

# Formation of Monodisperse Polyacrylamide Particles by Radiation-Induced Dispersion Polymerization. I. Synthesis and Polymerization Kinetics

Qiang Ye, Weidong He, Xuewu Ge, Haiting Jia, Huarong Liu, Zhicheng Zhang

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui, 230026, People's Republic of China

Received 27 September 2001; accepted 13 November 2001

**ABSTRACT:** Highly monodisperse polyacrylamide (PAM) microparticles were directly prepared by radiation-induced dispersion polymerization at room temperature in an aqueous alcohol media using poly(*N*-vinylpyrrolidone) (PVP) as a steric stabilizer. Monomer conversion was studied dilatometrically and polymer molecular weight was determined viscometrically. The gel effect was found evidently from the polymerization kinetics curves. The influence of the dose rate, monomer concentration, stabilizer content, medium polarity, polymerization temperature on the polymerization rate, and the molecular weight of the polymer was examined. The polymerization rate ( $R_p$ ) can be represented by  $R_p$

$\propto D^{0.15}[M]^{0.86}[S]^{0.47}[A/W]^{0.64}$  and the molecular weight of the polymer can be represented by  $M_w \propto D^{-0.19}[M]^{1.71}[S]^{0.43}[A/W]^{0.14}$  at a definite experimental variation range. The overall activation energy for the rate of polymerization is 10.57 kJ/mol (20–35°C). Based on these experimental results, the polymerization mechanisms were discussed primarily. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2567–2573, 2002

**Key words:** dispersion polymerization; polyacrylamide; radiation-induced; monodisperse particles; water-soluble polymers

## INTRODUCTION

There has been substantial interest in monodisperse polymer particles since Vanderhoff and Bradford announced their preparation of polystyrene particles with a highly uniform particle size in 1955.<sup>1</sup> A wide variety of applications of monodisperse particles have been found, including instrument calibration standards, column packing material for chromatographic separation,<sup>2,3</sup> support materials for biochemicals,<sup>4</sup> clinical examination,<sup>5</sup> catalyst carriers, coating and ink additives, and information-storage materials. All these successful applications are ultimately dependent upon the particle size and its distribution, the morphology of the particles, and the surface characteristics. Therefore, the control of particle size and particle uniformity has been focused on.

Various methods of producing monodispersed beads have been developed, such as suspension polymerization, emulsion polymerization, and dispersion polymerization. Dispersion polymerization is a very attractive method due to its inherent simplicity of the single-step process, which was first set up by ICI Corp. in the 1970s.<sup>6</sup> A typical example of this method is the dispersion polymerization of styrene in hydrocarbons,

alcohols, and alcohol–ether and alcohol–water mixtures. The reaction medium should dissolve both the monomer and stabilizer. In alcohols and other polar solvents, a wide range of polar organic polymers such as PVP, poly(vinyl alcohol), and cellulose derivatives have been used as the stabilizer. In many instances, the stabilizer may be grafted onto the surface of the polymer particles during the polymerization process.

Although water-soluble polymers have been recognized as being very useful in terms of technological applications and scientific investigations, up to now, very few studies have been reported in the case of dispersion polymerization. Only a few systems such as polymerization of *N*-vinylformamide,<sup>7,8</sup> 4-vinylpyridine,<sup>9</sup> 1-vinyl-2-pyrrolidone,<sup>10</sup> *N*-isopropylacrylamide,<sup>11,12</sup> and 2-hydroethyl methacrylate<sup>13,14</sup> are described in the literature. Ray and Mandal<sup>15,16</sup> reported the dispersion polymerization of acrylamide using poly(vinyl methyl ether) as the polymeric stabilizer and 2,2'-azobisisobutyronitrile or ammonium persulfate as the initiator.

In this work, a cobalt-60 gamma ray was used to initiate the dispersion polymerization of acrylamide. Such a type of work has scarcely been reported before.<sup>17,18</sup> Generally, radiation polymerization is one of the most convenient methods because of its nontemperature-dependent initiation and extremely large yield of radiation chemistry. Also, the radiation process can easily prepare a monodisperse polymer with-

Correspondence to: Q. Ye (yeqiang@ustc.edu.cn).

out the pollution of chemical initiators. In the present study, the dispersion polymerization of acrylamide with  $^{60}\text{Co}$  gamma-ray irradiation was made to examine the influence of the dose rate, monomer concentration, stabilizer content, medium polarity, and polymerization temperature on the polymerization rate and the molecular weight of polymers. Such kinetics studies of dispersion polymerization have not widely discussed before.

