Stability of Two-Phase Polymerization of Acrylamide in Aqueous Poly(ethylene glycol) Solution

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ABSTRACT: A poly(acrylamide) (PAM) aqueous dispersion with high solid was successfully synthesized through two-phase polymerization of acrylamide (AM) in aqueous poly(ethylene glycol) (PEG) solution. To prepare stable PAM aqueous dispersion, the effects of initiator, monomer and PEG concentration on the stability of the aqueous two-phase polymerization system were investigated in detail. Dynamic light scattering (DLS) was applied to study the evolution of the size and size distribution of the aqueous PAM droplet in the initial stage of polymerization. A droplet aggregation period was found in the initial stage, in which the PAM coagulum is easy to be generated below the conversion of about 5% due to high polymerization rate. By analyzing the effects of PEG on the stability of this polymerization system, it was found that PEG plays both precipitant and stabilizer role. When PEG concentration ranges from 12 to 24%, increasing its use would promote the droplet stabilization; however, when PEG concentration exceeds 28%, increasing its use may accelerate the droplet formation which does not further favor the droplet stabilization. Furthermore, the viscosity evolution during the polymerization under various reaction conditions was determined by rotational viscometer on line. When monomer concentration exceeded 8%, increasing the initiator or monomer concentration would result in that the polymer produced in the continuous phase could not be separated in time due to the high viscosity. All these results demonstrated that the slower the polymerization rate is, the more stable PAM aqueous dispersion will be. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1121–1133, 2011

Key words: aqueous two-phase polymerization; droplet aggregation; droplet stabilization; phase separation

INTRODUCTION

Poly(acrylamide) (PAM) has shown significant industrial applications and is widely used in a number of industrial fields such as waste water treatment, paper making, spinning, printing, and oil industries. The easiest method to prepare PAM is aqueous solution polymerization, the solvent is subsequently dried and the product is crushed down to powder to reduce transport cost. However, the viscosity of the aqueous solution polymerization system is very high, often giving rise to gels. And therefore, the dissolution time of the dry powder is very long. Although the inverse emulsion polymerization[1–4] and dispersion polymerization in aqueous tert-butyl alcohol (TBA)

media[5] overcome above-mentioned defect, the use of organic solvent such as hydrocarbon and toxic TBA will become pollutants to the environment again.

To overcome these disadvantages, in recent decades, two-phase polymerization of AM in aqueous media has received great attention as a green and effective approach for the preparation of PAM.[6–18] Through this polymerization process, PAM aqueous dispersions with low viscosity may be prepared. This kind of PAM aqueous dispersion does not contain any organic solvent, and could become solution instantaneously on the dilution with water. Regarding the two-phase polymerization in aqueous poly (ethylene glycol) (PEG) solution, early in the 1980s, Hosoda et al.[6] systematically studied the effect of PEG molecular weight on the stability of two-phase polymerization of sodium acrylate. They concluded that stable dispersion could be prepared only when the PEG molecular weight exceeded 8000. Compared with AM polymerization in aqueous salts media, the two-phase polymerization of AM in aqueous PEG solution does not need any stabilizer. Subsequently, Hu et al.[7] performed the two-phase polymerization of AM in aqueous PEG solution based on the phase diagram of PAM-PEG-water system. During the last few years, the two-phase polymerization of AM in

aqueous PEG solution was investigated systematically. Shan et al.[8–10] reported on the phase diagram of the PAM-PEG-water system, polymerization kinetics of this aqueous two-phase polymerization as well as the viscosity of its product. In these studies, it was found that stable PAM aqueous dispersion could not be prepared when the PEG molecular weight below 10,000. Furthermore, the viscosity of the final PAM aqueous dispersion increased with increasing amount of initiator, and the stability of the dispersion became bad. At the same time, PAM coagulum or gel was often present at a higher polymerization rate.

Recently, we reported on the droplet formation mechanism of the two-phase polymerization of AM in aqueous PEG solution.[11,12] After the macroradicals in the continuous phase attain the critical chain length, they separate from the continuous phase and aggregate to form the aqueous PAM droplets (dispersion phase). Thereafter, the polymerization performs in both the aqueous phases. It should be emphasized that small PAM droplet separated from the continuous phase ceaselessly, and many droplets aggregated with each other during the polymerization, which is quite different from the conversional dispersion polymerization. Therefore, to prepare stable PAM aqueous dispersion, and explain when and how the PAM coagulum and gel generate, it is of significant interest to investigate the droplet aggregation behavior and the viscosity evolution during the two-phase polymerization of AM in aqueous PEG solution.

In this article, the droplet aggregation in the initial stage of the polymerization was followed by dynamic light scattering (DLS) on line, meanwhile the viscosity evolution of the polymerization system was determined by rotational viscometer on line. Furthermore, digital optical phase-contrast microscope and transmission electron microscopy were used to examine the product and the droplet morphologies, respectively. We are particularly interested in the role of PEG acted in the aqueous two-phase polymerization system. Thus, the effects of PEG on the droplet stabilization during the aqueous two-phase polymerization were investigated systemically.

EXPERIMENTAL

Materials

Acrylamide (AM, 99.9%, Acros Organics) was of analytical grade and was dried *in vacuo* at 45°C. Ammonium persulfate (APS, Arkema) as a water-soluble initiators, poly(acrylamide) (PAM, Acros Organics) with a weight-average molecular weight of 1000, and poly(ethylene glycol) (PEG, Acros Organics) with the weight-average molecular weights of 4000, 6000, 10,000, and 20,000 were used as received without any purification. Deionized water was used throughout this work.

Polymerization procedure

The two-phase polymerization of AM in the aqueous solution of PEG was performed in a 500 mL glass jacket reactor with a five-necked cover equipped with a motor-driven Teflon stirrer, reflux condenser, argon inlet tube, thermometer, and sampling tube. PEG, AM, and water were added into the reactor, then the reaction mixture was heated to the appointed temperature and purged with argon for 30 min. Thereafter, the aqueous APS solution was injected to start the polymerization. The aqueous two-phase polymerization was carried out under the protection of argon throughout its course. The stirring speed was maintained at 100 rpm, and the temperature was kept constant. PEG20,000 was always used except as indicated.

Online measurement for the viscosity of the polymerization system

The reaction mixture containing initiator was introduced to fill up the chamber (about 50 mL) of the rotational viscometer (HAAKE VT550). Once the temperature reached 60°C, the measurement was started (time zero). To obtain the intrinsic viscosity of the polymerization system, the shear rate of the rotor was kept at a relatively low speed (15 rpm), and the viscosity was detected every 9 s.

