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ORIGINAL CONTRIBUTION

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Monodisperse micron-sized macroporous poly(styrene-*co*-divinylbenzene) particles by seeded polymerization

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Abstract Macroporous poly(styrene-*co*-divinylbenzene) particles were produced in a micron-size range by two-stage swelling and continuous polymerization. The molecular weight of the polystyrene seed particles was controlled by incorporating a urethane acrylate. It was found that the porosity of the particles produced by the seeded polymerization was dependent on the molecular weight of the seed polymer. As the molecular weight of the polystyrene seed increased, the porous particles produced became macroporous. Interestingly, the high molecular weight of the polystyrene seed had a negligible influence on the change of porosity of the seeded polymerized particles. It is believed that the viscosity of the swollen droplet phase remained pretty high with the change in composition because the polystyrene seed copolymerized with urethane cacrylate had many side chains.

Key words Porous poly(styrene-*co*-divinylbenzene) particles · Molecular weight · Urethane acrylate · Macroporous · Many side chains

Introduction

Conventional polymeric packing materials have been produced using suspension polymerization [1–3]. One disadvantage in this traditional process is a size distribution which is too broad. In the case of polydisperse column packing, the permeability of the column is mainly determined by the smallest particles, while its efficiency is controlled by the largest ones [4, 5]. Therefore, a tedious size classification must be followed to get the monodispersity that is essential for the high efficiency of the column packing.

The monodispersity in particle size can be achieved by employing seeded polymerization. For this purpose, several monomer swelling methods have been used, such as successive seed and polymerization by Vanderhoff and coworkers [6, 7], the activated swelling procedure (ASP) by Ugelstad and coworkers [8–11], the dynamic swelling method by Okubo and coworkers [12, 13], and others [14, 15]. In all processes proposed, once the monodispersity of the seed particles is determined, it could be continued to the final targeting particles. On the basis of these swelling methods, a variety of monodisperse polymer particles have been produced in a large size range up to hundreds of micrometers.

Chemically and mechanically stable porous packing materials, generally styrene (S)–divinylbenzene (DVB) copolymers in the presence of an inert diluent, are available [9, 16–18]. Ugelstad and coworkers [9–11] produced uniform microporous particles using ASP. Cheng et al. [18] reported a potential use of a poor solvent such as heptane as a diluent and discussed the pore formation during polymerization. Wang et al. [19] pointed out the importance of porogens in determining the characteristics of pore structure. As can be seen in much research, the pore size of the packing materials is very important for highly efficient separation. Most of all, monodisperse porous particles having macroporous structures are the most efficient materials for many separation processes [9, 10, 18–20]. Therefore, much work is concentrated on controlling the porosity of the porous polymer particles.

In this study, monodisperse micron-sized poly(styrene-*co*-divinylbenzene) [poly(S-*co*-DVB)] porous particles were produced by a two-stage seeding method. The monodisperse polystyrene (PS) particles produced by dispersion polymerization were utilized as seed particles. The molecular characteristics of the PS seeds were varied by adding urethane acrylate (UA) to the polymerization mixture. Here we present new results closely related to the characteristics of seeds. The porous properties and the morphology of the final porous particles were investigated with the molecular characteristics of the PS seeds, the diluent content, and the degree of cross-linking.

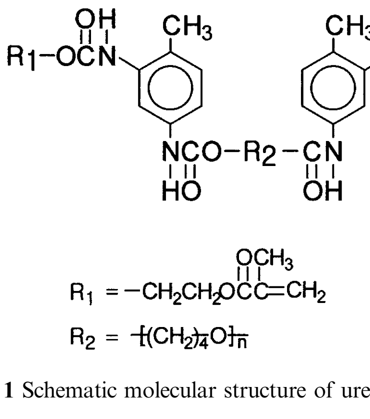
Experimental

Materials

Toluene diisocyanate (80% 2,4-isomer, Tokyo Chemical Industry) was vacuum distilled before use. Poly(tetramethylene glycol) ($M_w = 1.0 \times 10^3$ gmol^{-1}, Hyosung BASF), poly(vinylpyrrolidone) (PVP K-30, $M_w = 4.0 \times 10^4$ gmol^{-1}, Aldrich Chemical Co.), 1-chlorododecane (CD, TCI), and 2-methoxyethanol (Kanto Chemical Co.) were used as received. The inhibitors in 2-hydroxyethyl methacrylate (Aldrich), DVB (55 and 80% grade, Aldrich), and S(Aldrich) were removed through a removing column (Aldrich). Poly(vinyl alcohol) (PVA, $M_w = 8.8 \times 10^4$–9.2×10^4 gmol^{-1}, 87–89% hydrolyzed) was kindly supplied by Kuraray Co. 2,2-Azobis(isobutyronitrile) (AIBN, Junsei Chemical Co.) and benzoyl peroxide (BPO, Junsei) were recrystallized from methanol.

