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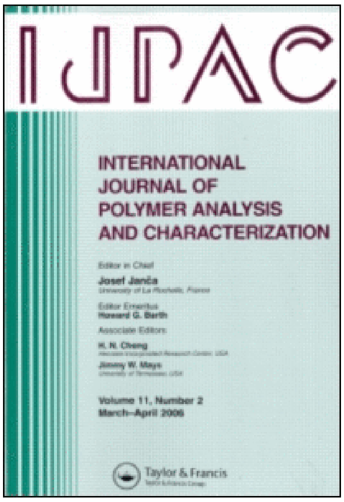

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Effects of Reaction Parameters on Particle Size, Molecular Weight, and Kinetics for Dispersion Polymerization of *n*-Butyl Acrylate

Ki-Chang Lee[a]; Jai-Hyuk Her[a]; Kwang-Jea Kim[b]
[a] Department of Polymer Science and Engineering, Engineering Research Institute, Gyeongsang National University, Jinju, Korea [b] Institute of Polymer Engineering, The University of Akron, Akron, Ohio, USA

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Effects of Reaction Parameters on Particle Size, Molecular Weight, and Kinetics for Dispersion Polymerization of *n*-Butyl Acrylate

Ki-Chang Lee,[1] Jai-Hyuk Her,[1] and Kwang-Jea Kim[2]
[1]Department of Polymer Science and Engineering, Engineering Research
Institute, Gyeongsang National University, Jinju, Korea
[2]Institute of Polymer Engineering, The University of Akron,
Akron, Ohio, USA

Abstract: Poly(acrylic acid) (PAA) prepared in the presence of *n*-dodecyl mercaptan (DDM) was used as a steric stabilizer for dispersion polymerization of *n*-butyl acrylate (BA). The effects of polymerization parameters such as alcohol/water ratios, concentration and molecular weight of PAA stabilizer, concentration and species of initiator, concentration of monomer, and polymerization temperature on number-average particle size and size distribution, weight-average molecular weight, molecular weight distribution, and polymerization rate were investigated. The effects of medium ratio, stabilizer and monomer concentration, and polymerization temperature were similar to those obtained in the conventional dispersion polymerization. However, the effect of molecular weight of PAA stabilizer showed significantly different trends than the existing results. As the molecular weight of PAA decreased, the molecular weight of poly(butyl acrylate) (PBA) and rate of polymerization increased, while the particle size of PBA decreased. This is due to the formation of PAA-*block*-PBA copolymers, which played a crucial role in particle stabilization.

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Correspondence: Ki-Chang Lee, Dept. of Polymer Science and Engineering, Engineering Research Institute, Gyeongsang National University, Jinju 660-701, Korea. E-mail: kclee@gnu.ac.kr

Keywords: Dispersion polymerization of *n*-butyl acrylate; Formation of PAA-*block*-PBA; *n*-Dodecyl mercaptan; Poly(acrylic acid); Polymerization rate;

INTRODUCTION

Monodispersed microspheres have a variety of applications in the fields of calibration standards, analytical chemistry, bioengineering, and coating, among others, due to their special properties, such as higher specific surface area, the ability of surface reaction, and stronger adsorption.[1–4] They can be prepared by the emulsion or suspension polymerization through processes of two or three steps, as described in previous studies.[5,6] However, these processes are complex, time-consuming, and difficult to implement in large scale.

Preparation of monodisperese particles of micrometer size by dispersion polymerization has been extensively studied because of the simplicity of the process. There are many reports on dispersion polymerization investigating the polymerization mechanism, effect of polymerization parameters, kinetics, modification with functional groups, cross-linking, polymerization processing, and other topics. The monomers studied were limited to general-purpose monomers such as styrene (St)[7–15] or methyl methacrylate (MMA).[7,16–21]

Very few reports are available on dispersion polymerization of *n*-butyl acrylate (BA) even though BA is a type of monomer widely used in industry. Wang et al. have recently reported dispersion polymerization of BA where they used one of the most common stabilizers (poly (*N*-vinyl pyrrolidone) (PVP)) and polymerization mediums (methanol/water mixture).[22–24] Most of the studies related to the dispersion polymerization of BA have been limited to the copolymerization of BA with St or MMA.[25–27] Furthermore, there are few publications reporting data on molecular weight and molecular weight distribution of poly (butyl acrylate) particles prepared by dispersion polymerization.

