Mechanism of the Droplet Formation and Stabilization in the Aqueous Two-Phase Polymerization of Acrylamide

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ABSTRACT: Aqueous two-phase polymerization of acrylamide has been carried out in an aqueous solution of poly(ethylene glycol) initiated by ammonium persulfate. The chemical composition of the product was characterized by FTIR, and the droplet size distribution in the initial stage of the polymerization was followed by dynamic light scattering. On the basis of the evolution of polyacrylamide aqueous droplets size distribution and morphology at every stage, a new mechanism of droplet formation was proposed. The experimental phenomenon that the small droplets always existed in the process of polymerization and some irregular shape droplets were formed in the product of aqueous two phase polymerization could be successfully explained by the new mechanism. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2859–2867, 2009

Key words: aqueous two-phase polymerization; polyacrylamide; poly(ethylene glycol); droplet formation; mechanism

INTRODUCTION

The water-soluble polymers, for example, polyacrylamide (PAM), can be widely applied in a number of industrial fields as a flocculant, a paper-making additive, and so on. In recent years, the preparation of water-soluble polymers through dispersion polymerization by using organic media as the continuous phase has been extensively studied[1–9]. The spherical particles in polydisperse and oval particles were produced in the system of the dispersion polymerization of acrylamide (AM) in water/*tert*-butyl alcohol medium using poly(vinyl methyl ether) (PVME) as the polymeric stabilizer.[1–3] A kind of PAM monodisperse microspheres in micronsize was prepared through a photoinitiated dispersion polymerization in an aqueous solution of ethanol at the room temperature.[5] Although a fast-soluble PAM with ultrahigh molecular weight can be synthesized via the dispersion polymerization in an aqueous alcohol medium, the extensive applications of this method are limited by its inherent defects in the pollution and recycle of used organic solvents.

Recently, the development of a green method for preparing water-soluble polymers has been drew more and more attentions. A new system of dispersion polymerization of AM without adding any organic solvent has been successfully developed in the aqueous solution of ammonium sulfate by Song and coworkers[10,11], Liu and coworkers,[12–14] and Wu et al.[15] It is believed that the newly produced polymers will separate from the aqueous solution of ammonium sulfate according to the principles of aqueous two-phase system.[10,11] With the help of stabilizer, poly(acryloyloxyethyl trimethyl ammonium chloride), the phase-separated polymer could be well dispersed in the aqueous solution of ammonium sulfate. The final dispersion of polymers can be directly used, and therefore, the process of separation and drying of solid products commonly used in aqueous solution polymerization as well as the redissolution of the products for applications become not necessary. As we all know, the aqueous solution of poly(ethylene glycol) (PEG) is one of the most commonly used compositions for the polymer aqueous two-phase system because of its excellent biological compatibility. However, only a few literatures about performing the polymerization in the aqueous solution of PEG for preparing water-soluble polymers have been reported. Hosoda et al.[16] successfully carried out the polymerization of sodium acrylate in the aqueous solution of PEG and studied

the molecular weight of the obtained polymer and viscosity of the system. Shan et al.[17–19] published their works about the polymerization of AM in the presence of aqueous PEG solution. The phase diagram of PAM-PEG-water system and the kinetics as well as the stabilization of the aqueous two-phase polymerization of AM were systemically investigated. It was found that the critical PAM concentration of phase separation was the lowest at 55°C, and decreased with the increase of PEG molecular weight. The effect of principal parameters on the kinetics and viscosity of the polymerization system was also investigated. The addition of emulsifier destroyed the stability of the latex dispersion system and resulted in a large viscosity.

In the present work, the aqueous two-phase polymerization of AM has been carried out in the aqueous solution of PEG without using any stabilizer. The initially homogeneous aqueous solution of monomer and PEG evolved to form an aqueous two-phase system as a result of phase separation of the newly produced polymers in the process of polymerization. The evolution of the droplet size and morphology at every stage of the aqueous two-phase polymerization of AM were studied. It is found that many results in the aqueous two-phase polymerization of AM were different from the previous investigation of the dispersion polymerization. We proposed a new mechanism for the formation and stability of the PAM aqueous droplets in the aqueous solution of PEG of the aqueous two-phase polymerization.

