Study on Synthesis and Morphology Control of Poly(4-vinylpyridine-*co*-butyl acrylate)/Poly(Styrene-*co*-butyl acrylate) Composite Microspheres

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ABSTRACT: Monodispersed crosslinked cationic poly(4-vinylpyridine-*co*-butyl acrylate) [P(4VP-BA)] seed latexes were prepared by soapless emulsion polymerization, using 2,2′-azobismethyl(propionamidine)dihydrochloride (V_{50}) as an initiator and divinylbenzene (DVB) or ethylene glycol dimethacrylate (EGDMA) as a crosslinker. The optimum condition to obtain monodispersed stable latex was investigated. It was found that the colloidal stability of the P4VP latex can be improved by adding an adequate amount of BA (BA/4VP = 1/4, w/w), and adopting a semicontinuous monomer feed mode. Subsequently, poly(4-vinylpyridine-*co*-butyl acrylate)/Poly(styrene-*co*-butyl acrylate) [P(4VP-BA)/P(ST-BA)] composite microspheres were synthesized by seeded polymerization, using the above latex as a seed and a mixture of ST and BA as the second-stage monomers. The effects of the type of crosslinker, the degree of crosslinking, and the initiators (AIBN and V_{50}) on the morphology of final composite particles are discussed in detail. It was found that P(4VP-BA)/P(ST-BA) composite microspheres were always surrounded by a PST-rich shell when V_{50} was used as initiator, while sandwich-like or popcorn-like composite particles were produced when AIBN was employed. This is because the polarity of the polymer chains with AIBN fragments is lower than for the polymer with V_{50} fragments, hence leading to higher interfacial tension between the second-stage PST-rich polymer and the aqueous phase, and between PST-rich polymer and P4VP-rich seed polymer. As a result, the seed cannot be engulfed by the PST-rich polymer. Furthermore, the decrease of T_g of the second-stage polymer promoted phase separation between the seeds and the PST-rich polymer: sandwich-like particles formed more preferably than popcorn-like particles. It is important knowledge that various

morphologies different from PST-rich core/P4VP-rich shell morphology, can be obtained only by changing the initiator, considering P4VP is much more hydrophilic than PST. The zeta potential of composite particles initiated by AIBN in seeded polymerization shifted from a positive to a negative charge. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1190–1203, 2002

INTRODUCTION

Polymer composite microspheres with various morphologies can be prepared via seeded emulsion polymerization by varying the process parameters. The composite microspheres provide a wide range of potential applications in various fields, from paints and organic opacifiers, to impact modifiers for plastics, to carriers for biomaterials.[1–4] For example, particles with a rubbery core and glassy shell are used in the field of toughening of thermoplastics, sound and vibration damping, and increasing fracture and fatigue resistance. Particles with inorganic core and polymeric shell show promising applications in electron materials and biotechnology.[5] To a large degree, the performance of the composite microspheres in an end-use application depends largely on the morphology of the microspheres. Therefore, the design and morphology control of the composite particle are crucial to meet the respective end use. In addition to their technological importance, a better understanding of the factors affecting the morphology of the composite particles will shed some light on the mechanism of the seeded emulsion polymerization.

It has been known that the morphology of composite microspheres, prepared by the seeded polymerization, depends on factors such as sequence and mode of monomer addition, monomer composition, hydrophilicity difference between the monomers, interfacial tensions, molecular weights of the formed polymers, and so forth. The morphology of the composite microspheres is controlled by thermodynamic and kinetic factors.[6] The equilibrium morphology of the final composite particles is determined by the thermodynamic factor, i.e., a morphology showing minimum free energy change should be realized. On the other hand, kinetic factors determine the ease with which the thermodynamically favored equilibrium morphology can be achieved. Control of particle morphology has been a challenge, particularly for the preparation of core-shell particles when the desired core polymer is more hydro-

philic than the shell polymer. So far, studies on the seeded polymerization mostly focused on the PST/PMMA system, where PMMA acted as a hydrophilic component and PST as a hydrophobic one. In 1985, Cho et al.[7] prepared PST/PMMA composite latex particles. When a water-soluble initiator $K_2S_2O_8$ was used, the occurrence of the half moon-like, the sandwich-like, and core shell morphologies were observed, depending on the polymerization condition. It was found that an anchoring effect, exerted by an ionic terminal group introduced by the ionic initiator, was the key factor in controlling the particle morphology. In 1990, Sheu et al.[8] schematically investigated the effects of crosslinking degree of seed and the second-stage polymer for the PST–PST system by using PST as a seed and ST as a second-stage monomer. They found that the crosslinking of the seed can promote phase separation between the seed and the second-stage polymer, and the morphology changed from spherical particles to nonspherical ellipsoidal or egg-like singlets, symmetric or asymmetric doublets, and ice cream cone-like or popcorn-like multiplets, as the crosslinking degree of the seed increased. The nonspherical particles resulted from enhanced phase separation between the second-stage polymer from the crosslinked seed network during polymerization. In 1992, Chen[9–11] and Jösson[12,13] independently prepared the so-called dumbbell-like PST/PMMA composite particles. They proved that the interfacial tensions between polymer and polymer and between polymer and water, were the key factors determining the equilibrium morphology of the resulting composite particle. All of the initiator, molecular weight, and emulsifier affect the value of the interfacial tension, therefore the morphology of the composite particles. Based on experimentally measured interfacial tension, El-Aasser's group[8–11] and Sundberg's group[14,15] theoretically predicted the morphology of the composite particles, and obtained good agreement with the observed morphology of the composite microspheres. Based on their theory,

PMMA core/PST shell composite particles are difficult to prepare, because the interfacial tension between PMMA and the aqueous phase is lower than that between PST and the aqueous phase in the general aqueous phase. However, Okubo et al.[16] successfully prepared PMMA core/PST shell microsphere by controlling the feed rate of ST at the second stage in the presence of the PMMA seed. Because the ST feed rate was very low, the ST monomer had no time to diffuse into the PMMA seed, and polymerized on the surface of the seed. This result suggests that various nonequilibrium morphologies can possibly be designed by controlling the kinetic factors.

In this study, we investigated the preparation and morphology control for P(4VP-BA)/P(ST-BA) system by the seeded emulsion polymerization. This system was selected here; because P4VP has a functional group, it can be chemically modified in acidity, basicity, and hydrophilic and hydrophobic properties: crosslinking, inside and between the particles, is easily performed. P4VP has been widely used in medicine, dye, ion-exchange materials, a functional membrane,[17–20] and so forth. The final purpose of this study is to obtain dumbbell-like or sandwich-like P4VP-rich/PSt-rich composite microspheres. By further modifying P4VP and PS domains to cationic and anionic domains, respectively, or only by modifying P4VP domains to hydrophilicity and keeping PST hydrophobicity, the cationic/anionic or hydrophilic–hydrophobic amphiphilic composite microspheres will be easily obtained. Such novel amphiphilic composite microspheres are designed to be used in the preparation of functional membranes.[21] For the preparation of P4VP-rich/PST-rich composite microspheres by seeded polymerization, the PST-core/P4VP shell morphology is usually formed, if using PST as a seed. To obtain microspheres with a dumbbell or sandwich-like, or other morphologies more than the PST core/P4VP shell by controlling kinetic factors, hydrophilic P4VP microspheres were selected as a seed. Unfortunately, probably because the considerable hydrophilicity of P4VP resulted in the formation of a "hairy layer" on the surface of the microsphere, the apparent diameter became larger. Consequently, the ionic density on the surface decreased, and the repulsive force between particles decreased. So, Ma et al[20] used partially quaternized reactive P4VP as an emulsifier to increase the repulsive force. The apparent diameter became larger and the apparent concentration of polymer particles increased. This would result in

