

Seeded Dispersion Polymerization

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ABSTRACT: Micron-size poly(*n*-butyl acrylate) (PBA) and polystyrene (PSt) particles were used as seed in second-stage seeded dispersion polymerizations. The effects of various polymerization parameters on the morphology of the structured particles resulting from the second-stage seeded dispersion polymerizations were studied, and a series of uniform micron-size structured particles was successfully prepared. In addition to the polymerization medium, the type of stabilizer (i.e., the molecular weight of the polyvinylpyrrolidone [PVP] stabilizer) that was used in the seed preparation and the subsequent seeded dispersion polymerization was found to be important. The final outcome of a seeded dispersion polymerization, that is, the morphology of the structured particles and the formation of secondary particles, was found to be primarily governed by thermodynamic factors. It was also found that the latex particles in these dispersion systems are virtually stabilized by the small amount of grafted PVP molecules. The dispersions maintain colloidal stability after repeated washing of the particles, which removes all of the soluble PVP. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2710–2720, 2002

Key words: seeded dispersion polymerization; microstructure; radical polymerization; morphology; particle nucleation; stabilization

INTRODUCTION

To prepare structured latex particles, three main methods of preparation have been considered and studied: First, the functionalization of latexes by copolymerization of a monomer with the addition of small amounts of a second monomer bearing a chemically reactive group such as carboxyl,^{1–4} amide,^{5,6} sulfate,^{7,8} sulfonate,⁹ and hydroxyl;^{10,11} second, the copolymerization of comonomers that markedly differ in their water solubility^{12,13} or reactivity ratios;^{14,15} and third, the polymerization in the presence of a polymer dispersion that is prepared in advance; that is, seeded emulsion polymerization.

Seeded emulsion polymerization is the most common method for the preparation of structured particles. In a typical seeded emulsion polymerization, the second monomer is polymerized in the presence of seed particles of the first polymer. A variety of morphologies of the structured latex particles such as core-shell, raspberry-like, sandwich-like, acorn-like, micro-domain, and inverted core-shell morphologies have been reported.^{16–22}

In a seeded emulsion polymerization of two or more components, the final morphology of the structured particles is determined by the interplay of thermodynamic and kinetic factors. The thermodynamic aspects would push the system toward the equilibrium morphology to attain the lowest free energy. Extensive studies^{19,21,23–26} have been carried out to predict the morphology of final particles from the point of view of interfacial tensions at the polymer/water and polymer/poly-

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mer interfaces. However, the reduction of the mobility of polymer chains from the high viscosity or cross linking in the polymer particle would result in a kinetic-controlled morphology.^{27,28}

Structured latex particles in the submicron-size range have been widely used in a variety of areas, as exemplified by the applications of core-shell-type structured particles. Latex particles that have a glassy core and rubbery shell are used in the coatings and adhesives industries to achieve a continuous latex film with improved cohesive strength^{29,30} while latex particles that have a rubbery core and a glassy shell are the basis for impact modifiers for glassy polymeric materials.^{31,32}

Micron-size structured particles are also needed in some applications. Poly(styrene-divinylbenzene) particles with a stable porous structure have been used in ion-exchange chromatography.³³ The same porous particles have been made hydrophilic by grafting a hydrophilic polymer to the residual double bonds in the cross-linked particle matrix for protein recovery applications.³⁴ Porous particles have been prepared through an activated swelling process.^{33,35}

Several techniques have been developed to prepare micron-size structured particles. Polystyrene/poly(methyl methacrylate) composite particles were prepared via emulsion polymerization by using a micron-size polystyrene seed that was prepared by dispersion polymerization.³⁶ A dynamic swelling method^{37,38} was used to prepare micron-size hollow polystyrene particles and polystyrene/poly(ethyl methacrylate) composite particles. Seeded dispersion polymerization has been employed to functionalize micron-size polystyrene particles.^{39–41} In principle, seeded dispersion polymerization has many potential advantages in the preparation of micron-size structured particles, compared with other methods. It does not involve the procedure of exchanging the reaction medium, and a higher solids content can be used than that in the other techniques mentioned above. The preparation of micron-size monodisperse poly(butyl acrylate) (PBA) particles has been described in a previous paper.⁴² The parameters that influence the particle size and distribution were investigated. Some unique features of the PBA dispersion system were discussed and compared with some other dispersion systems such as polystyrene (PSt) and poly(methyl methacrylate) (PMMA). In this article, a pair of polymers, that is, PBA and PSt, that exhibit large differences in their physical and chemical proper-

Table I Recipe for Preparing PBA Seed Particles by Dispersion Polymerization at 70°C

Ingredient	Weight (g)
BA	12.00
AIBN ^a	0.12
PVP K90 ^b	1.20
90% methanol/10% DDI water	120.00

^a 2,2'-azobis-(isobutyronitrile), Wako Chemicals USA Inc. (Richmond, VA).

