

J.-W. Kim
K.-D. Suh

Highly monodisperse crosslinked polystyrene microparticles by dispersion polymerization

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Abstract Highly monodisperse polystyrene microparticles cross-linked with urethane acrylates were produced by dispersion polymerization in ethanol solution in the presence of 2,2'-azobis(isobutyronitrile) initiator, polyvinylpyrrolidone stabilizer, and Aerosol-OT costabilizer. Different from conventional crosslinkers, the urethane acrylates employed as a crosslinker showed an excellent effect on maintaining the monodispersity of polystyrene microparticles even in the moderate crosslinker concentration. This was believed that the urethane acrylate helped forming the monomer-swellable surface of primary particles, because of its structurally long tetramethylene oxide groups in its molecule. However, at high concen-

tration of the urethane acrylate, the rough surface and the coagulum of particles were observed, which was attributed to the seriously decreased solubility of the monomer mixtures in ethanol solution. The solubility of the mixtures of styrene monomer and urethane acrylate in the media had a serious effect on the average particle size and morphology of the final particles. This could be confirmed by the measurement of cloud points and fractional conversions.

Key words Highly monodisperse polystyrene microparticles – the monomer-swellable surface – long tetramethylene oxide groups – the solubility of the monomer mixtures – cloud points and fractional conversions

J.-W. Kim · Prof. Kyung-Do Suh (✉)
Division of Chemical Engineering
College of Engineering
Hanyang University
Seoul 133-791
Korea

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, which are essential in the application of medical diagnostics [7, 8], liquid chromatography [9, 10], enzyme immobilization [11, 12], and drug delivery [13]. However, the common results of crosslinking of these polymer particles by dispersion polymerization have been broad size distributions, odd shape particles, and coagulum.

The crosslinked micron-sized polymer particles by dispersion polymerization started to appear in the work of Tseng et al. [14] and Margel et al. [15]. In their work, broad size distributions or coagulums of polystyrene particles were reported upon adding a small amount of crosslinker, such as divinylbenzene. Hattori et al. [16] could obtain comparatively stable dispersions of poly(styrene-co-divinylbenzene) only at high concentration of divinylbenzene. In their dispersion polymerization mechanism of divinylbenzene, they proposed that particle growth go on through the precipitation of the nucleated oligomers or particles onto the surface of the primary particles, which was because of the nonswellability of highly the crosslinked

poly(divinylbenzene) primary particles. Li et al. [17] also stressed on the role of the divinylbenzene monomers as a swelling agent of polydivinylbenzene primary particles in preparing the monodisperse crosslinked polydivinylbenzene particles by dispersion polymerization. However, from all resultant crosslinked particles, highly monodisperse crosslinked polymer particles could not be obtained successfully. This suggests that for the preparation of highly monodisperse crosslinked polymer particles, necessarily, monomer-swellaible primary particles are required.

In this work, in order to prepare highly monodisperse crosslinked polystyrene microparticles, we incorporated a urethane acrylate, designed with flexible tetramethylene oxide in the middle and two vinyl groups on both ends, as a crosslinker of the styrene monomer. When formed primary particles, this urethane acrylate was expected to help swelling of the primary particles by the styrene monomers in the media due to its flexible molecular characteristics. The effect of the concentration and molecular weight of the urethane acrylate and the property of dispersion medium on the particle size, the size distribution, and the morphology was examined. Finally, a dispersion polymerization mechanism for styrene and urethane acrylate in ethanol was proposed.

