Electron Microscopic Observation of Uniform Macroporous Particles. II. Effect of DVB Concentration

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ABSTRACT: The electron microscopic observation of uniform and macroporous poly(styrene-*co*-divinylbenzene) particles prepared by a two-step seeded polymerization method was performed. In the synthesis of uniform macroporous particles, the uniform polystyrene latices produced by a dispersion polymerization method with two different sizes and average molecular weights were utilized as the seed particles. The seed particles were first swollen with dibutylphthalate and then with a monomer phase, including styrene and divinylbenzene. The macroporous structure of the final particles was achieved by using a porogen mixture consisting of dibutylphthalate and linear polystyrene. The linear polystyrene part of the porogen solution was directly obtained from the seed latex. The macroporous particles with different diameters and porosities were produced by changing the divinylbenzene concentration between 25 and 100% in the repolymerization step. The effect of divinylbenzene concentration on the size and the surface morphology of the final particles were investigated by scanning electron microscopy. The internal structure of the final particles was analyzed by transmission electron microscopy. The results indicated that the average size of the final particles increased with the increasing divinylbenzene concentration. The increase in the DVB concentration also led to an increase in the average pore size. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2291–2302, 1999

Key words: porous particles; macroporous beads; polystyrene; dispersion polymerization; activated swelling method; monodisperse particles; large uniform particles

INTRODUCTION

The uniform macroporous particles are usually obtained in the form of styrene–divinylbenzene copolymer particles by the multistep seeded polymerization methods.[1–8] In the method developed by El-Aasser et al., linear polystyrene–hexane, linear polystyrene–toluene or linear polystyrene was used as the diluent phase for the synthesis of uniform particles with pore volumes up to 0.9 mL/g and specific surface areas up to 200 m^2/g.[4–5] They also found that the specific surface area and the pore volume significantly increased, and the median pore size decreased with the increasing divinylbenzene concentration in the monomer phase used for the swelling of seed particles.[4] Another multistep-seeded polymerization procedure was developed by Frechet and coworkers for the synthesis of uniformly sized porous poly(styrene-*co*-divinylbenzene) beads.[7–8] In their method, a porogenic mixture including linear polystyrene and dibutylphthalate or chlorododecane was utilized to create porosity within the seeded particles. This group reported that the pore volume and the specific surface area increased with the increasing divinylbenzene content of the monomer phase.[7]

In our previous study, we started the multistep polymerization procedure with reasonably large seed latex particles having relatively lower average molecular weight, and we obtained the polymeric part of the porogen mixture directly from

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the seed latex and an isomer mixture of divinylbenzene (DVB) was selected as the monomer phase for the swelling of seed particles.[9] Therefore, the final monodisperse macroporous particles were achieved with the repolymerization of DVB within the swollen seed particles. In the present study, we used a monomer phase, including both styrene and DVB, for the swelling of seed particles, and the final macroporous particles were obtained in the form of the styrene–divinylbenzene copolymer. The effects of divinylbenzene concentration on the average size, the surface morphology, and the pore structure of final particles were determined by electron microscopy.

EXPERIMENTAL

Materials

Styrene (Yarpet A.S., Turkey) was distilled under vacuum and stored in the refrigerator until use. The crosslinker, divinylbenzene (DVB; including 65% DVB *m*- and *p*-isomers and 33% ethylvinylbenzene isomers; Merck AG, Germany) was treated with aqueous NaOH solution (5% *w*/*v*) to remove the inhibitor. Dibutyl phthalate (Polisan A.S., Turkey), benzoyl peroxide (BPO; 97% of the active compound; Aldrich Chem. Co.), sodium dodecyl sulfate (SDS; Sigma Chemical Co., USA), and polyvinylalcohol (PVA; 87–89% hydrolyzed; M_{η}, 85.000–146.000; Aldrich Chem. Co.) were used without further purification. All polymerizations were performed by using distilled deionized water. Methylene chloride (MC; Merck AG) was selected as the solvent in the extraction of macroporous particles.

Preparation of Uniform Macroporous Particles

In this study, a modified form of the multistep polymerization procedure developed by Galia et al. was used to prepare uniform macroporous particles.[7] Based on the proposed modification, two different seed latices with different sizes, and average molecular weights were prepared by the dispersion polymerization of styrene. The seed letex preparation and the characterization procedures were described elsewhere.[9] The macroporous uniform latex particles were produced by a two-step seeded polymerization method starting from these latices. In a typical procedure, 0.2 mL of DBP was emulsified by ultrasonication within 15 mL of aqueous medium including 0.25% (*w*/*w*) SDS. 1 mL of aqueous dispersion including 0.12 *g* of PS seed particles was added into the aqueous DBP emulsion. The resulting dispersion was stirred with 250 rpm at +4°C for 24 h for complete absoption of DBP by the seed particles. In the second stage, DBP-swollen seed particles were reswollen with the monomer phase. For this step, 0.6 mL of the monomer phase, including 0.3 mL of styrene, 0.3 mL of DVB, and 0.04 g of BPO was emulsified by ultrasonication within 15 mL of aqueous medium, including 0.25% (*w*/*w*) SDS. The monomer emulsion was then mixed with the aqueous dispersion of DBP-swollen seed particles. The absorption of monomer phase by the DBP-swollen seed particles was conducted at +4°C for 24 h with a 250-rpm stirring rate. The resulting emulsion was transferred into the Pyrex polymerization reactor, together with 3 mL of 10% aqueous PVA solution, and purged with bubbling nitrogen for about 5 min. The repolymerization of monomer phase within the seed particles was conducted at 70°C for 24 h with a 120-cpm shaking rate in the sealed reactors. The repolymerization step provided large uniform and macroporous latex particles, together with some amount of small particles (i.e., about 1 μm), as a by-product. The final particle dispersion was washed with ethanol and water to remove small particles from the dispersion medium, absorbed DBP, and physically bound emulsifier from the large macroporous particles by applying a serum replacement method, including successive centrifugations. The detailed washing procedure was described elsewhere.[9]

Characterization of Uniform Macroporous Particles

The dried particles were extracted in a Soxhelet apparatus with methylene chloride for 24 h. The average particle size, size distribution, and surface morphology of particles were evaluated by a scanning electron microscope (JEOL, JEM 1200EX, Japan) before and after the extraction process.[9] The internal structure of macroporous particles were observed by the ultrathin sections of OsO_4-stabilized particles in a transmission electron microscope (JEOL, JEM 1200EX).[9]

RESULTS AND DISCUSSION

The effect of DVB concentration on the average size and the porosity of uniform macroporous particles were investigated by using two different seed latices, coded as SL1 and SL3, respectively.[9] In the first group of these runs, DVB concentra-

Table I The Effect of DVB Concentration on the Average Size of Uniform Large Latex Particles Produced by Using SL1 as the Seed Latex

DBP/SL (mL g)[a]	DVB (%)	D_p (μm)[b]	D_p/D_s (μm/μm)[c]
0.83	25	3.8	2.00
0.83	50	4.0	2.11
0.83	100	4.0	2.11
1.67	25	4.0	2.11
1.67	50	3.9	2.05
1.67	100	4.2	2.21

Seed latex properties: M_w, 5.4×10^4; M_w/M_n, 3.04; size, 1.9 μm.

DBP swelling: DBP-to-seed latex ratio, variable; SDS concentration, 0.25% (*w*/*w*); +4°C; 24 h, 250 rpm.

Monomer swelling: Monomer-to-seed latex ratio, 10 mL/g; BPO concentration, 66.7 mg/mL; SDS concentration, 0.25% (*w*/*w*); +4°C; 24 h, 250 rpm.

Repolymerization conditions: PVA, 1% (*w*/*w*); 70°C; 24 h; 120 cpm.

[a] DBP/SL represents the dibutylphthalate-to-seed latex ratio.

[b] D_p is the diameter of the final particle.