Measurement of the PAM content in the continuous phase

During the polymerization process, about 5 g reaction mixture was taken at various times. Once the sample was got out from the reactor, hydroquinone (0.05 g) was added to stop the polymerization. Thereafter, in addition to conversion determination, the PAM droplets (dispersion phase) were then removed by centrifugation at 12,000 rpm. A small portion of the continuous phase (supernatant) was diluted with 0.1 mol/L aqueous $NaNO_3$ solution for the gel permeation chromatography (GPC) measurement. Then the area ratio of PAM peak to PEG peak could be determined by GPC (Waters 1525 pump, 2414 differential refractometer detector, 717 automatic sample loader). The chromatographic system was made up of three columns connected in series, with stationary phases of PL aquagel-OH 60, 50, and 30, respectively. The mobile phase was 0.1 mol/L aqueous $NaNO_3$ solution, the flow rate was 0.8 mL/min, the sampling volume was 50 μL, and the
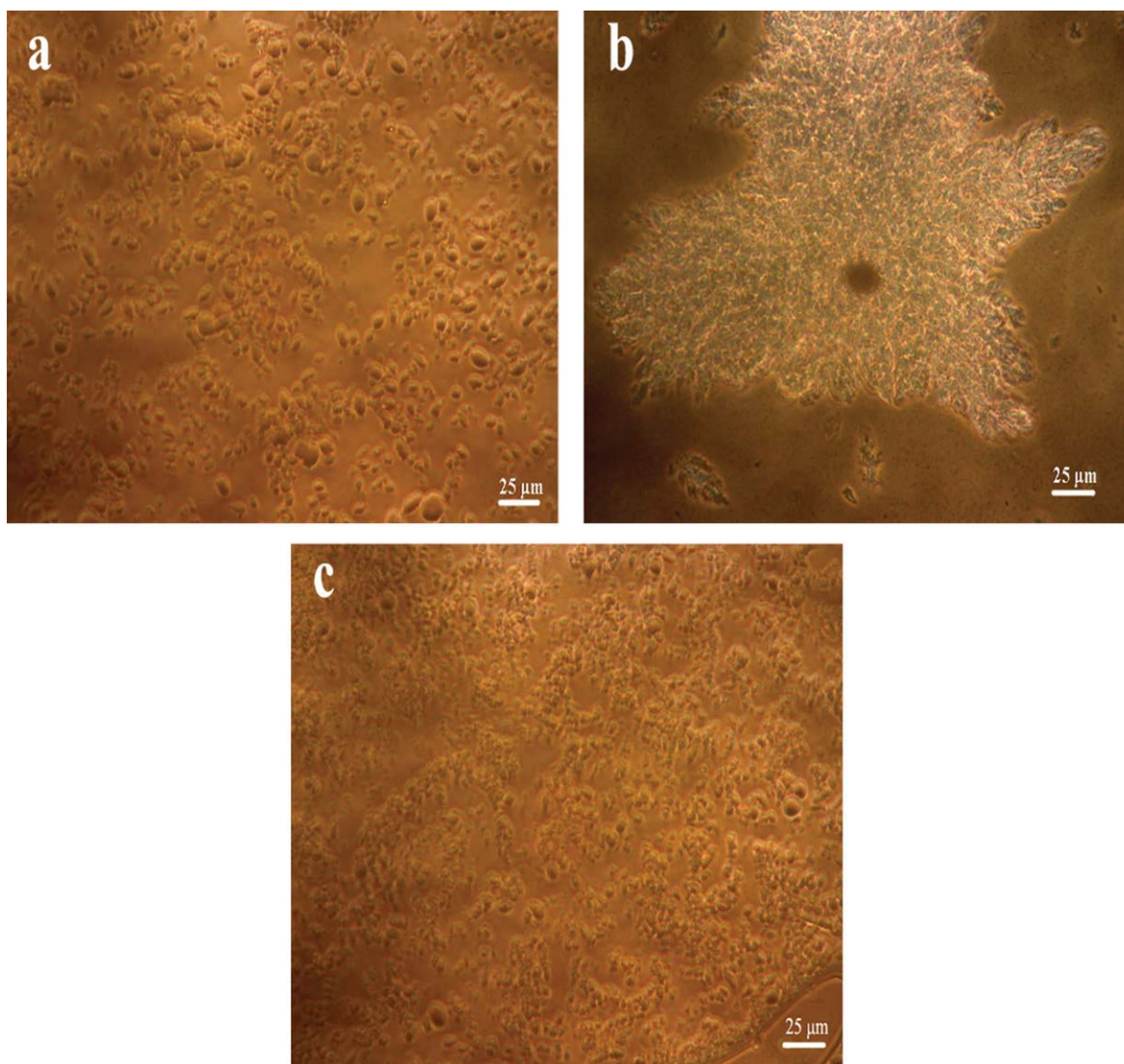
Figure 1 Shape of the product (monomer conversions are about 93%) prepared through aqueous two-phase polymerization of AM at 60°C under different APS concentration, (a) 0.0075%, (b) 0.0125%, (c) 0.0075% + 0.02% (PEG20,000 = 20 g, AM = 10 g, H_2O = 70 g, T = 60°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

column temperature was 30°C. Since the PEG amount inside the PAM droplets is very few, the PEG amount in the continuous phase nearly keeps constant. Therefore, the amount of PAM in the continuous phase could be calculated on the basis of the PEG content in the continuous phase in conjunction with the ratio of PAM to PEG determined by GPC.

Characterizations

The monomer conversion measurement and the DLS measurement was carried out as described in our previous studies.[11] The sample obtained from the aqueous two-phase polymerization was directly spread on a microslide, and its shape was examined by means of a digital optical phase-contrast microscope (NIKON BIOPHOT). The gel product was photographed by a digital camera (CANON SX200IS). The phase separation evolution of the aqueous two-phase system was observed by a digital optical polarizing microscope (NIKON ECLIPSE E600POL) with a heating platform (ED600). The PAM droplet morphology was observed by a transmission electron microscopy (TEM) (JEOL JSM-1230EXT20) using diluted redispersions in methanol. The ^{1}H-NMR experiments were carried out at room temperature with DMX (500 MHz) NMR spectrometer. The samples were usually completely dissolved in pure water (H_2O), and kept the aqueous PAM/PEG solution in the homogeneous region at room temperature. The heavy water (D_2O) kept in a sealed capillary was cast into the NMR tube and used as the external criterion. The weight-average molecular weight of PAM in the product was determined by
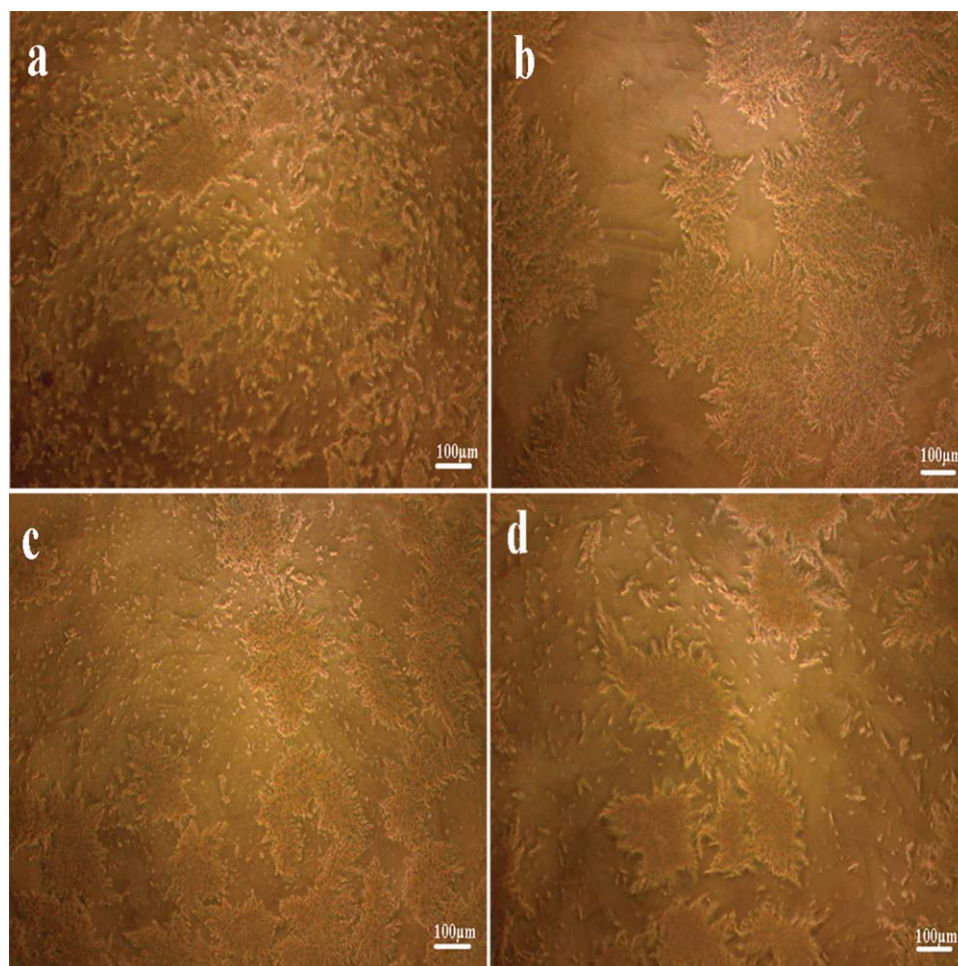
Figure 2 Shape of the product prepared through aqueous two-phase polymerization of AM at different conversion stages, (a) 5.42%, (b) 46.48%, (c) 65.67%, (d) 93.15% (PEG20,000 = 20 g, AM = 10 g, H_2O = 70 g, APS = 0.0125%, T = 60°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

GPC, the GPC measurement condition is the same as the measurement of the PAM content in the continuous phase.