entanglements between hairy polymers. The other problem is that free P4VP oligomer probably is produced, which will also reduce the stability of the particles by bridging or depletion flocculation.[22] In this study, by adding BA, copolymerization between BA and 4VP can reduce the hydrophilicity of the particle surface, and also promote the adsorption of copolymer on particles, therefore decreasing the amount of free P4VP oligomer. In addition, we also changed the monomer feed mode from a batch to a semicontinuous mode, to improve the stability of the latex. Another purpose of introducing BA to the polymerization system is to lower the glass transition temperature (T_g), which is favorable for future use in preparation of functional membranes. Therefore, as the first step in this study, we prepared P(4VP-BA) seed latex by soapless polymerization and investigated the effects of the monomer feed mode, the 4VP/BA ratio, the type and amount of crosslinker on the latex stability, particle size, and size distribution of the P(4VP-BA) seed. Next, we synthesized P(4VP-BA)/P(ST-BA) composite microspheres by seeded emulsion polymerization using the obtained P(4VP-BA) particle as a seed and a ST/BA mixture as the second-stage monomers. The influences of the type of the initiator, BA/ST ratio, crosslinking degree of the seed particle, and the second-stage polymer on the morphology of the final composite particles were investigated. The polymerization condition to obtain a dumbbell or sandwich-like microspheres is discussed.

EXPERIMENTAL

Chemicals

4-Vinylpyridine (4VP) (Merck, Schuchardt, Germany) was distilled under reduced pressure, after it was dried overnight with calcium hydride. Styrene (ST) and butylacrylate (BA) (Shanghai Chemicals Co.) was washed with 5% sodium hydroxide solution, followed by water, dried overnight with anhydrous sodium sulfate, and then distilled under vacuum. Ethylene glycol dimethacrylate (EGDMA) (Suzhou Anli Chemicals, C.P.) was distilled in the presence of methylene blue, followed by washing with saturated sodium chloride solution and water successively to remove the inhibitor, and then was dried overnight with anhydrous sodium sulfate. Divinylbenzene (DVB) (Shanghai Qunli Chemicals, C.P.,

Table I The Polymerization Conditions and the Results of Seed Latex by Soapless Emulsion Polymerization

Run No.	BA/4-VP (w/w)	C.D. (mol %)	Stability	d_n (nm) SEM	d_w (nm) SEM	d_w/d_n	ζ Potential (+mv)
301	1/4	DVB 2.0	unstable	589	680	1.154	31.6
304	1/4	DVB 2.0	stable	462	472	1.022	26.4
303	1/4	DVB 4.0	stable	405	413	1.020	33.5
308	1/4	EGDMA 3.0	stable	467	470	1.006	4.62
311	1/4	DVB 8.0	stable	338	342	1.012	34.7
312	1/4	DVB 16	stable	304	307	1.010	35.5
309	1/1	DVB 2.0	stable	297	324	1.091	26.4
310	4/1	DVB 2.0	stable	268, 78	271, 80	—	34.5

CD: degree of crosslinking; DVB: divinylbenzene; EGDMA: ethylene glycol methacrylate.

C.D. was expressed as the weight percentage of total monomers, and was calculated as: wt % = $W_c/(W_c + W_m)$, where W_c and W_m are the weight of crosslinker and monomers, respectively. Run 301: batch feeding mode, all the others by semicontinuous feeding (2 mL/h).

Initiator (V_{50})/monomer = 3.0 wt %, Total solid content equal to 5%, conversion is over 98%; Stirring speed: 350 rpm, polymerization temperature: 70°C.

55%) was washed with 10% sodium hydroxide solution, followed by water repeatedly, and then was dried with anhydrous calcium chloride. 2,2′-Azobis(methylpropionamidine) dihydrochloride (V_{50}) (Wako Pure Chemicals Industries, Ltd.) was recrystallized twice from acetone/water (50/50, v/v) mixture solvent. Azobisisobutyronitrile (AIBN) (Shanghai Chemicals, C.P.) was purified by recrystallization from ethanol and then dried at room temperature in a vacuum oven. Iodomethane (Shanghai Chemicals, A.R.) was distilled and used for the quaternization of P4VP domain. All the monomers were purged with nitrogen and kept at −10°C before use. Deionized water was used in all polymerizations.

Preparation of P(4VP-BA) Seed Microspheres

The P(4VP-BA) seed particles were prepared by soapless emulsion polymerization. The polymerization conditions, as well as the polymerization results, are listed in Table I. The 120 mL deionized water was charged to a 250-mL four-necked, round-bottom flask, equipped with a Teflon paddle-propeller mechanical stirrer, a reflux condenser, a thermometer, and a gas inlet tube, purged with nitrogen gas for 20 min, and then the temperature was elevated to 70°C. V_{50} (0.2250 g) was dissolved in 10 mL deionized water and thoroughly bubbled by nitrogen gas before being added. The monomer mixture (7.5 g), also purged with N_2 gas, was added to the reactor dropwise at a feeding rate of 2 mL/h, with the agitation speed of 350 rpm. The polymerization was carried out for 10 h under a nitrogen atmosphere. The BA/

4VP ratio was changed from 1/4 to 4/1 (w/w), and the content of crosslinker in the monomer was varied from 2.0 to 16 mol %. Two kinds of crosslinker (DVB and EGDMA) were used. The initiator/monomer ratio was fixed at 3.0 wt %, and monomer concentration at 5 wt %.

Preparation of P(4VP-BA)/P(ST-BA) Composite Microspheres

The P(4VP-BA)/P(ST-BA) composite microspheres was prepared by seeded polymerization. The 40-mL seed latex (2 g polymer) and 80 mL deionized water were charged to the reactor, bubbled with nitrogen gas for 30 min under agitation and then heated to 70°C. The AIBN (0.10 g) or V_{50} initiator (0.15 g) was dissolved in 10 mL ethanol or deionized water, respectively. The initiator solution was added and subsequently, the second-stage monomers (5.0 g) were added dropwise at a feed rate of 2 mL/h, after they were bubbled respectively with nitrogen gas for 30 min. The polymerization was performed for 10 h under nitrogen atmosphere to obtain the composite particles. For the preswelling method, all the second-stage monomers were charged before the seeded emulsion polymerization, and allowed to swell seeds for 24 h at room temperature. Then, the temperature was raised to 70°C to initiate polymerization. Monomer/seed polymer ratio was fixed at 5/2 (w/w), AIBN/monomer and V_{50}/monomer at 2 and 3 wt %, respectively. The content of crosslinker in the monomer was varied from 0.40 to 4.0 mol %, and two types of crosslinkers (DVB and EGDMA) were used.