[c] D_s is the diameter of the seed latex.

tion in the monomer phase (i.e., the concentration of isomer mixture comprising divinylbenzene and ethylvinylbenzene) was changed between 25 and 100% *v*/*v,* by using SL1 as the seed latex and by fixing the DBP-to-seed latex ratio to 0.83 g mL. The properties of seed latex and the synthesis conditions of large uniform particles are given in Table I. A scanning electron microscopy (SEM) photograph of the final particles produced with a 50% DVB concentration is given in Figure 1. As seen here, the final particles were obtained in the monodisperse form. The monodispersity observed with the other DVB concentrations was not different than that given in Figure 1. The average size values of final particles produced in this set are also given in Table I. As seen here, the average size values of the final particles produced in this set were around 4.0 μm, and the average size was slightly higher when the repolymerization was performed by using only DVB as the monomer phase (i.e., no styrene was used). The effect of DVB concentration on the surface morphology of the final particles before the methylene chloride extraction is shown in Figure 2. As seen here, the particle surface included only one crater-like pore in all samples. The size of holes increased with the increasing DVB concentration, and the surface holes of about 1 μm in size were observed for the particles produced by using only DVB. The pore structure on the particle surface was also checked after the methylene chloride extraction. The SEM photographs of the same beads after the extraction are given in Figure 3. As seen here, no significant change was observed on the particle size and surface morphology by the extraction.

In the second set, the DBP-to-seed latex ratio was fixed to a higher value (i.e., 1.67 mL/g), and the DVB concentration in the monomer phase was changed between 25 to 100% (based on volume) by using SL1 as the seed latex. The average size values of the particles produced with different DVB concentrations are given in Table I. The effect of DVB concentration on the size and monodispersity of final particles is shown in Figure 4. As seen here, highly monodisperse samples could be produced with all DVB concentrations. The SEM photographs indicating the surface morphology of particles produced in this set are given in Figure 5. These photographs were obtained after the methylene chloride extraction. As seen here, the surface morphology of particles produced with the lowest DVB concentration (25%) was significantly different, and the particle surface in Figure 5(A) included a higher number of smaller pores relative to the particles, including crater-like holes [i.e., Fig. 5(B) and (C)]. Similar to the tendency observed in the first set, the size of pores on the surface of particles increased by the increasing the DVB concentration. The transmission electron microscopy (TEM) photographs showing the internal structure of the particles produced by using 25 and 100% DVB are given in

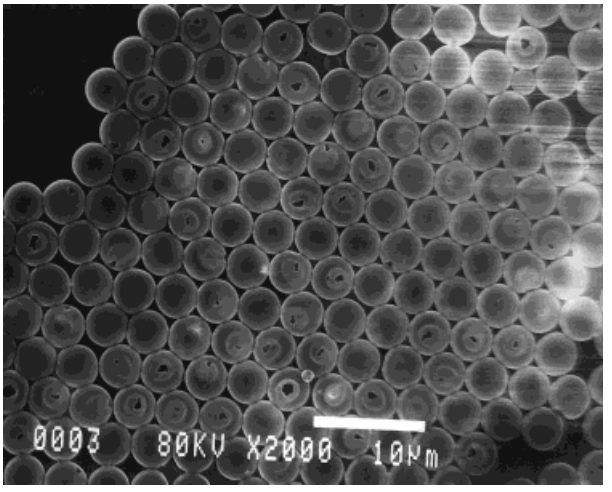

Figure 1 A SEM photograph of the final particles produced with 50% DVB concentration in the monomer phase (seed latex, SL1; DBP-to-seed latex ratio, 0.83 mL g; monomer-to-seed latex ratio, 10 mL/g; magnification, 2000×).

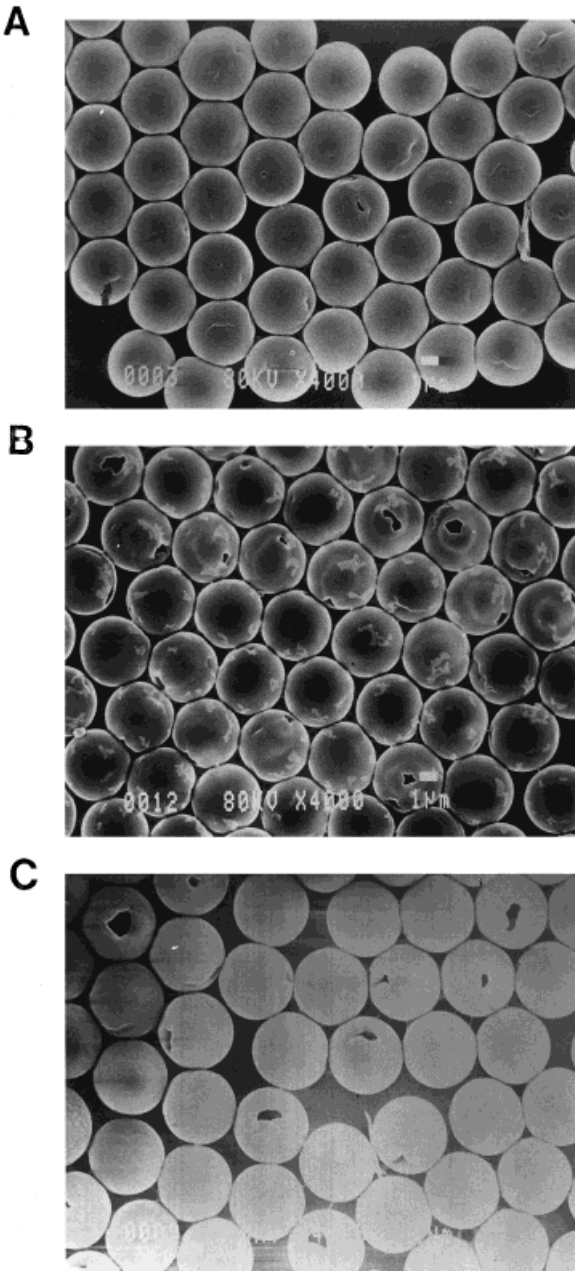

Figure 2 The effect of DVB concentration on the surface morphology of the final particles produced with the seed latex of SL1. These photographs were taken before the methylene chloride extraction [DBP-to-seed latex ratio, 0.83 mL/g; monomer-to-seed latex ratio, 10 mL/g; DVB concentration in the monomer phase (vol %)]: (A) 25, (B) 50, and (C) 100 (4000× magnification).

Figure 6. These photographs were also obtained after the methylene chloride extraction. As seen in these photographs, the pore volume (i.e., the porosity of the particle) was higher in the presence of higher DVB concentration.

Another uniform polystyrene latex coded as SL3 was also tried as the seed for the preparation of macroporous particles under identical conditions with the first two groups of experiments. Note that the average molecular weight of SL3