RESULTS AND DISCUSSION

Droplet aggregation behavior during polymerization

Figure 1(a) represents the shape of the product prepared with 20% PEG, 10% AM, and 0.0075% APS at 60°C (all the concentrations given as wt % are with respect to total weight of the reaction mixture throughout the article). It seems that the obtained polydisperse aqueous PAM droplets can be dispersed equably in aqueous PEG solution. The size of these droplets is smaller than 25 μm. When the APS concentration increased to 0.01%, stable product could also be prepared. However, sequentially increasing the APS concentration to 0.0125%, the PAM coagulum with the size exceeding 100 μm is present in the final product, as shown in Figure 1(b).

To explore when the coagulum started to generate, the shapes of the reactant at every stage during the polymerization were investigated. As shown in Figure 2, the coagulum has presented when the monomer conversion is only about 5%, then the coagulum increases and grows ceaselessly as polymerization proceeds. From Figures 1 and 2, we can see that if the polymerization rate is too high, the coagulum will be produced in the early stage of the polymerization system, and its size is much larger than that of stable PAM droplets. This kind of product with very high yield of coagulum was unstable and would be layered after preservation in container for several days; moreover, these coagulum need a long time (30–60 min) to be dissolved in water completely, whereas the stable product costs only about 5 min. It should be emphasized that if no coagulum was formed in the early stage, stable aqueous PAM dispersion would be prepared even though the polymerization rate became more rapid in the middle and last stage of the polymerization. For example, the initial recipe is the same as that of Figure 1(a),

however, when the monomer conversion reached about 25%, additional APS (0.02% with respect to total weight of the reaction mixture) was introduced into the reaction mixture, the final product was still stable as shown in Figure 1(c).

In conventional dispersion polymerization, the particle formation stage is transitory. After the particle formation stage, the aggregation between the particles does not occur, meanwhile the particle number nearly keeps constant (no new particles are produced). However, new small aqueous PAM droplet is separated from the continuous phase ceaselessly during the aqueous two-phase polymerization,[11] which is quite different from the conventional dispersion polymerization. To investigate the PAM droplet aggregation behavior in the early stage of the polymerization of AM in aqueous PEG solution, DLS was applied to study the evolution of the droplet size and size distribution, just as shown in Figure 3. At the beginning of this polymerization, the droplet size and numbers are relatively small, and therefore the PAM droplets can disperse stably in aqueous PEG solution. On the one hand, small droplets are separated from the continuous phase; on the other hand, these droplets grow continuously via the polymerization inside the droplets. Thus, the droplet size distribution becomes wide. Thereafter, the increased numbers and size of these droplets become enough to start aggregating with each other, which causes the droplet size distribution become narrow as shown in Figure 3(a). In Figure 3(b), the number-average droplet size increased from about 60 nm to 90 nm (conversion 2.14–4.05%), but its size reached about 300 nm when the conversion is 6.19%. These results suggested that in the initial stage of the polymerization, one period of droplet aggregation exists after a temporary period in which the droplet can exist stably, even though the polymerization rate is very slow. Therefore, if the polymerization rate increases, the droplet aggregation may be further aggravated. As studied earlier,[12] the droplet morphologies present significant difference in the middle stage of polymerization when using different amount of initiator. When the initial APS concentration was 0.0025%, only round and oval droplets were found at the conversion of about 20%; however, with the APS concentration increasing to 0.0075%, the stripe shape droplets were observed at the similar conversion stage. These phenomena indicate that the droplet aggregation becomes more acute when more initiator introduced when the conversion below 20%. If too many PAM droplets are separated instantaneously, these droplets would aggregate severely to form coagulum. Thus, lower polymerization rate should be kept to prevent the formation of coagulum in the early stage of polymerization.
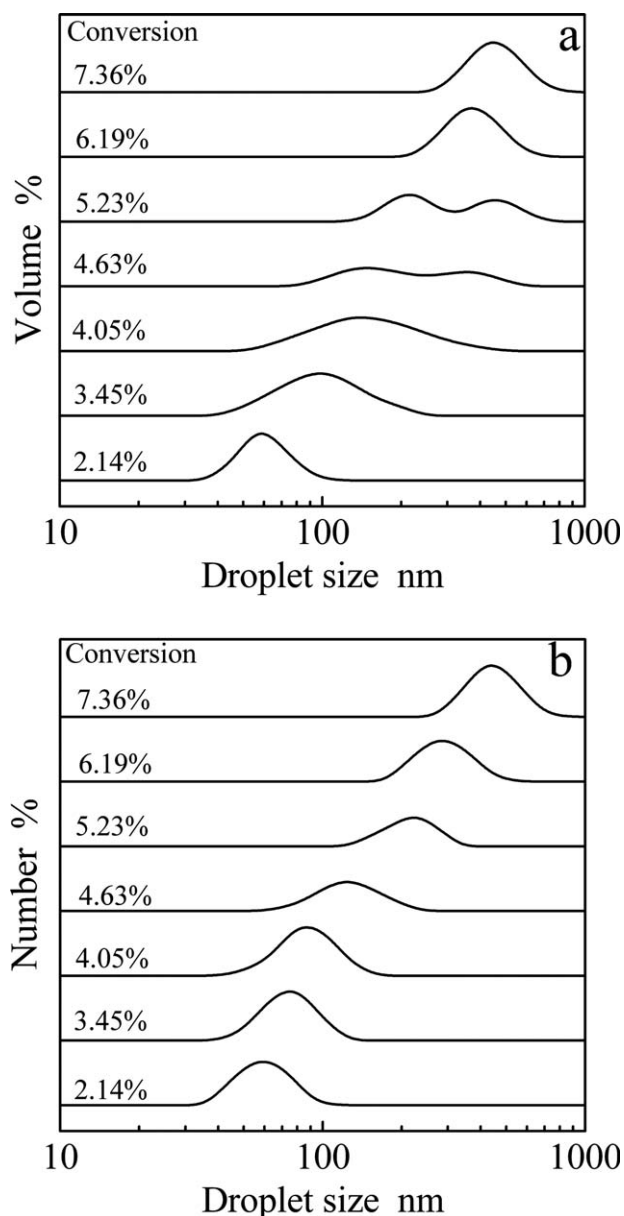

Figure 3 Evolution of the droplet size and distribution in the initial stage of polymerization (PEG20,000 = 12 g, AM = 4 g, H_2O = 84 g, APS = 0.0025%, T = 60°C).

