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ORIGINAL CONTRIBUTION

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Morphology of micron-sized polystyrene particles crosslinked with urethane acrylate

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Abstract The morphology of micron-sized polystyrene particles crosslinked with a urethane acrylate crosslinker was studied with different concentrations of urethane acrylate and medium solvency by means of simple dispersion polymerization. The urethane acrylate employed as a crosslinker showed an excellent effect on maintaining the monodispersity of the polystyrene particles at a moderate crosslinker concentration (to about 5 wt%) in terms of the monomer-swellable surface of primary particles. By enhancing the medium solvency, the amount of urethane acrylate incorporated was increased, while the monodispersity of the final particles was maintained. It was believed that the increase in solvency on adding xylene to ethanol solution helped the diffusion of the styrene monomers into the primary particles. At high concentration of urethane acrylate, however, nonspherical particles, ellipsoidal or egg-like singlets and asymmetric doublets, were observed. The increased crosslinking density seemed to repel the styrene monomers during particle growth.

Key words Morphology of micron-sized polystyrene particles – Urethane acrylate crosslinker – Monomer-swellable surface – Medium solvency – Nonspherical particles – Asymmetric doublets

Introduction

Recently, considerable interest has been concentrated on the development of polymer particles by dispersion polymerization [1–6], due mainly to their spherical shape and highly monodisperse size distribution. However, the common results of crosslinkling polymer particles by dispersion polymerization have been broad size distributions, oddly shaped particles, and coagula, even at low crosslinker concentration [6–9].

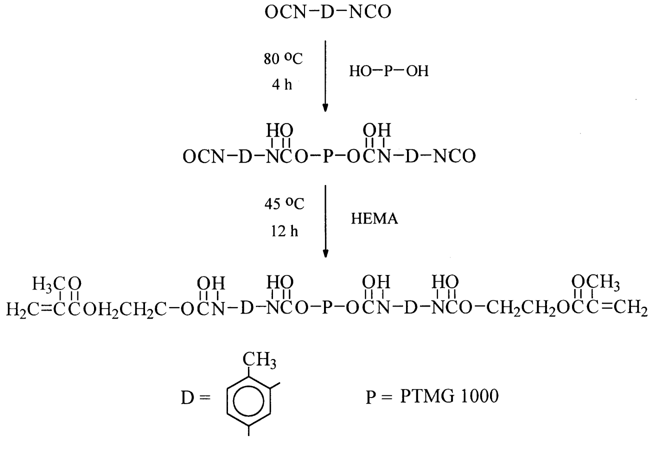
In the general dispersion polymerization mechanism for crosslinked polymer particles, it has been proposed that particle growth occurs through precipitation of nucleated oligomers and/or particles onto the surface of the primary particles, because of the nonswellability of the highly crosslinked primary particles [8, 9]. Based on this concept we successfully produced highly monodisperse crosslinked polystyrene microparticles [10]. As a useful monomer-swellable crosslinker, a urethane acrylate was designed with flexiable tetramethylene oxide in the middle and two vinyl groups at both ends enablings the formation of a crosslinked network. Owing to the flexible molecular structure of urethane acrylate, the styrene monomers in the ethanol medium could diffuse into the primary particles with ease during particle growth.

In this study, we obtained monodisperse micron-sized polystyrene particles crosslinked with a higher concentration of urethane acrylate by controlling the medium solvency. The effects of the concentration of urethane acrylate and of the medium solvency on the particle size, the size distribution, and the morphology were examined.

Experimental

Materials

Toluene diisocyanate (TDI, 80% 2,4-isomer, Tokyo Chemical Industry Co.) 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), and di-2 ethylhexyl ester of sodium sulfosuccinic acid (Aerosol-OT, American Cyanamid) were used as received. The inhibitors in hydroxyethyl methacrylate (HEMA, Aldrich) and styrene monomer (Junsei Chemical Co.) were removed through a removing column (Aldrich). 2,2-azobis(isobutyronitrile) (AIBN, Junsei) was recrystallized from methanol.



