

Novel Method of Preparation of a Charged Mosaic Membrane by Using Dipole-Like Microspheres.

II. Preparation of Dumbbell/Egg-Like Microspheres

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Received 9 March 2000; accepted 30 August 2000

ABSTRACT: The dumbbell-like/egglike microspheres of poly(4-vinylpyridine/*n*-butyl acrylate)/polystyrene [P(4VP/*n*BA)/PS] were prepared by soap-free seed emulsion polymerization. The effects of various polymerization parameters, such as the amount of ethyl acetate (EA) in the continuous phase, swelling time, degree of crosslinking of seed polymer, polymerization temperature, and compatibility of seed polymer and the secondary polymer, and so forth, on the formation of dumbbell-like/egglike morphology were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It was found that secondary particles could be eliminated either by drastically increasing the number of seed particles or by stripping EA from the seed latex by dialysis and evaporation under a vacuum. Swelling the seed particle with the secondary monomer was essential for the preparation of egglike microspheres. For the localization of PS domains on one side of the egglike particle, the most effective factors were to elevate the polymerization temperature up to 90°C and simultaneously to lower the compatibility of the polymer on the seed particle surface with the phase of PS, while using the uncrosslinked seed latex. Crosslinking the seed latex was not suitable for localizing the PS domains in the seed particle, especially when the degree of crosslinking exceeded 0.5 wt % of EGDMA. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2002–2017, 2001

Key words: dumbbell-like/egglike microsphere; poly(4-vinylpyridine/*n*-butyl acrylate)/polystyrene; ethyl acetate; charged mosaic membrane; dipole-like microsphere

INTRODUCTION

Composite latex particles offer a wide variety of physical properties to the end user and find applications in coatings, adhesives, graphic arts, impact-resistant thermoplastics, and biotechnologies, among other areas. The physical properties are achieved by balancing polymer composition, molecular weight, and latex particle morphology.

There is a wide variety of particle morphologies already reported. These include the familiar core-shell,^{1,2} “inverted” core-shell,^{1,3,4} sandwich structures,¹ dumbbell-like or hemispheres,^{1,5,6} and “confetti-like,” “raspberry-like,” and “void” particles.⁷ Because of their importance to the final properties of latex polymers, particle morphology is a subject of intense interest and a great deal of effort is being expended to learn how to control the final particle structure.^{8,9}

Seed emulsion polymerization is the most common preparative method for particles with various morphologies. With this method, the effects of

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Journal of Applied Polymer Science, Vol. 80, 2002–2017 (2001)
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various polymerization parameters on the formation of different morphologies have been widely investigated both thermodynamically and kinetically.^{1–14} Furthermore, the setting up of thermodynamic models and computer algorithms for predicting the morphology development have been also carried out by D. C. Sunderberg et al.,^{15,16} Chen et al.,¹⁷ and our research group.^{8,9} However, problems of phase separation during the polymerization create a more complex dependence of the particle morphology on polymerization parameters and conditions in the case in which the composite latex particles comprise two or more immiscible polymers, such as poly(4-vinylpyridine/*n*-butyl acrylate)/polystyrene [P(4VP/*n*BA)/PS] particles. It was found that almost every polymerization variable that one can think of can affect particle morphology and, in cases with the composite particle, morphology is determined from combinations of more than one parameter. This implies that it is possible to obtain any morphology observed in a certain polymerization system by properly adjusting the polymerization parameters, no matter what the thermodynamic equilibrium morphology of the polymerization system is. These considerations framed our background motivation for preparing dumbbell-like/egglike microspheres with the P(4VP/*n*BA)/PS polymerization system, even though the thermodynamic equilibrium morphology should be a so-called “inverted” core–shell structure resulting from the intensively hydrophilic seed polymer, P(4VP/*n*BA), and the hydrophobic secondary polymer, polystyrene.

Concerning the target morphology of this work, the dumbbell-like/egglike (hemisphere) morphology has been understood by many researchers as one of transient morphology. The factors that are essential to the formation of dumbbell-like morphology have been well investigated by Vanderhoff et al.,^{5,6} who employed seed emulsion polymerization of the PS/PS polymerization system. Moreover, a model for the formation of dumbbell-like microspheres has been postulated. These are good references for the preparation of dumbbell-like/egglike P(4VP/*n*BA)/PS composite particles.

For application of the morphologies, researchers' interests seemed to be focused on the core–shell or inverted core–shell morphology, which are the two extreme cases of the two-component morphologies. This is probably because of the practical advantages of core–shell structure, that is, the core–shell structure enables one to incorporate different properties of two or more mate-

rials into one microsphere. For example, the encapsulation technique, in which the core is a medicine and the shell is a polymer, has been widely studied and applied in the fields of mimicking biological cells^{18,19} and pharmaceutically controlled releases.^{20,21} On the other hand, the core–shell structure also supplied a new method for studies and applications of polymer blends or alloys, such as latex-based paints^{22,23} and engineering plastics.^{24,25} The core polymer can be effectively and uniformly dispersed in the matrix consisting of shell polymer, and the size and properties of their domains in the blends can be easily controlled. Consequently, all properties of polymer blends can be optimized for practical applications. Yamazaki^{26,27} investigated the polymethyl methacrylate/polyethylacrylate core–shell structure system, and claimed that the tensile strength, at 100% elongation of composite polymer latex film prepared by using core–shell particles, was more than fourfold higher than that of the random copolymer latex film. Furthermore, the core–shell structure has been employed as a model for studying the behavior of polymer blends.²⁸ For other morphologies, for example, hemisphere or raspberry-like, applications have not been reported. Therefore, this work is considered to be the first attempt for application of one of these morphologies, that is, the application of dumbbell-like/egglike microspheres.

In the previous study²⁹ we schematically showed a method to prepare charged mosaic membrane by using dipole-like microspheres, as well as the preparation and characterization of seed latex of P(4VP/*n*BA) by a modified soap-free emulsion polymerization. In this study, as a key step to attain that objective, we report on the preparation of dumbbell-like/egglike microspheres of P(4VP/*n*BA)/PS with the seed latex of P(4VP/*n*BA).

EXPERIMENTAL

Materials and Apparatus

Monomer styrene and *n*-butyl acrylate, solvents 2-butanone and 2-propanol, oil-soluble initiators benzoyl peroxide (BPO) and α, α' -azobisisobutyronitrile (AIBN), water-soluble crosslinker ethylene glycol dimethacrylate (EGDMA), oil-soluble crosslinker divinylbenzene (DVB), and hydrogen chloride (HCl; chemical grade, 35%) used for pH adjustment of the aqueous phase, were supplied

Table I Typical Recipe of the Seed Emulsion Polymerization

Seed Polymer (wt %) ^a	Monomer (wt %) ^b	Initiator V50 (wt %) ^c	Crosslinker (wt %) ^c	Water (wt %) ^d	Comments
2.5	2.5	2	Variable	Variable	pH

^a Based on the total amount of the ingredients and calculated with the solid content of seed latex.

^b Based on the total amount of the ingredients.

^c Based on the amount of monomer.

^d The final adjustment for maintaining the solid content of the resultant latex at 5 wt %.

by Kishida Chemical Industries (Japan). Water-soluble initiator 2,2'-azobis(2-amidinopropane) · 2HCl (V50) was supplied by Wako Pure Chemicals (Tokyo, Japan). Styrene and nBA were distilled under reduced pressure, and the two solvents under atmosphere. EGDMA and DVB were washed with 3 wt % alkaline solution three times, washed with distilled and deionized (DDI) water five times, and then dried with a 4-Å molecular sieve. The initiators V50, AIBN, BPO, and HCl were used without further purification.

Water used in all experiments was distilled and deionized, with a conductivity of 18 MΩ cm⁻¹ and measured pH value of 6.7, by employing a Milli-Q water purification system (Millipore, Bedford, MA).