Table I gives the average molecular weight of PAM ($\overline{M}_w$) prepared via the aqueous two-phase polymerization initiated by APS. With the APS concentration increasing, the $\overline{M}_w$ decreased firstly and then increased once coagulum presents. The index of molecular weight distribution (PDI) also increased significantly when coagulum appeared. To explain these phenomena, the difference of $\overline{M}_w$ evolution during polymerization between stable and unstable polymerization systems was investigated as shown in Figure 4. In a stable polymerization system, both the values of $\overline{M}_w$ and PDI increase slightly after the conversion exceeds 10% [Fig. 4(a)]. This could be attributed to the gel effect with the increase of PAM

APS concentration (wt %)	Conversion (%)	$\overline{M}_w$	PDI	Dispersion stability
0.0025	89.38	2.05×10^6	1.70	Stable
0.005	93.47	1.85×10^6	1.82	Stable
0.0075	95.38	1.61×10^6	2.10	Stable
0.01	95.76	1.47×10^6	2.57	Stable
0.0125	96.37	1.98×10^6	4.74	Coagulated
0.015	97.89	2.06×10^6	4.89	Coagulated

Polymerization conditions: AM = 10 g, PEG = 20 g, H_2O = 70 g, T = 60°C.

fraction inside the dispersion phase. However, in the polymerization systems in which coagulum presented, the $\overline{M}_w$ increased to a peak value until the conversion reached about 25%, and then began to decrease. Meanwhile the value of PDI increased obviously in the middle and last stage of polymerization [Fig. 4(b)]. This is because the radicals were embed and the radical termination rate slowed in the coagulum, hence the $\overline{M}_w$ attained the higher value. However, the droplet coalescence was gradually restrained due to increasing viscosity of the continuous phase with polymerization proceeding.[11] In other words, less and less coagulum would be produced in the middle and last stage of polymerization. Meanwhile, the monomers are difficult to diffuse into the coagulum presented at the early stage. Thus, the radical embedding reduced, and the molecular weight of PAM produced in the middle and last stage became lower. As a result, the $\overline{M}_w$ decreased and the value of PDI became large with the polymerization proceeding in the middle and last stage of polymerization. However, compared with that of stable product, the final $\overline{M}_w$ was enhanced because of the coagulum, and hence the abnormal evolution trend of $\overline{M}_w$ (Table I) can be easily understood.

Effect of PEG on the droplet stabilization

In a conventional dispersion polymerization system, the stabilizer usually could be adsorbed on the surface of the polymer particles by grafting with the polymers.[19,20] However, in our previous FTIR study,[11] it was verified that PEG could not be grafted with PAM. Therefore, the graft stabilizer mechanism could not be applied in this polymerization system. Figure 5 gives the ^{1}H-NMR spectra of PEG, PEG/PAM blends, and PAM in water. The most acute peak represents the water. It is evident that the chemical shift of ether groups of pure PEG at 3.589 ppm shifts to 3.887 ppm, while PAM is mixed in PEG water solution as shown in Figure

5(a). At the same time, in Figure 5(b), the amide peaks of PAM/water presented at the chemical shifts between 7 and 8 ppm almost disappear when PEG is blended. This finding appears to give support that the hydrogen bonding exists between ether groups in PEG and amide groups in PAM in the aqueous two-phase polymerization system. The amide hydrogen suffers more influence from ether, and becomes more flat and even not clearly shown. As a result, it is believed that some PEG molecules would interact with PAM molecules via hydrogen bonding and would be adsorbed around the aqueous PAM droplets.
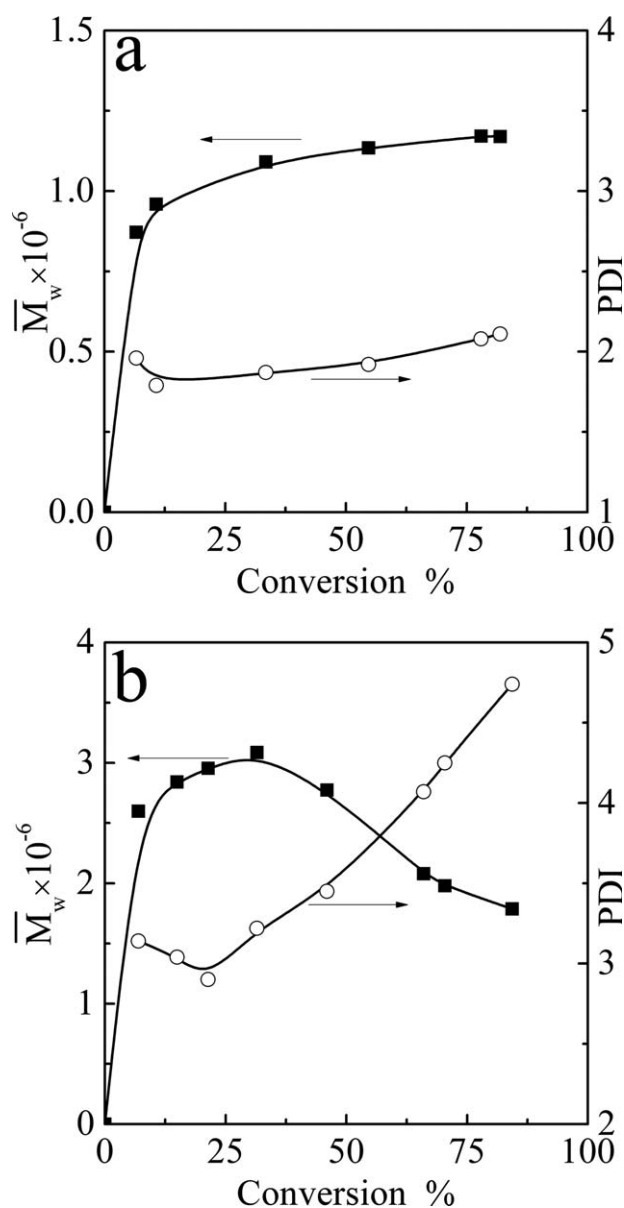

Figure 4 Evolution of molecular weight of PAM and its distribution during aqueous two-phase polymerization of AM, (a) AM = 6 g, PEG20,000 = 20 g, APS = 0.0075 g, H_2O = 74 g, T = 60°C, (b) AM = 10 g, PEG20,000 = 20 g, APS = 0.0125 g, H_2O = 70 g, T = 60°C.
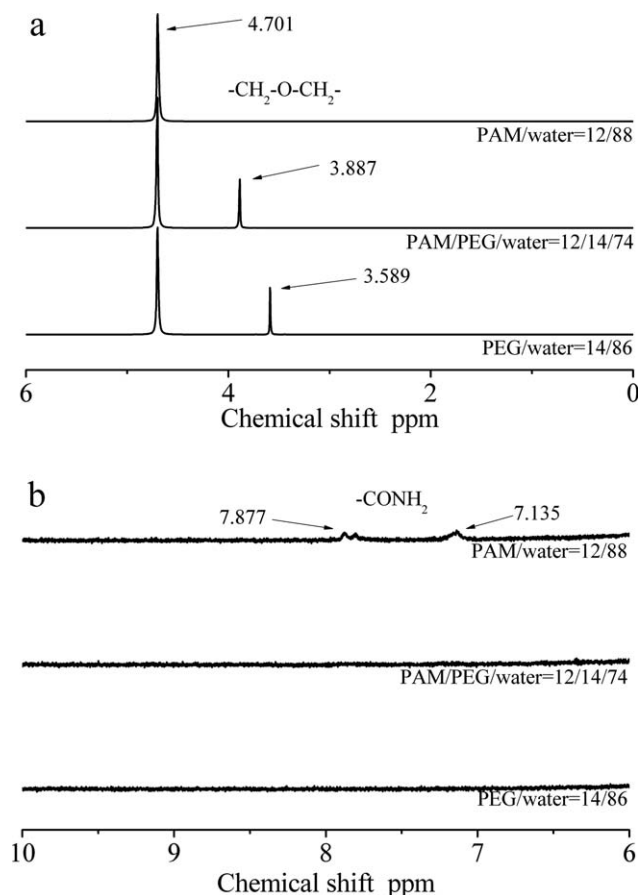
Figure 5 ^{1}H-NMR spectra of PAM1,000, PEG20,000 and their blends in water.