PS seed particles by dispersion polymerization

UA was synthesized as described in previous articles and was used as a cross-linker in the dispersion polymerization of PS seeds [21–23]. A schematic of a molecule of UA is shown in Scheme 1. Dispersion polymerization was followed as for our previous polymerization conditions. S, 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 spherical particles obtained were centrifuged for 10 min at 6,000 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.



Scheme 1 Schematic molecular structure of urethane acrylate

Table 1 The standard recipe for the production of seed polymer particles. 70 °C; 24 h; 10 wt% monomer concentration based on total weight

Ingredient	Weight (g)
Styrene	0.98
Urethane acrylate (2 wt%)	0.02 (variable)
Poly(vinylpyrrolidone) K-30	0.18
Aerosol-OT	0.04
2,2-Azobis(isobutyronitrile)	0.01
2-Methoxyethanol	4.39
Ethanol	4.39

Porous poly(S-*co*-DVB) particles by seeded polymerization

All the processes were carried out in a glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and a nitrogen gas inlet system. First, PS seed particles (0.5 g) redispersed in 0.25% sodium lauryl sulfate aqueous solution (40 g) by sonification were swollen with CD (0.5 g) emulsified by ultrasonic homogenization in 0.25% aqueous solution (10 g) for 10 h. The stirring speed was fixed at 200 rpm throughout the process. After the complete disappearance of CD emulsion droplets, the mixture (10 g) of S, DVB, toluene, and BPO (1 wt% of total monomers) was emulsified by the same method with CD and poured into the reactor. The swelling was continued for another 12 h at 30 °C. The swollen particles were stabilized with 5 wt% PVA aqueous solution and the concentration was fixed at 1% of the total content (250 g). Polymerization in the aqueous phase was inhibited by adding copper (II) chloride (0.5 g) [19, 25]. After deaerating with nitrogen gas, the polymerization was carried out at 80 °C for 10 h. The particles produced were repeatedly washed in water and methanol. Soxhlet extraction was followed using methylene chloride for 36 h to eliminate seed polymer and other impurities.

Characterizations

Molecular-weight distributions were measured using a model 410 gel permeation chromatography apparatus equipped with Styragel HR 1-4 columns from Waters Associates at 25 °C. The flow rate of the carrier solvent, tetrahydrofuran, was 0.5 ml min^{-1}. The surface morphology of the particles was observed with a scanning electron microscope (SEM, JSM-6300, Jeol). Specimens were prepared by diluting the particles 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 gold layer. The diameter of the particles was determined from SEM photographs. The viscosity was measured with a standard Ubbelohde viscometer in a thermostated bath at 25 ± 0.1 °C. The specific surface area, pore volume, and pore size of the porous particles were calculated from the Brunauer–Emmett–Teller isotherm of sorption/desorption of nitrogen.

Results and discussion

Molecular-weight control of PS seed particles

In general dispersion polymerizations of cross-linked polymer particles, it is known that the nonswellability of the cross-linked primary particles causes the primary particles to grow by the precipitation of the nucleated oligomers and/or particles onto their surfaces [26, 27].

On the basis of this dispersion polymerization mechanism, in our previous work [21, 22, 23], monodisperse cross-linked PS particles were produced using UA in the micron size range. One interesting point in our study is that from 3 wt% UA concentration (based on total monomer weight), the cross-linked network structure started to form, suggesting another possible technique to control the molecular weight of PS seed particles by dispersion polymerization. In most studies, the molecular weights of PS seed particles have been varied by adding an initiator or a chain-transfer agent [18, 19]. Uniquely, in this study, the molecular weight of PS seed particles was controlled by incorporating UA in the high-molecular-weight range.