Experimental

Materials

Toluene diisocyanate (TDI, 80% 2,4-isomer, Tokyo Chemical Industry Co., Ltd.) was vacuum distilled before use. Polytetramethylene glycol (PTMG, $M_w = 1.0 \times 10^3$, 1.4×10^3 , and 2.0×10^3 g mol⁻¹, Hyosung BASF), polyvinylpyrrolidone (PVP K-30, $M_w = 40 \times 10^3$ g mol⁻¹, Aldrich Chemical Co.), di-2-ethylhexyl ester of sodium sulfosuccinic acid (Aerosol-OT, American Cyanamid) were used as received. Inhibitor in 2-hydroxyethyl methacrylate (HEMA, Aldrich Chemical Co.) and styrene monomer (Junsei Chemical Co.) was removed through a removing column (Aldrich Chemical Co.). 2,2-azobis(isobutyronitrile) (AIBN, Junsei Chemical Co.) were recrystallized from methanol.

Synthesis of urethane acrylate crosslinkers

All reactions were carried out in the four-necked glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and nitrogen gas inlet system. 2 moles of TDI was poured into the glass reactor and nitrogen gas was inlet for 10 min to eliminate the residual moisture. Then, 1 mole of

PTMG was added slowly into the reactor. The reaction temperature was raised to 80 °C so that 2 mole of TDI reacted with the 1 mole of PTMG, resulting in the molecular structure having flexible tetramethylene oxides in the middle and isocyanates on end sides. In this stage, care must be taken of controlling the molar ratio of reaction, so as not to increase the molecular weight. The change of NCO value during reaction was determined using dibutylamine back titration method to find out the end point of reaction [18]. Continuously, after dissolving 1 wt% dibutyltindilaurate into the reactor again, 2 mole of HEMA was reacted to the residual isocyanate groups at 45 °C for 12 h, which capped the molecular ends with the reactive vinyl groups. The reaction end point was determined by the disappearance of NCO stretching peak (2270 cm⁻¹) through IR spectroscopy. Other detailed reaction procedures were followed from our previous works [19–21].

The reaction procedure and molecular structure are presented in Scheme 1. We named UA1, 2, and 3 for the urethane acrylates. Here the serial number, 1, 2, and 3 corresponds to the molecular weight of PTMG, 1.0×10^3 , 1.4×10^3 , and 2.0×10^3 g mol⁻¹.

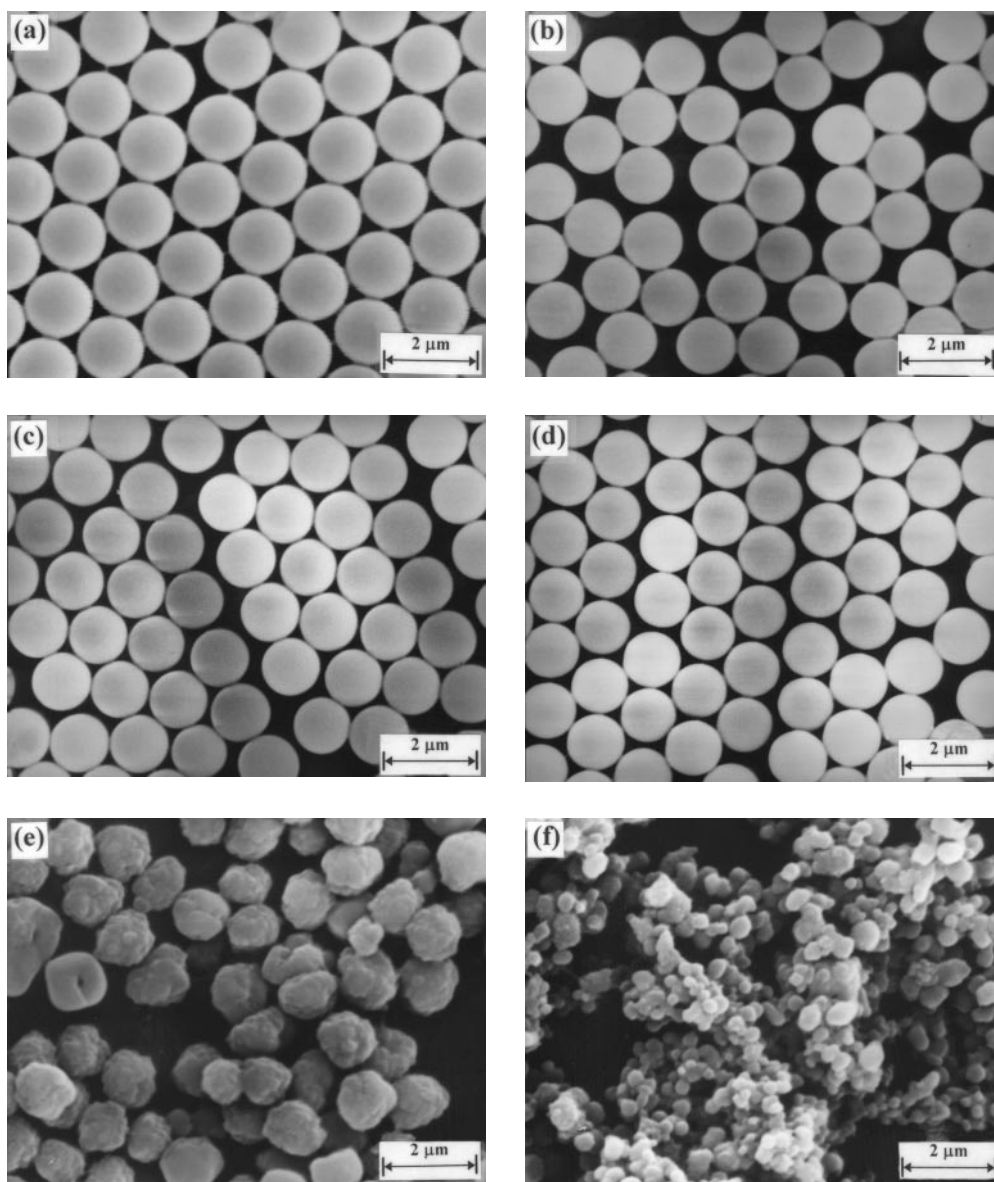
Dispersion polymerization of styrene and urethane acrylate

