

Investigation for Surface Morphology Variation of Monodisperse Polymer Particle

Dong Ok Kim, Jeong Hee Jin, Seok Heon Oh

Nano Technology Research Division, Research and Development Center, Hanwha Chemical Corporation, Yusung-Gu, Daejeon 305-804 S, Korea

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ABSTRACT: Monodisperse polymer particles composed of polystyrene (PS) and poly(1,6-hexanedioldiacrylate) were prepared via one-step seeded polymerization using PS as seed particles. For the study, the effects of the molecular weight of seed polymer particles, the ratio of the absorbed hexanediol dimethacrylate (HDDA) to the seed polymer particles (swelling ratio), and the seeded polymerization rate on the surface morphology of poly(St-HDDA) particles were investigated. It was observed that the crater-shaped

defect was at the surface of poly(St-HDDA) particles, independent of the molecular weight of seed polymer, and swelling ratio. But its surface morphology could be controlled by changing the rate of the seeded polymerization. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2385–2394, 2007

Key words: monodisperse polymer particles; seeded polymerization; swelling ratio; polymerization rate; surface morphology

INTRODUCTION

In recent years, monodisperse micron-sized polymer particles in the size range of 1–10 μm have been intensively investigated by both industry and academia, because they have, potentially, many applications in such areas, as microelectronics, information industry, and biomedical engineering.

Traditionally, micron-sized polymer particles have been synthesized by suspension polymerization. However, in spite of the simplicity of suspension polymerization, the size distribution of polymer particles becomes very broad because of the intrinsic nature of suspension polymerization. Thus, it is highly desirable to find an alternative process to obtain a very narrow distribution of micron-sized polymer particles.

Alternative methods for producing monodisperse micron-sized polymer particles have been developed, including (i) the successive seeding and polymerization from Vanderhoff et al.,¹ (ii) the activated swelling method from Ugelstad et al.,^{2–4} and (iii) the dynamic swelling method from Okubo et al.^{5,6}

About swelling method, one or two steps are needed, that is, seed polymer particles absorb monomer directly in one-step method but they need to be activated by absorbing a water-insoluble compound such as 1-chlorododecane at first and then absorb

monomer in two-step method. Thus, the swelling ratio and compatibility between the monomer and seed polymer determine the final size of polymer particles and their surface morphology.

In addition to the seeded polymerization, one-step aqueous dispersion polymerization has also been investigated by other research groups for the reason of its simplicity in preparing monodisperse micron-sized polymer particles.^{7–16}

Ogino et al. synthesized monodisperse polymer particles having the sizes in range of 4.1–7.5 μm from styrene (St) monomer and divinylbenzene (DVB) via the one-step swelling method, for which monodisperse polystyrene (PS) was used as seed particles. They reported that polymer particles thus prepared had pore structure at the surface, and the pore structure and pore size distribution were influenced by the ratio of the absorbed monomer to the seed polymer particles.¹⁷

Tuncel synthesized macroporous-structured polymer particles via a two-step seeded polymerization method using monodisperse PS particle as seed particles and dibutylphthalate as swelling agent. They reported that macroporous-structured polymer particles could be prepared, and the particle size and also the pore size increased with the amount of absorbed DVB.¹⁸

Kim et al. first prepared weakly crosslinked PS particles using urethane acrylate and then DVB was absorbed in the PS particles to obtain interpenetrated monodisperse particles. They observed that the surface of the interpenetrated particles changed from smooth to porous structure, as the amount of DVB

Correspondence to: D. O. Kim (sky2000cokr@hotmail.com).

was increased. They attributed the experimental observation to the microphase separation during polymerization.¹⁹

Owing to the very rigid nature, such crosslinked polymer particles based on St/DVB system have very limited applications. For instance, they are not suitable for such applications as the spacers for LCD panel and conductive particles. To overcome the difficulty associated with rigid nature, instead of DVB, it is desirable to use other crosslinking monomers having more flexible spacer units, such as ethyleneglycol dimethacrylate (EGDMA), butylene dimethacrylate (BDMA), or 1,6-hexanediol dimethacrylate (HDDA). But very little efforts have been reported on the subject.

In this article, we report on the results of our recent investigation on the effects of the molecular weight of seed polymer particles, the ratio of the absorbed HDDA to the seed polymer particles (swelling ratio), and the rate of seeded polymerization on the surface morphology of poly(St-HDDA) particles via one-step seeded polymerization using PS seed particles.

EXPERIMENTAL

Materials

For the preparation of seed polymer particles by dispersion polymerization, styrene (St) monomer (Junsei) was distilled under vacuum and stored in the refrigerator. 2,2'-Azobisisobutyronitrile (AIBN) was used as initiator and polyvinyl pyrrolidone (PVP, K-30) was used as dispersant.

For the seeded polymerization, hexanediol dimethacrylate (HDDA) was purchased from Alfa Aesar and used as crosslinking monomer without further purification. Benzoylperoxide (BPO, Lancaster), having 6-h half-life temperature at 73°C, was used as low-speed initiator and 2,2'-azobis(4,4'-dimethylvaleronitrile) (VT-65, Wako), having 6-h half-life temperature at 51°C, was used as medium speed initiator. In addition to the thermal initiators, UV initiator, camphorquinone, and 2-(dimethylamino) ethylmethacrylate (Aldrich) were used for fast polymerization. Poly(vinyl alcohol) (PVA, Aldrich), having a weight-average molecular weight of 85,000–146,000,

TABLE I
Standard Recipe for the Preparation of Seed Polymer Particles by Dispersion Polymerization

Chemicals	Amount (g)
Styrene	70
α -Methyl SM	10
Ethanol	432
Methyl-Cellusolve	122.5
Polyvinylpyrrolidone (K-30)	10
AIBN	2.5
Water	155.5

TABLE II
The Physical Properties of PS Seed Particles

	Diameter (μm)	M_w	C_v
Seed A	1.25	101,000	4.5
Seed B	1.30	37,000	4.3
Seed C	1.10	7,600	4.8

$$C_v (\%) = \sigma/D_n \times 100.$$

σ , Standard deviation of diameter; D_n , number average diameter.

was used as dispersant for polymerization and sodiumlaurylsulfate (SLS, Aldrich) was used as emulsifying agent for emulsification of monomer mixtures.