PS seed particles were produced by changing the concentration of UA by dispersion polymerization. SEM photograph of PS seed particles containing 2 wt% UA are shown in Fig. 1. All the particles were monodisperse and clear. The characteristics of the particles are summarized in Table 2. Below 3 wt% UA concentration, the molecular weight of the PS seed particles increased without a cross-linked network being formed. This means that the molecular weight of the seed polymers could be controlled by manipulating the amount of UA. At 3 wt% UA concentration, the cross-linking took place with an N value of 87.1 mol m^{-1} [28]. With these four PS seed particles, porous polymer particles were produced and a porous structure was observed.

Effect of seed molecular weight on porous properties

Monodisperse porous poly(S-*co*-DVB) particles were produced with only two-stage monomer swelling and polymerization. An optical microscope photograph of PS2 particles swollen with S, DVB, and toluene before polymerization is shown in Fig. 2. Regardless of the seed conditions, all the particles were uniformly swollen. After the polymerization and Soxhlet extraction process, porous poly(S-*co*-DVB) particles were obtained. An SEM photographs of poly(S-*co*-DVB) particles with different molecular weight of the PS seed particles is shown in Fig. 3: the particles were uniform in size. It is clear in Fig. 4 that each particle has a porous structure. As one can see, the porosity became macroporous with

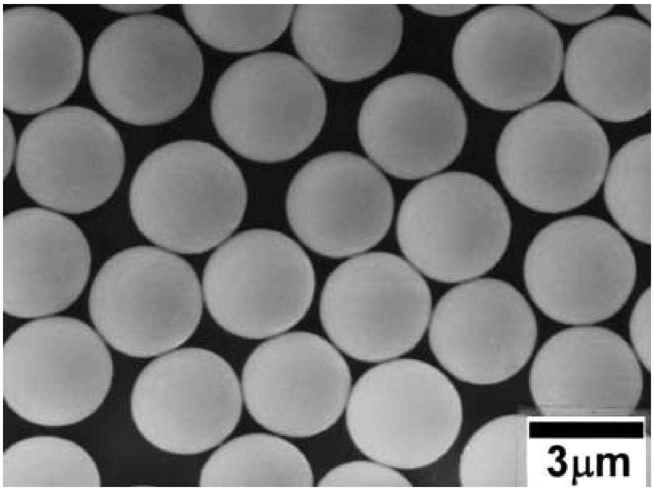


Fig. 1 Scanning electron microscope (*SEM*) photograph of polystyrene (*PS*) PS2 seed particles containing 2 wt% urethane acrylate (*UA*) (based on total monomer weight)

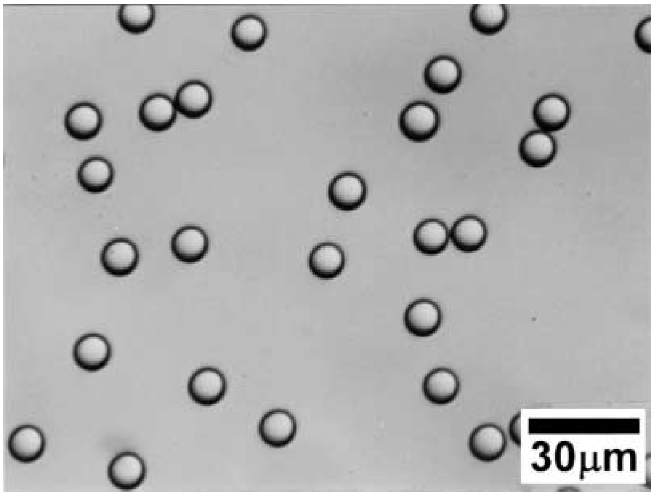


Fig. 2 Optical microscope photograph of PS2 particles swollen with styrene (*S*), diviylbenzene (*DVB*), toluene, and benzoyl peroxide (*BPO*)

Table 2 The characteristics of the seed polymer particles

Symbol[a]	D_n (μm)	Particle size distribution (D_w/D_n)	M_w (gmol^{-1})	Molecular-weight distribution (M_w/M_n)	N^b (mol m^{-3})
PS0	2.87	1.01	5.3×10^4	2.69	–
PS1	2.86	1.01	6.2×10^4	2.81	–
PS2	2.96	1.01	10.1×10^4	3.17	–
PS3	2.83	1.01	–	–	87.1

