

# Dispersion Polymerization of *n*-Butyl Acrylate

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

Emulsion Polymers Institute and Department of Chemical Engineering, Lehigh University, 111 Research Drive, Bethlehem, Pennsylvania 18015

Received 1 June 2001; accepted 13 September 2001

**ABSTRACT:** The dispersion polymerization of *n*-butyl acrylate (BA) was investigated using alcohol/water mixtures as the dispersion medium, 4,4'-azobis-(4-cyanopentanoic acid) as the initiator, and polyvinylpyrrolidone (PVP) as the stabilizer. The effects of polymerization parameters, such as the alcohol/water ratio in the medium and the type and concentration of the polymeric stabilizer, on the resulting particle size and size distribution were studied. The final particle size and the stability of the dispersion system were found to be greatly influenced by the type of alcohol used in the mixture; that is, methanol or ethanol, even though the apparent solubility parameters are almost the same for the two types of mixtures. Poly(butyl acrylate) particles with controlled size and size distribution (monodisperse), and gel content were successfully prepared in a 90/10 methanol/water medium. It was found that the particle size decreased with increasing initiator concentration. This is the opposite of what was previously reported in the dispersion polymerizations of styrene and methyl methacrylate. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2692–2709, 2002

**Key words:** dispersion polymerization; radical polymerization; particle size distribution; crosslinking; nucleation; stabilization

## INTRODUCTION

Dispersion polymerization has proven to be a useful polymerization technique for preparing micron-size polymer particles in a single step. A number of monomers have been used in dispersion polymerizations for the preparation of micron-size particles having narrow particle size distributions. Micron-size particles comprised of polymers having a glass transition temperature ( $T_g$ ) well above room temperature have found a wide variety of applications in such areas as column packing,<sup>1,2</sup> protein recovery,<sup>3</sup> immunoassay,<sup>4</sup> medical diagnostics,<sup>5</sup> and biomedical applications.<sup>6</sup> Polystyrene<sup>7–14</sup> (PSt), poly(methyl methacrylate)<sup>15–17</sup> (PMMA), and poly(divi-

nylbenzene) (PDVB)<sup>18–20</sup> are the most studied monomer systems. However, micron-size rubbery particles are needed in some applications, such as impact modification of brittle PSt materials.<sup>21</sup> Micron-size poly(butadiene-styrene) particles have been prepared<sup>22</sup> by dispersion polymerization for this purpose.

Dispersion polymerization is sometimes viewed as a modified precipitation polymerization. The critical characteristic for a dispersion polymerization is that the monomer to be polymerized must be soluble in the dispersion medium, whereas the polymer must be insoluble. The polymer particles, instead of forming macroscopic polymer precipitates, are formed in the presence of polymeric stabilizers. The early work in dispersion polymerization was confined to polymerization in aliphatic hydrocarbon fluids and has been well reviewed by the ICI (Imperial Chemical Industries) researchers.<sup>7</sup> During

Correspondence to: M. S. El-Aasser (mse0@lehigh.edu).

*Journal of Applied Polymer Science*, Vol. 84, 2692–2709 (2002)  
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the past 15 years, there has been a considerable interest in generalizing these results to more polar solvents as the continuous phase, by which the range of monomers that can be polymerized using this method have been greatly expanded. Hydroxypropyl cellulose (HPC),<sup>23</sup> poly(acrylic acid) (PAA),<sup>24</sup> and polyvinylpyrrolidone (PVP)<sup>10,11,25</sup> are the most frequently used stabilizers in polar media. The relative extent of the interaction between the reaction medium, the stabilizer, and the polymer that is being produced is considered to be one of the key factors that controls the final particle size.<sup>10,23,26</sup> Micron-size polystyrene particles were prepared in the homologous series of alcohols from methanol to octadecanol.<sup>23</sup> It was found that particle size increased with increasing carbon number up to pentanol and then decreased with increasing chain length to octadecanol.

The mechanism of dispersion polymerization is complex. A few mechanisms have been proposed to explain the experimental results. The key questions in mechanistic studies have been how the polymer nuclei are formed, what the role of the stabilizer is in the nucleation process, and ultimately, how these factors influence the final particle size and distribution. Three mechanistic models that are frequently mentioned include (1) aggregative nucleation, (2) coagulative nucleation, and (3) stabilization models. In the aggregative nucleation model, oligomers are formed in solution, and these aggregate among themselves until the surfaces of these unstable nuclei adsorb enough stabilizer to form stable particles. Coagulative nucleation, however, postulates that each oligomeric radical will grow to its critical solubility point ( $\theta$ -point) in the dispersion medium, precipitating to form a so-called precursor. These precursors will then form a nucleus either through homocoagulation among themselves or by continued propagation of the polymer chain. In the stabilization model,<sup>12-14</sup> the point at which homocoagulation stops is considered to be much more mechanistically important than the nucleation process. This stabilization point is greatly dependent on stabilizer factors such as concentration and molecular weight.

In this work, the dispersion polymerization of *n*-butyl acrylate (BA) is being investigated in the preparation of micron-size rubbery particles having a narrow particle size distribution. Because of a limited but significant solubility of poly(butyl acrylate) (PBA) in pure alcohols such as methanol, ethanol, and propanol, PBA particles can not be formed in these media. To decrease the solu-

bility of PBA in the medium while maintaining sufficient solubility of the monomer, ethanol/water or methanol/water mixtures are used as the polymerization media. The presence of water in the reaction medium increases the complexity of the polymerization system in terms of the difference in such properties as solvency between the water/alcohol medium and the monomer, the polymer, and the stabilizer. The effect of polymerization parameters, such as the type of the alcohol, the solvency of the medium, the concentration and molecular weight of the PVP stabilizer, the type and concentration of initiator, and the use of a cross-linking agent were investigated.

## EXPERIMENTAL

### Materials

The BA and styrene (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 the alcohols (methanol [MeOH] [Fisher Scientific], ethanol [EtOH] [200 proof, McCormick Distilling Co., Weston, MO], *n*-propanol [PrOH] [Fisher Scientific], and *n*-butanol [BuOH] [Fisher Scientific]); the azo-type initiators (2,2'-azobis[isobutyronitrile] [AIBN] and 4,4'-azobis[4-cyanopentanoic acid] [ACPA] [Wako Chemicals USA Inc., Richmond, VA]); the stabilizers (polyvinylpyrrolidone [PVP K90, PVP K30] [GAF, Wayne, NJ]; the co-stabilizer (Aerosol OTS [sodium dioctyl sulfosuccinate in petroleum distillate] [Cytec Industries, West Paterson, NJ]; and three cross linkers (allyl acrylate [AA] [Polysciences, Inc., Warrington, PA], divinylbenzene [DVB] [Fisher Scientific], and tetra[ethylene glycol]-dimethacrylate [EGDM] [Celanese, Dallas, TX]). Distilled-deionized (DDI) water was used in all experiments.

### Polymerization and Characterization

The dispersion polymerizations of BA were carried out according to the standard recipe given in Table I. Each of the polymerization parameters in the recipe was investigated. Although one or more parameters were varied as specified, other parameters were left the same. The ingredients were weighed and mixed in 2-oz glass bottles that were purged with nitrogen, capped, and sealed. The bottles were then placed in safety baskets

**Table I Standard Recipe for Dispersion Polymerization of *n*-Butyl Acrylate in a 90/10 (by Weight) Methanol/Water Mixture at 70°C**

Ingredient	Weight (g)
BA	1.5–12
AIBN <sup>a</sup> or ACPA <sup>b</sup>	0.0075–0.09
PVP K30 <sup>c</sup> or PVP K90 <sup>d</sup>	0.15–1.50
Aerosol OTS <sup>e</sup>	0–1.8
Allyl acrylate	0–0.12
MeOH/H <sub>2</sub> O <sup>f</sup>	27.00

<sup>a</sup> 2,2'-azobis(isobutyronitrile); Wako Chemicals USA, Inc. (Richmond, VA).

<sup>b</sup> 4,4'-azobis-(4-cyanopentanoic acid); Wako Chemicals USA, Inc.

<sup>c</sup> Polyvinylpyrrolidone, molecular weight 40,000 g/mol; GAF (Wayne, NJ).

<sup>d</sup> Polyvinylpyrrolidone, molecular weight 360,000 g/mol; GAF.

<sup>e</sup> Sodium dioctyl sulfosuccinate in petroleum distillate, Cytec Industries (West Paterson, NJ).

<sup>f</sup> Methanol content: 85%–94 wt %.

supported on a rotor and were tumbled end-over-end at 28 rpm in a constant temperature water bath at 70°C for 24 hr.

The viscosities of a series of PVP solutions in alcohol/water mixtures were measured at several shear rates and at room temperature using a Brookfield viscometer. The conversions of the resulting PBA latexes were measured gravimetrically. 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.

