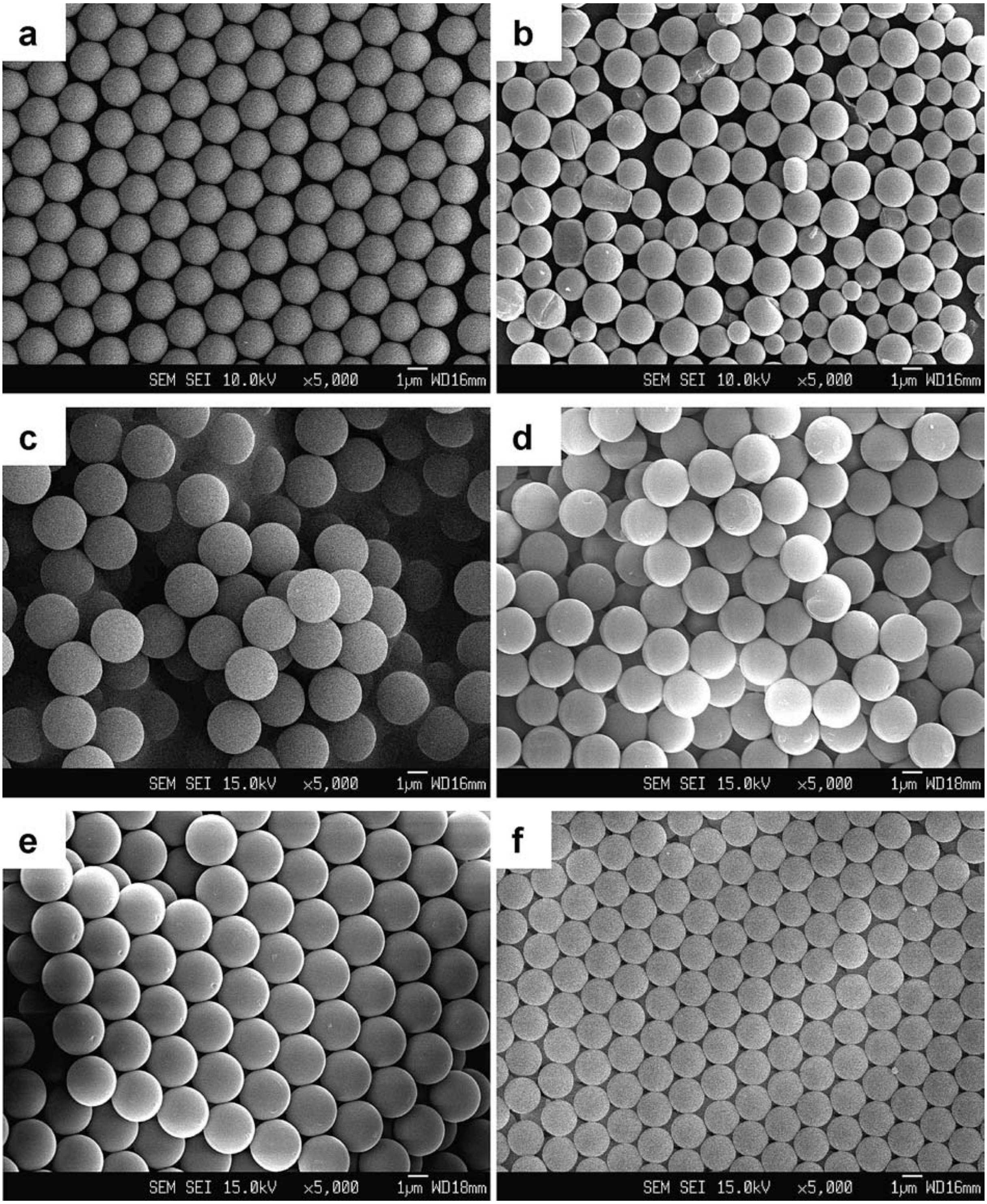


Fig. 3 SEM photographs of PS particles crosslinked with PDMSDA at different molecular weights and contents: PS3–550 (**a**), PS5–550 (**b**), PS5–1,700 (**c**), PS10–1,700 (**d**), PS10–4,000 (**e**), and PS20–4,000 (**f**)

toward the particle phase is more favourable resulting in faster polymerization rate.