In this study, poly(acrylic acid) (PAA) was prepared by solution polymerization in the presence of *n*-dodecyl mercaptan (DDM) as a chain transfer agent and then used in the dispersion polymerization of BA as a steric stabilizer. The dispersion polymerization of BA was carried out in mixtures of methanol/water and ethanol/water. The effects of polymerization parameters such as alcohol/water ratios, concentration and molecular weight of stabilizer, concentration and species of initiator, concentration of monomer, and polymerization temperature on the particle size and its distribution, molecular weight and its distribution, and reaction kinetics have been studied.

EXPERIMENTAL SECTION

Materials

BA (Aldrich) monomer was washed with 10 wt.% aqueous sodium hydroxide solution to remove the inhibitor. 2,2′-Azobis (isobutyronitrile) (AIBN, Junsei) as initiator was recrystallized in methanol. A mixture of methanol (Daejung Chemical) or ethanol (Daejung Chemical) with water was used as the polymerization medium. PAA ($\overline{M_v} = 61{,}700\,\mathrm{g/mol}$) prepared by solution polymerization was used as a particle stabilizer. All other materials were used without further purification, including 2,2′-azobis (2,4-dimethylvaleronitrile) (ADVN, Junsei), 2,2′-azobis (2-methylbutyronitrile) (AMBN, Wako Chemicals), benzoyl peroxide (BPO, Fluka), 1,4-dioxane (Daejung Chemical), *n*-dodecylmercaptan (DDM, Fluka), and petroleum ether (Daejung Chemical).

Synthesis of Poly(Acrylic Acid) as Steric Stabilizer

The mixture of acrylic acid (AA, 24 g), 1,4-dioxane (56 g), AIBN (0.01 g), and DDM (0, 0.12, 0.24 g) was added to a 250 mL round-bottom flask equipped with a reflux condenser, thermocouple, nitrogen purging inlet, and anchor-type stirrer, and it was stirred at 150 rpm and 65°C for 24 h under nitrogen. The prepared solution of PAA was added to petroleum ether (non-solvent) and maintained for 24 h. The precipitated PAA was recovered and dried at room temperature for 72 h under reduced pressure. The viscosity-average molecular weights of PAA prepared with 0, 0.5, and 1 wt.% of DDM concentration were 108,800, 61,700, and 34,000 g/mol, respectively (determined at aq. 1 M NaCl, 25°C, $K = 0.01547\,\mathrm{mL/g}$, $a = 0.9$).[28]

Dispersion Polymerization of *n*-Butyl Acrylate

The standard recipe for the dispersion polymerization of BA is given in Table I. The mixture of alcohol/water and PAA was added to a 250 mL round-bottom flask equipped with a reflux condenser, thermocouple, nitrogen purging inlet, and anchor-type stirrer, and the mixing temperature was raised gradually to 70°C under a nitrogen atmosphere at 150 rpm. When the temperature reached 70°C the mixture of BA and AIBN was added to the reaction flask, and the reaction was allowed to proceed for 24 h.

Table I. Standard recipe for dispersion polymerization of *n*-butyl acrylate

Ingredient	Weight (%)	Amount (g)
n-Butyl acrylate	9	14.4
AIBN	0.1	0.16
PAA[a]	0.9	1.44
Methanol/water	81/9	129.6/14.4
or	or	or
Ethanol/water	72/18	115.2/28.8
Total	100	160

Polymerization conditions: 70°C, 150 rpm for 24 h.
[a] Poly(acrylic acid); $\overline{M_v} = 61,700\,\text{g/mol}$.

