

## Dispersion Polymerization of Acrylamide in *t*-Butyl Alcohol/Water Media

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**Abstract:** We have performed dispersion polymerization of acrylamide in *tert*-butyl alcohol/water mixture – using hydroxypropyl cellulose and ammonium persulfate as the stabilizer and the initiator, respectively – to study the effects that the concentration of monomer, initiator, and stabilizer, the *tert*-butyl alcohol/water ratios as polymerization media, and the reaction temperature have on, among other things, the polymerization kinetics, particle sizes, and molecular weights. The polymerization rate increased upon increasing the concentration of the monomer, initiator, and stabilizer, the water content in the *tert*-butyl alcohol/water media, and the polymerization temperature. The average particle size of the lattices increased upon increasing the concentration of initiator, the polymerization temperature, and the water content in the *tert*-butyl alcohol/water media, but it decreased upon increasing the concentration of monomer and stabilizer. The viscosity-average molecular weight increased upon increasing the concentration of monomer and stabilizer and the water content in the *tert*-butyl alcohol/water media, but it decreased upon increasing both the concentration of initiator and the polymerization temperature.

**Keywords:** dispersion polymerization, acrylamide, dilatometer, polymerization kinetics, particle size and molecular weight.

### Introduction

The dispersion polymerization process has recently received a great attention because of its easiness and convenience in preparing monodisperse polymer particles of large size (1–10  $\mu\text{m}$ ) in a single step.<sup>1–15</sup> Preparation of micron size-monodisperse particles of polystyrene (PS)<sup>1–4,6,11</sup> or poly(methyl methacrylate) (PMMA)<sup>1,7</sup> has been studied intensely in polar media using such steric stabilizers as poly(vinyl pyrrolidone)(PVP),<sup>6,7,9,11</sup> hydroxypropyl cellulose,<sup>3,14</sup> poly(acrylic acid),<sup>5,15</sup> poly(vinyl methyl ether),<sup>16</sup> etc. In fact, dispersion polymerization can be as a modified precipitation polymerization in which flocculation is prevented and particle size is controlled by the presence of the steric stabilizer. Dispersion polymerization usually involves the polymerization of a monomer dissolved in an aqueous or non-aqueous media in the presence of an amphiphatic polymeric stabilizer to produce insoluble polymer particles dispersed in the continuous phase. The first studies of this technique were carried out in nonaqueous dispersion systems [NAD]<sup>17–19</sup> to prepare the PMMA particles in submicrometer size range by Barret.<sup>17</sup>

Later, Almog *et al.*<sup>1</sup> used this polymerization process in polar media to prepare monosize PS and PMMA particles up to 5  $\mu\text{m}$ . Most studies on dispersion polymerization deal with non-polar monomers both in non-polar<sup>17–19</sup> and polar media.<sup>1–16</sup> However, studies on dispersion polymerization of water soluble monomers yielding water soluble polymers are rather scarce and poorly understood.<sup>16,20,21</sup>

In the present study, we carried out dispersion polymerization of acrylamide in *t*-butyl alcohol/water mixture using hydroxypropyl cellulose and ammonium persulfate as the stabilizer and the initiator, respectively, and investigated the effects of concentration of monomer, initiator, stabilizer, and *t*-butyl alcohol/water ratios as polymerization media, and reaction temperature on the polymerization kinetics, particle size, and molecular weight, etc.

### Experimental

**Materials.** Acrylamide (AM, Junsei) and ammonium persulfate (APS, Shinyo) were used after recrystallization twice in chloroform and methanol, respectively. Hydroxypropyl cellulose(HPC, Aldrich,  $\overline{M}_v = 100,000$ ) was used without further purification. As the polymerization medium, *t*-butyl alcohol/distilled deionized-water mixtures were used.

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**Table I. Standard Recipe Used in Dispersion Polymerization of Acrylamide**

Ingredients	w/v (%)	Amount (g)
AM	3.5	3.5
HPC	4	4.0
APS	0.006 <sup>a</sup>	0.137
TBA/H <sub>2</sub> O	50/50 <sup>b</sup>	39/50

Polymerization conditions: 40°C (polymerization temp.), 120 cycles/min (revolution speed).

<sup>a</sup>mol/L. <sup>b</sup>v/v (%).

