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Monodisperse micron-sized polystyrene particles by seeded polymerization: effect of seed crosslinking on monomer swelling and particle morphology

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Abstract

Monodisperse micron-sized polystyrene particles were produced by seeded polymerization, and the effect of seed crosslinking on styrene monomer swelling and final particle morphology were considered. The monomer swelling procedure using crosslinked seed particles was predicted with a thermodynamic equation. Employing this equation, the crosslinking density of the seed particles could be determined from the rate of transport of the monomer molecules to the crosslinked seed particles. From a thermodynamic viewpoint, it was elucidated that the monomer swelling procedure was strongly dependent on the seed crosslinking density. Therefore, for an effective swelling of the monomer, an optimum seed crosslinking density was required. After polymerization of these swollen particles, highly monodisperse polystyrene particles could be obtained with a size range of over 10 μm. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Monomer swelling procedure; Seed crosslinking density; Highly monodisperse polystyrene particles

1. Introduction

Monodisperse micron-sized polymer particles have attracted wide interest in many fields including of standard calibration, biomedical examinations, chromatographic fillers, spacers, ink additives, catalytic substrates [1–3]. In all applications, the monodispersity of the particles produced played a crucial role in meeting their original requirements and in obtaining better efficiency.

For the production of monodisperse micron-sized polymer particles, several methods have been proposed. Vanderhoff et al. developed a successive seeding method in gravity-free conditions [4,5]. Similarly, Ugelstad et al. invented a useful two-stage swelling method for the production of various monodisperse micron-sized polymer particles. This method is characterized by the use of an oligomer of extremely low solubility in water as an effective swelling agent [1,6–8]. Recently, Okubo et al. suggested another swelling method—dynamic swelling method—that makes the seed polymers absorb a large amount of swelling monomers by treating the monomer soluble in the medium with slow, continuous, dropwise addition of water [9–11]. Some other unique techniques were also developed with the intention of producing these polymer particles [12–15]. However, the above-mentioned methods usually employed seed particles of linear polymers at the initial swelling stage. This is because the monodisperse micron-sized seed polymer particles that have a crosslinked network structure are difficult to prepare by conventional emulsion or dispersion polymerization methods [16–18].

In dispersion polymerizations of crosslinked polymer particles using divinyl monomers, it has been known that the non-swellability of the crosslinked primary particles caused the primary particles to grow by the precipitation of the nucleated oligomers and/or particles onto their surfaces [17,18]. This polymerization procedure enhances the possibility of generating the second particle formation during particle growth stage, which eventually leads to the polydisperse size distribution. Based on this dispersion polymerization mechanism, in our previous works [19–22], highly monodisperse micron-sized crosslinked polystyrene particles could be produced successfully by using a monomer-swellable crosslinker, urethane acrylate (UA). It was found that the styrene monomers in the medium readily diffused into the UA-crosslinked primary particles during the particle growth. When these crosslinked seed particles were used, it was expected that the swelling process of the seed particles could be understood more systemically.

In this study, the two-stage swelling procedure using

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crosslinked seed particles is elucidated by considering the thermodynamic equilibrium of the swollen particle with the monomers. The effect of seed crosslinking density on particle swelling and the final particle morphology is studied.

2. Thermodynamic consideration

Partial molar free energy, $\Delta\bar{G}^*$, of a monomer in the crosslinked polymer particles during swelling is composed of following three contributions:

$$\Delta\bar{G}^* = \Delta\bar{G}_\mathrm{m} + \Delta\bar{G}_\mathrm{t} + \Delta\bar{G}_\mathrm{el} \tag{1}$$

where $\Delta\bar{G}_\mathrm{m}$, $\Delta\bar{G}_\mathrm{t}$ and $\Delta\bar{G}_\mathrm{el}$ are the contributions of monomer–polymer mixing force, polymer network elastic–retractile force, and particle–water interfacial tension force, respectively.

Partial molar free energy change by the absorption of the monomer droplets developed by Morton et al. is given as follows [23]:

$$\Delta\bar{G} = \mathrm{R}T\left[\ln\phi_1 + \left(1 - \frac{1}{j}\right)\phi_2 + \phi_2^2\chi + \frac{2\bar{V}_1\gamma}{r\mathrm{R}T}\right] \tag{2}$$

where ϕ_1 is the volume fraction of the monomer, ϕ_2 the volume fraction of the polymer, j the ratio of molar volume of polymer and monomer, χ the monomer–polymer interaction parameter, γ the interfacial energy, r the radius of the particles, and $\bar{V}_1$ is the partial molar volume of the monomer.