General dispersion polymerization procedure was followed [14, 16]; AIBN, PVP, Aerosol-OT, styrene, urethane acrylate, and ethanol were weighed into 20 ml glass vials. After sealing in nitrogen atmosphere, the vials were submerged in a thermostated water bath and tumbled with the rotation speed of 40 rpm. The polymerization was carried out for 24 h at 70 °C. The obtained spheres 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 overnight. All ingredients used are summarized in Table 1.

Measurements

Molecular weight distributions were measured by a model 410 GPC equipped with Styragel HR 1-4 columns from Waters Associates at 25 °C. The flow rate of the carrier solvent, THF, was 0.5 ml min⁻¹. The average molecular weights calculated on the basis of the molecular weight versus retention volume curve of monodisperse polystyrene standards were $M_n = 1.8 \times 10^3 \sim 3.8 \times 10^3$ g mol⁻¹ and $M_w = 2.5 \times 10^3 \sim 5.2 \times 10^3$ g mol⁻¹.

Fig. 1 SEM photographs of polystyrene microparticles prepared by dispersion polymerization with the concentration of the urethane acrylate (UA1) at 70 °C for 24 h: 0.0 wt% (a), 0.5 wt% (b), 1.0 wt% (c), 3 wt% (d), 5 wt% (e), and 10 wt% (f) (based on total monomer weight)



In general, dispersion polymerization of styrene and conventional crosslinkers, such as divinylbenzene [12–15], broad size distributions and rough surface of the particles were the common observation upon adding a small amount of crosslinkers (more than 0.5 wt%). However, in the case of adding urethane acrylate as a crosslinker, highly monodisperse crosslinked polystyrene particles were obtained in the moderate concentration of the urethane acrylate. This can be elucidated by considering the surface characteristics of primary particles crosslinked by the urethane acrylates. Conventional crosslinkers form a hard and glassy surface of the primary particles, which eventually makes it difficult to swell the primary

particles by vinyl monomers in the medium [16, 17]. On the other hand, the primary particles crosslinked by the urethane acrylate can be easily swollen by the styrene monomers in the media during particle growth, because of the peculiar molecular structure of the urethane acrylate; long tetramethylene oxide groups in the backbone of the urethane acrylate molecule. This suggests that the monomer-swallowable primary particles play an important role in obtaining the highly monodisperse crosslinked polymer particles.