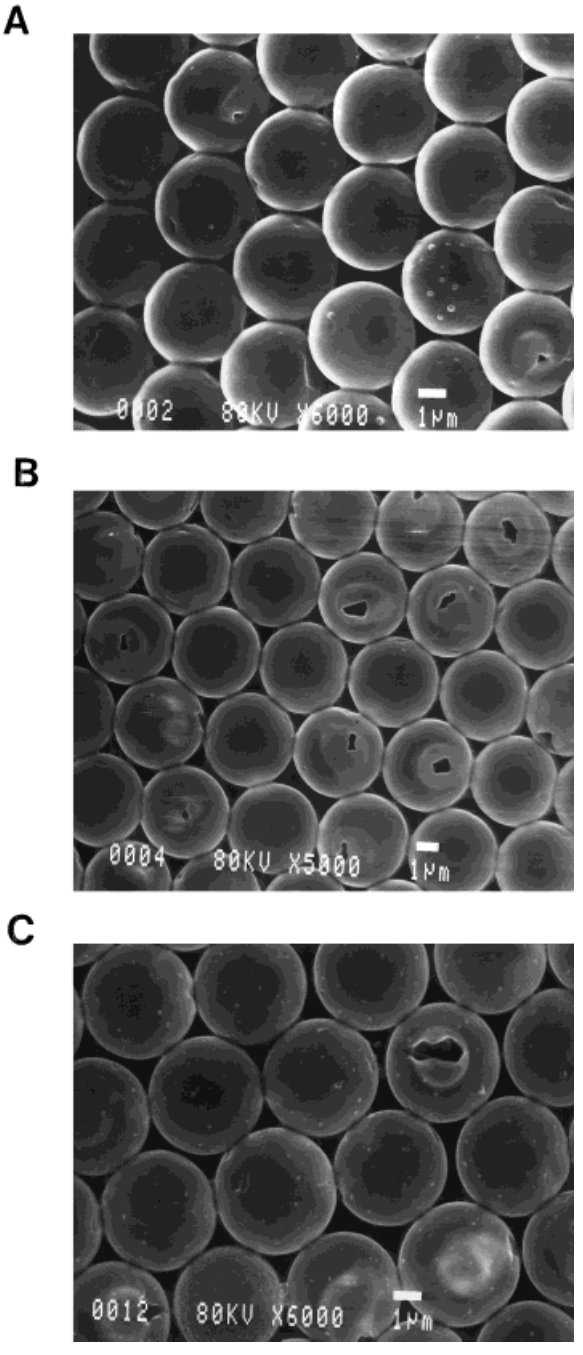

Figure 3 The effect of DVB concentration on the surface morphology of the final particles produced with the seed latex of SL1. These photographs were taken after the methylene chloride extraction [DBP-to-seed latex ratio, 0.83 mL/g; monomer-to-seed latex ratio, 10 mL/g; DVB concentration in the monomer phase (vol %)]: (A) 25, (B) 50, and (C) 100 [6000× magnification for (A) and (C) and 5000× for (B)].

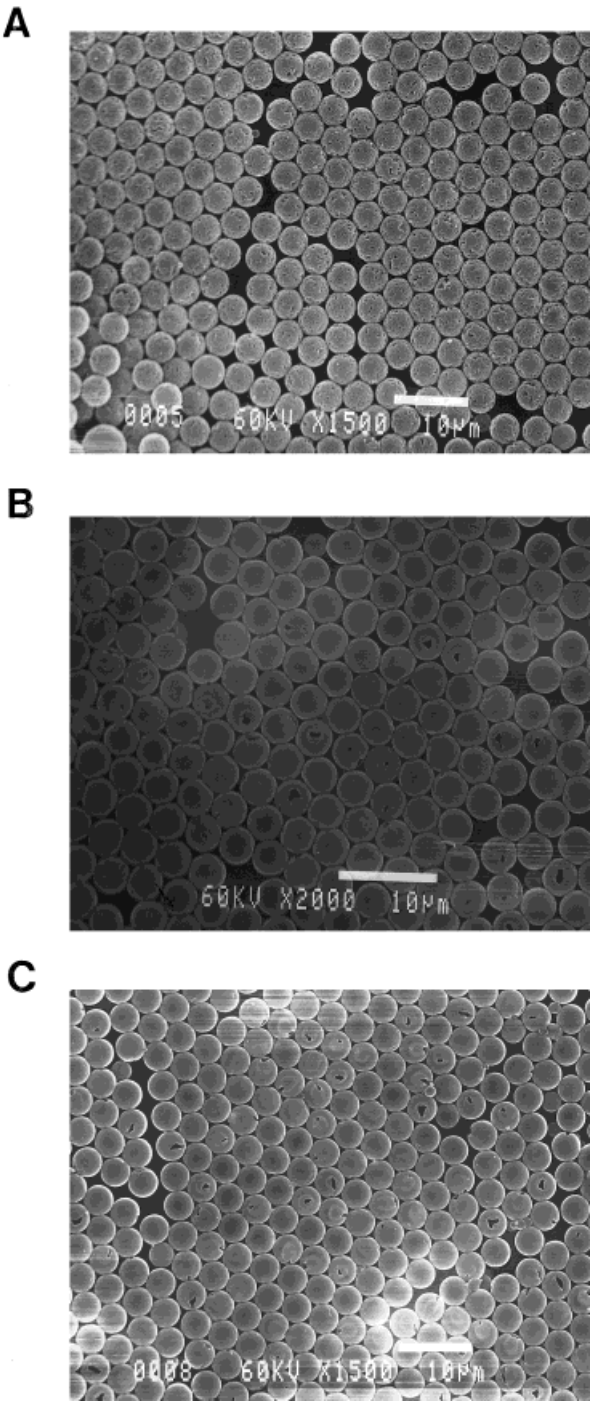

Figure 4 The effect of DVB concentration on the size and monodispersity of final particles produced with the seed latex of SL1 [DBP-to-seed latex ratio, 1.67 mL/g; monomer-to-seed latex ratio, 10 mL/g; DVB concentration in the monomer phase (vol %)]: (A) 25, (B) 50, and (C) 100 [1500× magnification for (A) and (C) and 2000× for (B)].

was significantly lower relative to that of SL1 (Table II). In the experiments with the seed latex of SL3, the monomer-to-seed latex ratio was fixed to 10 mL/g, and the DVB concentration in the monomer phase was changed at two levels (i.e., 25 and 100%) by fixing the DBP-to-seed latex ratio to

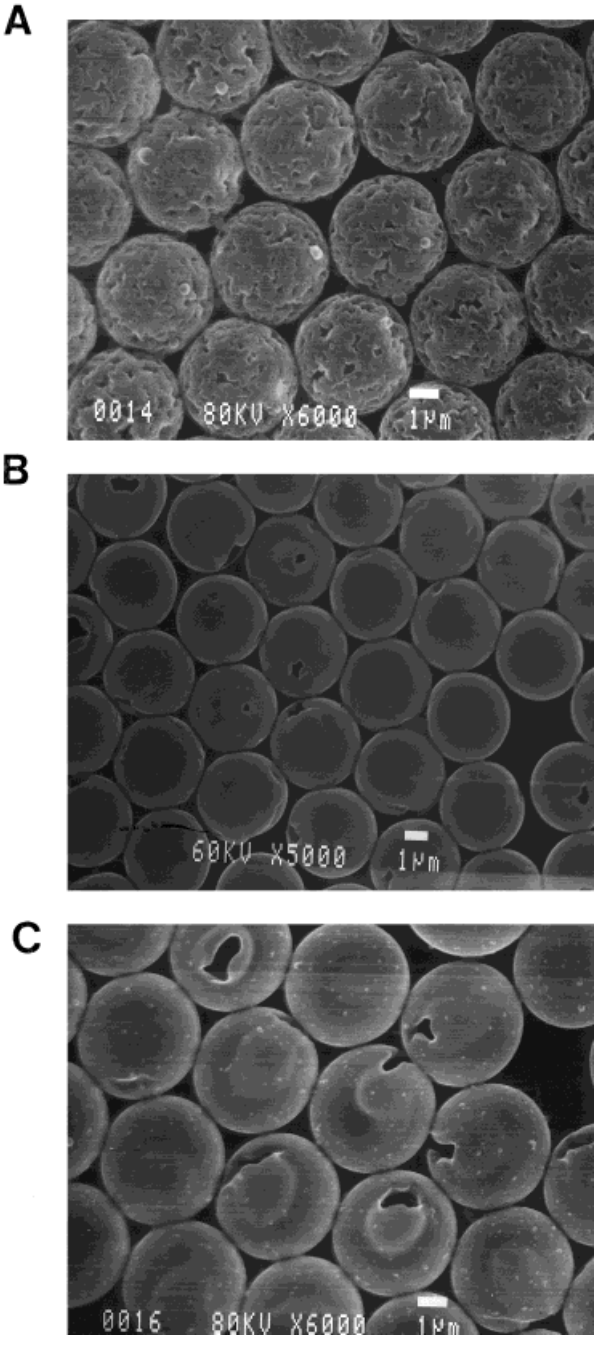

Figure 5 The effect of DVB concentration on the surface morphology of the final particles produced with the seed latex of SL1. These photographs were taken after the methylene chloride extraction [DBP-to-seed latex ratio, 1.67 mL/g; monomer-to-seed latex ratio, 10 mL/g; DVB concentration in the monomer phase (vol %)]: (A) 25, (B) 50, and (C) 100 [6000× magnification for (A) and (C) and 5000× for (B)].