Figure 5 shows the FT-IR spectra of PS particles crosslinked with various PDMSDA contents ($M_n = 1{,}700$ g/mol) after dispersion polymerization. The specific peaks of siloxane bond (–SiO–) and methyl groups (–CH_3) were confirmed in the region of 1,000–1,100 cm^{-1} and 1,260 cm^{-1}, respectively. Also, the

Table 2 Characteristics of crosslinked PS particles by dispersion polymerization

Symbol[a]	Content[b] (wt%)	M_n^c (g/mol)	D_n (μm)	PSD[d]	Remarks
PS0-0	Linear PS		2.72	1.01	Monodisperse
PS3-550	3	550	2.00	1.01	Monodisperse
PS5-550	5		–	–	Polydisperse
PS5-1700	5	1,700	2.64	1.01	Monodisperse
PS10-1700	10		2.33	1.01	Monodisperse
PS20-1700	20		–	–	Polydisperse
PS10-4000	10	4,000	2.56	1.01	Monodisperse
PS20-4000	20		1.80	1.01	Monodisperse

[a] PSα-β: α and β correspond to the wt% of PDMSDA and M_n of PDMS in the crosslinker, respectively
[b] The content of PDMSDA in the preparation of PS particles
[c] Molecular weight of PMDS used in the crosslinker
[d] Particle size distribution: D_w/ D_n

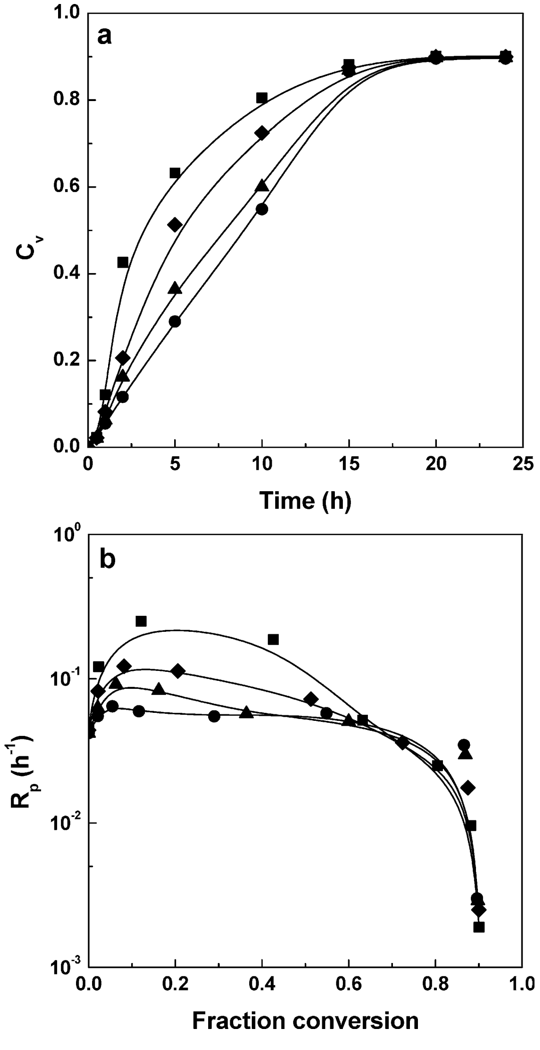


Fig. 4 Fractional conversion–polymerization time curves (**a**), and polymerization rate–fractional conversion curves (**b**) for PS particles crosslinked with various contents of PDMSDA (M_n = 1,700 g/mol): 0 wt% (*filled circles*), 5 wt% (*filled triangles*), 10 wt% (*filled diamonds*), and 20 wt% (*filled squares*)