EXPERIMENTAL

Materials

Acrylamide (AM, 99.9%, Acros Organics) was analytical grade and dried in vacuum to remove water at 45°C. Ammonium persulfate (APS, ARKEMA) as a water-soluble initiator or *t*-hexyl peroxyivalate (THPV, ARKEMA) as an oil-soluble initiator, and PEG with the molecular weight of 20,000 (PEG20000, Acros Organics) were used as received without any purification. Deionized water was used throughout this work.

Polymerization procedure and monomer conversion measurement

The aqueous 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 a sampling tube. 20 g PEG, 6 g AM, and 72 g water were added to the reactor and purged with argon

for 30 min at 35°C, then the reaction mixture was heated to 60°C (the temperature of each experiment was kept constant, except as indicated), and then 0.0075 g APS was dissolved into 2 g water and added to start the polymerization. The reactions were run for 10 h for a high monomer conversion.

The monomer conversion was determined by bromating method. About 1.0 g reactant sample and 100 mL of water was added into an iodine flask. 20 mL of 0.1 mol/L $KBrO_3$-KBr aqueous solution (prepared by dissolving 3 g potassium bromate and 25 g potassium bromide in 1 L water) was added into the sample solution. After 10 mL HCl aqueous solution (5 mol/L) was added, $KBrO_3$ reacted with KBr to produce Br_2, and then Br_2 could react with residual AM in the sample solution for the addition reaction. 10 mL of 20 wt % KI aqueous solution was used to react with the residual Br_2 to produce I_2. By titrating I_2 with the standard solution of $Na_2S_2O_3$, the total residual contents of AM could be determined through the calculation of the consumption of $Na_2S_2O_3$.

On-line measurement for the process of droplets formation

12 g PEG and 4 g AM were dissolved into 84 g water in a 35°C water bath. After the PEG and AM were completely dissolved, then 0.01 g APS was added to the mixture. The mixture was passed through a 0.2 μm pore-size filter (to remove the dust) into a quartz cell (1.0 × 1.0 × 5.0 cm) which was used as the reactor for the on-line measurement after being carefully cleaned with water and dried. Because the polymerization of AM is sensitive to oxygen, the small cell was sealed by a rubber stopple under the protection of argon. The cell was cleaned and positioned in the chamber of a dynamic light scanning (DLS) equipment (Zetasizer 3000HSA, Malvern). The chamber was kept at a constant temperature of 60°C. The formation, size, and size distribution of droplets were on-line measured by DLS. The detection was continuously carried out run by run, the individual measurements cost about 4 min and the overall reaction time for this experiment was about 30 min. As soon as the cell was positioned in the chamber of the DLS instrument, the measurement was started (time zero).

Characterization

The droplet size and size distribution in the process of polymerization (droplets growth) were measured with a laser particle size analyzer (Coulter LS320). The samples were usually dispersed in methanol. The droplet morphology was observed by transmission electron microscopy (TEM) (JEOL JSM-
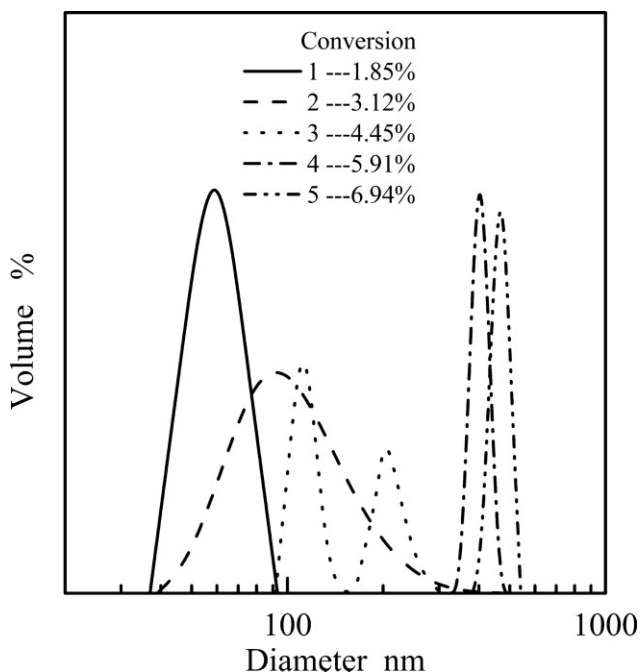
Figure 1 Droplets size distribution monitored by applying dynamic light scattering in the early stage of polymerization (PEG = 12 g, AM = 4 g, H_2O = 84 g, APS = 0.01 g).