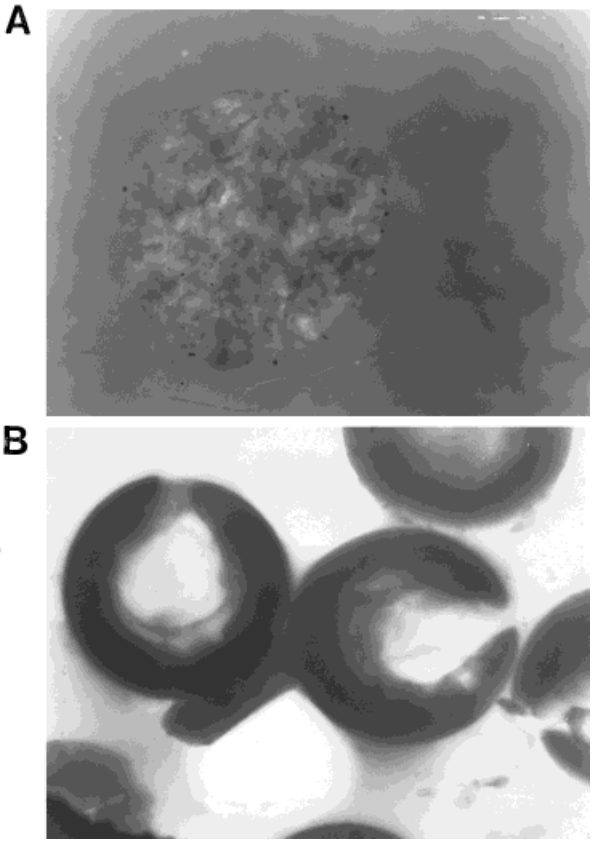

Figure 6 The TEM photographs showing the internal structure of the particles produced with the seed latex of SL1. These photographs were taken after the methylene chloride extraction [DBP-to-seed latex ratio, 1.67 mL/g; monomer-to-seed latex ratio, 10 mL/g; DVB concentration in the monomer phase (vol %)]: (A) 25 and (B) 100 [20.000× magnification for (A) and 6000× for (B)].

0.83 or 1.67 mL/g. Under these conditions, the monodisperse particles were also achieved with all DVB concentrations, as exemplified in Figure 7. The average size values of final particles produced with SL3 are given in Table II. As seen here, slightly higher bead size values were obtained when only DVB was used as the monomer phase. The surface morphology of the particles produced with different DVB concentrations and by using the seed latex of SL3 are shown in Figure 8. These photographs were obtained before the methylene chloride extraction. As seen here, the surface morphology of these particles was different than that observed with the seed latex of SL1. Reasonably smaller pores on the surface of the particles were produced in these runs. It should be noted that the molecular weight of SL3 was lower relative to SL1, and the decrease in the molecular weight of the polymeric part of porogen mixture caused a decrease in the average pore size, as discussed by Frechet and coworkers[8] and then by us[9] elsewhere. The surface morphology of particles were also examined by SEM after the extraction. These SEM photographs are given in Figure 9. As seen here, the extraction process caused no significant change on the surface of the particles having a sponge-like pore structure. The reasons of this result were explained in our previous study.[9] The TEM photographs showing the internal structure of the particles produced with the DBP-to-seed latex ratio of 1.67 mL/g are given in Figure 10. As seen in Figure 10(A), the porosity was very low for the beads produced with 25% of DVB concentration, although the existence of reasonably small pores on the surface of the same particles was detected by the SEM examination [i.e., Fig. 9(C)]. However, a sponge-like pore structure was observed for the internal part of the beads produced by using only DVB as the monomer phase [Fig. 10(B)]. Therefore, an increase in the bead porosity was again observed with the increasing crosslinker concentration in the monomer phase.

To achieve final particles having higher pore volumes starting from the seed latex of SL3, the

Table II The Effect of DVB Concentration on the Average Size of Uniform Large Latex Particles Produced by Using SL3 as the Seed Latex

M/SL (mL/g)	DBP/SL (mL/g)	DVB (%)	D_p (μm)	D_p/D_s (μm μm)
10	0.83	25	10.7	1.88
10	0.83	100	12.5	2.19
10	1.67	25	11.4	2.00
10	1.67	100	12.5	2.19
6	0.83	25	8.6	1.51
6	0.83	50	9.8	1.72
6	0.83	100	9.1	1.60
6	1.67	25	9.5	1.67
6	1.67	50	10.0	1.75
6	1.67	100	9.1	1.60

Seed latex properties: M_w, 1.99×10^4; M_w/M_n, 2.50; size, 5.7 μm.

DBP swelling: DBP-to-seed latex ratio, variable; SDS concentration, 0.25% (*w*/*w*); +4°C; 24 h; 250 rpm.

Monomer swelling: BPO concentration, 66.7 mg/mL; SDS concentration, 0.25% (*w*/*w*); +4°C; 24 h; 250 rpm.

Repolymerization conditions: PVA, 1% (*w*/*w*); 70°C; 24 h; 120 cpm.

[a] M/SL represents the monomer-to-seed latex ratio.

[b] DBP/SL represents the dibutylphthalate-to-seed latex ratio.

[c] D_p is the diameter of the final particle.

[d] D_s is the diameter of the seed latex.