#### Measurement of the Gel Content using a Butanol Extraction Method

The gel content of the PBA particles was determined by a solvent extraction method. This method involved dissolving 0.3 g of a PBA film, which was cast at room temperature and dried under vacuum for 12 hr, in 10 mL butanol and mixing it for 48 hr with end-over-end tumbling. The weight of dissolved polymers,  $W$ , which include non-cross-linked PBA,  $W_{\text{PBA}}$ , and all of the PVP,  $W_{\text{PVP}}$  (PVP is completely soluble in butanol), in the initial dispersion, was determined gravimetrically from the solids content in the supernatant after centrifugation at 5000 rpm for 2 hr at room temperature. The gel content was calculated as follows:

$$\text{Gel Content (\%)} = \frac{0.3 - W}{0.3 - W_{\text{PVP}}} \times 100 \quad (1)$$

where  $W_{\text{PVP}}$  was calculated from the amount of PVP that was used in the recipe for the dispersion polymerization.

## RESULTS AND DISCUSSION

### Effect of Polymerization Medium

To design a recipe for the dispersion polymerization of BA, it is important to study properties related to the interactions between monomer/medium, polymer/medium, and stabilizer/medium. The colloidal stability of the dispersion, the particle size, and the distribution of the particle size are virtually decided by these properties.

### Polymerizations in Alcohol/Water Media

Polymerizations of BA were carried out in different alcohol/water media according to the standard recipe given in Table II. Figure 1 shows the appearance of the reaction systems before and after the polymerizations. For the ethanol/water systems before polymerization, the reaction mixtures comprising 100 wt%, 70 wt%, and 50 wt% ethanol were good solvents for BA monomer, appearing as transparent and homogeneous solutions. When the ethanol concentration was reduced to 40 wt%, the solubility limit of the BA was exceeded and phase separation in the reaction mixture was observed. After polymerization in 100% ethanol, the system remained a transparent and homogeneous solution because ethanol is a good solvent for PBA. For the polymerizations in 70% and 50% ethanol media, the resultant PBA particles sedimented after several hours; the different sediment heights for these two cases reflect differences in the particle size. Finally, for the 40% ethanol case, no obvious sedimentation was observed after a few days, which indicates that

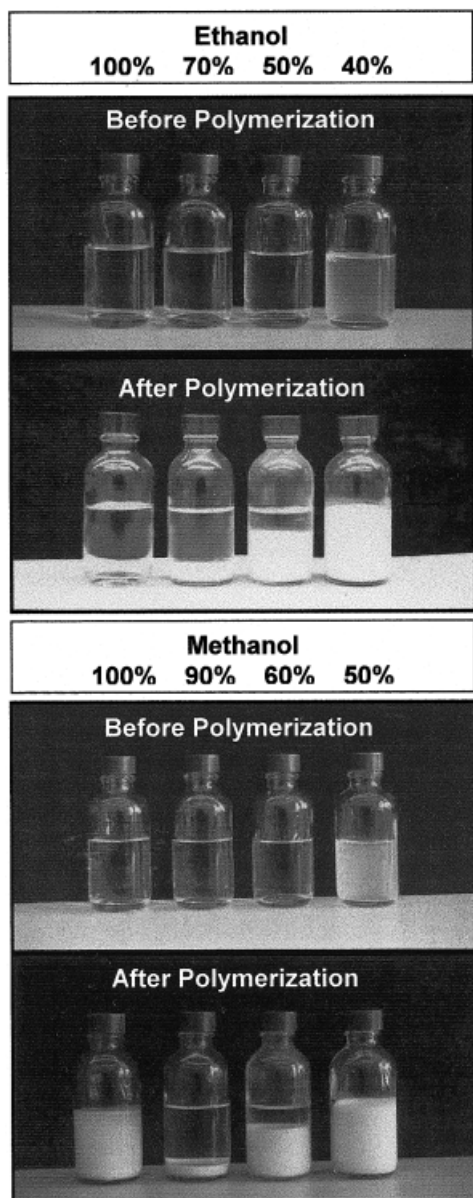
**Table II Recipe for Polymerization of *n*-Butyl Acrylate in Alcohol/Water at 70°C**

Ingredient	Weight (g)
BA	3.00
ACPA <sup>a</sup>	0.03
PVP K90 <sup>b</sup>	0.30
Alcohol/water medium <sup>c</sup>	27.00

<sup>a</sup> 4,4'-azobis-(4-cyanopentanoic acid), Wako Chemicals USA Inc.

<sup>b</sup> Polyvinylpyrrolidone, molecular weight 360,000; GAF.

<sup>c</sup> Ethanol or methanol (wt %) = 50%–100%.



**Figure 1** Appearance of reaction systems before and after the polymerization of *n*-butyl acrylate for different alcohol/water ratios, given as a weight percentage of alcohol in the medium.

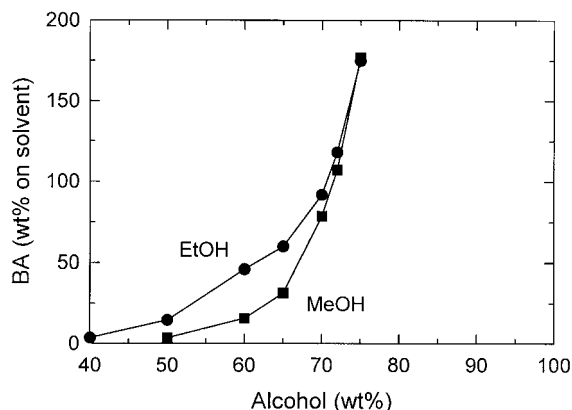
the PBA latex had a much smaller particle size. Similar phenomena were observed for the methanol/water system, except that the phase separation of the BA started at 50 wt% methanol. In the case of 100% methanol, the resulting latex was made up of particles having a broad size distribution, which appeared as a sediment comprised of large particles and a cloudy supernatant phase of small particles containing some dissolved PBA. By decreasing the alcohol/water ratio, the me-

dium goes from being a good solvent for both the monomer and the polymer to being a good solvent for the monomer while the polymer is insoluble and, finally, to being a poor solvent for both monomer and polymer. Consequently, the polymerization process would vary from a solution polymerization (e.g., in 100% ethanol) to a dispersion polymerization (e.g., in media with ethanol contents of 60 wt% to 70 wt% and methanol contents of 60 wt% to 90 wt%) and, finally, to an emulsion polymerization (ethanol  $\leq$  40 wt% and methanol  $\leq$  50 wt%).

This set of experiments qualitatively demonstrates the transitions of the polymerization process with the change in the solvency of the polymerization medium for the monomer and polymer. To select an appropriate polymerization medium for the dispersion polymerization of BA, however, it is necessary to quantitatively measure the solubilities of the BA monomer and PBA in different alcohol/water mixtures.

#### *Solubilities of BA and PBA in Alcohol/Water Media*

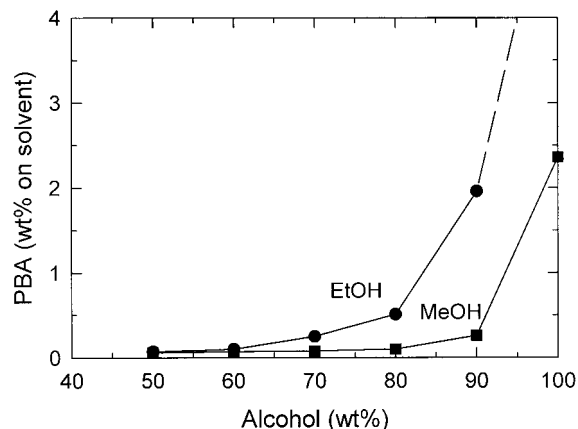
As mentioned previously, the medium for a typical dispersion polymerization has to be simultaneously a good solvent for the monomer and a poor solvent for the polymer. For most of the dispersion polymerization systems reported so far (e.g., St, MMA, and DVB), the polymerizations were carried out in pure alcohol media, which are usually good solvents for the given monomer and nonsolvents for the polymer. However, this was found not to be the case for the BA/PBA system. The saturation solubility of BA monomer in various alcohol/water media was determined experimentally. BA was titrated into a certain amount of the alcohol/water mixture, which was shaken frequently to observe any change. When the mixture changed from being transparent to slightly cloudy after shaking, the added amount of BA was recorded as exceeding its solubility limit. Figure 2 shows the BA weight percentage based on the solvent weight at the saturation point as a function of the alcohol content (wt%) in the alcohol/water media. At 40% ethanol and 50% methanol, the amounts of dissolved BA were less than 4% based on the solvent, which is much lower than the BA content used in the polymerizations (10% based on medium; see Table I). In both cases, phase separation was observed before the polymerization (Fig. 1); thus, these are not suitable media for conducting dispersion polymerizations. For alcohol contents of 50% ethanol and



**Figure 2** Effect of the ethanol or methanol content (wt%) in the solvent mixture on the saturation amount of *n*-butyl acrylate.