1230EXT20) using diluted redispersions in methanol. The transparence of the reacted solution was investigated by spectrophotometer (Shimadzu UV-3150). The final product was dissolved in water, and then the aqueous solution of polymers was precipitated in a large quantity of methanol. These operations were repeated several times to remove PEG and unreacted monomers. The washed polymers were dried at 40°C under vacuum to a constant weight, and the chemical composition of the product was characterized by FTIR.

RESULTS AND DISCUSSION

On-line measurement of droplets formation

Normally, the formation of particles completes in a short time for a typical dispersion polymerization system. The oligomer radicals with critical chain length precipitate, and coagulate to form nuclei. The nuclei continue to coagulate rapidly until the stabilizers adsorbed by these particles are enough to ensure their colloidal stability.[20] Liu and coworkers[12] established a distinct particle formation process in the copolymerization of AM with 2-methylacryloyl-xyethyltrimethyl ammonium chloride in an solution of ammonium sulfate and sodium chloride. They regard that as soon as the polymerization begins, polymers and polymer radicals coagulate with each other to form small regions of polymer phase (rather than nuclei) under stirring. After stopping stirring, the shapes of the small regions change from strings

to irregular blocks. Disperse trend in the small regions increases with increasing of the interfacial tension of the continuous phase and the polymer phase. Thus, smaller particles start to form as the interfacial tension becomes strong enough.

In the present work, to explore the process of droplets formation, DLS was used to investigate the appearance, the size, and size distribution of droplets in the initial stage of aqueous two-phase polymerization of AM in PEG aqueous solution. The DLS on-line measurements were repeated three times for every sample, and the characteristics of appearance time, the size, and size distribution of the droplets obtained for each run were similar. A typical evolution of droplet size and size distribution in the initial stage are shown in Figure 1, and which indicates that (1) the fact that no droplet could be detected indicates that the system was homogeneous at the beginning of the polymerization; (2) the nano-primary droplets about 30 nm in diameter appeared suddenly as a result of the phase separation of the PAM radicals with critical chains length from the continuous phase; (3) the average diameter of the droplets increased from about 60–500 nm as the conversion increase from about 1–7%; (4) the droplet size distribution was wide and even bimodal in some case at first, and then became narrow.

As described earlier, the solution was transparent at first and turned turbid soon. This process can be followed by a spectrophotometer through measuring the transparence of the reacting solution, and the results were shown in Figure 2. It indicates that the
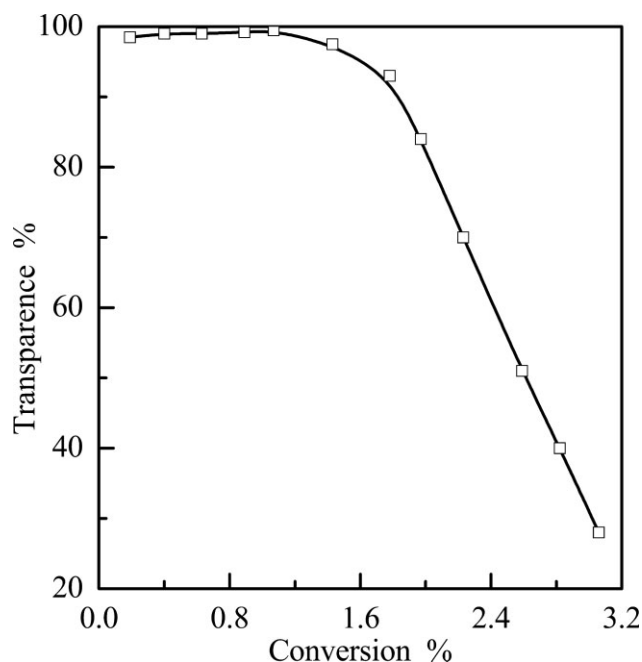

