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FORMATION OF MONODISPERSE POLYACRYLAMIDE PARTICLES BY DISPERSION POLYMERIZATION. I. SYNTHESIS AND POLYMERIZATION KINETICS

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ABSTRACT

Highly monodisperse polyacrylamide (PAM) microparticles were directly prepared by dispersion polymerization in aqueous alcohol media initiated by 2,2′-azobisisobutyronitrile (AIBN) 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 influences of initiator concentration, monomer concentration, stabilizer content, medium polarity, polymerization temperature on the polymerization rate and the molecular weight of polymer have been examined. The polymerization rate (R_p) can be represented by $R_p \propto [I]^{0.52}$, $[M]^{1.16}$, $[S]^{0.52}$, $[A/W]^{0.25}$ (at A/W value below 1.25), and the molecular weight of polymer can be represented by $M_w \propto [I]^{-0.22}$, $[M]^{1.46}$, $[S]^{0.25}$, $[A/W]^{0.19}$. The overall activation energy for the rate of polymerization is 48.10 kJ/mol (45−55°C). Based on these experimental results, the polymerization mechanisms were discussed primarily.

Key Words: Dispersion polymerization; Polyacrylamide; Monodisperse particles; Polymerization kinetics; Water-soluble polymers

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INTRODUCTION

There has been substantial interest in monodisperse polymer particles since J. W. Vanderhoff and E. B. Bradford announced their preparation of polystyrene particles with highly uniform particle size in 1955.[1] A wide variety of applications of monodisperse particles have been found, including instrument calibration standards, column packing material for chromatographic separation,[2,3] support materials for biochemicals,[4] clinical examination,[5] catalyst carriers, coating and ink additives, information storage materials, and so on. All these successful applications are ultimately dependent upon the particle size and 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 Corporation in the 1970s.[6] A typical example of this method is the dispersion polymerization of styrene in hydrocarbons, alcohols, alcohol-ether, and alcohol-water mixtures. The reaction medium should dissolve both 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 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,[7,8] 4-vinylpyridine,[9] 1-vinyl-2-pyrrolidone,[10] N-isopropylacrylamide [11,12] and 2-hydroethyl methacrylate [13,14] are described in the literature. Biswajit Ray [15,16] has 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 the present study, the dispersion polymerization of acrylamide using poly(N-vinylpyrrolidone) as sole stabilizer was made to examine the influence of initiator concentration, 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 been widely discussed before.

EXPERIMENTAL

Materials

Acrylamide (AM), obtained from Hubei Daxue Chemicals, Inc., was recrystallized from acetone. PVP (M_w 4×10^4, K-30) was supplied by Shanghai Chemical Reagent Co. *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 dispersion polymerization in different TBA water mixtures, in which the monomer is easily dissolved. Nitrogen with high purity was bubbled through the monomer solution at room temperature for about 15 min to get rid of oxygen. After that, the solution was directly fed into a special dilatometer [17] and held in a bath whose temperature can be accurately controlled by a regulator. The resulting 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 determined by further differentiation.

Viscosity Measurement

The molecular weight of the polymer was determined in 1M $NaNO_3$ aqueous solution with Ubbelode capillary viscometer at 30°C. The average molecular weight can be calculated with the Mark-Houwink relation:[18]

$$[\eta] = 3.37 \times 10^{-4}\, M_w^{0.66} (\mathrm{dL/g})$$

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-τ digital time correlator and a solid state laser (DPSS, out power $= \sim 400$ mV 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 $G(\Gamma)$.[19,20] For a pure diffusive relaxation, $(\Gamma/q^2)_{q\to 0, c\to 0}$ leads to the translational diffusion coefficient D or further to the hydrodynamic radius R_h via the Stocks-Einstein equation. The detail of LLS theory can be found elsewhere.[19,20] The polymer latex used in LLS was clarified by 0.8 μm 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 reaction 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 gel effect is observed evidently in the conversion-time curve. The linear portion of the curve extends to quite high conversion levels (~40–50%), showing no constant-rate region. Under normal conditions the R_p would have decreased with increasing conversion due to decreasing [M] at about 10% conversion. However, in the present case this decrease is fortuitously compensated by the gel effect up to a very high conversion level. The initiate rate of polymerization for a given run cannot be reproduced with a satisfactory accuracy because of the induction period. Therefore, the maximum reaction rate given by the slope of the linear part of the conversion-time curve was taken for determination of the kinetic relations.