Characterization of Seed and Composite Microspheres

Conversion

The monomer conversion was measured by gravimetry. Ten milliliters of emulsion were centrifuged and followed by decantation of the supernatant, then dried in a vacuum at 50°C and weighed. The conversion was calculated according to the following equation:

$$\text{conversion (\%)} = \frac{W_{ds}}{[W_{mo}/(W_{wa} + W_{mo})] \times W_{sa}} \times 100$$

where W_{ds}, W_{mo}, W_{wa}, and W_{sa} are the weight of the dried polymer latex, fresh monomer, water, latex sample, respectively. The result was obtained as an average value from three measurements.

SEM Observation

The morphology of seed particle was observed by scanning electron microscopy (SEM) (Model H800, Hitachi, Japan).

TEM Observation

The morphology of composite particles prepared by the seeded polymerization was observed by transmission electron microscopy (TEM) (Model H800, Hitachi, Japan). The TEM samples were prepared according to a similar procedure by Okubo,[23] one drop of emulsion was diluted and then cast on the copper mesh and dried at room temperature. The morphology was observed directly after the sample was stained with iodomethane vapor for 24 h in a sealed container.

Particle Size and Its Distribution

Average diameters of the seed particles were measured by counting 200 particles in SEM photographs. The number, weight average diameter of the particles D_n, D_w can be calculated by the following equation:

$$d_n = \sum n_i d_i / \sum n_i, \; d_w = \sum n_i d_i^4 / \sum n_i d_i^3,$$

where n_i is the intensity of the size distribution. The uniformity of the particles was calculated by the equation: $U = d_w/d_n$. The diameter of nonspherical particle was not given due to their anomalous morphologies.

Zeta Potential Analysis

The zeta potential of seed and composite latexes was measured in $10^{-3}M$ NaCl solution with a Microelectrophoresis Analyzer (Model JS94D, Shanghai Zhongchen Economy Development Co. Ltd.) after the latex was diluted to 1 wt ‰. The zeta potential was obtained as an average value of three time measurements.

DSC Measurement

The glass transition temperatures (T_g) of the composite particles were determined with a DSC2910 Modulated DSC (TA Instruments, U.S.A.) between $-10-150$°C, at a heating rate of 20°C/min. The samples for DSC were purified as follows: the latex was centrifuged (4500 rev/min for 45 min), followed by decantation of the supernatant: the solid was redispersed into deionized water and dialyzed for 1 week, and then was dried under vacuum at 50°C.
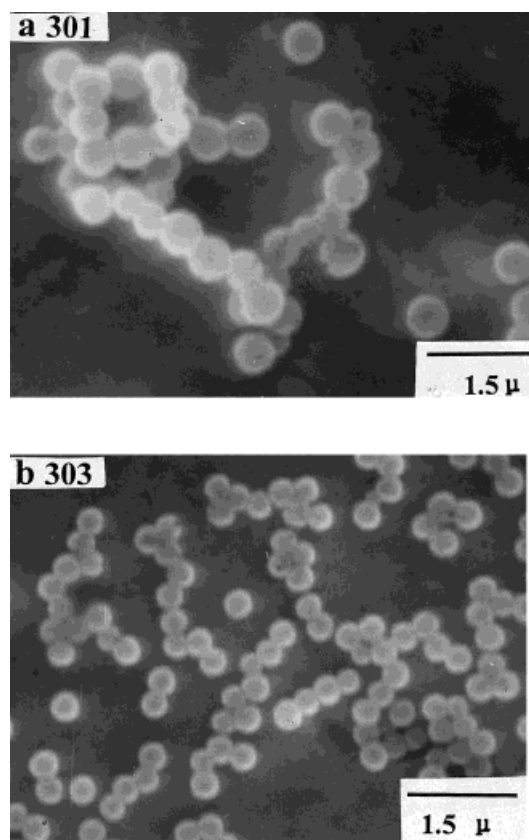

Figure 1 SEM photographs of P(4VP-BA) seed particles as a function of the monomer feed mode. DVB: 4.0 mol %. BA/4VP = 1/4 (w/w). (a) Batch feed mode; (b) semicontinuous feed mode.
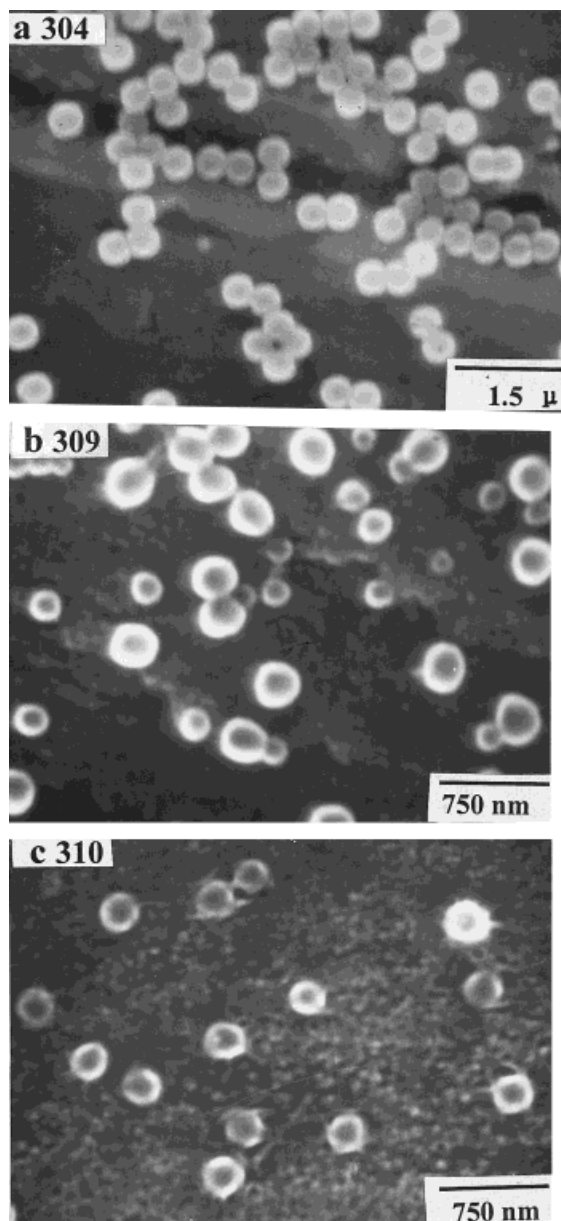
Figure 2 SEM photographs of P(4VP-BA) seed particles as a function of the BA/4VP ratio. DVB: 2.0 mol %. BA/4VP (w/w): (a) 1/4; (b) 1/1; (c) 4/1.

RESULTS AND DISCUSSION

Synthesis of P(4VP-BA) Seed Microspheres

The polymerization results of the P(4VP-BA) seed particles are shown in Table I, and the SEM photographs of the seed particles are shown in Figures 1–4.

Effect of Monomer Feed Mode

As seen from Table I and Figure 1, the monomer feed mode apparently affected the diameter and its distribution in the resultant particles. Comparing runs 301 to 304, where the BA/4VP ratio was fixed at 1/4 (w/w) and the DVB content in the monomer feed was fixed at 2.0 mol %, it was clear that the diameter of the microsphere by a batch feed mode was larger than that with a semicontinuous feed mode. Furthermore, it was observed that the latex prepared by the batch method is unstable: it tended to coagulate upon storage. Therefore, the semicontinuous monomer feed mode was employed in the following experiments.