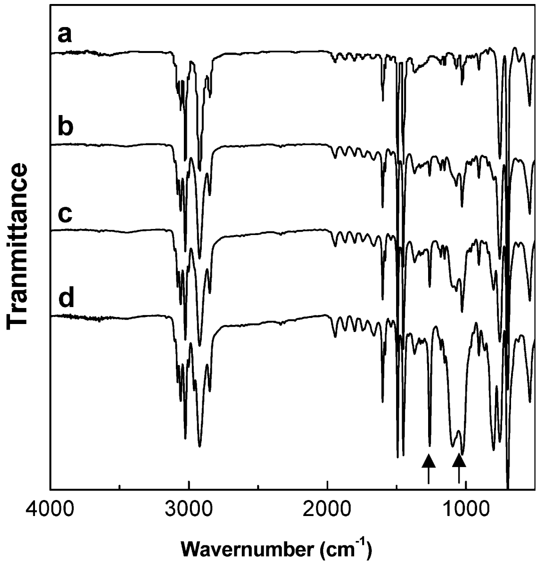


Fig. 5 FT-IR spectra of PS particles crosslinked with various contents of PDMSDA (M_n = 1,700 g/mol): 0 wt% (**a**), 5 wt% (**b**), 10 wt% (**c**), and 20 wt% (**d**)

intensity of peaks increased with increasing the PDMSDA concentration. The same trends were observed at the different molecular weight of PDMSDA (M_n = 550, 4,000 g/mol). From the results shown in Figs. 4 and 5, it leads to a general conclusion that the PDMSDA copolymerized with St, generated the slight crosslinking structure in the particles.

Monomer swelling capability

Various amounts of the second monomer (St) based on the weight of seed particles were swollen into the crosslinked PS particles to investigate the monomer swelling capacity. For an efficient monomer swelling,