For the preparation of PVP-free seed polymer particles via soap-free polymerization, potassium persulfate (KPS, Junsei) was used as initiator.

Polymerization

The polymerization procedure for the preparation of polystyrene (PS) seed particles via dispersion polymerization is as follows.

First, the chemicals summarized in Table I were put into a 500-mL round flask equipped with a mechanical stirrer and reflux condenser under a well-controlled temperature. The chemicals were stirred gently with nitrogen purging for 1 h to remove dissolved oxygen. Then, the temperature of the reactor was increased to 70°C and a predetermined amount of initiator was added to the reactor, and the polymerization reaction was continued for 12 h. The reactor was cooled down and the seed particles were separated using centrifugation, washed with methanol three times, and dried in a vacuum oven. The characteristics and photograph of seed particles thus prepared are summarized in Table II and Figure 1.

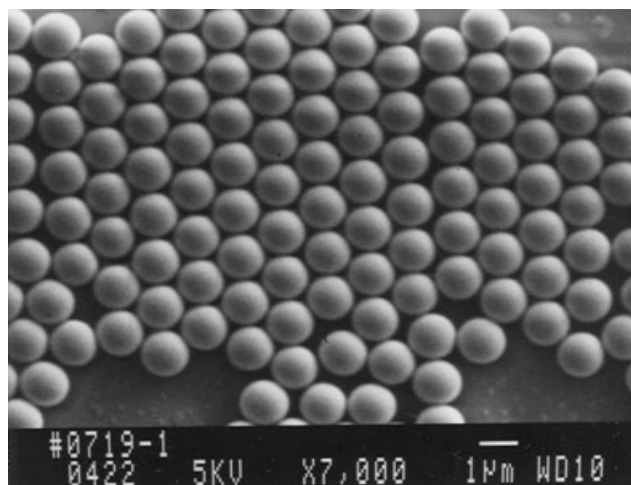


Figure 1 SEM photograph of the polystyrene seed particles (seed A).

TABLE III
Ingredients for the Materials Employed for the Synthesis of Polymer Particles by Seeded Polymerization

Chemicals	Amount (g)
HDDA	1
BPO	0.05
SLS (0.3%) solution	17
PVA (3%) solution	3

For the seeded polymerization, the chemicals summarized in Table III were added to a 50 mL vial and emulsified using ultrasonic homogenizer. A predetermined amount of seed particles was added to above-mentioned monomer emulsion and this vial was placed in a shaking incubator at room temperature for 24 h for monomer absorption. After the monomer absorption, a predetermined amount of PVA solution was added and polymerization was performed in a shaking bath under temperature control for 24 h. After the polymerization, the same sep-

aration and cleaning procedures employed for the seed polymerization were used to collect the poly(St-HDDA) particles.

Characterizations

The analysis of the particle size, the distribution of PS seed particles, and poly(St-HDDA) particles was performed using AccuSizer™ 740A (PSS.NICOMP, Santa Barbara, CA), and the surface and cross-sectional morphologies of the particles were examined by using SEM(JEM 1200EX, Japan) and TEM(ZEISS EM912).

RESULTS AND DISCUSSION

The effect of molecular weight of seed particles and swelling ratio

When crosslinked monodisperse poly(St-HDDA) particles were synthesized via one-step seeded polymerization using PS as seed particles, the crater-