Scheme 1 Schematic reaction procedure and molecular structure of urethane acrylate crosslinker

Synthesis of urethane acrylate crosslinker [10–13]

All reactions were carried out in a 4-necked glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and a nitrogen gas inlet system. TDI(2 mol) in the glass reactor was reacted with PTMG(1mol) at 80 °C for 4 h, resulting in the molecular structure having flexible tetramethylene oxides in the middle and isocyanates at the ends. Care must be taken to control the molar ratio of reaction, so as not to increase the molecular weight. The change in NCO value during the reaction was determined using the dibutylamine back-titration method to find out the end point of the reaction [14].

After dissolving 1 wt% dibutyltindilaurate in the reactor, 2 mol HEMA was reacted with the residual isocyanate groups at 45 °C for 12 h, which capped the molecular ends with reactive vinyl 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 urethane acrylate synthesized were $M_n = 1.8 \times 10^3$ g mol^{-1} and $M_w = 2.5 \times 10^3$ g mol^{-1} [10]. The reaction procedure and the molecular structure of the urethane acrylate synthesized are presented in Scheme 1.

Dispersion polymerization of styrene and urethane acrylate

The general dispersion polymerization procedure was followed [6, 8, 10]; AIBN, PVP, Aerosol-OT, styrene, urethane acrylate, ethanol, and xylene were weighed into 20 ml glass vials. All ingredients were homogeneously dissolved in an ethanol/xylene mixture. 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 °C for 24 h. The spheres obtained were centrifuged for 10 min at 6,000 rpm. The supernatant was decanted and the remaining precipitate was repeatedly washed by six centrifugations, and dried under vacuum at ambient temperature. All ingredients are summarized in Table 1.

Scanning electron microscope (SEM) measurements

The morphology and diameter of the polystyrene particles prepared were observed with SEM photographs (JSM-6300, JEOL). Specimens were prepared by diluting the particles recovered with distilled water and placing a drop on a cover glass. The drop was dried at room temperature and then coated under vacuum with a thin layer of gold. About 100 individual particle diameters were measured form SEM photographs and the average was taken. The polydispersity index (PDI) was obtained as follows:

Table 1 The standard recipe for the dispersion polymerization of styrene and urethane acrylate[a]

Ingredient	Weight (g)
Styrene	0.965
Urethane acrylate[b]	0.035
PVP K-30[c]	0.179
Aerosol-OT	0.045
AIBN[d]	0.010
Ethanol	8.252
Xylene[e]	0.525

[a] 70 °C; 24 h; 10 wt% of monomer concentration based on total weight.

[b] The weight percent of urethane acrylate was varied against styrene (3.5 wt% in this example).

[c] 2 wt% PVP K-30 based on total weight was added.

[d] 1 wt% 2,2′-azobis(isobutyronitrile), AIBN, based on monomer weight was added.

[e] Urethane acrylate/xylene was 1/15 (w/w).

$$D_{\mathrm{n}} = \frac{\sum_{i=1}^{n} d_i}{N} \quad , \tag{1}$$

$$D_{\mathrm{w}} = \frac{\sum_{i=1}^{n} d_i^4}{\sum_{i=1}^{n} d_i^3} \quad , \tag{2}$$

$$\mathrm{PDI} = \frac{D_{\mathrm{w}}}{D_{\mathrm{n}}} \quad , \tag{3}$$

where D_{n} is number-average diameter, D_{w} is the weight-average diameter, N is the total number counted, and d_i is the diameter of a particle i.

Results and discussion

Dispersion polymerization mechanism of urethane acrylate-crosslinked polystyrene particles