Figure 2 Transparence-conversion curves of the aqueous two-phase polymerization of AM (PEG = 20 g, AM = 6 g, H_2O = 74 g, APS = 0.0075 g).
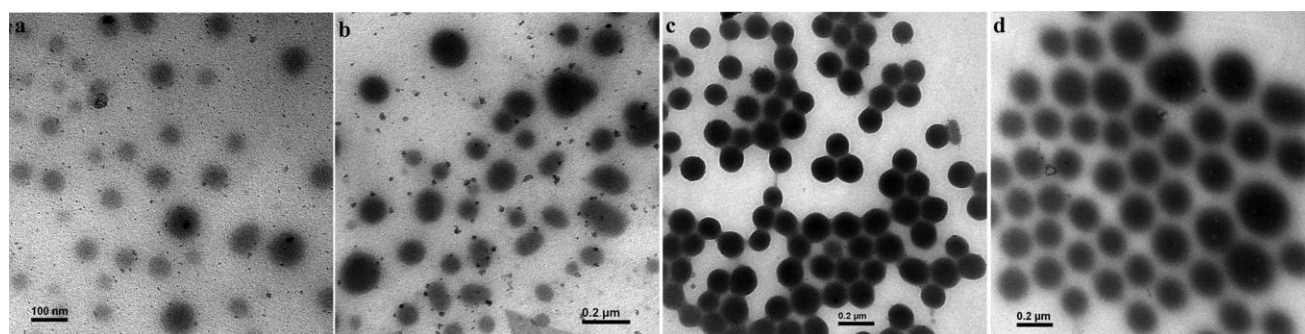
Figure 3 Droplet morphologies in the early stage; conversion: (a) 1.07%, (b) 2.43%, (c) 4.78%, (d) 5.82% (PEG = 12 g, AM = 4 g, H_2O = 84 g, APS = 0.01 g).

transparence kept constant at the beginning of the polymerization, and then declined suddenly when the conversion reached about 1% where could be considered as the phase separation point of the system. The morphologies of the droplets were observed by TEM. As shown in Figure 3, the droplet observed in the initial stage of polymerization is spherical but polydisperse, and the size range is from 30 to 90 nm. The value of the diameters may not exactly represent the true size of the droplet due to the loss of water during the TEM sample preparation and observation. However, it was a concentrated aqueous solution of PAM in the droplets resulting in a large viscosity in the interiors of them, as a result, the droplets prepared through the aqueous two-phase polymerization were strong enough to keep their original shapes. Thus, the morphologies of the droplets observed by TEM are believable. However, as the polymerization proceeded, some oval droplets formed in the product, although the conversion was still very low as shown in Figure 3(b). This indicates some coalescence of droplets occurred in this stage. The droplet size rapidly increased to about 150–200 nm, and the size distribution of droplets become uniform as shown in Figure 3(c,d). It is in agreement with the DLS results. These results seem to be different from both the experimental phenomena reported by Liu and coworkers[12], and the conventional dispersion polymerization.