Effect of BA/4VP Ratio

It was found that the colloidal stability of the latex was improved by adding an adequate amount of BA in the 4VP monomer. To confirm the effect of BA further, the BA/4VP ratio was varied from 1/4 to 4/1 (w/w), while the DVB content in the monomer feed was fixed at 2.0 mol %. The SEM photographs showing effect of BA are shown in Figure 2. As indicated by runs 304, 309, and 310, the diameter of P(4VP-BA) got smaller,
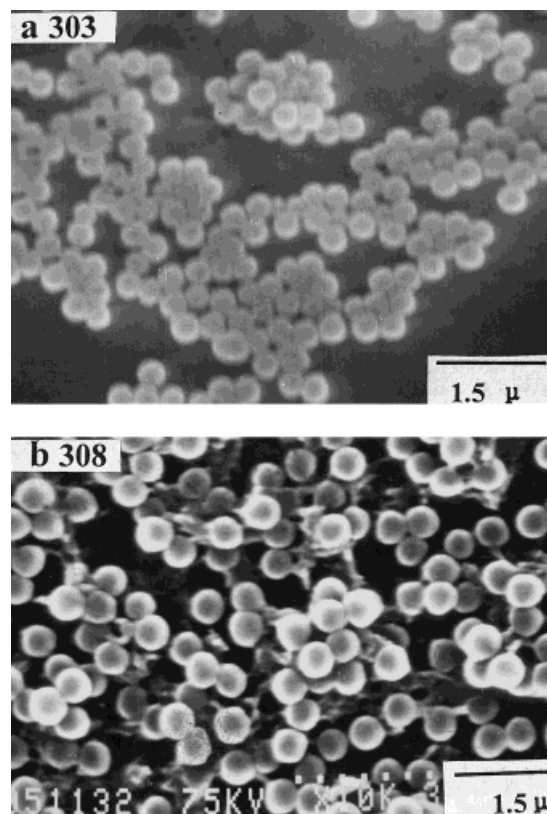

Figure 3 SEM photographs of P(4VP-BA) seed particles as a function of the crosslinker type. Crosslinker content: (a) 4.0 mol % DVB; (b) 3.0 mol % EGDMA.
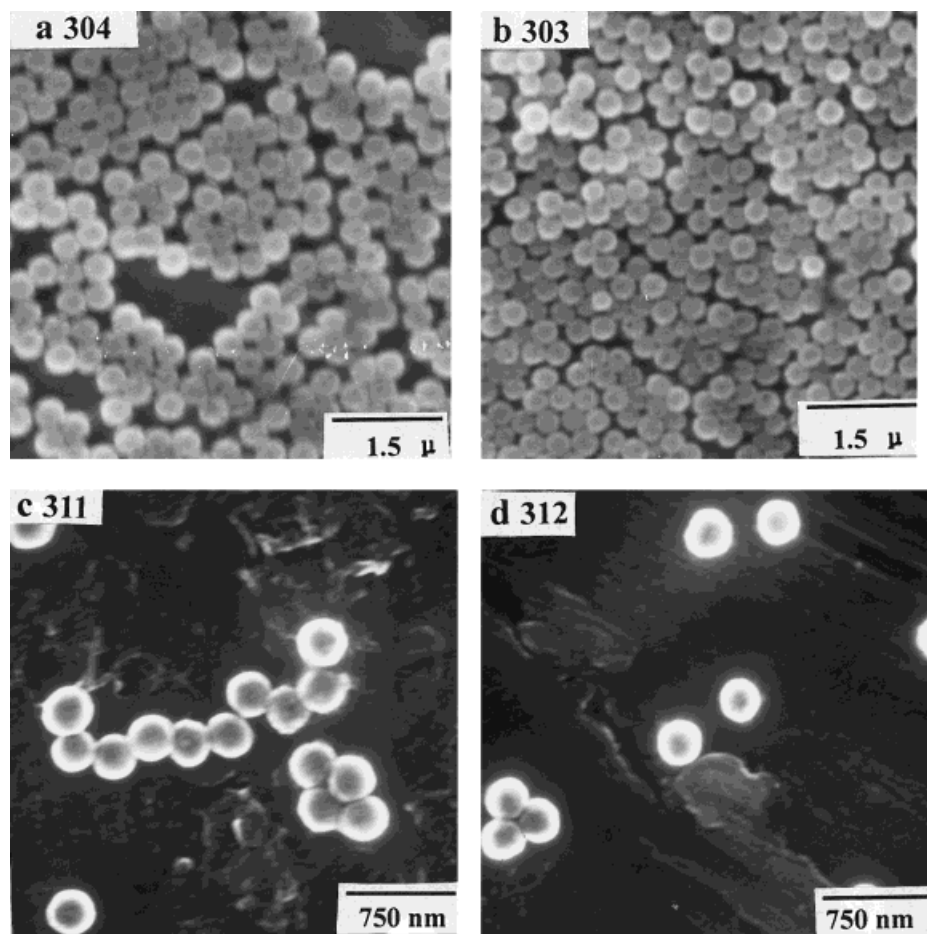
Figure 4 SEM photographs of P(4VP-BA) seed particles as a function of the crosslinking degree. BA/4VP = 1/4 (w/w). Crosslinker content (mol %): (a) 2.0; (b) 4.0; (c) 8.0; (d) 16.

and its distribution became broader with the increase of BA/VP ratio content in the monomer feed. When the BA/4VP ratio was 1/4 (w/w), particles with the narrowest size distribution were obtained, and the number-average diameter was 462 nm. As the BA/4VP ratio increased to 1/1, the diameter decreased to 297 nm, and the size distribution of particles got broader. When the BA/4VP ratio was increased further to 4/1, however, a bimodal size distribution consisting of 80 nm and 270 nm was revealed.

Effect of Type of Crosslinker and Crosslinking Degree

The crosslinked P(4VP-BA) seed particle was needed for morphology control in subsequent seeded polymerization. Therefore, the effect of the type of crosslinker and crosslinking agent on the size and size distribution of the particles were

also investigated, by fixing the BA/4VP ratio to 1/4 (w/w). The SEM photographs of the particles, prepared by using DVB and EGDMA as a crosslinker, respectively, are shown in Figure 3. From Figure 3 and Table I, it is evident that the diameter of the particle prepared by using EGDMA was larger than that with DVB. The DVB content in the monomer feed was changed from 2.0 to 16 mol % for which SEM photographs are shown in Figure 4. For the same crosslinker, DVB, the particle size became smaller with the increase of crosslinking degree.

