Effect of PVP in Dispersion and Seeded Dispersion Polymerizations

DANNI WANG, VICTORIA L. DIMONIE, E. DAVID SUDOL, MOHAMED S. EL-AASSER

Emulsion Polymers Institute and Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015

ABSTRACT: The outcome of seeded dispersion polymerizations of n-butyl acrylate (BA) and styrene (St) in terms of the success of growing the seed particles without nucleating new particles or generating coagulum was found to be dependent on the seed type (poly[n-butyl acrylate] [PBA] or polystyrene [PSt]), the second-stage monomer (BA or St), and the type of polyvinylpyrrolidone (PVP) stabilizer (PVP K30 or PVP K90). All seeds were first cleaned of excess stabilizer by medium replacement before the seeded polymerizations. In general, successful particle growth was achieved when the second-stage polymerization employed PVP K30 (1 wt%) as the stabilizer. In contrast, nearly all reactions employing PVP K90 (1 wt%) as the second-stage stabilizer resulted in the nucleation of a second crop of particles. These phenomena were further investigated by carrying out dispersion polymerizations using the supernatant obtained by separating the seeds from the second-stage media (containing monomer). The results paralleled those in the seeding studies and were explained by the presence of small amounts of grafted PVP created *in situ* during the preparation of the seeds. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2721–2732, 2002

Key words: radical polymerization; particle nucleation; particle size distribution; grafting

INTRODUCTION

Dispersion polymerization is a complex process that is popular for preparing micron-size monodisperse polymer particles in a single step. It begins as a homogeneous solution of monomer(s), solvent(s) (medium), stabilizer(s), and initiator (free radical in this case). With the production of free radicals, it develops into a heterogeneous process with many chemical and physical processes occurring simultaneously, as is partly illustrated in the schematic representation of Figure 1. The nucleation and stabilization of the particles are key to the formation of a dispersion with a narrow particle-size distribution. Nucleation can occur by a number of mechanisms including self-nucleation, aggregative nucleation, micellar nucleation (if micelles are present), and coagulative nucleation.[1]

The colloidal stability and particle size and size distribution in a dispersion polymerization system are ultimately determined by the choice of type and quantity of the stabilizer. Block and graft copolymers with segments that are insoluble in the dispersion medium will anchor the stabilizer to the growing polymer particles. It has been reported that the ratio of soluble block to anchor block is one important parameter.[2,3] These types of stabilizers are being used in anionic dispersion polymerizations of styrene in aliphatic hydrocarbon fluids such as hexane[4–6] and in dispersion polymerizations in supercritical car-
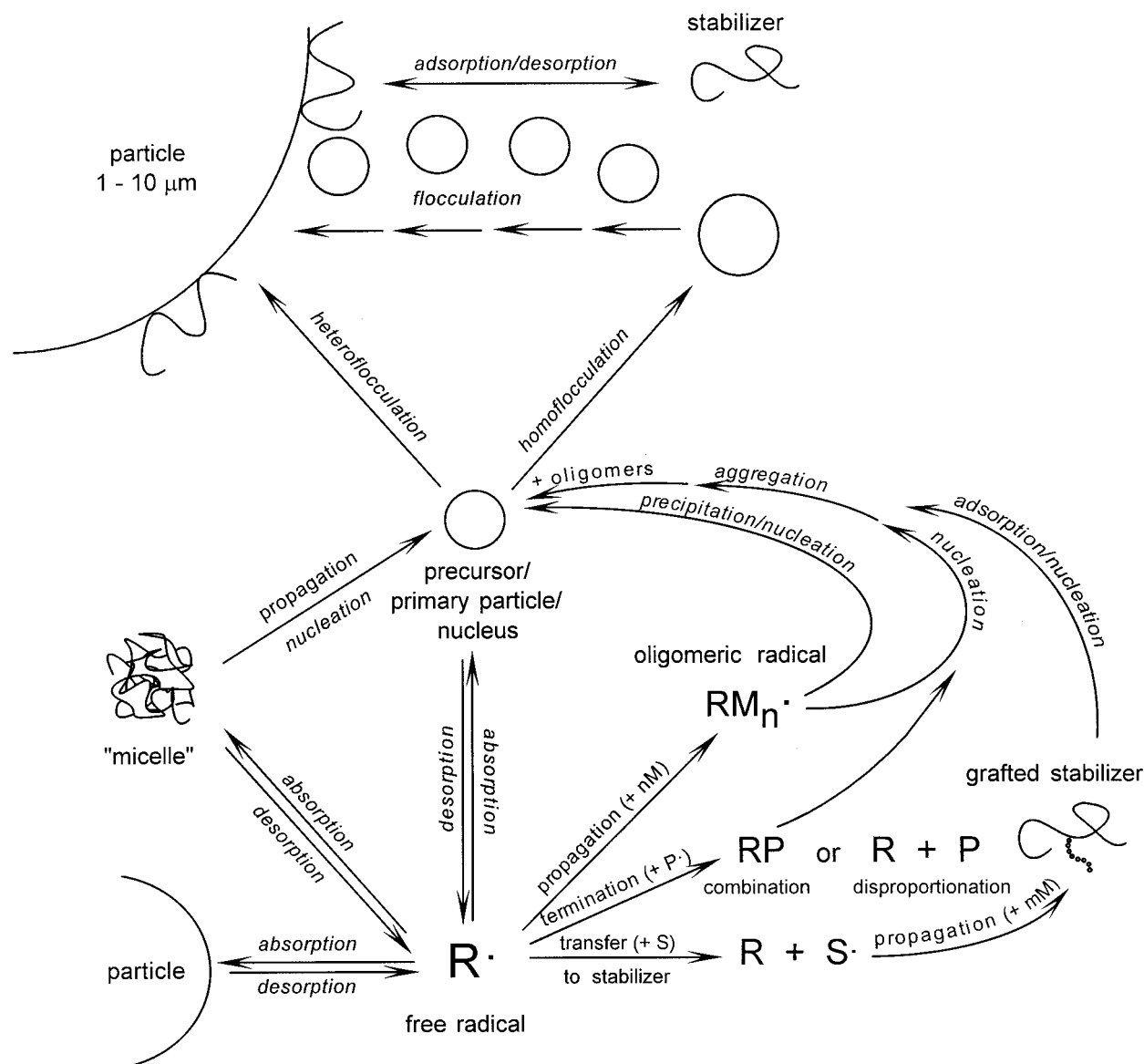
Figure 1 Schematic representation of mechanisms involved in free radical dispersion polymerizations used to prepare micron size polymer particles; words in italics represent physical processes.