Based on these results, the formation of droplets at the early stage of the polymerization could be described as follow. The reaction mixture was homogeneous at the start of polymerization. Once the initiator was introduced into the heated reaction mixture, free radicals were formed by initiator decomposition and propagated in the continuous phase. Free radicals with critical chain length separated from the continuous phase, these polymer radicals coagulated with each other to form nuclei, which continue to coagulate to form the nanoprimary droplets. The nanoprimary droplets were still not stable and further aggregated to form small

droplets rich in PAM. After this moment, the polymerization takes place in two locations. One is in continuous phase (rich in PEG), and the other is in dispersed phase (rich in PAM). In the subsequent stage after phase separation, the droplets were stable and grow mainly by polymerization inside the droplet. Because new smaller droplets were generated from continuous phase at the same time, the droplets size distribution became wide. However, the droplets became unstable with the increase of the number and size of the droplets, and aggregated with each other including the new generated small droplets. This presumption is confirmed by the formation of elliptical droplets shown in Figure 3(b). Anomalistic droplets were formed because of the high viscosity in the interiors of the droplets, which prevent the diffusion of PAM between the coalescing droplets. At that time, the viscosity of continuous phase was still low, and thus, the droplets aggregated quickly. The smaller droplets coagulated preferentially with each other. Both of them led to a narrow droplets size distribution.

Here, the period of droplets formation can be defined as from the time reaction started to the time that the nanoprimary droplets aggregated to form small droplets. In another word, the droplets formation stage finished when the small droplets began to aggregate, and the critical conversion of this period is about 3%.

Droplets growth and aggregation

According to the conventional mechanism of dispersion polymerization, the particle formation stage is transitory. After the particle formation stage, the number of mature particle will not change, whereas the sizes changes was mainly due to the polymerization inside the particle and the aggregation of small nuclei and oligo-radicals from the continuous phase.[21] Thus, there should be no small particle in existence. However, small droplets exist throughout the aqueous two-phase polymerization of AM in the aqueous
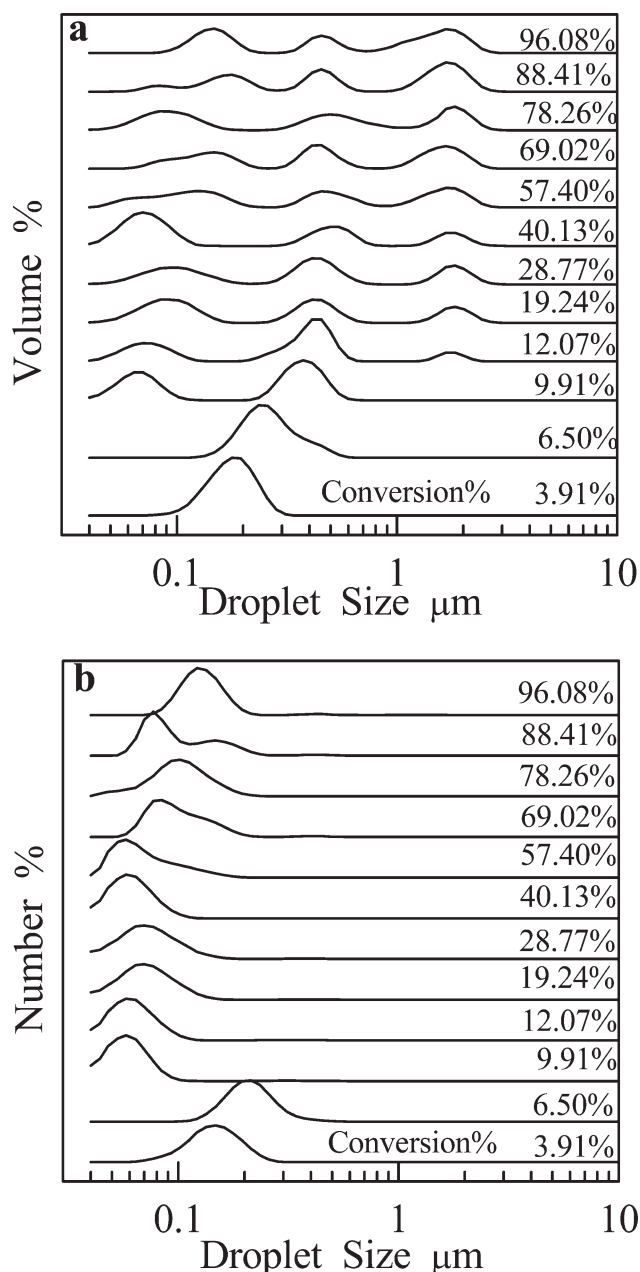
Figure 4 Relationship between the droplets size distribution and conversion of the aqueous two-phase polymerization of AM (PEG = 20 g, AM = 6 g, H_2O = 74 g, APS = 0.0075 g).

solution of PEG. It seems to be different from the present mechanism of dispersion polymerization.