^b Polyvinylpyrrolidone, molecular weight 360,000 g/mol; GAF (Wayne, NJ).

ties such as glass transition temperature, solubility in alcohol, and reactivity were used to investigate the mechanism of seeded dispersion polymerization. Micron-size structured particles having various morphologies were prepared through seeded dispersion polymerizations. This work opens up the possibility of preparing micron-size structured particles having a rubbery core and a PSt shell, which is considered suitable for impact modification of PSt.⁴³

EXPERIMENTAL

Materials

The *n*-butyl acrylate (BA) and styrene (St) (Fisher Scientific, Springfield, NJ) monomers were treated by passing them through inhibitor-removal columns (Signa-Aldrich, St. Louis, MO). All other materials were used without further purification, including the alcohols, methanol (MeOH) (Fisher Scientific) and ethanol (EtOH) (200 proof, McCormick Distilling Co., Weston, MO); the azo-type initiators, 2,2'-azobis-(isobutyronitrile) (AIBN) and 4,4'-azobis-(4-cyanopentanoic acid) (ACPA) (Wako Chemicals USA Inc., Richmond, VA); the stabilizer, polyvinylpyrrolidone (PVP K90, PVP K30) (GAF, Wayne, NJ); the costabilizer, Aerosol OTS (sodium dioctyl sulfosuccinate in petroleum distillate, Cytac Industries, West Paterson, NJ); and allyl acrylate (AA) crosslinker (Polysciences, Inc., Warrington, PA). Distilled-deionized (DDI) water was used in all experiments.

Polymerization and Characterization

Seed Preparation

The seed particles used in this study (PBA, crosslinked PBA [X-PBA], PSt, and P[BA-co-St])

Table II Recipe for Preparing PSt Seed Particles by Dispersion Polymerization at 70°C

Ingredient	Weight (g)
St	25.00
AIBN ^a	0.25
PVP K30 ^b	3.00
Methanol	100.00

^a 2,2'-azobis-(isobutyronitrile), Wako Chemicals USA Inc., Richmond, VA.

^b Polyvinylpyrrolidone, molecular weight 40,000 g/mol; GAF.

were prepared by dispersion polymerization according to recipes shown in Tables I, II, III, IV, and V. To prepare the "clean seed" for seeded dispersion polymerization, soluble stabilizer and other medium soluble species must first be removed from the seed latexes. Thus, the seed latex was sedimented and the supernatant replaced by the medium (dispersed and allowed to settle) until no solids could be found in the medium. Then the sedimented latex was simply redispersed in the medium by shaking to obtain the cleaned seed. The solids content of the cleaned latex was measured by gravimetry.

Seeded Dispersion Polymerization

All the seeded dispersion polymerizations in this study were carried out according to the standard recipe given in Table VI except for the one shown in Table VII for the PSt/(St-co-SSNa) system. The

Table III Recipe for Preparing Crosslinked PBA Seed Particles by Dispersion Polymerization at 70°C

Ingredient	Weight (g)
BA	12.00
Allyl acrylate (AA)	0.024–0.24
AIBN ^a	0.12
PVP K90 ^b or PVP K30 ^c	1.20 or 4.8
Aerosol OTS ^d	0.72 or 1.44
90% methanol/10% DDI water	120.00

^a 2,2'-azobis-(isobutyronitrile), Wako Chemicals USA Inc., Richmond, VA.

^b Polyvinylpyrrolidone, molecular weight 360,000 g/mol; GAF, Wayne, NJ.

^c Polyvinylpyrrolidone, molecular weight 40,000 g/mol; GAF.

^d Sodium dioctyl sulfosuccinate in petroleum distillate, Cytec Industries (West Paterson, NJ).

Table IV Recipe for Preparing PSt Seed Particles by Dispersion Polymerization at 70°C

Ingredient	Weight (g)
St	25.00
AIBN ^a	0.25
PVP K90 ^b	1.50
Methanol	100.00

^a 2,2'-azobis-(isobutyronitrile), Wako Chemicals USA Inc.

^b Polyvinylpyrrolidone, molecular weight 360,000 g/mol; GAF.

actual amount of cleaned latex that was needed for the seeded dispersion polymerization was dependant on the solids content of the cleaned seed latex. Additional reaction medium was added to the seed latexes until the total amount of the medium was 24.0 g. The polymerizations were carried out in 2-oz bottles, tumbled end-over-end at 28 rpm for 24 hr in a 70°C water bath. The conversions of the resulting second-stage structured latexes were measured by gravimetry. Optical microscopy and transmission electron microscopy (TEM) were used to examine the particle morphology.

Surface Change Density of Sulfonate Groups on Latex Particles Prepared with NaSS

Preparation of Ion-Exchange Resins

Mixed-bed ion-exchange resins (anionic Dowex 1 and cationic Dowex 50W; BioRad, Hercules, CA),

Table V Recipes for Preparing Poly(BA-co-St) Particles by Dispersion Copolymerization at 70°C

Ingredient	Weight (g)		
BA/St	70/30	50/50	30/70
Methanol/water	90/10	95/5	97/3
PVP K30 ^a	1.20	2.00	2.80
PVP K90 ^b	1.75	1.25	0.75
Aerosol OTS ^c	1.41	1.35	1.29
D_n (μm) ^d	2.2	3.5	3.0
PDI ^e	1.020	1.026	1.023

^a Polyvinylpyrrolidone, molecular weight 40,000; GAF.

^b Polyvinylpyrrolidone, molecular weight 360,000; GAF.

^c Sodium dioctyl sulfosuccinate in petroleum distillate, Cytec Industries.

^d D_n = Number-average particle diameter.

^e PDI = Polydispersity index (D_w/D_n , where D_w = weight-average particle diameter).

Table VI Standard Recipe for Seeded Dispersion Polymerization at 70°C

Ingredient	Weight (g)
Cleaned seed (polymer)	3.0
Second-stage monomer	3.0
ACPA ^a	0.03
PVP K30 ^b	0.06
Medium	24.00

^a 4,4'-azobis-(4-cyanopentanoic acid), Wako Chemicals USA Inc.