## EXPERIMENTAL

### Materials

Acrylamide (AM), obtained from Hubei Daxue Chemicals, Inc. (Wuhan, China), was recrystallized from acetone. PVP ( $M_w$   $4 \times 10^4$ , K-30) was supplied by the Shanghai Chemical Reagent Co. (Shanghai, China). *tert*-Butanol (TBA, A.R. grade) was fractionated prior to use. Deionized water was used throughout this work. Other reagents were of GR grade and used as received.

### Preparation of PAM microspheres by dispersion polymerization

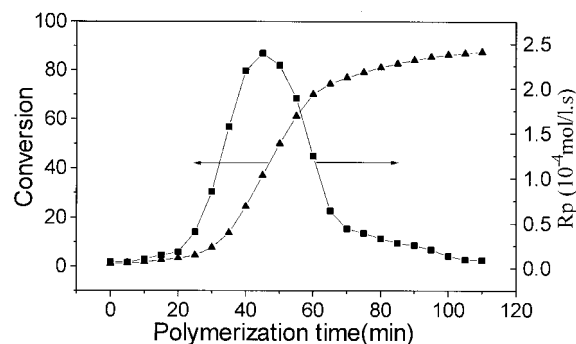
The syntheses of polymer particles were performed by gamma ray-induced dispersion polymerization in different TBA water mixtures, in which the monomer is easily dissolved. Nitrogen with a high purity was bubbled through the monomer solution at room temperature for about 15 min to get rid of the oxygen. After that, the solution was directly fed into a special dilatometer<sup>19</sup> and held in a bath whose temperature could be accurately controlled by a regulator. The polymerization was carried out at 25°C at a fixed dose rate with gamma rays. The resulted polymers were centrifuged at 7000 rpm and then washed with fresh TBA. This operation was repeated several times. The polymer conversion was recorded as a function of time with the dilatometer, and the polymerization rate was obtained by further differentiation.

### Viscosity measurement

The molecular weight of the polymer was determined in a 1M  $\text{NaNO}_3$  aqueous solution with a Ubbelohde capillary viscometer at 30°C. The average molecular weight can be calculated with the Mark-Houwink relation<sup>20</sup>:  $[\eta] = 3.37 \times 10^{-4} M_w^{0.66}$  (dL/g).

### Determination of particle size by light scattering

The polymer particle size and size distribution were measured on a modified commercial laser light scattering (LLS) spectrometer (ALV/SP-125) equipped with an ALV-5000 multi- $\tau$  digital time correlator and a



**Figure 1** Conversion versus time curve and polymerization rate versus time curve. Dose rate, 12.33 Gy/min; AM, 4 wt %; TBA/ $\text{H}_2\text{O}$ , 5/4; PVP, 6 wt %;  $T$ , 298 K.

solid-state laser (DPSS, out power =  $\sim 400$  mW at  $\lambda = 532$  nm). In dynamic LLS, the Laplace inversion of a measured intensity-intensity time correlation function  $G^{(2)}(t, q)$  in the self-beating mode results in a line-width distribution  $G(\Gamma)$ .<sup>21,22</sup> For a pure diffusive relaxation,  $(\Gamma/q^2)_{q \rightarrow 0, c \rightarrow 0}$  leads to the translational diffusion coefficient  $D$  or, further, to the hydrodynamic radius  $R_h$  via the Stocks-Einstein equation. The details of LLS theory can be found elsewhere.<sup>21,22</sup> The polymer latex used in LLS was clarified by 0.8- $\mu\text{m}$  Millipore filters to remove dust.