As above-mentioned, the hydrogen bonding would cause the PEG molecular chain to be aggregated and adsorbed on the surface of the aqueous PAM droplets. In other words, the thermodynamic stability of the PAM droplets mainly attributes to the steric stabilization of PEG, and therefore the PEG could acts as a stabilizer besides the precipitator in the polymerization of AM in aqueous PEG solution. Furthermore, the droplet aggregation could be restrained with increasing viscosity according to the droplet formation mechanism in aqueous two-phase polymerization.[11] It is easy to understand that increasing initial PEG amount may significantly enhance the system viscosity. From this point of view, increasing PEG concentration could enhance the droplet stabilization.

Table II gives the effect of PEG molecular weight on the product state. When PEG 4000 or 6000 was applied, the translucent jelly-like product was obtained, even though the PEG concentration increased to 32% or 36%. The stable aqueous PAM dispersion could not be prepared until the PEG10,000 concentration reached 28% or the PEG20,000 concentration reached 12%. As mentioned above, stable product could be prepared via increasing the PEG concentration when PEG10,000 was used. However, in Figure 6, the coagulum was always observed with the PEG concentration increasing from 14 to 28%, where the APS concentration was 0.0125%; in detail, even though the coagulum size seems to be smaller with PEG concentration increasing to 24%, its size become lager again when increasing PEG concentration to 28%. It seems that the increase of PEG concentration would enhance the droplet stabilization at first, but then aggravate the droplet aggregation. Thus, it is necessary to further understand the effect of PEG on the stability of aqueous two-phase polymerization system.

For the two-phase polymerization of AM in aqueous PEG solution, the viscosity of dispersion phase is obviously higher than that of continuous phase. As a result, the polymerization rate in dispersion phase is much faster because of the gel effect. With increasing amounts of PEG, more monomer would be distributed in the dispersion phase[12]; moreover, internal viscosity of the aqueous PAM droplets would be also enhanced resulting in lower termination rate of the radicals. Thus, with the PEG

TABLE II
Effect of PEG Molecular Weight on the Product Prepared via Two-Phase
Polymerization of AM in Aqueous PEG Solution

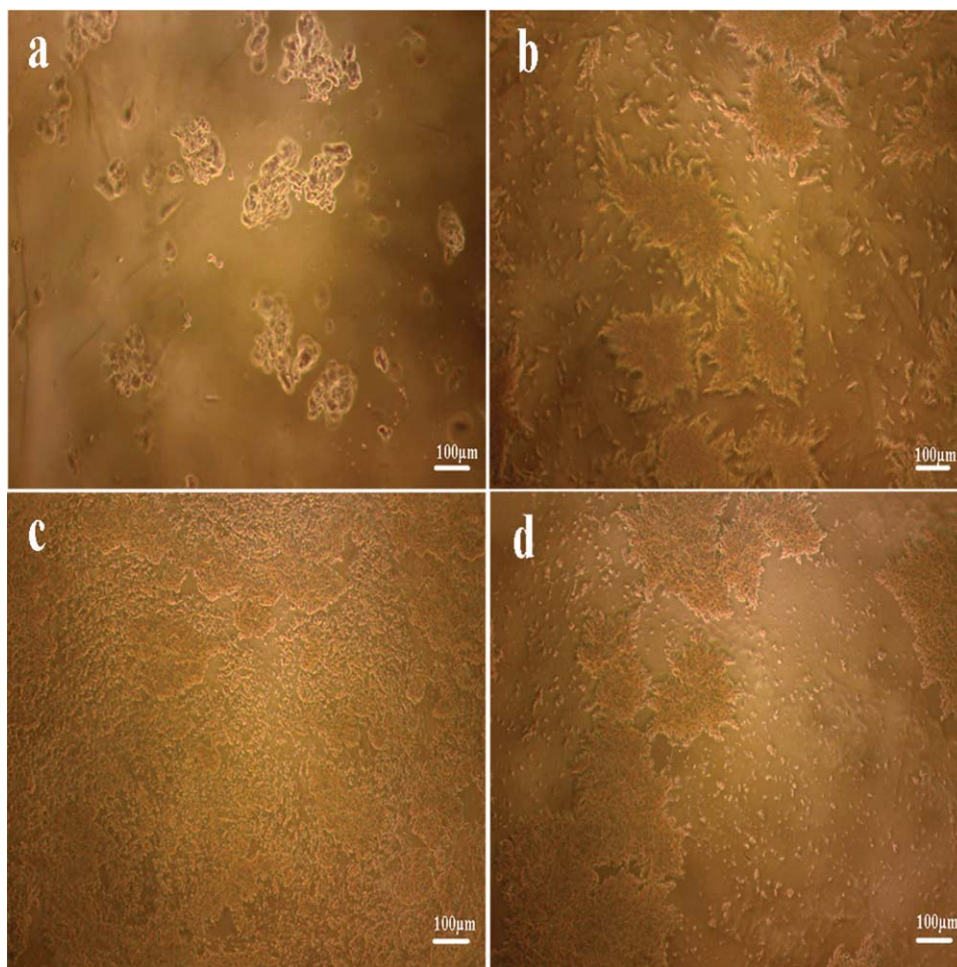| Molecular weight	PEG Concentration (%)	APS (%)	AM (%)	T (°C)	Dispersion stability
4000	32	0.0075	10	60	Coagulated
	36	0.0075	10	60	Coagulated
6000	28	0.0075	10	60	Coagulated
	32	0.0075	10	60	Coagulated
10,000	24	0.0075	10	60	Coagulated
	28	0.0075	10	60	Stable
20,000	12	0.0075	10	60	Stable
	16	0.0075	10	60	Stable
	20	0.0075	10	60	Stable

Figure 6 Shape of the product prepared through aqueous two-phase polymerization of AM in different concentrations of aqueous PEG solutions, (a) 14%, (b) 20%, (c) 24%, (d) 28% (PEG20,000 + H$_2$O = 90 g, AM = 10 g, APS = 0.0125%, T = 60°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

concentration increasing, the polymerization kinetic is accelerated,[9] and the final conversion increased; meanwhile, the $\overline{M}_w$ enhanced and the value of PDI reduced, as shown in Table III. On the one hand, more monomer polymerized inside the aqueous PAM droplets; on the other hand, the increase of PEG amount also enhanced the continuous phase viscosity and the steric stabilization of the droplets. Thus, when the PEG concentration increased from 20 to 28%, the droplet aggregation reduced to form round and big droplets as shown in Figure 7(a, b). However, in Figure 7(c, d), with the PEG concentration increasing sequentially to 32% or 36%, popcorn shape droplets with smaller size were presented in all view. It could be attributed that with the PEG concentration increasing, the critical chain length of PAM separated from the continuous phase becomes shorter and the droplet formation accelerates. This result highlighted the precipitator role of PEG, and the high viscosity of the continuous phase could not prevent these generated droplets from aggregation.