The reasons that the rate of polymerization and the molecular weight of the final polymers prepared by dispersion polymerization are lower than in

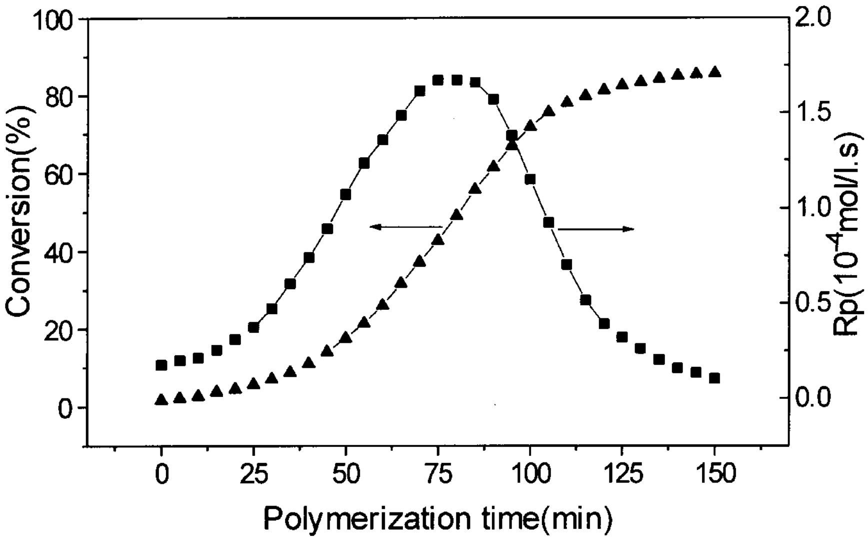

Figure 1. Conversion vs. time curve and polymerization rate vs. time curve. AM 6 wt%; TBA/H2O 5/4; PVP 6 wt%; AIBN 0.25 wt%; T 323 K.

conventional emulsion polymerization are due to the low monomer concentration in the polymer particles, low particle number, and very high average number of oligomeric radicals per particle. The relatively high number of oligomeric radicals existing in the monomer-swollen polymer particle is due to the large particle size and extremely high viscosity within the particles. The limited amount of monomer in the polymer particles is therefore shared by a large number of oligomeric radicals, resulting in a low molecular weight for the final polymers.

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 11% and 87% were shown in Fig. 2. It is clear that R_h changes from 148 nm to 231 nm, and its distribution becomes narrower with the increase of conversion. The polydispersity index at 87% conversion is about 1.02, indicating the monodispersity of particles. The monodispersity of a colloidal dispersion obtained from a synthetic process has been discussed by Lamer and Dineager,[21] and the authors have indicated that it is only when good stabilization and a short nucleation period coincide that monodispersity is achieved.

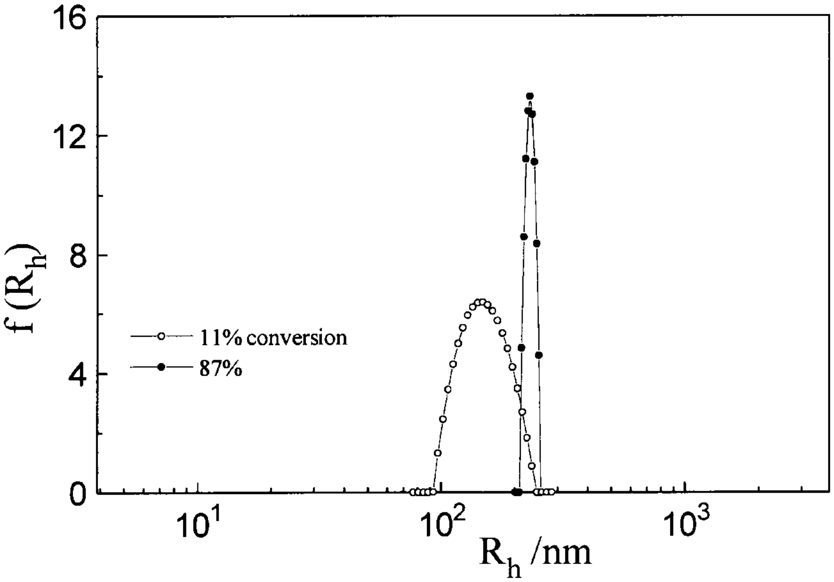

Figure 2. The hydrodynamic radius distribution $f(\langle R_h \rangle)$ of the PAM latex particles at two different conversions. AM 6 wt%; TBA/H_2O 5/4; PVP 6 wt%; AIBN 0.25 wt%; T 323 K.