bon dioxide.[7–9] From the point of view of cost and availability, however, homopolymers or statistical copolymers have drawn more attention. Degraded natural rubber was used as the stabilizer in some early studies.[10] Later on, it was found that poly(2-ethyl hexyl acrylate) in 2,2,4-trimethylpentane and hydroxypropylcellulose in water-based mixtures also function as effective steric stabilizers.[11,12] Polyvinylpyrrolidone (PVP),[13–17] hydroxypropyl cellulose (HPC),[18] and poly(acrylic acid) (PAA)[19] are some of the highly polar homopolymers that are used as stabilizers in disper-

sion polymerizations. Other stabilizer systems such as methacrylic acid/ethyl acrylate statistical copolymer,[20] poly(vinyl methyl ether),[21] and some thiol-ended polymers such as thiol-ended vinyl acetate/vinyl alcohol copolymer[22] and thiol-ended poly(ethylene oxide)[23] have also shown promise as stabilizers in dispersion polymerizations. One of the characteristics of these homopolymers or statistical copolymers is that they all contain labile hydrogen atoms (or sulfur atoms in thiol-ended polymers) that can be abstracted by a free radical, which then allows grafting of the mono-

mer to produce an amphipathic copolymer. It is believed that these *in situ*–formed amphipathic copolymers (illustrated in Fig. 1) end up on the particle surfaces acting as stabilizers by anchoring to the polymer particles. In a dispersion polymerization of styrene using HPC,[18] a kinetic analysis predicted a grafting probability of about 1 in 200 polystyrene chains. The grafting behavior was also studied by using infrared (IR) spectroscopy.[24] The same function can be efficiently provided by some macromonomers. Poly(ethylene oxide)[25,26] and poly(ethylene glycol)[27] macromonomers, which are terminated at one end with a reactive acrylate ester group, have proven to be effective for stabilizing dispersion systems.

The primary purpose of the earlier part of this study was to search for appropriate polymerization conditions for the preparation of micron-size poly(butyl acrylate) (PBA) particles having a narrow particle-size distribution and, subsequently, to prepare uniform micron-size structured particles through seeded dispersion polymerization in alcohol/water reaction media. The effects of various polymerization parameters on the particle size and size distribution, colloidal stability, and morphology of the micron-size particles have been studied. Micron-size PBA particles (1.5–4.0 μm) having narrow size distributions (PDI <1.05) were successfully prepared by dispersion polymerization,[28] and a series of uniform micron-size structured particles were prepared by seeded dispersion polymerization.[29] It was found that, in addition to the expected sensitivity to the concentration of the PVP stabilizer present in the second-stage polymerization, the outcomes of the seeded dispersion polymerizations were influenced dramatically by the type (i.e., the molecular weight) of the PVP stabilizer that was used. The stability and morphology of the structured particles were influenced by the PVP used both in the seed preparation and in the second-stage polymerization.

Compared with previous studies that were carried out by other researchers investigating the dispersion polymerization of styrene (St)[13,14] and methyl methacrylate (MMA),[15] the *n*-butyl acrylate (BA) monomer system has shown some trends that are essentially different from these monomer systems regarding the effect of some polymerization parameters. For instance, the particle size of the PBA dispersions decreased as the concentration of initiator increased, whereas the opposite trend was observed in both PSt (polystyrene) and PMMA systems. It was pointed out that

BA might graft more readily onto PVP than St or MMA because of the higher chain transfer tendency of PBA radicals.[28]

It is generally believed that the stabilization effect of PVP homopolymers in a dispersion polymerization results from some strong interactions, either chemical or physical, between the PVP molecules and the polymers that are being prepared. The *in situ* formation of PVP-graft-polymer (PVP-g-P) chains during the polymerization is a widely accepted mechanism. It has been reported that the characteristic IR absorbance of PVP could still be observed in PMMA particles that had been repeatedly washed with water.[15] These residual PVP molecules on the washed particles were said to be chemically bonded PVP.

In this work, the effects of PVP K30 and PVP K90 stabilizers on the dispersion polymerization of BA and St are studied. A comprehensive comparison of four dispersion systems, that is, PBA/PVP K30, PBA/PVP K90, PSt/PVP K30, and PSt/PVP K90, is made to obtain a better understanding of the process. A procedure for separating each fraction in a resultant PBA dispersion according to their individual solubilities in water and alcohol was developed. Proton nuclear magnetic resonance (NMR) was used to analyze these fractions to investigate the distribution of each component in the dispersion.

EXPERIMENTAL

Materials

The BA and St (Fisher Scientific, Springfield, NJ) monomers were treated by passing them through inhibitor-removal columns (Sigma-Aldrich, St. Louis, MO). All other materials were used without further purification, including methanol (MeOH) (Fisher Scientific), 2,2′-azobis-(isobutyronitrile) (AIBN) and 4,4′-azobis-(4-cyanopentanoic acid) (ACPA) (Wako Chemicals USA Inc., Richmond, VA), and PVP (PVP K90, PVP K30) (GAF, Wayne, NJ). Distilled–deionized (DDI) water was used in all experiments.

