# Electron Microscopic Observation of Uniform Macroporous Particles. I. Effect of Seed Latex Type and Diluent 

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#### Abstract

Uniform and macroporous polymer particles in the size range of 5-21 $\mu \mathrm{m}$ were prepared by a multistep seeded polymerization method. The uniform polystyrene particles in the size range of $1.9-7.5 \mu \mathrm{~m}$ were used as the seed particles in the preparation of macroporous beads. The seed particles with different sizes and molecular weights were produced by dispersion polymerization, by changing the type of dispersion medium and the initiator concentration. In the synthesis of macroporous particles, a two-step swelling procedure was employed. The seed latexes were first swollen by a low molecular-weight organic agent (i.e., dibutyl phthalate, DBP), then by a divinylben-zene-ethylvinylbenzene isomer mixture including an oil phase soluble initiator (i.e., benzoyl peroxide). The porous structure in the final beads was achieved by the polymerization of the monomer phase within the swollen seed particles including a mixture of linear polystyrene and DBP. The initiator concentration in the repolymerization step, the seed latex type (i.e., the diameter and the molecular weight of seed latex), DBP/seed latex, and the monomer/seed latex ratios were changed to achieve uniform polymer beads with different average sizes and pore structures. The average size, the size distribution, and the surface morphology of final beads were analyzed by Scanning Electron Microscopy. The internal structure of the beads were analyzed by Transmission Electron Microscopy. The results indicated that the average size of the final particles increased with increasing the seed latex diameter, DBP/seed latex, and monomer/seed latex ratios. The average pore size decreased with decreasing the molecular weight of the seed latex and increasing the DBP/seed latex and monomer/seed latex ratios. These tendencies were explained by the viscosity change of the porogen solution used in the repolymerization step. © 1999 John Wiley \& Sons, Inc. J Appl Polym Sci 71: 2271-2290, 1999


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## INTRODUCTION

The compact or macroporous large uniform particles are usually synthesized by applying multistep seeded polymerization techniques. ${ }^{1-10}$ Ugel-

[^0]stad et al. proposed a two-step microsuspension method to produce compact or macroporous particles of predetermined size in the range of $1-100$ $\mu \mathrm{m} .{ }^{1-3}$ The method was developed based on the activation of monosize seed particles by the introduction of a low molecular-weight material. ${ }^{3}$ The production of large uniform particles in the compact form were also achieved in microgravity during the space shuttle flights in the early of 1980 s. ${ }^{4}$

El-Aasser et al. prepared monodisperse macroporous polymer particles in the size range of 10 $\mu \mathrm{m}$ in diameter via seeded emulsion polymerization..$^{8,9}$ In their study, linear polymer (polystyrene seed) or a mixture of linear polymer and solvent or nonsolvent were tried as inert diluents to achieve macroporous structures with the pore diameters on the order of $1000 \AA$, and specific surface areas up to $250 \mathrm{~m}^{2} / \mathrm{g}$. The effects of diluent type, the crosslinker content, and the nature of polymer seed particles on the physical characteristics of macroporous uniform particles were determined. The same group also proposed a mechanism for the pore formation process in multistep seeded polymerization. ${ }^{9}$ In the proposed mechanism, the pore formation process was explained by the production, agglomeration, and fixation of the interior gel microspheres of polymer particles. ${ }^{9}$ Recently, Frechet et al. developed a multistage seeded polymerization method for the synthesis of uniformly sized porous poly(styrene-codivinylbenzene) beads $7.4 \mu \mathrm{~m}$ in size. ${ }^{11-13}$ They used a multistage seeded polymerization procedure starting with the monodisperse polystyrene particles ( $1.1 \mu \mathrm{~m}$ in size) produced by emulsifier free-emulsion polymerization. In their procedure, dibutyl phthalate was selected as the low molec-ular-weight organic compound to create porosity. They reported that the average weight of the linear polymer had a key effect on the pore size distribution, and higher molecular weight of the linear polymer provided larger pores. ${ }^{12}$

To produce a series of uniform porous particles with different average sizes and porosity properties, we used a modified form of multistep seeded polymerization method developed by Frechet et al. ${ }^{12,13}$ In our study, the uniform polystyrene particles in the size range of $1.9-7.5 \mu \mathrm{~m}$ were produced by dispersion polymerization. The size and the average molecular weight of seed particles were controlled by changing the polymerization conditions. These particles were directly used as the seed particles for the synthesis of uniform macroporous beads because the dispersion polymerization procedure provided sufficiently large polymeric particles having reasonably suitable average molecular weights as a polymeric porogen. Therefore, the final size and the porosity properties of the final particles could be controlled by changing the size and the molecular weight of seed latex. These modifications resulted in a decrease in the number of polymerization steps by the elimination of the first seeded polymerization in the original method. ${ }^{12}$ The effects of seed latex size and molecular weight, the diluent/seed latex,
the monomer/seed latex ratios on the average size, and the porosity properties of resultant particles were investigated.

## EXPERIMENTAL

## Materials

In the preparation of uniform polystyrene seed particles, 2,2'-Azobisisobutyronitrile (AIBN, BDH Chemicals Ltd., Poole, UK) and polyvinylpyrrolidone ( $M_{r}$ : 40.000, PVP K-30, Fluka Chemie AG, Buchs, Switzerland) were used as the initiator and the stabilizer, respectively. Ethanol (Merck AG, Darmstad, Germany) or 2-methoxyethanol (BDH Chemicals Ltd.) was used as a component of the dispersion media. Styrene (Yarpet A.S., Turkey) was distilled under vacuum and stored in the refrigerator until use. A divinylbenzene isomer mixture ( $65 \%$ divinylbenzene isomers and $33 \%$ ethylvinylbenzene isomers, Merck A.G.) was treated with aqueous NaOH solution ( $5 \% \mathrm{w} / \mathrm{v}$ ) to remove the inhibitor. Benzoyl peroxide (BPO, including $97 \%$ of the active compound, Aldrich Chem. Co., Milwaukee, WI) and sodium dodecyl sulfate (SDS, Sigma Chemical Co., St. Louis, MO) were selected as the initiator and the emulsifier, respectively, in the preparation of macroporous particles. Dibutyl phthalate (Polisan A.S., Turkey) was selected as the low molecular weight organic compound for the activation of seed particles. Polivinylalcohol (PVA, 87-89\% hydrolyzed, $M_{r}$ : 85,000-146,000, Aldrich Chem. Co.) was employed as the stabilizer in the repolymerization step. Ethanol and methylene chloride (MC, Merck AG) were used in the extraction of macroporous particles.