Characterization

The particle size of the latex was measured by an optical microscope (Leica LMDM), and particle size distribution (PSD) was determined as the ratio of the number ($\overline{D_n}$) and weight ($\overline{D_w}$) average diameters as follows:

$$\overline{D_n} = \sum_{i=0}^{N} D_i/N \tag{1}$$

$$\overline{D_w} = \sum_{i=0}^{N} D_i^4 \Big/ \sum_{i=0}^{N} D_i^3 \tag{2}$$

where N is the total number of particles counted and D_i is the diameter of particle i.

$$PSD = \overline{D_w}/\overline{D_n} \tag{3}$$

The conversion was measured by the gravimetric method, and polymerization rate was calculated from the slope of the curve of reaction time versus conversion. The molecular weight and molecular weight distributions (MWD) were obtained by gel permeation chromatography (GPC) using a refractive index detector (Shodex RI-101, Japan). Four columns in a series were used (Shodex GPC LF-G, LF-404 (x3)). Distilled tetrahydrofuran (THF) was used as a mobile phase (flow rate = 0.5 mL/min). The calibration was carried out by using monodisperse polystyrene standards (3, 4, 8, 30, 105, 225, and 403 kg/mol).

RESULTS AND DISCUSSION

Effects of Medium Ratio in Alcohol/H_2O

For 100 wt.% methanol and 90 ~ 100 wt.% ethanol, dispersion polymerization of BA occurred in clear-solution state throughout the polymerization without showing any turbidity, and then PBA with low molecular weights of 18,500 and 15,300 g/mol respectively was obtained. However, with increasing water content from 10 to 40 wt.% in the methanol/water system, the particle size decreased from 1.9 to 0.8 μm, the particle size distribution became wider from 1.01 to 1.27, and the molecular weight and molecular weight distribution increased from 59,600 to 274,200 g/mol and from 2.07 to 4.76, respectively. Similar results were also obtained in ethanol/water system.

Figure 1 shows the curve of polymerization rate versus conversion for the dispersion polymerization as a function of reaction medium in methanol/water system, indicating an increase in polymerization rate with increasing concentration of water. The polymerization rate for 100 wt.% methanol decreased continuously with reaction time where solution polymerization occurred. The solid line in Figure 1 shows the polymerization rates of six different reaction media measured at 30 min from the beginning of the reaction (the solid lines from all the curves of polymerization rate versus conversion in this article were measured at 30 min after initiation of reaction). This is also an indication that the polymerization rate and conversion increased with increasing water content in the medium.

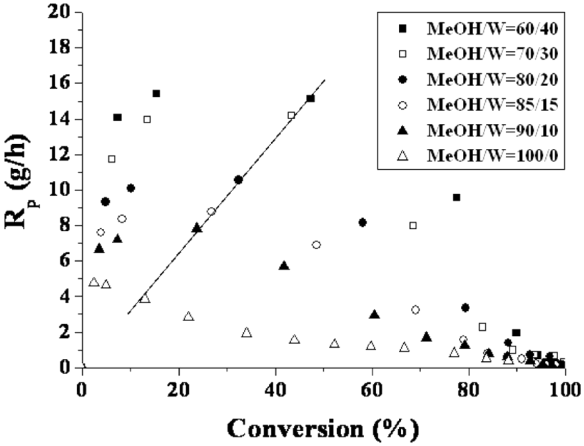

Figure 1. Effect of MeOH/Water medium ratio on polymerization rate.

Generally in dispersion polymerization, the oligomeric radicals are formed in the early stage of polymerization in the medium and then the particles are formed with the help of steric stabilizers, which are grafted or adsorbed onto the oligomeric radicals. After the formation of nuclei, particle growth takes place within the monomer-swollen polymer particles or from the surface of polymer particles through the capture of oligomeric radicals from the continuous phase.[2,26,29]

For 100 wt.% methanol and 90 ~ 100 wt.% ethanol medium, particle nuclei were not created due to the higher solvency of the medium to the chains of the formed PBA. The polymerization rates at the beginning of the polymerization increased suddenly with the start of the reaction, reached the top point, and then continuously decreased with the decrease of the monomer concentration in the medium. Consequently, the prepared PBA showed relatively low molecular weight and narrow molecular weight distribution.[10,26,29] On the other hand, with increase of water content from 10 to 40 wt.% in the reaction medium, the polarity of the reaction medium increases and the solubility of the formed oligomers decreases. Therefore, the particle size of the latex became smaller along with the increasing number of particle nuclei. Also, the polymerization mainly takes place within the particles with increase of water content. The increase of the molecular weight of PBA particles and the rate of polymerization can be explained by delayed radical termination within the particles due to increased viscosity.[26] The increase of the molecular weight distribution with increasing water content is also due to the coexistence of the high molecular weight polymer chains formed inside the particles and low molecular weight polymer chains generated from the continuous phase at the beginning of the reaction.[10]

Effects of PAA Concentration

In the methanol/water system, the particle size decreased from 1.9 to 1.2 μm, and the particle size distribution increased from 1.01 to 1.10 with increasing PAA concentration from 10 to 40 wt.% (based on monomer). Also the molecular weight and molecular weight distribution increased from 59,600 to 75,100 g/mol and from 2.07 to 3.07, respectively. Similar phenomena were observed in the ethanol/water system.