The average particle sizes, size distributions, and conversions obtained with the concentration of the urethane acrylate are listed in Table 2. The average particle size

Table 2 The effect of urethane acrylate concentration on the crosslinked polystyrene microparticles^{a)}

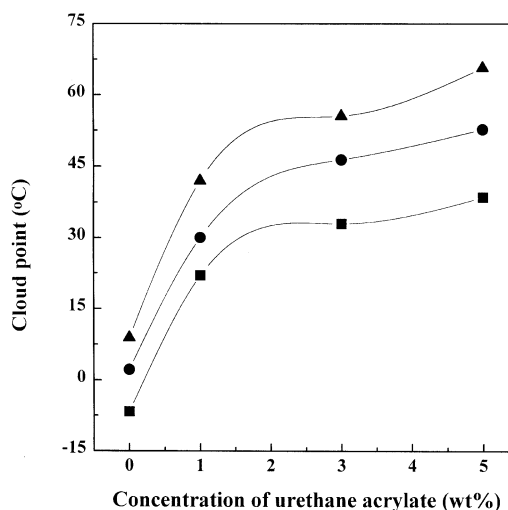
UA ^{b)}	Particle size [μm]		PDI (D_w/D_n)	Fractional conversion	Remarks
	D_n	D_w			
UA1-0.0	1.516	1.517	1.001	0.927	Monodisperse
UA1-0.5	1.340	1.341	1.001	0.925	Monodisperse
UA1-1.0	1.291	1.292	1.001	0.947	Monodisperse
UA1-3.0	1.245	1.247	1.002	0.942	Monodisperse
UA1-5.0	1.185	1.248	1.053	0.958	Odd shape, rough surface
UA1-10.0	—	—	—	—	Coagulum
UA2-3.0	0.859	0.888	1.034	0.925	Bimodal
UA2-3.0	0.795	0.827	1.038	0.945	Bimodal, rough surface

^{a)} 70 °C; 24 h; 10 wt% of monomer concentration based on total weight.^{b)} UA- α,β ; α,β corresponds to the concentration of the urethane acrylate based on total monomer weight.

decreased with the increase of the urethane acrylate concentration. Related to these results, the solubility of the monomers were observed relatively in ethanol solution. Figure 2 shows the cloud points obtained from TOA for the monomer mixtures in ethanol solution with respect to the concentration of the urethane acrylate. The cloud point increased, as the concentration of the urethane acrylate increased. This indicates that the solubility of the monomer mixtures in ethanol solution was lowered by adding urethane acrylate. Eventually, the lowered solubility increased the number of primary particles. So, the smaller particles were obtained. When the urethane acrylate concentration was increased to 5–10 wt%, a dispersion of rough surface and coagulum was observed, as shown in Fig. 1e and f. This can also be explained in terms of low solubility of the monomer mixtures, when a large amount of urethane acrylate was added.

Effect of dispersion medium

In order to examine the effect of the dispersion medium on the particle sizes and size distributions, the solvency of the medium was controlled by adding water or xylene. Figure 3 shows the SEM photographs of polystyrene particles crosslinked with 3 wt% of urethane acrylate (EtOH/water = 90/10 (a) 80/20 (b), EtOH/xylene = 95/5 (c), and 90/10 (d), w/w). The particle sizes, size distribution, and conversions are listed in Table 3. The average particle size decreased with the added amount of water and increased with xylene. The effect of the medium solvency can also be confirmed by the results of TOA, and shown in Fig. 2. The upward shift of the cloud points was observed with increasing the added amount of water. This explains well the effect of the medium solvency on the particle sizes and size distributions of the crosslinked particles; better solvency led to longer chain lengths of oligomers and larger par-

**Fig. 2** Cloud point for the monomer mixtures with the concentration of the urethane acrylate (UA1). The mixing ratio of ethanol to water was 74/26 (■), 72/28 (●), and 70/30 (▲), w/w

ticles while shorter critical chain lengths and smaller particles were favored for poor solvents [14, 16].