## Preparation of Uniform Polystyrene Seed Particles

The uniform seed particles were prepared by dispersion polymerization of styrene. The type of dispersion medium and the initiator concentration were changed to obtain uniform seed particles with different diameters and average molecular weights. ${ }^{14,15}$ Four different dispersion polymerization recipes were applied by using ethanol/ water or ethanol/2-methoxyethanol mixture as the dispersion medium. In a typical preparation, the dispersion medium was obtained by dissolving proper amount of stabilizer (i.e., PVP K-30) in a mixture of ethanol/water or ethanol/2methoxyethanol. The monomer phase was prepared by dissolving proper amount of initiator (i.e., AIBN) within the styrene. The monomer

Table I The Production Conditions of Seed Latexes

| Seed Latex Code | SL1 | SL2 | SL3 | SL4 |
| :--- | :---: | :---: | :---: | :---: |
| AIBN (g) | 0.14 | 0.16 | 0.40 | 0.24 |
| Styrene (mL) | 10.0 | 16.7 | 16.7 | 16.7 |
| Water (mL) | 10.0 | - | - | - |
| Ethanol (mL) | 90.0 | 50 | 50 | 35 |
| 2-Methoxyethanol (mL) | - | 50 | 50 | 65 |
| PVP K-30 (g) | 1.00 | 1.75 | 1.75 | 1.75 |

Polymerization conditions: temperature: $70^{\circ} \mathrm{C}$, time: 24 h , shaking rate: 120 cpm .
phase was mixed with the dispersion medium within the polymerization reactor. The resulting homogeneous solution was purged with bubbling nitrogen for 5 min at room temperature. The Pyrex glass cylinders having a total volume of 160 mL were used as the polymerization reactors. The sealed reactor was placed at the horizontal position within a shaking water bath equipped with a temperature control system. The polymerizations were performed at $70^{\circ} \mathrm{C}$ for 24 h with 120 cpm shaking rate. Four different dispersion polymerization recipes used for the synthesis of seed particles with different diameters are given in Table I.

After completion of the polymerization, the seed particles were washed with distilled water by a serum replacement method to remove the unreacted monomer and the dispersion medium components. For this purpose, the seed latexes were centrifuged at 4000 rpm for 5 min and the supernatant were removed. The seed particles were redispersed by vortex and sonication within a certain volume of distilled-deionized water. This procedure was applied two times for the new dispersion. A certain amount of aqueous suspension of latex particles was dried in a vacuum and the overall monomer conversion value ( $C_{M} \%$ ) was calculated by using the dry weight of latex particles. ${ }^{14}$ The dispersion polymerization recipes of I and II provided uniform particles with different sizes. However, a bimodal size distribution was obtained with the recipes of III and IV. To isolate the large uniform fraction from the bimodal batch by removing the low-sized particle fraction (i.e, about $1 \mu \mathrm{~m}$ ), the washing procedure was modified. After the first centrifugation at 4000 rpm , the aqueous dispersion of large particles ( 20 mL ) were centrifuged at 2000 rpm for 1 min and the supernatant including small particles were discarded. This operation was repeated several
times until no appreciable amount of low-sized particles were detected in the optical microscopy examinations of the large uniform particle dispersion ( 20 mL ). A certain volume of final dispersion $(4 \mathrm{~mL})$ was dried in vacuum at $60^{\circ} \mathrm{C}$ for 24 h , and the isolation yield of large seed particles (IY, \%) was calculated by using the dry weight of isolated fraction. The molecular weight of seed latexes were determined by an HPLC system (Waters, USA) by using methylene chloride as the eluent solvent within an Ultrastragel column at ambient temperature.

## Preparation of Macroporous Particles

A two-step seeded polymerization procedure was used for the synthesis of macroporous uniform latex particles. Dibutyl phthalate (DBP) was selected as the low molecular-weight organic compound for the activation of seed particles. In a typical procedure, 0.2 mL of dibutyl phthalate was emulsified within 15 mL of aqueous medium including $0.25 \%$ ( $\mathrm{w} / \mathrm{w}$ ) sodium dodecyl sulfate (SDS) as the emulsifier. For emulsification, the mixture of DBP-aqueous SDS solution was sonicated for 30 min in an ultrasonic bath (Bransonic 200, USA). Then, DPB was dispersed in the form of droplets about $1 \mu \mathrm{~m}$ in size. One milliliter of aqueous dispersion including 0.06 g polystyrene (PS) seed particles was added into the aqueous DBP emulsion. The resulting dispersion was stirred at $+4^{\circ} \mathrm{C}$ for 24 h with 400 rpm stirring rate for complete absorption of DBP by the seed particles. In the next step, the monomer phase, comprised of 0.6 mL divinylbenzene-ethylvinylbenzene isomer mixture and 40 mg BPO, was emulsified within another 15 mL of aqueous medium including $0.25 \%$ (w/w) SDS, by sonication for 10 min . In all runs, only divinylbenzene-ethylvinylbenzene isomer mixture (DVB) was used as the monomer phase for the swelling of seed particles. The monomer emulsion was mixed with the aqueous dispersion of DBP swollen seed particles. The resulting emulsion was stirred at $+4^{\circ} \mathrm{C}$ for 24 h with 400 rpm stirring rate for complete absorption of the monomer phase by the DBP swollen seed particles. At the end of this period, $10 \%$ aqueous PVA solution ( 3 mL ) was added, and the resulting emulsion was purged with bubbling nitrogen for 5 min . The reactor was sealed, and the repolymerization of monomer phase within the swollen seed particles was conducted at $70^{\circ} \mathrm{C}$ for 24 h with 120 cpm shaking rate. The repolymerization step provided macroporous latex particles. In some experiments, low-sized particles
about $1 \mu \mathrm{~m}$ were obtained as a by-product, together with the desired large macroporous particles.

## Characterization of Macroporous Particles

The overall monomer conversion in the repolymerization step was determined by a using a gravimetric procedure. The produced latex suspension was passed through a coarse filter ( $44 \mu \mathrm{~m}$ in size) to remove any coagulum, and the sample $(10 \mathrm{~mL})$ taken from this suspension was centrifuged at 5000 rpm for 10 min . In most cases, the centrifuged suspension contained large uniform particles as the desired product and low-sized particles (about $1 \mu \mathrm{~m}$ ) as the by-product. The centrifuge was continued up to the complete precipitation of both types of particles. The supernatant was discarded after the centrifuge. The particles were redispersed in 10 mL of ethanol, and the resulting dispersion was again centrifuged under similar conditions. This operation was repeated three times by using ethanol as the washing solvent. The final particle dispersion was dried in vacuum at $70^{\circ} \mathrm{C}$ for 8 h . The overall monomer conversion $\left(C_{M} \%\right)$, was calculated based on the following expression: where $M_{p}$ is the weight of dried particles, $M_{m}$ is the weight of the monomer used in the swelling of seed particles. $V_{R}$ and $V_{S}$ are the total volume of the produced latex suspension after the repolymerization step and the volume of the sample, respectively.

$$
\begin{equation*}
C_{M}(\%)=\left(V_{R} / V_{S}\right) \times\left(M_{p} / M_{m}\right) \times 100 \tag{1}
\end{equation*}
$$