Analyses

A scanning electron microscope (SEM; JEOL JSM-5310; JEOL, Peabody, MA), transmission electron microscope (TEM; Hitachi H-700H, Tokyo, Japan), Ubbelohde viscometer, FTIR spectrometer (Nicolet 360, Avatar; Nicolet Instruments, Madison, WI), and pH/ion meter (Horiba, F-23, claimed precision 0.01, Kyoto, Japan) were used.

The pH value of water was adjusted with HCl solution, and measured with a pH/ion meter.

Morphologies of the resultant particles were determined by using SEM and TEM. The preparation methods of the SEM and TEM specimen were the same as those of seed particles that were described in the previous study.²⁹

The FTIR spectrum was measured using a tablet of potassium bromide (KBr) mixed with the powder of dry latex.

Because there are no proper viscosity constants for the Mark-Houwink-Sakurada equation applicable for the P(4VP/St) copolymer, the molecular weight of the copolymer was estimated by the following equation, which was recommended for pure P4VP.³⁰ The intrinsic viscosity was determined in 2-butanone/2-propanol (6/1 v/v) at 25°C by using a Ubbelohde viscometer.

$$[\eta] = 38 \times 10^{-3} M^{0.57} \text{ (mL/g)}$$

Dialysis and Swelling

The seed latex was dialyzed with a seamless cellulose tube (27/32, Viskase Sales Corp.) in flowing tap water for 24 h, and thereafter, in DDI water

Table II Main Properties of the Seed Latex

Run	Particle Size (μm)	CV ^a (%)	Particle Number (×10 ⁻¹² /g latex)	Degree of Crosslinking (EGDMA wt %) ^b	Solid Content ^c (wt %)	Comments
1122	0.77	9.50	0.394	0	9.41	
1135	0.58	8.93	0.862	0	8.80	pH = 3.7 ^d
1130	0.53	6.52	1.224	0.5	9.54	pH = 3.7 ^d
1185	0.56	7.20	0.539	0	4.95	
1186	0.52	7.13	0.678	0.5	4.99	
1187	0.40	8.80	1.284	2.0	4.30	

^a Variation coefficient of particle size.

^b Based on the total amount of monomers.

^c Solid content of the resultant latex.

^d pH value of water used for preparing the latex; others unmentioned were pH 6.7.

for 24 h at ambient temperature. To obtain a seed latex free of EA, the dialyzed latex was further stripped in a vacuum at room temperature, until no bubble was released.

The swelling was carried out by charging the ingredients to a 30-ml bottle or ampoule, and then tumbling the bottle or ampoule end over end at ambient temperature.

Preparation and Characterization of Dumbbell-Like/Egglike Microspheres

The polymerization was carried out by the two kinds of methods that were described in the previous work²⁹ concerned with the preparation of seed latex. The differences were that, in the case of using an ampoule, it was deoxidized by a vacuum nitrogen-purging cycle. In the case of using a flask, the initiator was added ahead of the monomers, to prevent a high concentration of initiator from inducing the seed latex to coagulate. A typical recipe of seed emulsion polymerization is shown in Table I.

All the solid contents of the resultant latices were 5 wt %. The polymerization was performed at 70°C for 14 h with initiator V50 and for 20 h with AIBN and BPO, unless specified otherwise.

RESULTS AND DISCUSSIONS

Properties of the Seed Latices Used

The properties of the seed latices and some essential comments on the latices that were used are shown in Table II.

Additionally, the compatibility of both the seed polymer and the secondary polymer will be discussed later, and will be, in turn, related to the pH adjustment of the continuous phase and the protonated degree of pyridine groups in the seed polymer. FTIR spectra were employed to reveal the effects of pH adjustment, either in the stage of preparing seed latices or in the seed emulsion polymerization, and the protonated degree of the seed polymer. The transmittance of the 1640 cm^{-1} band, which was assigned to the stretching vibration of the $\text{C}=\text{N}^+-\text{H}$ group, and the 1600 cm^{-1} band, which was assigned to that of the $\text{C}=\text{C}$ group, were detected. The relative strength of these two bands can be considered as a qualitative scale of the extent to which the pyridine groups were protonated in the polymers. As shown in Figure 1, the protonated degree of the

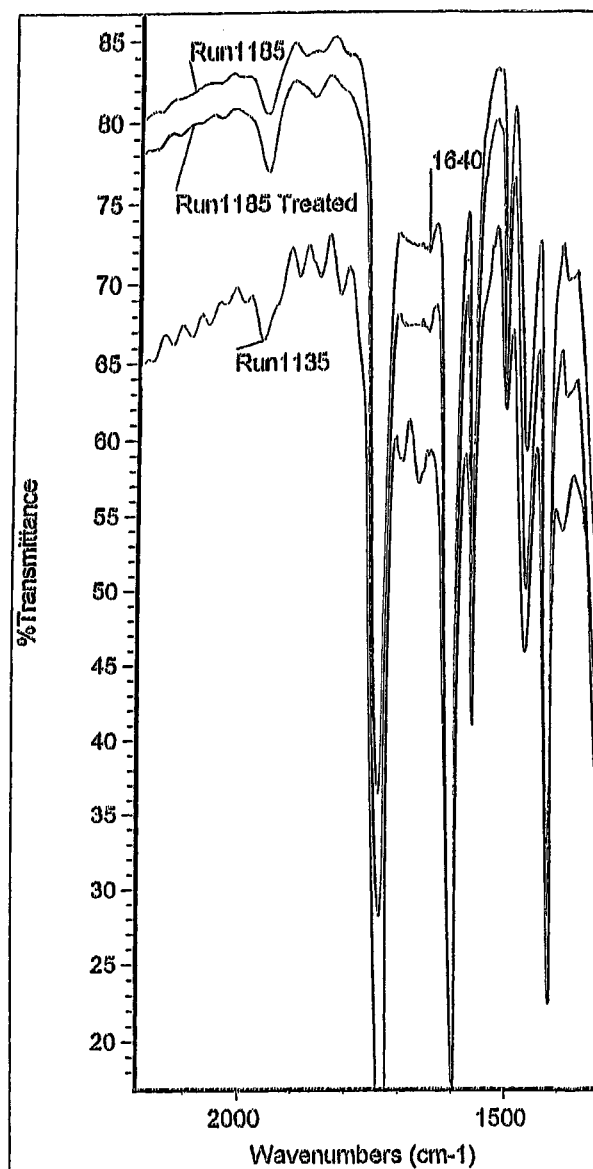


Figure 1 FTIR spectra of quaternized seed latices.

pyridine groups in the seed polymer was the highest in run 1135, which was prepared by adjusting the pH of the continuous phase prior to the emulsion polymerization, and the lowest one was run 1185, without any adjustment of the pH in the continuous phase; that of run 1185, treated with pH 3.3 of water, was moderate.