From Eq. (2), Ugelstad et al. proposed a thermodynamic equation for the swelling of the particles consisting of polymer, swelling agent and mixtures thereof [1,6–8]. The partial molar free energy was given as follows:

$$\Delta\bar{G} = \mathrm{R}T\left[\ln\phi_1 + \left(1 - \frac{1}{j_2}\right)\phi_2 + \left(1 - \frac{1}{j_3}\right)\phi_3 + \phi_2^2\chi_{12} + \phi_3^2\chi_{13} + \phi_2\phi_3\left(\chi_{12} + \chi_{13} - \frac{\chi_{23}}{j_2}\right) + \frac{2\bar{V}_1\gamma}{r\mathrm{R}T}\right] \tag{3}$$

where ϕ_1 is the volume fraction of the monomer, ϕ_2 the volume fraction of the swelling agent, ϕ_3 the volume fraction of the polymer, j_2 the ratio of molar volume of water-insoluble swelling agent and monomer, j_3 the ratio of molar volume of polymer and monomer, χ_{12} and χ_{13} are the interaction parameters of the monomer with swelling agent and polymer, respectively, and χ_{23} is the interaction parameter of the swelling agent with the polymer.

For the crosslinked polymer particle system, $1/j_3$ can be set equal to zero in Eq. (3), because a crosslinked polymer has limitless j_3 value. Therefore, Eq. (3) can be simplified as follows:

$$\Delta\bar{G} = \mathrm{R}T\left[\ln\phi_1 + \left(1 - \frac{1}{j_2}\right)\phi_2 + \phi_3 + \phi_2^2\chi_{12} + \phi_3^2\chi_{13} + \phi_2\phi_3\left(\chi_{12} + \chi_{13} - \frac{\chi_{23}}{j_2}\right) + \frac{2\bar{V}_1\gamma}{r\mathrm{R}T}\right] \tag{4}$$

The elastic free energy change, $\Delta\bar{G}_\mathrm{el}^*$ is an entropy term associated with the change in the configuration of the polymer network [24,25], and described as follows:

$$\Delta\bar{G}_\mathrm{el} = \mathrm{R}TN\bar{V}_1\left(\phi_3^{1/3} - \frac{\phi_3}{2}\right) \tag{5}$$

where N is the effective number of chains in the network per unit volume.

Consequently, the partial molar free energy, $\Delta\bar{G}^*$ of the monomer in the crosslinked polymer particles during swelling gives

$$\Delta\bar{G}^* = \mathrm{R}T\left[\ln\phi_1 + \left(1 - \frac{1}{j_2}\right)\phi_2 + \phi_3 + \phi_2^2\chi_{12} + \phi_3^2\chi_{13} + \phi_2\phi_3\left(\chi_{12} + \chi_{13} - \frac{\chi_{23}}{j_2}\right) + \frac{2\bar{V}_1\gamma}{r\mathrm{R}T} + N\bar{V}_1\left(\phi_3^{1/3} - \frac{\phi_3}{2}\right)\right] \tag{6}$$

At equilibrium states, the following thermodynamic equation can be obtained:

$$\ln\phi_1 + \left(1 - \frac{1}{j_2}\right)\phi_2 + \phi_3 + \phi_2^2\chi_{12} + \phi_3^2\chi_{13} + \phi_2\phi_3\left(\chi_{12} + \chi_{13} - \frac{\chi_{23}}{j_2}\right) + \frac{2\bar{V}_1\gamma}{r\mathrm{R}T} + N\bar{V}_1\left(\phi_3^{1/3} - \frac{\phi_3}{2}\right) = 0 \tag{7}$$

Particle radius r can be represented as follows:

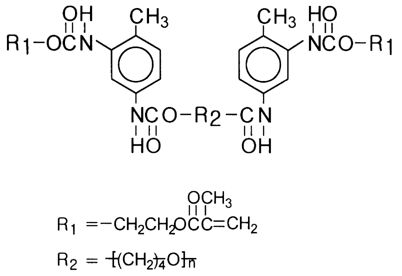
$$r = r_0\left[\frac{V_1 + V_2 + V_3}{V_3}\right]^{1/3} \tag{8}$$

where r_0 is the initial particle radius.

The rate of transport of the monomer molecules to the seed polymer particles through the aqueous medium can be determined by considering that the transport of monomer molecules is the rate determining process of molecular diffusion [8,26], as follows:

$$\frac{\mathrm{d}V_1}{\mathrm{d}t} = 4\pi r_\mathrm{s}N_\mathrm{s}DC\left[1 - \exp\left(\frac{\Delta\bar{G}^*}{\mathrm{R}T}\right)\right] \tag{9}$$

where D is the diffusion constant of the monomer molecules in the aqueous medium, C the solubility of the molecules in aqueous medium, r_s the radius of the swollen polymer



Scheme 1.

particles, and N_s the number of the swollen polymer particles. In Eq. (9), $\Delta\bar{G}^*$ can be obtained from Eq. (6).