To determine the isolation yield (IY) of macroporous particles, a certain amount of filtered latex sample ( 10 mL ) was centrifuged at 2000 rpm for about 1 min . Then, the supernatant including dominantly the low-sized particle fraction was removed. The precipitated particle fraction including dominantly larger macroporous particles were redispersed within 10 mL of distilled deionized water. The centrifuges were repeated until all the small particles were removed from the dispersion of large uniform particles. The isolated large macroporous particles were washed with ethanol three times to remove the diluent. The particles were again washed with distilled deionized water and redispersed. The final dispersion was dried in vacuum at $70^{\circ} \mathrm{C}$ for 8 h . The isolation yield of large macroporous particles (IY \%) was calculated by using eq. (2), where $M_{\text {LMP }}$ is the weight of the large macroporous particles within
the sample. The other symbols were the same with the those in eq. (1).

$$
\begin{equation*}
\operatorname{IY}(\%)=\left(V_{R} / V_{S}\right) \times\left(M_{L M P} / M_{m}\right) \times 100 \tag{2}
\end{equation*}
$$

The average size, size distribution, and the surface morphology of the final particles were evaluated by Scanning Electron Microscopy. The aqueous dispersion of large macroporous particles were prepared for electron microscopy by following the procedure used for the determination of isolation yield. The procedure for the determination of average size and size distribution of the large macroporous particles is given below: A small amount of aqueous dispersion of cleaned latex particles (about 0.1 mL ) was spread onto a copper disk, and the water was evaporated at room temperature. The dried macroporous particles were coated with a thin layer of gold (about 100 A ) in vacuum. The specimens were examined and photographed in a Scanning Electron Microscope (JEOL, JEM 1200 EX). For the taking of the SEM photographs, the magnification was adjusted to a proper value at which the taken photograph contained at least 100 particles (in most cases 250-300 particles were included in the obtained SEM photographs). For this purpose, the magnifications between 400 and $1200 \times$ were used for the SEM photographs of the macroporous particles in the size range of $4-20 \mu \mathrm{~m}$. By evaluating SEM photographs, the number $\left(D_{n}\right)$ average diameter of macroporous particles were calculated according to eq. (3), where, $N_{i}$ is the number of particles in diameter $D_{i}(\mu \mathrm{~m})$.

$$
\begin{equation*}
D_{n}=\sum N_{i} D_{i} / \sum N_{i} \tag{3}
\end{equation*}
$$

The size polydispersity index $(U)$ was calculated by using eq. (4), where, $D_{w}$ is the weightaverage diameter of porous particles ( $\mu \mathrm{m}$ ). The weight-average diameter was calculated by using eq. (5).

$$
\begin{align*}
U & =D_{w} / D_{n}  \tag{4}\\
D_{w} & =\left\{\sum N_{i} D_{i}^{6} / \sum N_{i} D_{i}^{3}\right\}^{1 / 3} \tag{5}
\end{align*}
$$

The surface morphology of porous particles was observed by the SEM photographs taken with 3000 or $4000 \times$ magnification. The internal structure of porous particles was examined by Transmission Electron Microscopy. For this analysis, the dried particles ( $100-200 \mathrm{mg}$ ) were fixed in $1 \%$ aqueous $\mathrm{OsO}_{4}$ solution and dehydrated in a


Figure 1 The SEM photographs of seed latexes used as starting material in the preparation of porous particles. Seed latex code: (A) SL1, (B) SL2, (C) SL3, (D) SL4. (magnification: $1200 \times$ ).
graded series of alcohols, then embedded in Araldit CY 212. Thin sections were cut serially ( $60-90 \mathrm{~nm}$ ) by Ultratom (LKB, UK) and mounted on 100 mesh grids and studied under a JEOL, JEM 1200EX electron microscope.

## Extraction of Porous Particles

The dried particles were extracted in a soxhelet apparatus with methylene chloride for 24 h . The extracted particles were washed with ethanol three times by applying serum replacement technique (i.e., centrifugation and decantation). Finally, the particles were again washed with distilled water two times and redispersed in the dis-tilled-deionized water.

## RESULTS AND DISCUSSION

## Preparation and Characterization of Seed Latexes

The SEM photographs of uniform seed latexes used in the preparation of macroporous beads are
given in Figure 1. The size distribution properties and the average molecular weights of the seed latexes are listed in Table II. As seen in Tables I and II, the seed latex produced in the dispersion medium including $90 \%$ ethanol and $10 \%$ water (i.e., SL1) had the smallest particle size. Highly polar character of the dispersion medium used in the synthesis of SL1 possibly provided the highest monomer conversion and the smallest particle size. ${ }^{14,15}$ The size polydispersity index value of SL1 $(U)$ was very close to 1 . The highest average molecular weight ( $M_{w}$ ) and the highest polydispersity index for the molecular weight $\left(M_{w} / M_{n}\right)$ were also obtained for this seed latex. The seed latexes with higher sizes and lower average molecular weights were synthesized by using eth-anol-methoxyethanol medium (Table I). The use of a dispersion medium containing $50 \%$ ethanol and $50 \%$ methoxyethanol with a lower AIBN concentration relative to the first recipe (i.e., $0.67 \%$ mol ) provided the seed latex particles $3.6 \mu \mathrm{~m}$ in size but with a lower molecular weight (i.e., SL2).

Table II The Properties of Seed Latexes

| Seed Latex | $C_{M}(\%)$ | IY $(\%)$ | $D_{n}(\mu \mathrm{~m})$ | $U\left(D_{w} / D_{n}\right)$ | $M_{w} \times 10^{4}$ | $M_{w} / M_{n}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| SL1 | 98.2 | 98.2 | 1.9 | 1.002 | 5.40 | 3.04 |
| SL2 | 90.6 | 90.6 | 3.6 | 1.006 | 4.62 | 2.92 |
| SL3 | 89.1 | 45.9 | 5.5 | 1.006 | 1.99 | 2.50 |
| SL4 | 57.4 | 31.1 | 7.4 | 1.011 | 2.75 | 2.71 |