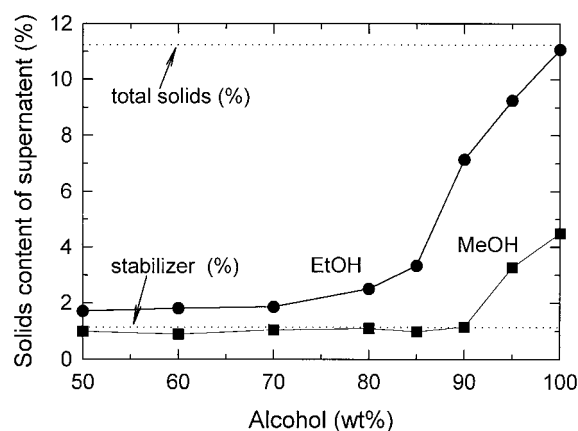
60% methanol, the amounts of dissolved BA were higher than 10% and, thus, represent the lower limits of these alcohol/water mixtures that can be used as dispersion polymerization media.

The second important criterion for a dispersion polymerization is that the polymer be "insoluble" in the medium. The saturation solubility of PBA was measured using the following procedure. A PBA latex was prepared in 90% methanol according to the recipe in Table I. The resulting latex was dried at room temperature, and 3 g of the dried PBA was added to 10 g of an alcohol/water mixture. This was tumbled end-over-end at room temperature for 48 hr and was then centrifuged at 5000 rpm at room temperature for 2 hr. The solids content of the supernatant was measured gravimetrically. As the PVP stabilizer is also soluble in the solvent, the dissolved PBA amount was simply calculated by deducting the PVP content on the basis of the recipe, assuming that all of the PVP was present in the supernatant. Figure 3 shows the weight percentage of the dissolved PBA, based on the solvent weight as a function of the alcohol content in the alcohol/water mixture. The solubilities of the PBA in the solvent mixtures containing 70% ethanol and 90% methanol were less than 0.5%; this increased substantially at higher alcohol contents. The poor solubility of PBA in both 70% ethanol and 90% methanol suggests that these two media are suitable for the dispersion polymerization of BA and should be near the upper limits for alcohol content in the alcohol/water mixtures that can be used as polymerization media. By considering the solubility of BA monomer and PBA in polymerization media having different alcohol/water ra-



**Figure 3** Effect of the ethanol or methanol content (wt%) in the solvent mixture on the saturation amount of poly(butyl acrylate).

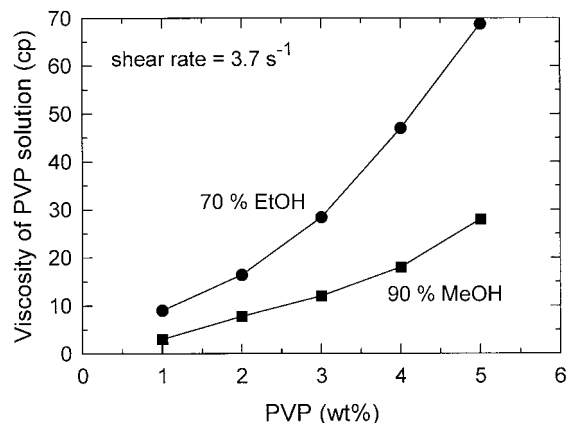
tios, it becomes apparent that dispersion polymerizations can only be carried out over a relatively narrow range of alcohol/water ratios; that is, 50%–70% for ethanol and 60%–90% for methanol. To ultimately select the medium for the dispersion polymerization of BA, polymerizations were carried out over a wider range of alcohol/water ratios according to the recipe shown in Table I. The polymerization products were centrifuged at 5000 rpm at room temperature for 2 hr, and the solids contents of the supernatants were measured gravimetrically. Figure 4 shows the results obtained as a function of the ethanol or methanol content (wt%). The total solids content



**Figure 4** Solids content of the supernatant of poly(butyl acrylate) products prepared in different alcohol/water media, given as a weight percentage based on the medium. The horizontal dotted lines indicated the total solids content and the stabilizer content (both given in wt%), based on the recipe.

and the stabilizer content (both given in wt%) based on the recipe are also shown in the figure. As shown in the graph, when the ethanol content was higher than 80% and the methanol content was higher than 90%, the solids content in the supernatant increased significantly. This suggests that appreciable amounts of PBA were soluble in the medium. For 100% ethanol, almost all of the PBA was dissolved, whereas for 100% methanol, 30% of the total PBA was dissolved. The size of the PBA particles that were prepared in both alcohol/water mixtures increased with increasing alcohol content. Although particles can still be formed in the media that contain up to 80% ethanol or 100% methanol, the systems became rather viscous when the ethanol and methanol contents were higher than 72% and 90%, respectively. Stable PBA particles having the largest particle sizes and narrow distributions were obtained in the media at these two upper limits; that is, at 2.0  $\mu\text{m}$  in the 72/18 ethanol/water mixture and at 2.4  $\mu\text{m}$  in the 90/10 methanol/water mixture.

Although the media comprising 72% ethanol and 90% methanol were considered to be suitable for carrying out dispersion polymerizations of BA on the basis of the solubility results presented above, significant differences in the outcomes of dispersion polymerizations of BA were observed in these two systems. Besides differences in the particle size and size distribution, remarkable differences in colloidal stability were noted. In contrast to the frequent coagulation and poor reproducibility encountered when the ethanol/water (72/28) medium was used, no coagulation was found to occur in the methanol/water (90/10) medium, even under much harsher conditions; that is, much lower PVP concentrations and higher shear rates (i.e., higher revolutions per minute in bottle polymerizations). From the point of view of the solubilities, there are some differences between these two systems. As shown in Figure 2, the 90% methanol medium was completely miscible with BA, whereas a solubility limit is seen for the 72% ethanol medium. In contrast, as shown in Figures 3 and 4, more polymer was found to be soluble in the 72% ethanol medium. These differences suggest that the extent of the interactions between the BA monomer, and hence the resultant oligomers, and the medium are different for these two types of alcohol/water mixtures. This would certainly influence the nucleation process and resulting particle size but may not be the



**Figure 5** Effect of polyvinylpyrrolidone concentration in 70% ethanol and 90% methanol aqueous mixtures on the solution viscosity; shear rate = 3.7 ( $\text{s}^{-1}$ );  $T = 25^\circ\text{C}$ .

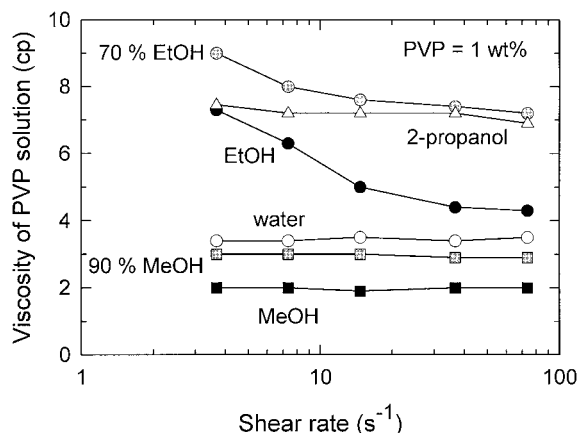
primary reason for the poor colloidal stability found in the ethanol/water system.

#### Viscosity of PVP Solutions

It seems that, to attain a “good” dispersion polymerization system, it is not enough to only consider the solubilities of monomer, polymer, and stabilizer in the medium. The stabilizing efficiency of the stabilizer in the polymerization medium certainly plays an important role in the polymerization process, even though its solubility does not seem to be affected by the nature of the medium—that is, PVP stabilizer is soluble in both ethanol/water and methanol/water media.

In an attempt to explain the significant difference in colloidal stability in the two media, the surface tensions of the two alcohol/water media and a series of PVP solutions in these media were measured. No significant differences were observed. Subsequently, the viscosity of a series of solutions comprised of PVP dissolved in alcohol/water mixtures was measured at room temperature using a Brookfield viscometer.

Figure 5 shows the viscosity of PVP in alcohol/water mixtures comprised of 70% ethanol and 90% methanol as a function of the amount of PVP. These were measured at a constant shear rate of 3.7  $\text{s}^{-1}$ . The 70% ethanol solutions had higher viscosities, which increased more with increasing PVP concentration than did the 90% methanol solution. For reference, the viscosities of pure ethanol and methanol at 25°C are 1.08 and 0.55 cp, respectively. The significantly larger difference in the viscosities shown in Figure 5 should be caused

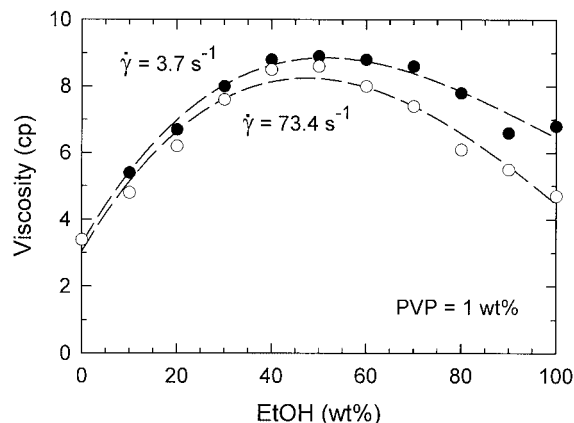


**Figure 6** Effect of shear rate on the viscosity of polyvinylpyrrolidone (PVP) solutions in different solvents; PVP = 1 wt%,  $T = 25^\circ\text{C}$ .

primarily by the different conformations of the PVP polymer in the two types of alcohol/water mixtures.