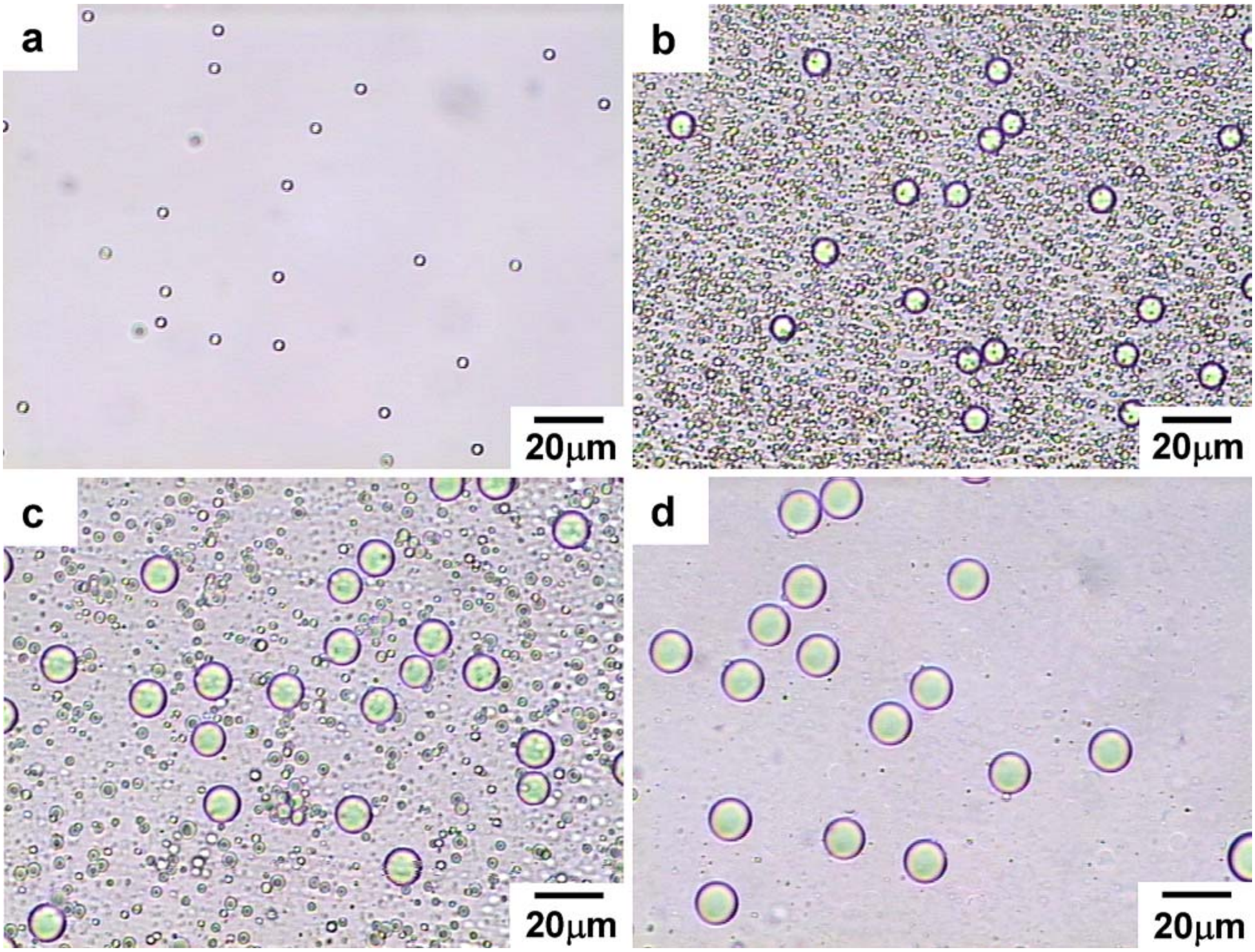


Fig. 6 OM photographs of the monomer swelling process: 0 min (**a**), 30 min (**b**), 180 min (**c**), and 360 min (**d**) using PS10–4,000 as seed particles

SLS and ethanol were mixed with the aqueous solution to facilitate the movement of St emulsions toward the seed particles (0.25 wt% SLS in EtOH/water = 1/5, g/g), and the swelling temperature was set at 30°C. The St emulsions were dissolved into the medium at high ethanol content and temperature. In Fig. 6, OM images of the monomer swelling procedure for PS10-4000 are exhibited by the swelling time. After 6 h of swelling, it was confirmed that the monomer was swollen into the PS seed particles uniformly and completely.

The monomer swelling of the seed particles having different crosslinking densities was carried out without the oligomer swelling step and the results are plotted as in Fig. 7. These swelling kinetics suggest that a swelling time of 6 h is sufficient to reach the equilibrium swelling state. According to the molecular weight of PDMSDA, the maximum swelling capacities of the seed particles were determined as follows: 50-fold at 550 g/mol, 70-fold at 1,700 g/mol, and 100-fold at 4,000 g/mol of PDMSDA based on the weight of the seed particles. Although 100-fold of monomer was used in the PS10-1700, the same swollen size was obtained when 70-fold of monomer was swollen, and all the emulsions remained in the medium. Furthermore, the swelling speed is decayed as the content of PDMSDA increased at the same molecular weight. This is supposed that volume expansion of seed particles is hindered by the crosslinking density of seed particles during the swelling stage [2, 22]. In Table 3, the crosslinking density of seed particles, *N*, was deduced from the transport rate of the monomer molecules to the seed particles following the thermodynamic consideration [24].

The swollen particles were stabilized with the PVA solution and then polymerized. Figure 8 shows the SEM photographs of polymer beads without the oligomer swelling step. Almost the same diameters of monomer swollen particles and polymer beads were obtained as compared to Figs. 6d and 8e, and also, the St emulsions were not observed in the medium after polymerization.