The evolution of droplets size distribution is shown in Figure 4. In the early stage, there is only one peak meaning a rapid aggregation of droplets which is in agreement with the DLS on-line measurement. However, smaller droplets turned out at about 10% of conversion, and bigger droplets with the size of 1–2 μm appeared when the conversion is about 12%. With the development of polymerization, more and more droplets smaller than 200 nm

formed, and a polydisperse droplets dispersion system was obtained finally. The formation process of droplets was followed through the morphological observation by TEM, and the results can be seen in Figure 5. The irregular shape droplet formed at low conversion stage, as shown in Figure 5(a,b). When the conversion reached about 22%, the droplets with beads string shape were observed [Fig. 5(c,d)]. After that the droplets with a stripe shape could be found in the system, as seen in Figure 5(e–h). It was clearly found that small droplets existed even when the conversion was about 84%. Ultimately, a kind of dispersion latex with small and big, spherical as well as stripe-shape droplets was obtained and this result corresponds with the droplets size distribution shown in Figure 4.

Theoretically, the growth of droplets may be attributed to two factors. One is the aggregation of the droplets depending on the viscosity of the continuous phase, and the other is the polymerization inside the droplets.

In the earlier stage of polymerization, the rapid aggregation took place because of the low viscosity of the system, therefore, bigger droplets formed with uniform dimension. Subsequently, the increasing viscosity of the system reduced the aggregation of the droplets, and some small droplets can be existed stably. However, a majority of droplets participated in the aggregation to form a string of beads-shape droplets shown in Figure 5(c,d), which became the stripe shape finally by the polymerization inside the droplets. With the development of polymerization, more and more water diffused from the continuous phase to the dispersion phase, and the viscosity of the system increased. The aggregation of droplets became difficult, and as a result, more and more small droplets appeared. The number size distribution of the droplets shown in Figure 4(b) in the process of the polymerization is different from the volume size distribution as shown in Figure 4(a). It is difficult to observe the droplets with the size of 1–2 μm in Figure 4(b). This indicated that the number of small droplet is much more than the bigger droplets. It can be seen that the number average size increased firstly and was similar with the volume average size distribution shown in Figure 4(a) at the low conversion stage, and then decreased in a short time. This result confirmed the aforementioned suggestion again.