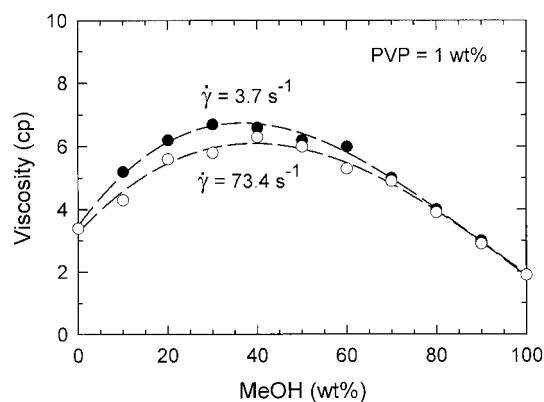
Figure 6 shows the viscosities of 1% PVP solutions in different solvents as a function of the shear rate. The viscosities of the solutions that used pure solvents increased in the following order: methanol < water < ethanol < propanol. Except for the ethanol solution, all other solutions showed an almost constant viscosity over the entire range of shear rates, which is typical for true polymer solutions without strong intermolecular interactions among the polymer chains. The viscosity of the ethanol solution, however, decreased with the increasing shear rate, a typical shear-thinning behavior, which usually indicates that some kind of intermolecular interaction is present in the system and that this interaction can be broken down by the shear. Similar shear thinning behavior was also observed in the ethanol/water mixture shown in Figure 6. In addition to this behavior, the viscosity of the PVP solution in 70% ethanol exhibited even higher values than those in either pure ethanol or water, whereas the viscosity in the 90% methanol solution lies in between those in the pure methanol and water.

Figure 7 shows the viscosity profiles of PVP solutions as a function of the ethanol content in the medium. It can be clearly seen that the viscosities, both at the high ( $73.4\text{ s}^{-1}$ ) and low ( $3.7\text{ s}^{-1}$ ) shear rates, increase with increasing ethanol content to a maximum at around 50% ethanol and then decrease. (It should be noted that even in the absence of the PVP, the viscosity of alcohol/water mixtures also increases to a maximum, albeit at



**Figure 7** Viscosity of polyvinylpyrrolidone (PVP) solutions in various ethanol/water mixtures, measured at high (filled symbols) and low (open symbols) shear rates; PVP = 1 wt%,  $T = 25^\circ\text{C}$ .

much lower values of viscosity.) After these maxima, the differences between the viscosities at the high and low shear rates increase with increasing ethanol content, reflecting the shear-thinning region. The parallel results for methanol/water solutions are shown in Figure 8, where the viscosities increase to a maximum value at around 40% methanol and then decrease. However, in this case, the shear thinning appears in the low alcohol content range (10%–0%). In both alcohol/water systems, relatively high viscosities were observed over certain ranges of alcohol/water ratios; that is, 40%–70% for ethanol/water solutions and 20%–50% for methanol/water solutions. The presence of excess values such as density, refractive index, and absolute viscosity is not rare in many



**Figure 8** Viscosity of polyvinylpyrrolidone (PVP) solutions in various methanol/water mixtures, measured at high (filled symbols) and low (open symbols) shear rates; PVP = 1 wt%,  $T = 25^\circ\text{C}$ .

binary mixtures such as ethanol/water and methanol/water mixtures. The higher viscosities of these alcohol/water mixtures is caused by the stronger associations, for example, hydrogen bonding, between alcohol and water molecules in these mixtures. The greater increase in the viscosity of the PVP solutions, compared with simple alcohol/water mixtures, suggests that the association between alcohol and water molecules enhances the interaction between PVP molecules in these mixtures. A separate experiment showed that the PBA dispersion remains stable after all the medium-soluble polymers are washed out by repeated replacement of the medium. This experimental result indicates that the polymer particles can be stabilized by grafted PVP. The presence of free PVP in the medium can either promote stabilization or cause flocculation of the dispersion through a depletion mechanism.<sup>26-29</sup> Strong interactions between the PVP molecules can lead to flocculation through bridging. The PVP solution comprising 70% ethanol is in the range where the high viscosity and shear thinning appear. However, the 90% methanol PVP solution shows a relatively low viscosity and no shear thinning. The PVP in this polymerization medium has proven to be much better at producing stable dispersions. This is only a preliminary picture of the influence of the solvency of the medium on the stabilizer efficiency, as the latter is also affected by other factors, such as the extent of graft formation on the PVP polymer, the properties of the particle surface, and the temperature, which warrant further investigation.

#### Effect of Methanol Content in the Medium

Dispersion polymerizations of BA in a methanol/water medium with varying methanol content were carried out according to the standard recipe given in Table I. In the recipe, the BA monomer concentration was maintained at 10 wt% based on the total weight. The ACPA initiator concentration was 1 wt% on monomer. Two kinds of stabilizer were used separately; PVP K30 was used at 20 wt%, or PVP K90 was employed at 5 wt%, based on the monomer weight. The costabilizer, Aerosol OTS, and the cross linker, AA, were not used. The methanol content in the medium was varied from 85% to 94% based on the total weight of the methanol/water mixture. The polymerizations were carried out at 70°C for 24 hr, and the final conversions were all greater than 90%.

Table III shows the effect of the methanol content in the medium on the PBA particle size and

**Table III Effect of the Methanol Content in the Medium on the Poly(Butyl Acrylate) Particle Size and Size Distribution**

Methanol (%)	PVP K30 <sup>a</sup> = 20%		PVP K90 <sup>b</sup> = 5%	
	$D_n^c$ ( $\mu\text{m}$ )	PDI <sup>d</sup>	$D_n$ ( $\mu\text{m}$ )	PDI <sup>d</sup>
85	1.9	1.039	1.5	1.112
88	2.4	1.034	2.2	1.034
90	2.9	1.028	2.5	1.018
92	4.0	1.027	4.1	1.025
94	7.6	1.087	9.7	1.067

<sup>a</sup> Polyvinylpyrrolidone, molecular weight 40,000 g/mol; GAF.

<sup>b</sup> Polyvinylpyrrolidone, molecular weight 360,000 g/mol; GAF.

<sup>c</sup>  $D_n$  = Number-average particle diameter.

<sup>d</sup> PDI = Polydispersity index ( $D_w/D_n$ , where  $D_w$  = weight-average particle diameter).

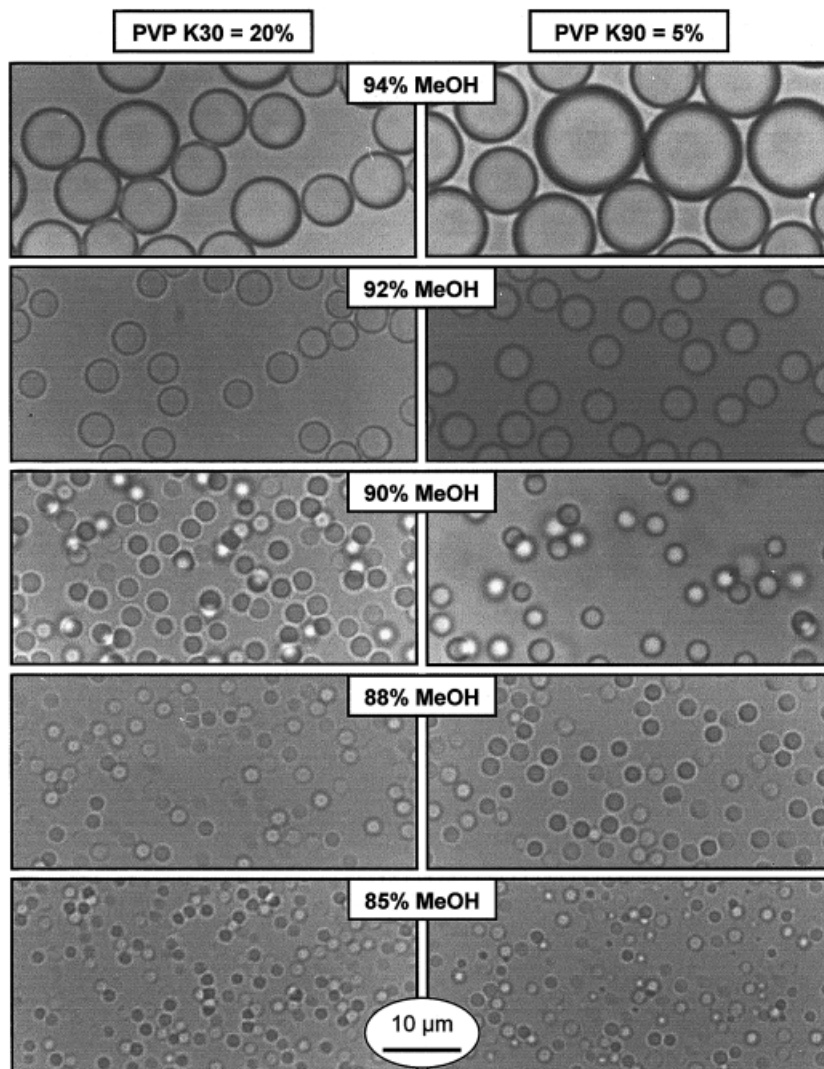
size distribution. Figure 9 shows optical micrographs of the resulting PBA particles. When PVP K30 was used, the PBA particle size varied from 1.9 to 7.6  $\mu\text{m}$ ; when PVP K90 was used, the PBA particle size varied from 1.5 to 9.7  $\mu\text{m}$ . These results demonstrate that the methanol content in the medium has a strong effect on the particle size.

