Preparation of Hemispherical Poly(4-Vinylpyridine-*co*-Butyl Acrylate)/Poly(Styrene-*co*-Butyl Acrylate) Composite Microspheres by Seeded Preswelling Emulsion Polymerization

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ABSTRACT: Seeded preswelling emulsion polymerization was carried out by using monodispersed poly(4-vinylpyridine-*co*-butyl acrylate) [P(4VP-BA)] particles as the seed, and styrene and butyl acrylate as the second-stage monomers under different polymerization conditions, to obtain hemispherical polystyrene (PST)-rich–P4VP-rich microspheres. Prior to polymerization, toluene was added into the preswelling system together with the second-stage monomers. It was found that, with the increase of the amount of toluene, the particle morphology showed a tendency toward desirable hemispherical structure, and the colloidal stability of composite latex was improved. When the weight ratio of toluene/seed latex was increased up to 7.5/40 (g/g), the stable hemispherical latex could be obtained. However, when toluene was not added, the coagulum formed on the wall of the reactor during polymerization, and the composite particles with multiple surface domains (such as sandwich-like, popcorn-like) were formed. In addition, the final morphology of composite particles was influenced by the polarity of the seed crosslinker and the hydrophilicity of the second-stage initiator, which could affect the mobility of poly(styrene-*co*-butyl acrylate) [P(ST-BA)] chains. The morphology development during the polymerization was investigated in detail, and a schematic model was derived to depict the formation mechanism of hemispherical P(4VP-BA)/P(ST-BA) composite microspheres. The results revealed that the mobility of the P(ST-BA) chains influenced the diffusion of the P(ST-BA) domains on the surface of the P(4VP-BA) matrix. When the mobility of the P(ST-BA) chains allowed small-size P(ST-BA) domains to coalesce into one larger domain, complete phase-separated morphology (hemisphere) could be achieved. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3811–3821, 2003

Key words: emulsion polymerization; colloid; composites; morphology; swelling

INTRODUCTION

In recent years, there has been a great deal of industrial interest in composite particles with precisely tailored physical properties. These composite particles provide a wide range of potential applications in the various fields, for example, coatings, adhesives, impact modifiers for plastics, and biomaterials. The particle morphology plays an important role in the aspect of deciding latex end-use applications. Therefore, the morphology design and control of the composite particles are crucial to meet the different demands. Composite particles with different morphology are usually prepared by seeded emulsion polymerization under different parameters and conditions, including water solubility of the monomers; the type, amount, and addition mode of other ingredients such as the initiator and crosslinking agent; the viscosity of the polymerization locus; and so forth. These parameters and conditions fall into two categories[1–5]: thermodynamic factors that determine the equilibrium morphology of the final composite latex particles, and kinetic factors that determine the ease with which the thermodynamically favored equilibrium morphology can be achieved.

A great deal of studies, which focused on the polystyrene (PST)/poly(methylmethacrylate) (PMMA),[6–10,13–15] PMMA/PST,[1,11–12,15] and PST/PST[4,16–18] system, have been done to investigate the effects of various polymerization parameters on composite particle morphology, and it has been found that almost every

polymerization variable which could be thought of could influence particle morphology. The complex dependence of composite particles morphology development on polymerization parameters and conditions leads to the difficulties of morphology controlling. At the same time, it provides a possibility of obtaining any morphology particles by adjusting the polymerization parameters, even to prepare the core-shell particles[11,12] where the desired core polymer is more hydrophilic than the shell polymer. This is our theoretical background for preparing hemispherical composite microspheres with poly(4-vinylpyridine-*co*-butyl acrylate) [P(4VP-BA)]/poly(styrene-*co*-butyl acrylate) [P(ST-BA)] by seeded preswelling emulsion polymerization. The final purpose of our study is to obtain hemispherical or dumbbell-like composite microspheres. By further modifying P(4VP-BA) and P(ST-BA) domains to cationic and anionic domains, respectively, or only by modifying P(4VP-BA) domains to hydrophilicity and keeping P(ST-BA) hydrophobicity, the cationic-anionic or hydrophilic-hydrophobic amphiphilic composite microspheres will be easily obtained. Such novel amphiphilic composite microspheres are designed for the preparation of functional membranes.[19,20]

In a previous article, Ma et al.[20] described the reason[21,22] and motivation that the system was selected here, and prepared monodispersed cationic P(4VP-BA) latex by controlling the process parameter, such as the BA/4VP weight ratio. Furthermore, by using the monodispersed cationic P(4VP-BA) latex as the seed, Ma et al.[20] discussed in detail the effect of polymerization parameters on the morphology of P(4VP-BA)/P(ST-BA) composite microspheres and prepared popcorn-like and sandwich-like composite microspheres. However, the hemispherical or dumbbell-like composite microspheres, which can satisfy our final goal, were not obtained. It was thought that crosslinking degree of the seed was too high and the mobility of PST-rich chains was limited, so that the morphology with complete phase separation could not be obtained and the mobility of polymer chains is related to the viscosity polymerization loci. Cho and Lee[1] studied the morphology development for PMMA/PST composite system and found the viscosity of polymerization loci decreased by the addition of the toluene solvent. Moreover, El-Aasser et al.[6] studied the morphology development for the PST/PMMA composite system and found that there existed mixed morphology of more than one. They pointed out that mixed morphology in the final latex was due to restricted chain mobility related to high internal viscosity during the final stage of the polymerization, and when the final composite latex was swollen with toluene, the diffusion resistance decreased and the mobility of polymer chains increased, the morphology changed from original sandwich-like structure to the hemi-

sphere, and the particles morphology showed a tendency toward a thermodynamically more favorable morphology. These provide some implications on decreasing the polymerization locus viscosity and enhancing the mobility of the polymer chains to obtain the desired hemispherical or dumbbell-like composite microspheres.