^b Polyvinylpyrrolidone, molecular weight 40,000 g/mol; GAF.

were used clean the latexes (in water) before conductometric titration. The anionic resin (Dowex 1) was first eluted consecutively with 3 N sodium hydroxide and DDI water to convert the Cl⁻ on the resin to the OH⁻ form. Both resins were thoroughly washed with DDI water before mixing. The resins were mixed in a weight ratio of 51/49 Dowex 50W/Dowex 1 and then washed again with DDI water. The purity of the resins was monitored by measuring the conductivity of the DDI water.

Cleaning of Latexes

A latex sample was diluted by adding water to achieve a solids content of about 5%. The resin was added in a ratio of 1/1 with the solid polymer. The latex and resin were mixed for 2 hr, using a magnetic stirrer, and then the resins were removed by filtration. This ion-exchange procedure was repeated five times.

Conductometric Titration

To determine the amount of sulfonate groups on the latex particles, 30 g of the cleaned latex (~5% solids) was titrated with 0.02 N NaOH. The conductance was monitored continuously. A minimum in the conductance curve is indicative of the strong acid (SO₃⁻) endpoint. The surface charge is calculated on the basis of the amount of latex polymer and the amount of titrant.

RESULTS AND DISCUSSION

Seeded Dispersion Polymerization of PBA/BA

The details of the procedure to prepare PBA particles with various particle sizes have been de-

scribed in the previous paper.⁴² The polymerization parameters that influence the particle size and the size distribution were also discussed. The PBA seed particles used here were prepared by dispersion polymerization according to the recipe shown in Table I. Figure 1(left) shows an optical micrograph (OM) of the PBA seed particles. The particle size is 2.0 μm, and the distribution is narrow.

Using these PBA particles as seed, a PBA/BA seeded dispersion polymerization in 90% methanol was carried out according to the recipe given in Table VI. After the second-stage polymerization, the particle size increased from 2.0 μm to about 2.3 μm without the formation of any small particles, as shown in the micrograph reproduced in Figure 1 (right). This particle size (2.3 μm) is in accordance with the expected size. This indicates that the second-stage PBA was indeed incorporated into the PBA seed particles.

Seeded Dispersion Polymerization of PSt/St

PSt/St seeded dispersion polymerizations have been previously conducted in a pure ethanol medium.³⁹ As the polymerization conditions in the previous study differed from the conditions used in this work, it was considered worthwhile to carry out PSt/St seeded dispersion polymerization under these conditions.

The PSt seed particles used here were prepared by dispersion polymerization according to the recipe shown in Table II. Figure 2 (left) shows an OM of the PSt seed particles. The particle size is 2.0 μm, and again the distribution is narrow. Using these PSt particles as seed, a PSt/St-seeded dispersion polymerization in pure methanol was

Table VII Recipe for PSt/(St-co-SSNa) Seeded Dispersion Polymerization at 70°C

Ingredient	Weight (g)
Cleaned PSt seed	5.0
St	1.0
SSNa ^a	0.06
ACPA ^b	0.01
PVP K30 ^c	0.01
90% ethanol/10% DDI water	24.00

^a Styrene Sulfonic Acid Sodium Salt, Polysciences Inc. (Warrington, PA).

^b 4,4'-azobis-(4-cyanopentanoic acid), Wako Chemicals USA Inc.

^c Polyvinylpyrrolidone, molecular weight 40,000 g/mol; GAF.

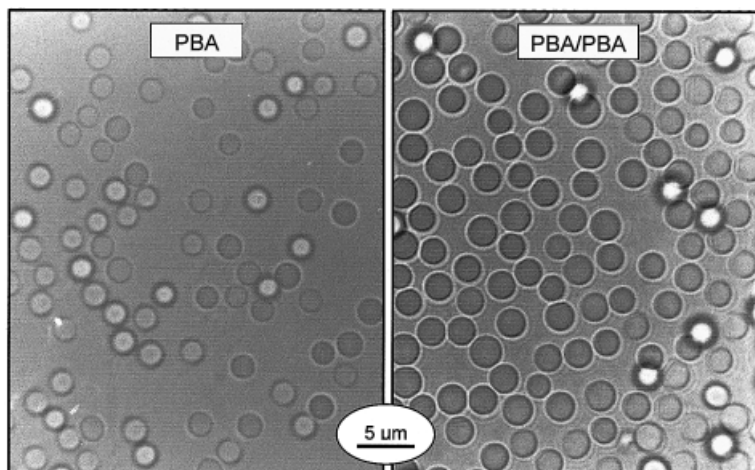


Figure 1 Optical micrographs of poly(*n*-butyl acrylate) (PBA) seed particles prepared by dispersion polymerization (left) and the PBA/PBA (50/50 by weight) structured particles produced by seeded dispersion polymerization. Seed/monomer = 1/1; Methanol/water = 90/10; $T = 70^{\circ}\text{C}$.

carried out. After the seeded dispersion polymerization, the particle size increased from $2.0\ \mu\text{m}$ to about $2.3\ \mu\text{m}$ without the formation of any small particles, as shown in the micrograph reproduced in Figure 2 (right). Again, these results indicate that the second-stage polymer PSt was incorporated into the PSt seed particles.