The increase of the methanol content in the medium increases the solvency of the medium for the polymer and, as a result, oligomeric radicals with longer critical chain lengths would be formed before particle nucleation. According to the coagulative nucleation model, these oligomeric radicals with higher molecular weight would form a large surface area when they reach the  $\theta$ -point and form nuclei, and then they would undergo homocoagulation until the surface area and/or the number of these coagulated species is small enough to be stabilized by the PVP molecules (grafted and/or adsorbed). According to the stabilization model, the point at which the homocoagulation stops and the number of particles is fixed is called the stabilization point. The final particle size, consequently, is decided by the occurrence of this point. Thus, the particle size increases with increasing methanol content and/or the solvency of the medium. This result is in accordance with the conclusions that have been made for St and MMA dispersion systems.

#### Effect of Monomer Concentration

Dispersion polymerizations of BA in methanol/water mixtures were carried out by varying the





**Figure 9** Optical micrographs of poly(butyl acrylate) particles prepared by dispersion polymerization using different methanol/water media.

initial BA concentration. In the recipe (see Table I), 90% methanol was used as the medium. The BA monomer content was varied from 1.5 to 9.0 g; that is, 5%–30%, based on the total weight. The ACPA initiator concentration was maintained at 1 wt% on monomer; that is, 0.015–0.09 g. PVP K90 was used as stabilizer at a level of 10 wt% based on monomer; that is, 0.15–0.9 g. Thus, both the initiator and stabilizer concentrations increased with increasing monomer content. This design was chosen because of the convention of basing the initiator and stabilizer concentrations on the monomer. However, the obvious disadvantage is that in reality the three variables are changing simultaneously, which makes interpretation of the results difficult at best. The costabi-

lizer and the cross linker were not used in this set of experiments. The polymerizations were carried out at 70°C for 24 hr and the final conversions were all greater than 90%.

Table IV shows the effect of varying the monomer concentration on the PBA particle size and size distribution. Figure 10 shows optical micrographs of these PBA particles. When the BA concentration was increased from 5% to 30%, the PBA particle size first decreased and then slightly increased again. A similar tendency was also observed in the dispersion polymerization of MMA, in which the PMMA particle size exhibited a minimum at about 10 wt% monomer. However, in the latter study, all other component concentrations were held constant except for the monomer. In the

**Table IV** Effect of the Monomer Concentration on the Poly(Butyl Acrylate) Particle Size and Size Distribution

Butyl Acrylate on Total (wt %)	$D_n^a$ ( $\mu\text{m}$ )	PDI <sup>b</sup>
5	2.9	1.029
10	2.1	1.018
15	1.7	1.017
20	1.8	1.024
25	2.1	1.055
30	2.2	1.098

<sup>a</sup>  $D_n$  = Number-average particle diameter.

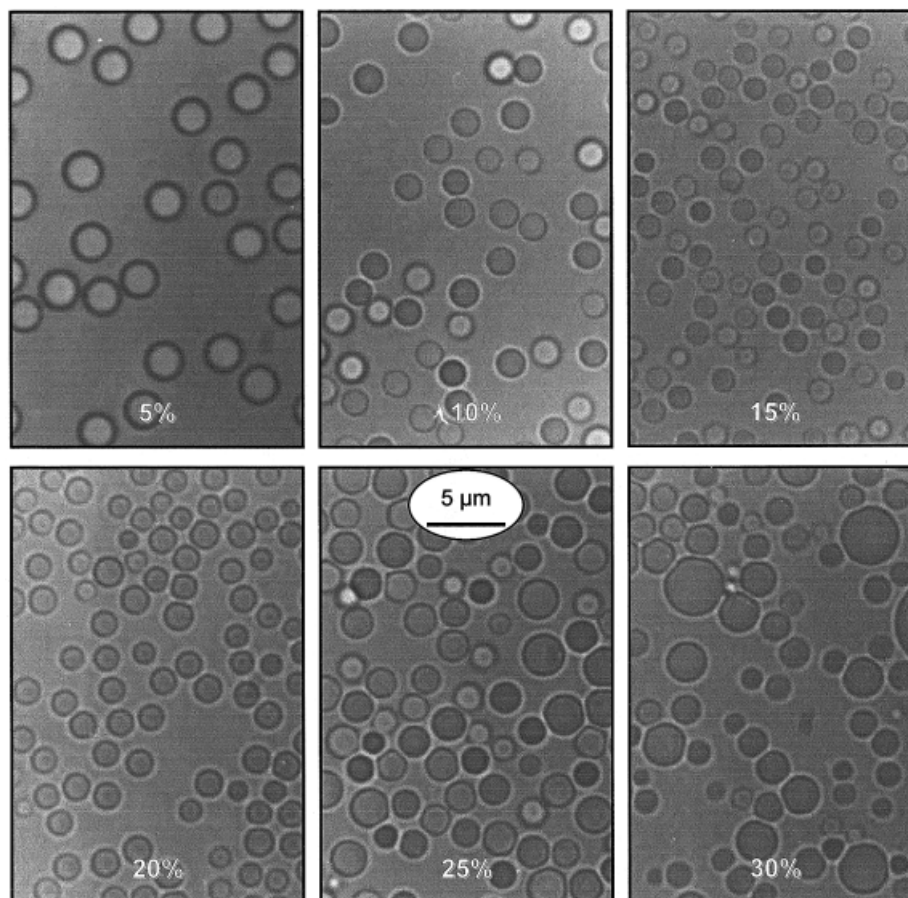
<sup>b</sup> PDI = Polydispersity index ( $D_w/D_n$ , where  $D_w$  = weight-average particle diameter).

BA system, the minimum particle size was attained at about 15% monomer; when the BA concentration was higher than 20%, the particle size

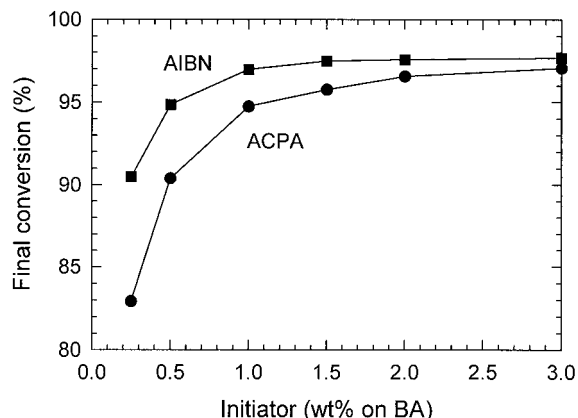
distributions broadened. As stated above, the interpretation of these results is difficult. Increasing the monomer concentration increases the solvency of the medium for the polymer and the rate of the formation of the oligomeric radicals (increasing initiator and monomer concentrations), which typically would lead to larger particles. However, the increase in monomer may also decrease the solvency of the medium for the PVP stabilizer, which could lead to more adsorption in addition to the increase in the amount of PVP, which would also promote more adsorption. The latter effects would lead to the generation of smaller and, therefore, more numerous particles, as seen for the 5%–15% BA data.

#### Effect of Type and Concentration of Initiator

The initiator type and concentration were varied in the next series of dispersion polymerizations of BA in methanol/water mixtures. In these recipes,



**Figure 10** Optical micrographs of poly(butyl acrylate) particles prepared by dispersion polymerization in 90/10 methanol/water medium using different monomer concentrations (wt% *n*-butyl acrylate on total).



**Figure 11** Effect of the type and concentration of initiator on the final conversion in dispersion polymerizations of *n*-butyl acrylate at 70°C for 24 hr.

the 90% methanol medium was used; the monomer concentration was 10 wt% based on total weight; the stabilizer, PVP K90, was used at a 10 wt% level, based on the monomer. Two kinds of initiator, AIBN and ACPA, were used. These two initiators have similar structures except that ACPA has two carboxyl groups, which give it a higher solubility in the medium. The 10-hr half-life decomposition temperatures are 64°C for AIBN (measured in toluene) and 69°C for ACPA (measured in water).<sup>30</sup> The costabilizer and the cross linker were not used in this set of experiments.