Polymerization Kinetics

In this study, the influences of various polymerization parameters, including polymerization temperature, stabilizer concentration, initiator concentration, monomer concentration, and solvency of the medium, were investigated systematically. The standard recipes and synthesis parameters used in this study are given in Table 1. The amount of each ingredient was kept constant in all experiments except as indicated.

Effect of Initiator Concentration

The dependence of the conversion on the reaction time at different initiator concentration is shown in Fig. 3. The correlation between the initiator concentration and the polymerization rate (R_p) and the molecular weight (M_w) of polymer are also displayed in Fig. 3 and can be expressed as the following: $R_p \propto [I]^{0.52}$, $M_w \propto [I]^{-0.22}$. The overall R_p increases and M_w decreases with the increase of initiator concentration. The results conform to the general polymerization kinetics. As the initiator concentration increases, 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.

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.[22] When the monomer concentration was more than 10 wt%, the dispersion was so unstable that the coagulation happened. The polymerization conversion-time curves obtained at various monomer concentrations are shown in Fig. 4. From the slope of the conversion-time curves, $R_p \propto [M]^{1.16}$ and $M_w \propto [M]^{1.46}$ are obtained. It should be noted here that the

Table 1. Recipes and Synthesis Parameters for the Dispersion Polymerization of Acrylamide

	Standard Recipe or Parameter	Experimental Variation
Initial monomer content (wt%)	6.0	3.0 ~ 10.0
Polarity of dispersion medium (TBA/H_2O w/w)	1.25/1	0.3/1 ~ 1.7/1
Stabilizer Content (wt%)	6.0	2.0 ~ 6.0
Initiator Content (wt%)	0.25	0.15 ~ 0.45
Temperature (°C)	50	45 ~ 55

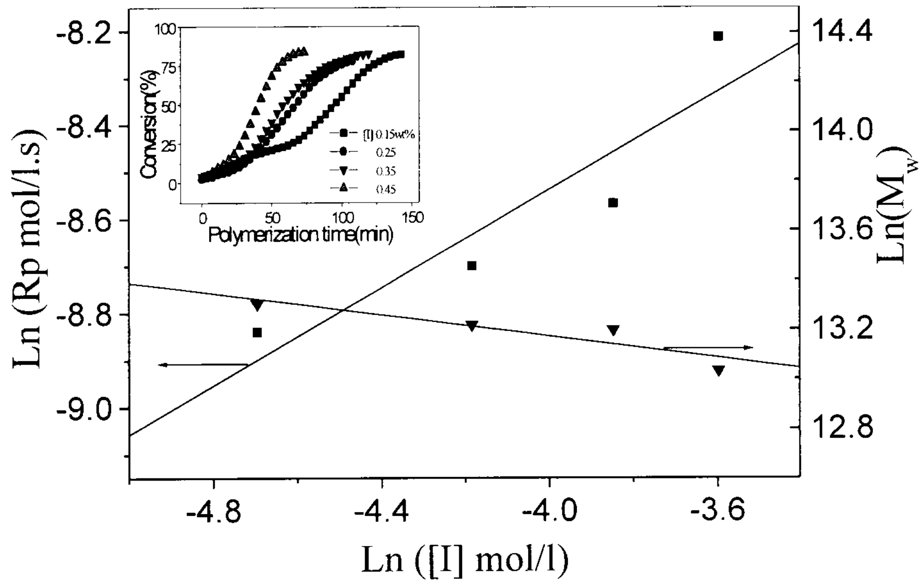

Figure 3. The effect of initiator concentration on polymerization. AM 6 wt%; TBA/H_2O 5/4; PVP 6 wt%; T 323 K.

monomer entry into the particle phase to sustain the solid state polymerization would be different for acylamide 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.[22,23] In the case of acrylamide, it has been suggested by Ray [15] that polyacrylamide particles are swollen by the dispersion medium and the monomer enters into the particles through the solvent channels. Figure 4 also indicates the relationship between the molecular weight of 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 α-hydrogens as possible chain transfer sites, is used as a steric stabilizer. The effect of stabilizer content on polymerization kinetics is shown in Fig. 5 as $R_p \propto [S]^{0.52}$ and $M_w \propto [S]^{0.25}$. When the PVP content was less than 2%, particles with bimodal size distribution or coagulum were obtained. The curve in Fig. 5 also tells us that the polymerization rate increases in general and polymer molecular weight increases with increasing PVP concentration. This result may be explained that a higher stabilizer concentration causes faster stabilizer adsorption, and hence for a given