This set of experiments and those described in the previous section demonstrate that seeded dispersion polymerizations can be successfully conducted in which the second-stage monomer is the same as that used to prepare the original seed

particles. These two sets of experiments served as benchmark studies, performed to achieve a better understanding of the polymerization conditions required for the seeded dispersion polymerizations. Structured particles where the second-stage polymer is chemically and/or physically different from the seed polymer are needed for practical applications. One of the approaches to prepare such structured particles is to employ small amounts of a functional monomer (e.g., sodium styrene sulfonate) to create heterogeneities within the seed particles.

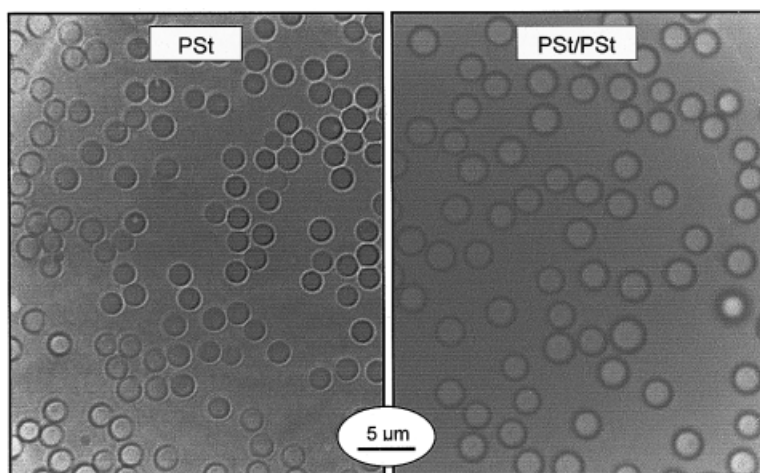


Figure 2 Optical micrographs of polystyrene (PSt) seed particles prepared by dispersion polymerization (left) and the PSt/PSt (50/50 by weight) structured particles produced by seeded dispersion polymerization. Seed/monomer = 1/1; $T = 70^{\circ}\text{C}$.

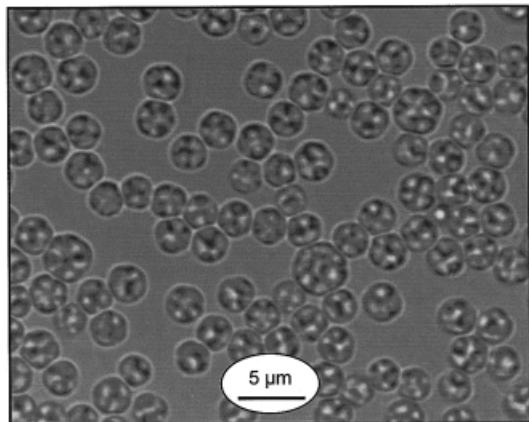


Figure 3 Optical micrograph of the morphology of the poly(*n*-butyl acrylate)/polystyrene (50/50 by weight) structured particles produced by seeded dispersion polymerization. Seed/monomer = 1/1; methanol/water = 90/10; $T = 70^{\circ}\text{C}$.

Seeded Dispersion Polymerization of PSt/(St-SSNa)

Seeded dispersion polymerization can be used to prepare micron-size monodisperse particles possessing groups that give the surface a charge, such as $-\text{SO}_3^- \text{Na}^+$. Here, the same $2 \mu\text{m}$ PSt particles were used in seeded dispersion copolymerizations of St and SSNa, using the recipe given in Table VII. After the second-stage polymerization, the increase in the particle size can barely be observed because the ratio of seed to

monomer was only 5/1. However, other experimental evidence indicates that the second-stage copolymer was indeed incorporated into the seed particles. First, no small particles were observed after the seeded dispersion polymerization. Second, sulfonate groups were found on the surface of the particles by conductometric titration. The amount of the sulfonate groups was determined to be $1.59 \mu\text{mol/g}$ of polymer, or about one sulfonate group for every three square nanometers of the particle surface.

To prepare micron-size structured particles in which another polymer phase is present, a series of seeded dispersion polymerizations using second-stage monomers that are different in composition to the seed polymer were conducted.

Seeded Dispersion Polymerization of PBA/St

PBA seed particles were prepared by dispersion polymerization according to the recipe given in Table I. Using these as seed, a PBA/St seeded dispersion polymerization in 90% methanol was carried out according to the standard recipe given in Table VI. Figures 3 and 4 show the morphology of the resulting PBA/PSt structured particles. In the OM of Figure 3, the structured particles appear to possess a uniform morphology. No new small particles can be noted. Materials with differing refractive indices can be observed within the particles. Figure 4 shows TEM micrographs of these particles, obtained using two different pre-

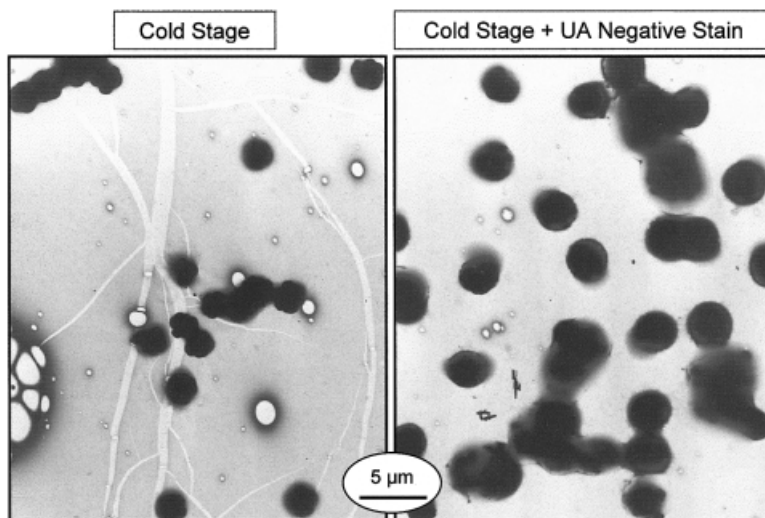


Figure 4 Transmission electron micrographs of the morphology of the poly(*n*-butyl acrylate)/polystyrene (50/50 by weight) structured particles produced by seeded dispersion polymerization. (Left: cold-stage; right: cold-stage and negative staining by uranyl acetate). Seed/monomer = 1/1; methanol/water = 90/10; $T = 70^{\circ}\text{C}$.