Figure 11 shows the effect of the type and concentration of initiator on the final conversions obtained for dispersion polymerizations of BA at 70°C for 24 hr. The final conversions increased with increasing initiator. The use of AIBN resulted in slightly higher conversions compared with ACPA, whereas the conversions reached at least 95% when the initiator concentration was higher than 1 wt% on monomer. Table V shows the effect of the initiator type and concentration on the PBA particle size and size distribution obtained in these dispersion polymerizations (the corresponding final conversions are shown in Fig. 11). In both cases, the PBA particle size slightly decreased with increasing initiator concentration. These results differ from those reported previously for the dispersion polymerizations of St<sup>11</sup> and MMA,<sup>16</sup> in which the particle size increased with increasing initiator concentration.

At higher initiator concentrations, more oligomeric radicals would be created. The presence of a larger number of oligomeric radicals in the me-

dium can influence the number of particles in two different ways: forming larger numbers of particles if sufficient stabilizer is available to stabilize these particles, which would lead to a smaller final particle size; or increasing the coagulation rate, resulting in fewer particles, which would certainly lead to a larger final particle size. At this point, it is necessary to discuss the nature of the stabilizer in these dispersion polymerizations. Some consider that the PVP itself can adsorb, albeit to a relatively small degree, to stabilize the particles. Others contend that only graft copolymer, formed *in situ*, can act as stabilizer. It is likely that reality lies in between and that this reality is dependent on the specific system being studied. Some results obtained here support grafting as an important stabilization mechanism in the dispersion polymerization of BA, in contrast to other results seen for styrene and MMA dispersion polymerizations. This can be shown by the remarkably different results of dispersion polymerizations of BA and St using “recycled” PVP stabilizer. The recycled PVP stabilizers were obtained from the supernatants of each latex dispersion, that is, PBA, PSt, and PMMA, by centrifugation at 5000 rpm for 20 min after initial dispersion polymerizations were carried out using PVP K30 stabilizer. Three sets of dispersion polymerizations of BA, St, and MMA were conducted by using the corresponding recycled PVP stabilizers under the same polymerization conditions as those of the initial dispersion polymerizations. The resultant particle size of the PBA particles

**Table V** Effect of the Type and Concentration of the Initiator on the Poly(Butyl Acrylate) Particle Size and Size Distribution

[Initiator] on Butyl Acrylate (wt %)	AIBN <sup>a</sup>		ACPA <sup>b</sup>	
	$D_n^c$ (μm)	PDI <sup>d</sup>	$D_n$ (μm)	PDI
0.25	2.0	1.020	2.2	1.017
0.50	2.1	1.023	1.9	1.017
1.00	2.0	1.018	2.1	1.019
1.50	1.8	1.022	1.9	1.024
2.00	1.9	1.022	1.9	1.029
3.00	1.8	1.025	1.9	1.026

<sup>a</sup> 2,2'-azobis(isobutyronitrile); Wako Chemicals USA, Inc.

<sup>b</sup> 4,4'-azobis(4-cyanopentanoic acid); Wako Chemicals USA, Inc.

<sup>c</sup>  $D_n$  = Number-average particle diameter.

<sup>d</sup> PDI = Polydispersity index ( $D_w/D_n$ , where  $D_w$  = weight-average particle diameter).

was much smaller than that obtained from the original dispersion polymerization, whereas the particle size of the PSt and PMMA latexes were almost the same as those of the original dispersion polymerizations. These results indicate that more extensive grafting occurred in the dispersion polymerization of BA, where much of the grafted PVP was available through separation of the supernatant. It is expected then that the effect of initiator concentration on the final particle size is likely to be dependent on the competition between the rates of coagulation and graft formation. Therefore, depending on the specific type of polymer, medium, and stabilizers, an increasing initiator concentration can increase, have little influence on, or decrease the final particle size.

#### Effect of Concentration and Molecular Weight of Stabilizer

Two kinds of stabilizer were used separately based on the recipe given in Table I (i.e., PVP K30 or PVP K90); the amount was varied from 0.015 to 1.5 g; that is, 5 wt% to 50 wt% based on the monomer. In the recipe, the BA monomer concentration was maintained at 10 wt% based on the total weight (i.e., 3 g); the ACPA initiator was 1 wt% on monomer. The costabilizer and the cross linker were not used here. The polymerizations were carried out at 70°C for 24 hr, and the final conversions were all greater than 90%.

Table VI shows the influence of PVP type (molecular weight) and concentration on the resulting PBA particle size and size distribution. Using the same PVP concentrations (by weight), larger particles were obtained with PVP K30. As expected, the particle size decreased with increasing stabilizer concentration for both PVP systems. The particle size distributions became narrower with increasing PVP K30 concentration. Figure 12 shows optical micrographs of these PBA particles. The higher molecular weight PVP K90 seems to be a more efficient stabilizer for the PBA particles; that is, compared with PVP K30. Less PVP K90 was needed to attain the same particle size. Note that the PBA particles are about the same size for the systems that used 5% PVP K90 and those that used 20% PVP K30 (i.e., the molar concentration of PVP K-30 is about 36 times that of PVP K90).

However, it was reported that broader particle size distributions were obtained in dispersion polymerizations of St<sup>11</sup> and MMA<sup>16</sup> when PVP K90 was used, compared with their PVP K30 counterparts.

**Table VI** Effect of the PVP Molecular Weight and Concentration on the Poly(Butyl Acrylate) Particle Size and Size Distribution

PVP Type	PVP on Butyl Acrylate (wt %)	$D_n^b$ ( $\mu\text{m}$ )	PDI <sup>c</sup>
PVP K30 <sup>a</sup>	5	4.2	1.114
	10	3.9	1.075
	20	3.1	1.041
	30	2.8	1.035
	40	2.2	1.034
	50	1.9	1.036
PVP K90 <sup>d</sup>	5	2.6	1.052
	10	2.1	1.024
	20	1.8	1.023
	30	1.5	1.020
	40	1.3	1.021
	50	1.1	1.021

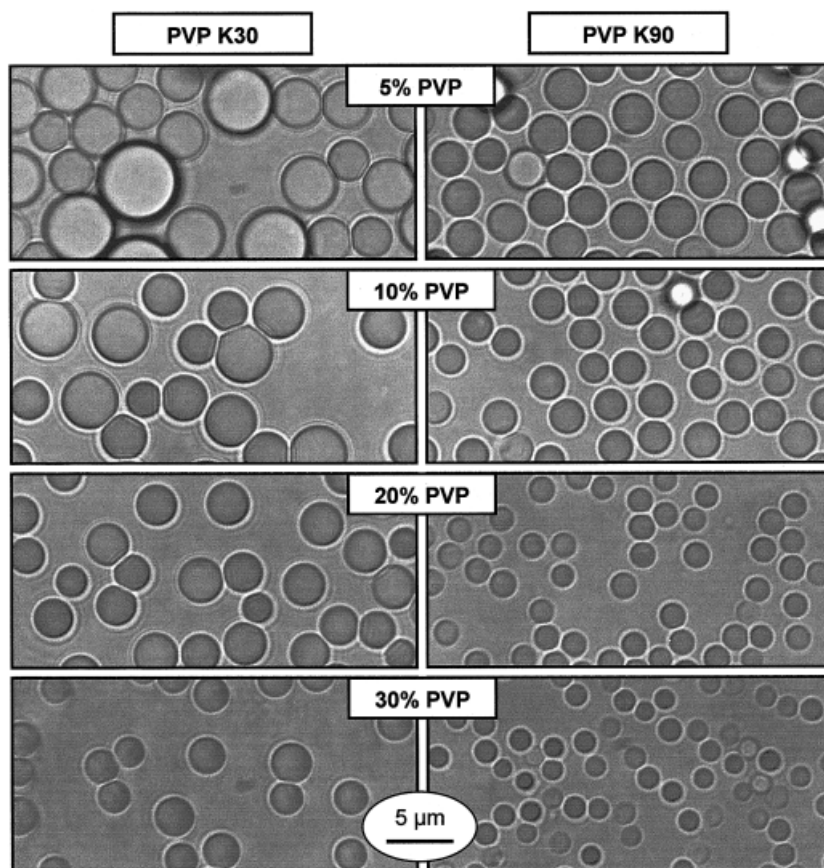
<sup>a</sup> Polyvinylpyrrolidone, molecular weight 40,000; GAF.

<sup>b</sup>  $D_n$  = Number-average particle diameter.

<sup>c</sup> PDI = Polydispersity index ( $D_w/D_n$ , where  $D_w$  = weight-average particle diameter).

<sup>d</sup> Polyvinylpyrrolidone, molecular weight 360,000; GAF.