Effect of molecular weight of urethane acrylate

The dispersion polymerization of styrene and urethane acrylate was carried out with the urethane acrylates synthesized changing the molecular weight of PTMG, in order to examine the effect of the flexibility of urethane acrylates. Figure 4 shows the SEM photographs of polystyrene particles crosslinked with 3 wt% of urethane acrylates synthesized with PTMG ($M_w = 1.4 \times 10^3 \text{ g mol}^{-1}$ (a) and $2.0 \times 10^3 \text{ g mol}^{-1}$ (b)). In Table 2, the average particle sizes and the size distribution are summarized. Bimodal

Fig. 3 SEM photographs of polystyrene microparticles crosslinked with 3 wt% of urethane acrylate (UA1) in ethanol/water (=90/10 (a) and 80/20 (b), w/w) and ethanol/xylene (=95/5 (c) and 90/10 (d), w/w) solutions

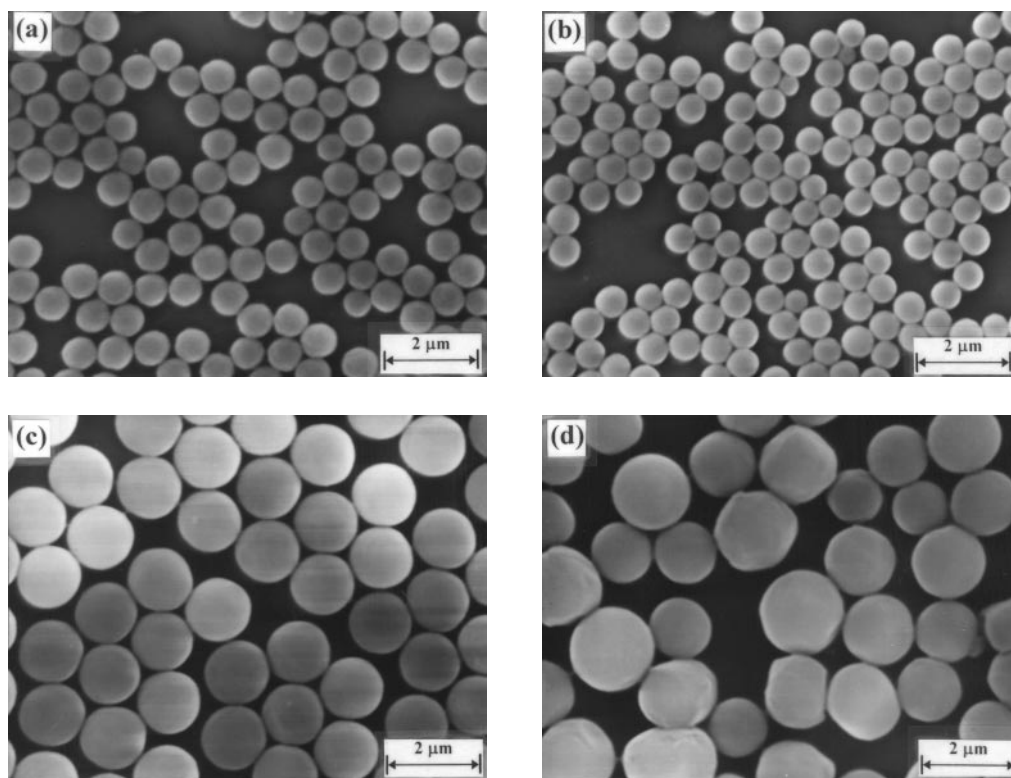


Table 3 The effect of medium solvency on the crosslinked polystyrene microparticles^{a)}