treatments of the samples. In Figure 4 (left), where the sample was placed in a cold stage, some spherical aggregates (dark areas), which are the PSt domains, can be observed. In Figure 4 (right), where the sample was placed in the cold stage after being treated with a negative stain, uranyl acetate, a lighter-appearing material on the outer side of the dark domains can be observed. These suggest that the PBA remains on the outside of the PBA/PSt particles even though it was used as the seed (as in inverted core/shell latexes). From the thermodynamic point of view, it is easy to understand this phase-reversal phenomenon. PBA is more hydrophilic than PSt, and the polymer/medium interfacial tension of the structured particle is reduced with PBA present on the outside of the particles. The shapes of the PSt domains inside the structured particles comprised of a number of smaller spheres indicates that a complete migration and fusion of the polystyrene among these small domains did not occur at 70°C, the temperature at which the seeded dispersion polymerization was carried out.

Seeded Dispersion Polymerization Using X-PBA Seeds

In an attempt to prevent the formation of the second-stage PSt inside the structured particles, the “hardness” of the PBA seed particles was increased by increasing the degree of cross linking. The details of the effect of different cross linkers on the PBA particles and the measurement of the gel content of the particles are described elsewhere.⁴² A series of cross-linked-PBA (X-PBA) seed particles were prepared via dispersion polymerization using allyl acrylate (AA) as a cross linker according to the recipe given in the Table III. The amount of AA was varied from 0.024 to 0.24 g (i.e., 0.2 wt% to 2 wt% based on the monomer). Two kinds of stabilizer and costabilizer systems were used: 1.2 g PVP K90 (10 wt% on monomer) plus 0.72 g Aerosol OTS (6 wt% on monomer), and 4.8 g PVP K30 (40 wt% on monomer) plus 1.44 g Aerosol OTS (12 % on monomer weight). The gel contents of these X-PBA particles are shown in Figure 5 as a function of the amount AA. The resulting PBA seed particles were examined by optical microscopy. The particle sizes were all around 2.0 μm , and the distributions were narrow. Using these X-PBA particles as seed, X-PBA/St and X-PBA/BA seeded dispersion polymerizations in 90% methanol were carried out according to the recipe given in Table VI. The

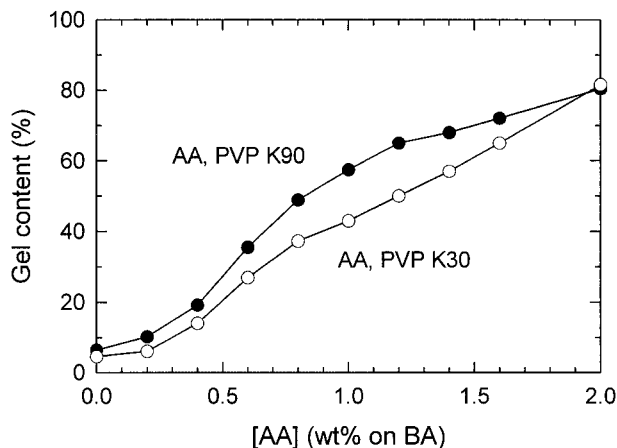


Figure 5 Effect of the concentration of the allyl acrylate crosslinking agent on the gel content of poly(*n*-butyl acrylate) particles.

morphologies of the resulting structured particles were similar to those obtained for PBA/PBA and PBA/PSt (Figs. 1 and 3) when the gel contents of the X-PBA seed were lower than 70% and 60%, respectively; that is, uniform spherical X-PBA/PBA particles and small PSt domains inside the X-PBA particles. However, when the gel contents of the X-PBA seeds were higher than these two values, the results of the seeded dispersion polymerizations exhibited dramatic changes in particle morphology. Figure 6 shows the OMs of the resulting X-PBA/PSt and X-PBA/PBA, obtained by using the X-PBA seeds with gel-contents of 64% and 72%, respectively. The X-PBA/St system (left) coagulated because of the formation of a large number of submicron PSt particles. In contrast, for the X-PBA/PBA system (right), in addition to the formation of some small PBA particles, several separated PBA domains can be observed protruding from the surface of the X-PBA seed particles. A similar morphology was also observed for the X-PBA particles having a gel content of 90%.⁴² It seems that the interfacial tensions between the high-gel X-PBA and PSt or even PBA greatly increase when the gel content of the X-PBA reaches a certain level. It was shown elsewhere⁴² that the gel content in the X-PBA particles increased rapidly to about 60% with the addition of 1 wt% to 2 wt% AA and then slowly increased to 90% with additional amounts of AA (up to 5 wt%). At the higher AA concentrations, an increase in the crosslinking density of the existing crosslinked network may result, rather than an increase in the gel content. This result also suggests that the crosslinked network in the