Based on the previous work,[20] the solvent toluene was added into the seed latex together with the second-stage monomer in this study, and the seed latex was swollen by the mixture of toluene and second-stage monomer for 24 h at ambient temperature prior to polymerization (seeded preswelling emulsion polymerization) to obtain the monomer-solvent-swollen seed particles with the low viscosity. At the same time, to increase the mobility of PST-rich chains, the second-stage polymer P(ST-BA) was not crosslinked.

Therefore, in this study, the composite microspheres P(4VP-BA)/(ST-BA) were prepared by seeded preswelling emulsion polymerization with monomer and solvent toluene. The effect of solvent toluene on the composite particle morphology was discussed. In addition, the influences of the seed particles' crosslinker and the second-stage initiator on the final morphology were investigated. For a better understanding of the parameters affecting the morphology of the composite particles, the morphology development of composite particles during polymerization under the different polymerization conditions was investigated. The formation mechanism of hemispherical morphology, which represents a desirable and thermodynamically favored situation, was described.

EXPERIMENTAL

Experimental materials

The following monomers were used: 4-vinylpyridine (4VP), styrene (ST), and *n*-butyl acrylate (BA). The initiators were as follows: water-soluble 2,2'-azobis(2-amidinopropane), 2HCl (V-50), and oil-soluble azobisisobutyronitrile (AIBN). Polar ethylene glycol dimethacrylate (EGDMA) and nonpolar divinylbenzene (DVB) were used as crosslinkers. Toluene was used as solvent. Among these reagents, 4VP, ST, BA, AIBN, EGDMA, and DVB were supplied by Kishida Chemical Industries Co. Ltd. (Tokyo, Japan), and V-50 and toluene were purchased from Wako Pure Chemical Industry Co. Ltd. (Tokyo, Japan). All monomers were distilled under reduced pressure, and the solvent toluene was distilled. EGDMA and DVB were washed with 3 wt % alkaline solution three times, washed with distilled-deionized water (DDI) five times, and then dried with a 4 Å molecular sieve. The initiators V-50 and AIBN were used without further purification.

Water used in all experiments was distilled and deionized (DDI) by employing a Milli-Q water purifi-

TABLE I
The Polymerization Conditions[a] and Results of the Monodisperse P(4VP-BA) Seed Latex

Run no.	Crosslinker	Content of crosslinker (wt% based on monomer)	Colloidal stability	d_n[b] (nm)	Particle yield[c] (%)
101	EGDMA	10	Stable	377	100
102	DVB	10	Stable	396	100

[a] Polymerization temperature: 70°C. Initiator: V-50.
[b] d_n, number-average diameter of seed microspheres.
[c] Polymer yield: polymer precipitate was not included.

cation system with the conductivity of $18M \ \Omega \ cm^{-1}$ and measured pH value of 6.7 (Millipore, Tokyo, Japan).

Preparation of monodispersed P(4VP-BA) seed latex

The P(4VP-BA) seed latices were prepared by soap-free emulsion polymerization, and semicontinuous addition mode of monomer was used to obtain uniformly structured microspheres. The polymerization conditions and results are listed in Table I. The 440 mL deionized water was charged to a four-necked reactor, equipped with a stirrer, a spiral condenser, a nitrogen inlet, and a dropping funnel with a nitrogen inlet. The initiator V-50 (0.5 g) was thoroughly dissolved in 35 g deionized water and was then added into the reactor. Then, the system was bubbled with nitrogen gas for 60 min under stirring. At the same time, the monomer and crosslinker mixture (25 g) also was bubbled with nitrogen gas for 60 min after being fed in the dropping funnel and then was added to the reactor dropwise at a feeding rate of 8.3 g/h at 70°C under an agitation speed of 300 rpm. The polymerization was carried out for 12 h under the nitrogen blanket. The BA/4VP ratio was fixed at 1/4 (w/w). After the polymerization, the seed latex was filled in a seamless cellulose tube and dialyzed under flowing tap water for 24 h, and thereafter, in distilled-deionized water for 24 h at ambient. Figure 1 shows scanning electron micrographs (SEM) of the seed latices Run 101 and Run 102. The resulting latex particles were monodispersed.

Preparation of P(4VP-BA)/P(ST-BA) composite microspheres

The P(4VP-BA)/P(ST-BA) composite microspheres were prepared by seeded preswelling emulsion polymerization. A standard recipe for polymerization is shown in Table II. All the ingredients (145 g) except the initiator solution were fed in a five-neck reactor with an agitator, a spiral condenser, a nitrogen inlet, a rubber stopper for sampling, and a dropping funnel with a nitrogen inlet for adding the initiator. The swelling was carried out for 24 h at ambient temperature under stirring. Then the initiator aqueous solution (15 g including 0.12 g initiator) was charged in the dropping funnel. The whole system was bubbled with the nitrogen gas for 1 h before elevating the temperature, and the initiator was added into the reactor when the reaction temperature reached 70°C. The polymerizations were performed for 24 h at 70°C. The stirring rate was fixed at 300 rpm. The polymerization was performed under the nitrogen blanket.