In conventional dispersion polymerization of crosslinked polymer particles, particle growth is considered to be achieved by the precipitation of polymers or oligomers onto the primary particles, because of the nonswellability of the highly crosslinked primary particles [6–9]. Therefore, the broad size distributions and rough surface of the particles were common observations upon adding a small amount of crosslinker, such as divinylbenzene (more than 0.5 wt%). This can be illustrated by considering the unique dispersion polymerization mechanism in the particle growth stage [8]. Conventional crosslinkers form a hard and glassy surface on the primary particles, which eventually makes it difficult to swell the primary particles using vinyl monomers in the medium [9]. In our case, using urethane acrylate as a crosslinker [10], highly monodisperse crosslinked polystyrene particles were obtained even at a moderate urethane acrylate concentration (to 3 wt%) by means of simple dispersion polymerization. This is attributed to the surface characteristics of the primary particles crosslinked by urethane acrylates. The primary particles crosslinked by urethane acrylate can be readily swollen by the styrene monomers in the media during particle growth because of the long tetramethylene oxide groups in the backbone of the urethane acrylate molecule. This suggests that monomer-swellable primary particles play a key role in obtaining monodisperse crosslinked polymer particles.

Even though the urethane acrylate crosslinker helped the styrene monomer diffusion into the primary particle polymer phase, we also obtained particles with rough surfaces above 3 wt% concentration of urethane acrylate. The enhanced crosslinking of the primary particles seemed to prevent the styrene monomers from diffusing into the primary particles: this is similar to the conventional dispersion polymerization of crosslinked polymer particles.

Effect of dispersion medium solvency

In order to help the diffusion of the monomers into the primary particles, the medium solvency was controlled by adding xylene to the ethanol solutions. Figure 1 shows SEM photographs of the crosslinked polystyrene particles with changing weight ratio of urethane acrylate (3.5 wt%) to xylene.

As shown in Fig. 1a, when dispersion polymerization was carried out in ethanol solution, 3.5 wt% concentration of urethane acrylate resulted in rough surfaces of the final crosslinked polystyrene particles. However, as the amount of xylene added to the medium increased, the rough surfaces of the particles disappeared (Fig. 1b, c). Especially, when the weight ratio of urethane acrylate to xylene was 1/15 (w/w), highly monodisperse polystyrene particles were obtained; however, when a large amount of xylene was added, broadening of the size distribution was observed (Fig. 1d). It was believed that the higher solvency of the medium increased the concentration of the growing oligomers and the growth rate of the oligomer chains, resulting in favorable secondary nucleation during particle growth [6].

Figure 2 shows the particle size and polydispersity of the crosslinked polystyrene particles with different weight ratios of urethane acrylate (3.5 wt%) to xylene (w/w). The particle size increased with increasing amount of xylene. This was because better solvency led to longer chain lengths of oligomers and larger particles [6, 10]. The crosslinked polystyrene particles for which the weight ratio of urerthane acrylate to xylene was 1/15 showed the best monodispersity, indicating that the solubility of the monomer mixture of urethane acrylate and styrene was well-matched in this composition. From these results, it was found that the most desirable weight ratio of urethane acrylate to xylene was about 1/15 (w/w). Under this medium condition, nucleation during particle growth seemed to be suppressed by diffusion. An oligomer initiated in the medium is favorably captured by an existing particle before it grows to some threshold degree of the polymerization [6, 15].

Effect of concentration of urethane acrylate

Figure 3 shows SEM photographs of the crosslinked polystyrene particles with different urethane acrylate concentration. By adding xylene to enhance the medium solvency, the monodisperse crosslinked polystyrene

