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ORIGINAL CONTRIBUTION

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Morphological investigations of crosslinked polystyrene microspheres by seeded polymerization

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Abstract Crosslinked polystyrene microspheres with novel surface and inner morphologies were synthesized by seeded polymerization following a seed-swelling method, using uncrosslinked polystyrene microspheres as seeds and a mixture of toluene, styrene (St), and divinylbenzene (DVB) as the swelling agent. With the increasing toluene/(St + DVB) ratio, the crosslinked particles changed from smooth-surfaced spheres to deformed spheres with dimples or heavy dents at the surface. A single hole inside the spherical particles was produced at low St/DVB ratio, while higher St/DVB ratios gave irregular dented or dimpled particles. Ultrathin cross-section observation by TEM revealed a non-uniformly crosslinked inner structure.

Key words Seed-swelling – dispersion polymerization – crosslinked microsphere – morphology

Introduction

Recently, monodisperse polymer microspheres have gained a lot of research interest due to their various particle morphologies and novel characteristics, such as large specific surface area, strong adsorption capability, remarkable aggregation effects, and surface reactive ability. Monodisperse polymer microspheres have found lots of applications in such fields as standard calibration, biomedical and clinical examinations, HPLC fillers, catalyst carriers, coating and ink additives, information storage materials, and so on [1–3].

Crosslinked polystyrene (PS) microspheres, due to their stiffness, susceptibility to chemical modification, and adaptivity in a wide pH range, have been utilized as chromatographic supports for ion exchangers [4, 5], and photoconductive materials by introducing fullerene to the microsphere surface [6], etc. Crosslinked PS spheres may be prepared by suspension polymerization [7], with a particle size larger than 100 μm and a broad size distribution which may be unfavourable in some applications. Dispersion polymerization may lead to monodisperse micron-sized spheres, but the crosslinker content needs to be less than 1%, which, otherwise, will result in particles with irregular shape [8]. The seed swelling method [9–13] has been a very effective pathway to prepare various polymer microspheres with narrow polydispersity, high crosslink density, as well as easily controllable particle size. Nevertheless, the theory about this technique is far from perfection and thus extensive investigation is of necessity.

Smooth-surfaced spherical particles can be easily achieved by emulsion polymerization, however, seeded emulsion polymerization may sometimes give nonspherical abnormal particles, most of which originate from the combination of different incompatible polymers particles [14]. There are also reports [15–18] on abnormal particles based on the same polymer particles, for example, a series of abnormal particles, including singlets, doublets, and multiplets, was observed in seeded emulsion polymerization using crosslinked PS as seeds. The nonspherical latex particles were attributed to phase separation induced by the incompatibility between constituent polymers. Rudin et al. reported the preparation of monodisperse particles barring deformities by dispersion polymerization at high DVB concentrations, e.g., 1–6% based on the total monomer content [8]. By dynamic swelling, Okubo et al. observed the formation of a core-shell microsphere with a hole inside using DVB and toluene as the swelling agent [13].

The effects of temperature, monomer concentration, initiator concentration, stabilizer concentration and dispersion medium on the particle size of PS microspheres by dispersion polymerization have been previously studied in our laboratory [19], and the polymerization procedure will be briefly summarized in the Experimental section. Persistent spectral hole burning was realized at room temperature for Nile Blue molecules-doped monodisperse micronsized PS microspheres based on morphology-dependent resonances [20, 21]. When attempts were made to prepare larger particles by a seed-swelling technique, we found some interesting morphologies of polystyrene microspheres brought about by various factors, as will be demonstrated in this paper.

Experimental

Materials

Styrene (St) was distilled under reduced pressure before polymerization. Divinylbenzene (DVB) obtained from Merck is a mixture of meta and para isomers with a purity of 55% (the rest 35% is ethylvinylbenzene). 2,2-Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were purified by recrystallization in ethanol and chloroform, respectively. Polyvinylpyrrolidone (PVP, Mw = 360 000), sodium dodecylsulfate (SDS), ethanol, toluene, dibutyl phthalate (DBP), etc., were used as received.