Polymerization and Characterization

Four kinds of seed particles were prepared according to the recipes given in Table I. Each ingredient was adjusted in such a way that all four kinds of particles had a similar particle size regardless of the type of stabilizer used. These par-

Table I   Standard Recipes for Preparing Poly(Butyl Acrylate) (PBA) and Polystyrene (PSt) Seed Particles by Dispersion Polymerization at 70°C

Polymer-PVP	PBA-K90	PBA-K30	PSt-K90	PSt-K30
Monomer (g)	12	12	25	25
PVP[a] (g)	1.2	4.8	1.5	3.0
AIBN[b] (g)	0.12	0.12	0.25	0.25
Medium (g)	90% Methanol	90% Methanol	Methanol	Methanol
	120	120	100	100

[a] Polyvinylpyrrolidone; molecular weight: K90 = 360,000; K30 = 40,000 g/mol; GAF.
[b] 2,2′-azobis(isobutyronitrile); Wako Chemicals USA, Inc.

ticles were than cleaned following the procedure described elsewhere.[29] Seeded dispersion polymerizations were then carried out according to the standard recipes shown in Table II. The dispersion polymerizations were conducted in either 2- or 8-oz bottles depending on the total volume of the ingredients for each polymerization. The ingredients were weighed and mixed in glass bottles, which were purged with nitrogen, capped, and sealed. The bottles were then placed in safety baskets supported on a rotor and tumbled end-over-end at 28 rpm in a constant-temperature water bath at 70°C for 24 hr.

The conversions of the resulting PBA latexes were measured by gravimetry. An optical microscope was used to examine the particle size and size distribution. A particle size histogram was constructed from measurements of over 500 individual particles from the enlarged micrographs.

¹H NMR Spectra

¹H NMR (Bruker MSL, 500 MHz, Billerica, MA) was used to analyze the components in each fraction of the PBA dispersion. We accumulated 800 scans with a repetition delay of 3 sec. The dried polymers were dissolved by using an appropriate deuterated solvent; that is, deuterated acetone (CD_3COCD_3) and deuterated water (D_2O). To achieve complete dissolution of some fractions of the PBA dispersion, mixtures of CD_3COCD_3 and D_2O were also used as a solvent. Tetramethylsilane (TMS) was used as internal standard.

RESULTS AND DISCUSSION

Seed Preparation by Dispersion Polymerization

To exclude the influence of the particle size of the seed particles on the seeded dispersion polymer-

izations, four kinds of PBA and PSt seeds with similar particle size and size distributions were prepared by using PVP K90 and PVP K30 stabilizers according to Table I. The optical micrographs presented in Figure 2 show that the resulting seed particles have a similar size of about 2.2 μm and narrow size distributions (PDI < 1.01). It was found that the overall stabilization ability of PVP K90 is higher than that of PVP K30. Less PVP K90 was needed for preparing PBA or PSt polymer particles of the same size. For example, the required amount of PVP K30 was four times that of PVP K90 by weight, or 36 times the molar amount, to produce the same size PBA particles. This difference was somewhat less for preparing PSt particles (two times by weight or eighteen times in moles). It seems that a stronger enhancement in stabilization by changing from the lower molecular weight PVP K30 to the higher molecular weight PVP K90 was observed in the PBA systems. The different effects of the stabilizer on preparing each type of polymer particle are possibly caused by different rates of graft formation on the PVP through chain transfer

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

Ingredient	Weight (g)
Cleaned seed (poly[butyl acrylate], polystyrene)	3.0
Monomer (butyl acrylate, styrene)	3.0
ACPA[a]	0.03
Additional PVP (K90, K30)[b]	0.06
90% or 100% Methanol	24.00

[a] 4,4′-azobis-(4-cyanopentanoic acid), Wako Chemicals USA Inc.
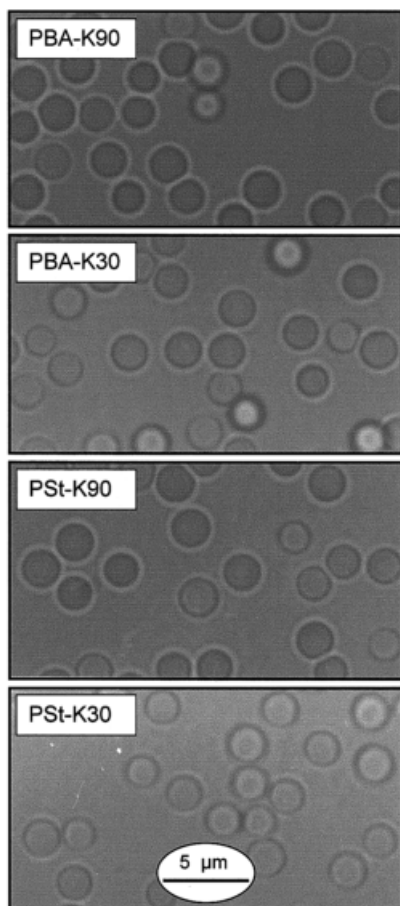[b] Polyvinylpyrrolidone, molecular weight: K90 = 360,000; K30 = 40,000 g/mol; GAF.

Figure 2 Optical micrographs of poly(butyl acrylate) and polystyrene seed particles prepared by dispersion polymerization.

from PBA and PSt radicals. The results shown in Table I indicate that there may be another factor that can influence the effect of the stabilizer in a specific dispersion polymerization system; that is, the molecular structure of the grafted PVP molecule. The number of particles is normally fixed in the early stages of a typical dispersion polymerization, producing particles having a narrow particle-size distribution. This is determined by the amount of stabilizer that is available to stabilize nuclei formed in the nucleation stage. It was found that micron-size PSt particles having a narrow size distribution can be prepared relatively easily, using the low molecular weight PVP K30, compared with the preparation systems that use PVP K90 as the stabilizer.