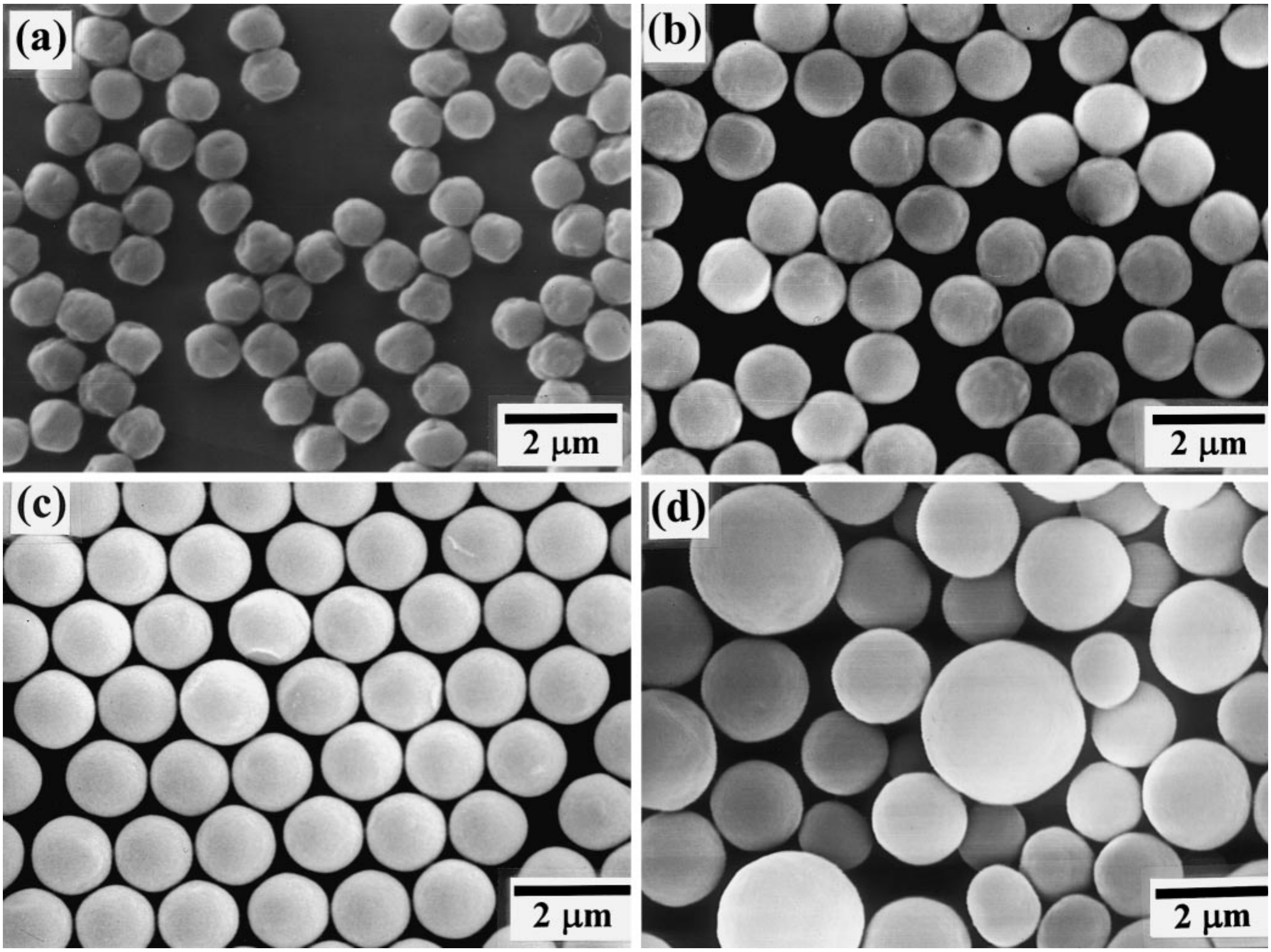


Fig. 1a–d Scanning electron microscope (SEM) photographs of crosslinked polystyrene particles with changing amount of xylene added to urethane acrylate. Urethane acrylate/xylene in ethanol (w/w) **a** 1/0, **b** 1/7, **c** 1/15, and **d** 1/20. The concentration of urethane acrylate was 3.5 wt% based on the total monomer weight

particles were possibly produced to about 5 wt% concentration of urethane acrylate.

In our previous work [10], at these concentrations of urethane acrylate, the crosslinked polystyrene particles displayed broad size distributions and rough surfaces in ethanol solution, which was attributed to the too low solubility of the monomer mixture of styrene and urethane acrylate in ethanol. However, by adding xylene to the ethanol medium, the styrene monomers in the medium were readily captured by the crosslinked primary particles, which eventually resulted in the restriction of new primary particle formation. In this way the monodisperse final particle could be obtained.

Figure 4 shows a SEM photograph of the polystyrene particles crosslinked with 4.5 wt% urethane acrylate at high magnification. It was peculiar that the surface of the particle was very clear. This confirms that particle growth occurred predominantly by styrene monomer diffusion from the medium, even in the crosslinking procedure of dispersion polymerization.