[a] PSα; α corresponds to the concentration of urethane acrylate (weight percent based on total monomer weight)

[b] Effective number of chains in cross-linked network determined from the monomer transport rate [28]

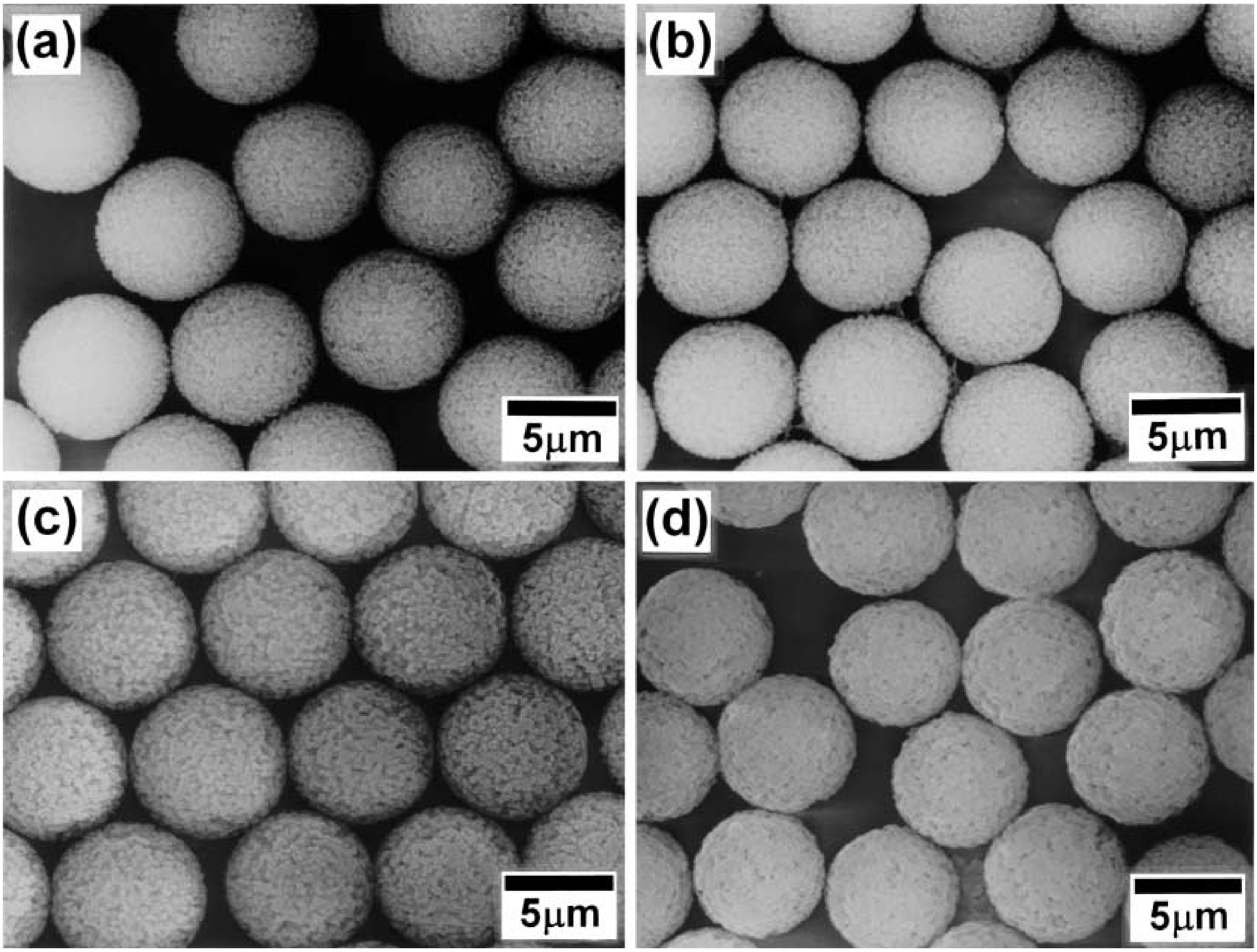


Fig. 3 SEM photographs of porous poly(S-*co*-DVB) particles produced with varying molecular weights of PS seed particles: **a** PS0-30-40, **b** PS1-30-40, **c** PS2-30-40, and **d** PS3-30-40