Cleaning the Seed Latex

To remove the extra stabilizer from the seed latexes, a cleaning procedure was applied before

use in the second-stage seeded polymerizations. This was accomplished as follows. The latex was allowed to sediment, and the polymerization media used in the seeded dispersion polymerizations of BA and St, that is, 90% methanol and pure methanol, respectively, replaced the supernatant. The sedimented particles were then simply redispersed by shaking. This process was repeated until the supernatant solids content was reduced to a negligible level (<0.1%). The progression of the solids contents is shown in Figure 3. After several washes, the final solids contents of the supernatants were low, as shown by the percentages in Figure 3. The nonzero values indicate that some solubility equilibrium between the medium and the seed particles exists, where PBA and PVP K90 show relatively higher final solids contents in the medium compared with those of the PSt and PVP K30 systems, respectively. Both PBA and grafted PVP K90 have higher solubilities in the polymerization media.

Seeded Dispersion Polymerization Using the Four Kinds of Seed Particles

Using the four cleaned seed latexes, seeded dispersion polymerizations were carried out according the standard recipes shown in Table II. Table III qualitatively summarizes the outcome of these polymerizations using the 16 combinations of four types of cleaned seeds (polymer-stabilizer combinations: PBA-K90, PBA-K30, PSt-K90, and PSt-K30), with BA and St as second-stage monomers and PVP K90 and PVP K30 as second-stage stabilizers. Compared with the relatively large amounts of PVP stabilizer that were required to prepare the original seed particles (10–40 wt%
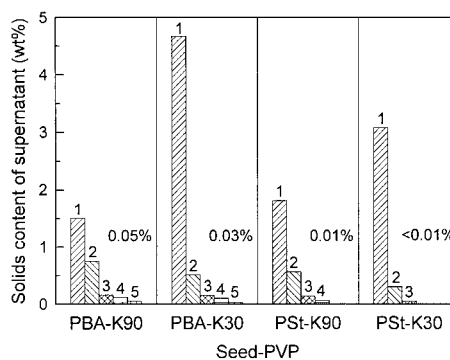

Figure 3 Supernatant solids contents found after each sedimentation cycle during the process for cleaning the seed latex particles; the final solids content is given above each set of data.

Table III Results of the Seeded Dispersion Polymerizations

	Seed[a]			
2nd-Stage[b]	PBA-K90	PBA-K30	PSt-K90	PSt-K30
BA-K90	::o::	::o::	o	X
BA-K30	o	o	X	X
St-K90	::o::	::o::	::o::	::o::
St-K30	o	o	o	o

[a] PBA = poly(butyl acrylate); PSt = polystyrene.

[b] BA = butyl acrylate; St = styrene.

::o:: = Many new small particle generated in addition to some growth of the larger seed particles; o = uniform particles produced without any newly formed small particles; X = the system coagulated.

PVP based on monomer; Table I), only 2 wt% PVP stabilizer (based on monomer) was used in the seeded dispersion polymerizations to avoid secondary nucleation. The final results of these polymerizations are classified with regards to the particle size and size distribution produced. A general trend that can be seen from Table III is that, except for the four PSt/BA systems (upper-right corner of Table III), new particles were generated when PVP K90 was used as the additional stabilizer, whereas stable dispersions with no new particles were obtained when PVP K30 was used. To explain these results, however, more information about the influence of the additional stabilizer and the second-stage monomer on the system is needed.

Effect of the Additional PVP in the Seeded Dispersion Polymerization

The results shown above indicate that the molecular weight of the PVP stabilizer used in the different stages of the dispersion polymerization greatly influence the final results of the seeded dispersion polymerizations. For the specific systems represented in Table III, new small particles were found only in the systems in which PVP K90 was used as the additional stabilizer. However, during the development of the reported recipes, new particles were found to be formed in many cases in the seeded dispersion polymerizations even when PVP K30 was used as the additional stabilizer. These newly formed particles were small (<0.5 μm) and stable despite the fact that the seeds were cleaned and the amount of additional PVP stabilizer was quite low. However, to determine whether the low amount of additional

PVP could possibly be the reason for the formation of these small particles, dispersion polymerizations were carried out using the recipe in Table IV, which is the same as Table II except that no seed was present. Optical micrographs of the resulting particles are shown in Figure 4. In these pictures, only large micron-size particles are observed. Because the amounts of stabilizer used in these polymerizations are lower than those used for the preparation of the seed particles, the particles are larger than the seed particles, and the size distributions are broader. This was not unexpected.

Aging of the Seed Particles

It was found that the final outcome of a seeded dispersion polymerization varies on the "aging" of the cleaned seed. Coagulation occurred frequently when the seeded dispersion polymerization was carried out using freshly cleaned seed particles without the additional PVP stabilizer, whereas a stable dispersion with a large number of new small particles was obtained by using aged seed particles; for example, using particles 48 hr after their cleaning was completed. This result indicates that a "cleaned" seed obtained according to the procedure described above is not at an equilibrium state in terms of the solubility of various components in the medium. These components may include PVP that does not desorb quickly or that is entrapped in the surface region of the particles and PVP that is grafted with PBA or PSt, which itself does not desorb readily. These subsequently desorb into the medium given a sufficient amount of time.

Addition of Second-Stage Monomer

As mentioned above, the establishment of the equilibrium adsorption of species in the cleaned

Table IV Recipe for Dispersion Polymerization Using the Low PVP Levels Employed in the Seeded Dispersion Polymerizations at 70°C

Ingredient	Weight (g)
Monomer (butyl acrylate, styrene)	3.0
ACPA[a]	0.03
PVP (K90, K30)[b]	0.06
90% or 100% Methanol	24.00

[a] 4,4′-azobis-(4-cyanopentanoic acid), Wako Chemicals USA Inc.