**Dispersion Polymerization.** All polymerizations were carried out in a dilatometer, which consisted of a 40 mL Erlenmeyer flask with attached capillary column.<sup>22</sup> All the ingredients as shown in Table I were mixed and dissolved clearly in a glass bottle and purged with O<sub>2</sub>-free nitrogen gas for 5 min, after which the mixture was added into dilatometer. The dilatometer was then placed in constant temperature water bath maintained at 40°C and magnetic stirred. Volume contraction with time was measured for 24 hrs.

**Conversion and Particle Size.** The final conversion of the samples was determined gravimetrically after removing unreacted monomer and excessive steric stabilizer by washing in excess amount of acetone. The PAM dispersions (about 10 mL) were treated with acetone (50 mL). The particles were then centrifuged out. The isolated particles were redispersed in acetone (50 mL) and sedimented again by centrifugation. The sedimented particles were dried in a vacuum oven at 40°C for 48 hrs.

The particle sizes were examined by scanning electron microscopy (SEM, Jeol Jsm 6400). A drop of the PAM dispersion was diluted in about 2–3 mL of acetone and one drop of the diluted dispersion was coated on the aluminum stud and was dried at room temperature overnight. The samples were sputter coated with gold, and examined at 15 kV. The particle size of the latices was measured on photographs and particle size distributions (PSD) were determined from the ratio of number ( $\overline{D}_n$ )- and weight ( $\overline{D}_w$ )-average diameters as follows.

$$\overline{D}_n = \frac{\sum_{i=0}^N D_i}{N}$$

$$\overline{D}_w = \frac{\sum_{i=0}^N D_i^4}{\sum_{i=0}^N D_i^3}$$

$$\text{Polydispersity Index (PDI)} = \frac{\overline{D}_w}{\overline{D}_n}$$

where,  $N$  is the total number of particles counted (about 100 particles) and  $D_i$  is the diameter of particle  $i$ .

**Viscosity-average Molecular Weight.** The intrinsic viscosity was measured in 0.5 NaCl at 25°C using an Ubbelohde viscometer. The following equation<sup>16</sup> was used to calculate  $\overline{M}_v$  from  $[\eta]$ :

$$[\eta] = 7.19 \times 10^{-6} (\overline{M}_v)^{0.77}$$

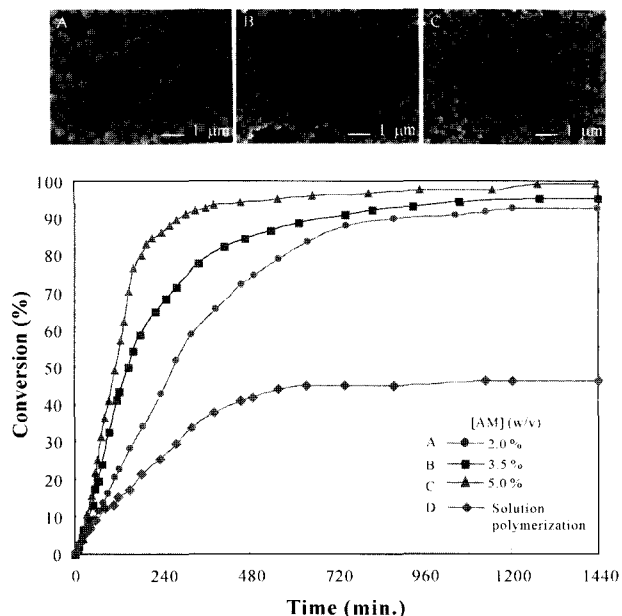
## Results and Discussion

**Effect of Monomer Concentration.** In order to study the effect of monomer concentration, AM was varied with three different concentrations (i.e., 2.0, 3.5, and 5.0% w/v) and the amount of the other components was the same as those listed in Table I. Figure 1 and Table II show the monomer conversion with the polymerization time, SEM photographs, and the average particle size and molecular weight of the latices, respectively. The polymerization rate and viscosity average molecular weight increased with increasing monomer concentration, but the average particle diameter decreased. The increase in polymerization rate and molecular weight suggest that considerable polymerization has taken place inside the particles through the capture of oligomeric radicals from the continuous phase by the particles. These radicals subsequently underwent polymerization inside the particles and grew to higher molecular weights due to the gel effect. Compared curve B with curve D in Figure 1, higher polymerization rate in curve B also infers polymerization inside the particles. As far as the average particle diameter is concerned, it is the inverse of what was observed for the dispersion polymerization of nonpolar monomers in polar solvents. That is, the particle diameter in the present case was proportional to the solubility parameter ( $\delta$ ) of the medium.  $\delta$  of the medium (*t*-butyl alcohol: water = 50:50 wt%) and acrylamide are 17.4 and 9.5–14.5<sup>23</sup>(cal/cm<sup>3</sup>)<sup>1/2</sup>, respectively. Since other ingredients besides the solvent components were used in small quantities, the contributions of only *t*-butyl alcohol and water were taken into account in the solubility evaluation. Thus, the increase in the AM concentration would result in the decrease in  $\delta$  of the medium, and at the same time result in the decrease in the solvency of the medium toward the