Figure 2 shows the log-log plot of particle size versus PAA concentration and the micrographs of the resulting particles. Figure 3 presents the plots of the polymerization rate versus conversion of dispersion polymerization depending on the various concentrations of PAA stabilizer. The dependence of particle size on the PAA concentration in methanol/water and ethanol/water systems exhibited the slopes −0.34 and −0.23, respectively. In the dispersion polymerization

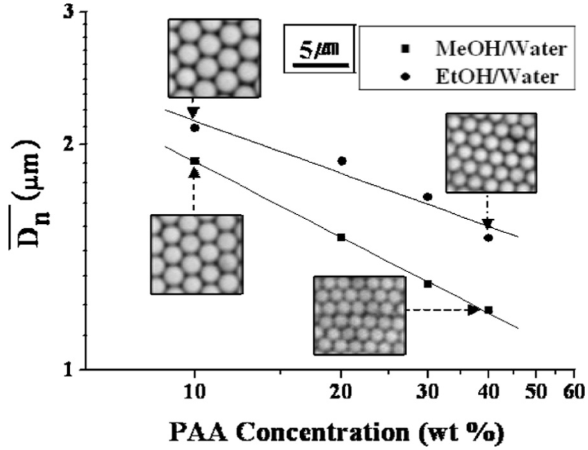

Figure 2. Effect of PAA concentration on particle size.

of BA in methanol/water reported by Wang et al.[22] the dependence of particle size on the PVP K-30 concentration exhibited the slope −0.35. Generally in dispersion polymerization, the particle size decreases with increasing concentration of stabilizer due to increasing stabilization efficiency, and polymerization rate and molecular weight increase and vice versa.[2,8,10,26,29] Therefore, the polymerization rate increased with increasing PAA concentration from 10 to 40 wt.% due to the increasing

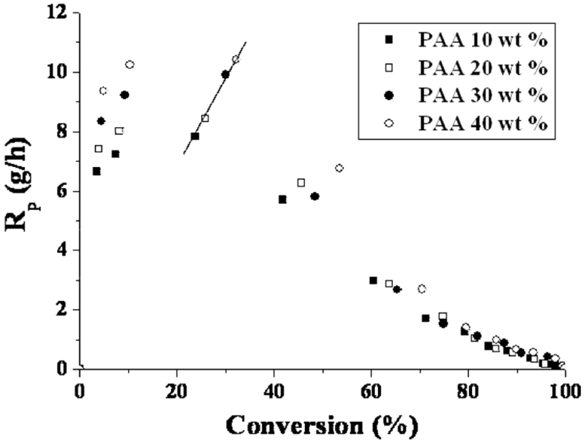

Figure 3. Effect of PAA concentration on polymerization rate (MeOH/water = 90/10, wt./wt.%).

Table II. Effect of the molecular weight of PAA on the particle size and molecular weight

	MeOH/water (90/10, w/w)				EtOH/water (80/20, w/w)			
$\overline{M_v}$ of PAA (g/mol)	$\overline{D_n}$ (μm)	PSD	$\overline{M_w}$ (g/mol)	MWD	$\overline{D_n}$ (μm)	PSD	$\overline{M_w}$ (g/mol)	MWD
34,000	1.7	1.01	66,200	2.42	2.0	1.01	41,900	2.32
61,700	1.9	1.01	59,600	2.07	2.1	1.01	28,200	2.17
108,800	2.3	1.08	47,900	2.14	2.6	1.09	22,500	1.93

9.0 wt.% monomer, 90 wt.% alcohol/water (based on total), 10 wt.% PAA, 1.11 wt.% AIBN (based on monomer), 70°C, and 150 rpm for 24 h.

number of particles and the dominant polymerization inside the particle, as shown in Figure 3.