3. Experimental

3.1. Materials

Toluene diisocyanate (TDI, 80% 2,4-isomer, Tokyo Chemical Industry (TCI) Co., Ltd) was vacuum distilled before use. Polytetramethylene glycol (PTMG, $M_w = 1.0 \times 10^3$ g mol^{-1}, Hyosung BASF), polyvinylpyrrolidone (PVP K-30, $M_w = 4.0 \times 10^4$ g mol^{-1}, Aldrich Chemical Co.), 1-chlorododecane (CD, TCI), and 2-methoxyethanol (Kanto Chemical Co., Inc) were used as received. Polyvinyl alcohol (PVA, $M_w = 8.8 \times 10^4 \sim 9.2 \times 10^4$ g mol^{-1}, 87 ~ 89% hydrolyzed) was kindly supplied from Kuraray Co., Ltd. 2,2-azobis(isobutyronitrile) (AIBN, Junsei Chemical Co.) and benzoyl peroxide (BPO, Junsei) were recrystallized from methanol.

3.2. Synthesis of UA crosslinker [19–22]

Reaction was carried out in a four-necked glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and a nitrogen gas inlet system. Two moles of TDI were poured into the glass reactor under a nitrogen atmosphere. Then, 1 mol of PTMG was added slowly into the reactor. The reaction was carried out at 80°C for 4 h so as to obtain a molecule with flexible polytetramethylene oxide in the middle and isocyanates on the outside. The required NCO value during the reaction was determined using dibutylamine back titration method [27]. Continuously, after dissolving 1 wt% dibutyltindilaurate into the reactor, 2 mol of 2-hydroxyethyl methacrylate (HEMA) was reacted to the residual isocyanates at 45°C for 12 h, capping the molecular ends with the reactive acryl groups. The reaction end point was determined by the disappearance of the NCO stretching peak (2270 cm^{-1}) through IR spectroscopy. The average molecular weights of the UA measured by a Model 410 GPC were $M_n = 1.8 \times 10^3$ g mol^{-1} and $M_w = 2.5 \times 10^3$ g mol^{-1}. The molecular structure of UA is presented in Scheme 1.

Table 1
The standard recipe for the dispersion polymerization of styrene and UA (70°C; 24 h; 10 wt% of monomer concentration based on total weight)

Ingredient	Weight (g)
Styrene	0.970
UA[a]	0.030$^{\text{variable}}$
PVP K-30	0.179
Aerosol-OT[b]	0.045
AIBN	0.010
2-Methoxyethanol	4.389
Ethanol	4.389

[a] Concentration of UA = 3 wt% in this sample.

[b] Costabilizer: di-2 ethylhexyl ester of sodium sulfosuccinic acid (Aerosol-OT, American Cyanamid).

3.3. Seed particles by dispersion polymerization [19,20]

Styrene, UA, AIBN, PVP, 2-methoxyethanol, and ethanol were weighed into 50 ml glass vials. After sealing in a nitrogen atmosphere, the vials were submerged in a thermostated water bath and tumbled with a rotation speed of 40 rpm at 70 ± 0.1°C for 24 h. The spheres obtained were centrifuged for 10 min at 6000 rpm. The supernatant was then decanted and the remaining precipitate was repeatedly washed by four centrifugations and dried under vacuum at ambient temperature. All the ingredients used are summarized in Table 1.

3.4. Two-stage swelling and polymerization

Two-stage swelling and polymerization was also carried out in a 4-necked glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and a nitrogen gas inlet system. Firstly, seed particles (0.1 g) redispersed in 0.25% sodium lauryl sulfate (SLS) aqueous solution (40 g) by 10 min sonication were swollen with CD (0.1 g) emulsified by ultrasonic homogenizing in 0.25% aqueous solution (10 g) at 30°C for 10 h. The stirring speed was fixed at 200 rpm throughout the process. After complete disappearance of the CD droplets, 100 g of 0.25% SLS solution was added. Then, the mixture of styrene monomer (10 g) and BPO (1 wt% to styrene) was poured into the reactor. The swelling was continued for another 6 h at 30°C. The swollen particles were stabilized with 5 wt% PVA aqueous solution and its concentration was fixed at 1% of the total content (250 g). Polymerization in the aqueous phase was inhibited by adding sodium nitrite (0.01 g) [28,29]. After deaerating with nitrogen gas, the polymerization was carried out at 80°C for 10 h. The particles produced were repeatedly washed by decantation in water and ethanol and dried under vacuum at ambient temperature.

3.5. Particle observation

Swelling of the seed particles was monitored by optical microscope (OM, Nikon Microphot Fax) and the diameter change was recorded at different time intervals. Particles