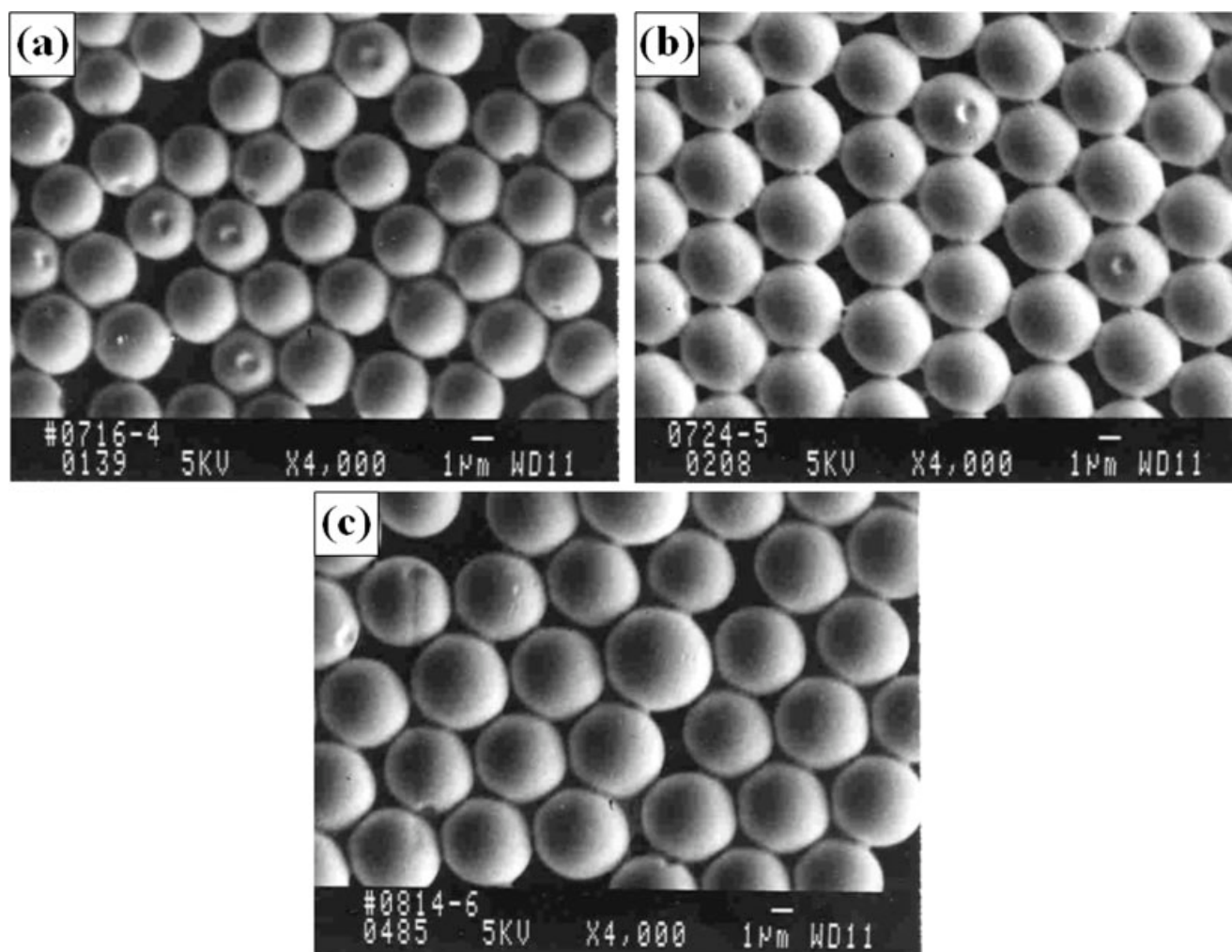


Figure 2 SEM photographs of the poly(St-HDDA) particles with different molecular weights of seed polymer at 70°C: (a) seed A (C_v : 5.3), (b) seed B (C_v : 5.0), and (c) seed C (C_v : 5.5) ($\times 4000$ magnification).

shaped defect was observed on the particle surface as shown in Figure 2. This kind of phenomenon is usually referred to as phase separation caused by the lack of compatibility between the seed polymer and crosslinked polymer, and it is dominated especially when the molecular weight of seed polymer exceeds a critical value for phase separation.

In this study, we observed variations of surface morphology of the crosslinked poly(St-HDDA) particles at a fixed swelling ratio (S/R:50), but we varied the molecular weight of the seed polymers, as shown in Figure 1, to determine a critical molecular weight of the seed polymer for crater-shaped defect. Figure 2 shows that crater-shaped defects were always observed, independent of molecular weight of the seed polymers, and the size of crater defect was increased with increasing molecular weight of the seed polymer. This observation indicates that more active phase separation occurs when the molecular weight of seed polymer is increased.

However, very large amounts of chain transfer agent were necessary to lower the molecular weight of seed particles, which in turn would have an adverse effect on making the particle size distribution narrow. Thus, in this study, we could not prepare seed polymer whose molecular weight was lower than 7600. The surface morphology of poly(St-HDDA) particles was also observed with a fixed molecular weight of seed polymer (37,000) and varying the swelling ratio from 20 to 200. In Figure 3, we observe crater-shaped defects, independent of the swelling ratio, but the size was decreased with increasing swelling ratio. It was almost impossible to remove crater-shaped defect from the particle surface by simply adjusting the molecular weight of the seed particles and swelling ratio.

However, the polymer particles with such defects are not suitable for applications in microelectronics such as ball spacers for such applications in LCD panel and conductive particles requiring a certain

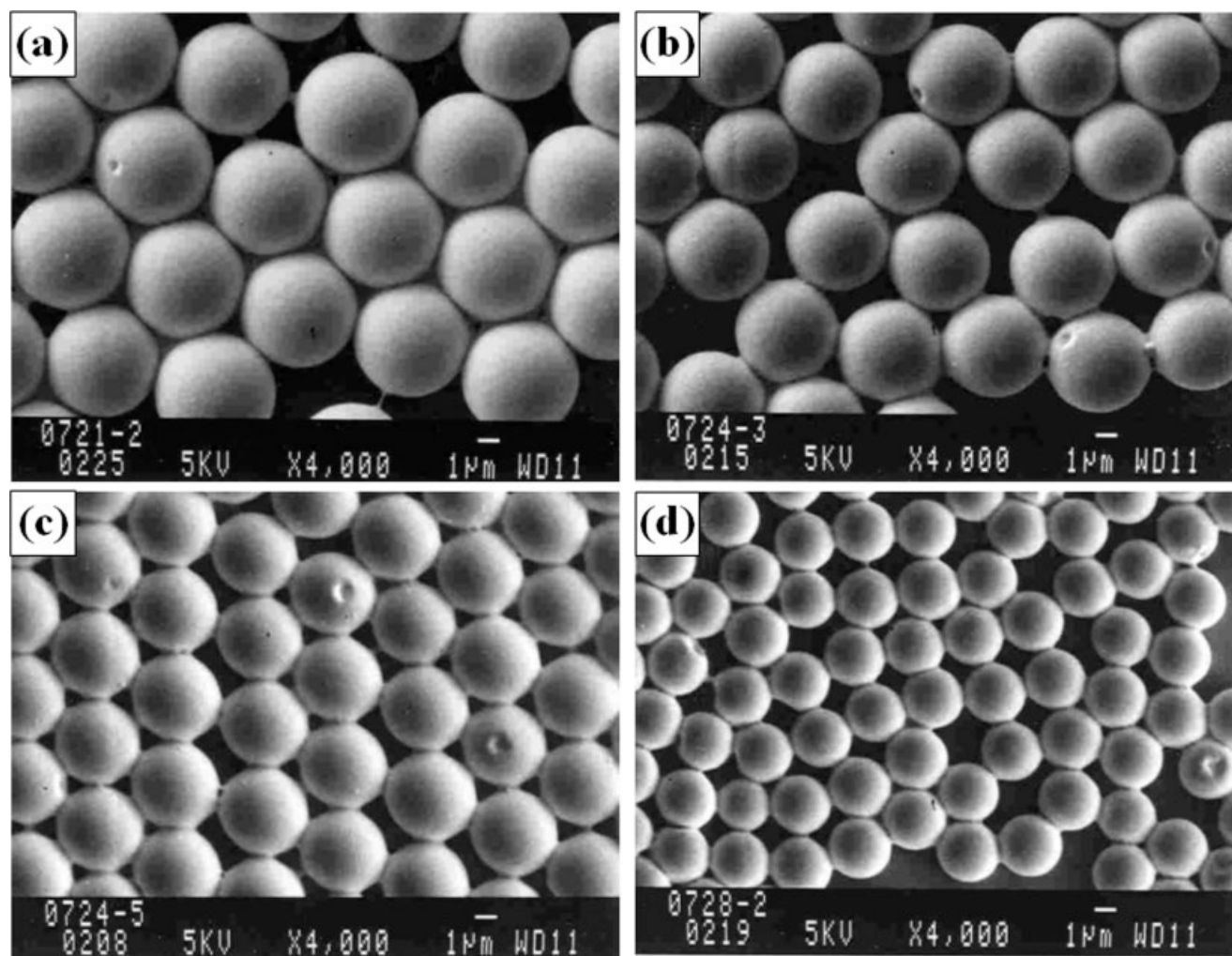


Figure 3 SEM photographs of the poly(St-HDDA) particles with different swelling ratios (S/R) at 70°C: (a) S/R: 200 (C_v : 5.6), (b) S/R: 100 (C_v : 4.9), (c) S/R: 50 (C_v : 5.1), and (d) S/R: 20 (C_v : 5.4).

minimum level of mechanical properties, while the surface defects may have an adverse effect on the mechanical properties. The detailed discussion of the effect of the surface defects on the mechanical properties will be presented in the future.