The size polydispersity index of SL2 was slightly higher relative to that of SL1 (Table II). However, the seed latexes of SL1 and SL2 did not contain any small particles. Then, the serum replacement was only used for removal of the unreacted monomer. Due to this reason, the isolation yields were equal to the monomer conversions for these latexes. In the polymerization recipe for the synthesis of SL3, a 2.5 -fold higher AIBN concentration was selected relative to that in the preparation of SL2. The other polymerization conditions were completely the same for these two recipes. Therefore, it was aimed to produce the seed particles with lower molecular weight and higher size relative to SL2 by increasing the initiator concentration. ${ }^{14-17}$ This polymerization recipe provided a latex dispersion including a dominant fraction of large uniform particles together with a certain amount of small particles (i.e., bimodal size distribution). Therefore, the large uniform particle fraction $5.5 \mu \mathrm{~m}$ in size could be isolated by the elimination of low-sized particles (i.e., about $1 \mu \mathrm{~m}$ in size) with the successive application of the serum replacement method. In the synthesis of SL3, the overall monomer conversion and the isolation yield of the large particle fraction were 89.1 and $45.9 \%$, respectively. The difference between these two values (i.e., $43.2 \%$ ) was roughly equal to the fraction of small particles removed from the latex suspension. This result indicated that about half of the polymerized monomer was in the form of low-sized particles at the end of polymerization. A more apolar dispersion medium relative to that used in the synthesis of SL1 was used for the synthesis of SL3. The initiator concentration was also kept at a reasonably high level for the formation of large particles. In the dispersion polymerization process, the higher rate of free radical initiation produces a shorter kinetic chain length in the growing oligomers. Then, larger particles composed of a lower molecular weight polymer are produced because fewer nuclei are generated. ${ }^{14-17}$ However, the oligomer absorption ability of large particles is lower due to their smaller surface area. Then, the oligomers in solution can
continue to nucleate during the later stages of the polymerization. ${ }^{17}$ The nucleations occurred in the presence of lower monomer and initiator concentrations (i.e., in the later stages of polymerization) provide smaller particles relative to those formed with the first nucleation. The size polydispersity index value of the isolated fraction was 1.006 (Table II). This value showed that the size distribution was reasonably narrow in the isolated fraction. The seed particles having $5.5 \mu \mathrm{~m}$ in size had the lowest molecular weight and the lowest molecular-weight polydispersity index among the other seed latexes (Table II). The composition of dispersion medium used for SL2 was changed for the synthesis of SL4. In the synthesis of this latex, a dispersion medium including $35 \%$ ethanol and 65\% methoxyethanol was utilized with a lower AIBN concentration in the monomer phase (i.e, $1.0 \% \mathrm{~mol}$ ). This modification provided a latex including reasonably large and uniform particles $7.4 \mu \mathrm{~m}$ in size, together with an appreciable amount of low-sized particles. The large uniform particles in this batch were isolated and redispersed within distilled water for obtaining the largest seed latex used in this study. The monomer conversion and the isolation yield of large particles were 57.4 and $31.1 \%$ based on the monomer charged into the reactor, respectively (Table II). Because no significant amount of coagulation was observed in this polymerization, the difference between these two values (i.e., $26.3 \%$ ) roughly indicated the corresponding fraction of small particles. Note that the medium used for the synthesis of SL4 was the most apolar one among the other dispersion polymerizations because the volume fraction of methoxyethanol (more apolar constituent of the dispersion medium) was fixed to the highest value. In the dispersion polymerization process, the polarity of dispersion medium was one of the most important parameter controlling the size and the molecular weight of the final particles. ${ }^{18-21}$ The solubility of oligomers formed at the earlier polymerization times increase with the decreasing polarity of the dispersion medium. Therefore, the growing oli-
gomers can reach relatively longer chain lengths by remaining in the dissolved form. ${ }^{14,15,19-21}$ The first nucleation of the longer oligomeric chains provides a fewer number of nuclei leading to a fewer number of larger particles. As explained above, this case extends the nucleation period and leads to the formation of smaller particles by the successive nucleation steps at the late stages of polymerization.

## Initiator Concentration in the Repolymerization Step

To select an appropriate benzoyl peroxide (BPO) concentration for the repolymerization of the monomer phase within the swollen seed particles, the BPO concentration was changed between 17$66.7 \mathrm{mg} / \mathrm{mL}$. The emulsifier (i.e., SDS) concentration was $0.25 \%(\mathrm{w} / \mathrm{w})$, both in the swelling and repolymerization steps. The initiator effect was tested by using SL1 as the seed latex. In these experiments, the dibutyl phthalate/seed latex ratio was fixed to $6.67 \mathrm{~mL} / \mathrm{g}$. The seed particles were swollen at $+4^{\circ} \mathrm{C}$ by a monomer phase including the isomer mixture of divinylbenzene and ethylvinylbenzene and BPO. The monomer/seed latex ratio was fixed to $10 \mathrm{~mL} / \mathrm{g}$. The repolymerizations were conducted at $70^{\circ} \mathrm{C}$ for 24 h with a 120 cpm shaking rate. The SEM photographs of porous particles produced with different initiator concentrations are given in Figure 2. The number-average size and the size polydispersity index values are also presented in Table III. As seen in Figure 2 and Table III, the initiator concentration in the repolymerization step was not an effective parameter on the average size and the uniformity of the resultant particles. No significant change was also observed in the surface morphology by the initiator concentration in the studied range. However, an agglomeration was observed in the particle dispersion obtained by the BPO concentration of $17 \mathrm{mg} / \mathrm{mL}$. The agglomeration was eliminated by the alcohol washing and sonication of the final aqueous dispersion including 0.25\% SDS. The aggregation behavior possibly originated from the lower monomer conversion with the lower initiator concentration. Therefore, a sufficiently high value (i.e., $66.7 \mathrm{mg} / \mathrm{mL}$ ) was selected for BPO concentration in the synthesis of porous particles with different seed latexes.

## Seed Latex Type

The effect of seed latex properties on the average size and the size distribution of macroporous par-


Figure 2 The SEM photographs of porous particles produced with different initiator concentrations starting from SL1 as the seed latex. The DBP/seed latex ratio: $6.67 \mathrm{~mL} / \mathrm{g}$, monomer/seed latex ratio: $10 \mathrm{~mL} / \mathrm{g}$; BPO concentration ( $\mathrm{mg} / \mathrm{mL}$ ): (A) 17, (B) 40 , (C) 66.7 . (magnification: $4000 \times$ ).
ticles were investigated by using different polystyrene seed latexes with different sizes and molecular weights (Table II). For the constant

Table III The Variation of Average Size and Size Distribution of Porous Particles With the Initiator Concentration in the Repolymerization Step

| BPO Concentration <br> $(\mathrm{mg} / \mathrm{mL})$ | $D_{n}(\mu \mathrm{~m})$ | $U\left(D_{w} / D_{n}\right)$ | $D_{n} / D_{s n}$ |
| :---: | :---: | :---: | :---: |
| 17.0 | 4.9 | 1.010 | 2.58 |
| 40.0 | 4.7 | 1.008 | 2.47 |
| 66.7 | 4.9 | 1.011 | 2.58 |

Swelling conditions: seed latex: $0.06 \mathrm{~g}, \mathrm{DBP} /$ seed latex: $6.67 \mathrm{~mL} / \mathrm{g}$, monomer/seed latex: $10 \mathrm{~mL} / \mathrm{g}$.
amount of seed latex (i.e., 0.06 g ), DBP/seed latex and monomer phase/seed latex ratios were fixed to 1.67 and $10 \mathrm{~mL} / \mathrm{g}$, respectively. A monomer phase including BPO and the isomers of divinylbenzene and ethylvinylbenzene was used for the reswelling of DBP swollen seed particles. In this
group of experiments, BPO concentration in the monomer phase was $66.7 \mathrm{mg} / \mathrm{mL}$. The emulsifier (i.e., SDS) concentration was $0.25 \%$ (w/w), both in the swelling and repolymerization steps. The repolymerization was conducted at $70^{\circ} \mathrm{C}$ for 24 h with a 120 cpm shaking rate. The SEM photographs of porous particles are given in Figure 3. The overall monomer conversions, the isolation yields, and the average size values are presented in Table IV. As seen here, satisfactory monomer conversions were obtained in the repolymerization step for all cases. However, the isolation yield of porous particles decreased with the increasing seed particle size. The difference between the overall monomer conversion and the isolation yield of porous particles mainly showed the fraction of low-sized particles because no significant coagulum was observed in these experiments after repolymerization. In the existence of nearly constant monomer conversion, the increase in the


Figure 3 The SEM photographs of porous particles produced with different seed latexes, $\mathrm{DBP} /$ seed latex ratio: $1.67 \mathrm{~mL} / \mathrm{g}$, monomer/seed latex ratio: $10 \mathrm{~mL} / \mathrm{g}$; seed latex code and magnification: (A) SL1, $1500 \times$; (B) SL2, $1200 \times$; (C) SL3, $1200 \times$; and (D) SL4, $1200 \times$.