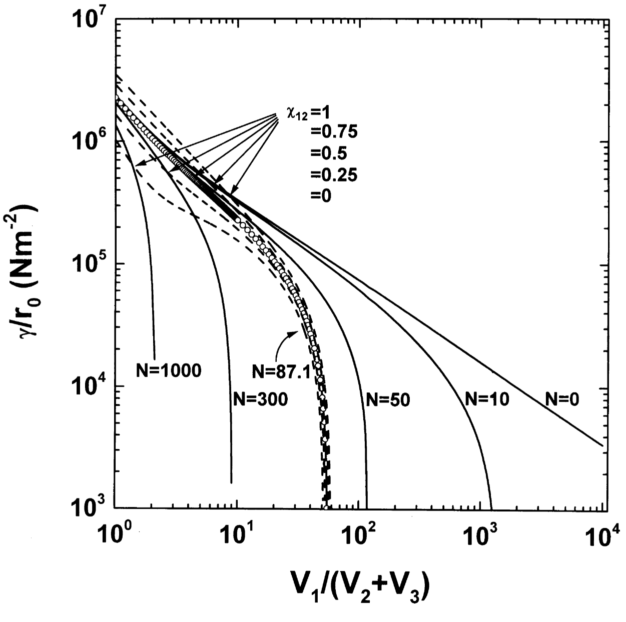


Fig. 1. Variation of simulated monomer swelling ratio ($V_1/(V_2+V_3)$) with the seed diameter (γ/r_0) at different χ_{12} and crosslinking density (N, mol m^{-3}) of seed particles under the conditions of $\chi_{13}=0.5$, $\chi_{23}=0$, $j_2=5$, $V_2=V_3=0.5$, $\bar{V}_1=10^{-4}$ m^3 mol^{-1}, $T=303$ K and $\gamma=5$ mN m^{-1}.

produced were observed with a scanning electron microscope (SEM, JSM-6300, JEOL). In order to determine the particle diameter, about 100 individual particles were counted from SEM photographs and the average was taken.

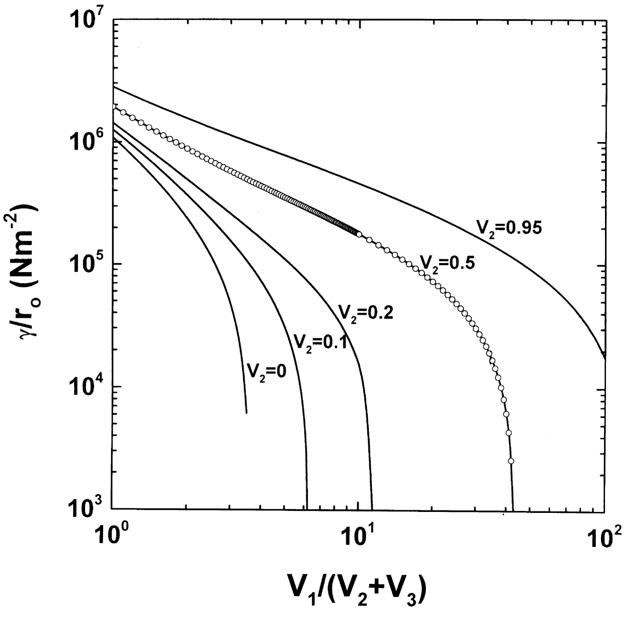


Fig. 2. Variation of simulated monomer swelling ratio ($V_1/(V_2+V_3)$) with the seed diameter (γ/r_0) at different j_2 values under the conditions of $\chi_{12}=\chi_{13}=0.5$, $\chi_{23}=0$, $N=87.1$ mol m^{-3}, $V_2=V_3=0.5$, $\bar{V}_1=10^{-4}$ m^3 mol^{-1}, $T=303$ K and $\gamma=5$ mN m^{-1}.

4. Results and discussion

4.1. Thermodynamics of two-stage monomer swelling

For the production of micron-sized polymer particles, much research employs the two-stage polymerization method [6–15]. However, they have been limited by the use of seed particles of linear polymer. This is because it is not easy to produce crosslinked micron-sized seed particles by means of conventional emulsion or dispersion polymerization. However, recently we have succeeded in producing monodisperse micron-sized polystyrene particles having a crosslinked network structure by a simple dispersion polymerization technique [19–22]. Urethane acrylate as a useful crosslinker was employed to treat the surface characteristics of the primary particles during particle formation stage. Primarily, in this study, we tried to understand the effect of seed crosslinking on the monomer swelling procedure from a thermodynamic viewpoint in the two-stage swelling method.

Fig. 1 shows the equilibrium monomer swelling with the seed diameter at selected crosslinking densities of seed particles and the interaction parameter between the monomer and swelling agent, which is simulated from Eq. (7). It is obvious in Fig. 1 that the swelling capacity is significantly dependent on the crosslinking density of seed particles. The swelling capacity is sharply reduced with the crosslinking density of seed particles. For example, more than 10-fold swelling cannot be achieved with a crosslinking density of over 300 mol m^{-3}. Therefore, it can be inferred from the simulation that slightly crosslinked seed particles are a prerequisite to an effective swelling in cases where crosslinked seed particles are used. In the crosslinked seed system, the monomer–swelling agent interaction parameter has little influence on the swelling capacity.