The viscosity-average molecular weight was also determined by an approximate method. These are 1.27 and 1.15×10^5 g/mol for the latex of run 1122 and run 1135, respectively. They indicated that the molecular weight of seed polymer was not affected by lowering the pH of the con-

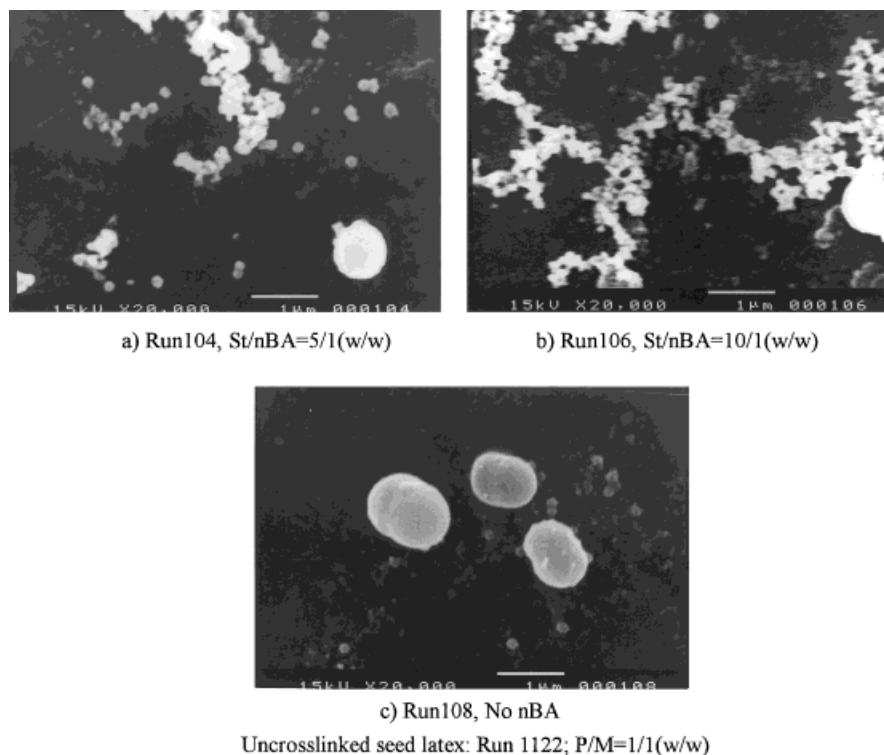


Figure 2 Effect of nBA on the morphologies of resultant particles.

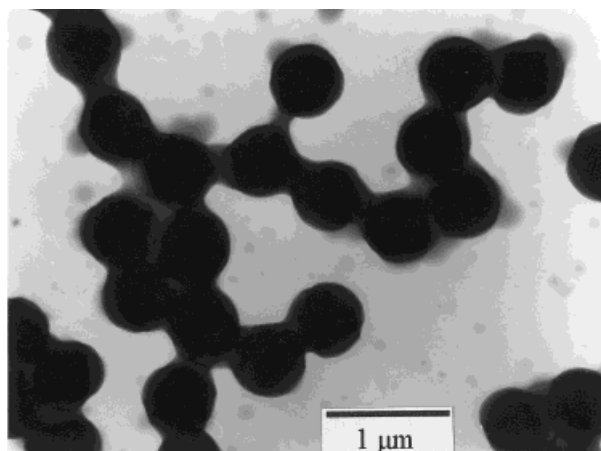
tinuous phase in the stage of preparing seed latex.

Control of New Particles during the Seed Emulsion Polymerization

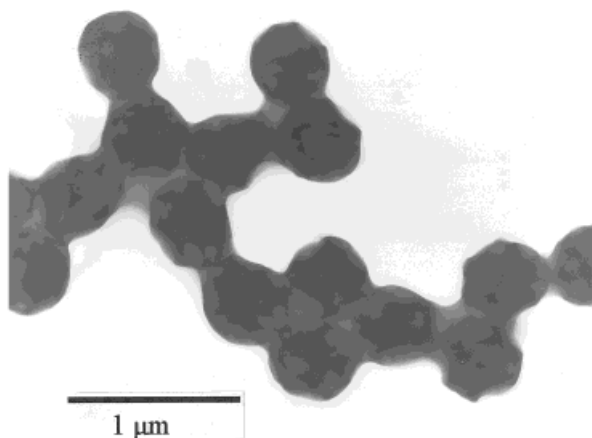
The seed emulsion polymerization was conducted in an ampoule, and the uncrosslinked seed latex (run 1122) was employed without any posttreatment. The secondary monomer was a mixture of styrene and *n*-butyl acrylate with 5/1, 10/1, and 1/0 S/nBA (w/w) ratios. The purpose of adding nBA to styrene was not only to modify the interfacial tensions of PS/P4VP and PS/water but also to enhance the miscibility of seed polymer and the secondary polymer. As we know, the terminal morphology of microspheres is determined by the thermodynamic factors of the polymerization system. With respect to obtaining dumbbell-like microspheres from P4VP and PS, it should be desirable to lower the interfacial tension of hydrophobic PS/water, to increase the surface area of PS domains in water as high as possible. Moreover, it is also desirable to prevent secondary particles from being generated during the polymerization by means of promoting the miscibility of seed and

second-stage monomer. Therefore, an additional small amount of nBA was added. The SEM photographs of the resulting particles are shown in Figure 2.

As shown in Figure 2, numerous new particles were generated, accompanied with a large amount of coagulum during the polymerization, regardless of the addition of nBA during the polymerization. Meanwhile, the dumbbell-like morphology was formed (run 108) only with the recipe without charging any nBA. This implies that the generation of secondary particles was not prevented by promoting the miscibility of seed polymer with the second-stage monomer and, also, that it was not effective to add nBA to modify the interfacial tensions of PS/water for the preparation of dumbbell-like microspheres. Moreover, the generation of secondary particles was not prevented by means of further crosslinking of the secondary polymer with 0.5 wt % of EGDMA, either. Therefore, based on these results, the next objective was to find a way to eliminate the new particles generated during the polymerization and, reasonably, an increase of the number of seed particles was considered as a first step.



a) Seed number: $3.9 \times 10^{13}/\text{g-Lx}$ (Run1186)



b) Seed number: $7.70 \times 10^{13}/\text{g-Lx}$ (Run1187)

The number was calculated based on the whole amount of resultant latex,
Stained by CH_3I vapor for 3 days (Black portion: P(4VP/nBA))

Figure 3 Effect of the number of seed particles on the generation of new particles.

According to the Fitch–Tsai theory of emulsion polymerization,³¹ the generation of new particles is determined by the rates of oligoradical capture by primary particles and coagulation. These two rates are greatly affected by the number of primary particles. If the number of primary particles is high enough, new particles will not form. However, in the present case, it seemed impossible to drastically increase the number of seed particles without changing other properties of the seed particles. For example, when using the seed latex (run 1122) of which the solid content was 10 wt %, the solid content of the resultant latex should not be over 10 wt %, to prevent coagulation resulting

from the addition of ionic initiator (V50). Hence, the number of seed particles was unable to be drastically increased. If latices such as run 1186 and run 1187 were used, other problems arose with the changes of the particle size and crosslinked degree, which, in turn, affected the morphology of resultant particles. Figure 3 shows the results of using the seed latices of runs 1186 and 1187 while maintaining the solid content of the resultant latex at 5 wt % and P/M equal to 1/1 (w/w). As shown in Figure 3, the secondary particles decreased as the number of seed particles increased. When run 1187 latex with a smaller size was used as seed latex, the secondary parti-

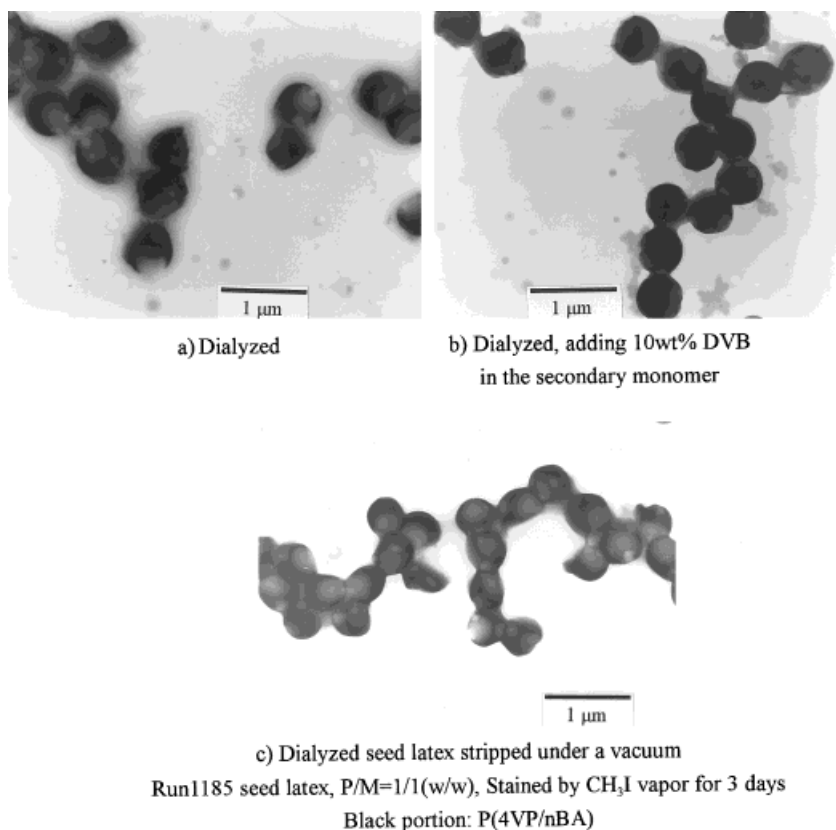


Figure 4 Effect of the amount of EA on the generation of new particles.