**Table II. Effect of AM Concentration in Dilatometer-Polymerization**

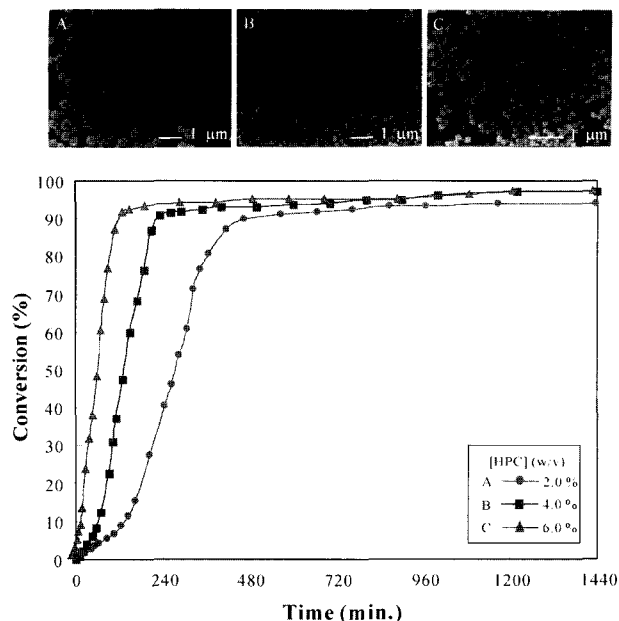
Samples	[AM] (%) w/v	$\overline{D}_n$ (μm)	$\overline{D}_w$ (μm)	PDI	$\overline{M}_v$ (× 10 <sup>5</sup> )
A	2.0	0.43	0.51	1.19	3.15
B	3.5	0.34	0.38	1.13	4.66
C	5.0	0.18	0.25	1.37	7.09

Polymerization conditions: [HPC]: 4.0%(w/v), [APS]: 6.0 mol/L (× 10<sup>-3</sup>), TBA/H<sub>2</sub>O: 50/50%(v/v), 40°C.



**Figure 1.** Conversion vs. time curves for 3 different AM concentrations and SEM pictures of the resulting PAM latices.

◆Solution polymerization conditions: [AM] : 3.5%(w/v), [APS] : 6.0 mol/L( $\times 10^{-3}$ ), Medium : H<sub>2</sub>O, 40°C.

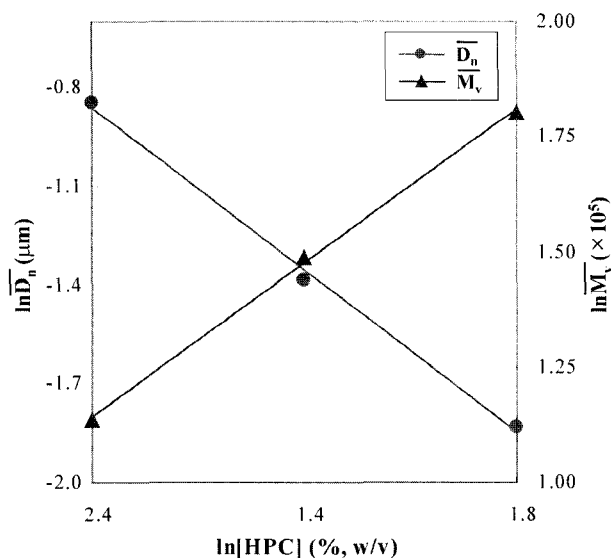


**Figure 2.** Conversion vs. time curves for 3 different HPC concentrations and SEM pictures of the resulting PAM latices.

HPC stabilizer. As a result, the adsorption of the HPC stabilizer would be more facile, resulting in the facilitation of primary stabilization and leading to a great number of primary stabilized particles and hence a lower ultimate particle size as the monomer concentration is increased.