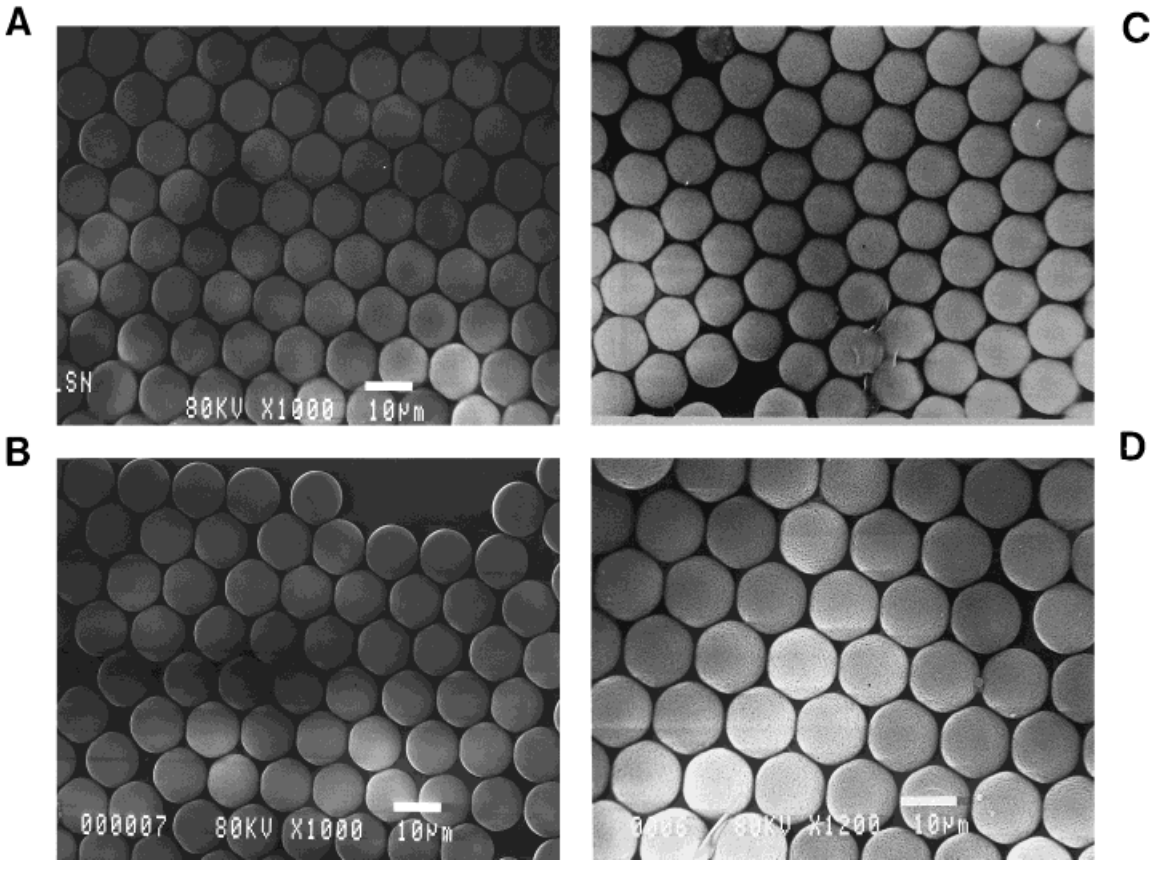

Figure 7 The effect of DVB concentration on the size and monodispersity of final particles produced with the seed latex of SL3 [monomer-to-seed latex ratio, 10 mL/g; DBP-to-seed latex ratio (mL/g); DVB concentration in the monomer phase (vol %)]: (A) 0.83, 25; (B) 0.83, 100; (C) 1.67, 25; (D) 1.67, 100 [1000× magnification for (A), (B), and (C) and 1200× for (D)].

monomer-to-seed latex ratio was reduced by increasing the amount of seed latex. Therefore, the linear polymer concentration in the porogen solution increased before the repolymerization step. For this reason, an increase in the porogen viscosity was achieved relative to the previous set carried out with the seed latex of SL3. In this set, the monomer-to-seed latex ratio was fixed to 6 mL/g and the DBP-to-seed latex ratio was changed at two levels (i.e., 0.83 and 1.67 mL/g). At each DBP-to-seed latex ratio, the DVB concentration in the monomer phase was changed between 25 and 100% by using the seed latex of SL3. The monodispersity of final particles produced with different DVB concentrations are shown by the SEM photographs in Figure 11 and 12 for the DBP-to-seed latex ratios of 0.83 and 1.67 mL/g, respectively. As seen in these figures, the monodispersity was reasonably good for all samples obtained in this set. The average size values of these particles are also given in Table II. The monodisperse particles between 8.6–10.0 μm in size were produced in this group of experiments. The lower monomer-to-seed latex ratio (i.e., 6 mL/g) led to a decrease in the average size of the final particles relative to those achieved in the previous set in which the monomer-to-seed latex ratio was 10 mL/g. The detailed surface morphology of the particles produced with the monomer-to-seed latex ratio of 6 mL/g are given in Figure 13 and 14. These photographs were taken with the methylene-chloride-extracted beads. At constant DVB concentration, reasonably larger pores on the particle surface were observed with the monomer-to-seed latex ratio of 6 mL/g relative to those with the monomer-to-seed latex ratio of 10 mL/g (see Fig. 9). On the other hand, the number and the average size of pores on the particle surface increased with the increasing DVB concentration. This finding was especially clear for the DBP-to-

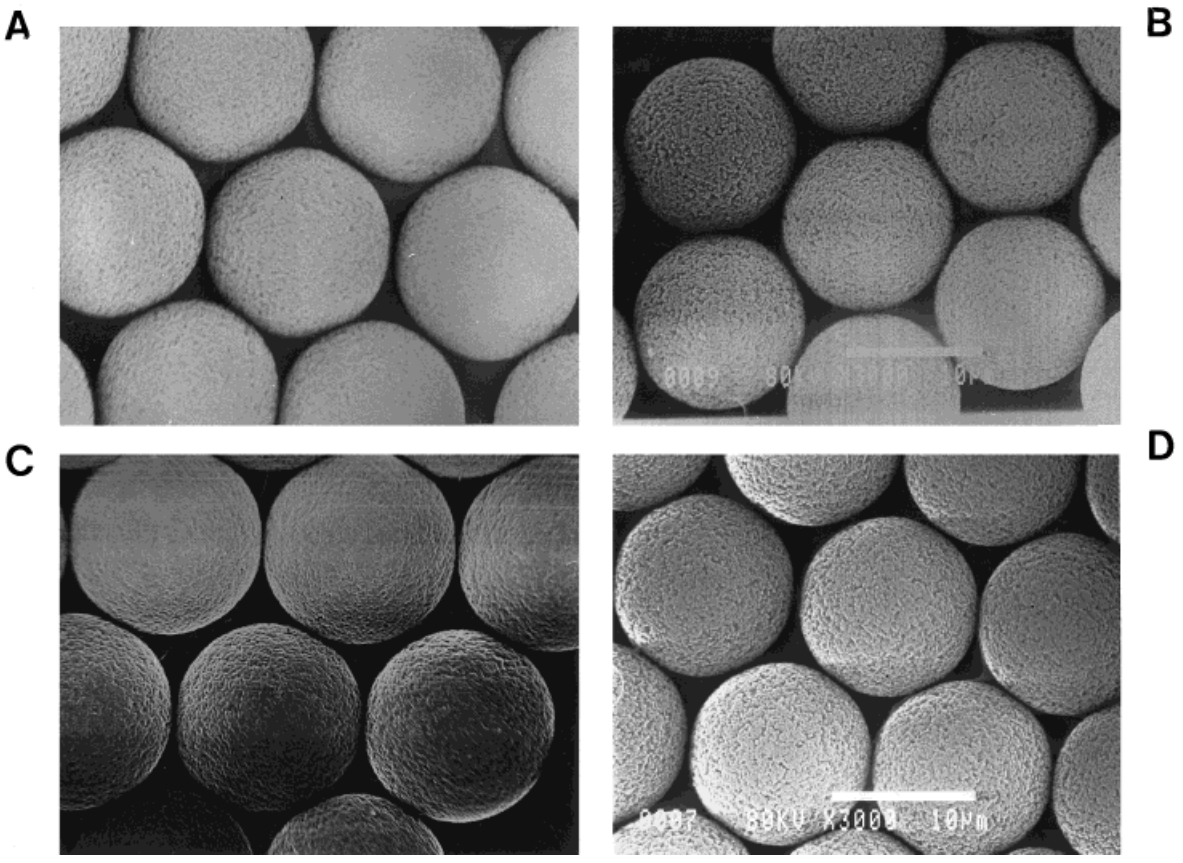

Figure 8 The effect of DVB concentration on the surface morphology of the final particles produced with the seed latex of SL3. These photographs were taken before the methylene chloride extraction [monomer-to-seed latex ratio, 10 mL/g; DBP-to-seed latex ratio (mL/g); DVB concentration in the monomer phase (vol %)]: (A) 0.83, 25; (B) 0.83, 100; (C) 1.67, 25; (D) 1.67, 100 [4000× magnification for (A) and (C) and 3000× for (B) and (D)].

seed latex ratio of 1.67 mL/g (Fig. 14). The internal structures of the beads produced in this set were exemplified with the TEM photographs of the particles produced with the DVB concentrations of 25 and 100% in Figure 15. As seen here, no significant pore formation occurred with 25% of DVB concentration when the monomer-to-seed latex ratio was 6 mL/g. However, a clear increase in the porosity when only DVB was used as the monomer phase. For this case, the internal part of the beads produced with a lower monomer-to-seed latex ratio (i.e., 6 mL/g) included larger pores relative to that obtained with the monomer-to-seed latex ratio of 10 mL/g (i.e., Fig. 10). Larger pore size may be explained by the increase in the viscosity of porogen solution with the increasing amount of seed latex (i.e., a decreasing monomer-to-seed latex ratio). By considering the mechanism proposed by Cheng et al. for the pore formation process,[4] it may be concluded that the larger microspheres or agglomerates are formed during the repolymerization step when the viscosity of the porogen mixture, including DBP and linear polystyrene, is higher. For this reason, the voids between the fixed larger agglomerates or microspheres become larger within the forming macroporous particles, which, in turn, leads to an increase in the pore size.