Effects of Molecular Weight of PAA

Table II shows the effect of molecular weight of PAA on the particle size and size distribution, molecular weight, and molecular weight distribution of PBA latexes prepared as given in Table I. In the methanol/water system, the particle size and size distribution increased

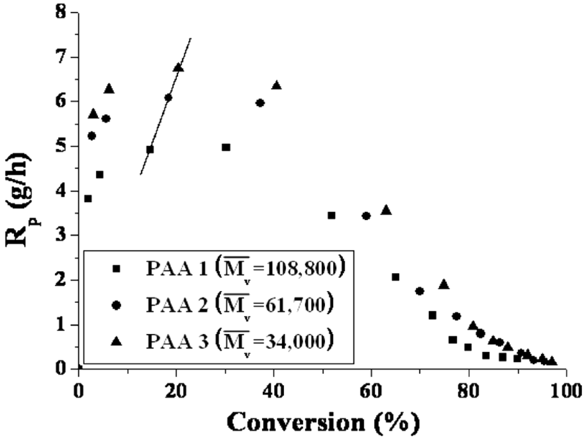

Figure 4. Effect of molecular weight of PAA on polymerization rate (EtOH/water = 80/20, wt./wt.%).

from 1.7 to 2.3 μm and from 1.01 to 1.08 respectively, and molecular weight and distribution decreased from 66,200 to 47,900 g/mol and from 2.42 to 2.14, respectively with increasing molecular weight of PAA from 34,000 to 108,800 g/mol. Similar phenomena were also observed in the ethanol/water system.

Figure 4 shows the plot of the polymerization rate versus conversion depending on the molecular weight of PAA in the ethanol/water system, indicating that the polymerization rate decreased with increasing molecular weight of PAA. Similar phenomena were also observed in the methanol/water system.

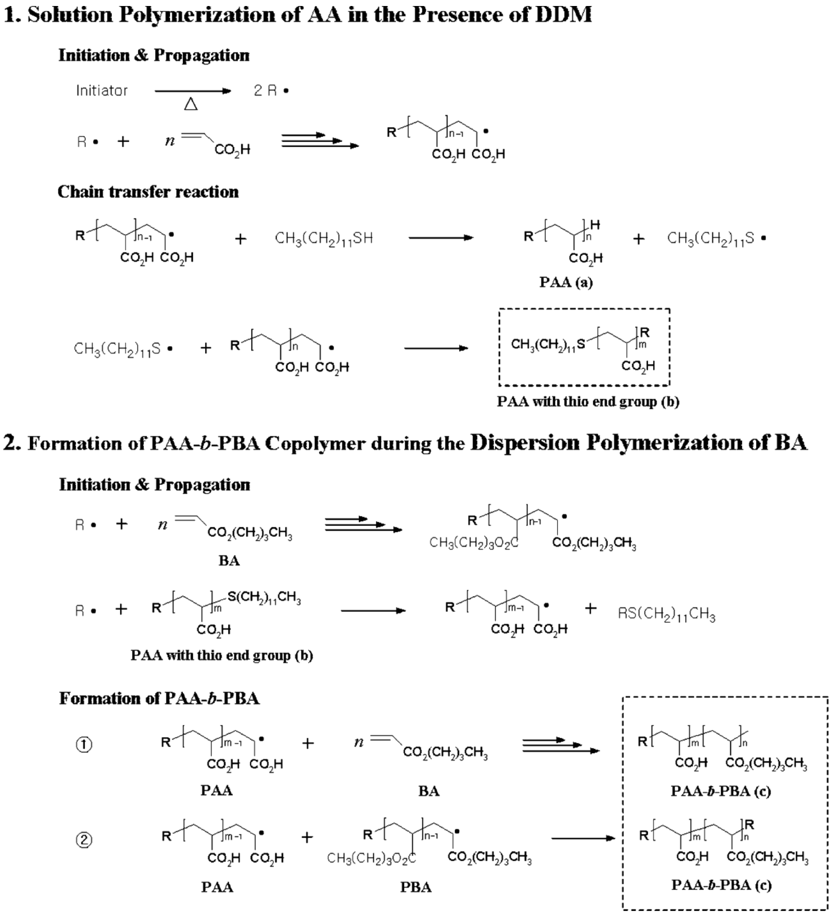

Figure 5. Reaction mechanism of the solution polymerization of AA with DDM and the formation of PAA-*block*-PBA.