**Effect of Stabilizer Concentration.** The polymerizations were performed with three different HPC concentrations (i.e., 2.0, 4.0, and 6.0% w/v) at a constant APS initiator concentration of 0.006 mol/L in a dispersion medium containing *t*-butyl alcohol and water (50/50% v/v) based on the polymerization conditions as described in Table I. Figure 2 and Figure 3 show the monomer conversion with the polymerization time, SEM photographs, and the log-log plots of particle diameter( $\overline{D}_n$ ) vs stabilizer concentration and of viscosity average molecular weight vs. stabilizer concentration, respectively. The polymerization rate increased with increasing HPC concentration. The average particle diameter decreased and the viscosity average molecular weight increased with increasing stabilizer concentration, resulting in  $\overline{D}_n \propto [\text{HPC}]^{-0.49}$  and  $\overline{M}_v \propto [\text{HPC}]^{0.33}$  relationships. A higher stabilizer concentration provides larger adsorption area onto stabilizing particles, resulting in a greater number of particles of smaller size. The increase in the polymerization rate and molecular weight with increasing HPC concentration suggests considerable polymerization taking place inside the particles due to higher monomer concentration and larger surface area.

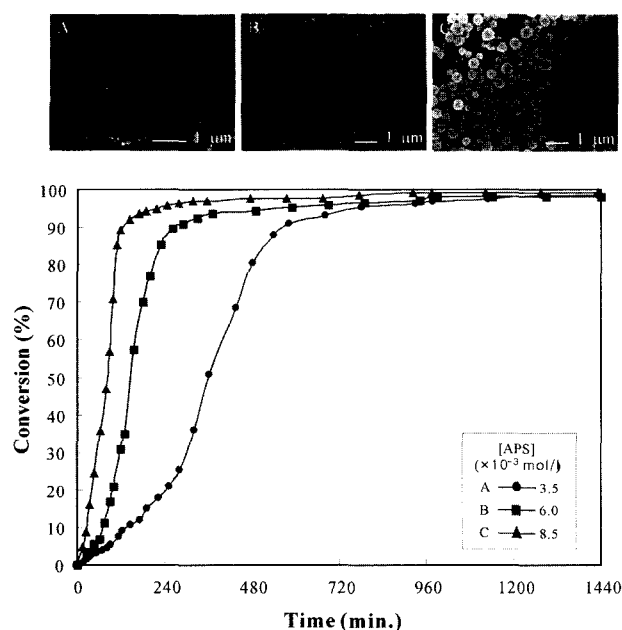
**Effect of Initiator Concentration.** In order to investigate



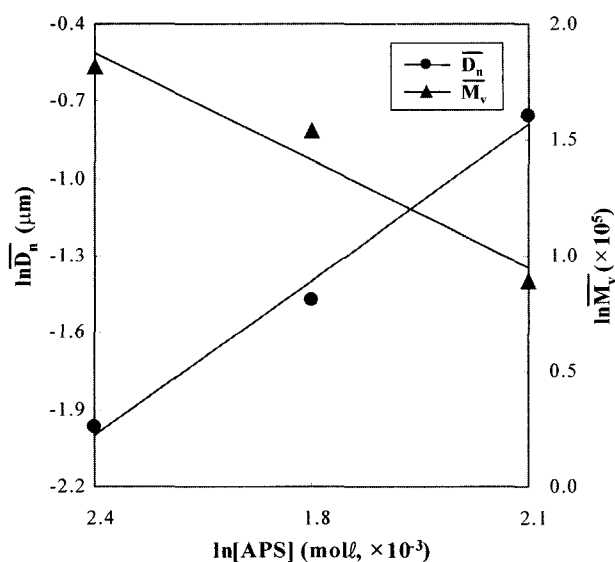
**Figure 3.** Relationship between  $\overline{M}_v$  and particle size in 3 different HPC concentrations.

the effect of initiator concentration, the polymerizations were carried out with three different APS concentrations (i.e., 0.0035, 0.006, and 0.0085 mol/L) at AM concentration of 5.0%(w/v) and HPC concentration of 4%(w/v) in a dispersion medium containing *t*-butyl alcohol and water (50/50% v/v) based on the polymerization conditions as described in Table I. Figures 4 and 5 show the monomer conversion with the polymerization time, SEM photographs, and the log-log

plots of particle diameter ( $\overline{D}_n$ ) vs. stabilizer concentration and of viscosity average molecular weight vs. stabilizer concentration, respectively. The average particle diameter increased and the viscosity average molecular weight decreased with increasing initiator concentration, resulting in  $\overline{D}_n \propto [\text{APS}]^{0.60}$  and  $\overline{M}_v \propto [\text{APS}]^{-0.46}$  relationships. The increase in the initiator concentration causes an increase in the number of free radicals and in the polymerization rate. This led