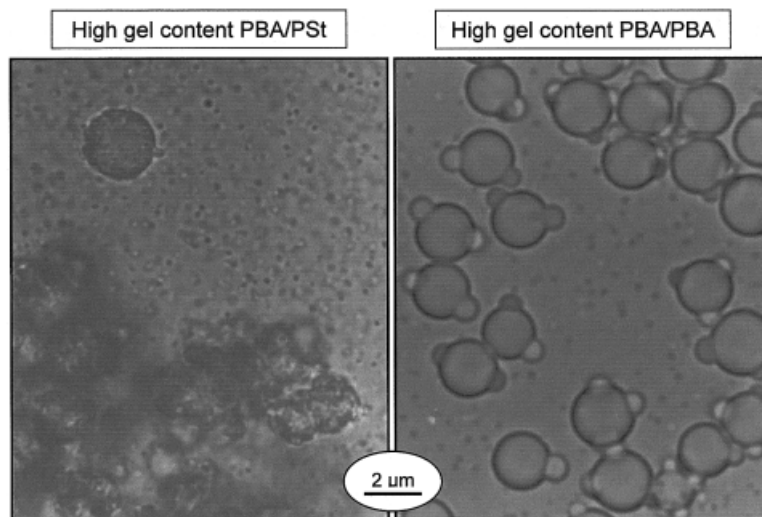


Figure 6 Optical micrographs of the structured particles produced by seeded dispersion polymerization using a high gel content poly(*n*-butyl acrylate) seed (left: gel content = 64%; right: gel content = 72%). Seed/monomer = 1/1; Methanol/water = 90/10; $T = 70^{\circ}\text{C}$.

particles would not grow in a uniform manner in terms of the shape as well as the cross-linking density. Thus, the cross-linked-PBA network is not uniformly distributed in the surface layer of the X-PBA particles. For the low-gel-content X-PBA seed particles, the interfacial tension effect is relatively weak, whether they are covered by linear PBA polymer chains or a lightly cross-linked PBA network. When the second-stage polymer, either PBA or PSt, precipitates onto the low-gel X-PBA particles from the medium, the surface layer is essentially the same as the non-cross-linked PBA particles, as shown in Figures 1 and 3. With increasing AA, the total volume of the crosslinked network increases, along with the increase in the crosslink density of the existing network. Thus, larger areas of the crosslinked network can be exposed on the surface of the particles. Under such a situation, the interfacial tension effect is strong and phase separation occurs even between the highly cross-linked PBA areas and the second-stage PBA, which is primarily linear polymer. Several possible reasons can account for the formation of such morphology. First, the linear polymer regions on a X-PBA particle may have a greater ability to capture second-stage oligomeric radicals than the highly cross-linked regions. Second, the monomer concentration or the partitioning of the second-stage monomer can be higher in the linear regions than in the highly cross-linked regions. Third, even if

linear second-stage PBA polymer chains can be formed in the highly cross-linked regions, the difference in the mobility of these two types of PBA polymer, that is, linear versus cross linked, could eventually “squeeze” the linear PBA chains out of the crosslinked networks. Thus, it may be postulated that the second-stage PBA domains grow in the regions of the X-PBA seed particles where linear PBA chains or a lightly cross-linked X-PBA network exist. For the second-stage PSt, the overall interfacial tension effect is so strong that the majority of the St forms new particles. As a result of the absence of sufficient stabilizer to stabilize the great increase in the total surface area formed by the large number of PSt particles, the system coagulated. From this analysis, a series of PBA seed particles that contain uniform cross-linking networks with different cross-linking densities and 100% gel contents would be of interest for these experiments. Unfortunately, these ideal X-PBA particles were not obtained.

Seeded Dispersion Polymerization Using Copolymer Seeds

The preparation of a series of monodisperse micron-size P(BA-co-St) seed particles with different copolymer compositions was described previously.⁴² Using these P(BA-co-St) particles as seed, a series of seeded dispersion polymerizations of BA and St was carried out in the same manner according to the recipe given in Table VI.

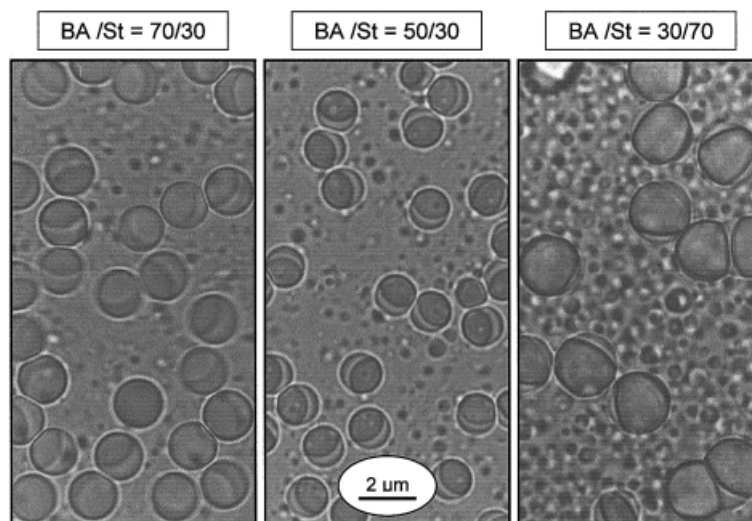


Figure 7 Optical micrographs of the structured particles produced by seeded dispersion polymerization of BA using different P(BA-co-St) seed particles. Seed/monomer = 1/1; Methanol/water = 90/10; T = 70°C.