The particle size and polydispersity of the crosslinked polystyrene particles with increasing urethane acrylate concentration at a urethane acrylate to xylene weight ratio of 1/15 (w/w) are shown in Fig. 5. The particle sizes did not change significantly with the concentration of urethane acrylate. However, the polydispersity of the particles obtained became comparatively high with increasing urethane acrylate concentration. It appears that the styrene monomer diffusion into the primary particle was somewhat hindered by the increased crosslinking density of the primary particle surfaces [9].

Nonspherical particle formation

It was very interesting that nonspherical particles, ellipsoidal or egg-like singlets, were observed (Fig. 3d). These nonspherical particles suggest that there is a phase

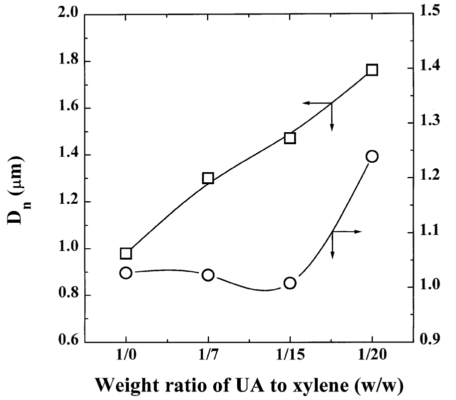
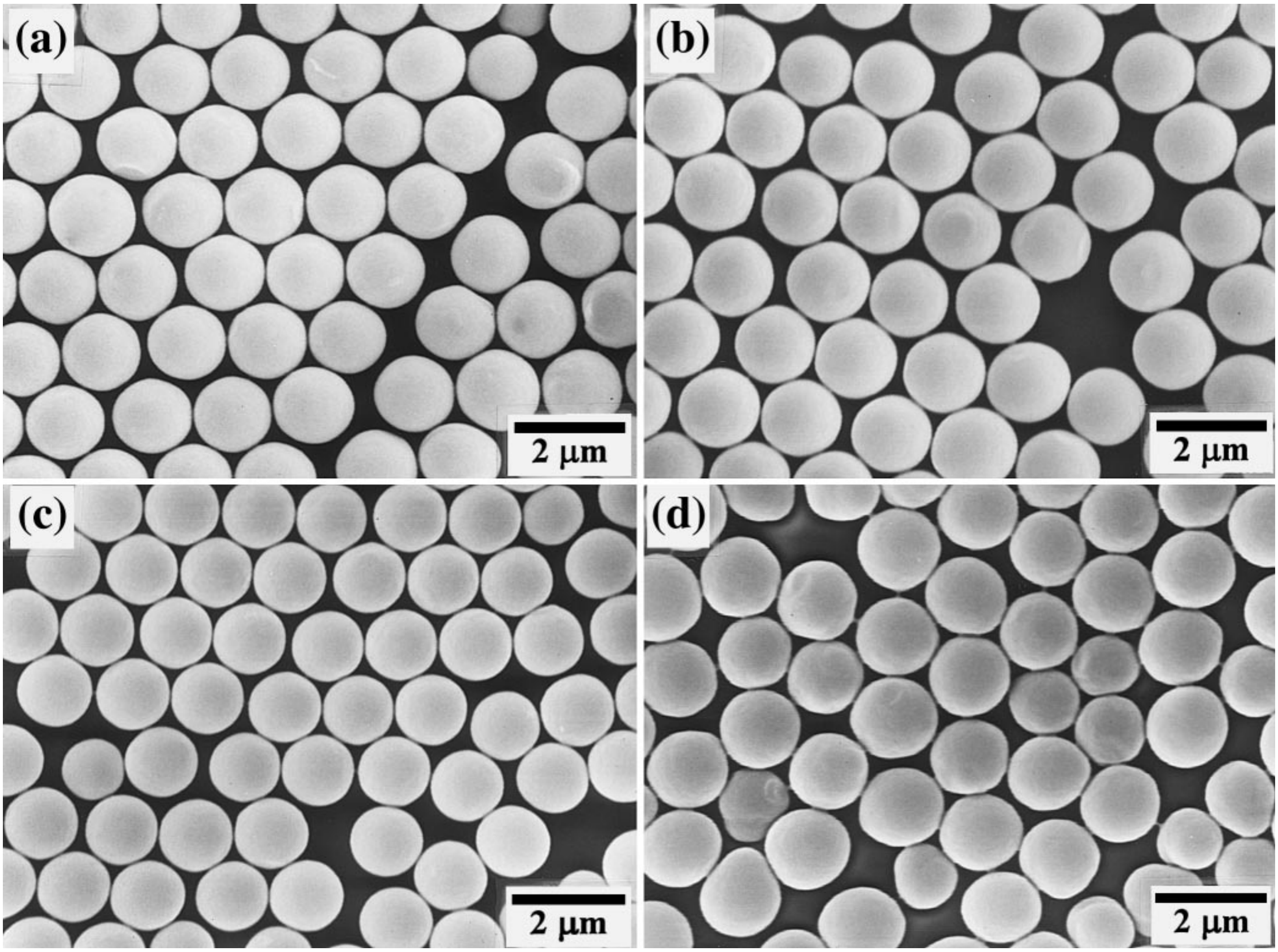