cles completely disappeared. It was clear that increasing the number of seed particles could eliminate the secondary particles.

Unfortunately, however, the dumbbell-like morphology was not obtained; instead, raspberry-like microspheres were formed. This implied that the 2 wt % crosslinked degree was too high to use for the preparation of dumbbell-like microspheres.

The unique way to increase the particle number of uncrosslinked seed latex was to prepare the seed latex with lower solid content, because the particle size decreased as the solid content decreased, consequently increasing the number of particles. However, decreasing the solid content too much contradicts the original purpose of this work. Therefore, another way to eliminate the secondary particle must be found.

Compared with a conventional seed emulsion polymerization, the presence of ethyl acetate in the continuous phase, which was present in the seed latex, should be considered in this polymerization system. It has been established that the existence of EA in the continuous phase greatly affected the properties and morphologies of the

P(4VP/St) latex by a soap-free emulsion polymerization.³² For example, while 2 wt % of EA existed in the polymerization system, a bimodal distribution of particle size was observed. This result is quite relevant to this study because the amount of EA in the continuous phase is estimated to be around 2 wt %, based on the total amount of the continuous phase of the seed emulsion polymerization. Moreover, the two polymerization systems are similar in most aspects, except that the seed particles exist prior to the emulsion polymerization in the current work. Therefore, the existence of EA was probably the reason for the generation of secondary particles.

Figure 4 shows the amount of EA in the continuous phase affecting the morphology of resultant particles. Because the coagulation took place during the dialysis of run 1122 latex, the run 1185 latex was used as the seed latex. Figure 4 shows the morphologies of resultant latices when using the seed latices, of which, for Figure 4(a) and (b) EA was removed by dialysis, and for Figure 4(c) by stripping the dialyzed seed latex under a vacuum until no bubbles were released. In the case of Figure 4(c), all of EA was considered to be re-

moved from the seed latex. It was observed that the secondary particles decreased as the amount of ethyl acetate decreased, regardless of the addition of crosslinker, and finally disappeared when seed latex free of EA was used. Therefore, it was clear that the existence of EA in the seed emulsion polymerization system was another reason for the generation of new particles.

However, the domains of polystyrene in the particles were not localized in the surface of the resultant particles, and a thin layer of seed polymer covered the PS domains. Furthermore, if the PS phase was crosslinked with DVB, as shown in Figure 4(b), it was found that all of the PS domains seemed to be embedded further into that of the seed particle. This indicated that the PS domains were probably occluded in the seed particles, in agreement with the results of Sheu et al.^{10,11} Therefore, a method to localize the PS domains on the surface of seed particles must be found.

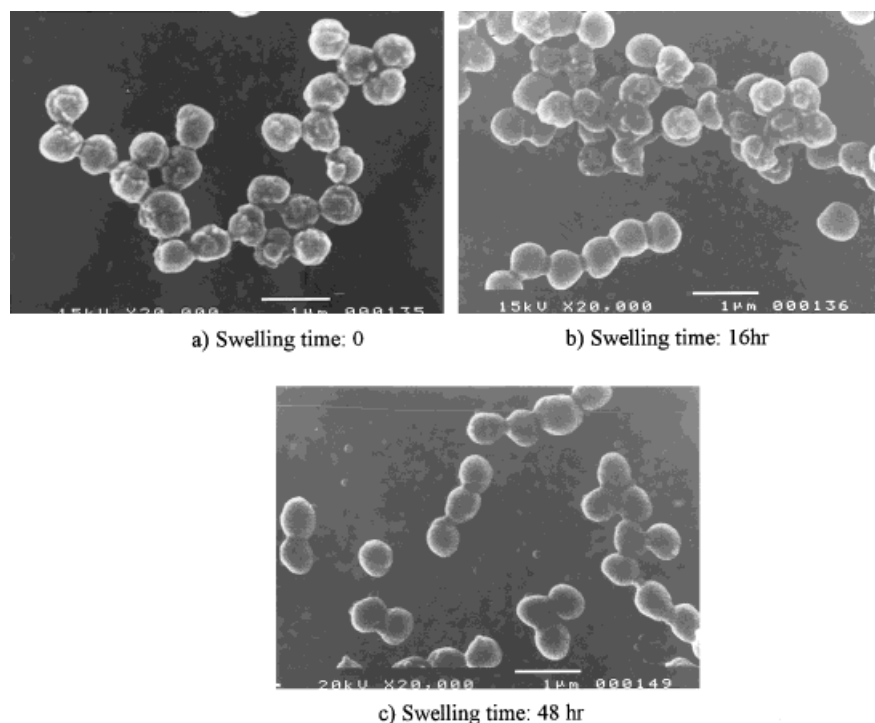
Two methods were investigated in this study. The first one was to promote the polarity of the seed polymer, that is, to decrease the miscibility of the two polymers by protonation of the pyridine groups in the seed particles, so as to force the PS domains to appear on the surface of seed parti-

cles. The second one was to crosslink the seed polymer.

Formation of Egglike Microspheres

The seed latex of run 1135 was used, which was prepared by adjusting the pH of the continuous phase to 3.7 prior to the emulsion polymerization.²⁹ This means that the 4VP monomer was protonated before the polymerization, and therefore, as shown in Figure 1, the protonated degree of the whole seed polymer was the highest.

Because the miscibility of seed polymer and the secondary polymer was decreased, a problem of inefficient swelling before the seed polymerization arose. Smith and Ewart³³ assumed that, during the emulsion polymerization, the monomer concentration in polymerizing particles was independent of conversion as long as monomer droplets were present in the system. Morton and coworkers³⁴ reported a fast diffusion rate of toluene into PS latex particles. In those cases where the latex particles were small ($D \leq 1000 \text{ \AA}$). Chung-Li et al.³⁵ showed that, when larger seed particles were used, the diffusion of monomer into the seed PS particles could be a slow process. Matsumoto and coworkers³⁶ claimed that the particle mor-



Uncrosslinked seed latex: Run1135; P/M=1/1(w/w); Swollen at room temperature

Figure 5 Effect of swelling time on the morphology.