Table IV The Properties of Porous Particles Produced With Different Seed Latexes

| Seed Latex Type | $C_{M}(\%)$ | $I Y(\%)$ | $D_{n}(\mu \mathrm{~m})$ | $U\left(D_{w} / D_{n}\right)$ | $D_{n} / D_{s n}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| SL1 | 98.1 | 92.1 | 4.2 | 1.007 | 2.21 |
| SL2 | 95.8 | 84.2 | 7.6 | 1.012 | 2.11 |
| SL3 | 94.4 | 73.6 | 12.5 | 1.015 | 2.27 |
| SL4 | 93.0 | 63.2 | 16.2 | 1.022 | 2.19 |

Swelling conditions: seed latex: $0.06 \mathrm{~g}, \mathrm{DBP} / \mathrm{seed}$ latex: $1.67 \mathrm{~mL} / \mathrm{g}$, monomer/seed latex: $10 \mathrm{~mL} / \mathrm{g}$.
isolation yield also indicated a decrease in the fraction of low-sized particles with the decreasing seed latex size. This result may be explained as follows: in the case of a constant amount of seed latex, the number and the total surface area of the seed particles increase with the decreasing seed latex size. In the monomer swelling step, the monomer can be absorbed more efficiently from the aqueous phase by the higher number of seed particles having a higher total surface area. Then, the amount of monomer that is not absorbed by the seed particles ( i.e., the amount remained within the aqueous phase after the monomer swelling step) decreases. The second crop of lowsized particles are possibly produced by the polymerization of nonadsorbed monomer in the repolymerization step. Therefore, the fraction of lowsized particles increases with the increasing seed latex size because more nonabsorbed monomer is available within the aqueous phase in this case. As seen in Figure 3, the final particle size increased with increasing the seed latex size. The size polydispersity index value was higher for the porous particles produced with the seed latex with a higher size and wider size distribution (Table IV), because any size defect present in the seed latex was magnified during the swelling of seed particles. ${ }^{11}$ The ratio of average size of porous particles to the average size of seed particles ( $D_{p n} / D_{s n}$ ) was roughly the same for all seed latexes. The observed $D_{p n} / D_{s n}$ values indicated that 9.3-11.5 times the volume increase could be achieved with the monomer/seed latex ratio of 10 $\mathrm{mL} / \mathrm{g}$ and a $\mathrm{DBP} /$ seed latex ratio of $1.67 \mathrm{~mL} / \mathrm{g}$. The detailed surface morphologies of these particles before the methylene chloride extraction are shown in Figure 4, by the SEM photographs taken with higher magnifications. As seen in Figure 4(A) and (B), crater-like pores were observed on the surface of the final particles produced with the seed latexes with higher molecular weights (i.e., SL1 and SL2). However, the surface of uniform particles produced with the seed latexes having lower molecular weights contained a large
number of smaller pores [i.e., SL3 and SL4 in Fig. 4(C) and (D)]. The surface morphologies of the same particles after the methylene chloride extraction are shown in Figure 5. As seen in Figures 4 and 5, no significant change was observed in the surface morphology after the methylene chloride extraction. This result may be explained as follows: in the repolymerization step, the formation possibility of uncrosslinked polymer chains was so low because the crosslinker concentration was so high (i.e., approximately $65 \%$ ) in the monomer phase within the swollen seed particles. For this reason, the extractable part of the final particles was dominantly comprised of soluble polystyrene coming from the seed latex. The monomer/seed latex ratio was fixed to $10 \mathrm{~mL} / \mathrm{g}$ (i.e., 0.6 mL monomer for the 0.06 g seed latex) in these experiments. In the case of complete conversion of monomer in the repolymerization step, the concentration of soluble polystyrene coming from the seed latex will be about $10 \%$ within the final particle structure. Additionally, some part of the linear polystyrene can also be removed, together with DBP, during the alcohol washing after the repolymerization, which in turn, also reduces the amount of linear polymer that can be extracted by the methylene chloride. Therefore, no appreciable change was observed in the surface morphology after the methylene chloride extraction because the concentration of soluble polymer was possibly so low (i.e., lower than $10 \%$ ) within the particle structure obtained after the alcohol washing. The TEM photographs showing the cross-sectional view (i.e., the internal structure) of the extracted macroporous beads are given in Figure 6. The comparison of Figures 5 and 6 indicated that the pore structure on the particle surface was very similar to that of the internal part for each sample. Figure 6 also showed the effect of seed latex molecular weight on the porosity of final particles. As seen in Figure 6(A) and (B), only large voids were observed in the internal part of the final particles produced with the seed latexes having higher molecular weights. An internal structure


Figure 4 The SEM photographs showing the surface morphology of porous particles produced with different seed latexes (the photographs were taken before the methylene chloride extraction). DBP/seed latex ratio: $1.67 \mathrm{~mL} / \mathrm{g}$, monomer/seed latex ratio: 10 $\mathrm{mL} / \mathrm{g}$; seed latex code and magnification: (A) SL1, $4000 \times$; (B) SL2, $4000 \times$; (C) SL3, $3000 \times$; and (D) SL4, $4000 \times$.
including small pores with a reasonably narrow pore size distribution (i.e., sponge-like pore structure) could be achieved with the seed latexes having lower molecular weights [Fig. 6(C) and (D)]. In our multistep seeded polymerization procedure, the polymeric part of the porogen solution was obtained directly from the monosize polystyrene seed particles. A decrease in the seed latex molecular weight involves a decrease in the viscosity of the porogen solution. Our results indicated that the average pore size decreased with the decreasing viscosity of the porogen solution. A similar tendency for the effect of the molecular weight of the polymeric part of the porogen solution on the porosity of uniform polymer particles was reported elsewhere by Wang et al. ${ }^{13}$ In their study, the polymeric part of the porogen was produced by a separate seeded polymerization step,
and the molecular weight of the polymer produced in this step was decreased by increasing the initiator concentration. They reported that a clear decrease in the average pore size occurred by increasing the initiator concentration in the seeded polymerization step. ${ }^{13}$

## DBP/Seed Latex Ratio

The effect of the DBP/seed latex ratio on the average size and the porosity of porous particles were studied with the seed latexes having the lowest and the highest average molecular weights (i.e., SL1 and SL3).