Characterization of seed and composite microspheres

The conversion of the monomer was determined gravimetrically; that is, a known amount of latex was dried and weighed. The size and morphology of particles were observed by SEM (JEOL JSM-5310) and transmission electron microscopy (TEM) (Hitachi H-700H). The SEM sample was prepared as follows: one drop of dilute latex (1×10^{-4} g/mL) was cast on a stage covered with an aluminum film; after drying,
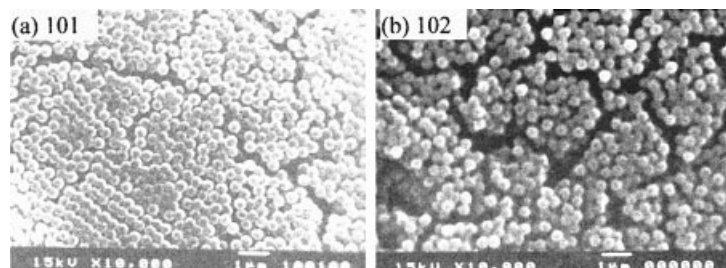

Figure 1 SEM photos of the seed latices.

TABLE II
The Synthesizing Recipes and Results of Composite Microspheres by Seeded Preswelling Emulsion Polymerization[a]

Run	Seed latex	Initiator type	Solvent	Solvent amount (g)	Seed amount (g)
1011	Run 101	V-50	Toluene	7.5	2
1012	Run 101	AIBN	Toluene	7.5	2
1013	Run 101	V-50	Toluene	0	2
1014	Run 101	AIBN	Toluene	0	2
1017	Run 101	V-50	Toluene	3.75	2
1019	Run 101	V-50	Toluene	5	2
1021	Run 102	V-50	Toluene	7.5	2
1022	Run 102	AIBN	Toluene	7.5	2

[a] Seed latex (including water) = 40 (g); solid amount: 5 (wt %) $\times$ 40 (g) = 2 (g).
ST = 4.8 (g), BA = 1.2(g). ST/BA = 4/1 (wt/wt); (ST + BA)/P(4VP-BA) = 3/1 (wt/wt).
Water was added by letting (seed latex + monomer + toluene + water) = 145.0 (g).
Initiator = 0.12 g, which was added in the system after being dissolved in 14.88 (g) water.

it was coated with a thin gold film. The particle's size was determined by direct measurement of 200 particles/sample in SEM photos. The TEM specimen was prepared as follows: one drop of dilute latex (1×10^{-4} g/mL) was cast on a copper mesh covered with thin carbon film and dried at room temperature; then the P4VP domain was stained with iodomethane (CH_3I) vapor in a sealed container for 2 days at room temperature. Therefore, the dark part stands for the P(4VP-BA) domain, and the bright part stands for P(ST-BA) domain in the TEM photos.

RESULTS AND DISCUSSION

Effect of the solvent toluene on the morphology and colloidal stability of composite microspheres

The viscosity of the polymerization locus (related to the chain mobility) is one of the main parameters controlling the particle's morphology in a composite polymer latex system. To decrease the viscosity of the polymerization locus, the solvent toluene was added into the system together with the second-stage monomer prior to polymerization. After the polymerization was finished, by carefully observing the surface of resulting emulsion, no thin oil-layer (toluene) was found. That meant that the toluene still existed inside of the composite microspheres. The conditions and

TABLE III
The Effect of the Toluene Solvent on the Composite Latex

Run	Toluene (g)	Colloidal stability	Particle yield (%)
1013	0	Unstable	36
1017	3.75	Unstable	65.5
1019	5.0	Stable	92.1
1011	7.5	Stable	98

results of polymerization are shown in Table III. The SEM and TEM photos of particles are given in Figure 2.

From Figure 2, it was obvious that the solvent toluene influenced the final morphology of particles. When no toluene was added into the preswelling system, the mixture of popcorn-like particles and sandwich-like particles [Fig. 2(a–b)] were formed. When 3.75 g of toluene was added, the mixture of sandwich-like and hemispherical particles [Fig. 2(c–d)] were formed. When 5 g of toluene was added, the mixture of hemispherical and sandwich-like particles [Fig. 2(e–f)] were also formed. Compared with Fig. 2(c–d), however, the number of sandwich-like particles decreased greatly. As toluene was increased to 7.5 g, almost only hemispherical particles [Fig. 2(g–h)] were found. This implied that with the increase of the amount of toluene added into the preswelling system, the particle morphology showed a tendency toward hemispherical structure. This was because that the swelling with toluene decreased the viscosity of the polymerization locus and enhanced polymer chain mobility; accordingly, the diffusion resistance of the P(ST-BA) domains on the surface of the P(4VP-BA) matrix was decreased during the final polymerization stage. As a result, PST domains can coalesce to one large domain, and the morphology with complete phase separation was realized. Therefore, when 7.5 g of toluene was used, desired hemispherical particles [Fig. 2(g–h)] were obtained.