Preparation of polystyrene seed particles by dispersion polymerization

Micron-sized monodisperse PS seed particles were prepared under the dispersion polymerization conditions in Table 1, as determined in a previous article [19]. The dispersion polymerization of styrene was carried out at 70 °C for 24 h under a nitrogen atmosphere in a four-necked, round-bottom flask equipped with a mechanical stirrer, a reflux condenser, a thermometer, nitrogen gas inlet and outlet. After a typical centrifugal purification method, the seed particles were dispersed into an ethanol/water (v/v = 1 : 1) mixture for further use. PS seed particles were observed with a Hitachi S-520 scanning electronic microscope (SEM).

Table 1 Preparation of micronsized monodisperse PS seed particles by dispersion polymerization[a)]

Ingredient	Styrene	AIBN	PVP	Ethanol
Content (g)	25	0.25	1.25	65

[a)] N_2 atmosphere; reaction temperature: 70 °C for 24 h; stirring rate: 350 rpm.

Seed swelling and preparation of large crosslinked PS particles

A typical seed-swelling procedure is as follows: 6 ml of the ethanol/water dispersion of polystyrene seed particles (seed content, 0.068 g/ml) was treated with an emulsion which was prepared from DBP (1.4 ml), BPO (0.24 g), SDS (0.15 g) and deionized water (100 ml). The first step of swelling was carried out at room temperature for 24 h with stirring at 125 rpm. Here, DBP was added to facilitate good swelling by lowering the interfacial tension between the particle surface and water. Then, toluene (20 ml) was added to the mixture while maintaining the stirring. After 12 h, St(10 ml), DVB (10 ml) and an aqueous solution of PVP (1.5 g in 35 ml of water) were added to the dispersion. The swelling was continued at room temperature for another 24 h with stirring at 125 rpm. The superfluous swelling agent was removed afterwards.

The dispersion was polymerized at 70 °C under nitrogen atmosphere for 24 h with slow stirring. The crosslinked PS particles were observed with a Hitachi S-520 scanning electronic microscope.

Observation of ultrathin cross-sections of particles

Crosslinked PS particles were exposed to OsO_4 vapor at room temperature for 24 h in the presence of 1% OsO_4 solution, and then dipped in an epoxy matrix, cured at room temperature for 24 h and microtomed. The ultrathin cross-sections were observed with a Hitachi HU–11B transmission electronic microscope (TEM).

Diameter measurements

Number-average diameter ($\bar{D}$) and standard deviation (δ) are determined by measuring the diameter of the particles in the SEM photographs as follows:

$$\bar{D} = \frac{\sum_{i=1}^{n} D_i}{n}; \quad \delta = \sqrt{\frac{\sum_{i=1}^{n}(D_i - \bar{D})^2}{n-1}} .$$

(n is the number of particles counted for calculation, usually 300).

Results and discussion

PS seed microspheres

Figure 1a shows the SEM photograph of a typical PS seed microsphere. The diameter of this PS seed microsphere is 2.4 μm, with standard deviation of about 0.1 μm. These microspheres will be used as seeds for the following experiments, unless otherwise stated.

Effect of diluents on morphology of crosslinked microspheres

The effects of diluents on particle size and morphology of crosslinked PS microspheres are shown in Table 2 and Fig. 1b–d. All particles appear to be spherical. It is obvious that large particles with a narrow size distribution were produced using toluene as the diluent, while hexane and heptane gave quite smaller particles with a broader distribution. No small particles formed during seed swelling and the following polymerization, as verified by SEM observation, which suggests no secondary nucleation during these periods. Therefore, in the following experiments, toluene was chosen as the diluent.

Fig. 1 SEM photographs of (a): uncrosslinked PS seeds prepared under conditions listed in Table 1; (b–d): crosslinked PS microspheres Nos. 1–3 in Table 2