In the first set, the $\mathrm{DBP} /$ seed latex ratio was changed between $0.83-6.67 \mathrm{~mL} / \mathrm{g}$, by fixing the monomer phase/seed latex ratio to $10 \mathrm{~mL} / \mathrm{g}$ and by using SL1 as the seed latex (i.e., the latex parti-


Figure 5 The SEM photographs showing the surface morphology of porous particles produced with different seed latexes (the photographs were taken after the methylene chloride extraction). $\mathrm{DBP} /$ seed latex ratio: $1.67 \mathrm{~mL} / \mathrm{g}$, monomer/seed latex ratio: 10 $\mathrm{mL} / \mathrm{g}$; seed latex code and magnification: (A) SL1, $2500 \times$; (B) SL2, $3000 \times$; (C) SL3, $3000 \times$; and (D) SL4, $2500 \times$.
cles with the average molecular weight of 5.40 $\times 10^{4}$ ). The monomer phase included only the divinylbenzene-ethylvinylbenzene isomer mixture and BPO in the second swelling step. BPO concentration in the monomer phase was 66.7 $\mathrm{mg} / \mathrm{mL}$ in all runs. The emulsifier (i.e., SDS) concentration was $0.25 \%(\mathrm{w} / \mathrm{w})$, both in the swelling and repolymerization steps. The repolymerizations were conducted at $70^{\circ} \mathrm{C}$ for 24 h with a $120-\mathrm{cpm}$ shaking rate. The average size and the size polydispersity index values of porous particles produced with different DBP/seed latex ratios are given in Table V. The SEM photographs of porous particles produced with the lowest and the highest DBP/seed latex ratios are presented in Figure 7. As seen here, a crater-like pore structure on the particle surface was observed when the seed latex of SL1 was used. However, the
number of craters was higher on the surface of each particle for the sample produced with the highest DBP/seed latex ratio [Fig. 7(B)]. The internal structure of the same beads produced with the seed latex of SL1 was exemplified with the TEM photographs in Figure 7(C) and (D). Although the internal structure of the beads obtained with the lowest DBP/seed latex ratio ( 0.83 $\mathrm{mL} / \mathrm{g}$ ) included large voids [Fig. 7(C)], a more regular pore structure could be achieved with the highest DBP/seed latex ratio [Fig. 7(D)]. In our study, the linear polymer obtained by the dissolution of seed latex particles within the DBP was used as the polymeric part of the porogen solution. Therefore, an increase in the DBP/seed latex ratio caused a decrease in the concentration of the linear polymer in the porogen solution, which in turn, resulted in a decrease in the viscosity. In the


Figure 6 The TEM photographs showing the internal structure of porous particles produced with different seed latexes (the photographs were taken after the methylene chloride extraction). DBP/seed latex ratio: $1.67 \mathrm{~mL} / \mathrm{g}$, monomer/seed latex ratio: 10 $\mathrm{mL} / \mathrm{g}$; seed latex code and magnification: (A) SL1, $7500 \times$; (B) SL2, $10000 \times$; (C) SL3, $5000 \times$; (D) SL4, $2000 \times$.

Table V The Variation of Average Size and Size Distribution of Porous Particles With the DBP/Seed Latex (DBP/SL) Ratio

| Seed Latex | M/SL $(\mathrm{mL} / \mathrm{g})$ | $\mathrm{DBP} / \mathrm{SL}(\mathrm{mL} / \mathrm{g})$ | $D_{n}(\mu \mathrm{~m})$ | $U\left(D_{w} / D_{n}\right)$ | $D_{n} / D_{s n}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| SL1 | 10 | 0.83 | 4.2 | 1.007 | 2.21 |
| SL1 | 10 | 1.67 | 4.2 | 1.008 | 2.21 |
| SL1 | 10 | 3.33 | 4.3 | 1.012 | 2.21 |
| SL1 | 10 | 6.67 | 4.9 | 1.011 | 2.58 |
| SL3 | 10 | 1.83 | 12.4 | 1.010 | 2.25 |
| SL3 | 10 | 3.33 | 12.5 | 1.015 | 2.27 |
| SL3 | 10 | 6.67 | 13.4 | 1.019 | 2.47 |
| SL3 | 10 | 0.42 | 8.6 | 1.024 | 2.44 |
| SL3 | 5 | 0.83 | 8.6 | 1.008 | 1.51 |
| SL3 | 5 | 1.67 | 9.3 | 1.008 | 1.51 |
| SL3 | 5 |  | 1.009 | 1.63 |  |

[^1]

Figure 7 The SEM and TEM photographs of porous particles produced with different DBP/seed latex ratios and by using SL1 as the seed latex. Monomer/seed latex ratio: 10 $\mathrm{mL} / \mathrm{g}, \mathrm{DBP} / \mathrm{seed}$ latex ratio ( $\mathrm{mL} / \mathrm{g}$ ) and magnification: (A) $0.83,4000 \times$; (B) $6.67,4000 \times$; (C) $0.83,7500 \times$; (D) $6.67,5000 \times$.
existence of SL1, reasonably high viscosity of a porogen solution with a lower DBP/seed latex ratio provided an internal structure including only large voids [Fig. 7(C)]. The more regular pore structure with the highest $\mathrm{DBP} /$ seed latex ratio [Fig. 7(D)] may be explained by the lower viscosity of the porogen solution. However, the viscosity of the porogen solution was still high, even at the highest DBP/seed latex ratio, because the seed latex of SL1 had the highest molecular weight. Therefore, a sponge-like pore structure could not be achieved with this seed latex even when a reasonably high DBP/seed latex ratio ( $6.67 \mathrm{~mL} / \mathrm{g}$ ) was used in the swelling of seed particles [Fig. 7(D)].

The effect of the DBP/seed latex ratio on the size and the porosity of final particles was also investigated by using SL3 as the seed latex (i.e., the latex particles with the average molecular
weight of $1.99 \times 10^{4}$ ). The experimental conditions were the same with those of the previous set. The SEM photograph indicating the uniformity of final particles produced by the DBP/seed latex ratio of $0.83 \mathrm{~mL} / \mathrm{g}$ was given as an example in Figure 8(A).