It was interesting that, when no toluene was added into the preswelling system, the precipitate was found to adhere on the wall of reactor during the polymerization, and the precipitate layer was thick after the polymerization completed. When 3.75 g of toluene was added, only the thin-layer precipitate was found on the wall of the reactor. When 5 or 7.5 g of toluene was added, no precipitate was found. The effect of
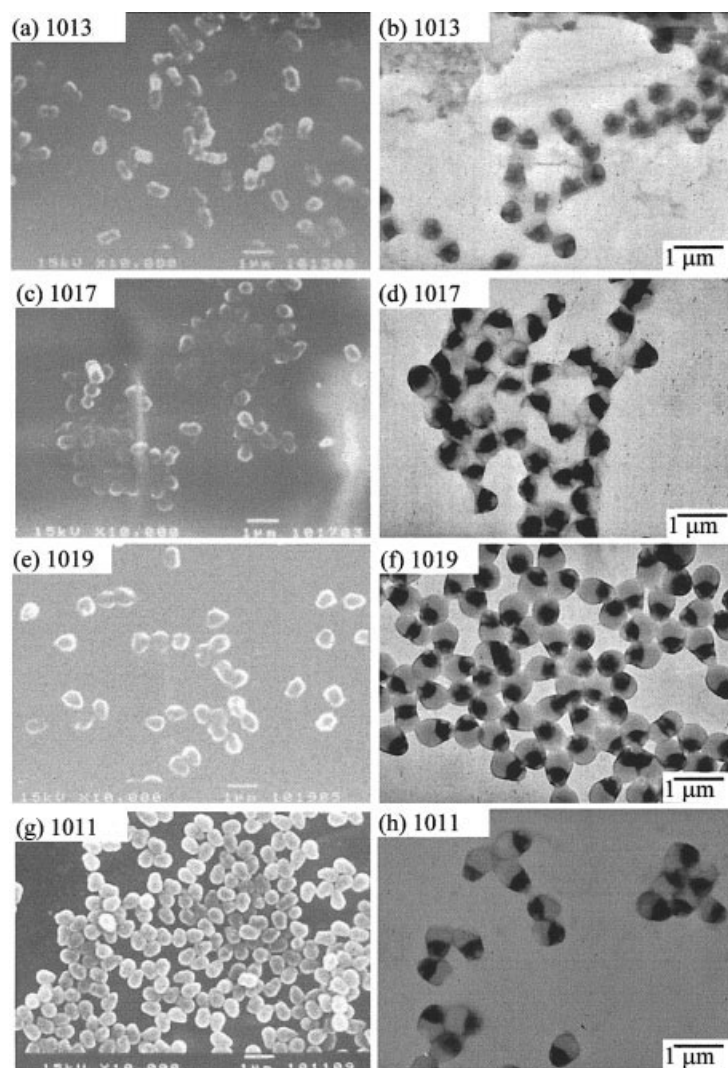
Figure 2 SEM and TEM photos of composite particles. (a, c, e, g): SEM; (b, d, f, h): TEM. (a, b): Run 1013 (no toluene); (c, d): Run 1017 (3.75 g toluene); (e, f): Run 1019 (5 g toluene); (g, h): Run 1011 (7.5 toluene).

toluene on colloidal stability of emulsion and particle yield are shown in Table III. The particle yield was measured without including the precipitate. The results indicated that the solvent toluene could effectively improve the colloidal stability of latex during the polymerization. Probably the swelling of toluene enhanced the mobility of the polymer chains so that the P(ST-BA) domains tended to converge. At the same time, the terminal ionic group (fragment of V-50) also can move to the surface and was favorably distributed on the surface of polymer particle, because of the low viscosity in the particle. Thus, the particle surface charge density increased. When they approached each other during the seeded polymerization, a stronger repulsive force was generated to drive them apart.

Concluding with the increase of the amount of toluene added into the preswelling system, both the decrease of the precipitate and the formation of desir-able hemispherical composite microspheres were attributed to the enhancement of polymer chain mobility. According to the experimental results, when the weight ratio of toluene/seed latex was increased to 5/40 (g/g), the stable composite latex was formed, and was increased to 7.5/40 (g/g), the hemispherical composite particles were obtained.

Effect of the seed crosslinker and second-stage initiator on morphology of composite microspheres

The above results indicated that the formation of hemispherical particles required considerable chain mobility to allow microdomains polymerized in the second stage to coalesce to one single domain. Furthermore, it was considered that the hydrophilicity of seed network and polymer chain formed in the second stage should affect the mobility of polymer chain; consequently, it affected the morphology of the parti-

TABLE IV
Effect of the Crosslinking Agent of Seed Particles and the Initiator
of the Second Stage on Composite Microsphere

Run[a]	Seed latex	Initiator type	Colloidal stability	Particle yield (%)
1011	Run 101	V-50	Stable	98
1012	Run 101	AIBN	Stable	91
1021	Run 102	V-50	Stable	79.6
1022	Run 102	AIBN	Unstable	10.2
1022*	Run 102	AIBN[b]	Stable	49.1

[a] Toluene amount: 7.5 g.
[b] The initiator AIBN of Run 1022* was added into the system before preswelling.

cles, because the relatively hydrophilic network can swell more in the aqueous phase, and hydrophilic polymer formed in the second stage was able to move more easily at the interface between particle and water. To better understand the effect of polymerization parameters on the polymer chain's mobility, the two latices, which were crosslinked by EGDMA and DVB, respectively (the recipe is shown in Table I), were used as the seed, and V-50 and AIBN were, respectively, used as the second-stage initiator. The toluene amount was fixed at 7.5 g. The polymerization results are given in Table IV. Figure 3 shows TEM photos of composite microspheres prepared.