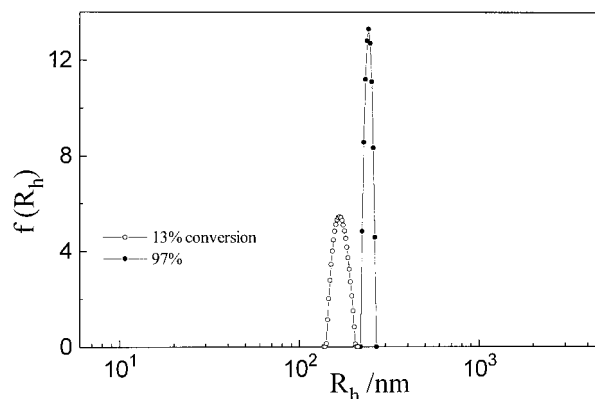
## RESULTS AND DISCUSSION

### Variation of polymerization rate with conversion

At the initial stage, the turbidity of the reaction mixtures was near zero. However, after a certain irradiation time, the turbidity started to increase. Figure 1 shows the typical conversion-time curve, generally S-shaped. In fact, the curve can be reproduced with a measurement error below 3%. The influence of the gel effect is observed evidently in the conversion-time curve. The linear portion of the curve extends to quite high conversion levels ( $\sim 40$ – $50\%$ ). The maximum reaction rate was taken for determination of the kinetic relations. It is specially pointed out that the polymerization conversion easily reaches a higher value than that of the same system using a chemical radical initiator at high temperature.<sup>23</sup> This may be due to the higher activity and efficiency of free primary radicals produced by irradiation with gamma rays.

### Particle-size analysis

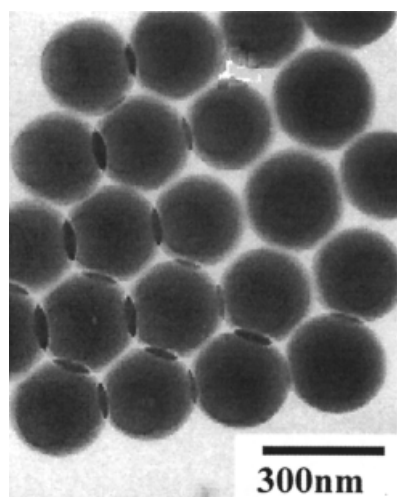
The hydrodynamic radius ( $R_h$ ) and its distribution of polymer latex particles were determined by dynamic light scattering, and the results at the conversion of 13% and almost 100% are shown in Figure 2. It is clear that  $R_h$  changes from 167 to 242 nm, and its distribution becomes narrower with increase of the conversion. The polydispersity index (PDI) at almost 100%



**Figure 2** Hydrodynamic radius distribution  $f(R_h)$  of the PAM latex particles at two different conversions. Dose rate, 12.33 Gy/min; AM, 4 wt %; TBA/H<sub>2</sub>O, 5/4; PVP, 6 wt %;  $T$ , 298 K.

conversion is about 1.01, indicating the monodispersity of the particles. Figure 3 shows latex particles of a polymer at 13% conversion photographed by transmission electron microscopy (TEM). The particle radius of the polymer latex was estimated as around 125 nm. It is easily understood that the particle size observed in the TEM photo is smaller than is the value determined by LLS.

The monodispersity of a colloidal dispersion obtained from a synthetic process was discussed by Lamer and Dineger,<sup>24</sup> and the authors indicated that monodispersity is only obtained when the initiation and nucleation stage is very short compared with the overall reaction time. Also, the period of repetitive nucleation must be made so short that monodispersity arises by subsequent uniform growth on the existing nuclei. The gamma ray produces a greater rate of free-radical formation and initiation in the radiation



**Figure 3** TEM photographs of PAM microspheres. Dose rate, 12.33 Gy/min; AM, 4 wt %; TBA/H<sub>2</sub>O, 5/4; PVP, 6 wt %;  $T$ , 298 K.

**TABLE I**  
Recipes and Synthesis Parameters for the Dispersion Polymerization of Acrylamide

	Standard recipe or parameter	Experimental variation
Initial monomer concentration (wt %)	4.0	3.0–10.0
Polarity of dispersion medium (TBA/H <sub>2</sub> O w/w)	1.25/1	0.3/1–3.5/1
Stabilizer content (wt %)	6.0	2.0–8.0
Dose rate (Gy/min)	12.33	8.25–45.03
Temperature (°C)	25	20–35

polymerization.<sup>25</sup> The formation of nuclei is finished in a short time after irradiation (about  $10^{-6}$  s). Insoluble polymer particles are formed as soon as the chain length reaches its solubility limit. After the nuclei formation step, the number of the particles becomes constant at a polymerization conversion below 10% with the irradiation time of 5–30 min. The induction period and the nucleation period are both quite short, and the radicals produced after the irradiation time do not contribute to the formation of new nuclei<sup>25</sup>; thus, it can easily lead to monodispersity.