the increase in the molecular weight of the PS seed particles. This means that the large pores were generated during the phase-separation for higher molecular weights of PS seed particles. The larger radius of gyration of the high-molecular-weight PS is responsible for these large pores. To elucidate the effect of the radius of gyration caused by the high-molecular-weight PS, the viscosities were measured at the same condition of the monomer swelling state before polymerization and the results are shown in Fig. 5. The viscosity was enhanced by the increase of the molecular weight of the PS seed particles. It was evident from this result that the molecular weight of the PS seed particles played an important role in controlling the pore size of poly(S-*co*-DVB) particles during the phase-separation. One interesting thing in this observation is that the porous structure also appeared in the case of the slightly cross-linked PS seed particles (Fig. 3d). In an experiment carried out without employing toluene, a similar result was obtained. This means that alternatively, the porous polymer particles can be produced by only controlling the degree of cross-linking in the presence/absence of diluent. The porous properties of poly(S-*co*-DVB) particles are summarized in Table 3. The pore size (D_p), pore volume (V_p), and specific surface area (A_p) could be characterized in the macroporous range.

Effect of other parameters on the porous properties

At the high molecular range of the PS seed particles (PS2), the effect of the contents of toluene and DVB on the porosity of poly(S-*co*-DVB) particles was observed. A SEM photograph of PS2-25-50 particles (50% toluene content in the total monomer mixture) is shown in Fig. 6. The porosity is enhanced at high content of diluent because at lower viscosity, the phase-separation induced by the collapse of growing S–DVB chains is favorable [18–20]. In our study, however, the higher content of toluene had negligible influence on the porous

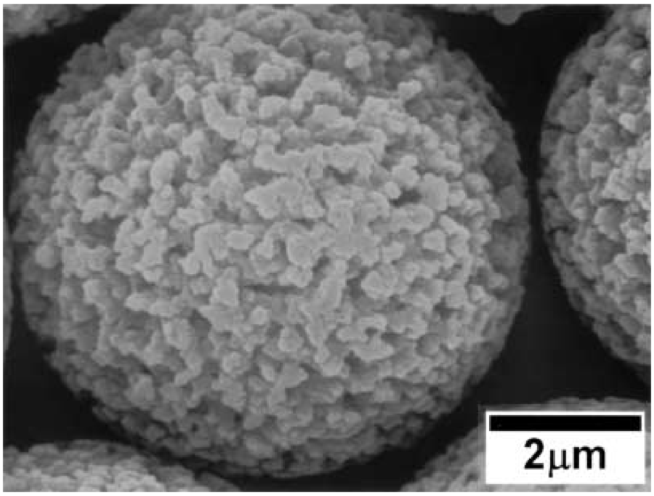


Fig. 4 SEM photograph of porous poly(S-*co*-DVB) particles (PS2-30-40) at high magnification

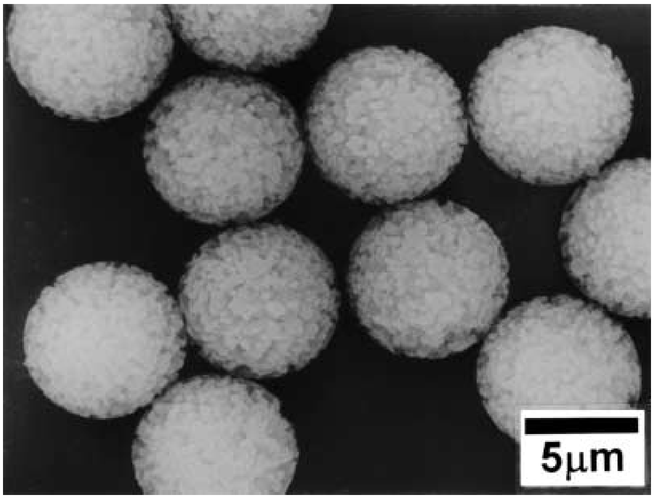


Fig. 6 SEM photograph of porous poly(S-*co*-DVB) particles (PS2-25-50) at high toluene content