The effects of the monomer feed mode, the BA/4VP ratio, and the crosslinker on the particle size and size distribution can be explained as follows. Two possible nucleation mechanisms for soapless emulsion polymerization have been previously proposed: homogeneous nucleation and micellar nucleation.[24,25] For the hydrophilic monomers,

Table II Recipe and Characterization for Composite Latex Particles in Seeded Emulsion Polymerization

Run No.	Seed	Shell Monomers BA/ST (w/w)	C. D. (mol %)	Feeding Mode	Initiator Type	ζ Potential (mv)
404-1	304	1/4	DVB 4.0	Batch	V_{50}	+26.8
404-2	304	1/4	DVB 4.0	Semicontinuous	V_{50}	+23.1
404-3	304	1/4	EGDMA 4.0	Semicontinuous	V_{50}	+23.5
404-4	304	1/4	DVB 2.0	Semicontinuous	V_{50}	+14.0
404-5	304	1/4	EGDMA 2.0	Semicontinuous	V_{50}	+21.9
408-1	308	1/4	EGDMA 4.0	Semicontinuous	V_{50}	+11.6
408-2	308	1/4	DVB 4.0	Semicontinuous	V_{50}	+11.7
404-6	304	1/4	DVB 0.40	Semicontinuous	AIBN	−8.87
404-9	304	1/4	EGDMA 0.4	Semicontinuous	AIBN	+5.73
404-7	304	1/4	EGDMA 0.5	Semicontinuous	AIBN	−3.67
404-8	304	2/3	EGDMA 0.5	Semicontinuous	AIBN	+9.90
408-3	308	1/4	DVB 0.6	Semicontinuous	AIBN	−13.8
408-4	308	1/4	EGDMA 0.3	Semicontinuous	AIBN	−11.0

C.D.: degree of crosslinking. C.D. (wt %) = $W_c/(W_c + W_m)$, where W_c and W_m are the weight of crosslinker and monomer, respectively.

Monomer/seed polymer: 5/2 (w/w).

V_{50}/monomer = 3.0 wt %, AIBN/monomer = 2.0 wt %, total solid content = 5%, conversion is over 98%.

Stirring speed: 350 rpm, reaction temperature: 65°C.

such as 4VP and MMA, nucleation in the soapless polymerization should follow an homogeneous nucleation mechanism. The initiation of polymerization starts in the aqueous phase through the decomposition of the initiator, followed by the addition of monomers dissolved in water. The growth of the oligomeric radical proceeds in the aqueous phase up to a critical chain length. On exceeding this critical length, the oligomeric radical precipitates from the aqueous phase and form a water-insoluble polymer in the form of spherical particle (primary particle, nucleus). The primary particles are unstable, and they coagulate to a large stable particle. Then, the stable growing particle absorb monomers, which diffuse through the aqueous phase from the monomer droplets, to carry out the polymerization. When monomer was fed by the batch mode, the 4VP polymerized preferentially because the solubility of 4VP in the aqueous phase is higher (refer to 2.9 g 4VP in 100 g water at 20°C and 0.16 g BA in 100 water at 25°C, respectively) and the reactivity ratio is larger [refer to the bulk reactivity ratio, r_1 = 4.3, and r_2 = 0.23 for 4VP(1)/BA(2)]. Therefore, the critical polymer chain length is larger, causing a lower growing particle number. As a result, the diameter of the particles became larger. When the semicontinuous monomer feed mode was employed, a

higher fraction of BA can be copolymerized with 4VP in the aqueous phase to form the nucleus in the initial stage, due to the relatively "monomer-starved" condition. Therefore, the critical polymer chain length decreased, causing a larger particle number; hence, particle size decreased. As the particle size decreased, the colloidal stability of the latex was improved.

When a small amount of BA was added, the occurrence of free P4VP oligomer could be prevented; hence, the colloidal stability of the latex can be improved. Additionally, when the BA/4VP ratio increased, the hydrophilicity of the copolymer was reduced and the critical polymer chain length got shorter, causing a higher growing particle number. Therefore, the particle size became smaller. In the case of high BA/4VP ratio (4/1, w/w), the reason for the bimodal size distribution is not known exactly. Although we expected a "monomer-starved" condition, it did not occur, because the polymerization rate was slower than that of monomer feeding. Probably because of the disparate aqueous solubility and reactivity of 4VP and BA, as well as the monomer ratio, 4VP was consumed preferentially to BA. Even when 4VP was consumed, nucleation of BA still existed. As a result, the particles produced first consisted of more P4VP polymer and yielded larger particles,
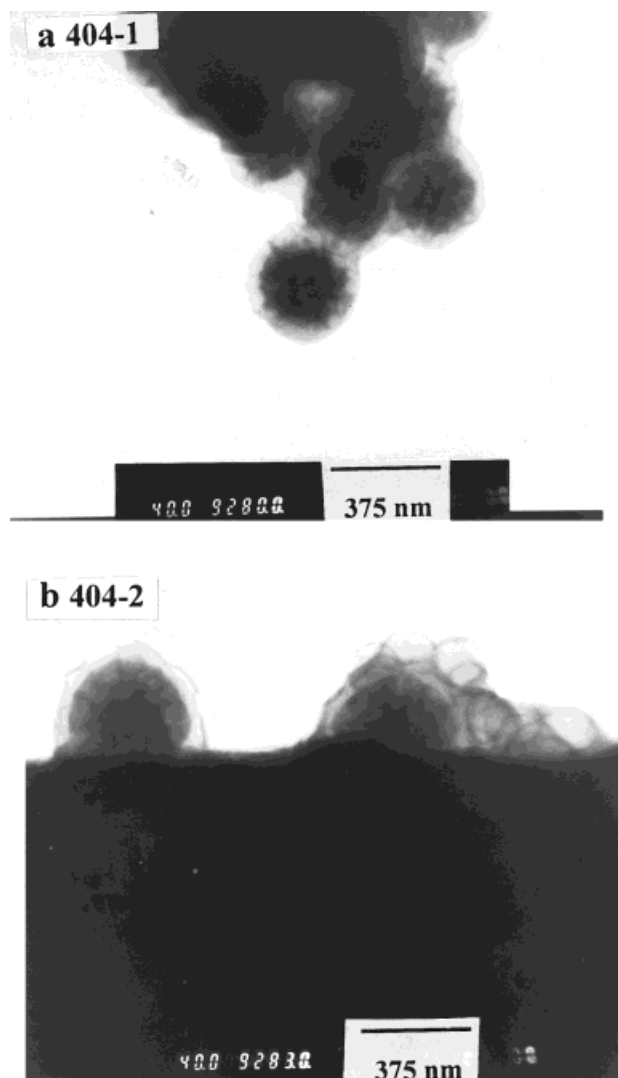
Figure 5 TEM photographs of P(4VP-BA)/P(ST-BA) composite particles as a function of monomer feed mode. Seed: run 304. DVB: 4.0 mol %. BA/ST = 1/4 (w/w). Initiator: V_{50}. Monomer feed mode: (a) Batch (preswelling) feed mode; (b) semicontinuous feed mode. (P4VP domain was stained with CH_3I).

while the later-produced particles were composed of more BA content and yielded smaller particles. Therefore, a bimodal particle size distribution was formed.

When EGDMA was used as a crosslinker, the critical chain length was larger because its hydrophilicity is higher than that of DVB. As a result, the particle number became smaller and then the particle size got larger. For the same reason, a higher fraction of DVB was copolymerized with 4VP to form a primary particle as the DVB content increased. Therefore, the critical polymer

chain length decreased, causing an increase of the particle number; hence, the particle size decreased. From the above results, we can also find that the crosslinking effect is coupled to the hydrophobicity of the DVB monomer.

As described above, the most stable latex with a narrow size distribution was obtained when the BA/4VP ratio was 1/4 (w/w). Therefore, runs 304 and 308 were selected as the seeds in subsequent seeded emulsion polymerizations for preparation of P(4VP-BA)/P(ST-BA) composite microspheres.