Medium property ^{b)}	Particle size [μm]		PDI (D_w/D_n)	Fractional conversion	Remarks
	D_n	D_w			
EtOH/water = 100/0	1.245	1.247	1.002	0.942	Monodisperse
EtOH/water = 90/10	0.736	0.745	1.012	0.902	Relatively monodisperse
EtOH/water = 80/20	0.638	0.659	1.033	0.894	Slightly rough surface
EtOH/xylene = 95/5	1.417	1.419	1.001	0.921	Monodisperse
EtOH/xylene = 90/10	1.549	1.611	1.040	0.905	Slight aggregate

^{a)} 70 °C; 24 h; 10 wt% of monomer concentration based on total weight; 3 wt% of UA1 based on styrene.

^{b)} The mixing ratio of ethanol to water or xylene (w/w).

size distributions in Fig. 4a and rough surfaces in Fig. 4b were observed instead of the monodispersity together with the decrease of average particle sizes. To elucidate this point, the solubility of the monomer mixtures with ethanol solution was considered in Fig. 5. The shear increase of the cloud point could be observed, showing the serious decrease of the solubility of the monomer mixtures at high molecular weight of PTMG. This seemed to be attributed to the increased hydrophobicity of the urethane acrylates, when the molecular weight of PTMG increased [19–21]. Therefore, even though the flexibility of the urethane acryl-

ate was improved, monodisperse polystyrene particles could not be expected in this study.

Polymerization kinetics in dispersion polymerization of styrene and urethane acrylate

Figure 6 shows the fractional conversion for polystyrene crosslinked with varying the urethane acrylate concentration microparticles as a function of polymerization time (0.0 wt% (■), 1.0 wt% (●), and 3.0 wt% (▲)) at 70 °C in

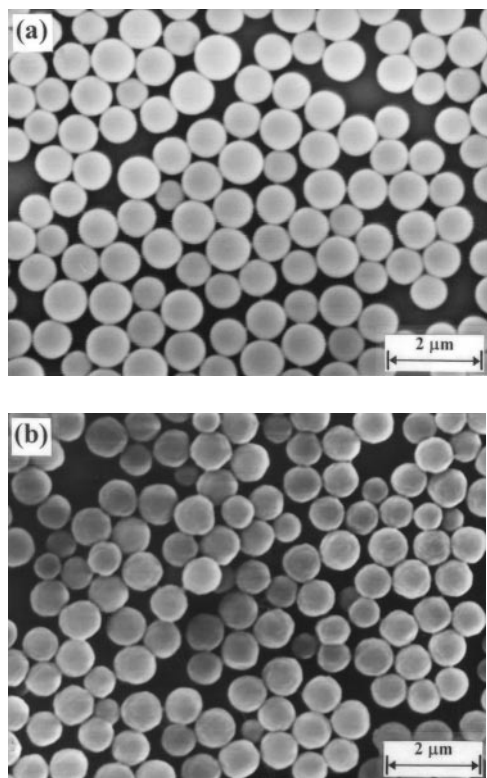


Fig. 4 SEM photographs of polystyrene microparticles prepared by dispersion polymerization at 3 wt% of urethane acrylate (UA2 (a) and UA3 (b)) at 70 °C for 24 h in ethanol

ethanol. As the concentration of the urethane acrylate increased, the polymerization rate increased. As is shown in Fig. 2, the solubility of the mixtures of styrene monomer and urethane acrylate in ethanol solution was lowered with the increase of the urethane acrylate concentration, finally generating an increased number of nuclei [4, 14]. This indicates that total surface area was increased. Therefore, the equilibrium distribution of monomer towards the particle phase was more favourable, which eventually results in a faster polymerization rate. Similar trends could be observed in the effect of the molecular weight of the urethane acrylates. Figure 7 shows the fractional conversion for polystyrene microparticles crosslinked with UA1 (■) and UA2 (●). The polymerization rate also increases, as the molecular weight of urethane acrylate increased.