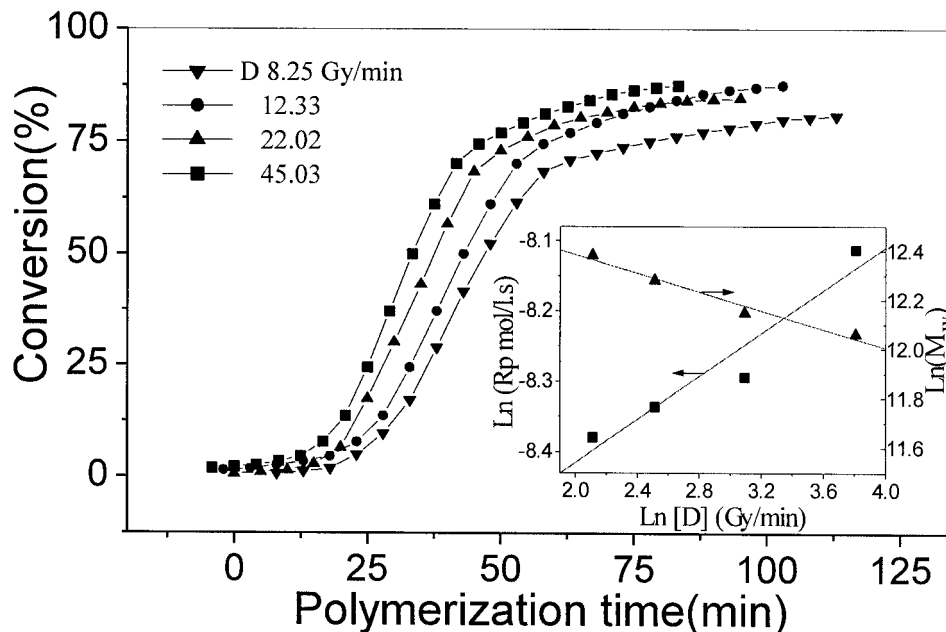
### Polymerization kinetics

In this study, the influence of various polymerization parameters, including the polymerization temperature, stabilizer concentration, irradiation dose rate, monomer concentration, and solvency of the medium, were investigated systematically. The standard recipes and synthesis parameters used in this study are given in Table I. The amount of each ingredient was kept constant in all experiments except as indicated.

#### Effect of irradiation dose rate

The dependence of the conversion on the reaction time at different irradiation dose rates is shown in Figure 4. The correlation between the irradiation dose rate and the polymerization rate ( $R_p$ ) and the molecular weight ( $M_w$ ) of the polymer are also displayed in Figure 4 and can be expressed as the following:  $R_p \propto [D]^{0.15}$ ;  $M_w \propto [D]^{-0.19}$ . The overall  $R_p$  increases and  $M_w$  decreases with increase of the irradiation dose rate. The results conform the general polymerization kinetics. As the irradiation dose rates increase, the rate of free-radical formation becomes greater. The higher rate of free-radical initiation leads to faster monomer consumption but also results in a shorter kinetic chain length.

The rate of polymerization increases with the dose rate with an approximate 0.15 order dependence. This order was less than that of conventional radical polymerization. This result can be rationalized: The polymerization may proceed simultaneously in the solu-