Investigation of crater-shaped defect

As described previously, the surface defects on the crosslinked poly(St-HDDA) particles are formed because of the phase separation between the seed polymer and crosslinked polymer. Figure 4 gives direct evidence of phase separation in such a system. In Figure 4, we observe that the separated phases are located at the surface of the particles and this is in good agreement with the observations in Figure 3.

This observation clearly explains that phase separation occurs between the seed polymer and crosslinked polymer during the polymerization and segregated seed polymer part (linear polymer) moved toward the particle surface and shrank with the degree of crosslinking polymerization because shrinking stress may be concentrated on the relatively weak linear polymer part when the polymerization shrinkage happens, and this phenomenon seems to give rise to crater-shaped defect.

Effect of seed polymerization method

When phase separation occurs in poly(St-HDDA) ($S/R: >20$) particle, it is not difficult to imagine that small hydrophobic dispersant phase, seed polymer (PS), would be located in the center of polymer particle and form core (PS)/shell [poly(HDDA)] structure, because this would be a more thermodynamically stable structure. We observe, however, crater-shaped defect on the surface of the particle, instead of core/shell structure. From this observation, we can specu-

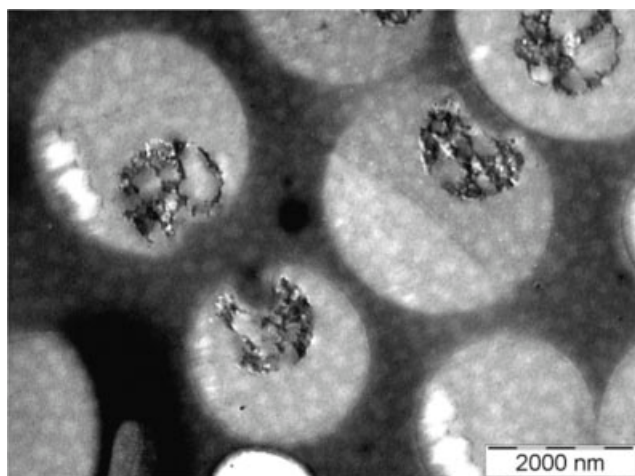


Figure 4 TEM photograph describing the cross section of the poly(St-HDDA) particles.

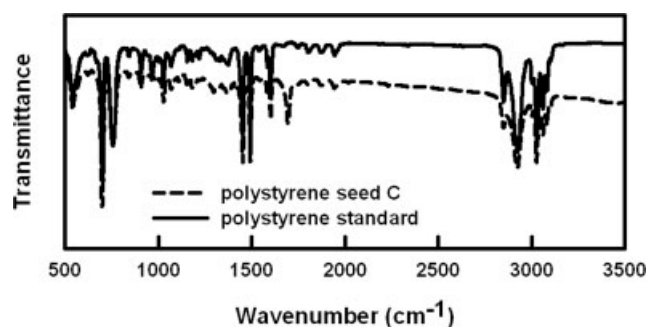


Figure 5 Variations of FTIR spectra of PS seed particles and PS standard.

late that there are still certain amounts of PVP remaining at the surface of seed polymer particle after the cleaning of seed polymer particles, because they are chemically grafted onto the seed polymer particles during the seed polymerization. This phenomenon made the PS phase be located near the surface of the polymer particles and not at the center of polymer particle. Namely, hydrophilicity of PVP seems to be responsible for the phenomenon. From the comparison of the FT-IR spectrum of PS seed particles with PS standard given in Figure 5, we can observe the peak for the carbonyl group of PVP at 1695 cm^{-1} , and it implies that a certain amount of PVP still remains at the surface of the seed particles even after seed polymer particles were cleaned with deionized water and methanol several times. Thus, the mechanism for forming crater-shaped defect on the particle surface is suggested schematically in Figure 6 on the basis of the previous observations.

According to the suggested mechanism, the grafted PVP plays a key role in forming crater-shaped defect. To support the earlier discussion, we synthesized PVP-free PS seed particles ($1.1\text{ }\mu\text{m}$; $C_v: 5.8$) via soap-free polymerization separately and prepared cross-

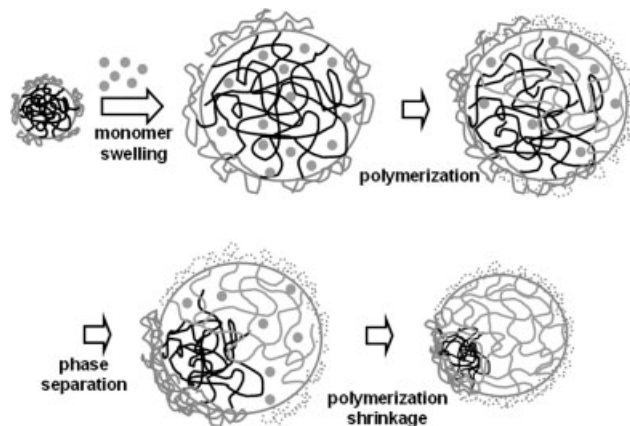


Figure 6 Schematic of the proposed model for the crater-shaped defect on the poly(St-HDDA) particle: (black: PS, gray: HDDA, dotted line: PVA, and dark gray solid line: grafted PVP).