When Run 101 was used as the seed latex, the system (Run 1011) initiated by hydrophilic V-50 formed hemispherical composite microspheres [Fig. 3(a)] as described above; the system (Run 1012) initiated by hydrophobic AIBN formed a mixture of hemispherical and sandwich-like composite microspheres [Fig. 3(b)]. This is because that when the small-size P(ST-BA) domains formed during the polymerization, they were driven to the surface of seed particles. Approaching to the water interface, P(ST-BA) chains with V-50 end was more hydrophilic than P(ST-BA) chains with the AIBN end so that its chain mobility was higher at the interface between particle and water. Therefore, the system initiated by V-50 had the higher possibility to form the complete phase-separated hemispherical composite microspheres. This was proven in the following investigation of morphology development.
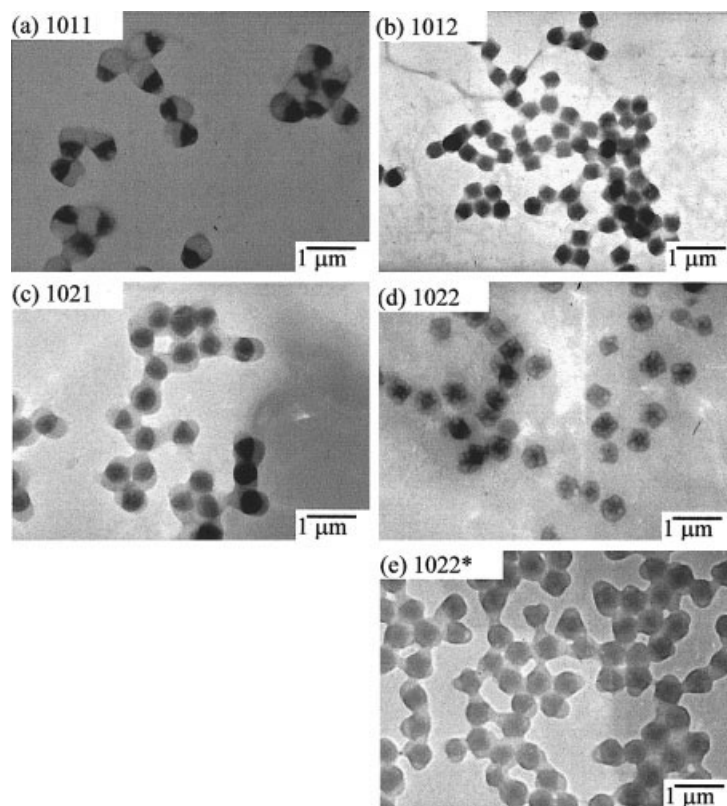

Figure 3 TEM photos of composite microspheres of Run 1011, Run 1012, Run 1021, Run 1022, and Run 1022*.
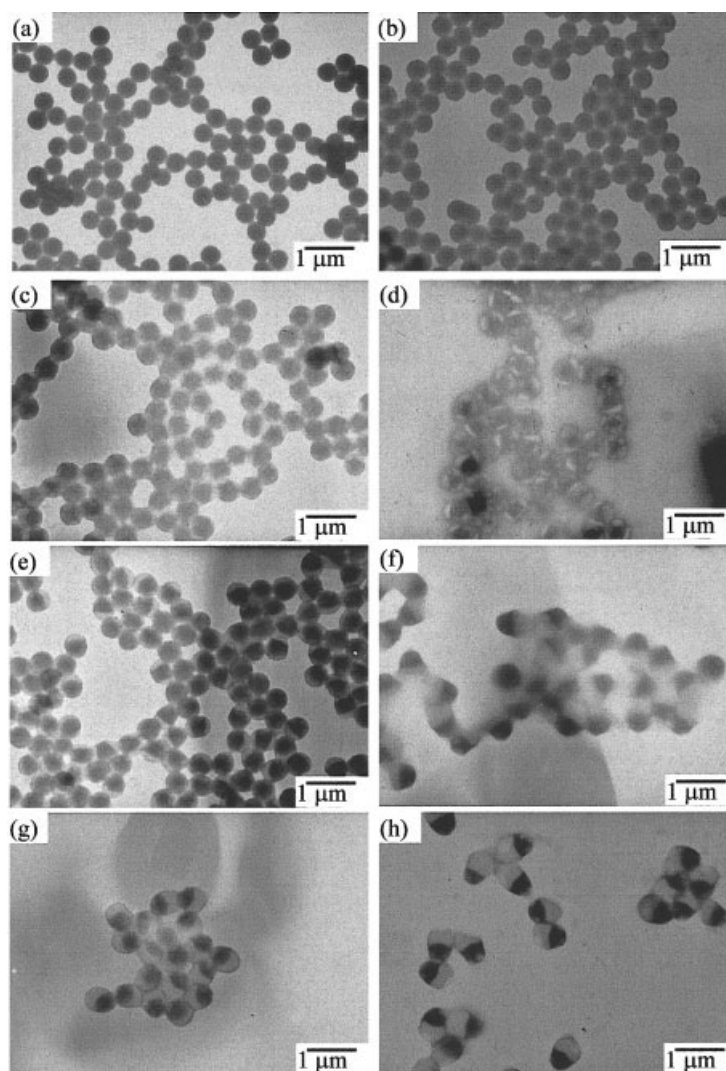
Figure 4 TEM photos of the Run 101, and the Run 1011 at different polymerization times. (a) Run 101 seed; (b) swelling for 24 h; polymerization time (monomer conversion): (c) 10 min (13.2%); (d) 20 min (17.2%); (e) 30 min (23.3%); (f) 40 min (28.6%); (g) 50 min (31.8%); (h) 24 h (95.2%).