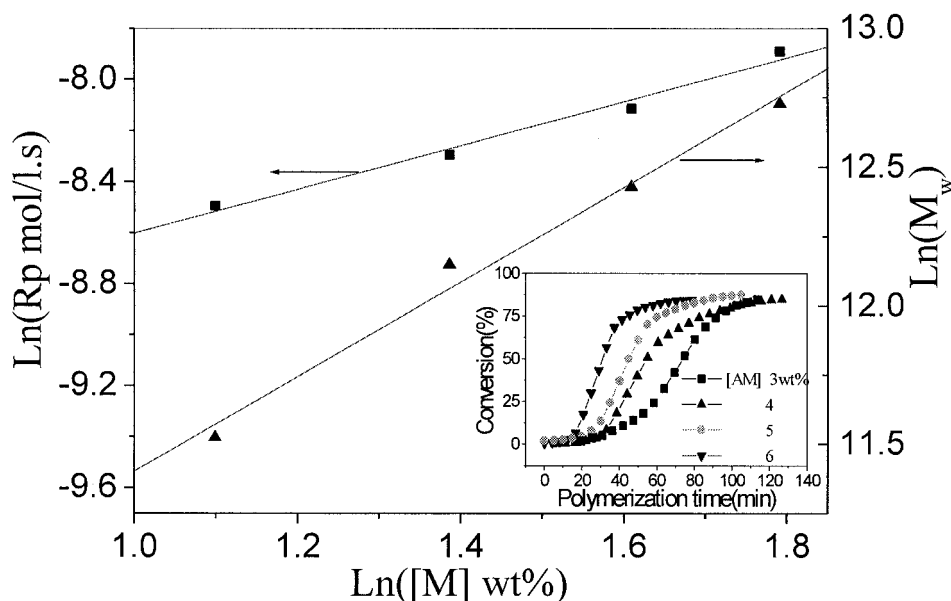
**Figure 4** Conversion versus time at different irradiation dose rates S. AM, 4 wt %; TBA/H<sub>2</sub>O, 5/4; PVP, 6 wt %; T, 298 K.

tion phase and in the particle phase. In the early stages, the polymerization takes place primarily in the solution phase, thus its rate should increase with the concentration of free radicals, which at low conversions is directly related to the dose rate, usually with 0.5–1.0 order dependence. After the conversion exceeds 40–50%, the reaction primarily proceeds through a heterogeneous mechanism in the particle phase. Such a process does not involve the formation of any new polymer chains and would be, therefore, expected to be independent of the irradiation dose rate. The presence of the two distinct kinetic regions is

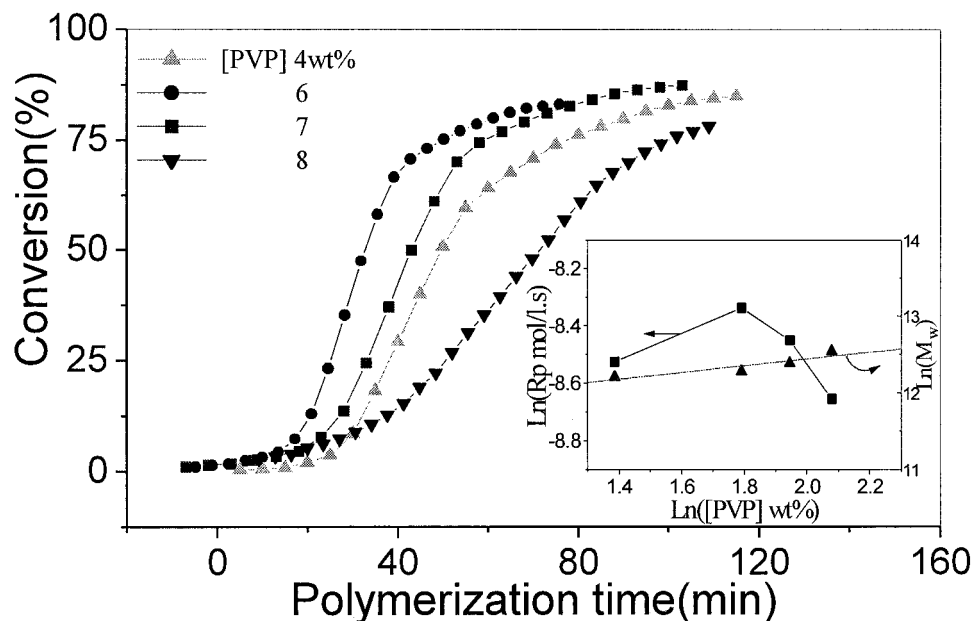
indicative of the competition between the solution and heterogeneous polymerization processes and maybe the latter predominates.

#### Effect of monomer concentration

The initial monomer concentration is important because the particle number is determined by the monomer concentration very early in the reaction.<sup>26</sup> When the monomer concentration was more than 10 wt %, the dispersion was so unstable that coagulation oc-



**Figure 5** Effect of monomer concentration on polymerization. Dose rate, 22.02 Gy/min; TBA/H<sub>2</sub>O, 5/4; PVP, 6 wt %; T, 298 K.