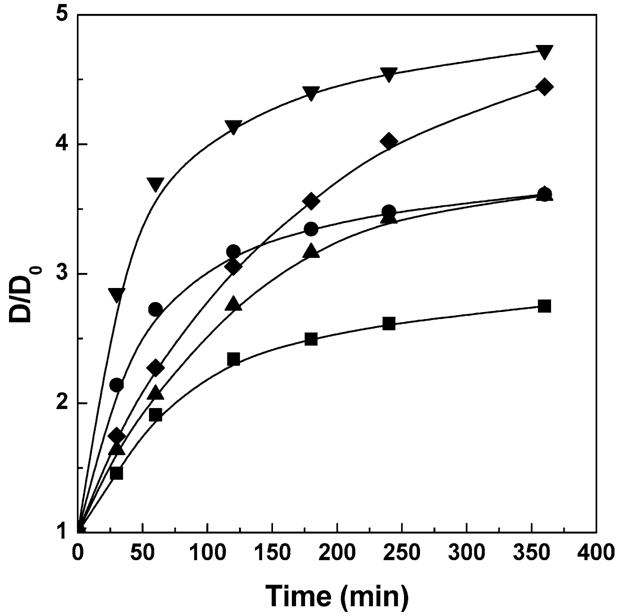


Fig. 7 Particle diameter change versus the swelling time using different crosslinked seed particle: PS3–550 (*filled squares*), PS5–1,700 (*filled circles*), PS10–1,700 (*filled triangles*), PS10–4,000 (*filled inverted triangles*), and PS20–4,000 (*filled diamonds*)

Table 3 Characteristics of PS microspheres by seeded polymerization

PS seed particles			Swelling ratio[b]	D_n^c (μm)	PSD[d]
Symbol	D_n (μm)	N (mol/m^3)[a]			
PS3–550	2.00	149.0	50	5.31	1.01
PS5–1,700	2.64	118.2	70	8.92	1.01
PS10–4,000	2.56	92.5	100	11.44	1.01

[a] The crosslinking density of the PS seed particles, which was derived from our previous works [22]

[b] The amount of the monomer based on the PS seed particles

[c] The diameter of PS microspheres after seeded polymerization

[d] Particle size distribution: D_w/D_n

Because of the hydrophobicity of PDMS and a large content of PDMSDA in the seed particles, de-swelling of monomer was efficiently prevented when oligomer swelling step was eliminated in the seeded polymerization.

Monodispersity of the seed particles is one of the key factors to determine the monodisperse polymer beads after the seeded polymerization. Polydisperse and rough surfaced of polymer beads (Fig. 8b) were produced by using polydisperse seed particles as shown in Fig. 3b, since the secondary nucleation of monomer occurred during the polymerization. On the other hand, monodisperse polymer beads (Fig. 8a) having smooth and clear surface were obtained when monodisperse seed particles (Fig. 3a) were employed. The same trend was confirmed when the PS seed particles crosslinked with different molecular weights of PDMSDA (Fig. 8c, e). However, when highly crosslinked seed particles were used in the seeded polymerization, peculiar morphologies (doublet structure) appeared after polymerization as shown in Fig. 8d, f. This happens because the second monomer (St) gets readily swollen into the seed particles without morphological changes due to the large content of flexible PDMSDA crosslinker in the seed particles, but the seed polymer domain and the second monomer domain get separated during seeded polymerization because of the high crosslinking density of seed particles.

Conclusions

Monomer swelling capacity and morphological change of monodisperse PS particles having different crosslinking densities were investigated. Flexible PDMSDA crosslinkers containing three different molecular weights were synthesized and co-polymerized with St through dispersion polymerization. The generation of crosslinked structure in the PS particles was examined by using the polymerization kinetics and FT-IR measurements. Monodisperse crosslinked PS particles were employed as seed particles in the seeded polymerization, and their monomer swelling capacities were determined according to the molecular weight of PDMSDA. In addition, monodisperse polymer beads were prepared without the oligomer swelling step due to the hydrophobic property of PDMS. Although no morphological changes appeared in the swelling stage, peculiar morphologies (doublet structure) appeared after polymerization when highly crosslinked seed particles were used in the seeded polymerization.