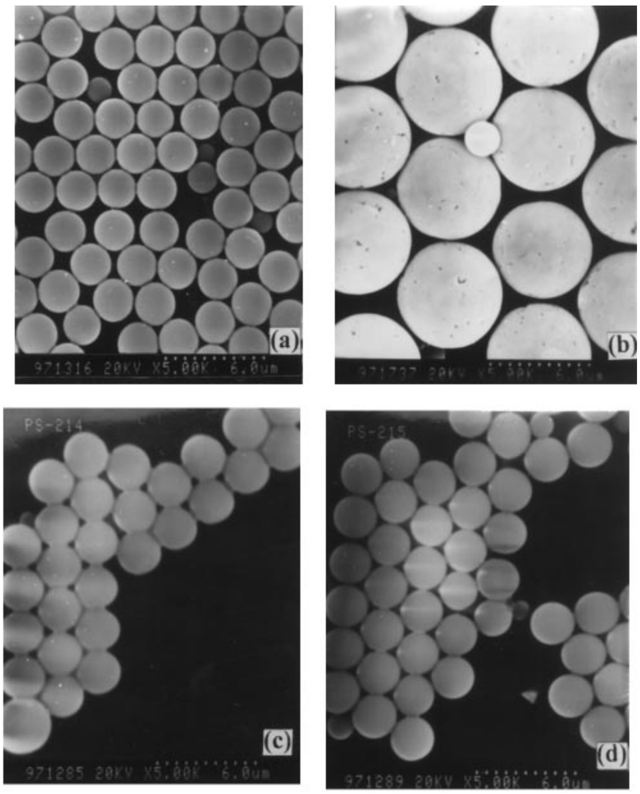

Table 2 Effect of diluents on the morphology of crosslinked microspheres[a)]

Serial no.	Diluent[b)]	$\bar{D}/\mu$m	δ/μm	Morphology
1	Toluene	5.8	0.1	Sphere
2	*n*-Hexane	2.6	0.2	Sphere
3	*n*-Heptane	2.5	0.1	Sphere

[a)] $\bar{D}$ of seed is 2.4 μm, and δ is 0.1 μm.
[b)] The diluent (20 ml), St (10 ml), and DVB (10 ml) were included in the swelling agent.

Table 3 Effect of toluene/(St + DVB) ratios on the morphology of crosslinked microspheres[a)]

Serial no.	Toluene/(St + DVB), v/v	$\bar{D}/\mu$m	δ/μm	Morphology
4	1:2	3.6	0.7	Sphere
5	1:1	3.2[c)]	0.6	Many small dimples (Spheroid)
6	2:1	3.9[c)]	0.4	Many small dimples (Spheroid)
7	4:1	3.6[c)]	0.6	Many heavy dents
4′	1:2[b)]	—[d)]	—[d)]	Sphere, with mini particles
7′	4:1[b)]	—[d)]	—[d)]	Sphere, with mini particles

[a)] $\bar{D}$ of seed is 1.7 μm, and δ is 0.3 μm; the total amount of toluene, St and DVB was 40 ml; St/DVB ratio was 1:1 (v/v).
[b)] Toluene/St ratio, and total amount of toluene and St was 40 ml.
[c)] $\bar{D}$ was calculated as ideal spheres.
[d)] Particle diameters were not calculated because of a huge difference between large and small particles.

Effect of toluene/(St + DVB) ratio on the morphology of crosslinked microspheres

In this series, the total amount of toluene, styrene, and DVB was kept at 40 ml, with the St/DVB ratio of 1:1(v/v). As seen in Table 3 and Fig. 2, the ratio of toluene/(St + DVB) does not have significant effects on particle size and size distribution, but leads to dramatic difference in morphology. At the toluene/(St + DVB) ratio of 1:2, the particles attained were spherical with a smooth surface (Fig. 2a); but irregular spherical particles with many dimples were produced with ratio of 1:1 (Fig. 2b) and 2:1