[b] Polyvinylpyrrolidone, molecular weight: K90 = 360,000; K30 = 40,000 g/mol; GAF.

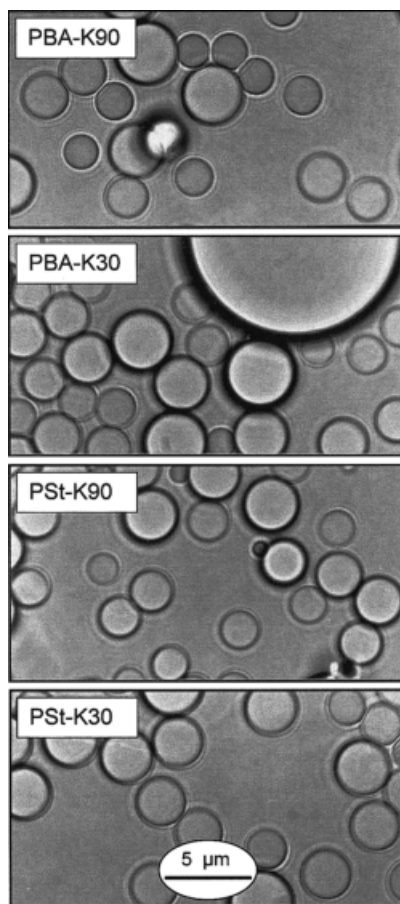**Figure 4** Optical micrographs of particles prepared by dispersion polymerizations using the polyvinylpyrrolidone levels indicated in Table IV.

Figure 5 Schematic of the process for removing the seed particles after the extraction by the second-stage monomer.

seed latexes seems to be a slow process. By the addition of the second-stage monomer in the seeded dispersion polymerization, the equilibrium can also be affected between the seed particles and the reaction medium now containing monomer. Because the seeded dispersion polymerization is conducted at 70°C, it is difficult to determine the equilibrium under such conditions without polymerization. However, to simulate this new equilibrium in the presence of the second-stage monomers, the cleaned seed, the corresponding polymerization medium, and the second-stage monomer were mixed as shown in the standard recipe for the seeded dispersion polymerizations given in Table II without the additional PVP stabilizer and the ACPA initiator. Trace amounts of methyl hydroquinone (MEHQ) and 4-tert-butylcatechol inhibitors were added to the BA and St systems, respectively, to prevent polymerization. The mixtures were then agitated
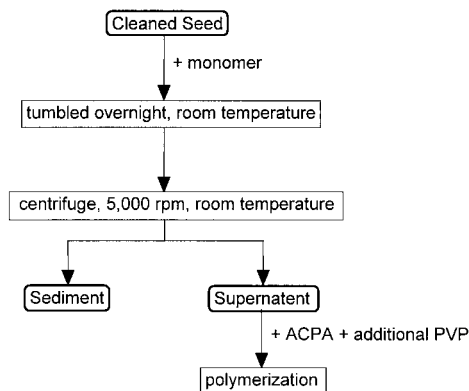
at room temperature overnight. The supernatant, which contains the initially charged methanol/water medium, the monomer, and any additional extracted solids from the cleaned seed particles, was separated from the particles by centrifugation at 5000 rpm for 2 hr at room temperature. The process is shown in Figure 5. The solids contents of the supernatant phase were measured gravimetrically, and the results are shown in Figure 6. Compared with the final solids contents after the seed cleaning process shown in Figure 3, additional solids were extracted after the addition of the second-stage monomer. As shown in Figure 6, higher quantities of solids were extracted from the seed particles by the media containing their own monomers; that is, the solids contents found in the PBA/BA and PSt/St systems were higher than those obtained in the PBA/St and PSt/BA systems. Also, more solids were extracted from
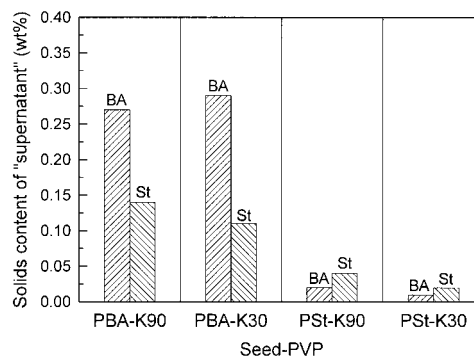

Figure 6 Solids contents of the supernatant phases after the extraction from the cleaned seeds using the second-stage monomer.

Ingredient	Weight (g)
"Supernatant"[a]	27.0
ACPA[b]	0.03
Additional PVP (K90, K30)[c]	0.06

[a] The medium containing the second-stage monomer after extraction of the seed, as shown in the process in Figure 5.
[b] 4,4'-azobis-(4-cyanopentanoic acid), Wako Chemicals USA Inc.
[c] Polyvinylpyrrolidone, molecular weight: K90 = 360,000; K30 = 40,000 g/mol; GAF.

the PBA seed systems than from the PSt seed systems.

Eight parallel experiments were also carried out as described above without the addition of the inhibitors. By using the supernatants from these eight extractions, 16 dispersion polymerizations were carried out with the addition of ACPA initiator and either PVP K90 or PVP K30 stabilizer, according to the recipe shown in Table V. The dispersion polymerizations in this set of experiments can be considered as having been carried out in media that closely simulate the media in the seeded dispersion polymerizations shown in Table III, the only but significant difference being the absence of the seed particles. The 16 results are shown in Table VI; similar to the results reported in Table III, there are three types of results. Except for the four PSt/BA systems (upper-right corner of Table VI), small particles were formed when PVP K90 was used as the additional stabilizer, whereas near seed-size particles were formed when PVP K30 was used. For the PSt/BA systems, particles were formed with sizes that were much larger than the respective seed particles, except for the particles obtained from the PSt-K90/BA-K90 system, which were nearly the same size as the seed. By comparing each corresponding result shown in Tables III and VI, it is interesting to find that there are three pairs of relationships between these results: 1) when small particles were reported in Table VI, new small particles were also noted in Table III; 2) when near seed-size particles were formed as given in Table VI, particles were reported in Table III without the formation of any new particles; and 3) when larger than seed-size particles were formed in the dispersion polymerization shown in Table VI, coagulation occurred in the seeded dispersion polymerization reported in Table III. The