In the high viscosity stage, the polymerization inside the droplet plays a key role in the growth of droplets, because little aggregation happened. At this stage, small droplets generated slowly from the continuous phase and the droplets size increased slowly. It should be emphasized that the small droplets are always present in the process of polymerization clearly shown in Figure 5(g) even in very high
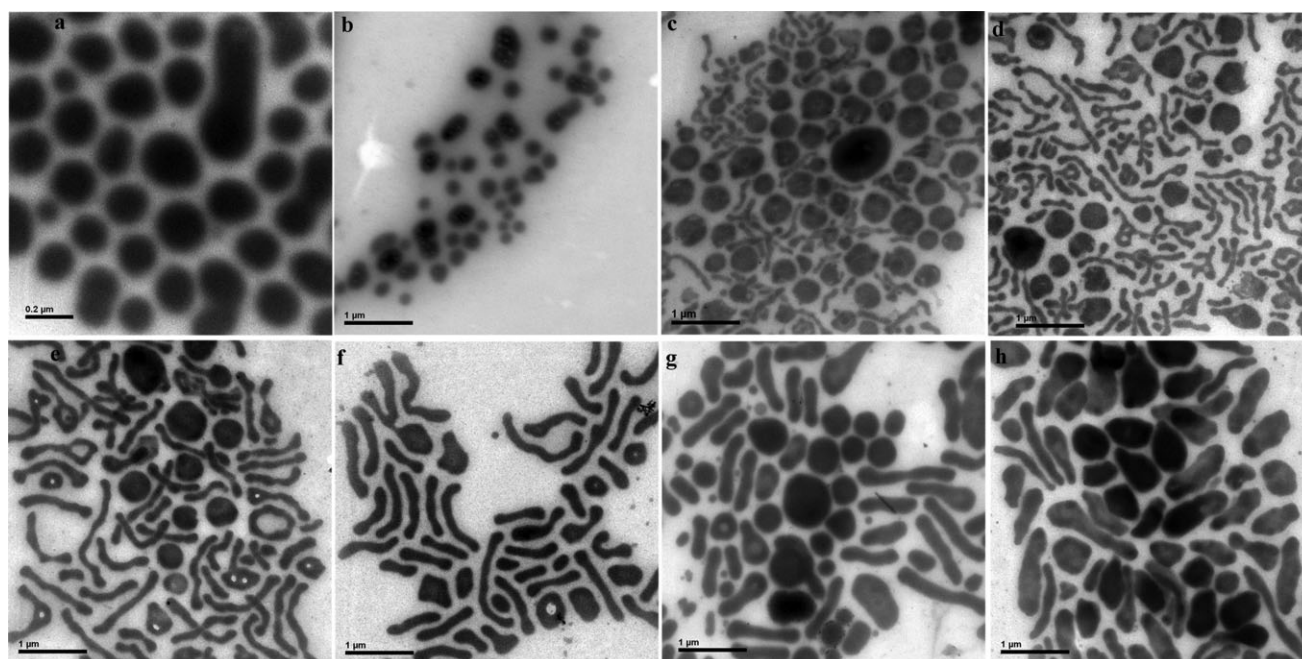
Figure 5 Droplet morphologies at every stage; Conversion: (a) 3.30% (b) 6.82% (c) 22.02% (d) 39.83% (e) 59.35% (f) 70.95% (g) 83.96% (h) 97.92% (PEG = 20 g, AM = 6 g, H_2O = 74 g, APS = 0.0075 g).

conversion stage. The phenomena shown in Figure 5 are consistent with the droplet size distribution shown in Figure 4.

Ye et al.[8] also observed small particle in conventional dispersion polymerization of AM in water/tert-butyl alcohol medium when the stabilizer (PVP) concentration was lager than 7%. They regarded this phenomenon may be due to the high viscosity of the continuous phase too.

Droplets stabilization

As for the process of dispersion polymerization, it has been recognized that stabilizer plays a crucial role in dispersion polymerization. Therefore, many reports have been focused on the effects of various stabilizers, such as PVP, hydroxypropyl cellulose (HPC), and PVME on the stability of the droplets or particles. Paine[22] compared the function of the adsorption of ungrafted stabilizer with that of grafted stabilizer in the stabilization of the particles, and concluded that the latter played a significant role for the stabilization of the dispersion polymerization of styrene in which the homopolymer like HPC was used as stabilizer. A similar conclusion has been draw by El-Aasser and coworkers[20,23] when they investigated the polymerization of methyl methacrylate with PVP as stabilizer.