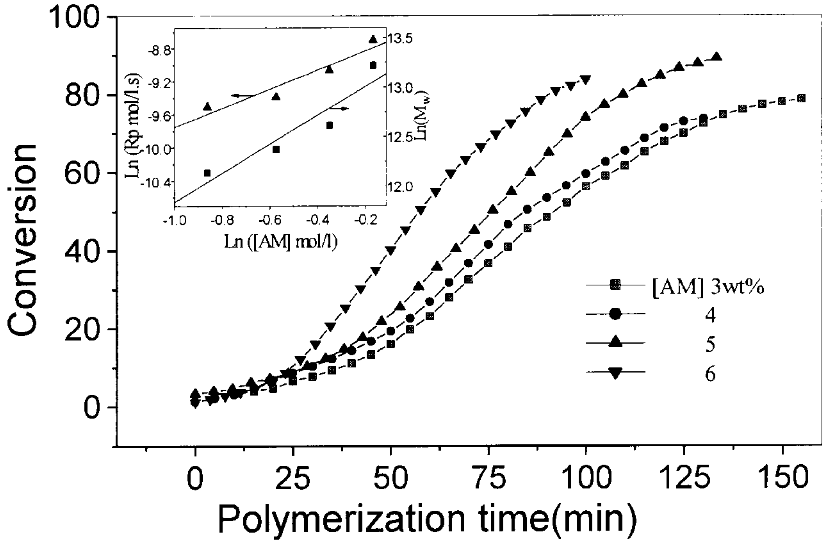

Figure 4. The polymerization rate vs. conversion curves at various monomer concentration. TBA/H_2O 5/4; PVP 6 wt%; AIBN 0.25 wt%; T 323 K.

duration a greater number of particles with 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 rise, and the reaction rate will increase.

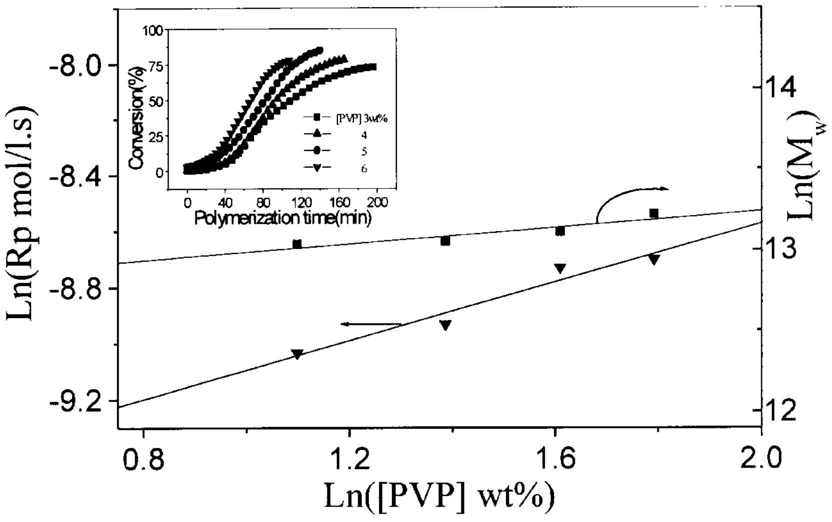

Figure 5. The effect of stabilizer content on polymerization. AM 6 wt%; TBA/H_2O 5/4; AIBN 0.25 wt%; T 323 K.

The increase of the molecular weight with the stabilizer concentration suggests that the polymerization has taken place considerably 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.[22]

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 mixture) also affected the rate of the dispersion polymerization of AM as shown in Fig. 6. The influence of the ratio of alcohol/water (A/W) on polymer molecular weight is also shown in Fig. 6: $M_W \propto [A/W]^{0.19}$. 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 0.7 to 1.25, the polymerization rate increased. This may be explained that TBA is a nonsolvent for PAM, but water is a good solvent. The addition of TBA to water makes the solvent increasing 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 a 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