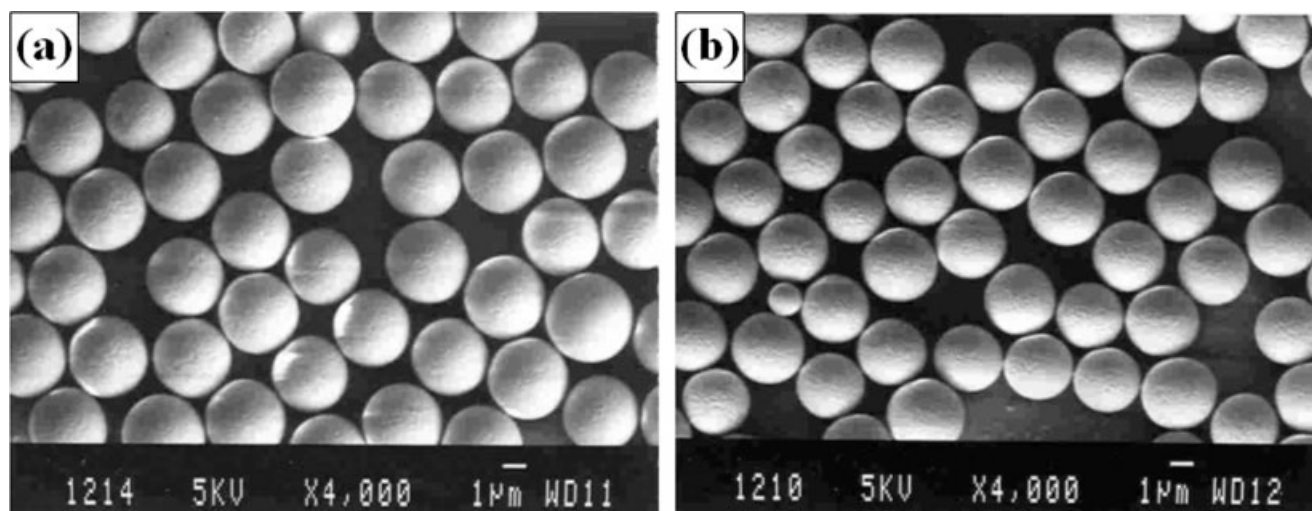


Figure 7 SEM photographs of the poly(St-HDDA) particles, which were prepared using soap-free emulsion polymerized seed particles at 70°C: (a) S/R: 60 (C_v : 6.5) and (b) S/R: 40 (C_v : 6.2) (4000 \times magnification).

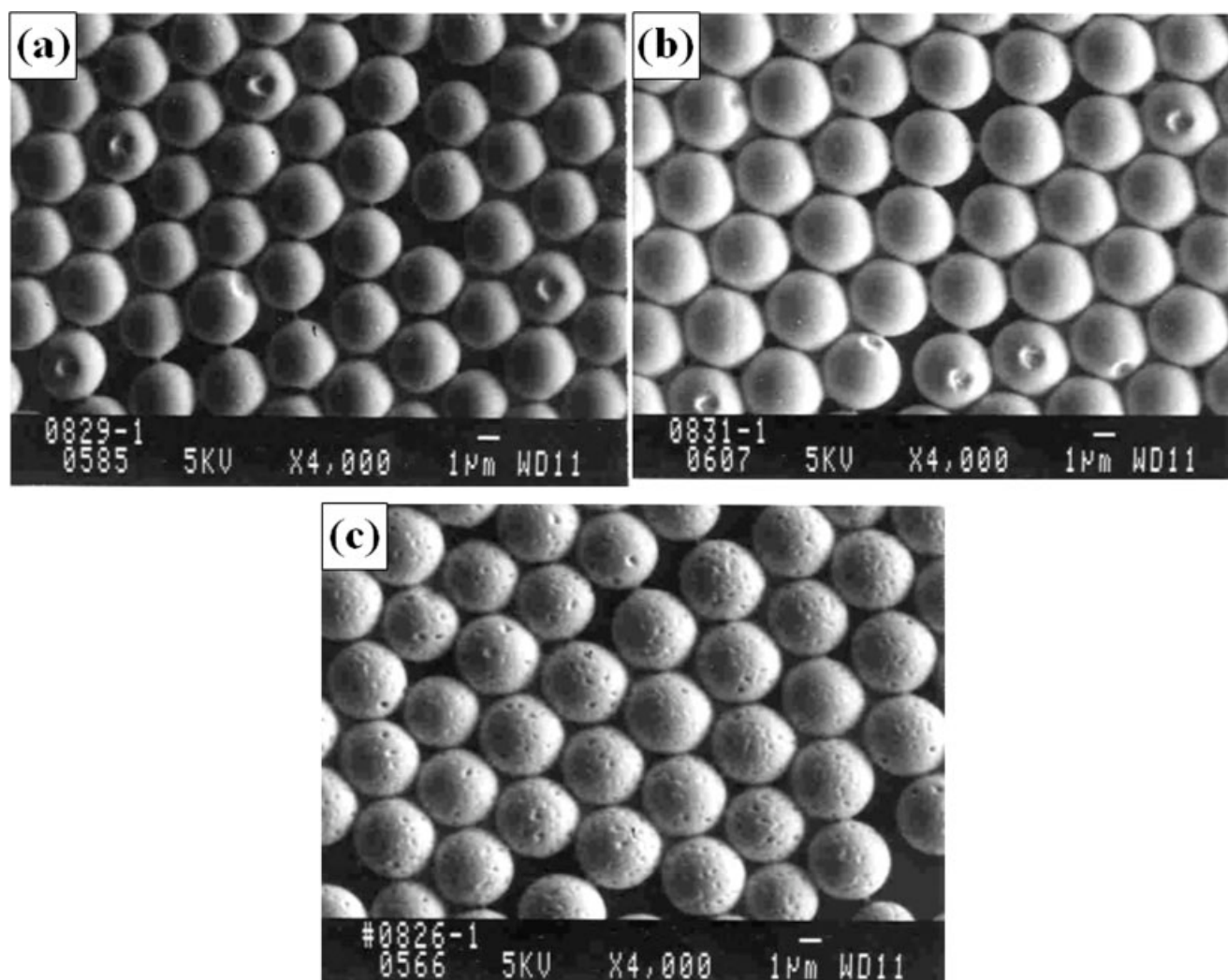


Figure 8 SEM photographs of the poly(St-HDDA) polymer particles having different molecular weights at 80°C: (a) seed A (C_v : 5.5), (b) seed B (C_v : 5.1), and (c) seed C (C_v : 5.4), (4000 \times magnification).

linked poly(St-HDDA) particles, and then examined the surface morphology using SEM. As shown in Figure 7, although the molecular weight of the seed polymer (M_w : 363,000) is very high, smooth surface morphology can be observed. This observation enables us to conclude that the grafted PVP is the origin of crater-shaped defect.