Synthesis of P(4VP-BA)/P(ST-BA) Composite Microspheres

The results for the preparation of P(4VP-BA)/P(ST-BA) composite particles by seeded polymerization are listed in Table II. Compared with the seed particles, the diameter and surface characteristics of the composite particles changed a lot. Only the diameter of particles with morphology of the core-shell structure was measured. For the case of sandwich-like or popcorn-like morphological particles, the diameter was not measured due to their anomalous structure. For example, the diameter of run 404-4 composite particles increased to 573 nm from 460 nm of the seed and few secondary particles was observed. The zeta potential of composite particles became lower than that of the seed. When AIBN was used as an initiator in the seeded polymerization, the zeta-potential got much lower than in the case of V_{50}, and some samples changed from positive to negative values. This is because V_{50} is a cationic initiator, while the radical of AIBN is a nonionic one. The zeta potential is a consequence of ion adsorption. As the seeded emulsion polymerization proceeded, the PST-rich polymer with AIBN fragments accumulated on the surface of the core, which reduced the positive charge density on the surface of the composite particle. The variation of morphology of the particles led to a corresponding change of zeta potential. This result has something in common with the result of Okubo et al.'s research.[26] They prepared the core-shell composite particles by the heterocoagulation of cationic small particles onto an anionic large polymer particle. The zeta potential of the final composite particles showed a positive value because the anionic core is surrounded by positively charged microspheres.

In addition, two distinct T_gs were observed for each composite particle. One was around 110°C, corresponding to the P4VP-rich seed polymer, an-
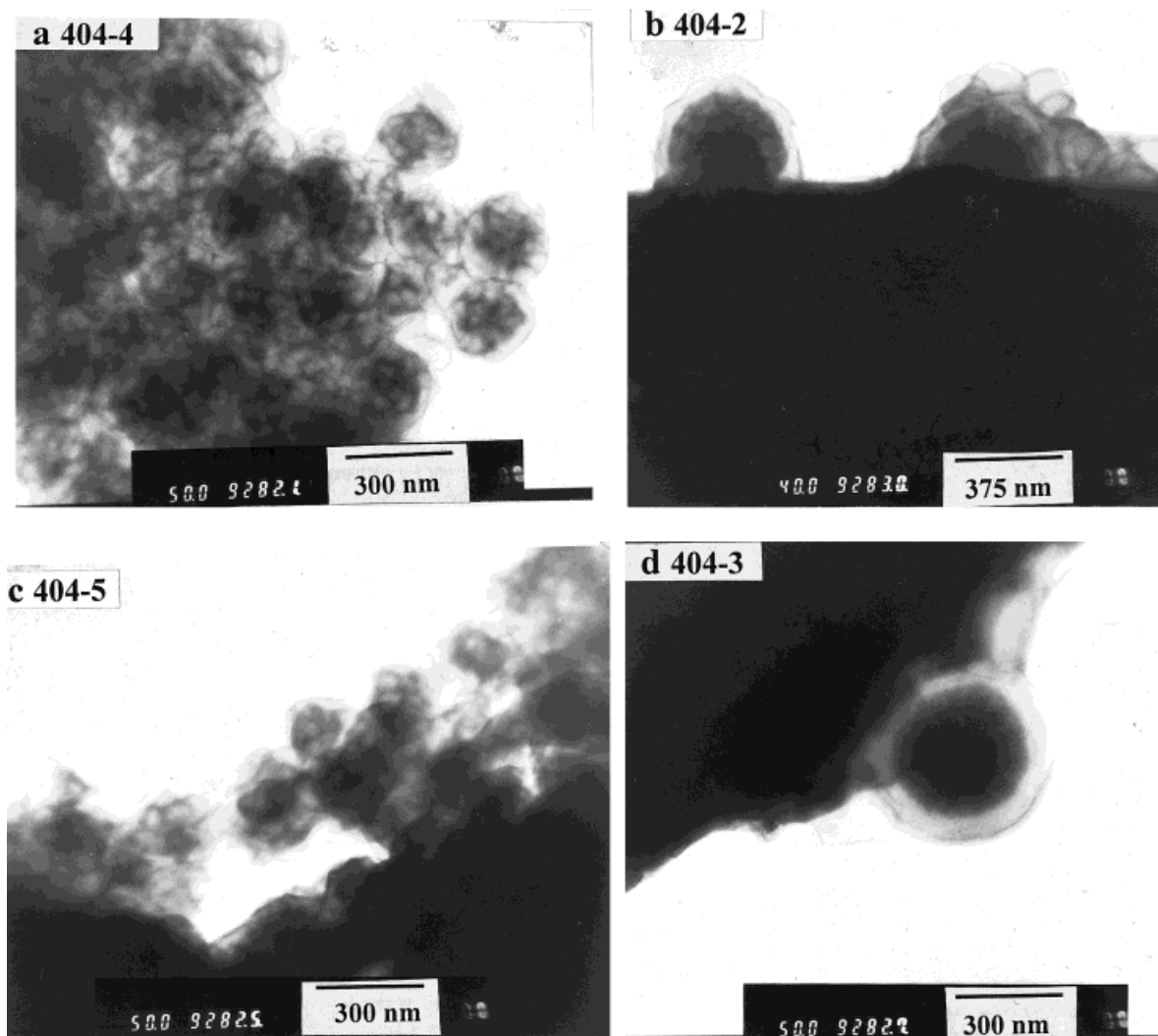
Figure 6 TEM photographs of P(4VP-BA)/P(ST-BA) composite particles as a function of crosslinking degree. Seed: run 304. BA/ST = 1/4 (w/w). Initiator: V_{50}. Crosslinker content (mol %): (a) 2.0 (DVB); (b) 4.0 (DVB); (c) 2.0 (EGDMA); (d) 4.0 (EGDMA). (P4VP domain was stained with CH_3I).

other one was at about 70°C, which belonged to PST-rich polymer formed at the second stage.

Morphology Control of the P(4VP-BA)/P(ST-BA) Composite Particles

The TEM photographs of P(4VP-BA)/P(ST-BA) composite microspheres are shown in Figures 5 to 9, where P4VP-rich domain was stained with iodomethane vapor. For some TEM samples, coagulation occurred, which has some negative effect on the observation. But we can still see the internal structure of the composite particles. As seen from TEM photographs in Figures 5 to 9, it is clear that the inner region of the composite par-

ticle is darker. This implies that the inner region of the composite particles corresponds to P4VP-rich phase, and the outer part corresponds to the PST-rich polymer formed at the second stage. To obtain various morphologies and search for a polymerization condition to obtain dumbbell or sandwich-like P(4VP-BA)/P(ST-BA) composite microspheres, monomer feed mode, initiator type, crosslinker type, and crosslinking degree of the seed and second-stage polymer were changed.