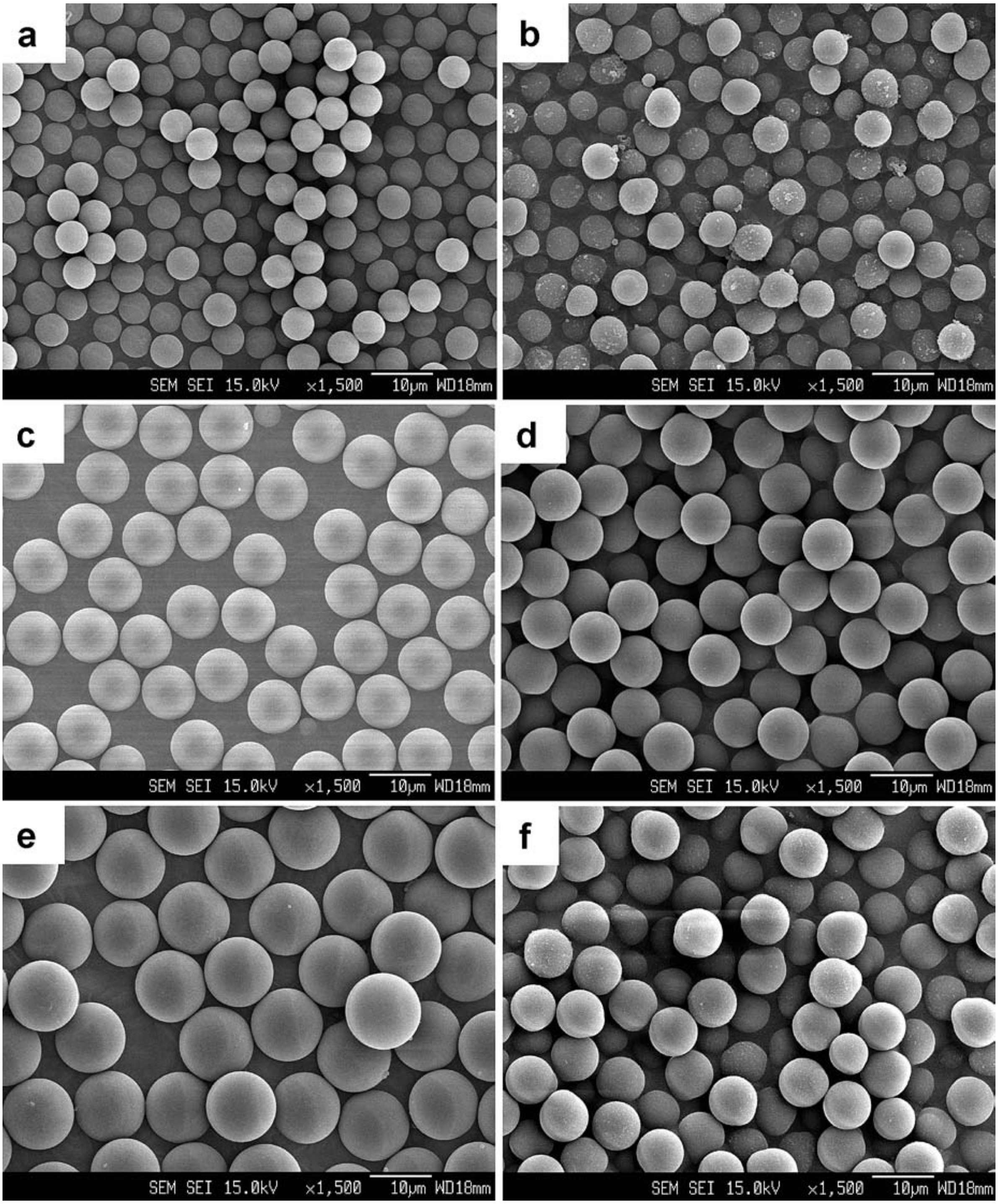


Fig. 8 SEM photographs of the polymer beads through seeded polymerization using different crosslinked seed particles: PS3–550 (**a**), PS5–550 (**b**), PS5–1,700 (**c**), PS10–1,700 (**d**), PS10–4,000 (**e**), and PS20–4,000 (**f**)

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