In light of above-mentioned, the role of PEG acted in the aqueous two-phase polymerization is complex. The increase of PEG concentration would result in various and even reverse effects on the droplet stabilization. On the one hand, the increase of PEG concentration would increase the viscosity of the PEG continuous phase to slow the PAM droplet

TABLE III
Effect of PEG Concentration on the Properties of the Product

PEG (wt %)	Conversion (%)	$\overline{M}_w$	PDI	Dispersion stability
8	88.37	1.12×10^6	2.76	Coagulated
12	93.28	1.47×10^6	2.49	Stable
16	95.27	1.51×10^6	2.48	Stable
20	95.38	1.61×10^6	2.10	Stable
24	96.27	1.80×10^6	1.89	Stable
28	96.86	1.93×10^6	1.74	Stable

Polymerization conditions: AM = 10 g, PEG + H$_2$O = 90 g, APS = 0.0075 g, T = 60°C.
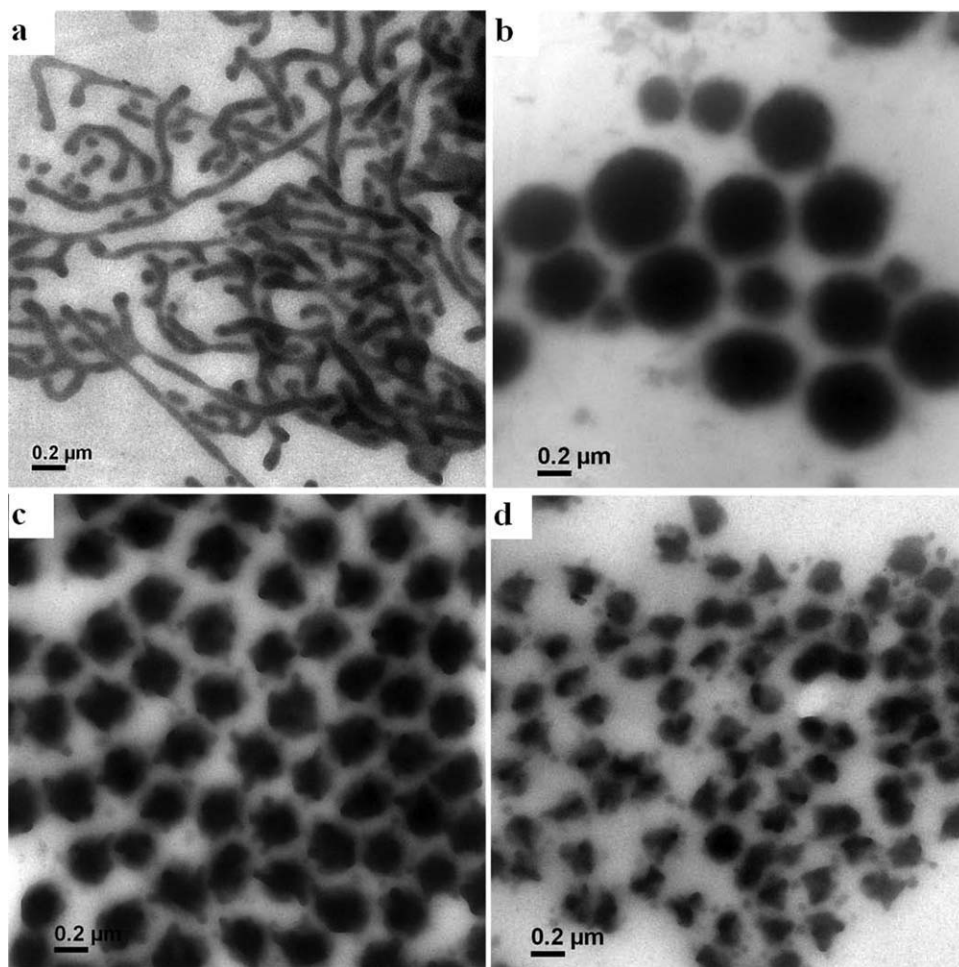
Figure 7 Droplet morphologies prepared through aqueous two-phase polymerization of AM in different aqueous PEG concentration, (a) 20%, (b) 28%, (c) 32%, (d) 36% (AM = 2 g, PEG20,000 + H_2O = 98 g, APS = 0.01%, T = 60°C).

coalescence and enhance the steric stabilization of the aqueous PAM droplets; on the other hand, the increase of PEG concentration would accelerate the PAM droplet formation, leading to more aggregation of droplets. Thus, the increase of PEG concentration would promote the droplet stability to some extent, but could not effectively prevent severe aggregation of the droplets when the polymerization rate is high as shown in Figure 6.

Viscosity evolution during polymerization

During the two-phase polymerization of AM in aqueous PEG solution, the viscosity of the polymerization system increases with the development of polymerization.[11] It is known that although the PAM content in the continuous phase is very low according to the phase diagram of PEG-PAM3,000,000-H_2O system,[9] however, extremely high viscosity of aqueous PAM solution is enough to enhance the viscosity of the polymerization system. Therefore, the increase of the viscosity during polymerization could be attributed to two factors: one is
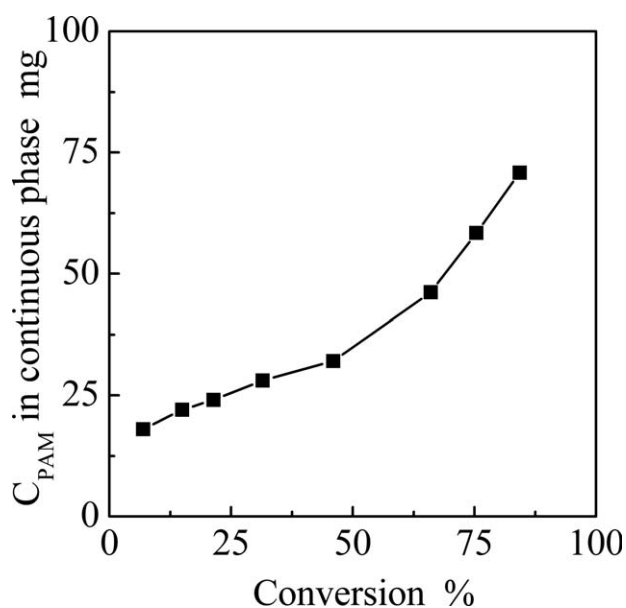

Figure 8 PAM content evolution in the continuous phase for the aqueous two-phase polymerization of AM in aqueous PEG solution (PEG20,000 = 20 g, AM = 10 g, H_2O = 70 g, APS = 0.0075%, T = 60°C).
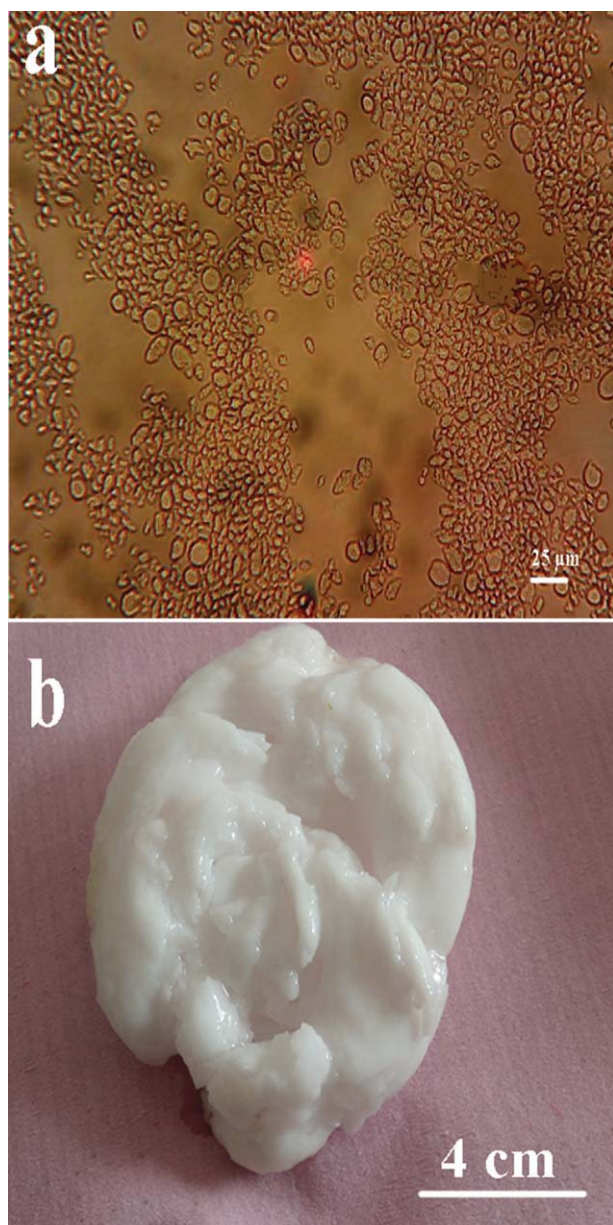
Figure 9 Shape of the product prepared through aqueous two-phase polymerization of AM in aqueous PEG solutions under different APS concentration, (a) 0.0025%, (b) 0.0050% (AM = 16g, H_2O = 64 g, PEG20,000 = 20 g, T = 60°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the diffusion of water from the continuous phase to the dispersion phase; the other is the increase of PAM content (C_{PAM}) in the continuous phase as shown in Figure 8. Weissenberg effect (climbing-up) was usually observed at the middle stage of polymerization when the monomer concentration exceeded 10%, although no coagulum was found in the final product [Fig. 9(a)]. If the viscosity increases sharply, the polymerization heat could not be released successfully leading to the massive gel products [Fig. 9(b)]. Thus, it is very important to