The effects of using copolymer seeds prepared with different BA/St ratios on the morphology of the resulting P(BA-co-St)/PBA structured particles are shown in Figure 7. As the St content in the seed increased, the area of the second-stage PBA domain (lighter areas) in the resulting structured particles decreased, and the amount of small homopolymer PBA particles increased. For the P(BA-co-St)/PSt systems, contrary to expectations, coagulation and the formation of new particles occurred for the two systems where the high-St content seeds were used (i.e., P[BA-co-St] with BA/St ratios of 5/5 and 3/7). The P(BA-co-St)/PSt system that used the copolymer seed having a 7/3 BA/St ratio formed uniform structured particles that appeared to be almost the same as the PBA/PSt particles shown in Figure 3.

Seeded Dispersion Polymerization of PSt/BA

Massive coagulation occurred in the PSt/PBA system when the PSt seed particles were prepared according to the recipe given in Table II (the seeded polymerizations were carried out according to the recipe given in Table VI). In both recipes for the seed and the structured particles, PVP K30 was used as the stabilizer. By changing the type of PVP stabilizer (the molecular weight of the PVP) used in different stages of these dispersion polymerizations, stable PSt/PBA structured particles could be successfully prepared without any coagulation. The PSt seed particles were pre-

pared according to the recipe given in Table IV using PVP K90 as stabilizer, and the seeded polymerizations of BA were carried out according to the recipe given in Table VIII, which is almost the same as the standard recipe for all the other seeded dispersion polymerizations as shown in Table VI, except that PVP K90 was used as the additional stabilizer instead of PVP K30. Figure 8 shows an OM of the structured particles resulting from the seeded dispersion polymerization of PSt-K90/BA-K90; uniform “half-moon” structured particles were formed, and no new small particles were observed. This result indicates that the type of PVP stabilizer (or the molecular weight of the PVP) used in the two stages of the seeded dispersion polymerizations can greatly influence the final results of the seeded dispersion polymeriza-

Table VIII Recipe for PSt/BA Seeded Dispersion Polymerization at 70°C

Ingredient	Weight (g)
Cleaned PSt seed	3.0
BA	3.0
ACPA ^a	0.03
PVP K90 ^b	0.06
90% methanol/(10% DI water)	24.00

^a 4,4'-azobis-(4-cyanopentanoic acid), Wako Chemicals USA Inc.

^b Polyvinylpyrrolidone, molecular weight 360,000 g/mol; GAF.

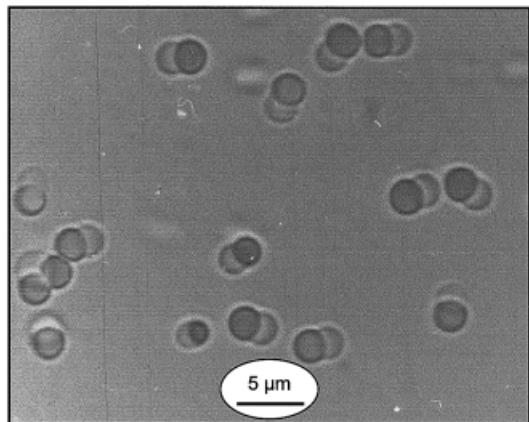


Figure 8 Optical micrograph of the polystyrene/poly(*n*-butyl acrylate) structured particles produced using polyvinylpyrrolidone K90 both in preparing the polystyrene seed and in the seeded dispersion polymerization. Seed/monomer = 1/1; methanol/water = 90/10; $T = 70^{\circ}\text{C}$.

tions. A general trend that can be drawn from the results of the dispersion polymerizations described above is that structured particles are relatively easy to obtain when a "soft" seed is used in systems where a thermodynamically unfavorable process is involved; for example, the precipitation of styrene oligomeric radicals onto the PBA particle surface in the PBA/PSt system. Compared with the PBA/PSt system, some seeded dispersion polymerization systems seem to be more thermodynamically favorable; for example, PSt/PBA with PVP K30 stabilizer, X-PBA/PBA, and the P(BA-co-St)/PBA, in which seed polymer having less compatibility with the medium is supposed to be covered by a PBA shell that is more compatible with the medium. However, the formation of new particles or coagulum caused by the formation of large amounts of new particles in these systems can still occur for kinetic reasons.

SUMMARY

Seeded dispersion polymerizations were carried out in methanol/water mixtures to prepare micron-size structured particles that exhibit various morphologies. The type of the stabilizer, that is, the molecular weight of the PVP stabilizer, used in the seed preparation and the subsequent seeded dispersion polymerization was found to be important, as was the polymerization medium. The final outcome of a seeded dispersion polymer-

izations, in terms of the morphology of the structured particles and the formation of secondary particles, is influenced primarily by thermodynamic factors.