particle sizes obtained in the dispersion polymerizations shown in Table VI reflect the efficiencies of the stabilizer systems, which include the PVP and grafted PVP from the seed serum plus the additional PVP stabilizer. The formation of the submicron-size particles in the dispersion polymerizations shown in Table VI would seem to indicate the presence of a relatively large quantity of the grafted PVP in the system, and this results in the formation of new small particles in the seeded dispersion polymerization, as shown in Table III. However, the formation of the larger than seed-size particles in a dispersion polymerization indicates the presence of little grafted PVP in the system. Coagulation is the result in the seeded dispersion polymerizations. It is noted that this kind of result was only found in the PSt/BA systems. Figure 6 does show that the lowest amounts of solids were found in the supernatants of the PSt/BA systems. As mentioned previously, the majority of the grafted PVP still present in a cleaned seed system is strongly associated with the polymer particles through either polymer chain entanglements or adsorption. The desorption of these from the particle surface requires the movement of polymer chains at the particle surface. The PSt that is prepared via dispersion polymerization has a much higher molecular weight than the corresponding PBA.[30] The high glass-transition temperature and the high molecular weight of the PSt polymer in this layer can result in a stronger association between the grafted PVP and the PSt particles. The only exception in the PSt/BA seeded dispersion polymerizations is the PSt-K90/BA-K90 system, where a sufficient amount of stabilizer seems to be present because of the use of the PVP K90 stabilizer.

Table VI Results of Polymerizations of the Supernatant

	Seed[a]			
2nd-Stage[b]	PBA-K90	PBA-K30	PSt-K90	PSt-K30
BA-K90	::::	::::	o	O
BA-K30	o	o	O	O
St-K90	::::	::::	::::	::::
St-K30	o	o	o	o

[a] PBA = poly(butyl acrylate); PSt = polystyrene.
[b] BA = butyl acrylate; St = styrene.
:::: = Submicron small particles, much smaller than the seed particles; o = particle size close to the seed particle size; O = much larger particles than the seed particles.
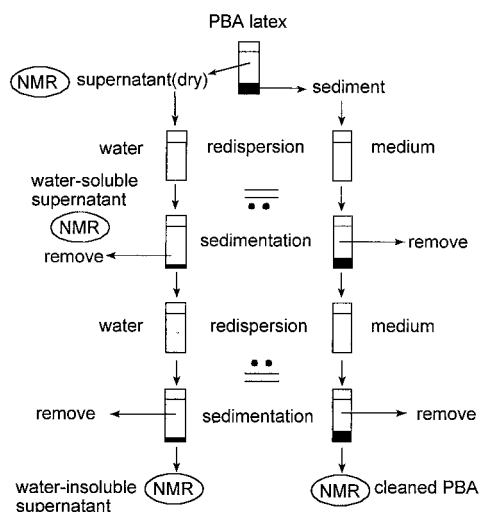
Figure 7 Schematic diagram of the separation process of each component having different solubilities in a poly(butyl acrylate) dispersion in methanol/water medium.

It must be emphasized that the results shown in Tables III and VI are not universal because the equilibrium of the grafted PVP in a seeded dispersion polymerization is influenced by a variety of polymerization parameters such as the type and concentration of the second-stage monomer, the procedure that is used to clean the seed, and the aging time of the seed particles before polymerization. Uniform particles can be obtained without the additional stabilizer even for some of the polymerization systems shown in Table III. Thus, to reach an acceptable reproducibility, it is crucial to follow a consistent procedure for each specific polymerization. For the seeded dispersion polymerizations shown in Table III, for instance, the time period between the final wash of the seed particles and the start of the second-stage polymerization at 70°C was approximately 2 hr.

Separation and NMR Characterization of Components in the Seed Latex

To characterize the grafted PVP formed in a dispersion polymerization of BA, different fractions of the PBA dispersion system were separated using the washing procedure illustrated in Figure 7. Four samples marked NMR in the figure were analyzed using ^{1}H NMR. As described in the previous section, the supernatant was obtained from the latex after centrifugation at 5000 rpm for 2 hr at room temperature. The clear supernatant was dried, and the solids obtained were labeled "NMR

supernatant (dry)." This material was then separated into water-soluble and water-insoluble components according to the procedure shown on the left side of Figure 7. The dried solids were redispersed in water, and the water-soluble supernatant sample was then obtained by centrifugation. The water-insoluble solids from the centrifugation were then repeatedly washed with water until no solids could be detected in the supernatant by gravimetry. The final solid material was labeled "water-insoluble supernatant." As shown on the right side of Figure 7, the sediment obtained in the first centrifugation of the latex was washed repeatedly with the reaction medium until no solids could be detected in the supernatant by gravimetry. The final PBA polymer sample was used in the NMR analysis and was labeled "cleaned PBA." The ^{1}H NMR spectra of the four samples described above are shown in Figure 8. As presented elsewhere,[28] the amount of solids in the supernatant was noticeably higher than the total amount of PVP in the recipe, which indicates that a PBA component must be present in the supernatant. The spectrum at the top of Figure 8 shows that characteristic peaks of the protons in the $-CH_3$ group in PBA ($\delta = 1.05$ ppm) and the $-N-CH_2-$ group in PVP ($\delta = 3.3$ ppm) are present in the supernatant. As described previously, the PBA latex particles prepared using this supernatant as the medium (plus stabilizer) resulted in much smaller particles than the original polymerization from which the supernatant resulted. Although it is difficult to distinguish grafted PVP from a simple blend of PVP and PBA polymer by using ^{1}H NMR, the high stabilization efficiency of the material in the supernatant suggests that
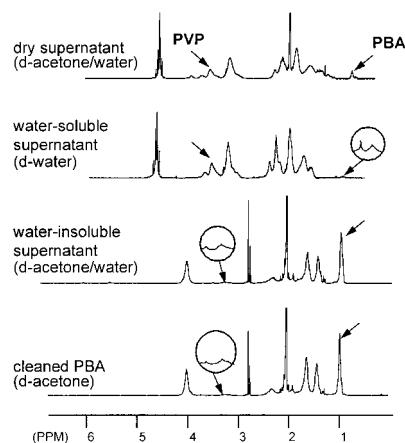