Fig. 2 Particle size and polydispersity of crosslinked polystyrene particles with the weight ratio of urethane acrylate (3.5 wt%) to xylene (w/w)

separation during the particle growth stage. For more detailed observation of the effect of the concentration of urethane acrylate on the phase separation, crosslinked polystyrene particles at higher concentrations of urethane acrylate were produced and their morphologies are shown in Fig. 6. As the concentration of urethane acrylate increased, the nonspherical singlet particles became asymmetric doublet particles. Moreover, the number of doublet particles increased.

Related to the formation of these nonspherical particles, there seemed to be a phase separation of the styrene monomers from the crosslinked network of the primary particles during the particle growth stage. As was shown in Fig. 3, no phase separation was observed below 5 wt% concentration of urethane acrylate. This result suggests that the crosslinked polystyrene network induced the phase separation; the styrene monomers in the primary particle phase were expelled in the course of particle growth because of the elastic-retractive force [16, 17].

Fig. 3a–d SEM photographs of crosslinked polystyrene particles with different urethane acrylate concentrations **a** 3.5 wt%, **b** 4.0 wt%, **c** 4.5 wt% and **d** 5.0 wt%. The weight ratio of urethane acrylate to xylene was 1/15 (w/w)



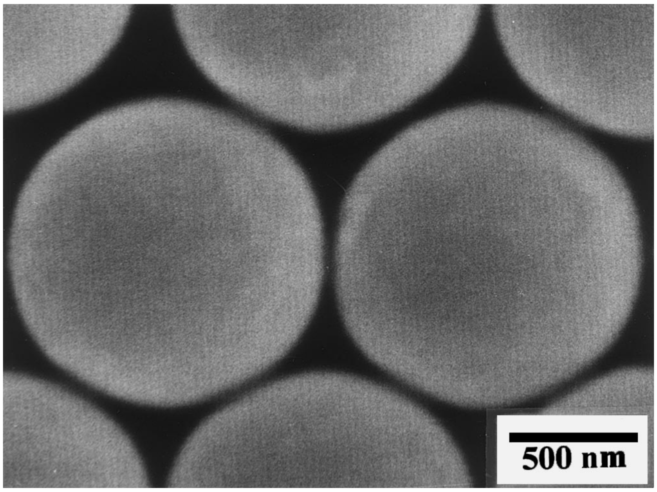


Fig. 4 SEM photograph of polystyrene particles crosslinked with 4.5 wt% urethane acrylate at high magnification. The weight ratio of urethane acrylate to xylene was 1/15 (w/w)