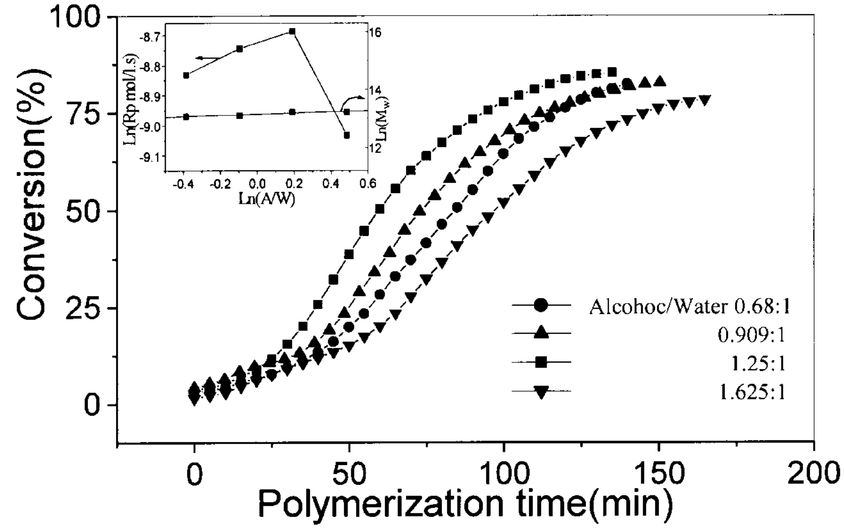

Figure 6. The conversion vs. time curves at different alcohol/water ratio. AM 6 wt%; PVP 6 wt%; AIBN 0.25 wt%; T 323 K.

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 particle ensures that the growing oligomeric radicals initiated in solution are captured efficiently. And this also leads to solid-phase polymerization that gives higher molecular weight polymer because of the gel effect.[23]

However, with a further increase of A/W above 1.25, the polymerization rate decreases. This can be explained that the transport of 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 radical 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 the increase in TBA concentration.

Effect of Polymerization Temperature

Figure 7 displays the effect of temperature on polymerization. According to the Arrenhenius Equation, the apparent activation energy for R_p and M_w is 48.10 and −57.90 KJ/mol, respectively. Although the relationship between the molecular weight of polymer and the polymerization tempera-

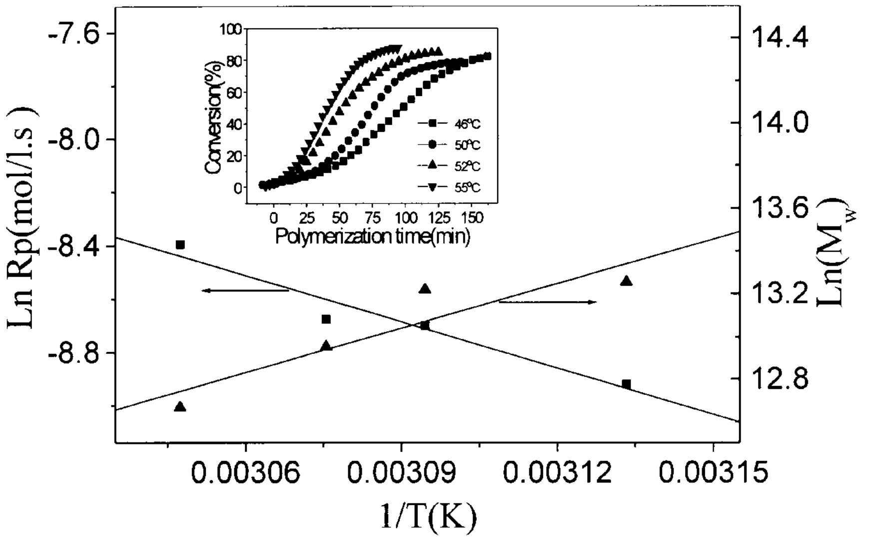

Figure 7. The effect of temperature on polymerization. AM 6 wt%; TBA/H_2O 5/4; PVP 6 wt%; AIBN 0.25 wt%.

ture (1/T) is somewhat scattered, as seen in Fig. 7, M_w tends to decrease with the temperature. These results also conform to the general polymerization.

CONCLUSION

In this work, the specific features of the dispersion polymerization of AM initiated by AIBN with PVP as the steric stabilizer in TBA/water have been studied. In general, the conversion-time curves are S-shaped because of the gel effect. It is discovered that the polymerization rate increases with the increase of initiator concentration, monomer concentration, stabilizer concentration, alcohol/water ratio at its value below 1.25, and the rise of temperature. And the polymer molecular weight increases with increasing stabilizer concentration, increasing monomer concentration, decreasing initiator concentration, decreasing polymerization temperature, and decreasing aqueous weight fraction. The effects of various polymerization parameters on particle size and size distribution as the second part will be forward in the near future. Further research is in progress.

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