Effect of Monomer Feed Mode

The TEM photographs of the composite microspheres with a batch monomer feed mode and

semicontinuous phase, respectively, are shown in Figure 5, where DVB was fixed at 4.0 mol %, the BA/ST ratio was fixed at 1/4 (w/w), run 304 was used as a seed, and V_{50} was used as an initiator. Comparing Figure 5(a) and (b), it is evident that the small PST-rich domains were most uniformly distributed inside of the P4VP-rich seed particle when the batch method was used, while there was a more clear interface between the core and shell in the case of semicontinuous feed mode. This is because the preswelling method (batch mode) allowed the monomers to diffuse into the interior of the core and polymerized inside. However, the crosslinking of the seed limited the complete phase separation between P4VP-rich and PST-rich polymers: small PST-rich domains were formed inside the network of seed particles. When the semicontinuous feed mode was used, on the other hand, monomer had no time to migrate into the particle, and most of the monomer polymerized on the surface of the seed, due to the "monomer starved" condition. As a result, a clear interface between the core and shell was observed. In a thermodynamic sense, the hydrophilic core part of the composite particles should migrate to the outside to form a PST-rich core/P4VP shell structure. In the present system, however, the P4VP-rich core was likely to be surrounded by PST-rich shell, because the crosslinking of the seed limited chain mobility of the seed polymer.

Effect of Crosslinker and Crosslinking Degree of the Second-Stage Polymer

The TEM photographs of composite microspheres by changing the crosslinker and crosslinking degree of the second-stage polymer, are shown in Figure 6, where run 304 was used as a seed with V_{50} as an initiator. Comparing Figures 6(a) and (b), or (c) and (d), it is clear that the P4VP-rich phase and the PST-rich phase interpenetrated each other when the crosslinking degree was lower, while P4VP-rich core/PST-rich shell particles were likely to be formed when the crosslinking degree was higher, irrespective of DVB or EGDMA. When the crosslinking degree was lower, the mobility of the PST-rich polymer chain was higher (the viscosity of the polymerization location was lower). Therefore, the PSt-rich polymer can migrate into the interior of the core and formed the fine domain inside.

Effect of Crosslinker Type of the Seed Polymer

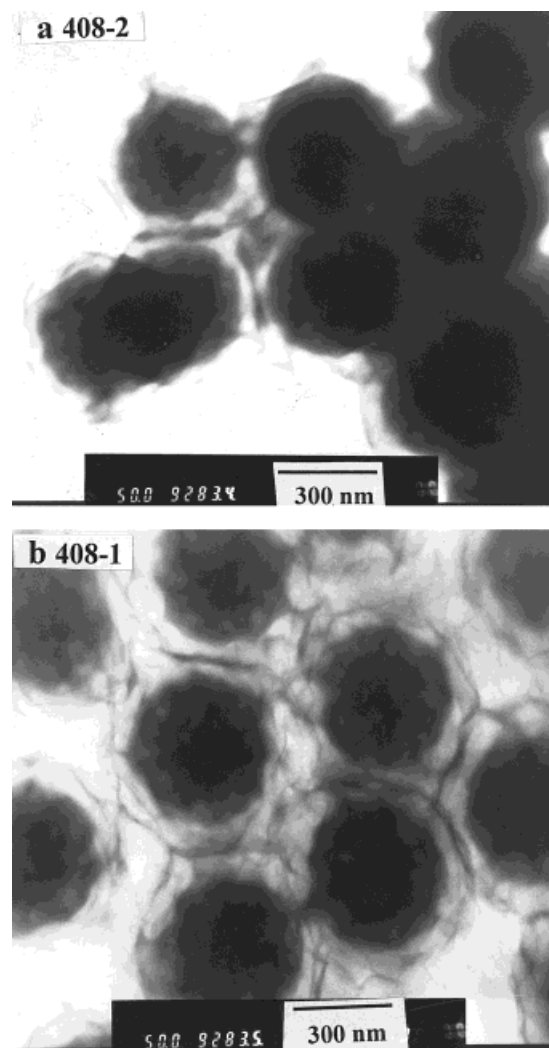It was found that the type of crosslinker also had an influence on the morphology of the P(4VP-BA)/

Figure 7 TEM photographs of P(4VP-BA)/P(ST-BA) composite particles as a function of the crosslinker type. Seed: run 308. BA/ST = 1/4 (w/w). Initiator: V_{50}. Crosslinker: (a) DVB (4.0 mol %); (b) EGDMA (4.0 mol %). (P4VP domain was stained with CH_3I).

P(ST-BA) composite particles. Run 308 was also used as a seed, to compare with the result using run 304. The TEM photographs are shown in Figure 7. Comparing Figures 6(b) and (d) with Figures 7(a), (b), the fine light domains were observed more clearly in the core when run 308 was used as a seed. This result implies that the second-stage monomer migrates into the seed more easily, and polymerized there. The small PST-rich phase was uniformly distributed inside of the P4VP-rich phase. This is because the hydrophilicity of EGDMA is higher than that of DVB: the seed can be swollen by the monomer better in the former case, although its crosslinking degree is higher.
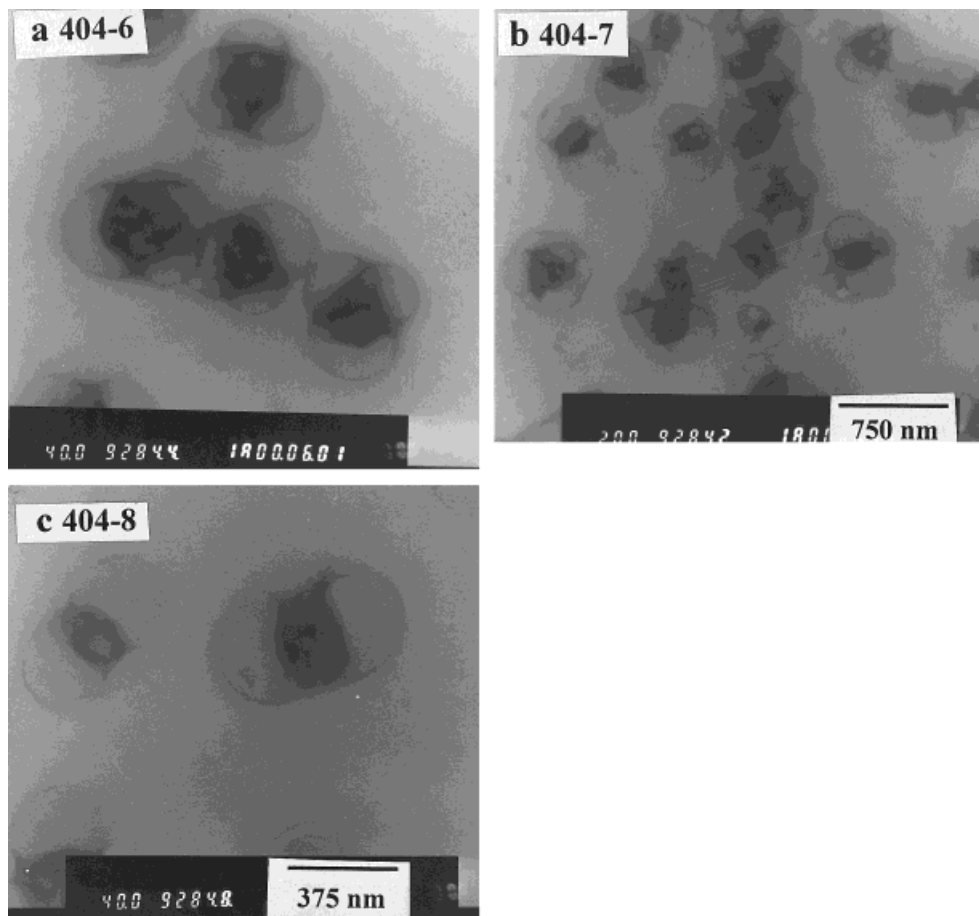
Figure 8 TEM photographs of P(4VP-BA)/P(ST-BA) composite particles as a function of the crosslinker type and BA/ST ratio. Seed: run 304. Initiator: AIBN. (a) DVB (0.4 mol %), BA/ST = 1/4 (w/w); (b) EGDMA (0.5 mol %), BA/ST = 1/4 (w/w). (c) EGDMA (0.5 mol %), BA/ST = 2/3 (w/w). (P4VP domain was stained with CH_3I).