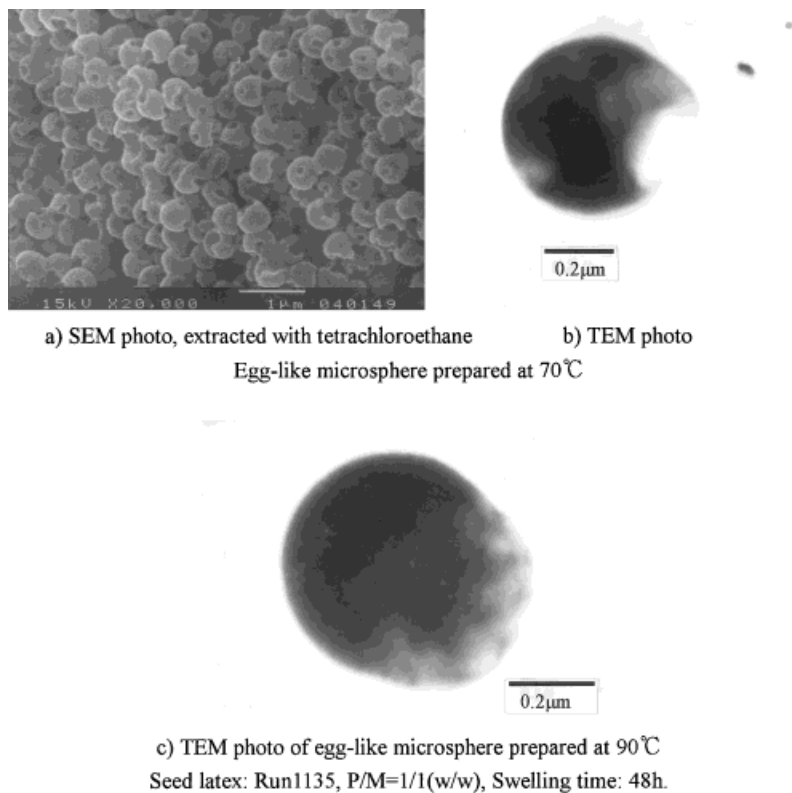


Figure 6 Morphology of egglike microspheres prepared at 70 and 90°C.

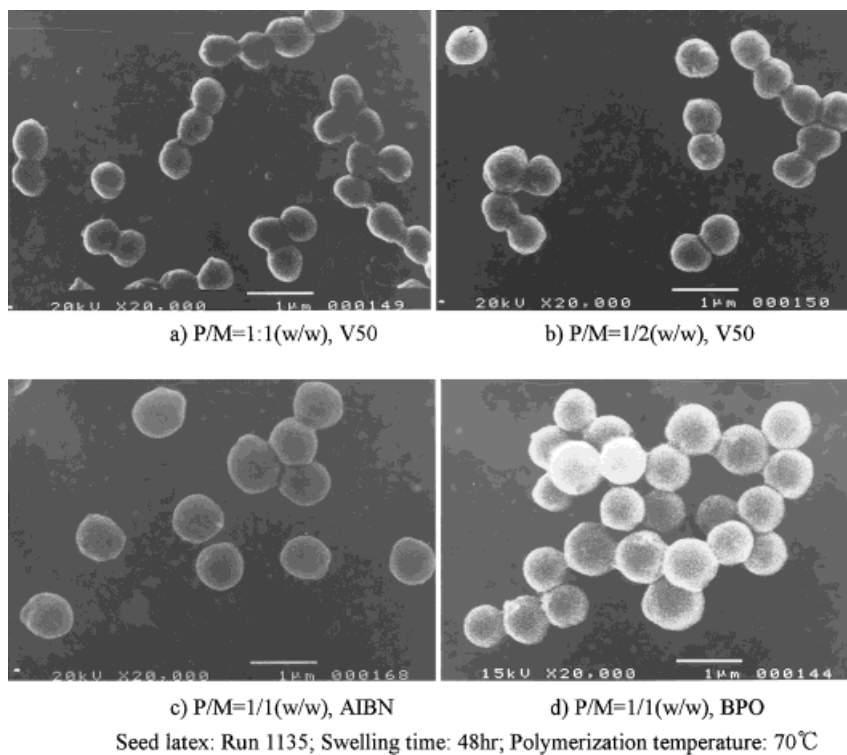
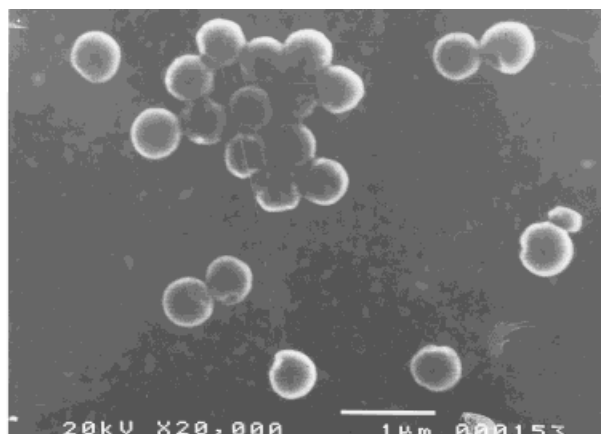
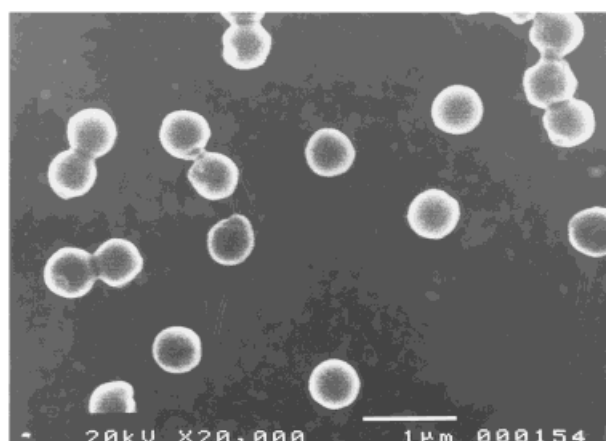


Figure 7 Effect of P/M and initiators on egglike microspheres prepared at 70°C.



a) 20wt%EGDMA, hydrophilic crosslinker



b) 20wt%DVB, hydrophobic crosslinker

Seed latex: Run1135, P/M=1/1(w/w), Swelling time: 48h, Polymerization temperature: 70°C

Figure 8 Effect of crosslinker on egglike microspheres prepared at 70°C.

phology was affected by the swelling state. Min et al.³⁷ reported that the swelling state affected the formation of graft copolymers and morphology change of PBA/PS composite latex particles in long-term duration. However, Cho and Lee¹ claimed that swelling times did not affect the particle morphology in the PMMA/PS polymerization system.

In this seed emulsion polymerization system, it is clearly shown in Figure 5 that the morphology was significantly affected by the swelling time. The surfaces of the resultant particles became smoother as the swelling time lengthened. After swelling for 48 h, particles with irregular surface disappeared, and egglike particles with smooth surface were obtained. This result indicates that swelling was essential for the formation of egglike

microspheres because of the poor miscibility of monomer and seed polymer.

Localization of PS Domains on One Side of the Egglike Particle

As noted, an egglike shape was obtained, although, as shown in Figure 6(a) and (b), the PS domains seemed occluded inside of the egglike particles, rather than localized at a head of the "egg." This morphology does not satisfy the requirement for preparation of the dipole-like microspheres.