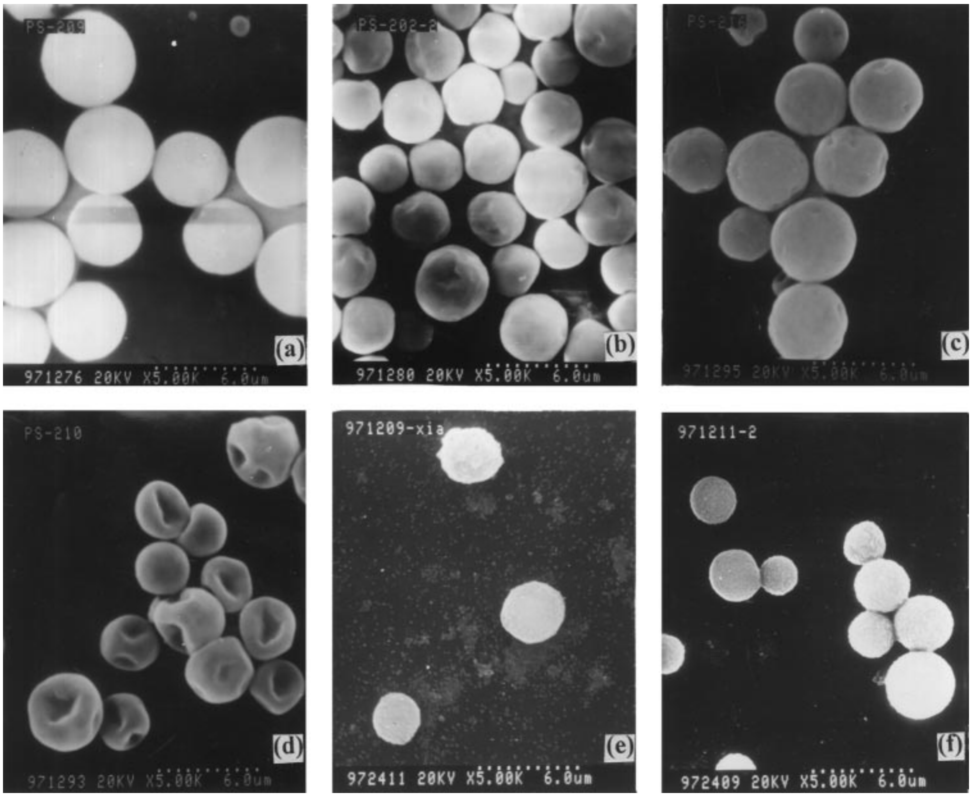

Fig. 2 SEM photographs of (a–d): crosslinked PS microspheres Nos. 4–7 in Table 3; (e) and (f): uncrosslinked PS microspheres Nos. 4′ and 7′ in Table 3, respectively

(Fig. 2c), respectively. As the ratio increased to 4:1, almost every particle contained heavy dents (Fig. 2d).

In the stage of seed swelling, PS seed microspheres were well swollen by the mixture of toluene, styrene and DVB; the PS chain was actually dissolved in the solvent mixture inside each swollen particle, considering the high ratio of swelling agent to seed. The round shape of swollen particles was well maintained [22] according to the observation with an optical microscope. After polymerization has taken place, DVB may form a crosslinked network (based on DVB and St) at the early period due to its higher reactivity than styrene. The network was reported as heterogeneous [23, 24]. Then inside the microsphere (loci of polymerization), two phases of crosslinked polymer-rich and toluene-rich would form during polymerization, respectively. The particle would contract as the polymerization proceeded [25], leading to the decrease in particle diameter and consequently the increase of interfacial tension. But the existence of crosslinked network may resist the contraction when the amount of DVB and St was high (e.g., toluene/(St + DVB) ratio of 1:2). The formed crosslinked network was strong enough to maintain the spherical shape. With the increasing amount of toluene, the crosslinked network became weak, however, and was subject to deform during polymerization, as it is not strong enough to resist the increase of interfacial tension and volume contraction, which resulted in dimples or dents at the particle surface.

For comparisons, a polymerization of St was performed without using DVB in seed swelling, where the toluene/St ratios were 1:2 and 4:1 [Nos. 4′ and 7′ in Table 3], respectively. SEM photographs of the particles produced are shown in Fig. 2e and f. At the toluene/St ratio of 1:2, many small particles aggregated at the surface of seed microspheres and a large quantity of new mini particles (about 0.1 μm) formed, as shown in Fig. 2e. Similar results were obtained when the ratio was 4:1 (Fig. 2 f), but with less amount of mini particles. However, neither dimples nor dents were observed in both cases and the diameters of the particle produced were smaller than those with DVB, i.e., Nos. 4 and 7 in Table 3. The mini particles came from secondary nucleation. At the toluene/St ratio of 4:1, the larger spherical particles in Fig. 2f (compared to mini ones) were the consequence of no existence of crosslinked network, where the swollen particle may contract rather uniformly and expel toluene gradually during polymerization. However, these particles were smaller than those particles (Fig. 2d) with DVB used in the swelling agent, whereas the crosslinked network in the latter case might maintain the original spherical shape when sphere

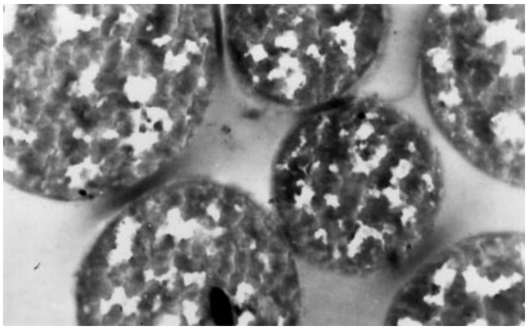

Fig. 3 TEM photograph of an ultrathin cross-section of crosslinked PS microspheres No. 4 in Table 3 (× 5000)