Figs. 2 and 3 show the effect of the swelling agent on the equilibrium monomer swelling at the condition of seed crosslinking. Even though the seed particles are crosslinked, the molar volume ratio and the volume fraction of the swelling agent play an important role in determining the swelling capacity. For an enhanced swelling of the monomer, a swelling agent with lower molar volume ratio and larger volume fraction is required. This result shows a good agreement with the cases where seed particles of linear polymers are employed [6–8]. Therefore, it can be deduced that even in the crosslinked seed system, the presence of the swelling agent in the swollen particles enhances the swelling capacity.

Partial molar free energy change was simulated with the monomer swelling ratio at different crosslinking densities of seed particles from Eq. (6) and is shown in Fig. 4. In the swelling of linear seed particles, the main contribution to total partial molar free energy, $\Delta\bar{G}^*$ is the mixing force, $\Delta\bar{G}_\mathrm{m}$. The contribution from the interfacial tension force, $\Delta\bar{G}_\mathrm{t}$ is negligible when the seed particles are large [30]. Therefore, $\Delta\bar{G}^*$ remains negative over the swelling ratio,

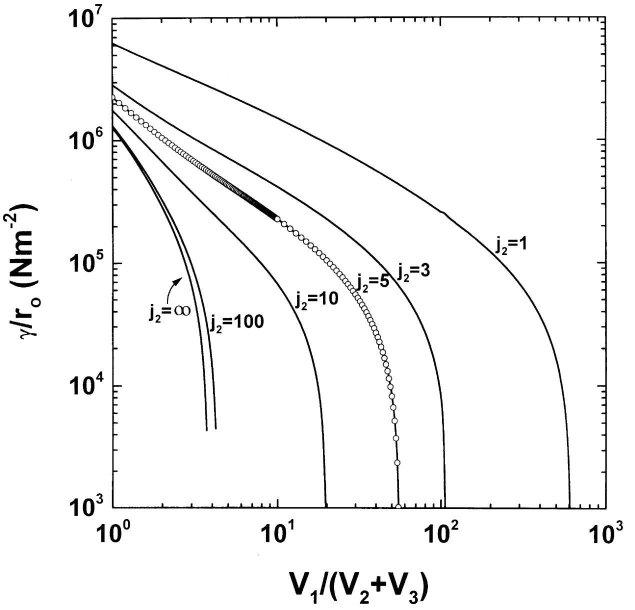


Fig. 3. Variation of simulated monomer swelling ratio ($V_1/(V_2+V_3)$) with the seed diameter (γ/r_0) at different V_2 values under the conditions of $\chi_{12} = \chi_{13} = 0.5$, $\chi_{23} = 0$, $N = 87.1\ \mathrm{mol\ m^{-3}}$, $j_2 = 5$, $V_2 = V_3 = 0.5$, $\bar{V}_1 = 10^{-4}\ \mathrm{m^3\ mol^{-1}}$, $T = 303$ K and $\gamma = 5\ \mathrm{mN\ m^{-1}}$.

meaning that the seed particles can swell to thousands of times their original size [8]. However, in the swelling of crosslinked seed particles, the elastic–retractile force, $\Delta\bar{G}_{\mathrm{el}}$ makes a positive contribution to $\Delta\bar{G}^*$, resulting in restrained particle swelling. So, the crosslinked seed particles showed positive $\Delta\bar{G}^*$ even at decades of swelling ratio. From these results, we could find that in the case of crosslinked seed particles, relatively acceptable monomer swelling is achieved at low crosslinking density (around $100\ \mathrm{mol\ m^{-3}}$).

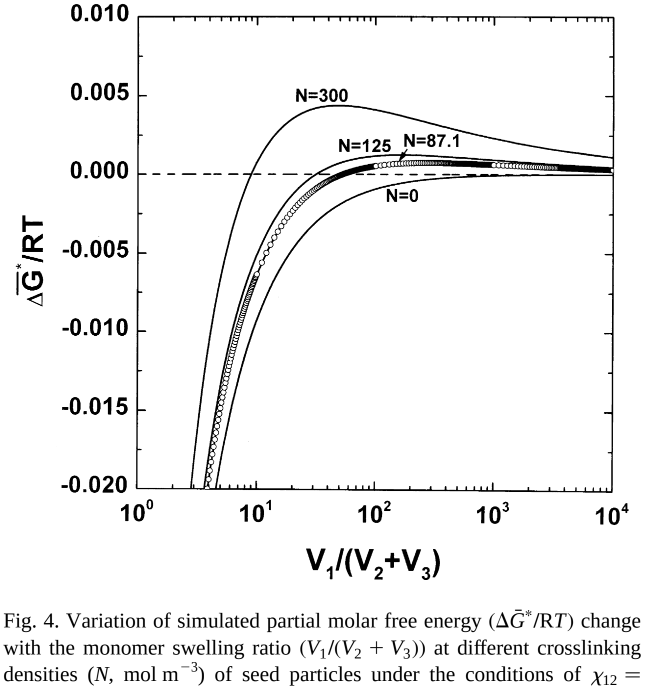


Fig. 4. Variation of simulated partial molar free energy ($\Delta\bar{G}^*/RT$) change with the monomer swelling ratio ($V_1/(V_2+V_3)$) at different crosslinking densities (N, $\mathrm{mol\ m^{-3}}$) of seed particles under the conditions of $\chi_{12} = \chi_{13} = 0.5$, $\chi_{23} = 0$, $j_2 = 5$, $V_2 = V_3 = 0.5$, $\bar{V}_1 = 10^{-4}\ \mathrm{m^3\ mol^{-1}}$, $T = 303$ K, $\gamma = 5\ \mathrm{mN\ m^{-1}}$ and $r_0 = 1.5 \times 10^{-6}$ m.