Mechanism for the dispersion polymerization of the crosslinked polystyrene microparticles

The mechanisms for the dispersion polymerization from monofunctional monomers [1, 4, 14] and bifunctional

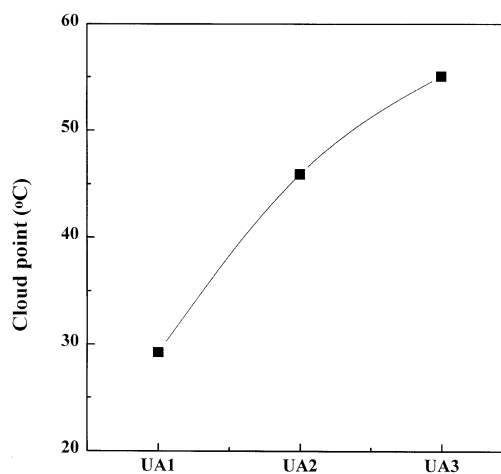


Fig. 5 Cloud point for the monomer mixtures with the flexibility of the urethane acrylates. 3 wt% of urethane acrylate was added in ethanol/water (= 70/30, w/w) solution

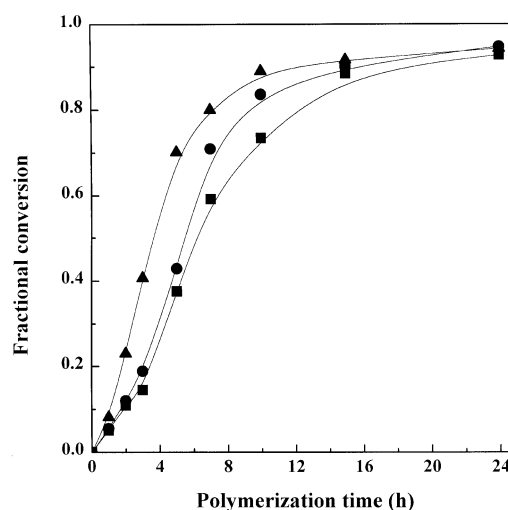


Fig. 6 Fractional conversion with the polymerization time at various urethane acrylate (UA1) concentration: 0.0 wt% (■), 1.0 wt% (●), 3.0 wt% (▲), at 70 °C in ethanol

monomers [16, 17] have been proposed to understand the formation and growth of the polymer particles. Here, we suggest a mechanism for the formation of the crosslinked polystyrene microparticles, based on the previously proposed mechanisms and present works. A schematic representation is given in Fig. 8. At the start of the process, styrene monomer, urethane acrylate, stabilizer, and co-stabilizer are present homogeneously in the medium (a). Upon heating to the reaction temperature, the initiator decomposes and the free radicals react with styrene monomers and the urethane acrylates to form oligomer radicals

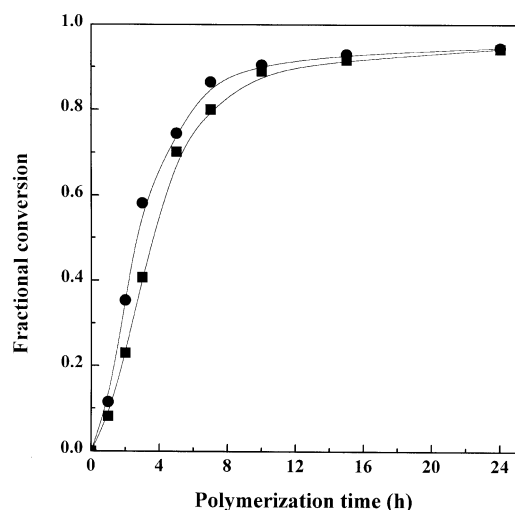


Fig. 7 Fractional conversion with the polymerization time at 70 °C in ethanol. 3 wt% of UA1 (□), and UA2 (●) was added

(b). When reached a critical chain length, the oligomers precipitate to form the primary particles crosslinked with the urethane acrylates. During the primary particle formation, stable primary particles can be formed through the absorption of stabilizers and costabilizers (c). Then, the crosslinked primary particles grow either by styrene monomer absorption or by oligomer radical adsorption until all monomers are consumed (d).