For modifying this egglike microsphere, that is, to localize as well as to enlarge the PS domain on the surface of seed particles, the following polymerization factors were modified according to re-

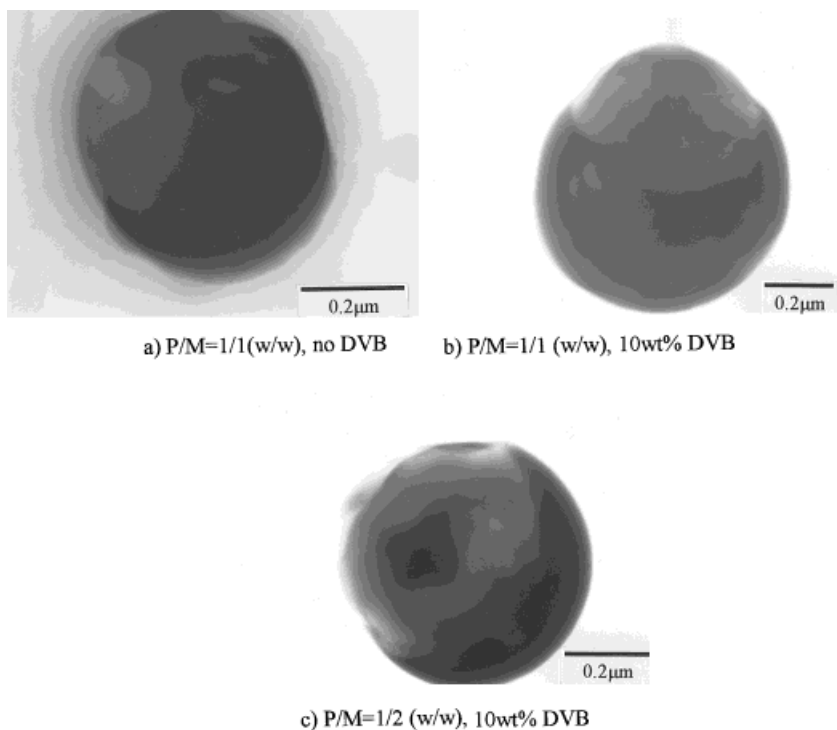
sults reported by other authors,¹⁻¹⁷ such as elevating the seed emulsion polymerization temperature, changing the seed polymer/monomer ratio, addition of benzene as a solvent, and using the hydrophobic crosslinker, divinyl benzene, and initiators AIBN and BPO, in the stage of seed emulsion polymerization. It was found that the most important factor for localizing the PS phase was the reaction temperature in this seed emulsion polymerization system. As shown in Figure 6(c), when the temperature was elevated up to 90°C, the PS domains were localized on one head of the “egg,” although a thin layer of seed polymer covered the PS phase. The other factors seemed ineffective and neither the portion of PS domains on the surface was remarkably increased, nor was the localization of PS domains in the seed particles improved. For example, when the seed polymer/monomer ratio was increased from 1/1 to 1/2 (w/w), as shown in Figure 7(b), the whole volume of the resultant particle seemed increased, but the volume of PS domains on the surface (the smaller portion of the “egg”) was not obviously increased. This indicated that increasing the amount of monomer increased just the volume of

all the domains occluded in the seed particles. When using the hydrophobic initiators, the shapes of the resultant particles, shown in Figure 7(c) and (d), became spherical rather than egglike in shape. This implies that the PS domains entered further into the seed particles because of the lack of ionic groups anchored on the PS domains. When using as high as 20 wt % of the hydrophobic DVB and hydrophilic EGDMA, respectively, the shape of the resultant particles shown in Figure 8 became more spherical.

These results indicated that the compatibility of run 1135 seed polymer and secondary polymer was too poor to allow the monomer dwelling in the seed particle to move freely during the seed emulsion polymerization. Therefore, only by elevating the temperature of the seed emulsion polymerization to as high as 90°C [Fig. 6(c)] was the monomer able to move relatively freely in the seed particles.

Removal of the Thin Layer Covered on the Phase of PS

Based on this consideration, the polarity of seed polymer was increased by merely adjusting the



Seed latex: Run1185, Using the water of pH3.30, Swelling time: 48h, Polymerization temperature: 90°C, Stained by CH₃I vapor for 3 days (Black portion: P(4VP/nBA))

Figure 9 Morphologies of egglike microspheres prepared in the continuous phase of pH 3.3.

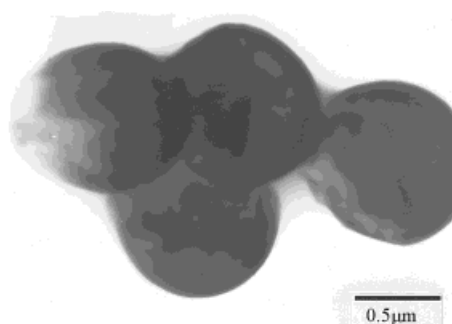
pH of the continuous phase prior to the seed emulsion polymerization: water of pH 3.3 was used in the seed emulsion polymerization, while using run 1185 latex as the seed polymer. Additionally, for comparison, seed emulsion polymerization using run 1185 seed latex with ordinary DDI water (pH 6.7) was also carried out at 90°C. The results are shown in Figures 9 and 10.

When using water of pH 3.3, as shown in Figure 9(a), there were some white “spots” on the thin layer of seed polymer covering the PS phase. This seemed to indicate that the thin cover on the PS phase was ruptured. When the PS phase was crosslinked with 10 wt % of DVB, the layer covering the PS phase, shown in Figure 9(b), seemed much thinner, and the size of the PS phase appearing on the particle surface increased. Furthermore, when the seed polymer/monomer ratio was increased to 1/2, and simultaneously crosslinked with 10 wt % DVB, as shown in Figure 9(c), the localized PS phase was significantly increased, and interestingly, there was only a black “patch” remaining on the surface of the PS phase. These results indicated that, when water

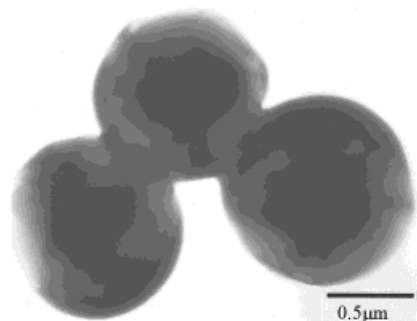
of pH 3.3 was used, shrinkage of the thin layer of seed polymer covering the PS phase took place. At some points, as the volume of the crosslinked PS phase increased, the thin layer was eventually ruptured. The black patch shown in Figure 9(c) probably resulted from the shrinkage of the thin layer of seed polymer that initially covered the surface of the PS phase.

On the other hand, when using ordinary DDI water, as shown in Figure 10, the thin layer of seed polymer covering the PS phase still existed. Neither an increase in the amount of styrene nor an increase in the degree of crosslinking of the PS phase caused it to rupture.

It was shown earlier in Figure 1 that the protonated degree of run 1185 treated with water of pH 3.3 was moderate compared with that of run 1135 and initial run 1185. Therefore, it is suggested that the value of water with pH 3.3 was only to protonate the pyridine group in the surface polymer of the seed particle. Hence, the removal of the thin layer probably was the result of the following two factors: (1) the end groups of polymer chains, which derived from the fragment



a) P/M=1/2 (w/w), no DVB



b) P/M=1/2 (w/w), 10wt% DVB

Seed latex: Run1185, Using the ordinary DDI water, Swelling time: 48h, Polymerization temperature: 90°C, Stained by CH₃I vapor for 3 days (Black portion: P(4VP/nBA))

Figure 10 Morphologies of egglike microspheres prepared by using DDI water.

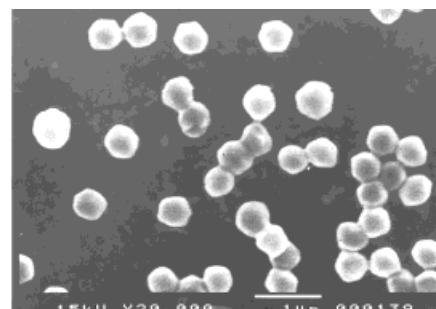
of initiator V50 and from decomposition, and were anchored on the surface of the PS phase, were thoroughly protonated, enough to stabilize the PS phase in water, and (2) the compatibility of seed polymer on the surface with PS became unfavorable because of the protonated surface seed polymer, consequently forcing the thin layer to shrink. Meanwhile, good miscibility of seed polymer and styrene inside the seed particles should be secured, because, to localize the secondary polymer, the monomer should be freely transported inside of the seed particle during the seed emulsion polymerization. From the above-noted results, these were considered to be the conditions for preparing dumbbell-like particles by seed emulsion polymerization.