control the viscosity of the reaction system during the polymerization.

The viscosity of the polymerization system was measured on line as shown in Figure 10. The viscosity increases smoothly with the development of polymerization as expected in Figure 10(a), while 10% AM, 0.01% APS, and 20% PEG were added. The final conversion was about 90%, when the viscosity measurement was finished. However, increasing the APS concentration to 0.04%, the viscosity increases acutely in Stage I, and then increases gently in Stage II. Thereafter, the viscosity again enhances quickly
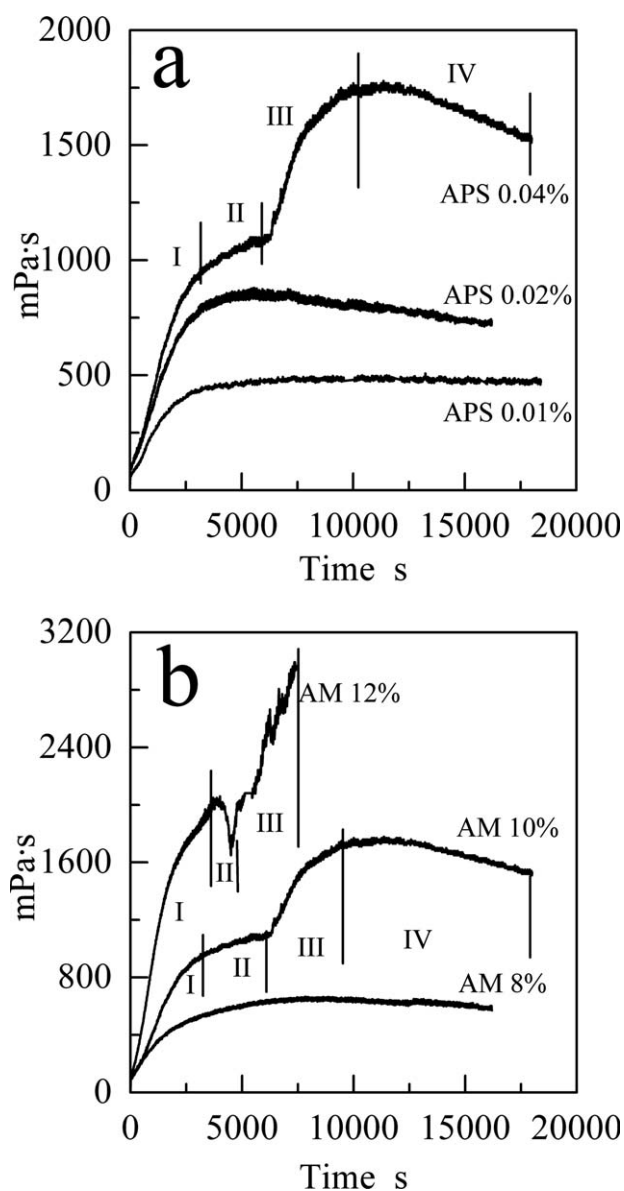

Figure 10 Effects of the initiator and monomer concentration on the viscosity evolution of the aqueous two-phase polymerization of AM in aqueous PEG solution, (a) PEG20,000 = 20 g, AM = 10 g, H_2O = 70 g, T = 60°C, 15 rpm; (b) PEG20,000 = 20 g, AM + H_2O = 80 g, APS = 0.04%, T = 60°C; the viscosity was determined at 60°C, and the shear rate was 15 rpm.
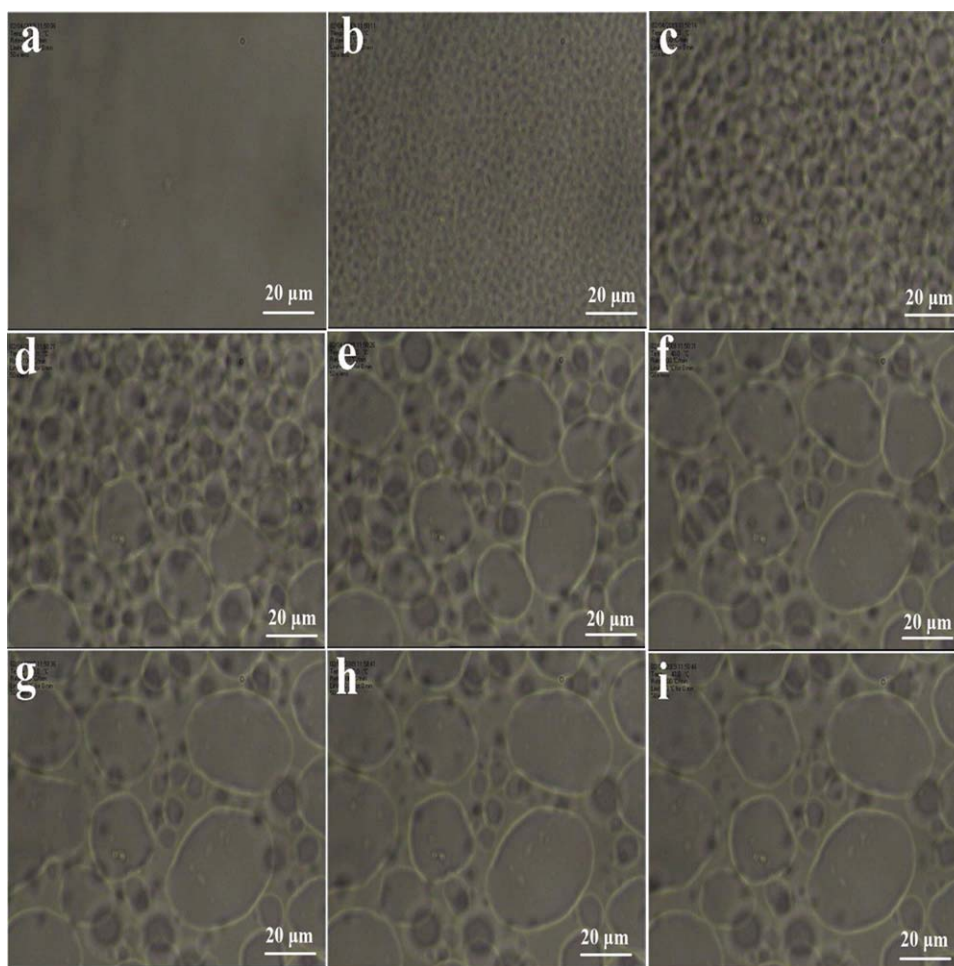
Figure 11 Evolution of phase separation of the PAM-PEG-water system after the temperature jumped from 30 to 40°C instantaneously at, (a) 0 s, 30°C, (b) 5 s, 40°C, (c) 10 s, 40°C, (d) 15 s, 40°C, (e) 20 s, 40°C, (f) 25 s, 40°C, (g) 30 s, 40°C, (h) 35 s, 40°C, (i) 40 s, 40°C, respectively, (PAM1,00 = 14%, PEG20,000 = 14%, H$_2$O = 72%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the peak value (Stage III); finally, the viscosity decreases a little in Stage IV of the polymerization as shown in Figure 10(a). Keep the APS concentration at 0.04% and increase the AM concentration to 12%, the viscosity at Stage II even decreased a little, however, the viscosity increased significantly again until exceeding the peak load of the apparatus (Stage III) as shown in Figure 10(b). The evolution trend of the viscosity with increasing amount of initiator is conformity with the increase of the monomer concentration, which suggests that the viscosity evolution of the polymerization system is closely relevant to the polymerization rate.