It was observed that the PBA particle size distribution became broad and the colloidal stability of the dispersion became poor when the concentration of PVP stabilizer was lower than 1%. If the polymer particles are actually stabilized primarily by grafted PVP, it would be of interest to know how many of these grafted PVP molecules are needed to stabilize the particles in a dispersion system. Although it is difficult to directly obtain this number by measurement, a rough estimation can be made by a simple calculation. Assume that 2- $\mu\text{m}$  polymer particles are prepared from a dispersion system that contains 10 g monomer and 1 g PVP K90 stabilizer in the reaction medium. A study using small-angle neutron scattering (SANS)<sup>31</sup> indicated that the radius of gyration of a typical random coil polymer chain (e.g., polystyrene in cyclohexane) with a molecular weight on the order of  $10^5$  is about 100 Å. Thus, it is reasonable to assume that the radius of gyration of a PVP K90 molecule, which has a molecular weight of  $3.6 \times 10^5$ , is roughly 100 Å in alcohol/water medium. By comparing the total surface area of the polymer particles and the area that can be covered by these PVP coils, it can be calculated that about 0.06 g of the PVP (i.e., 6%) is needed for a full coverage of the whole surface of the polymer particles. That is, if grafting is the only means of stabilization, six PBA-graft-PVP molecules must be formed from a hundred PVP



**Figure 12** Optical micrographs of poly(butyl acrylate) particles prepared by dispersion polymerization using different amounts (wt%) of polyvinylpyrrolidone K30 and K90 stabilizer.

molecules. Considering the low chain transfer constant to polymer for most radicals ( $\sim 10^{-3}$ – $10^{-4}$ ), a certain concentration of PVP molecules is needed for the formation of enough grafted polymer to stabilize the particles. Thus, most of that 1 g of PVP remains unreacted to generate the 60 mg of grafted PVP. This can also explain why a dispersion can remain stable after removing all of the solids in the supernatant; and in most cases the weight of the solids removed is higher than the initial amount of PVP added because of the presence of some grafted PVP molecules and because of some soluble polymer chains having low molecular weights.

#### Effect of Costabilizer

The amount of costabilizer, Aerosol OTS, was varied from 0.075 to 1.8 g (i.e., from 2.5 wt% to 60 wt%) based on the monomer, as indicated in Table I. In these recipes, the 90% methanol medium

was used; the monomer concentration was 10 wt%, based on the total recipe weight; the initiator, ACPA, was 1 wt% on monomer; and PVP K30 and PVP K90 were used separately at different levels as shown in Table VII. The cross linker was not used. The polymerizations were carried out at 70°C for 24 hr, and the final conversions were all greater than 90%.

Table VII shows the influence of the concentration of costabilizer on the size and size distribution of the PBA particles that were prepared using different types and amounts of PVP. The sizes of the PBA particles that were prepared by using PVP K90 at either 5% or 10% concentration do not show any significant changes with the addition of Aerosol OTS costabilizer. For the PVP K30 systems, however, the particle sizes became smaller with the addition of 2.5% Aerosol OTS, and the particle size distribution became narrower for the system with 5% PVP K30. No obvious changes

**Table VII Effect of the Costabilizer Aerosol OTS Content on the Poly(Butyl Acrylate) Particle Size and Size Distribution**

Aerosol OTS on BA (wt %) <sup>a</sup>	$D_n^b$ ( $\mu\text{m}$ )/PDI <sup>c</sup>			
	PVP K90 <sup>d</sup>		PVP K30 <sup>e</sup>	
	5%	10%	5%	20%
0	2.6/1.057	2.2/1.018	4.2/1.114	3.1/1.041
2.5	2.7/1.054	2.1/1.022	3.6/1.022	2.7/1.032
5	2.5/1.055	2.0/1.019	3.5/1.021	2.7/1.029
10	2.8/1.083	2.3/1.024	3.5/1.023	2.7/1.028
20	2.6/1.063	2.2/1.058	3.2/1.028	2.6/1.044
40	2.5/1.056	2.3/1.038	3.3/1.019	2.7/1.069
60	2.7/2.867	2.3/1.048	3.4/1.017	2.7/1.070

<sup>a</sup> Sodium dioctyl sulfosuccinate in petroleum distillate, Cytec Industries.

<sup>b</sup>  $D_n$  = Number-average particle diameter.

<sup>c</sup> PDI = Polydispersity index ( $D_w/D_n$ , where  $D_w$  = weight-average particle diameter).

<sup>d</sup> Polyvinylpyrrolidone, molecular weight 360,000; GAF.

<sup>e</sup> Polyvinylpyrrolidone, molecular weight 40,000; GAF.

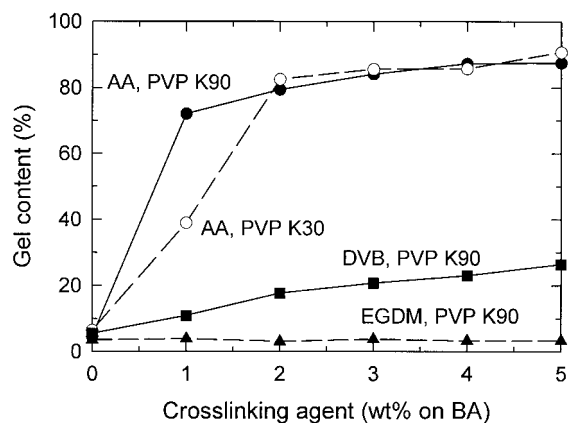
can be observed when the Aerosol OTS concentration was higher than 2.5% in all four systems. These results indicate that the costabilizer can help stabilizing nuclei to form more particles to some degree only in the case where the stabilization efficiency of the stabilizer is poor; that is, with PVP K30. For PVP K90 systems, the stabilization by the PVP K90 is relatively good and no effect of the costabilizer was evident.

### Effect of Cross Linker

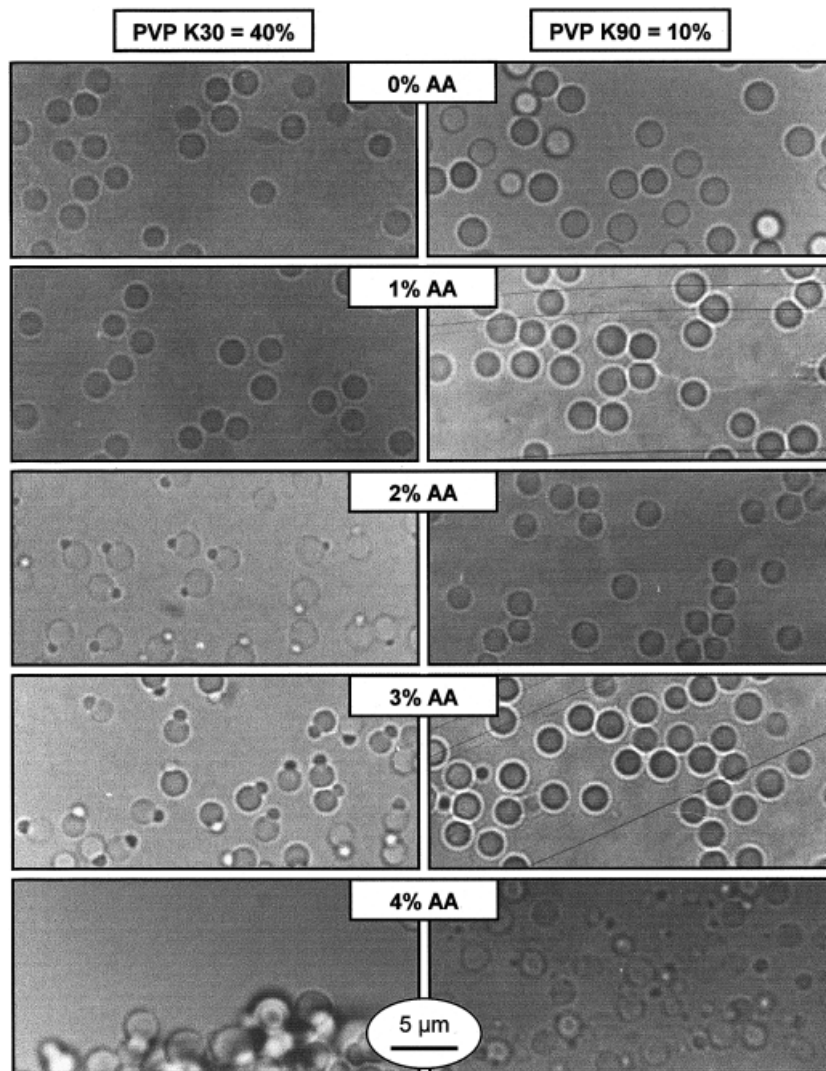
Three kinds of cross linker were used in dispersion polymerizations of BA: tetra-(ethylene glycol) dimethacrylate (EGDM), divinylbenzene (DVB), and AA. The amounts of these cross linkers were varied from 0 to 0.15 g (0 wt% to 5 wt% based on the monomer). In these recipes, the 90% methanol medium was used; the monomer concentration was 10 wt% based on the total recipe weight; and the initiator, ACPA, was 1 wt% on monomer. Two kinds of stabilizer and costabilizer systems were used in this set of experiments: 0.3 g PVP K90 (10 wt% on monomer) plus 0.18 g Aerosol OTS (6 wt% on monomer), and 1.2 g PVP K30 (40 wt% on monomer) plus 0.36 g Aerosol OTS (12 wt% on monomer). The polymerizations were carried out at 70°C for 24 hr, and the final conversions were higher than 90%. The gel content was measured by a butanol extraction method. It should be mentioned that particles with broad PSDs were obtained in the absence of the costabilizer. This effect of the costabilizer on

the particle size distribution was not observed in the systems without the cross linker.