**Figure 6** Conversion versus time curves at various stabilizer contents. Dose rate, 12.33Gy/min; AM, 4 wt %; TBA/H<sub>2</sub>O, 5/4; T, 298 K.

cured. The effect of the monomer content on the polymerization kinetics is shown in Figure 5. From the slope of the conversion–time curves,  $R_p \propto [M]^{0.86}$  and  $M_w \propto [M]^{1.71}$  are obtained. The order of  $R_p \sim [M]$  was also less than that of conventional radical polymerization. This is likely due to the diffusion of the monomer-to-particle phase becoming the main factor to control the polymerization reaction at higher conversions. It should be noted here that the monomer entry into the particle phase to sustain the solid-state polymerization would be different for acrylamide than for methyl methacrylate or styrene. In the latter two cases, the monomers are soluble in the respective polymers so that the monomer is partitioned between the particle phase and the dispersion medium.<sup>26,27</sup> In the case of acrylamide, it was suggested by Ray and Mandal<sup>15</sup> that polyacrylamide particles are swollen by the dispersion medium and the monomer enters into the particles through the solvent channels. Figure 5 also indicates the relationship between the molecular weight of the polymer and the monomer concentration. It can be seen that  $M_w$  increases with the monomer concentration.

#### Effect of stabilizer concentration

In the present system, a water and alcohol soluble polymer (PVP), which possesses active  $\alpha$ -hydrogens as possible chain-transfer sites, was used as a steric stabilizer. Figure 6 shows the conversion–time curves obtained at various stabilizer contents. When the PVP content was less than 3%, particles with a bimodal size distribution or coagulum were obtained. The curve in

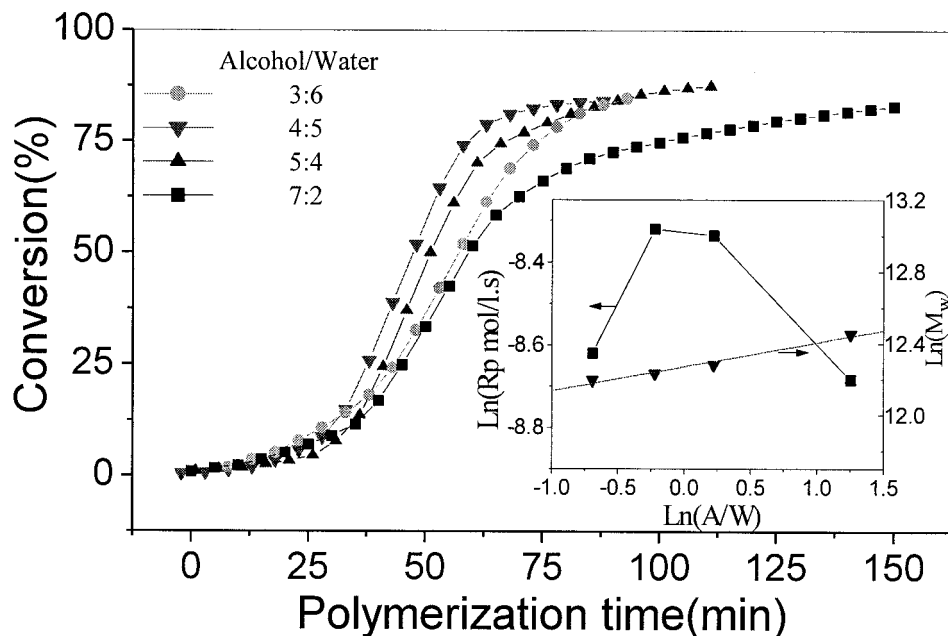
Figure 5 also tells us that the polymerization rate increases, in general, and the polymer molecular weight increases with increasing PVP concentration if its concentration is less than 6 wt %. This result may be explained that a higher stabilizer concentration causes a faster stabilizer adsorption, and, hence, for a given duration, a greater number of particles with a smaller size will be stabilized during the primary stabilization process. As a result, the total interfacial area will be larger, the capture ability of primary radicals will increase, and the reaction rate will increase. Further increase of the stabilizer concentration above 6% leads to the decrease of the polymerization rate. The reason may be that the viscosity of the polymerization system increases quickly with a further increasing PVP concentration.