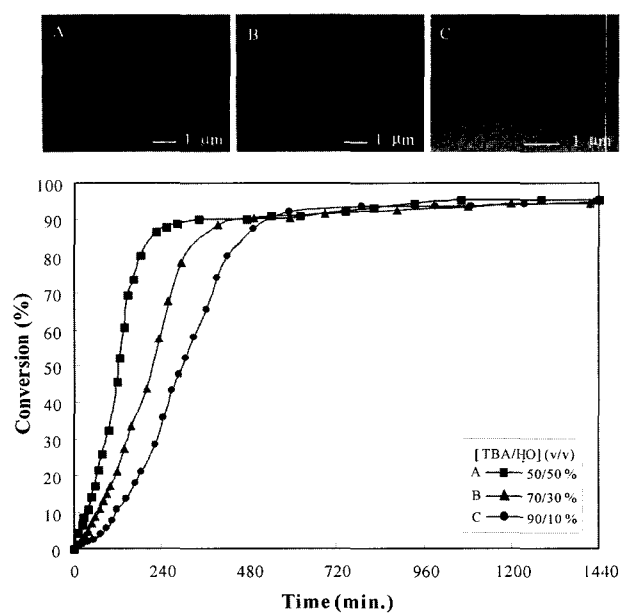
**Figure 4.** Conversion vs. time curves for 3 different APS concentrations and SEM pictures of the resulting PAM latices.



**Figure 5.** Relationship between  $\overline{M}_v$  and particle size in 3 different APS concentrations.

to low molecular weight polymer chains which had good solubility in the medium. In dispersion polymerization, the nucleation occurs when the polymer chains reach a certain molecular weight in which they become insoluble in the dispersion medium. At high initiator concentration, due to low concentration of high molecular weight chains in the medium, a few nuclei were produced, leading to a few larger size.

**Effect of TBA Content in the Medium.** Table III and Figure 6 show the results of the polymerization experiments in which the concentration of *t*-butyl alcohol was varied from 50 to 90 vol%, while the concentrations of the other components were kept constant as shown in Table I. The polymerization rate, viscosity average molecular weight of the PAM and the particle size increased with a decrease in *t*-butyl alcohol concentration. *t*-Butyl alcohol is a nonsolvent for PAM, but water is a good solvent. Addition of *t*-butyl alcohol to water makes the solvent increasingly poorer for PAM, such that the polymer becomes insoluble at *t*-butyl alcohol concentrations greater than 40 vol%. Thus, the sol-



**Figure 6.** Conversion vs. time curves for 3 different TBA contents and SEM pictures of the resulting PAM latices.

**Table III.** Effect of TBA Content in Dilatometer-Polymerization

Samples	[TBA/H <sub>2</sub> O] (%, v/v)	$\overline{D}_n$ ( $\mu\text{m}$ )	$\overline{D}_w$ ( $\mu\text{m}$ )	PDI	$\overline{M}_v$ ( $\times 10^5$ )
A	50/50	0.31	0.35	1.14	4.53
B	70/30	0.16	0.18	1.12	3.31
C	90/10	0.09	0.10	1.09	2.75

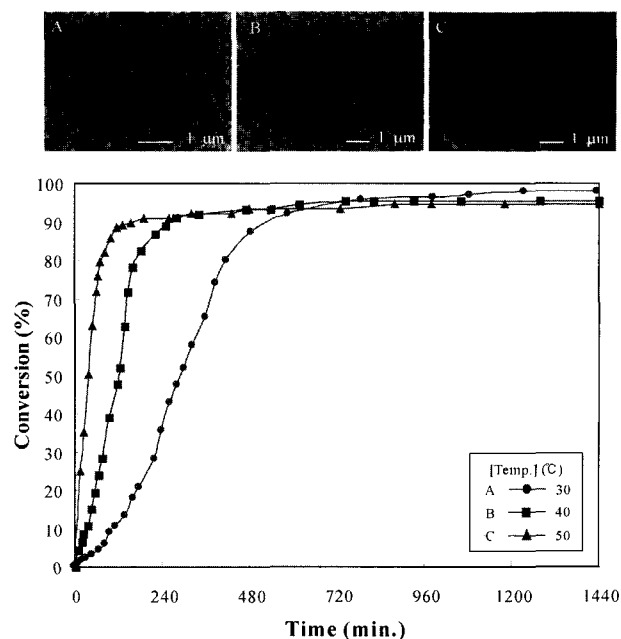
Polymerization conditions: [AM]: 3.5% (w/v), [APS]: 6.0 mol/L ( $\times 10^{-3}$ ), [HPC]: 2.0% (w/v), 40°C.