When Run 102 was used as the seed latex, the system (Run 1021) initiated by hydrophilic ionic V-50 formed sandwich-like composite microspheres [Fig. 3(c)], although the latex system (Run 1022) initiated by hydrophobic nonionic AIBN was quite unstable and produced particles with very fine P(ST-BA) domains that uniformly distributed in P(4VP-BA) matrix [Fig. 3(d)]. To obtain stable latex of Run 1022, the initiator AIBN was added before the preswelling (Run 1022* as the tab). During the polymerization, no coagulum was observed, and finally the stable latex was formed though the particle yield was not high. Cho and Lee[1] also found that when AIBN was used as the second-stage initiator, the coagulum could be minimized by sufficient premixing AIBN and PMMA (seed)/styrene system at ambient. The Run 1022* particles were the mixture of sandwich-like and popcorn-like [Fig. 3(e)]. The difference of Run 1021 and Run 1022* was also

due to the difference of the hydrophilicity of two initiators.

Run 1011 that seed particles crosslinked by polar EGDMA formed hemispherical particles, and Run 1021 that seed particles crosslinked by nonpolar DVB formed sandwich-like particles. This implied that the mobility of P(ST-BA) chain in the P(4VP-BA-EGDMA) seed was relatively higher compared with that in the P(ST-BA-DVB) seed in the aqueous solution. This is because the hydrophilicity of EGDMA is higher than that of DVB; the network in the former case can be swollen more than that in the latter case. Hence the relatively higher mobility of the P(ST-BA) chains contacting with P(4VP-BA-EGDMA) domain allowed the smaller P(ST-BA) domains to move to one large domain on the surface of P(4VP-BA-EGDMA) matrix. On the other hand, the mobility of the P(ST-BA) chains contacting with P(4VP-BA-DVB) domain were rela-
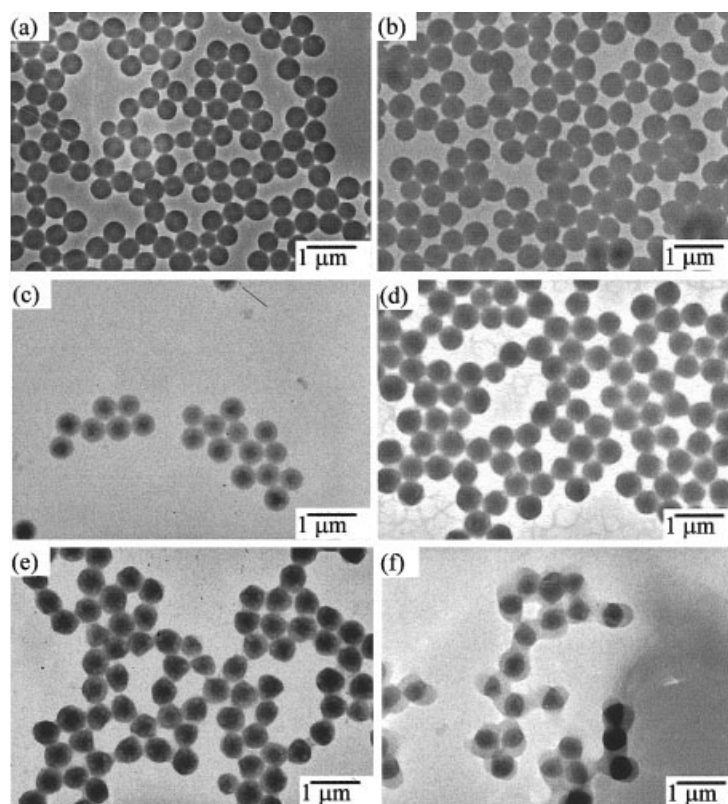
Figure 5 TEM photos of the seed Run 102, and the Run 1021 at different polymerization times. (a) Run 102 seed; (b) swelling for 24 h; polymerization time (monomer conversion): (c) 30 min (14.5%); (d) 60 min (23.3%); (e) 150 min (47.4%); (f) 24 h (79.6%).

tively low to enhance the difficulty of the diffusion of P(ST-BA) domains on the surface of P(4VP-BA-EGDMA) matrix.

Morphology development of composite microspheres during polymerization

As described above, the morphology of composite particles is complicated and varied because the numerous parameters are involved in their preparation (e.g., the amount of the solvent toluene, the crosslinking agent and degree of the seed, and the second-stage initiator). Therefore, it is worthwhile to investigate the morphology development of composite particles under different polymerization conditions for a better understanding of the parameters affecting the morphology of the composite particles and determining the formation mechanism of hemispherical morphology.

Here, the morphology development of Run 1011, Run 1021, and Run 1022* particles during the polymerization were investigated. Latex samples were taken at different times and shortstopped; the morphology of the latex particles during preswelling and polymerization was determined by TEM.