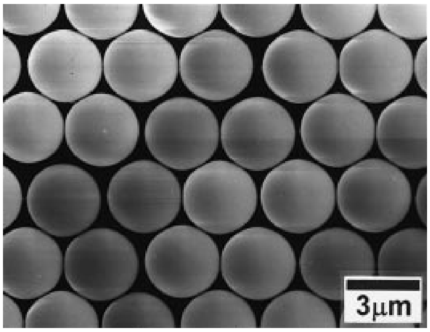


Fig. 5. SEM photograph of polystyrene seed particles containing 3 wt% UA.

4.2. Swelling kinetics

As a useful crosslinker, the UA represented in Scheme 1 was proposed. In this study, the monodisperse micron-sized polystyrene particles crosslinked with UA were produced by dispersion polymerization and used as seed particles [19–22]. Fig. 5 shows the SEM photograph of the polystyrene particles crosslinked with 3 wt% UA. The particle characteristics are summarized in Table 2.

Fig. 6 shows the swelling kinetics with the swelling time at different crosslinking densities of the seed particles. One can observe that as the content of UA increased, the swelling speed is decayed. This is because the crosslinked network of the seed particles hindered the particle expansion

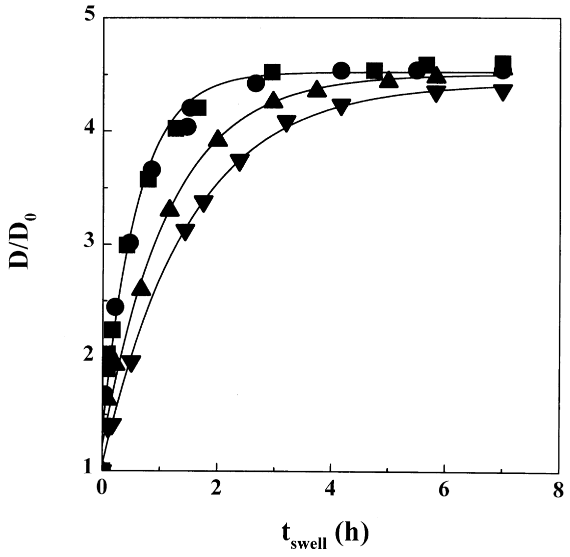


Fig. 6. Particle diameter change with the swelling time at different seed crosslinking: UA 0 wt% (-■-); 1 wt% (-●-); 3 wt% (-▲-); and 3.5 wt% (-▼-). Each solid line is the fitted one from Eq. (9). Initiator, BPO was not added in this kinetic observation in order to exclude the solubility change of styrene monomer in the aqueous medium.

Table 2
The particle characteristics of seed particles

Symbol[a]	D_n (μm)	PDI[b]	M_w (g mol^{-1})	N (mol m^{-3})	Remarks
PS-0	3.35	1.01	5.3×10^4	–	Monodisperse
PS-1	3.20	1.01	6.2×10^4	–	Monodisperse
PS-3	3.18	1.01	–	87.1	Monodisperse
PS-3.5	3.22	1.01	–	126.5[c]	Monodisperse; slightly rough surface

[a] PS-α: α corresponds to the concentration of UA (wt%, based on total monomer weight).

[b] Polydispersity index.

[c] There can be some deviation by the doublet form of the seed particle during swelling.

[30]. These swelling kinetics suggest that 6 h swelling time is sufficient to reach the equilibrium swelling state. From the transport rate of the monomer molecules to the seed polymer particles through the aqueous medium, the crosslinking density of the seed particles was determined, based on Eq. (9). The results are listed in Table 2. The crosslinked polystyrene particles containing 3 or 3.5 wt% UA were located in the proper range that was suggested from the simulation of Fig. 4.