Figure 8 ^{1}H NMR spectra of each component as separated by the procedure depicted in Figure 7.

grafted PVP is present in the supernatant, as a blend of the two homopolymers would not have such an effect. To confirm this, and by considering the solubility of PBA in the methanol/water (90/10) supernatant, the dry solids from the supernatant were then washed with water until nothing more could be extracted. The second spectrum in Figure 8 shows that a small amount of PBA is present in the water-soluble supernatant, which can be identified as the grafted PVP having a high percentage of PVP. Similarly, the third spectrum of the water-insoluble supernatant component represents the grafted PVP in which longer PBA grafted lengths or multiple PBA grafts are present, which causes the grafted PVP to become water insoluble. The bottom spectrum shows that there is still a small amount of PVP in the cleaned PBA even after repeated washing with water. It seems that grafted PVP polymers are present in the different loci of the dispersion system and that the extent of adsorption on the particles depends on the relative composition of the anchoring (PBA branch) and soluble (PVP chain) portions in the grafted polymer. These grafted polymers may play different roles in a dispersion polymerization. The absolute quantities of the grafted PVP in the different loci should be reflected by the PBA in the water-soluble supernatant, the PVP in the water insoluble-supernatant, and the PVP in the cleaned PBA, as shown in the second, third, and fourth spectra in Figure 8, respectively. The amounts of these materials, however, are so small that quantitative analysis is almost impossible. For most free radicals, the chain transfer constant to polymer is about 10^4.[31] Therefore, it is reasonable to estimate that the grafted PVP is less than a few thousandths of the total PVP. To demonstrate the stabilization effect of this trace amount of grafted polymer on the size of the final particles, the recycled PVP obtained from the supernatant of a dispersion polymerization can be used as the stabilizer.

Dispersion Polymerization Using Recycled PVP

Dispersion polymerizations were carried out according the recipes shown in Table I. The resulting dispersions were centrifuged at 5000 rpm for 2 hr at room temperature. The solids content of each supernatant, which was clear in appearance, was measured gravimetrically. The results are shown in Figure 9. The numbers that appear above the left bars represent the ratios of the supernatant solids to the PVP contents in the
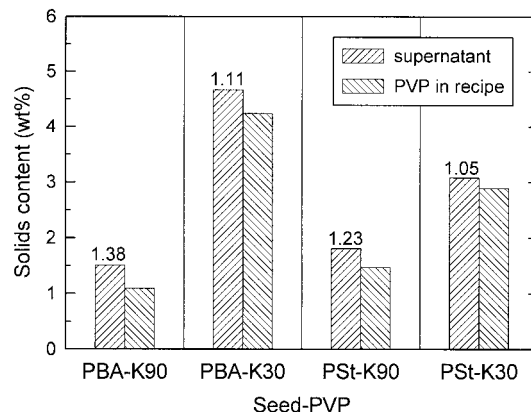

Figure 9 Supernatant solids contents for the four seed latexes compared to the polyvinylpyrrolidone content in the recipes.

recipes. In all four systems, the ratio is higher than one, with the highest value shown for the PBA-K90 system and the lowest for the PSt-K30 system. It was discussed in the previous sections that the extra solids in the supernatant are generated from the grafted segments in the PVP plus some low molecular weight PBA having solubility in the medium. The polymerizations were again carried out by following the same recipes in Table I but using recycled PVP rather than fresh PVP as the stabilizer. Figure 10 shows optical micrographs of the resulting particles. All four latexes resulted in particles that were obviously smaller in size than the corresponding ones that were originally prepared using PVP stabilizer as shown in Figure 2. The change in the PBA-K90 case is dramatic, while in the case of PSt-K30 the change is relatively small. This set of experiments demonstrates the strong stabilization ability of trace amounts of grafted PVP formed in the medium during the dispersion polymerization.

SUMMARY

Parallel seeded dispersion polymerizations of BA and St were carried out to determine which systems produce particle growth without nucleating new particles or generating coagulum. Variables included the seed type (PBA and PSt) and the stabilizer used to prepare the seed (PVP K30 and PVP K90), the second-stage monomer (BA and St), and the stabilizer added to the second stage. The medium was either 90% methanol and 10% water or 100% methanol, depending on the monomer. Con-
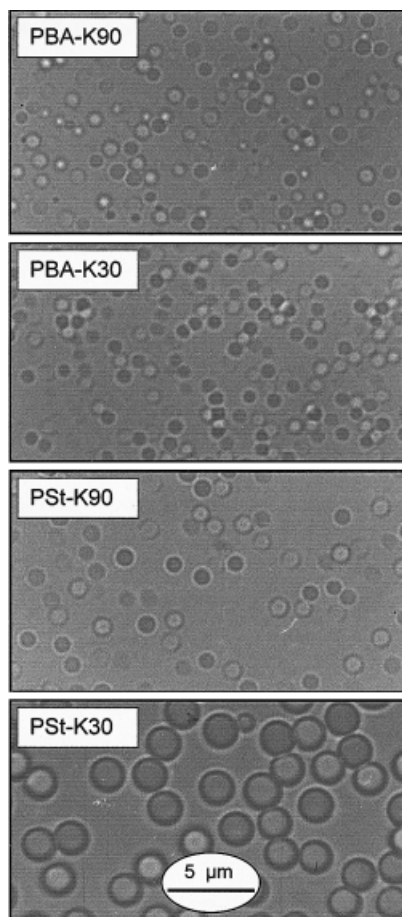
Figure 10 Optical micrographs of particles prepared by using recycled polyvinylpyrrolidone.