The average size and the size polydispersity index values of final particles produced in this set are given in Table V. As seen here, the uniform porous particles in the size range of $12.4-13.6$ $\mu \mathrm{m}$ were achieved. Note that higher size values were observed with the higher DBP/seed latex ratios. For a certain DBP/seed latex ratio, a higher polydispersity index value corresponding to a wider size distribution was obtained in this set relative to the previous one. This result indicated that the volume swelling ratios of all seed particles were closer to each other when the multistep swelling process was started with the


Figure 8 The SEM photographs of porous particles produced with the seed latex of SL3 and with different DBP/seed latex ratios (the photographs were taken before the methylene chloride extraction). Monomer/seed latex ratio: $10 \mathrm{~mL} / \mathrm{g}, \mathrm{DBP} / \mathrm{seed}$ latex ratio ( $\mathrm{mL} / \mathrm{g}$ ) and magnification: (A) $0.83,1000 \times$; (B) $0.83,3000 \times$; (C) $1.67,3000 \times$; (D) 6.67, $3000 \times$.
smaller seed particles. This case is possibly related to the higher total surface area of SL1 relative to SL3. Note that the size polydispersity index value also increased with the increasing DBP/seed latex ratio. The SEM photographs indicating the surface morphology of the final particles produced by different DBP/seed latex ratios and by using SL3 as the seed latex are given in Figure 8. These photographs were taken before the methylene chloride extraction. As seen in Figure 8(B) and (D), a sponge-like pore structure on the particle surface could be achieved with all $\mathrm{DBP} /$ seed latex ratios. The surface morphology observed for a certain $\mathrm{DBP} /$ seed latex ratio in Figure 8 was reasonably different than that obtained with the seed latex of SL1 at the same conditions (Fig. 7). It should be noted that no
significant change was observed in the surface morphology of these beads after extraction with methylene chloride. The TEM photographs, indicating the internal structure of the final beads produced with different DBP/seed latex ratios by using SL3 as the seed latex, are given in Figure 9. As seen here, the sponge-like pore structure was also observed within the internal part of the beads produced by using either low or high DBP/ seed latex ratios. By comparing Figure 9(A) and (B), it was also possible to see a slight decrease in the pore size with increasing the DBP/seed latex ratio. Even with a low DBP/seed latex ratio ( 0.83 $\mathrm{mL} / \mathrm{g}$ ), as was used in the existence of SL3 seed particles, an internal structure including dominantly small pores ( $<100 \mathrm{~nm}$ ) could be achieved. By comparing the TEM photographs in Figures 7


Figure 9 The TEM photographs showing the internal part of porous particles produced with different DBP/ seed latex ratios and by using SL3 as the seed latex (the photographs were taken after the methylene chloride extraction). Monomer/seed latex ratio: $10 \mathrm{~mL} / \mathrm{g}$, DBP/ seed latex ratio ( $\mathrm{mL} / \mathrm{g}$ ) and magnification: (A) 1.67 , $5000 \times$; (B) $6.67,3000 \times$.
and 9 , it could be concluded that the molecular weight of the seed latex was more effective than the $\mathrm{DBP} /$ seed latex ratio for controlling the average pore size.

The effect of the DBP/seed latex ratio on the average size and the porosity of final particles was also examined by using a different monomer/ seed latex ratio and SL3 as the seed latex. In these experiments, the $\mathrm{DBP} /$ seed latex ratio was changed between $0.42-1.67 \mathrm{~mL} / \mathrm{g}$ by fixing the monomer/seed latex ratio to a lower value (i.e., 5.0 $\mathrm{mL} / \mathrm{g}$ ). The other experimental conditions were the same with the those of the previous set. The SEM photographs showing the size distribution of final particles produced with a monomer/seed latex ratio of $5.0 \mathrm{~mL} / \mathrm{g}$ are given in Figure 10. The average size values of these particles are given in

Table V. As seen here, the porous beads $8.6-9.3$ $\mu \mathrm{m}$ in size were synthesized in this set of experiments. The average particle size with a certain

A


B


C


Figure 10 The SEM photographs showing the monodispersity of porous particles produced by using the seed latex of SL3 and with the monomer/seed latex ratio of $5.0 \mathrm{~mL} / \mathrm{g}$, magnification: $1200 \times$ for all photographs, DBP/seed latex ratio (mL/g): (A) 0.42 , (B) 0.83 , (C) 1.67 .


Figure 11 The SEM photographs showing the surface morphology of porous particles produced with the seed latex of SL3 and with different DBP/seed latex ratios. Monomer/ seed latex ratio: $5 \mathrm{~mL} / \mathrm{g}$, magnification: $4000 \times$ for $\mathrm{A}-\mathrm{C}$, and $3000 \times$ for $\mathrm{D}-\mathrm{F}, \mathrm{DBP} /$ seed latex ratio ( $\mathrm{mL} / \mathrm{g}$ ): (A) 0.42 , (B) 0.83 , (C) 1.67 , (D) 0.42 , (E) 0.83 , (F) 1.67. The photographs of A-C were taken before the methylene chloride exraction, while the others ( $\mathrm{D}-\mathrm{F}$ ) were obtained with the extracted beads.

DBP/seed latex ratio was smaller relative to the corresponding run in the previous set because the monomer/seed latex ratio was kept at a lower
value. The surface morphology of these beads before and after the methylene chloride extraction are given in Figure 11. The internal structures of


Figure 12 The TEM photographs showing the internal part of porous particles produced with different $\mathrm{DBP} /$ seed latex ratios and by using SL3 as the seed latex (the photographs were taken after the methylene chloride extraction). Monomer/seed latex ratio: $5 \mathrm{~mL} / \mathrm{g}$, $\mathrm{DBP} /$ seed latex ratio ( $\mathrm{mL} / \mathrm{g}$ ) and magnification: (A) $0.42,5000 \times$; (B) $1.67,5000 \times$.
these beads after the methylene chloride extraction were also exemplified with the TEM photographs in Figure 12. The comparison of Figures 11 and 12 indicated that the pore structures on the surface and within the internal part of the beads were very similar for a certain particle sample. When the monomer/seed latex ratio was fixed to $5.0 \mathrm{~mL} / \mathrm{g}$, larger pores in the form of craters were observed, especially with the low $\mathrm{DBP} /$ seed latex ratios relative to the sponge-like pore structures achieved in the previous set (i.e., Fig. 9). The effect of the DBP/seed latex ratio on the pore structure of uniform beads was more clearly observed with the monomer/seed latex ratio of $5 \mathrm{~mL} / \mathrm{g}$. As seen in Figures 11 and 12, the pore size either at the surface or at the internal part of the beads clearly decreased with increasing the $\mathrm{DBP} /$ seed latex ratio.

As stated before, the increase in the DBP/seed latex ratio involved a decrease in the viscosity of the porogen solution, leading to a decrease in the average pore size of the final particles. A mechanism was proposed by Cheng et al. for the pore formation process in the uniform large latex particles. ${ }^{9}$ According to this mechanism, the first stage in the pore formation process was described as the production and agglomeration of low-energy and highly crosslinked microspheres by the phase separation taking place between the crosslinked copolymer (i.e., the copolymer of ethylvinylbenzene and divinylbenzene in our case), and the phase including linear polystyrene + nonsolvent within the forming particle. The fixation and binding of microspheres and agglomerates occurred in the second stage, and the voids between the fixed microspheres were filled with the linear polymer and nonsolvent. ${ }^{9}$ By considering the proposed mechanism and our results, it may be concluded that the larger microspheres or agglomerates are produced 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. Therefore, the average pore size increases with the increasing viscosity of the porogen solution. It should be noted that not only the decrease in the DBP/seed latex ratio, the changes in the other synthesis conditions (i.e., seed latex molecular weight and monomer/seed latex ratio) providing an increase in the viscosity of porogen solution also lead to the formation of internal structure with larger pores.