The results obtained in this study indicate the opposite of the phenomena[2,26,29] observed in conventional dispersion polymerization. The viscosity-average molecular weights of PAA stabilizers prepared with 0, 0.5, and 1 wt.% of DDM concentration were found to be 108,800, 61,700, and 34,000 g/mol, respectively. In radical polymerization, the chain transfer reaction terminates the propagation of chain and creates new radicals; simultaneously, the molecular weight of the resulting polymer decreases.[30] Figure 5 represents the scheme of the reaction mechanism of the solution polymerization of AA with DDM and the formation of PAA-*block*-PBA. The PAA (a) and PAA with thio end group (b) are prepared by the chain transfer reaction of AA with DDM. Also, the molecular weight of PAA decreases but the amount of PAA with thio end group (b) increases with increasing the concentration of DDM. Miyazaki et al.[31] reported the effect of poly(vinyl acetate/vinyl alcohol) copolymer with a thio end group as a steric stabilizer on dispersion polymerization of styrene. The reactive thio group acts as a site of formation of the polystyrene-*block*-poly(vinyl acetate/vinyl alcohol) copolymer, which was utilized as an effective dispersant in the polymerization. Bourgeat-Lami and Guyot[32,33] also produced stable monodisperse polystyrene lattices using thio-ended poly(ethylene oxide) (POE-SH) as reactive stabilizer. Comparison with PVP showed that the POE-SH compounds give lower particle size and higher molecular weight polymers. The high stabilizing efficiency is probably due to the high probability of transfer to the stabilizer. In this study, PAA with thio end group (b) acts as a site of formation of the PAA-*block*-PBA copolymer (c), which was also utilized as an effective steric stabilizer in the dispersion polymerization of BA.

In order to determine the quantity of PAA-*block*-PBA copolymers present in the PBA latex particles, the PBA latex was first separated into supernatant and PBA particles by centrifugation at 4000 rpm for 10 min. The resulting PBA particles at the bottom were redispersed in water for 30 min and centrifuged at 10,000 rpm for 10 min, and the supernatants were removed. The cleaning process with water was repeated five times and the remaining products were vacuum dried at room temperature for 48 h. Finally, the dried product dissolved in methanol was titrated with 0.1 N NaOH. Table III shows the titration results for the PAA-*block*-PBA copolymers prepared with three different PAA stabilizers, present in the PBA particles. In general, the amounts of NaOH needed for the titration of the AA portion in the PAA-*block*-PBA copolymers increased with decreasing molecular weight of PAA stabilizer, implying that more of the PAA-*block*-PBA copolymer was formed with decreasing molecular weight of PAA stabilizer and contributed more in the particle stabilization. As a result, the particle size of PBA latex decreased and the

Table III. Titration of PAA-*block*-PBA copolymer

$\overline{M_v}$ of PAA (g/mol)	DDM (wt.%)[a]	NaOH (mg)[b]
34,000	1.0	22.53
61,700	0.5	12.32
108,800	0	4.41

Titrated with 0.1 N NaOH/methanol, 1% phenolphthalein solution.

[a] Based on BA weight in Table I.

[b] Amount of NaOH required for the titration of PAA-*block*-PBA copolymer.

molecular weight and polymerization rate increased due to the increasing efficiency of particle stabilization.

Effects of AIBN Concentration and Initiator Species

The effect of AIBN ($t^{1/2} = 289\,\text{min}$) concentration was investigated by changing concentration from 1 to 3 wt.% (based on monomer). Also, the dispersion polymerization of BA was carried out by using four different initiators: ADVN ($t^{1/2} = 58\,\text{min}$), AMBN ($t^{1/2} = 500\,\text{min}$), and BPO ($t^{1/2} = 1049\,\text{min}$), as well as the AIBN. Figures 6 and 7 show the plots of polymerization rate versus conversion dependence on the concentration of AIBN and species of initiator, respectively. The polymerization rate increased with increasing concentration of AIBN or decreasing half-lifetime of the initiator. The particle size distributions