ditions for preparing each of the seed latexes were selected such that all four seeds had about the same particle size (2.2 μm) and possessed narrow distributions. Before conducting the seeded polymerizations, the seed latexes were cleaned of excess stabilizer by repeated replacement of the medium. Seed, monomer, and stabilizer were varied in the second-stage polymerizations, and the resulting dispersions were examined for secondary particle formation and coagulum. Successful particle growth was achieved when the second-stage polymerization employed PVP K30 (1 wt%) as the stabilizer, except when the seed was PSt and BA was the second-stage monomer (coagulum resulted). In contrast, the nucleation of a second crop of particles occurred in most of the reactions employing PVP K90 (1 wt%) as the second-stage stabilizer. Again, cases employing PSt as seed and BA in the second stage were the exception; the seed prepared with PVP K90 was grown successfully, whereas that prepared with PVP K30 coagulated.

These phenomena were further investigated by carrying out dispersion polymerizations using the supernatants separated from the second-stage polymerization recipes before carrying out the reactions. The resulting particles had characteristics that paralleled those in the seeding studies. All these results were explained by *in situ* synthesis of varying amounts of grafted PVP (depending on the monomer and PVP), which could be desorbed from the seed particles—particularly in the presence of monomer. This grafted material is considered to be an ideal stabilizer in these dispersion polymerizations.

The PBA dispersion was further characterized by separating the components and analyzing them for the presence of grafted polymer by ^{1}H NMR spectroscopy. The presence of PVP-graft-PBA was confirmed, but the amounts were too small to be quantified.

REFERENCES

1. Sudol, E. D. In Polymeric Dispersions: Principles and Applications; Asua, J. M.; Ed., NATO ASI Series E, No. 335, Kluwer Academic: Dordrecht, The Netherlands, 1996, p. 141.
2. Dawkins, J. W.; Stone, T.; Yeadon, G. Polymer 1977, 18, 1179.
3. Taylor, G. Ph.D. Thesis, Loughborough University, 1977.
4. Schwab, F. C.; Murray, J. G. Polym Sci Technol 1985, 35, 381.
5. Stampa, G. B. J. Appl. Polym Sci 1970, 14, 1277.
6. Awan, M. A.; Dimonie, V. L.; El-Aasser, M. S. J Polym Sci Part A Polym Chem 1996, 34, 2633.
7. Canelas, D. A.; DeSimone, J. M. Polym Prepr Am Chem Soc Div Polym Chem 1996, 37, 542.
8. Canelas, D. A.; Betts, D. E.; DeSimone, J. M. Macromolecules, 1996, 29, 2818.
9. DeSimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; McClain, J. B.; Romack, T. J.; Combes, J. R. Science 1994, 265, 356.
10. Barrett, K. E. J., Ed. Dispersion Polymerization in Organic Media; Wiley: London, 1975.
11. Lok, K. P.; Ober, C. K. Can J Chem 1985, 83, 209.
12. Egan, L. S.; Winnik, M. A.; Croucher, M. D. J. Polym Sci Polym Chem Ed 1986, 24, 1895.
13. Tseng, C. M.; Lu, Y. Y.; El-Aasser, M. S.; Vanderhoff, J. W. J Polym Sci Part A Polym Chem 1986, 24, 2995.
14. Lu, Y. Y.; El-Aasser, M. S.; Vanderhoff, J. W. J Polym Sci Part B Polym Physics 1988, 26, 1187.

15. Shen, S.; Sudol, E. D.; El-Aasser, M. S. J Polym Sci Part A Polym Chem 1993, 31, 1393.

16. Saenz, J. M.; Asua, J. M. J Polym Sci Part A Polym Chem 1996, 34, 1977.

17. Stejskal, P.; Hratochvil, P.; Helmstedt, M. Langmuir 1996, 12, 3389.

18. Paine, A. J. J Polym Sci Part A Polym Chem., 1990, 28, 2485.

19. Okubo, M.; Ikegami, K.; Yamamoto, Y. Colloid Polym Sci 1989, 267, 193.

20. Laus, M.; Dinnella, C.; Lanzarini, G.; Casagrande, A. Polymer 1996, 37, 343.

21. Digar, M. L.; Bhattacharyye, S. N.; Mandal, B. M. Polymer 1994, 35, 377.

22. Miyazaki, M.; Terada, K.; Sato, T.; Maruyama, H.; Okaya, T. J Appl Polym Sci 1996, 60, 2149.

23. Paine, A. J. J Colloid Interface Sci 1990, 138, 157.

24. Shen, S.; Sudol, E. D.; El-Aasser, M. S. J Polym Sci Part A Polym Chem 1994, 32, 1087.

25. Kawaguchi, S.; Winnik, M. A.; Ito, K. Macromolecules 1995, 28, 1159.

26. Capek, I.; Riza, M.; Akashi, M. Polym J 1992, 24, 959.

27. Morrison, B. R. B.S. Thesis, University of Sydney, 1987.

28. Wang, D.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M.S. J Appl Polym Sci 2002, 84, 2692.

29. Wang, D.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M.S. J Appl Polym Sci 2002, 84, 2710.

30. Wang, D. Ph.D. Dissertation, Lehigh University, 1997.

31. Odian, G. Principles of Polymerization accepted 3rd ed.; Wiley: New York, 1991.