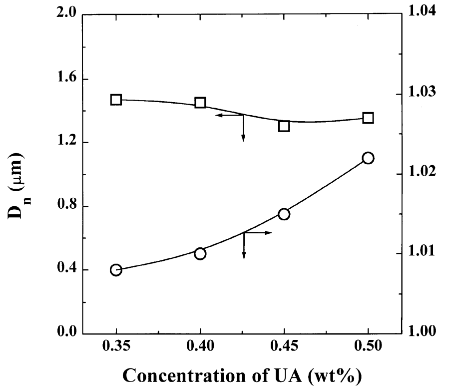


Fig. 5 Particle size and polydispersity of crosslinked polystyrene particles with concentration of urethane acrylate. The weight ratio of urethane acrylate to xylene was 1/15 (w/w)

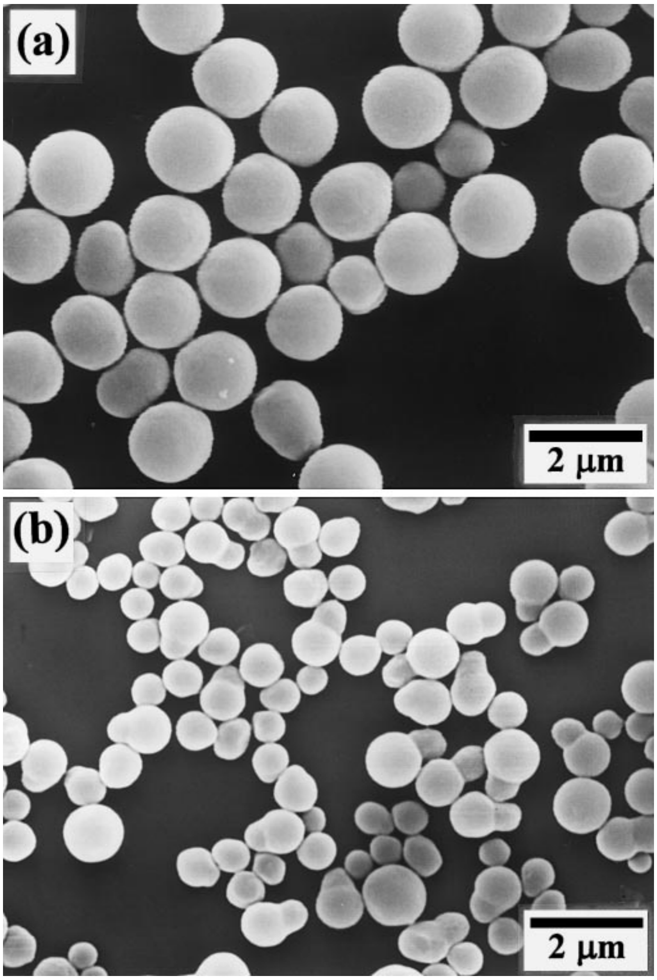


Fig. 6 SEM photographs of crosslinked polystyrene particles at a urethane acrylate concentration of **a** 6.0 wt% and **b** 7.0 wt%. The weight ratio of urethane acrylate to xylene was 1/15 (w/w)

In this procedure, it should be noted that the new domains started to be formed from the internal phase of the primary particle. This result strongly suggests that particle growth of the polystyrene particles crosslinked with urethane acrylate occurred by the styrene monomer swelling in the primary particle phase.

Conclusions

Monodisperse micron-sized polystyrene particles crosslinked with urethane acrylate crosslinker were produced and their morphologies were observed with different concentrations of urethane acrylate and medium solvency. The matching of the medium solvency with the monomer mixture of the urethane acrylate and the styrene monomer played an important role in obtaining monodisperse crosslinked polystyrene particles. It was found that the most desirable weight ratio of urethane acrylate and xylene was 1/15 (w/w). Monodisperse crosslinked polystyrene particles were possibly produced upto about 5 wt% concentration of urethane acrylate. It was believed that the increase in solvency on adding xylene to ethanol solution helped the diffusion of the styrene monomers into the primary particles. However, at high concentration of urethane acrylate (above 5 wt%) nonspherical particles, ellipsoidal or egg-like singlets and asymmetric doublets, were observed. This nonspherical particle formation suggested that particle growth occurred by the monomer swelling in the primary particle phase, even in the crosslinked state.

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