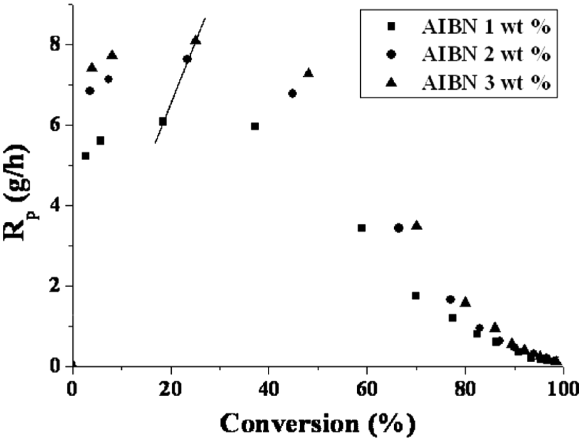

Figure 6. Effect of concentration of AIBN on polymerization rate (EtOH/water = 80/20, wt./wt.%).

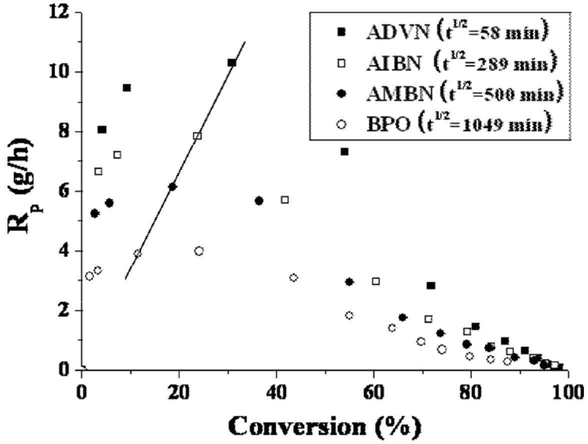

Figure 7. Effect of species of initiator on polymerization rate (MeOH/water = 90/10, wt./wt.%).

of these PBA latexes are found to be monodisperse and about the same irrespective of the concentration of AIBN. (methanol/water: 1.9(±0.1) μm, ethanol/water: 2.1(±0.1)μm).

The molecular weight and molecular weight distribution also decreased with increasing concentration of AIBN or decreasing half-lifetime of the initiator. Generally in dispersion polymerization, the polymerization rate and particle size increase, and the molecular weight of the resulting latexes decreases with increasing concentration of the initiator (or decreasing initiator's half-lifetime).[2,9,10,26,29] However, no substantial change in particle size has been observed in this study. In order to examine this further, three dispersion polymerizations of BA with 1, 2, and 3 wt.% of AIBN were carried out by using the corresponding supernatants recovered from the first polymerizations under the same polymerization conditions as shown in Table I, except for the PAA stabilizer. The resulting particle sizes of the PBA latexes were all smaller than those obtained from the first dispersion polymerizations, and the differences in particle size between the first and the second increased with increasing AIBN concentration, as shown in Figure 8. These results suggest that more efficient PAA-*block*-PBA stabilizers were formed with increasing initiator concentration and resulted in a smaller particle size of the latexes in the second polymerization. The reason the AIBN concentration is irrespective of the particle size in the first polymerization is believed to be the competition between the rates of coagulation and the formation of PAA-*block*-PBA steric stabilizer. Similar results were reported by Wang et al.[22] in the dispersion polymerization of BA.

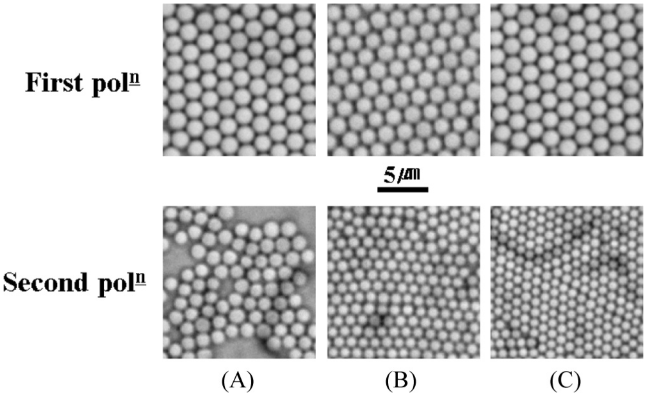

Figure 8. Optical micrographs of PBA particles prepared with three different concentrations of AIBN in the first polymerizations and prepared with their supernatants in the second polymerizations. (A) 1 wt.%, (B) 2 wt.%, (C) 3 wt.% AIBN, MeOH/water = 90/10, wt./wt.%.