The results of our study indicated that the porosity (i.e., the pore volume) increased with the increasing DVB concentration for either crater-like or sponge-like pore structures obtained with the SL1 and SL3 seed latices, respectively. This result may be explained by the pore formation mechanism proposed by Cheng et al.[4] According to this mechanism, the process of pore formation comprised two main steps. These were production and agglomeration of highly crosslinked gel mi-

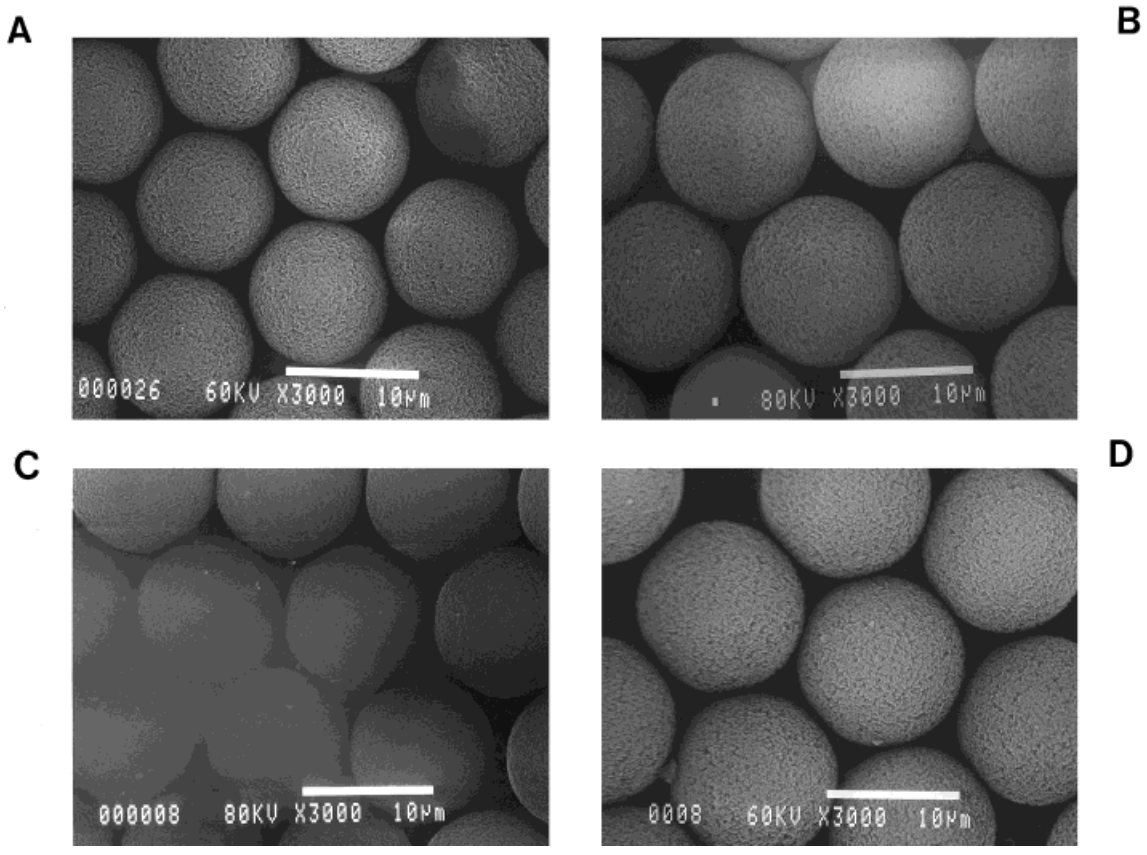

Figure 9 The effect of DVB concentration on the surface morphology of the final particles produced with the seed latex of SL3. These photographs were taken after the methylene chloride extraction [monomer-to-seed latex ratio, 10 mL/g; DBP-to-seed latex ratio (mL/g); DVB concentration in the monomer phase (vol %)]: (A) 0.83, 25; (B) 0.83, 100; (C) 1.67, 25; (D) 1.67, 100 (3000× magnification).

crospheres within the particle and the binding together of microspheres/agglomerates for the fixation of network structure. In our study, constant volume of porogenic mixture (constant amount of seed latex and dibutyl phthalate) was used while changing the DVB concentration in the monomer phase. Therefore, the porosity increase with the increasing DVB concentration was observed while the volume of the porogenic mixture was constant. After the copolymerization step, the fixed microspheres or agglomerates within the formed bead structure are swollen by some part of the porogen solution. However, another part of porogen is located within the voids between the fixed gel microspheres (i.e., within the macropores). In the case of higher DVB concentration within the monomer phase, the degree of crosslinking of the fixed gel microspheres is expected to be higher, which decreases their porogen absorption capacity. The largest part of porogen solution is possibly located within the voids. Then, an efficient phase separation occurs when the crosslinker concentration is higher. Thus, the macroporosity of the final beads increases with the increasing DVB concentration. The phase separation efficiency may be defined as the ratio of volume of porogen within voids after copolymerization (i.e., total pore volume) to the used porogen volume at the beginning of copolymerization (i.e., total volume of nonsolvent plus seed latex used in the run). In the case of higher macroporosity, the volume fraction of porogen within the voids will be higher after the copolymerization.

To determine the effect of DVB concentration on the porosity of uniform particles, the porous properties of particles produced by different polymerization methods were measured by different techniques. Galia et al. developed a multistage polymerization procedure using linear polystyrene and 1-chlorodecane mixture as a diluent for

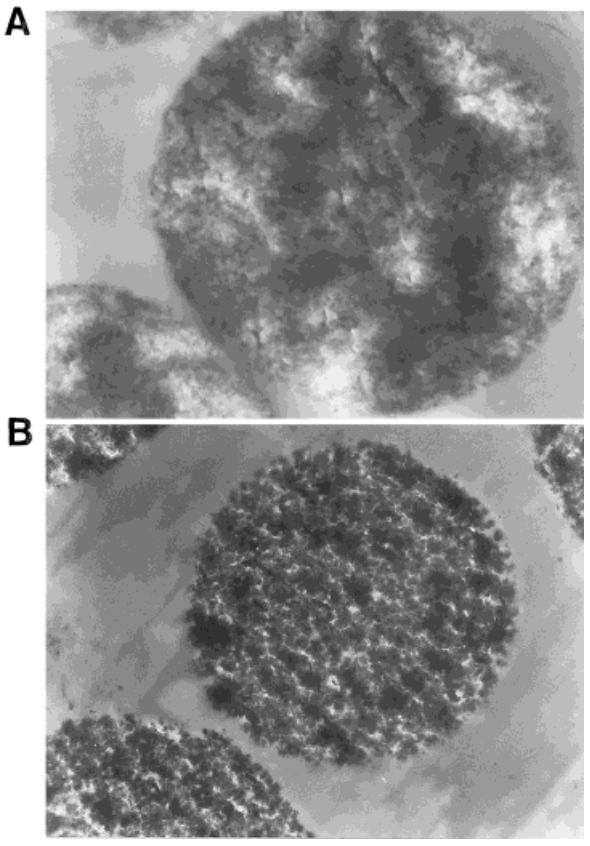

Figure 10 The TEM photographs showing the internal structure of the particles produced with the seed latex of SL3. These photographs were taken after the methylene chloride extraction [DBP-to-seed latex ratio, 1.67 mL/g; monomer-to-seed latex ratio, 10 mL/g; DVB concentration in the monomer phase (vol %)]: (A) 25 and (B) 100 [3000× magnification for (A) and 5000× for (B)].