Investigation on Run 1011

Figure 4 shows TEM photos of the Run 101 and the Run 1011 at different polymerization times. After swelling for 24 h at ambient temperature [Fig. 4(b)], it was found that the size of swollen particles increased on the basis of the size of the seed particles [Fig. 4(a)] (from 377 to 410 nm). This is quite strange because TEM observation was carried out after the specimen was dried. Probably this was because monomer and toluene penetrated into the seed network to allow the network to become swollen, and the particle became soft enough when it contained toluene and monomer. While toluene and monomer were evaporating, the particles flattened on the TEM grid, resulting in a large apparent diameter. After polymerization for 10 min [Fig. 4(c), 13.2% conversion], many fine P(ST-BA) domains formed and distributed in P(4VP-BA) matrix, and the size of P(ST-BA) domains distributed in the edge was relatively large. After 20 min [Fig. 4(d), 17.2%] and 30 min [Fig. 4(e), 23.3%], P(ST-BA) domains mainly distributed on the surface of particle, and the numbers of P(ST-BA) phase domains decreased greatly and the size of domains increased. After 40 min [Fig. 4(f), 28.6%] and 50 min [Fig. 4(g), 31.8%], P(ST-BA) phase domain almost converged to
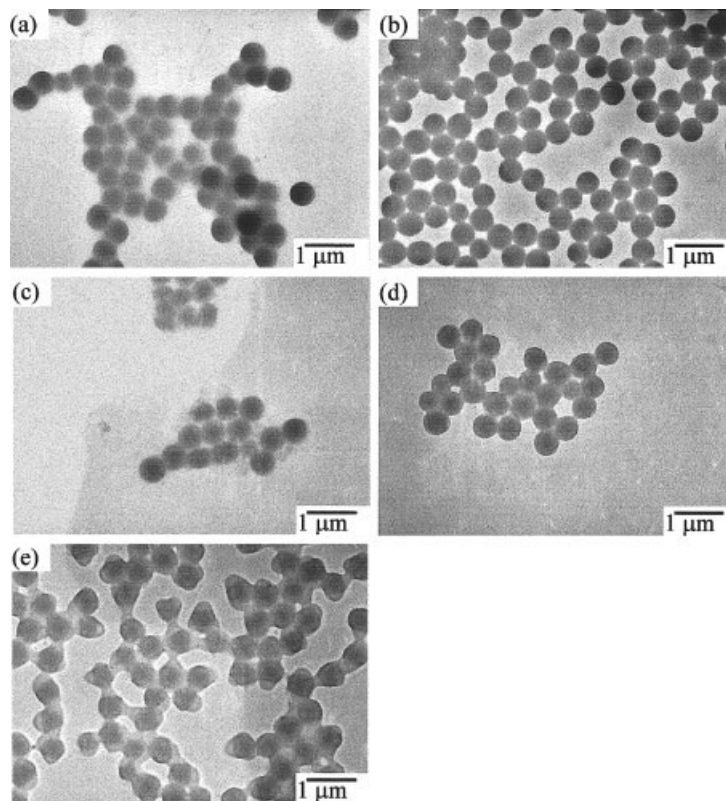
Figure 6 TEM photos of the Run 1022* at different polymerization times. (a) Swelling for 24 h; polymerization time (monomer conversion): (b) 30 min (5.2%); (c) 60 min (5.9%); (d) 150 min (10.8%); (e) 24 h (49.1%).

one domain on the P(4VP-BA) phase and formed hemispherical particles. After 24 h [Fig. 4(h), 95.2%], the size of P(ST-BA) domain increased significantly. The above phenomenon was explained as follows: because of the phase separation, the new-formed microdomains of P(ST-BA) were driven to the periphery of the particles in all directions to form many small-size new domains at the initial stage of polymeriza-

tion, because of the effect of elastic force in the crosslinked seed particle. Gradually, these small domains were driven out of the P(4VP-BA-EGDMA) phase, and the numbers of P(ST-BA) domains decreased greatly and the size of domains increased. The swelling of the seed with toluene decreased the diffusion resistance of P(ST-BA) domains on the surface of P(4VP-BA) phase. Therefore, P(ST-BA) domains could
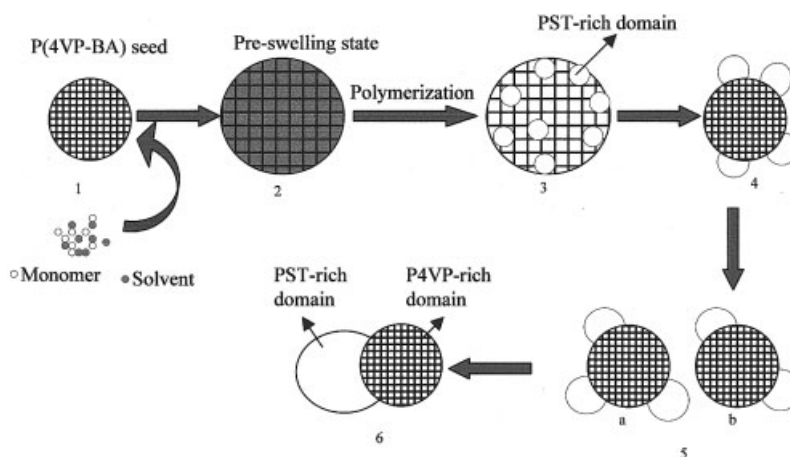

Figure 7 A schematic model of hemisphere-structured formation mechanism for hydrophilic-seed/hydrophobic-second-polymer composite microspheres.

converge to one large domain and finally formed hemispherical composite microspheres [Fig. 4(h), 95.2%], which are desirable for our purpose.