4.3. Particle change with swelling procedure

Fig. 7 shows the OM photographs of the swollen particles with the concentration of UA in the seed particles at a selected swelling time. The linear and 3 wt% UA-crosslinked seed particles were uniformly swollen and maintained spherical shapes throughout the swelling procedure. In Fig. 7(e) and (f), it was interesting to observe that 3.5 wt% UA-crosslinked seed particles started to separate

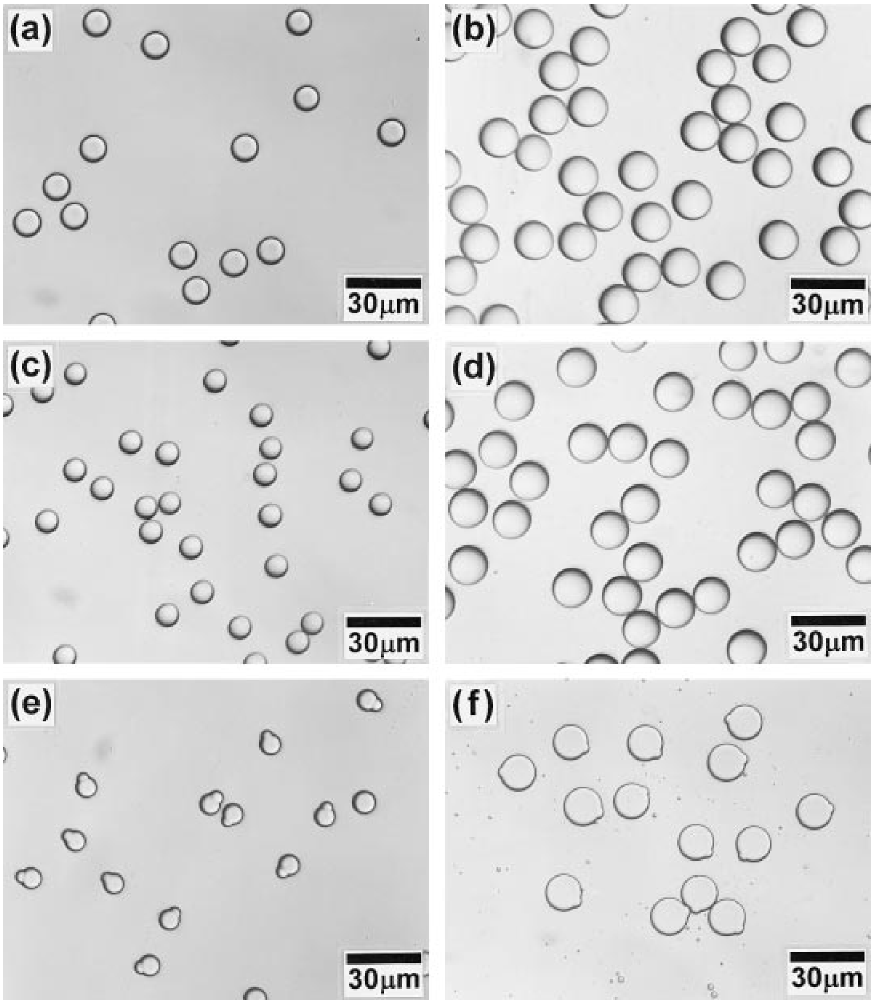


Fig. 7. OM photographs of the monomer-swollen particles 0.5 h after (UA (a) 0 wt%; (c) 3 wt%; and (e) 3.5 wt%)) and 6 h after (UA (b) 0 wt%; (d) 3 wt%; and (f) 3.5 wt%)).

into two parts (doublet morphology) after 0.5 h swelling and grew continuously on only one side. The schematic swelling procedure shown in Fig. 8 gives a better visualization of such an asymmetric swelling. Up to an optimum crosslinking density, the crosslinked network of the seed particles is released by the swelling monomer. So, the crosslinked seed particles with 3 wt% UA could be evenly swollen to their equilibrium state (d). On the contrary, at high crosslinking density, the particles are readily swollen along the weak point of the crosslinked network, instead of swelling evenly on their surfaces. Moreover, due to the high crosslinked density of the seed particles, the equilibrium swelling state is reached before complete monomer diffusion into the swelling particles. Therefore, small monomer droplets could be observed in Fig. 8(f). These droplets did not disappear even after 24 h swelling.

4.4. Particle morphology after seeded polymerization

After swelling, the swollen particles were polymerized. The SEM photographs of the particles produced by the seeded polymerization are shown in Fig. 9.

The particles produced using the seed particles of linear and slightly crosslinked polystyrene displayed monodisperse size distribution, a clear surface, and a spherical shape (Fig. 9(a) and (b)). The particle characteristics are listed in Table 3. The result in the case of usage of linear polystyrene as seed particles shows the same tendency as that of much research on the production of monodisperse micron-sized polymer particles in seeded polymerization [4–14]. However, it should be noticed that even in the case of using slightly crosslinked polystyrene as seed particles, the monodisperse polystyrene particles were possibly produced by the seeded polymerization, which led to the network structure of *semi*-IPN (interpenetrated network).

In Fig. 9(c), the polystyrene particles polymerized with the seed particles of higher crosslinking density showed somewhat peculiar morphology. Every particle had an occlusion in its inner phase. That was believed to be the seed domain separated from the second polymerized polystyrene phase, which is possible keeping in mind that the doublet particles shown in Fig. 7 were composed of the seed polymer domain (small side one) and the styrene domain (large side one). At an elevated temperature (polymerization temperature, 80°C), the elastic–retractile force of the crosslinked seed particles would be more enhanced [24,30]. Alternatively, the miscibility between the crosslinked polystyrene seed phase and the polymerizing polystyrene phase would also increase [24]. Therefore, the resultant morphology after polymerization seemed to be spherical and to include the seed domains in their inner phase (the theoretical approach related to this phenomenon is underway).