vency of the medium toward the PAM and the HPC stabilizer would decrease gradually with an increase in *t*-butyl alcohol concentration in the present dispersion polymerization (50~90 vol%). As a result, the adsorption of the stabilizer would be more facile from solvents richer in *t*-butyl alcohol. This would lead to a lower ultimate particle size as the *t*-butyl alcohol concentration is increased. As regards the effect of the medium on the molecular weight, the results are found to be against the general trend of higher molecular weight associated with smaller particle size.<sup>1,13</sup> For the general heterogeneous polymerizations, the transport process of the monomer into the particles during the polymerization is very important and sensitive to the molecular weight of the resulting polymer. For the present case, the transport of acrylamide monomer into particles occurs through the solvent channels of the swollen particles. As mentioned above, *t*-butyl alcohol is a nonsolvent for PAM and an increase in the *t*-butyl alcohol content of the medium would decrease the extent of swelling for the polymerizing-PAM particles and thus the concentration of AM monomer in the particles. This effect would result in a decrease of the polymerization inside the particles, polymerization rate, and in a decrease of molecular weight with an increase in *t*-butyl alcohol content.

**Effect of the Polymerization Temperature.** Table IV and Figure 7 show the results of the polymerization experiments on the effect of the polymerization temperature. The polymerization recipe used was as same as that in Table I except that the polymerization temperature was varied from 30 to 50°C. The polymerization rate and average particle diameter increased with increasing the polymerization temperature, but the viscosity average molecular weight decreased. The increase in the polymerization temperature causes an increase in the number of free radicals generated during the polymerization, resulting in the increase of polymerization rate. This led to low molecular weight polymer chains which had good solubility in the medium. At high polymerization temperature, due to low concentration of high molecular weight chains in the medium, a few nuclei were produced, leading to a few larger size.

## Conclusions

Dispersion polymerization of acrylamide was carried out in the media of *t*-butyl alcohol/water mixtures to investigate the effects of concentration of monomer, initiator, stabilizer,



**Figure 7.** Conversion vs. time curves for 3 different AM concentrations and SEM pictures of the resulting PAM latices.

and *t*-butyl alcohol/water ratios in media, and reaction temperature on the polymerization kinetics, particle size, and molecular weight, etc. Important results are as follows.

- The polymerization rate increased with increasing concentration of monomer, initiator, stabilizer, water content in *t*-butyl alcohol/water media, and polymerization temperature.

- The average particle size of the latices increased with increasing concentration of initiator and polymerization temperature, and water content in *t*-butyl alcohol/water media, but decreased with increasing concentration of monomer and stabilizer.

- The viscosity average molecular weight increased with increasing concentration of monomer, stabilizer, and water content in *t*-butyl alcohol/water media, but decreased with increasing concentration of initiator and polymerization temperature.

- $\overline{D}_n \propto [\text{HPC}]^{-0.49}$ ,  $\overline{D}_w \propto [\text{APS}]^{0.60}$ ,  $\overline{M}_v \propto [\text{HPC}]^{0.33}$ , and  $\overline{M}_v \propto [\text{APS}]^{0.46}$  relationships were found from the log-log plots.

- PAM latices of about 0.1~0.5  $\mu\text{m}$  with 195,000~

**Table IV.** Effect of Polymerization Temperature in Dilatometer-Polymerization

Samples	Temperature (°C)	$\overline{D}_n$ ( $\mu\text{m}$ )	$\overline{D}_w$ ( $\mu\text{m}$ )	PDI	$\overline{M}_v$ ( $\times 10^5$ )
A	30	0.15	0.25	1.64	7.78
B	40	0.36	0.43	1.18	4.64
C	50	0.47	0.52	1.11	1.95

Polymerization conditions: [AM]: 3.5% (w/v), [HPC]: 4.0% (w/v), [APS]: 6.0 mol/L ( $\times 10^{-3}$ ), TBA/H<sub>2</sub>O: 50/50% (v/v).

778,000 in  $\overline{M}_v$  were prepared throughout the study and the resulting latices were all dissolved in water instantly.

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