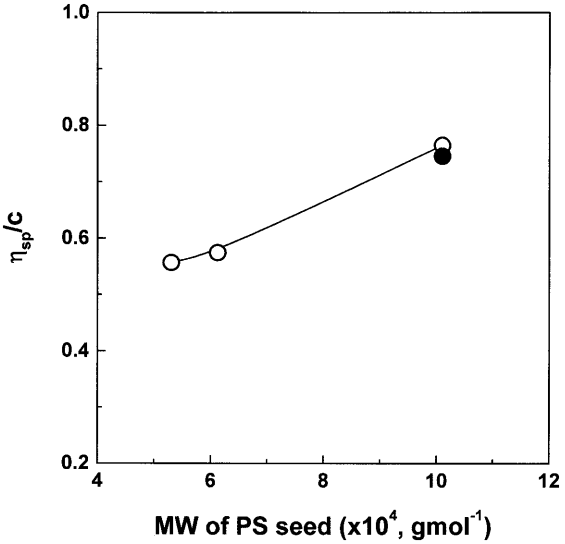


Fig. 5 Viscosity change of PS seed particles dissolved in a mixture of S, DVB, and toluene with the following molecular weights S: DVB: toluene 3:3:4 (○), S: DVB: toluene 2.5:2.5:5 (●). The first *open circle* is the viscosity of the solution containing the PS seed polymer produced in the absence of UA

morphology and properties (Table 3). These results seem to be related to the viscosity of the swollen droplet phase governing the collapse of growing S–DVB copolymer in the mixture of PS seed polymer, monomers, and toluene. In Fig. 5, the viscosity of the monomer mixtures containing a higher content of toluene is plotted and compared with that containing a lower one. It was found that the difference in the viscosities of the two was small. In order to elucidate this peculiar viscosity behavior, the molecular structure of the PS seed copolymerized with UA must be considered. UA has two acryl groups on both molecular ends. Then, PS chains would have many side chains from the radical polymerization of the other acryl group of UA during the propagation reaction. Therefore, PS copolymerized with UA could maintain its viscosity up to a high content of toluene. As a result, the formation of a pore structure was not so dependent on the content of diluent at high molecular weight of PS seeds.

A SEM photograph of PS2-60-40 (60% DVB content in the total monomer mixture) is shown in Fig. 7. The porous characteristics are listed in Table 3. The PS2-60-40 particles polymerized second with only DVB showed

Table 3 Characteristics of porous polymer particles determined with Brunauer–Emmett–Teller measurements. 80 °C; 10 h; 4 wt% solid content based on total weight

Symbol[a]	D_n (μm)	Particle size distribution (D_w/D_n)	Specific surface area (m^2/g)	Pore volume (ml/g)	Mean pore size (nm)
PS0-30-40	6.78	1.01	37	0.09	9.5
PS1-30-40	6.72	1.01	34	0.08	12.5
PS2-30-40	7.13	1.01	22	0.04	18.2
PS3-30-40	6.53	1.01	18	0.03	18.7
PS2-25-50	7.20	1.01	23	0.05	12.8
PS2-60-40[b]	6.91	1.01	211	0.23	2.8

[a] PSα-β-γ; α is the urethane acrylate concentration in seed particles, β is the divinylbenzene concentration, and γ is the toluene concentration in the monomer mixture by weight percent

[b] In this sample, divinylbenzene of 80% grade was used

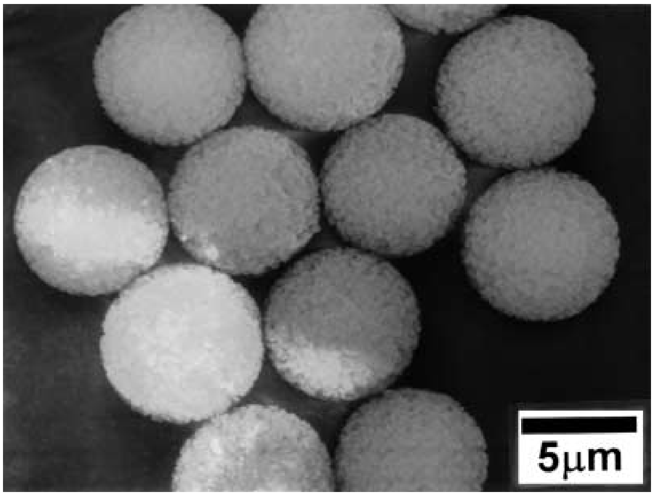


Fig. 7 SEM photograph of porous poly(S-*co*-DVB) particles (PS2-60-40) at high concentration of DVB