Table 4 Effect of St/DVB ratios on the morphology of crosslinked microspheres[a)]

Serial no.	St/DVB, v/v	$\bar{D}/\mu$m	δ/μm	Morphology
8	3:1	4.7[b)]	0.2	Many small dimples
9	2:1	4.2[b)]	0.2	Deeply-dented spheres
10	1:1	3.8[b)]	0.2	Shallowly-dented spheres
11	1:1	4.9	0.2	Sphere

[a)] $\bar{D}$ of seed is 2.6 μm, and δ is 0.1 μm; toluene amount was 20 ml, and the total amount of St and DVB was also 20 ml.
[b)] $\bar{D}$ was calculated as ideal spheres.

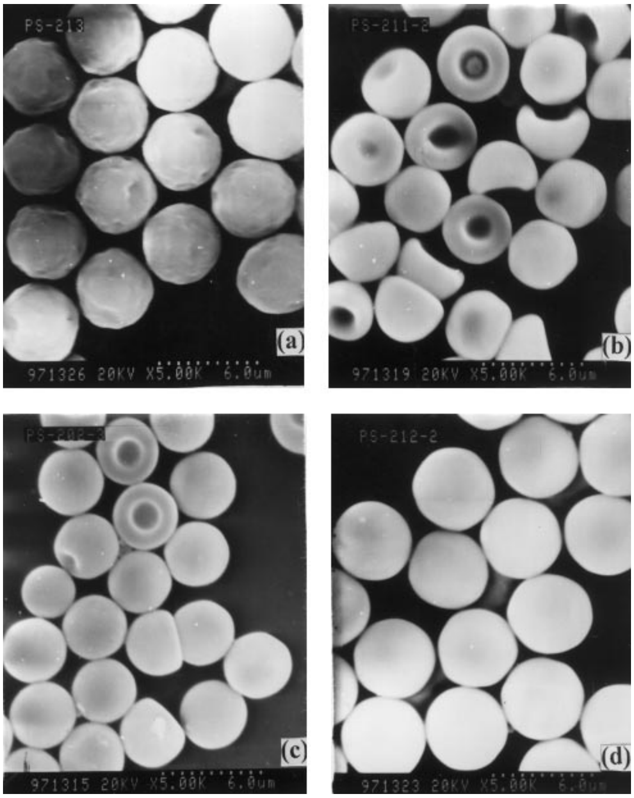

Fig. 4 SEM photographs of (a–d): crosslinked PS microspheres Nos. 8–11 in Table 4

contracted, but actually the network was not strong enough to keep the shape and thus deformed to dented spheres (Fig. 2d).

The inner structure (ultrathin cross-section) of crosslinked microspheres (No. 4 in Table 3) was observed by TEM to further corroborate the above viewpoints. A lot of tiny irregular pores were observed inside the microsphere (Fig. 3), which suggests the phase separation between toluene and crosslinked polymer. The tiny pores were due to the existence of toluene inside the microsphere. The non-uniformity of crosslinked polymer was epitomized as some dark regions and less dark regions elsewhere.

Effect of St/DVB ratio on the morphology of crosslinked microspheres

The total amount of St, DVB and toluene was always 40 ml and toluene/(St + DVB) ratio was kept at 1:1 (v/v). As shown in Table 4 and Fig. 4, no obvious dependence of particle size on St/DVB ratio was observed. The spherical particles have a rough surface with many dimples at the St/DVB ratio of 3:1. When the St/DVB ratio decreased to 2:1 and 1:1, smooth-surfaced round particles with a deep dent (Fig. 4b) and with a shallow dent (Fig. 4c) were obtained, respectively. The spherical appearance of some particles in Fig. 4b and c was due to their projections from different view angles, where the dent was visually invisible. The dent was deeper in the former than in the latter, which suggests the crosslinked network of the former was weaker. The particles are perfectly round spheres after further decreasing the St/DVB ratio to 1:2.