Use of Crosslinked Seed Latices

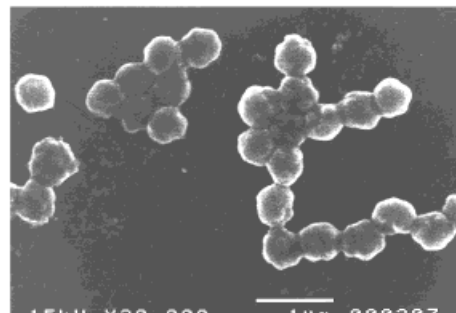
It was reported in the previous study²⁹ that, besides maintaining 10 wt % of solid content in the seed latices, and the addition of 10 wt % EA, the pH of the continuous phase must be adjusted to 3.7 prior to the emulsion polymerization. However, even in this case, the degree of crosslinking did not exceed 0.5 wt % of EGDMA. This means that once the seed polymer was crosslinked, a part of the pyridine groups must be protonated. Using this seed latex, as shown in Figure 11, raspberry-like microspheres were obtained, even when elevating the polymerization temperature up to 90°C. This indicates that the miscibility of seed polymer and styrene was too poor to allow the monomer to move inside the seed particles because of the presence of a crosslinked polymeric network and the protonated polymer chains.

Therefore, crosslinked seed latices without protonation were prepared by lowering the solid content to 5 wt %. In these cases, the degree of crosslinking attained 2 wt % EGDMA without adjusting the pH of the continuous phase.

Figure 12 shows the morphologies of particles prepared by using the seed latex with a degree of crosslinking of 0.5 wt % EGDMA. It was found that the PS domains also became localized by elevating the polymerization temperature up to 90°C. However, the thin layer covering the PS phase still existed and was not removed by using the pH 3.3 water in the seed emulsion polymerization. As shown in Figure 13, the covering layer seemed to become much thicker. The PS phase cannot be seen from the outside of the seed particle, which is understandable because the thin layer was a crosslinked polymer layer.



a) Polymerized at 70°C



b) Polymerized at 90°C

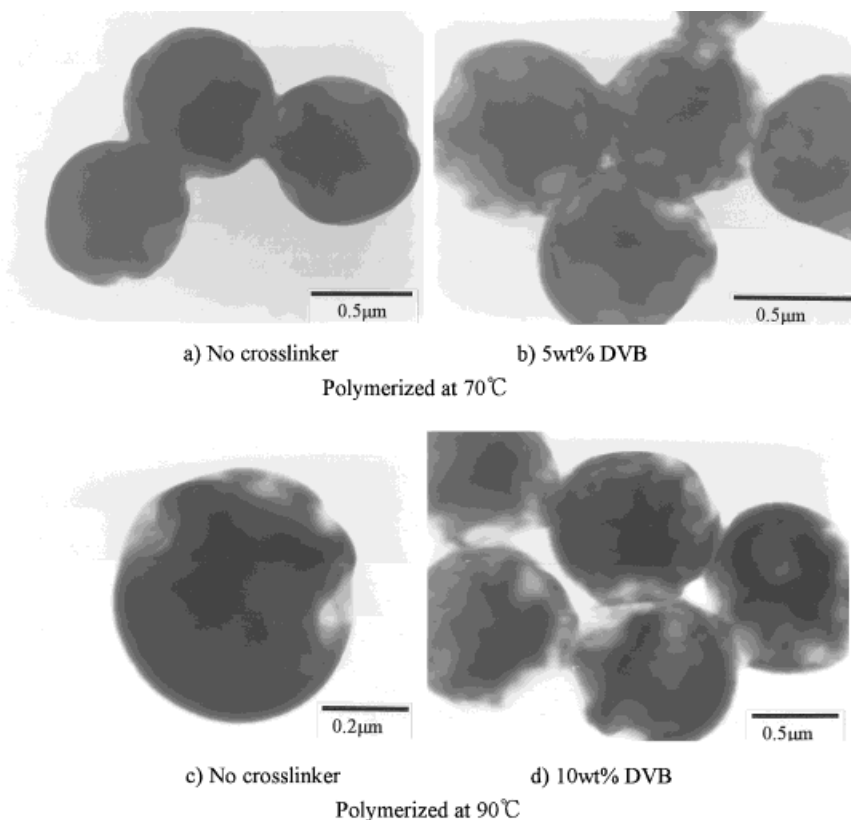
Seed latex: Run1130, P/M=1/1(w/w), Swelling time: 48h

Figure 11 SEM photographs of raspberry-like particles prepared by using protonated seed latex crosslinked with 0.5 wt % EGDMA.

The morphologies of particles using the seed latices with more than 0.5 wt % of EGDMA are shown in Figure 14. It was observed that the raspberry-like microspheres were obtained. Additionally, altering other polymerization factors, such as the polymerization temperature and addition of solvent, for example, could not change the raspberry-like morphologies to dumbbell-like/egglike morphologies. This means that increasing the degree of crosslinking of seed particles cannot localize the domains of PS in the seed particle.

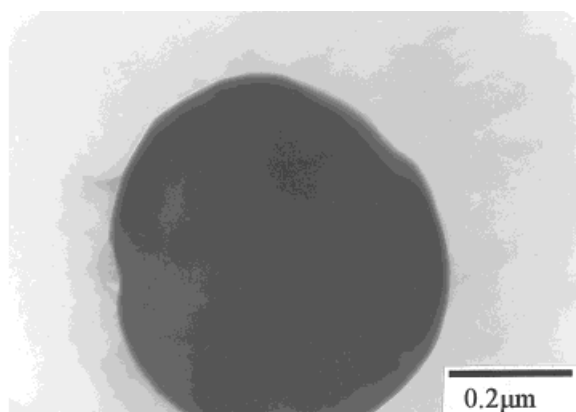
CONCLUSIONS

For the preparation of dumbbell-like/egglike microspheres, it was not sufficient to add nBA to modify the interface of PS/water as well as to increase the compatibility of seed polymer with PS. New particles generated during the seed emulsion polymerization could be eliminated either by increasing the number of seed particles or by stripping EA from the continuous phase of seed latices. Swelling time was a key factor for the formation of egglike microspheres with a smooth



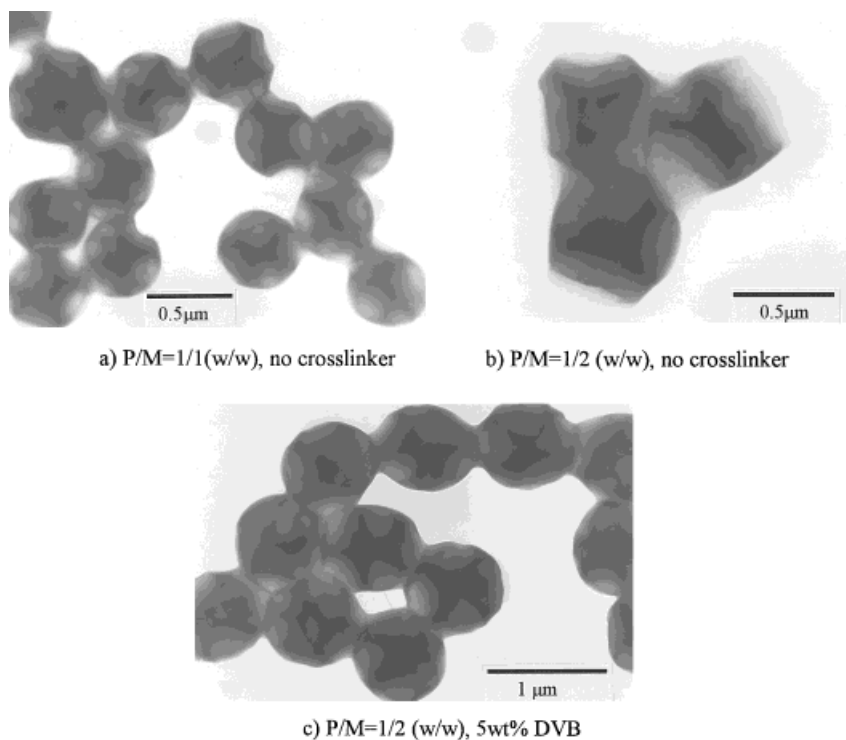
Seed latex: Run1186, P/M=1/1(w/w), Swelling time: 48h, Using the ordinary DDI water,
Stained by CH_3I vapor for 3 days (Black portion: P(4VP/nBA))

Figure 12 Morphologies of microspheres prepared by using seed latex crosslinked with 0.5 wt % EGDMA.