Figure 13 shows the effect of the type and concentration of cross linker on the gel content of the resulting PBA particles. It was found that the EGDM had almost no effect on the gel content of the resulting PBA particles; that is, as the EGDM amount increased from 0% to 5%, the gel content remained at a low and constant value of about 3.5%. When DVB was used as the cross linker, the gel content increased with increasing DVB but did not go higher than 30%. However, the gel content quickly increased with increasing AA concentration; when the amount of AA was higher



**Figure 13** Effect of the concentration of the crosslinking agents on the gel content of poly(butyl acrylate) particles.

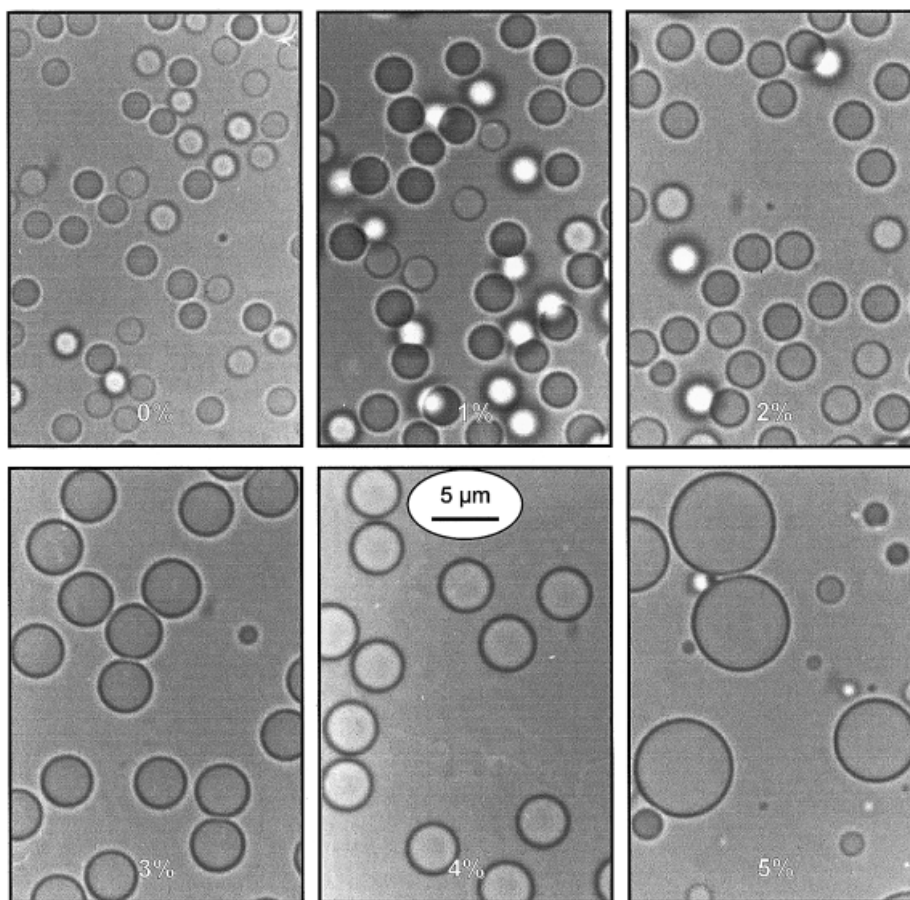


**Figure 14** Optical micrographs of poly(butyl acrylate) particles prepared by dispersion polymerization using different amounts of allyl acrylate cross linker.

than 2 wt%, based on BA, the gel content was higher than 80%. These results indicate significant differences in the cross-linking efficiencies of these three cross linkers in the dispersion polymerization of BA. In contrast, both EGDM and DVB were used successfully as cross-linking agents in dispersion polymerizations of St<sup>11</sup> and MMA.<sup>16</sup> The different effects of the cross linkers on the final gel fractions for the resultant polymers suggest that the reactivity ratios of the monomer and the cross linker should be considered when a cross linker is selected.

The gel contents varied in a similar manner when the two PVP stabilizers were used, increasing with increasing AA. When the amount of AA was higher than 2 wt% on BA, the gel contents

were almost the same for the two stabilizer systems, as shown in Figure 13. However, obviously different morphologies of the PBA particles in the high-gel regions were observed for the two stabilizer systems. Figure 14 shows optical micrographs of the PBA particles. When the amount of AA was lower than 2 %, the gel contents were lower than 70%, and normal spherical particles could be observed for both PVP stabilizers. When the amount of AA exceeded 2 wt% and the gel contents were higher than 70%, the PVP K90 system still produced spherical particles, but the PVP K30 system resulted in nonspherical morphologies with identifiable phase separation. When the amount of AA was higher than 4%, some coagulation and secondary small particles



**Figure 15** Optical micrographs of poly(butyl acrylate) particles prepared by dispersion polymerization using different amounts of tetra-(ethylene glycol) dimethacrylate (wt% based on total monomer).

were observed in the system. For the nonspherical particles, it seems that phase separation occurred between the linear polymer and the cross-linked polymer. The reason that this kind of morphology was not observed in the PVP K90 systems is not understood.

Although it seems that EGDM is not an effective cross linker for increasing the gel content of the PBA particles, as indicated in Figure 13, it does have a strong effect on the resulting PBA particle size. The PBA particle size quickly increased from 2 to 5  $\mu\text{m}$  when the EGDM concentration was increased from 0% to 5%. Figure 15 shows optical micrographs of the PBA particles. The presence of EGDM in the system could increase the solubility of the oligomeric radicals comprised of BA/EGDM, which would certainly increase the final particle size.

Another conclusion that can be made from the results of this set of experiments and the results

obtained by others is that the presence of a cross linker affects the stabilization. Particles with broader particle distributions and coagulum were frequently obtained when the cross-linker concentration was increased. The presence of the cross linker, especially during the nucleation period, may cause the inter- or intra-cross-linking of PVP molecules, which would reduce the amount of effective stabilizer and the number of grafted PVP chains. The effectiveness of the costabilizer, as mentioned above, in preparing monodisperse particles in this set of experiments also indicates less effective stabilization by the PVP in the presence of a cross linker.

#### Effect of Comonomer

In order to prepare P(BA-co-St) particles with various copolymer compositions, dispersion polymerizations were carried out with three BA/St



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

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

<sup>a</sup> Polyvinylpyrrolidone, molecular weight 40,000; GAF.

<sup>b</sup> Polyvinylpyrrolidone, molecular weight 360,000; GAF.

<sup>c</sup> Sodium dioctyl sulfosuccinate in petroleum distillate, Cytec Industries.

<sup>d</sup>  $D_n$  = Number-average particle diameter.

<sup>e</sup> PDI = Polydispersity index ( $D_w/D_n$ , where  $D_w$  = weight-average particle diameter).

monomer weight ratios of 70/30, 50/50, and 30/70 according to the standard recipe shown in Table II. The polymerizations were carried out at 70°C for 24 hr, and the final conversions were higher than 90%. The resulting particles exhibited broad PSDs with the presence of a large amount of small particles. Efforts were made to achieve a narrow distribution in particle size by varying the concentration and the type of PVP stabilizers, that is, PVP K30 or PVP K90; however, the resultant PSDs of the copolymer particles were not obviously improved.

Copolymer particles with relatively narrow PSDs were finally obtained by using mixed PVP K30/PVP K90 stabilizer systems. Table VIII shows the recipes developed for preparing P(BA-co-St) particles by dispersion copolymerization. Note that for the various BA/St ratios, different PVP K30/K90 mixtures were used as the stabilizer system, and different methanol/water mixtures were used as the medium. The resulting micron-size copolymer particles had quite narrow size distributions, as shown in Table VIII. These results reinforce the general observation that dispersion polymerizations are quite sensitive to the composition of the system. To obtain narrow particle size distributions, adjustment of this composition must often take place to find the suitable range of conditions producing monodisperse particles.

## SUMMARY

The preparation of micron-size poly(*n*-butyl acrylate) latex particles via dispersion polymerization

was investigated with the goal of producing particles of varying sizes and possessing narrow particle size distributions. Polyvinylpyrrolidone (PVP K30 and K90) was used as the stabilizer. Successful polymerizations of styrene and methyl methacrylate in ethanol and methanol could not be extended to BA because of the significant solubility of the PBA in these media. Instead, alcohol/water mixtures were used successfully to prepare micron-size, monodisperse PBA particles. The best results were obtained using a 90/10 methanol mixture as the medium and PVP K90 as the stabilizer. Other variables studied included the initial monomer concentration; the type and concentration of initiator; and the presence of a costabilizer (Aerosol OTS), cross-linking agents, and a comonomer (styrene). The sensitivity of the polymerization to all variables was noted.

In contrast to the trends found in most other dispersion polymerizations, the particle size was found to decrease with increasing initiator concentration. The presence of significant amounts of grafted PVP in the supernatant was indicated in recycling experiments. The competition between grafting, adsorption, and flocculation is considered an essential area of future investigation to explain the experimental observations.

Financial support from the Emulsion Polymers Liaison Program is greatly appreciated.

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