In Figure 10(b), when 8% AM and 0.04% APS were added, the final product contained a lot of coagulum, but the viscosity increases smoothly as polymerization proceeds. Moreover, as described earlier, the coagulum usually presents in the early stage of polymerization. Thus, the abnormal trend of viscosity evolution in the middle and last stage of polymerization would not be resulted from the coag-

ulum formation. In the most instances, the phase equilibrium between the continuous phase and the dispersed phase can be reached rapidly. It means that the polymer can be separated from continuous medium instantly. However, if too many polymers were produced in the continuous phase instantly, these generated polymers could not be separated and dispersed in time. Until the polymerization rate was relatively slowed, these overfull polymers in the continuous phase would be separated gradually and the viscosity would return to the normal state. It is evident in Figure 10(a) that the accelerating polymerization and increasing viscosity cause lots of generated PAM to be held up in the continuous phase, and further enhance the viscosity of the polymerization system. In other words, the high viscosity of polymerization system in the last of Stage I (indicated in the upper line, where APS concentration is 0.04%) is partially maintained by the overfull PAM in the continuous phase. However, the decreasing polymerization rate and continuously accumulated

PAM in the continuous phase, drive most of the PAM to be separated gradually. In the one hand, less PAM in the continuous phase reduces the polymerization viscosity; on the other hand, the proceeding polymerization would increase the viscosity. Thus, the viscosity in Stage II increases gently and even decreases a little. As polymerization proceeding, the viscosity increases quickly again in Stage III. At the same time, the continuous increase of the viscosity makes the phases separation become slower and slower. Thus, even though the polymerization rate is not rapid in the Stage III of polymerization, small parts of PAM could not be separated timely. Consequently, the viscosity decreases after the polymerization almost stops (Stage IV).

In the conventional dispersion polymerization, the polymer produced in the continuous phase can be separated rapidly due to the low viscosity of polymerization system. It is known that the velocity of phase separation would be significantly slowed with the viscosity increasing.[21–23] To confirm that the PAM produced in the continuous phase during the middle and last stage of polymerization needed time to precipitate, the phase separation of PAM1,000-PEG-H$_2$O system was examined. Figure 11 clearly reveals the evolution of phase separation of PAM1,000-PEG-H$_2$O system while the temperature jumped from 30 to 40°C instantaneously. It nearly took 30 s to finish phase separation completely in such a relatively low viscosity system. For the two-phase polymerization of AM in aqueous PEG solution, the viscosity of the most time of polymerization is usually higher than that of the PAM1,000-PEG-H$_2$O system. Thus, the explanation for above-mentioned abnormal viscosity behavior from the point of view of phase separation rate is believable. It should be emphasized that the viscosity of initial stage polymerization is still very low, and therefore, it does not conflict with the rapid phase separation and droplet formation at the early stage of polymerization.

The effect of PEG concentration on the evolution of the polymerization system viscosity was shown in Figure 12. As expected, the polymerization system viscosity decreased gradually with decreasing the PEG concentration. It should be noted in Figure 12 that the viscosity in the last stage declined more quickly to a lower value with decreasing amount of PEG. This is because the reduction of the polymerization system viscosity accelerates the phase separation. Similarly, when fewer amount of PEG was introduced, the viscosity in Stage II (indicated in the bottom line, where PEG concentration is 12%) increased slowly and even decreased a few; meanwhile the increase of viscosity in Stage III was greatly restrained. All of these phenomena could be interpreted in terms of the phase separation rate.
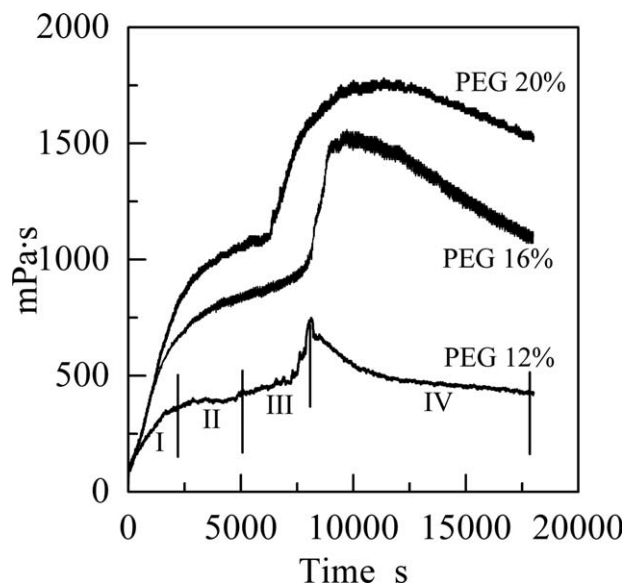

Figure 12 Effects of the PEG concentration on the viscosity evolution of the aqueous two-phase polymerization of AM in aqueous PEG solution (AM = 10 g, PEG20,000 + H$_2$O = 90 g, APS = 0.04%, T = 60°C; the viscosity was determined at 60°C, and the shear rate was 15 rpm).

From this part of research, it can be concluded that when AM concentration reached 10% or more, we can reduce the PEG concentration to 12% to decrease the viscosity of the polymerization system.

CONCLUSIONS

Two-phase polymerization of AM in aqueous PEG solution was successfully carried out with APS as the initiator, and the stable conditions for this polymerization system were investigated systemically. It was found that stability of this polymerization is quite different from the conventional dispersion polymerization. In the early stage of polymerization, the aggregation of PAM droplets was significant, and coagulum was easy to be produced below the conversion of about 5% due to high polymerization rate. The viscosity evolution during the aqueous two-phase polymerization were systemically measured on line, it was suggested that if the polymerization rate is high, the phase equilibrium between the continuous phase and the dispersion phase would not be reached instantly in the middle and last stage of polymerization. In this situation, gel product may be produced. Therefore, controlling a lower polymerization rate is vital for the preparation of stable PAM dispersions. In this polymerization system, when PEG concentration ranges from 12 to 24%, increasing its use would promote the droplet stability; however, when PEG concentration exceeds 28%, increasing its use may accelerate the droplet formation which does not further favor the droplet

stabilization. When the AM concentration kept at 10%, the concentrations for obtaining stable PAM aqueous dispersion were as follows: for PEG20,000, its better use ranged from 12 to 24%; for APS, its largest use is 0.01%. However, the largest use of APS should be decreased to 0.0025%, when the AM concentration increased to 16%.

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