producing uniform porous particles.[7] The macropore volume of the particles produced by their method was roughly insensitive to the DVB concentration in the repolymerization step. They reported that the total pore volume of the uniform particles determined by mercury porosimeter (i.e., the volume of pores in the size range of 10–1000 nm) was not significantly affected by the DVB concentration changed between 40–80%.[7] They also found that the total pore volume measured by nitrogen adsorption method (i.e., the volume of micropores determined by BET, <2–50 nm) clearly increased by the increasing DVB concentration. On the other hand, Cheng et al. developed a different multistage polymerization procedure for the synthesis of uniform macroporous particles, in which the linear polystyrene and *n*-hexane mixture was used as a diluent.[4] A clear increase in the pore volume measured by mercury porosimetry (i.e., the volume of the pores larger than 10 nm) with the increasing DVB concentration was reported by this group.[4] In their study, the increase in the pore volume was explained by the higher degree of phase separation occurring

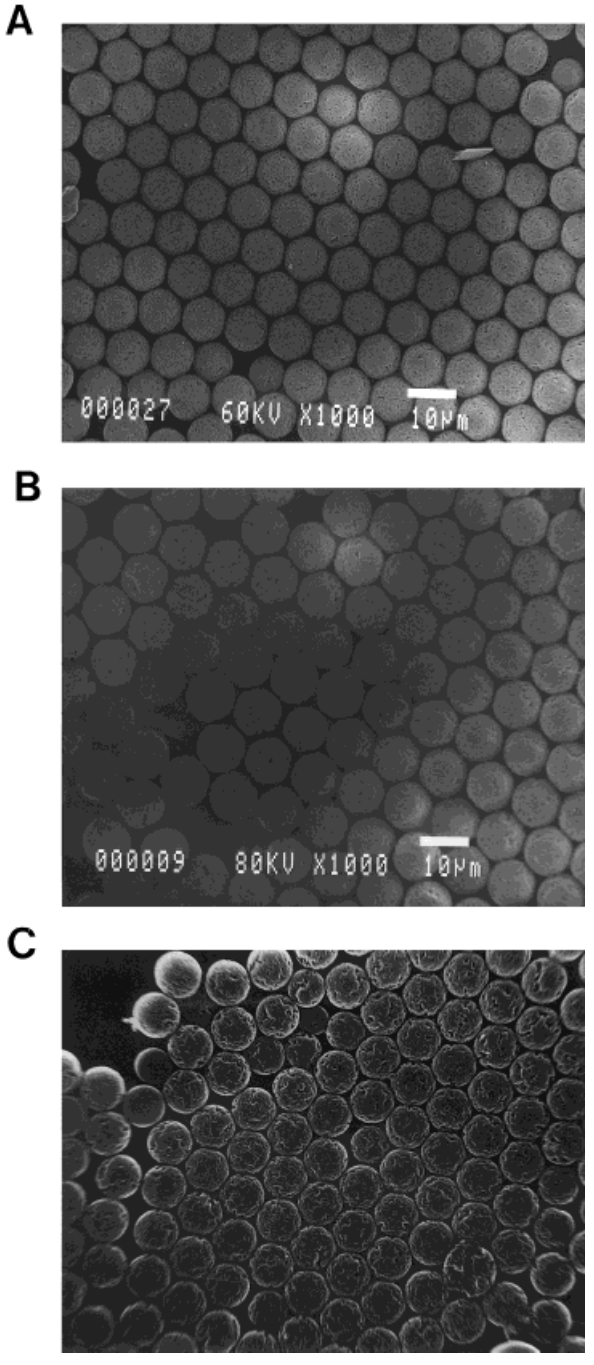

Figure 11 The effect of DVB concentration on the size and monodispersity of final particles produced with the seed latex of SL3 [DBP-to-seed latex ratio, 0.83 mL/g; monomer-to-seed latex ratio, 6 mL/g; DVB concentration in the monomer phase (vol %)]: (A) 25, (B) 50, and (C) 100 (1000× magnification).

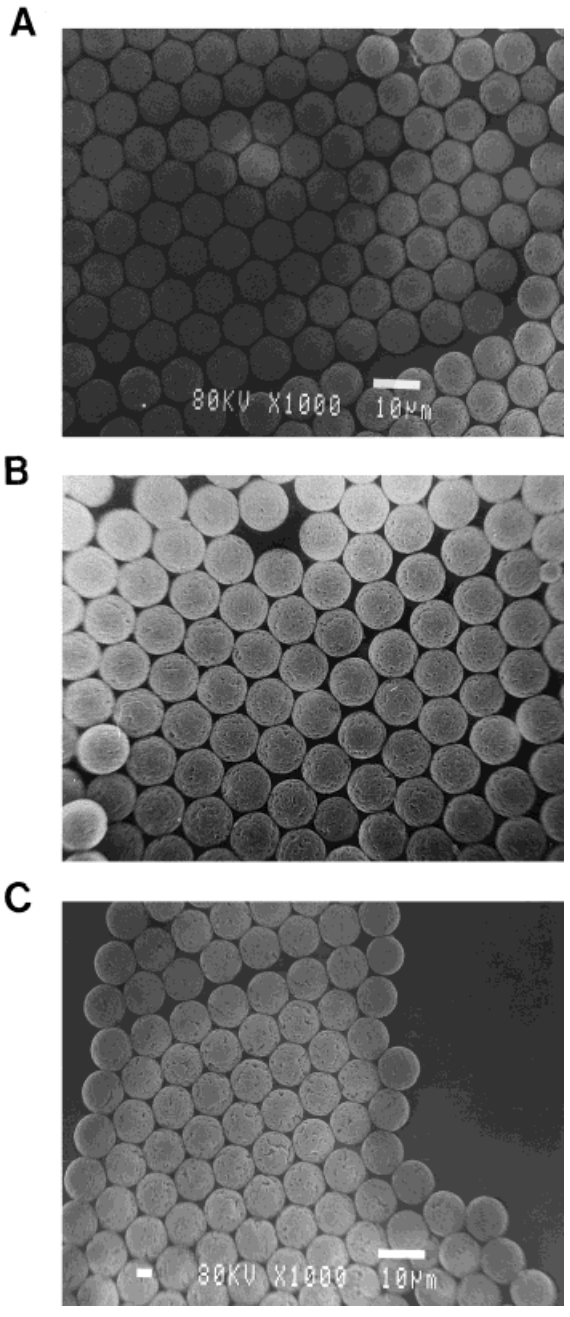

Figure 12 The effect of DVB concentration on the size and monodispersity of final particles produced with the seed latex of SL3 [DBP-to-seed latex ratio, 1.67 mL/g; monomer-to-seed latex ratio, 6 mL/g; DVB concentration in the monomer phase (vol %)]: (A) 25, (B) 50, and (C) 100 (1000× magnification).

in the existence of higher DVB concentration within the swollen particles.[4] In our study, we used a porogen mixture, including dibutylphthalate and linear polystyrene, directly coming from the seed latex for the synthesis of uniform porous particles, and the increase in the porosity (i.e., the pore volume) with the increasing DVB concentration was shown both by the SEM and TEM photographs. This increase was observed for either