Effects of BA Concentration

In methanol/water system, the particle size increased from 1.9 to 3.5 μm with increasing concentration of BA from 9 to 30 wt.% (based on total). Also, the molecular weight and molecular weight distribution increased from 59,600 to 268,500 g/mol and from 2.07 to 4.28, respectively. Similar phenomena were also observed in the ethanol/water system. Figure 9

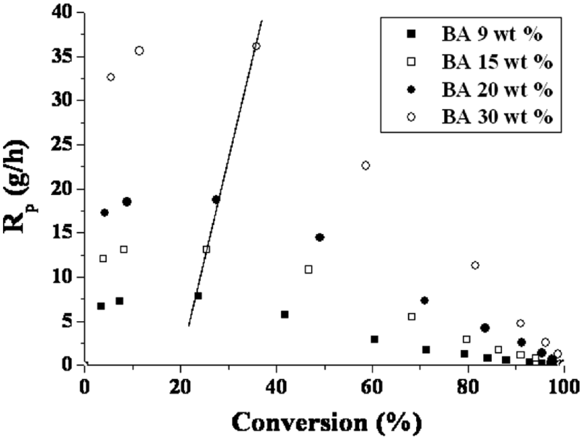

Figure 9. Effect of BA concentration on polymerization rate (MeOH/water = 90/10, wt./wt.%).

shows the curves of polymerization rate versus conversion for the polymerizations in the methanol/water system. The polymerization rate increased with increasing concentration of BA, and similar results were also shown in the ethanol/water system.

The increase of monomer concentration would increase the solvency of the medium for the polymer formed at the initial stage of the polymerization, resulting in an increase of critical chain length of the growing oligomer molecules and, at the same time, the decrease in the adsorption rate of the stabilizer. These features lead to the formation of larger particles. The increase in polymerization rate and molecular weight and its distribution would also be related to both the dominant polymerizations occurring in polymer particles and the increase of the monomer concentration.[2,10]

Effects of Polymerization Temperature

In the ethanol/water system, the particle size increased from 1.8 to 3.5 μm, and the particle size distribution was uniform with increasing polymerization temperature from 65° to 75°C. The polydisperse particles were also prepared at 55° ∼ 60°C. The molecular weight and molecular weight distribution decreased with increasing reaction temperature from 55° to 75°C. Similar phenomena were also observed in the methanol/water system. The results related to the increase of polymerization temperature can be explained similarly to those adopted in the effect of the initiator concentration. A higher polymerization temperature generates higher polymerization rates due to the increase in the decomposition rate of the initiator, leading to larger size particles with lower molecular weights.[26]

CONCLUSIONS

The dispersion polymerization of *n*-butyl acrylate (BA) was investigated using alcohol/water mixtures as the dispersion medium, 2, 2′-azobis (isobutyronitrile) (AIBN) as the initiator, and polyacrylic acid (PAA) as the stabilizer. PAA was prepared by solution polymerization with n-dodecyl mercaptan (DDM). The effects of polymerization factors, such as the alcohol/water ratio in the medium, concentration and molecular weight of PAA, concentration of AIBN and BA, and polymerization temperature on the resulting particle size and particle size distribution, molecular weight and molecular weight distribution, and kinetics were studied. The effects of medium ratio, concentration of stabilizer and monomer, and polymerization temperature were similar to those reported in the conventional dispersion polymerization. However, the particle size decreased and the molecular weight and polymerization rate increased with decreasing molecular weight of PAA stabilizer. This is the opposite of what was previously reported. This fact is due to the formation of PAA-*block*-PBA copolymers by the chain transfer reaction of PAA having thio end group with BA during dispersion polymerization and their utilization as an effective steric stabilizer. No variation of particle size with respect to the AIBN concentration was also observed, which is believed to be due to the competition between the rates of coagulation and the formation of PAA-*block*-PBA steric stabilizer. The dependence of particle size on the PAA concentration in methanol/water and ethanol/water systems exhibited the slopes −0.34 and −0.23, respectively. PAA stabilizers having thio end group were used successfully in making micron-sized, monodispersed PBA dispersions.

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