smaller D_p, larger A_p, and higher V_p than PS2-30-40. This can be explained by the fact that as the content of DVB in the monomer mixture increases, the inner microspheres formed by the phase separation become smaller and denser owing to the high cross-linking [18, 20]. Consequently, small D_p, large A_p, and high V_p could be obtained at a high content of DVB. However, the improvement in the porous characteristics was not so significant as expected from the literature [9, 10, 19]. We thought this also stemmed from the effect of the side chain in the PS seed copolymerized with UA. Many side chains present in the swollen phase would restrict the effective formation of smaller inner microspheres by locking in their phases, interpenetrating network structure, resulting in slightly favored phase-separation of S–DVB copolymers.

Formation of porous structures

The procedure for the formation of porous polymer particles has been proposed to understand the porous characteristics [16–20]. Initially, PS seed particles are dissolved in the mixture of S, DVB, toluene, and BPO because it itself is a good solvent for PS (when cross-linked PS seed used, it is expanded by the monomer mixture). After the initiation, the growing S–DVB copolymers started to collapse by losing their solvation sheath in the monomer mixture. As the polymerization continued, the S–DVB copolymers are separated to generate inner microspheres. Finally, a viscous cross-linked poly(S-*co*-DVB) phase is formed.

The porous characteristics, such as pore size, pore volume, and surface area are influenced by the molecular weight of the PS seed particles, the degree of cross-linking, and the diluent content. In this study, we tried to understand the pore formation procedure of poly(S-*co*-DVB) particles using PS seed particles produced by the dispersion polymerization of S and UA. A schematic representation of the formation of porous poly(S-*co*-DVB) particles with different molecular weight of PS seed particles is shown in Fig. 8. The porosity was successfully controlled by manipulating the molecular weight of the PS seed with UA. The PS seed of low molecular weight showed microscopic phase separation of S–DVB copolymers. In contrast, the PS seed of high molecular weight displayed macroscopic phase-separation. Even in the case of the cross-linked PS seed, macroporous poly(S-*co*-DVB) particles could be obtained. In the system using a high-molecular-weight PS seed, the side chains created during the copolymerization of UA with growing PS diminished the effect of the degree of cross-linking of the second polymer and the dilution of the polymerizing droplet phase. Since the toluene used in this study was a good solvent for all the ingredients, the pore volume was not sufficiently high as listed in Table 3. The growing S–DVB chains seemed to collapse readily after the extraction of toluene; however, it is expected that the pore volume can be enlarged by replacing the diluent with poor solvents such as heptane [18].

Conclusions

Porous poly(S-*co*-DVB) particles were produced in a macroporous region by changing the molecular weight of the PS seed particles, the contents of DVB and toluene, and their morphology and porous characteristics were studied. The molecular weight of the PS seed particles was successfully controlled with UA. The porous structure was dependent on the molecular weight of the PS seed particles. It was found that the content of

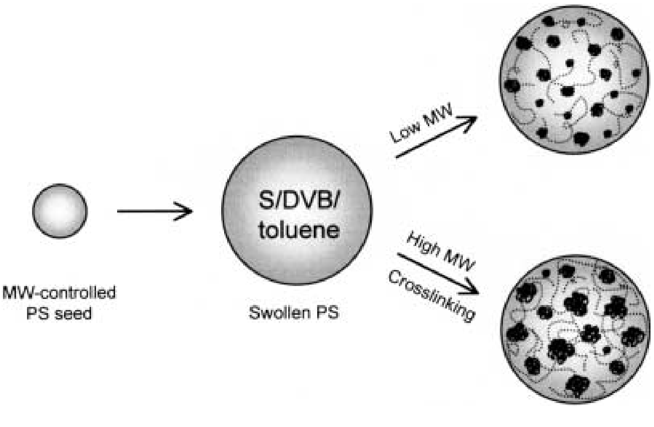


Fig. 8 Schematic representing the formation of porous poly(S-*co*-DVB) particles

toluene did not have a serious influence on the change in the porosity at high molecular weight of the PS seed particles, which is due to many side chains created by UA. The formation of a porous structure by the seeded polymerization utilizing the cross-linked seed particles provided an alternative approach to the production of porous particles for further study.

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