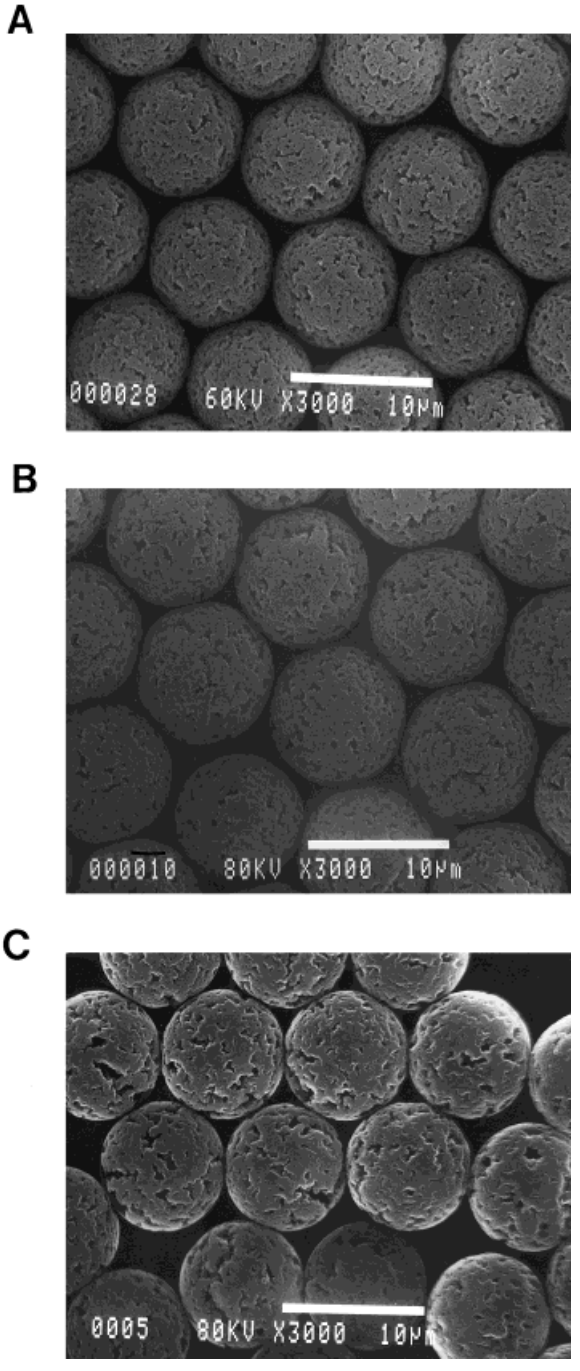

Figure 13 The effect of DVB concentration on the surface morphology of final particles produced with the seed latex of SL3. These photographs were taken after the methylene chloride extraction [DBP-to-seed latex ratio, 0.83 mL/g; monomer-to-seed latex ratio, 6 mL/g; DVB concentration in the monomer phase (vol %)]: (A) 25, (B) 50, and (C) 100 (3000× magnification).

the particles with sponge-like pore structure having an average pore size of about 100 nm or the particles with crater-like pore structure having pores usually larger than 500 nm.

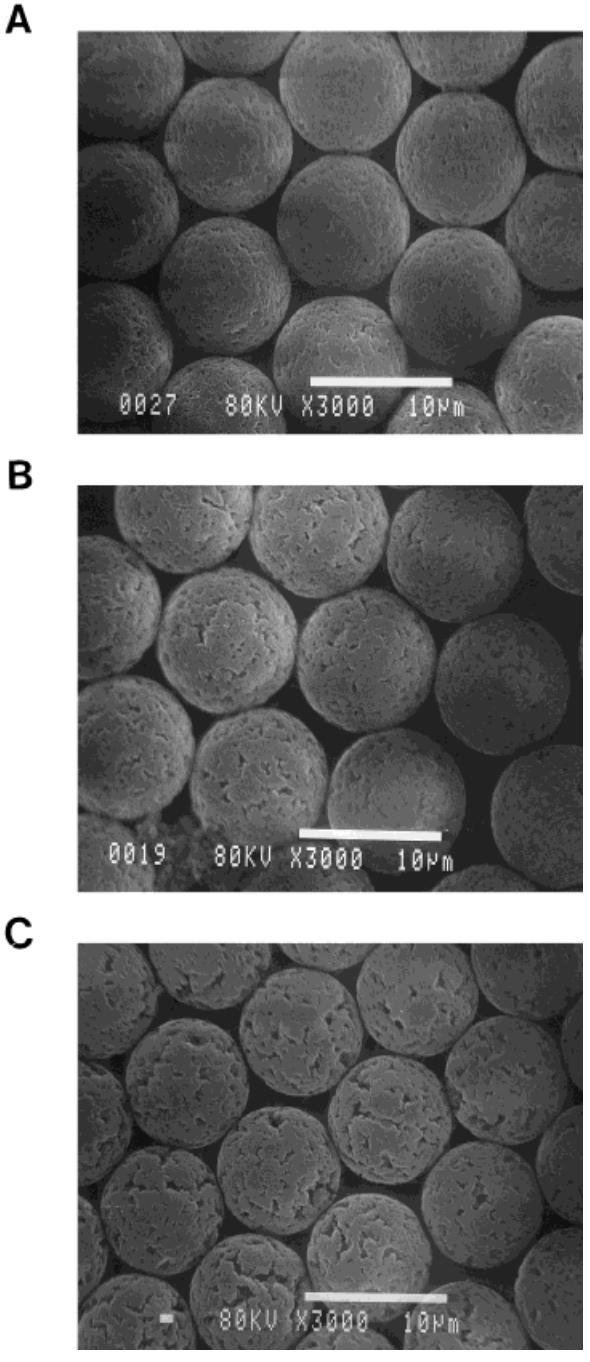

Figure 14 The effect of DVB concentration on the surface morphology of final particles produced with the seed latex of SL3. These photographs were taken after the methylene chloride extraction [DBP-to-seed latex ratio, 1.67 mL/g; monomer-to-seed latex ratio, 6 mL/g; DVB concentration in the monomer phase (vol %)]: (A) 25, (B) 50, and (C) 100 (3000× magnification).

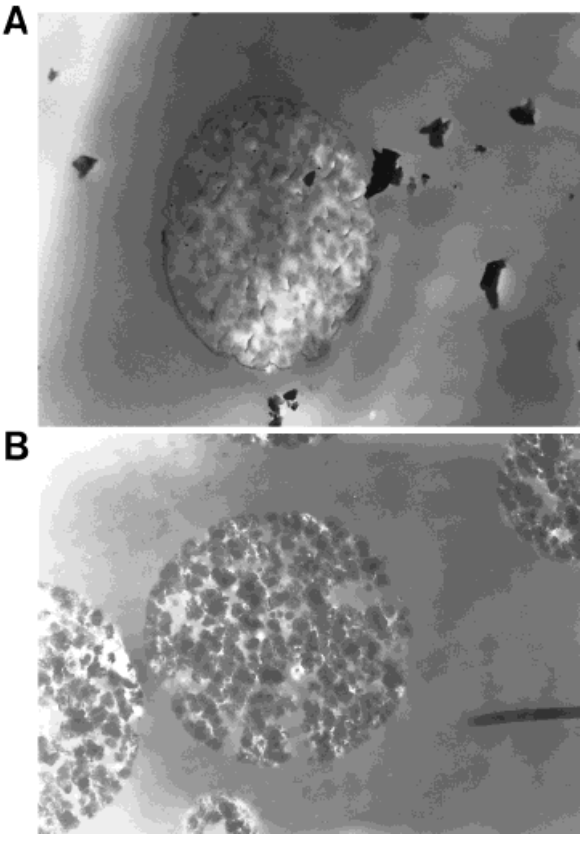

Figure 15 The TEM photographs showing the internal structure of the particles produced with the seed latex of SL3. These photographs were taken after the methylene chloride extraction [DBP-to-seed latex ratio, 1.67 mL/g; monomer-to-seed latex ratio, 6 mL/g; DVB concentration in the monomer phase (vol %)]: (A) 25 and (B) 100 [5000× magnification for (A) and 4000× for (B)].

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