Effect of seeded polymerization rate

Using Figure 6, we explained that crater-shaped defect originated from the phase separation of PS phase toward the particle surface because of the PVP. Thus, based on the idea that if the polymerization rate can be controlled faster than that of phase separation, different kinds of surface morphology can be obtained. We performed a series of experiments and investigated the relationship between the surface morphology and polymerization rate by changing the initiator from BPO to VT-65 and UV initiator.

Figure 8 gives SEM micrographs describing the results of polymerization performed using BPO with a fixed swelling ratio (40) and different seed polymer particles.

As shown in Figure 2, the size of the crater-shaped defect increases with increasing molecular weight of seed polymer. However, peculiarly enough, the surface morphology was changed to porous structure in the case of lowest seed molecular weight.

Figure 9 gives SEM micrograph describing the changes of the surface morphology of the polymer particles given in Figure 8 when the initiator BPO was replaced with VT-65. The surface morphology having crater-shaped defect is changed to porous structure for Figure 8(a), but changed to rough structure for Figure 8(b). And porous structure changed to rough structure for Figure 8(c). These results indicate that not only changing the molecular weight of seed polymer but also changing the polymerization rate can control the surface mor-

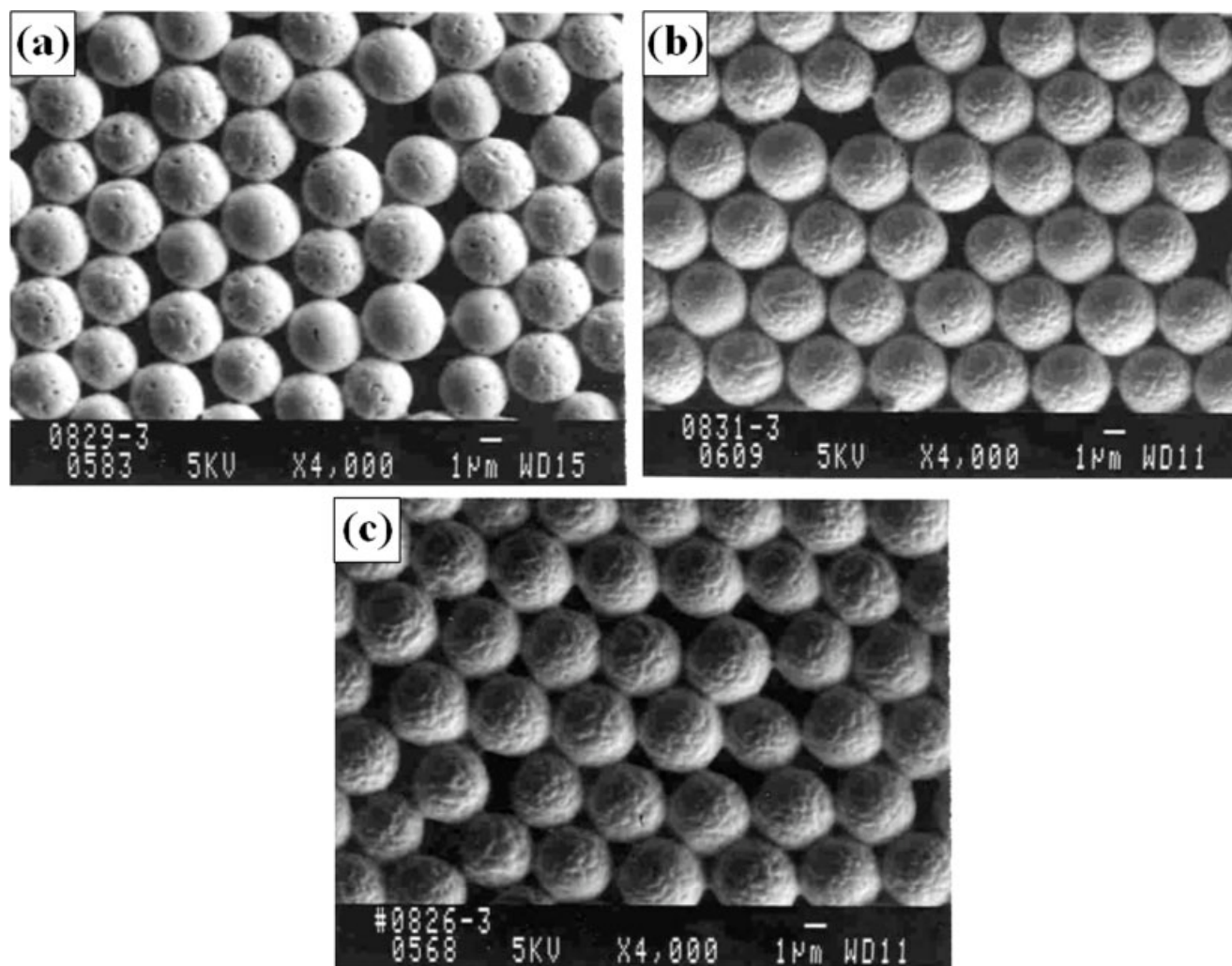


Figure 9 SEM photographs of the poly(St-HDDA) particles having different molecular weights at 80°C: (a) seed A (C_v : 5.8), (b) seed B (C_v : 5.3), and (c) seed C (C_v : 5.6) (4000× magnification).