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REFERENCES

1. Fordyce, D. B.; Dupre, J.; Toy, W. *Ind Eng Chem* 1959, 51, 115.
2. Muroi, S. *J Appl Polym Sci* 1966, 10, 713.
3. Egusa, S.; Makuuchi, K. *J Polym Sci Polym Chem Ed* 1982, 20, 836.
4. Hoy, K. L. *J Coat Tech* 1979, 51, 27.
5. Ohtsuka, Y.; Kawaguchi, H.; Sugi, Y. *J Appl Polym Sci* 1981, 26, 1637.
6. Tamai, H.; Iida, A.; Suzawa, T. *Colloid Polym Sci* 1984, 262, 77.
7. Vanderhoff; J. W.; van den Hul, H. J. *J Colloid Interface Sci* 1981, 26, 1649.
8. Tsauro, S. L.; Fitch, R. M. *J Colloid Interface Sci* 1987, 115, 450.
9. Weiss, R. A.; Turner, S. R.; Lundberg, R. D. *J Polym Sci Polym Chem Ed* 1985, 23, 525.
10. Kawaguchi, H.; Sugi, Y.; Ohtsuka, Y. *J Appl Polym Sci* 1981, 26, 1649.
11. Okubo, M.; Ymada, A.; Matsumoto, T. *J Polym Sci Polym Chem Ed* 1980, 16, 3219.
12. Misra, S. C.; Pichot, C.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Polym Lett Ed* 1979, 17, 567.
13. Kawaguchi, H.; Hoshino, H.; Amagasa, H.; Ohtsuka, Y. *J Colloid Interface Sci* 1984, 97, 465.
14. Emelie, B.; Pichot, C.; Guillot, J. *J Disp Sci Technol* 1984, 5, 393.
15. Rios, L.; Pichot, C.; Guillot, J. *Makromol Chem* 1980, 181, 677.
16. Okubo, M.; Katsuta, Y.; Matsumoto, T. *J Polym Sci Polym Lett Ed* 1980, 18, 481.
17. Okubo, M.; Katsuta, Y.; Inoue, K.; Nakamae, K.; Matsumoto, T. *J Adhesion Soc Jpn* 1980, 16, 278.
18. Lee, D. I. In *Emulsion Polymers and Emulsion Polymerization*; Bassett, D. R.; Hamielec, A. E., Eds.; ACS Symp. Series 165, American Chemical Society: Washington, DC, 1981; p. 405.
19. Dimonie, V. L.; El-Aasser, M. S.; Vanderhoff, J. W. *Polym Mat Sci Eng* 1988, 58, 821.
20. Dimonie, V. L.; El-Aasser, M. S.; Vanderhoff, J. W.; Klein, A. Graduate Research Progress Reports, Emulsion Polymers Institute, Lehigh University, 1986, 26, 33.
21. Chen, Y. C.; Dimonie, V. L.; El-Aasser, M. S.; *J Appl Polym Sci* 1991, 42, 1049.
22. Chern, C. S.; Poehlein, G. W. *J Polym Sci Polym Chem Ed* 1990, 28, 3073.

23. Chen, Y. C.; Dimonie, V. L.; El-Aasser, M. S.; *J Appl Polym Sci* 1992, 45, 487.
24. Muroi, S.; Hashimoto, J.; Josol, K. *J Polym Sci Polym Chem Ed* 1984, 22, 1345
25. Sundberg, D. C.; Cassasa, A. J.; Pantazopoulos, J.; Muscato, M. R.; Kronberg, B.; Berf, J. *J Appl Polym Sci* 1990, 41, 1425.
26. Durant, Y. G.; Sundberg, D. C. In *Technology for Waterborne Coatings*; Glass, E. J., Ed.; ACS Symposium Series 663, American Chemical Society: Washington, DC, 1997.
27. Cho, I.; Lee, K. W. *J Appl Polym Sci* 1985, 30, 1903.
28. Lee, D.; Kawamura, T.; Stevens, E. F. In *Future Directions in Polymer Colloids*; El-Aasser, M. S.; Fitch, R. M., Eds.; Martinus Nijhoff, Dordrecht, 1987; p. 47.
29. Vanderhoff, J. W.; Bradford, E. B.; Carrington, W. K. *J Polym Sci Symp* 1973, 41, 155.
30. Sperling, L. H. *Introduction to Polymer Science*; Wiley: New York 1992.
31. Sperling, L. H. *J Polym Sci Macromol Rev* 1977, 12, 141.
32. El-Aasser, M. S.; Segall, I.; Dimonie, V. L. *Macromol Symp* 1996, 101, 517.
33. Ugelstad, J.; Soderberg, L.; Berge, A.; Bergstrom, J. *Nature (Lond)* 1983, 303, 95.
34. Ellingsen, T.; Aune, O.; Ugelstad, J.; Hagen, S. *J Chromatogr* 1990, 535, 147.
35. Ugelstad, J.; Mørk, P. C.; Kaggurud, K. H.; Ellingsen, T.; Berge, A. *Adv Colloid Int Sci* 1980, 13, 101.
36. Shen, S.; El-Aasser, M. S.; Dimonie, V. L.; Vanderhoff, J. W.; Sudol, E. D. *J Polym Sci Part A Polym Chem* 1991, 29, 857.
37. Okubo, M.; Minami, H. *Colloid Polym Sci* 1996, 274, 433.
38. Okubo, M.; Yamashita, T.; Suzuki, T.; Shimizu, T. *Colloid Polym Sci* 1997, 275, 288.
39. Lu, Y. Y. Ph.D. Dissertation, Lehigh University, 1988.
40. Okubo, M.; Ikegami, K.; Yamamoto, Y. *Colloid Polym Sci* 1989, 267, 193.
41. Okubo, M.; Ikegami, K.; Yamamoto, Y. *Colloid Polym Sci* 1991, 269, 217.
42. Wang, D.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S., *J Appl Polym Sci* 2002, 84, 2692.
43. Tuncel, A.; Kahraman, R.; Erhan, P. *J Appl Polym Sci* 1994, 51, 1485.