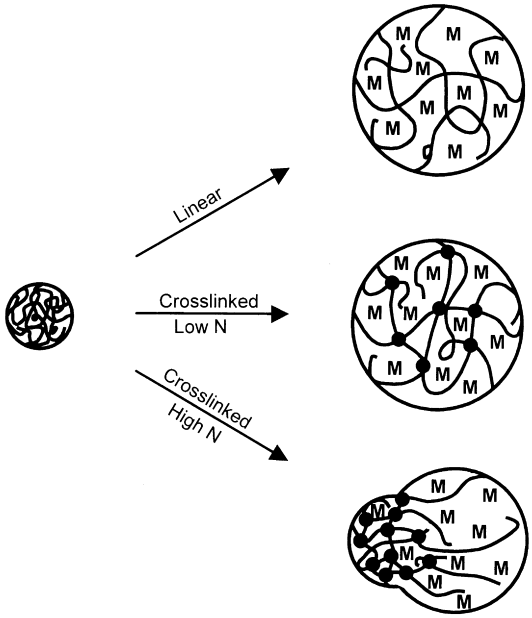


Fig. 8. Schematic representation of the monomer-swollen particles with the crosslinking density of the seed particles.

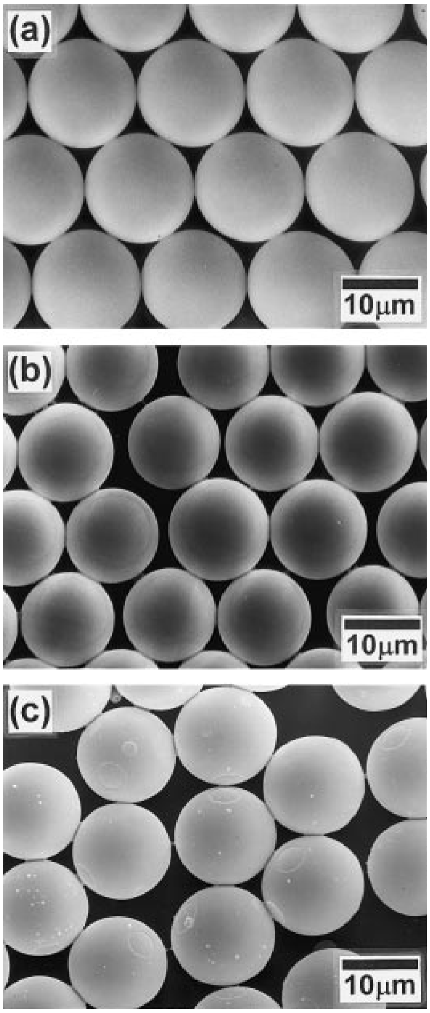


Fig. 9. SEM photographs of the polystyrene particles obtained after seeded polymerization with the seed polymers containing UA: (a) 0 wt%; (b) 3 wt%; (c) 3.5 wt%.

Table 3
The particle characteristics after seeded polymerization (80°C; 10 h; 4% solid content based on total weight)

Symbol[a]	D_n (μm)			Remarks
	Calculated	Measured	PDI[b]	
PS-0-100	15.31	14.77	0.01	Monodisperse
PS-1-100	14.62	14.32	0.01	Monodisperse
PS-3-100	14.53	14.27	0.01	Monodisperse
PS-3.5-100	14.72	14.30	0.01	Phase separation; some small particles
PS-3-150[c]	16.62	15.14	0.03	Many small particles

[a] PS-α-β: α corresponds to the concentration of UA (wt%, based on total seed weight) and β to the swelling ratio of monomer against the seed particle (w/w).

[b] Polydispersity index.

[c] At 150-fold swelling ratio there were many small emulsion droplets even after 24 h swelling.

5. Conclusions

The influence of seed crosslinking on monomer swelling and final particle morphology was studied using the two-stage swelling method. It was found in thermodynamic consideration that the crosslinking of the seed particles shifted the partial molar free energy of the monomer in the particles towards the positive side. Therefore, to obtain a reasonable swelling ratio of the monomer, slightly crosslinked seed particles were a prerequisite. In monomer swelling kinetics, the seed crosslinking retarded the monomer diffusion speed due to the elastic–retractile force. From the swelling history, the crosslinking density of the seed particles could be simulated successfully. The polystyrene particles produced from the seeded polymerization were spherical and very clear in the case of using properly crosslinked seed particles. In particular, when the crosslinked seed particles are seeded-polymerized with divinyl monomers, it is expected in further applications that polymer composite particles having a *full*-IPN structure can be produced.

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