Seed latex: Run1186, P/M=1/1(w/w), Using the water of pH3.30, Crosslinker: 10wt% DVB,
Swelling time: 48h, Polymerization temperature: 90°C, Stained by CH_3I vapor for 3 days
(Black portion: P(4VP/nBA))

Figure 13 TEM photograph of the particle prepared in the continuous phase of pH 3.3 and by using crosslinked seed latex.



a) P/M=1/1 (w/w), no crosslinker
 b) P/M=1/2 (w/w), no crosslinker
 c) P/M=1/2 (w/w), 5wt% DVB
 Seed latex crosslinked with 0.75wt% of EGDMA, Polymerization temperature: 90°C,
 Stained by CH₃I vapor for 3 days (Black portion: P(4VP/nBA))

Figure 14 Morphologies of microspheres prepared by using seed latex with high degree of crosslinking.

surface feature. However, the morphology of such egglike microspheres was the one where the PS domains were occluded in the seed particles, rather than localized on one head of the “egg.” To modify this egglike microsphere, that is, to localize the PS domains in the resultant particle, and to enlarge the volume of PS phase appearing on the surface, various polymerization factors were investigated, such as polymerization temperature, the P/M ratio, the crosslinking degree of the PS phase, the addition of solvent to enhance the mobility of styrene and PS, and so forth. The most effective polymerization factor to localize the PS domains in the resultant particles was the temperature of polymerization. The PS domains were localized by conducting the seed emulsion polymerization at 90°C, if the seed latices, with a degree of crosslinking lower than 0.5 wt % of EGDMA, were employed. Concerning the thin layer covering the localized PS phase, a continuous phase of pH 3.3 in the seed emulsion polymerization stage would eliminate it, except for the case using crosslinked seed latex. Crosslinking the seed latex with EGDMA was not effective for

localization of PS domains in the resultant particle, and therefore, not essential for the preparation of dumbbell-like/egglike microspheres.

The egglike microspheres, which were considered useful for the preparation of dipole-like microspheres, were prepared by using uncrosslinked seed latex (without prior protonation), in a continuous phase of pH 3.3, and then conducting the seed emulsion polymerization at 90°C after swelling for 48 h.

REFERENCES

1. Cho, I.; Lee, K.-W. *J Appl Polym Sci* 1985, 30, 1903.
2. Hourston, D. J.; Satgurunathan, R.; Varman, H. *J Appl Polym Sci* 1986, 31, 1955.
3. Muroi, S.; Hashimoto, H.; Hosoi, K. *J Polym Sci Polym Chem Ed* 1984, 22, 1365.
4. Lee, D. I.; Ishikawa, T. *J Polym Sci Polym Chem Ed* 1983, 21, 147.
5. Stutman, D. R.; Klein, A.; El-Aasser, M. S.; Vanderhoff, J. W. *Ind Eng Chem Prod Res Dev* 1985, 24, 404.

6. Vanderhoff, J. W.; Sheu, H. R.; El-Aasser, M. S. in *Scientific Methods for the Study of Polymer Colloids and Their Applications*; Candau, F.; Ottewill, R. H., Eds.; Kluwer Academic: Dordrecht, 1990; p. 529.
7. Okubo, M.; Katsuta, Y.; Matsumoto, T. *J Polym Sci Polym Lett Ed* 1982, 20, 45.
8. Ma, G.-H.; Nagai, M.; Omi, S. *J Colloid Interface Sci* 1999, 214, 264.
9. Ma, G.-H.; Nagai, M.; Omi, S. *J Colloid Interface Sci* 1999, 219, 110.
10. Sheu, H. R.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Polym Chem Ed* 1990, 28, 629.
11. Sheu, H. R.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Polym Chem Ed* 1990, 28, 653.
12. Jönsson, J.-E.; Hassander, H.; Jansson, L. H.; Törnell, B. *Macromolecules* 1994, 27, 1932.
13. Winzor, C. L.; Sundberg, D. C. *Polymer* 1992, 33, 4269.
14. Sundberg, D. C.; Durant, Y. G. in *Polymeric Dispersions: Principles and Applications*; Asua, J. M., Ed.; Kluwer: London, 1997; pp. 177–188.
15. Sundberg, D. C.; Casassa, A. P.; Pantazopoulos, J.; Muscato, M. R. *J Appl Polym Sci* 1990, 41, 1425.
16. Sundberg, E. J.; Sundberg, D. C. *J Appl Polym Sci* 1993, 47, 1277.
17. Chen, Y.-C.; Dimonie, V. L.; Shaffer, O. L.; El-Aasser, M. S. Presented at the International Symposium on Polymeric Microspheres; Fukui, Japan, October 1991; pp. 45–50.
18. Chang, T. M. S.; Kuntarian, N. *Enzyme Eng* 1978, 4, 193.
19. Grunwald, J.; Chang, T. M. S. *Biochem Biophys Res Commun* 1978, 81, 565.
20. Kedzierwicz, F.; Darne, X.; Etienne, A.; Lemut, J.; Hoffman, M.; Maincent, P. *J Microencapsul* 1997, 15, 227.
21. Lin, S.-Y.; Chen, K.-S.; Teng, H.-H. *J Microencapsul* 1998, 15, 383.
22. Devon, M.; Gardon, J.; Roberts, G.; Rudin, A. *J Appl Polym Sci* 1990, 39, 2119.
23. Eliseeva, V. I. *Prog Org Coatings* 1985, 13, 195.
24. Rajatapiti, P.; Dimonie, V. L.; El-Aasser, M. S. in *Polymeric Dispersions: Principles and Applications*; Asua, J. M., Ed.; Kluwer: London, 1997; p. 189.
25. Paul, D. R. in *Polymer Blends*; Paul, D. R.; Barlow, J. W., Eds.; Academic: New York, 1978; Vol. 2, Chapter 12.
26. Yamazaki, S. *Kobunshi Ronbunshu* 1976, 33, 663.
27. Yamazaki, S. *Shikizai Kyokaishi* 1977, 50, 267.
28. Hobbs, S. Y.; Dekkers, M. E.; Watkins, V. H. *Polymer* 1988, 29, 1598.
29. Ni, H.-M.; Ma, G.-H.; Nagai, M.; Omi, S. *J Appl Polym Sci* 2000, 76, 1731.
30. Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989; pp. II–153.
31. Fitch, R. M. in *Polymer Colloids: A Comprehensive Introduction*; Academic Press: New York, 1997; p. 9.
32. Ni, H.-M.; Ma, G.-H.; Nagai, M.; Omi, S. *J Appl Polym Sci* to appear.
33. Smith, W. V.; Ewart, R. H. *J Chem Phys* 1948, 16, 592.
34. Morton, M.; Kaizerman, S.; Altier, M. W. *J Colloid Sci* 1954, 9, 300.
35. Chung-Li, Y.; Goodwin, J. W.; Ottewill, R. H. *Prog Colloid Polym Sci* 1976, 60, 163.
36. Matsumoto, T.; Okubo, M.; Shibao, S. *Kobunshi Ronbunshu* 1979, 33, 575.
37. Min, T. I.; Klein, A.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Polym Chem Ed* 1983, 21, 2845.