When the DVB amount is high enough (e.g., St/DVB = 1:2, v/v), the crosslink density would be high enough to maintain the spherical shape of the particles during polymerization, resulting in perfectly round spheres (Fig. 4d). With decreasing DVB content, the crosslink density decreased, thus it is not so strong to resist the volume contraction and interfacial tension increase during polymerization, giving rise to the formation of a heavy dent (Figs. 4b and c) and many dimples (Fig. 4a) as a result of toluene escaping.

Effect of St/DVB ratio on inner structure of crosslinked microspheres

TEM photographs of ultrathin cross-section for samples 8–11 (Table 4), are shown in Fig. 5. Some tiny pores are

Colloid & Polymer Science, Vol. 276, No. 8 (1998)

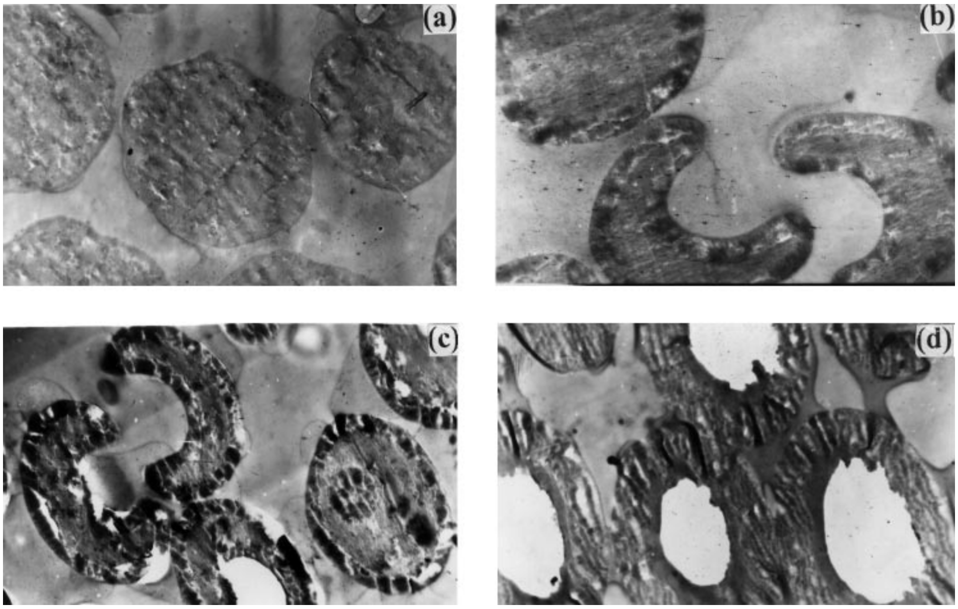

Fig. 5 TEM photographs of ultrathin cross-section of crosslinked PS microspheres (a–d): Nos. 8–11 in Table 4 (×5000)

rather uniformly distributed in Fig. 5a. There are some light and dark regions, suggesting the nonuniformity of the crosslinked structure. Figure 5b–d show a somewhat core-shell structure with a darker shell, which is a highly crosslinked region. At the St/DVB ratio of 1:2, a big hole formed because of the inclusion of toluene within the crosslinked shell (Fig. 5d).

Before polymerization, the well-swollen particles were observed to be spherical with an optical microscope. It is much different from the result of El-Aasser et al. [17, 18], who, using crosslinked PS spheres as seeds and a mixture (St + DVB) as the swelling agent, obtained irregular spheres after swelling. In a system studied by Kobayashi [12], they always got almost spherical particles regardless of St/DVB ratio when uncrosslinked PS was used as seeds and St/DVB as the swelling agent, due to that no phase separation took place during polymerization. By dynamic swelling, Okubo et al. [13] observed the formation of a core-shell microsphere with a hole inside, as a result of using crosslinked PS as seeds and a mixture of toluene and DVB as the swelling agent; because of the very high crosslinked density (exclusively from DVB polymerization), no deformed particles resulted. In our system, the co-existence of toluene, DVB, and styrene in the swelling agent is crucial to the formation of deformed particles and the novel inner morphologies. The different toluene/(St/DVB) ratios and different St/DVB ratios are the driving forces for such novel morphologies as described above.

In addition, it was found during experiments that the seed-swelling procedure (e.g., swelling temperature and addition speed of the swelling agent) and the seed diameter also played important roles in the formation of irregular morphologies; further investigation is under way and will appear in a forthcoming paper.

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