Table VI The Variation of Average Size and Size Distribution of Porous Particles With the Monomer/Seed Latex (M/SL) Ratio

| Seed <br> Latex | $\mathrm{M} / \mathrm{SL}$ <br> $(\mathrm{mL} / \mathrm{g})$ | $D_{n}(\mu \mathrm{~m})$ | $U\left(D_{w} / D_{n}\right)$ | $D_{p} / D_{s n}$ |
| :--- | :---: | :---: | :---: | :---: |
| SL2 | 5 | 6.3 | 1.006 | 1.75 |
| SL2 | 10 | 7.6 | 1.012 | 2.11 |
| SL2 | 15 | 7.6 | 1.011 | 2.11 |
| SL3 | 4 | 8.6 | 1.010 | 1.56 |
| SL3 | 5 | 9.3 | 1.009 | 1.69 |
| SL3 | 10 | 12.5 | 1.015 | 2.27 |
| SL4 | 4 | 13.3 | 1.019 | 1.79 |
| SL4 | 7 | 16.5 | 1.018 | 2.22 |
| SL4 | 10 | 16.2 | 1.022 | 2.19 |
| SL4 | 15 | 21.6 | 1.054 | 2.96 |

[^2]
## Monomer/Seed Latex Ratio

The effect of the monomer/seed latex ratio on the average size and the porous structure of final beads was investigated by using three different seed latexes (i.e., SL2, SL3, and SL4). To change the monomer/seed latex ratio, the amount of seed latex was changed by fixing the volume of the monomer phase to 0.6 mL within 35 mL of the total polymerization volume. In these experiments, the $\mathrm{DBP} /$ seed latex ratio was fixed to 1.67 and the monomer/seed latex ratio was changed to between 4 and $15 \mathrm{~mL} / \mathrm{g}$. A further increase in the monomer/seed latex ratio resulted in significant defects in the monodispersity of the final macroporous beads. A monomer phase including the divinylbenzeneethylvinylbenzene isomer mixture and BPO was used in the reswelling of DBP swollen seed particles. The emulsifier (i.e., SDS) concentration was $0.25 \%$ (w/w), both in the swelling and repolymerization steps. The repolymerization was conducted at $70^{\circ} \mathrm{C}$ for 24 h , with a 120 cpm shaking rate. The average size values of macroporous particles are listed in Table VI. As seen here, the average size of porous particles increased with the increasing monomer/seed latex ratio because a greater amount of monomer for the swelling of each particle was available when the monomer/seed latex ratio was higher. For the macroporous particles produced with the each seed latex, the size polydispersity index value increased with increasing the monomer/ seed latex ratio. The number and the total surface area of the seed particles were lower for the higher monomer/seed latex ratios because the monomer/seed latex ratio was increased in the runs by decreasing the amount of seed latex. The lower surface area for the absorption of the monomer phase by the seed particles possibly leads to the wider size distribution in the macroporous ones. The surface morphology of macroporous particles produced with the seed latex of SL2 did not significantly change with the monomer/seed latex ratio. A crater-like pore structure (i.e., reasonably large pores around $1-2 \mu \mathrm{~m}$ ) was observed on the surface of all particles produced with different monomer/seed latex ratios between $5-15 \mathrm{~mL} / \mathrm{g}$. This structure was exemplified in the section of "seed latex type" for the porous particles produced with the monomer/seed latex ratio of $10 \mathrm{~mL} / \mathrm{g}$ [(Fig. 4(B)]. It should be emphasized that SL2 was the seed latex having the highest average molecular weight among the tried seed latexes in this


Figure 13 The SEM photographs showing the surface morphology of porous particles produced with the seed latex of SL3 and with different monomer/seed latex ratios. DBP/seed latex ratio: $1.67 \mathrm{~mL} / \mathrm{g}$, monomer/ seed latex ratio ( $\mathrm{mL} / \mathrm{g}$ ) and magnification: (A) $4,4000 \times$; (B) $5,4000 \times$; (C) $10,3000 \times$.
set. The variation of surface morphology of the final particles with the monomer/seed latex ratio was exemplified in Figures 13 and 14 for the


Figure 14 The SEM photographs showing the surface morphology of porous particles produced with the seed latex of SL4 and with different monomer/seed latex ratios. DBP/seed latex ratio: $1.67 \mathrm{~mL} / \mathrm{g}$, monomer/seed latex ratio ( $\mathrm{mL} / \mathrm{g}$ ) and magnification: (A) $4,3000 \times$; (B) $7,3000 \times$; (C) $10,4000 \times$; (D) $15,3000 \times$.
macroporous particles produced by starting from the seed latexes of SL3 and SL4, respectively. As seen in Figure 13, the surface morphology of the beads produced with the seed latex having the lowest average molecular weight (i.e., SL3) was drastically affected by the monomer/seed latex ratio. The increase in the monomer/seed latex ratio resulted in a significant decrease in the average pore size on the surface of the macroporous beads. A similar tendency to that with the seed latex of SL3 was also observed with the macroporous beads produced by using the seed latex of SL4 having a slightly higher average molecular weight relative to that of SL3 (Fig. 14). The TEM photographs indicating the internal porous structure of the beads produced with the seed latex of SL4 are given in Figure 15. As seen here, the aver-
age pore size within the internal structure also decreased with the increasing monomer/seed latex ratio. Note that the pore size distribution on the bead surface was very similar to that in the internal structure for each macroporous bead sample.

The linear polymer concentration in the medium consisting of DBP, monomer, and linear polymer within the swollen particles decreased with the increasing monomer/seed latex ratio before the repolymerization step. This case involved a decrease in the viscosity of the same medium. The decrease in the viscosity led to a significant decrease in the average pore size of the final beads when the average molecular weight of the linear polymer coming from the seed particles was sufficiently low (i.e., in the existence of SL3 or SL4 seed latexes). However, possibly due to the


Figure 15 The TEM photographs showing the internal part of porous particles produced with the seed latex of SL4 and with different monomer/seed latex ratios. $\mathrm{DBP} /$ seed latex ratio: $1.67 \mathrm{~mL} / \mathrm{g}$, monomer/seed latex ratio ( $\mathrm{mL} / \mathrm{g}$ ) and magnification: (A) $4,3000 \times$; (B) $7,2500 \times$; (C) $10,3000 \times$.
reasonably high molecular weight of linear polymer obtained by the dissolution of SL2 within DBP and monomer phase, the viscosity within the shape template particles did not decrease sufficiently by increasing the monomer/seed latex ratio. Therefore, no significant change in the pore structure of the final particles prepared with SL2 was observed.

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[^1]:    M/SL: monomer/seed latex ratio ( $\mathrm{mL} / \mathrm{g}$ ).

[^2]:    Swelling conditions: monomer phase: $0.6 \mathrm{~mL}, \mathrm{DBP} /$ seed latex: $1.67 \mathrm{~mL} / \mathrm{g}$.