The effect of the stabilizer content on  $M_w$  is also displayed in Figure 6 as  $M_w \propto [S]^{0.43}$ . The increase of the molecular weight with the stabilizer concentration suggests that the polymerization has considerably taken place inside the particle phase through the capture of oligomeric radicals from the continuous phase. These radicals subsequently undergo solid-phase polymerization and grow to higher molecular weights due to the gel effect.<sup>26</sup>

#### Effect of medium polarity

The solvent plays an important role in the preparation of polymer particles, as described in a series of research articles. The composition of the reaction medium [alcohol/water (A/W) mixture] also affected the rate of the dispersion polymerization of AM as shown





**Figure 7** Conversion versus time curves at different A/W ratios. Dose rate, 12.33 Gy/min; AM, 4 wt %; PVP, 6 wt %; T, 298 K.

in Figure 7. The influence of ratio of A/W on polymer molecular weight is also shown in Figure 7:  $M_w \propto [A/W]^{0.14}$ . When the TBA concentration was reduced to 30%, no particles were formed instead of a translucent viscous solution. As the ratio of A/W increased from 0.5 to 0.8, the polymerization rate increased. This may be explained by that TBA is a nonsolvent for PAM, but water is a good solvent. Addition of TBA to water makes the solvent increasingly poorer for PAM, such that the polymer becomes insoluble at TBA concentrations greater than 30%. Thus, the solvency of the medium toward the PAM grafts (PAM-g-PVP) would decrease gradually with the concentration used in the present dispersion polymerization. As a result, the adsorption of the grafted stabilizer would be more facile. This would mean that primary stabilization will be facilitated, leading to a greater number of primary stabilized particles and, hence, a lower ultimate particle size as the TBA concentration is increased. A large total surface area and density of smaller particles ensures that the growing oligomeric radicals initiated in solution are captured efficiently. Also, this also leads to solid-phase polymerization that gives a higher molecular weight polymer because of the gel effect.<sup>27</sup>

However, with further increase of A/W above 1.0, the polymerization rate decreases. This can be explained by that the transport of the acrylamide monomer to the particles form solid-phase polymerization in the present case occurs through the solvent channels of the swollen particles. Since the extent of swelling decreases with an increase in the TBA content of the medium, the access of the growing polymer radi-

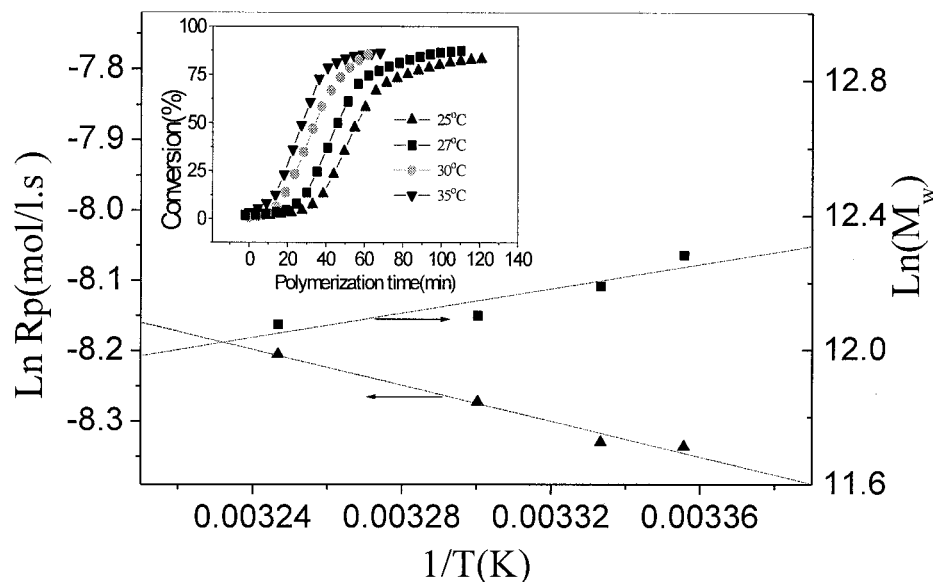
cal inside a particle to monomer and, hence, the contribution of solid-phase polymerization will decrease analogously. This latter effect would result in a decrease of the polymerization rate with an increase in the TBA concentration.