In conventional dispersion polymerization of the crosslinked polymer particles, the particle growth is considered to be achieved by the precipitation of polymers or oligomers onto the primary particles, because of the non-swelling of the highly crosslinked primary particles [16, 17]. The main difference of urethane acrylate-crosslinked polymer particles from general ones in the mechanism is the swellability of the primary particles during particle growth (stage (c)). Therefore, the styrene monomers in the medium can be readily absorbed by the crosslinked primary particles, which resulted in highly monodisperse final particles. However, at high concentration of the urethane acrylate (more than 5 wt% based on styrene monomer), the urethane acrylate may produce new primary particles faster than they can be captured by the initial particles, which leads to the precipitation of the new primary particles onto the initial particles. This seems to be attributed to too lowered solubility of the mixtures of styrene monomer and urethane acrylate in the medium. Therefore, similar result to the conventional crosslinked polymer particles could be obtained, as shown in Fig. 1e and f; broad size distributions and rough surfaces.

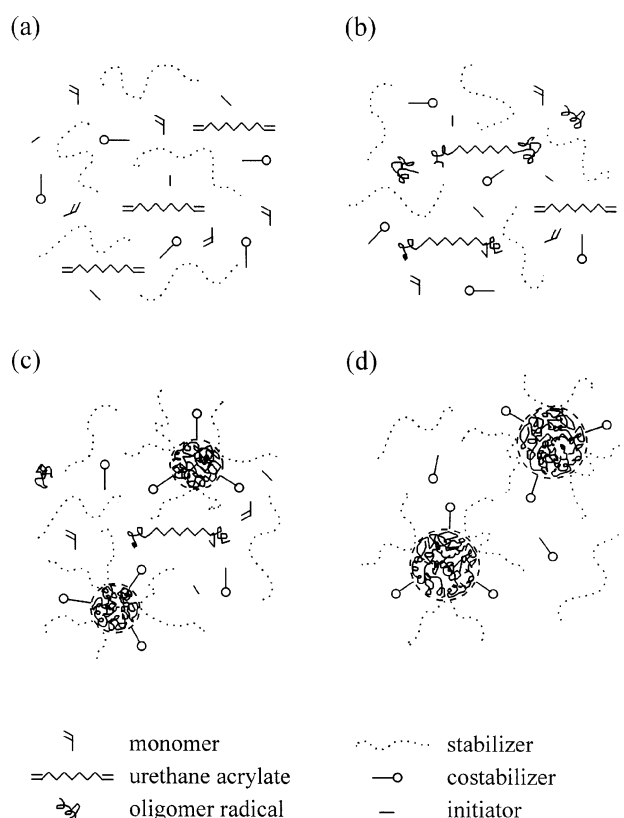


Fig. 8 A schematic representation for the particle nucleation and particle formation in the dispersion polymerization of styrene and urethane acrylate in ethanol

Conclusion

Highly monodisperse crosslinked polystyrene microparticles were produced directly by dispersion polymerization of styrene and urethane acrylate. The concentration of the urethane acrylate have a serious effect on the solubility of the monomer mixture in the medium. Highly monodisperse size distribution of the crosslinked particles was considered to be attributed to the monomer-swelling surface of primary particles, because of long tetramethylene oxide groups in the backbone of urethane acrylate molecules. Because of highly monodisperse crosslinked particle structure, the application to the preparation of monodisperse composite particles by a simple swelling procedure was possible in further study.

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