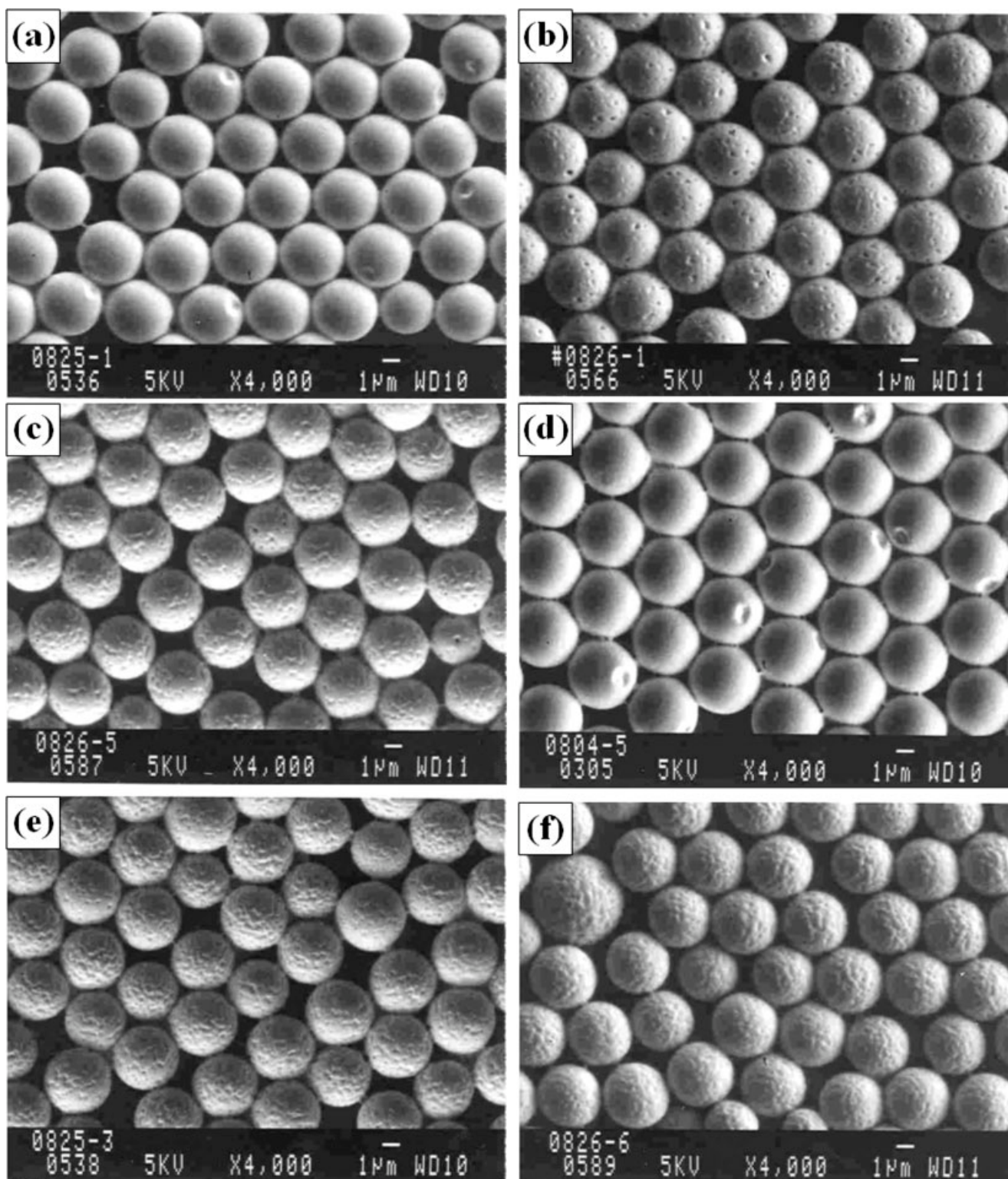


Figure 10 SEM photographs of the poly(St-HDDA) particles having different initiator and polymerization temperature: (a) BPO (C_v : 5.5, 70°C), (b) BPO (C_v : 5.4, 80°C), (c) BPO (C_v : 5.5, 90°C), (d) VT-65 (C_v : 5.5, 40°C), (e) VT-65 (C_v : 5.6, 70°C), and (f) VT-65 (C_v : 5.6, 90°C) (4000 \times magnification).

phology of polymer particles. Namely, increasing the polymerization rate can change the surface morphology of crosslinked poly(St-HDDA) particle from the crater-shaped defect to porous structure or rough

structure without adjusting the molecular weight of seed polymer.

As supplementary experiments, a series of experiments were conducted by varying the polymeriza-

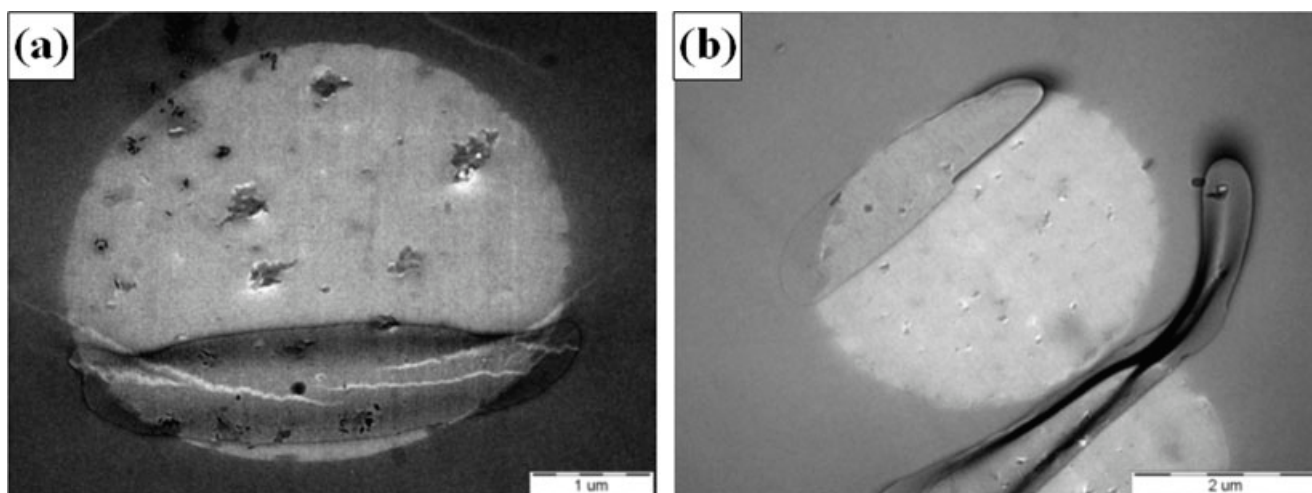


Figure 11 TEM photographs describing the cross section of the poly(St-HDDA) particles: (a) Figure 9(b) and (b) Figure 9(c).

tion rate at different polymerization temperatures for a given initiator using seed A.