#### Effect of polymerization temperature

Figure 8 displays the effect of temperature on the polymerization. According to the Arrhenius equation, the apparent activation energy for  $R_p$  and  $M_w$  is 10.57 and  $-15.16$  kJ/mol, respectively. This is much less than that initiated by the free-radical initiator at high temperature. It is easy to understand that the activation energy for the initiation reaction is zero in the case of radiation-induced polymerization. Although the relationship between the molecular weight of polymer and the polymerization temperature ( $1/T$ ) is somewhat scattered, as seen in Figure 8,  $M_w$  tends to decrease with the temperature.

## CONCLUSIONS

In this work, the specific features of the dispersion polymerization of AM initiated by gamma rays with PVP as the steric stabilizer in TBA/water were studied. This method takes advantage of the specialties of radiation induction; highly uniform polymer microspheres were obtained with high conversion. In general, the conversion-time curves are S-shaped because of the gel effect. It was discovered that the polymerization rate increases with increase of the dose rate, monomer concentration, and temperature, the stabi-



**Figure 8** Effect of temperature on polymerization. Dose rate, 12.33 Gy/min; AM, 4 wt %; TBA/H<sub>2</sub>O, 5/4; PVP, 6 wt %.

lizer concentration at a value below 6%, and the aqueous weight fraction at a value more than 1.0. Also, the polymer molecular weight increases with increasing stabilizer concentration, increasing monomer concentration, decreasing dose rate, decreasing polymerization temperature, and decreasing aqueous weight fraction. The effects of various polymerization parameters on the particle size and size distribution, as the second part of the study, will be available in the near future. Further research is in progress.

## References

- Vanderhoff, J. W.; Bradford, E. B. *Polymer Colloid I*; Plenum: New York, 1971.
- Ugelstad, J. *J Polym Sci Polym Symp* 1985, 72, 225.
- Christopher, K. O. *J Polym Sci Polym Lett Ed* 1985, 23, 103.
- Lok, K. P.; Ober, C. K. *Can J Chem* 1985, 63, 209.
- Okubo, M. *Colloid Polym Sci* 1987, 265, 957.
- Barrett, K. E. J. *Dispersion Polymerization in Organic Media*; Interscience: New York, 1987.
- Uyama, H.; Kato, H.; Kobayashi, S. *Chem Lett* 1993, 261.
- Uyama, H.; Kato, H.; Kobayashi, S. *Polymer J* 1994, 26, 858.
- Takahashi, K.; Miyamori, S.; Uyama, H.; Kobayashi, S. *Macromol Rapid Commun* 1997, 18, 471.
- Daniel, H.; Miloslav, K.; Jiri, S. *J Polym Sci Polym Chem* 2000, 38, 653.
- Pelton, R. H. *Colloids Surf* 1986, 20, 247.
- Pelton, R. H.; Pelton, H. M.; Morphesis, A.; Rowell, R. L. *Langmuir* 1989, 5, 816.
- Takahashi, K.; Miyamori, S.; Uyama, H.; Kobayashi, S. *J Polym Sci Polym Chem Ed* 1996, 34, 175.
- Horak, D. *J Polym Sci Polym Chem Ed* 1999, 37, 3785.
- Ray, B.; Mandal, B. M. *Langmuir* 1997, 13, 2191.
- Ray, B.; Mandal, B. M. *J Polym Sci Polym Chem* 1999, 37, 493.
- Xu, Z. L.; Zhang, Z. C.; Zhang, M. W. *J Disper Sci Technol* 1999, 20, 1647.
- Yoshida, M.; Kobota, T.; Asano, M.; Kumakura, M. *Colloid Polym Sci* 1986, 267, 986.
- Zhang, Z. C.; Jiang, P. Y.; Zhang, M. W. *J Radiat Res Radiat Process* 1990, 8, 100.
- Kabanev, V. A. *J Polym Sci Symp* 1973, 173, 42.
- Berne, B.; Pecora, R. *Dynamic Light Scattering*, 2nd ed.; Plenum: New York, 1991.
- Wu, C.; Guo, J.; Chu, B. *Macromolecules* 1989, 22, 633.
- Ye, Q. Zhang, Z. C., unpublished results, 2001.
- Lamer, V. K.; Dinegar, R. H. *J Am Chem Soc* 1975, 72, 4847.
- Naka, Y.; Kaetsu, I.; Yamamoto, Y.; Hayashi, K. *J Polym Sci A* 1992, 29, 1197.
- Paine, A. J. *Macromolecules* 1990, 23, 3109.
- Paine, A. J. *Macromolecules* 1990, 23, 3104.