Effect of the Initiator Type

From the above results, it is apparent that the composite microspheres were always surrounded by a PST-rich shell, and dumbbell or sandwich-like microsphere is difficult to prepare, when V_{50} is used as an initiator. This is because V_{50} is hydrophilic and the interfacial tension between PST-rich polymer with the V_{50} fragment and the water is lower. As a result, the PST-rich polymer can engulf the seed. To enhance the phase separation between P4VP-rich and PST-rich polymers, expecting to obtain dumbbell-like composite microspheres, a relatively hydrophobic initiator AIBN was used in the seeded emulsion polymerization. The TEM photographs are shown in Figures 8 and 9, where runs 304 and 308 was used as a seed, respectively.

As expected, sandwich or popcorn-like composite microspheres were obtained when AIBN was used, irrespective of monomer composition and seed type. This is because AIBN is a relatively hydrophobic initiator, and the polymer chains with AIBN fragments show lower polarity than those with V_{50} fragments, hence leading to higher interfacial tension between the polymer and the aqueous phase, and between the two polymers.[11] Therefore, the phase separation between polymers was enhanced, and the PST-rich polymer could not engulf the seed any more; hence, sandwich or popcorn-like composite particles were obtained.

As shown in Figure 8(a) and (b), the morphology change is not as apparent, when changing crosslinker in the seeded polymerization from DVB to EGDMA, and increasing the crosslinking agent from 0.4 mol % (DVB) to 0.5 mol % (EGDMA) and popcorn-like microspheres with triplets were obtained. However, as shown in Fig-
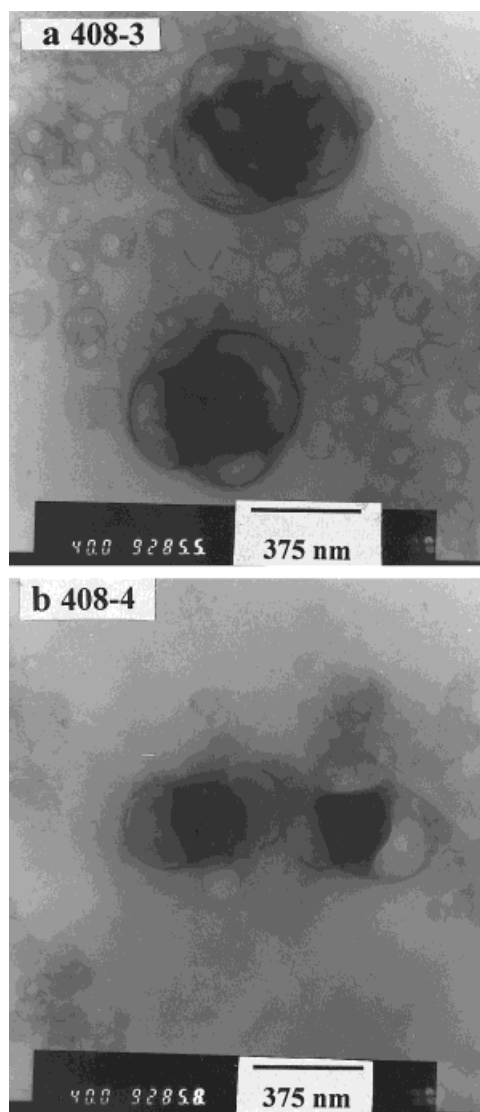
Figure 9   TEM photographs of P(4VP-BA)/P(ST-BA) composite particles as a function of the crosslinker type. Seed: run 308. BA/ST = 1/4 (w/w). Initiator: AIBN. (a) DVB (0.6 mol %), (b) EGDMA (0.3 mol %). (P4VP domain was stained with CH_3I).

ure 8(c), when the BA/ST ratio was increased from 1/4 to 2/3 (w/w) and EGDMA content was kept at 0.5 mol %, the composite microspheres formed a sandwich-like morphology with doublets. Thermodynamically, morphology with doublets is more stable than that with triplets.[9] Because the mobility of the second-stage polymer with higher content BA increased due to its lower T_g, the P(ST-BA) domain can move to two places from three locations. Hence, thermodynamically favored morphology was produced.

Figure 9 shows the results using DVB and EGDMA as a crosslinker, respectively, and run

308 as a seed. Similar to the case of run 304, popcorn-like composite microspheres were obtained, even when EGDMA was decreased to 0.3 mol %.

From the above results, it can be concluded that phase separation was promoted, and sandwich or popcorn-like composite microspheres could be prepared by changing initiator from V_{50} to AIBN. It is important to know that sandwich-like microspheres can be obtained by using AIBN, even for the P4VP/PST system. For this system, a PST-core/P4VP shell morphology is usually formed, because the hydrophilicity of P4VP is much higher than that of PST. However, dumbbell-like composite microspheres were not obtained, even by decreasing the crosslinker content to 0.3 mol %. This is probably because the crosslinking degree of the seed was too high and the mobility of PST-rich chains was limited, so that the equilibrium morphology with complete phase separation could not be obtained. It is considered that the dumbbell-like composite microsphere structure is favored more than the sandwich-like microsphere structure for the preparation of the desired functional membrane as described previously.[21] We will, in future work, decrease the crosslinking degree of the seed further to a low value, and search for an optimum condition for obtaining dumbbell-like microspheres.

CONCLUSION

Monodispersed cationic P(4VP-BA) particles can be prepared by soapless emulsion polymerization, controlling the process parameters. By adding an adequate amount of BA into the polymerization system, and employing a semicontinuous monomer feed mode, one can improve the stability of the latex. The optimum BA/4VP ratio is 1/4 (w/w). The particle size decreased with the increase of the BA/4VP ratio and crosslinker content. Using the above hydrophilic latex as a seed, P(4VP-BA)/P(ST-BA) composite particles were prepared by seeded emulsion polymerization with V_{50} or AIBN as an initiator. It was found that the morphology of the composite microspheres was affected largely by the initiator. By using AIBN as an initiator, phase separation was enhanced and sandwich-like or popcorn-like composite particles can be produced, while the particles were always engulfed by a PST-rich shell when V_{50} was used. This result is ascribed to the polarity of the poly-

mer chains with AIBN fragments being lower than that of the polymer with the V_{50} fragment, hence leading to higher interfacial tension between the PST-rich polymer and the aqueous phase, and between the PST-rich polymer and P4VP-rich seed polymer. It is important to know that sandwich, popcorn-like morphology, and other morphologies different from PST-rich core/P4VP-rich shell morphology, can be obtained by only changing the initiator, considering that P4VP is much more hydrophilic than PST. The zeta potential of composite particles, initiated by AIBN in seeded polymerization, shifted from a positive to a negative charge.

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