As shown in Figure 10, when BPO was used, crater-shaped defect was observed at 70°C and porous structure at 80°C, but rough structure was observed at 90°C. However, when VT-65 was used, crater-shaped defect was observed at 40°C, but rough structure was observed at 80 and 90°C. These observations clearly indicate that an increase in polymerization temperature has the same effect as changing initiator from BPO to VT-65.

In addition to surface morphologies, the cross-sectional morphologies of Figure 10(b,c) were also observed using TEM in Figure 11. As shown in Figure 11, both particles have discontinuous phase-separated domains at the surface and inside of particles, but porous structure particle has more distinctive phase separation than rough structure particle. It is not diffi-

cult to imagine that there is an intricate relationship between polymerization rate and degree of phase separation in poly(St-HDDA) particle system. Moreover, in the case of UV initiator, smooth surface morphology and no phase separation were obtained as shown in Figure 12. Thus, it can be concluded that this phenomenon occurred because the rate of polymerization is much higher than that of phase separation. On the basis of the earlier observations, the mechanisms for the variations of each surface morphology are proposed schematically in Figure 13.

CONCLUSIONS

In this study, we have investigated the surface morphology of crosslinked monodisperse poly(St-HDDA) particles prepared by one-step seeded polymerization using PS seed particles.

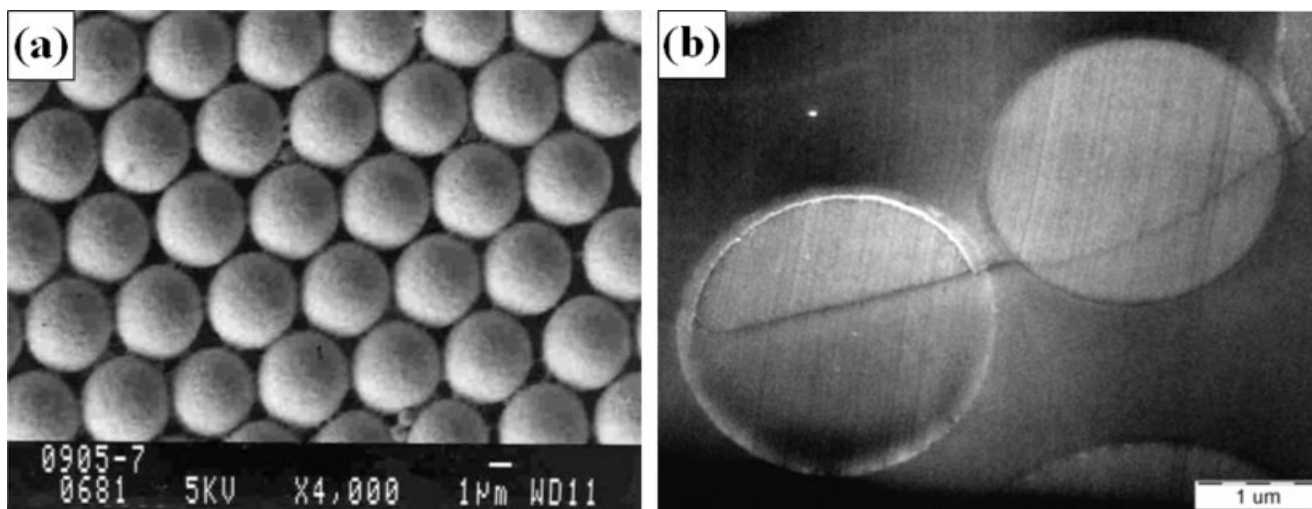


Figure 12 SEM and TEM photographs describing the surface and cross section of the poly(St-HDDA) particles, which were prepared using UV initiator at 25°C (S/R:60): (a) SEM (C_v : 5.5, 4000× magnification) and (b) TEM.

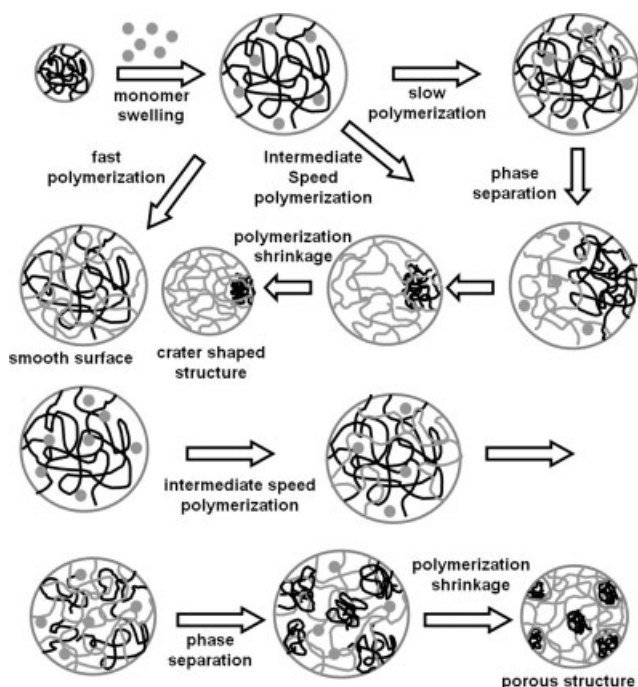


Figure 13 Schematic of the proposed model for the change of surface morphology of the poly(St-HDDA) particle: (black: PS and gray: HDDA).

In the PS (dispersion polymerization)/poly(HDDA) system, crater-shaped defect was observed irrespective of the molecular weight of seed polymer and swelling ratio, but it was not observed in PS (soap-free polymerization)/poly(HDDA) system. This observation drove to the conclusion that the origin of the crater-shaped defect is the PVP, which is remained on the surface of seed particles.

In addition to the earlier observations, we have demonstrated that the surface morphology of the crosslinked poly(St-HDDA) can be controlled from crater-shaped defect to porous structure, rough structure, or smooth surface by increasing polymerization rate.

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