Investigation on Run 1021

Figure 5 shows TEM photos of the Run 102, and the Run 1021 at different polymerization times. The initial morphology development of Run 1021 was similar to Run 1011. After swelling for 24 h at ambient temperature [Fig. 5(b)], the size of swelling particles increased based on seed particles [Fig. 5(a)] (from 358 to 396 nm). After polymerization for 30 min [Fig. 5(c), 14.5% conversion], and 60 min [Fig. 5(d), 23.3% conversion], many small-size domains of P(ST-BA) have formed and distributed mainly in the edge of P(4VP-BA) phase, which made the edge of the particles look gray in the TEM photos. After 150 min [Fig. 5(e), 47.4%], the domains became larger. However, compared with Run 1011, because of limited mobility of the P(ST-BA) chains contacted with P(4VP-BA-DVB) phase, finally Run 1021 formed sandwich-like particles [Fig. 5(f), 79.6%], but not hemispherical or dumbbell-like particles.

Investigation on Run 1022*

Figure 6 shows TEM photos of the Run 1022* at different polymerization times. Similarly, after swelling for 24 h at ambient [Fig. 6(a)], the size of swelling particles increased on the basis of seed particles [Fig. 5(a)] (from 358 to 392 nm). After polymerization for 30 min [Fig. 6(b), 5.2% conversion], many microdomains of P(ST-BA) formed and disturbed in P(4VP-BA) matrix. After 60 min [Fig. 6(c), 5.9%], and 150 min [Fig. 6(d), 10.8%], many small-size P(ST-BA) domains formed and mainly distributed in the edge of P(4VP-BA) phase, which made the edge of the particles look gray in the TEM photos. Compared with Run 1021, P(ST-BA) chains with hydrophobic AIBN terminal group in the aqueous solution was less hydrophilic. Accordingly, the mobility of P(ST-BA) chains with AIBN fragment was lower than those with V-50 fragment at the interface between the particle and water. Therefore, for Run 1022*, the diffusion of P(ST-BA) domains on the surface of P(4VP-BA) phase became more difficult during the final polymerization stage; finally the mixture of sandwich-like and popcorn-like composite microspheres [Fig. 6(e), 49.1%] were obtained.

Based on the above observations of morphology development of composite microspheres, for a hydrophilic-seed/hydrophobic-second-polymer system, a formation mechanism of a complete phase-separated morphology (hemispherical) was proposed. This mechanism is depicted schematically in Figure 7. In

stage 1, the solvent and the second-stage monomer together were added into the crosslinked seed latex, and the seed network was not yet swollen. In stage 2, the seed network was swollen to the equilibrium and the monomer-solvent was uniformly distributed in the seed network. As a result, the seed network was relatively relaxed. In stage 3, after heating the system to 70°C, the addition of initiator solution induced the formation of polymers in the seed network and then developed to many microdomains of P(ST-BA), because the polymerization started at different points in a particle as the radical entered and was consumed constantly. The polymerization rate in the initial stage was quite fast, and there was no time for the microdomains to coalesce to one domain. As the polymerization proceeded, microdomains of P(ST-BA) were driven to the periphery of the swelling network. In stage 4, with the polymerization proceeded further, the P(ST-BA) domains were driven out of the seed network in all directions and distributed on the surface of network matrix. Meanwhile, with the increase of polymer yield, the numbers of P(ST-BA) domains decreased and the size increased. In stage 5, the size of P(ST-BA) domains further increased. Meanwhile, the P(ST-BA) domains on the surface of seed matrix diffused each other and coalesced because of the principle of the free energy minimization, which led to the formation of the sandwich-like and popcorn-like composite microspheres. In stage 6, if the mobility of second-stage polymer chains is high enough to allow the complete diffusion and coalescence of P(ST-BA) domains on the surface of the matrix, finally the complete phase-separated hemispherical composite microspheres are achieved.

CONCLUSION

For the P(4VP-BA)/(ST-BA) composite latex system prepared by seeded preswelling emulsion polymerization, the swelling with toluene effectively decreased the polymerization locus viscosity and increased the mobility of polymer chains. When the seed was crosslinked by EGDMA and the second-stage polymerization was initiated by V-50, with the increase of toluene amount added into preswelling system, the P(ST-BA) domains of popcorn-like or sandwich-like particles were likely to overcome the diffusion resistance to converge to one domain during the final polymerization stage. That implied that the hemispherical particles were obtained. According to the studies of the effect of the different parameters on the final morphology, it was concluded that the mobility of P(ST-BA) chains was crucial to determine the final morphology of P(4VP-BA)/P(ST-BA) system. When the mobility was high enough to allow the new P(ST-BA) domains on the surface of P(4VP-BA) phase to move to one large domain during the final polymer-

ization, the hemispherical particles could be achieved. The addition of toluene also enhanced the colloidal stability of composite latex at the time of a decrease in the number of P(ST-BA) domains on the P(4VP-BA) matrix.

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