The IR spectra of PEG, commercial PAM, and purified PAM prepared by aqueous two-phase polymerization are shown in Figure 6. The absence of peak at 1110 cm^{-1} (C—O—C) in the spectrum of

PAM prepared by the aqueous two-phase polymerization indicates that there is no copolymer generated. Therefore, the droplets rich in PAM, dispersed stably in the aqueous two-phase polymerization system with APS as initiator, mainly attributed to the relatively high viscosity of continuous phase, and to
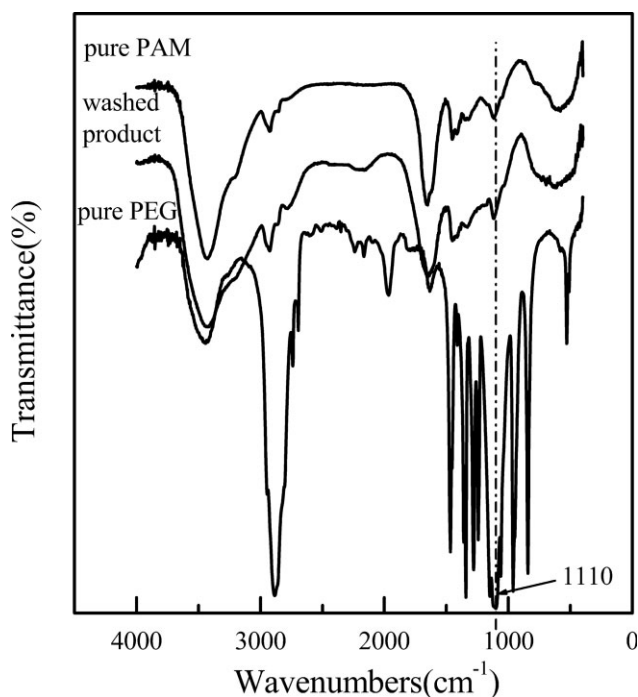

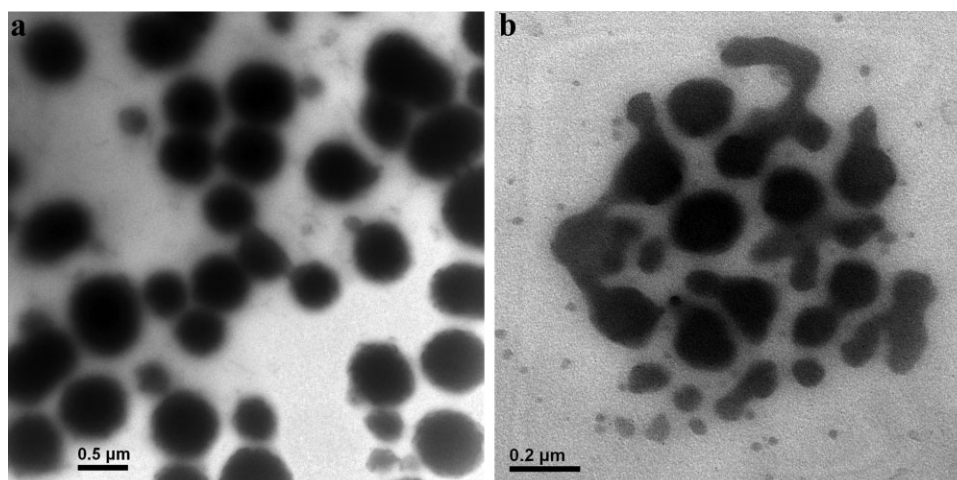**Figure 6** FTIR spectra of the pure PAM PEG and the washed product.

Figure 7 Droplet morphologies with various initiators. (a)APS = 0.01 g, (b)THPV = 0.0089 g (PEG = 28 g, AM = 2 g, H_2O = 70 g).

electrostatic effect of the ionic sulfate end group especially in the early stage.

The importance of the sulfate end groups toward droplet stability is confirmed by the fact that the system using THPV as the initiator yielded some strip-shape droplets instead of the spherical droplets in the system initiated by APS, as shown in Figure 7. The products shown in Figure 7(a,b) were prepared with 28% of PEG and 2% of AM at 60°C with the same molar amount of the different initiators. Although the decomposition rate of THPV is faster than that of APS, the kinetics of polymerization initiated by THPV is slower than that of the system initiated by APS, according to the results in Figure 8. The obvious differences in the kinetics of the system initiated by APS and THPV lies in the low water solubility of the latter, which made the polymerization mainly take place in the continuous phase and the interface of the droplet, and made the droplets prepared with THPV smaller than that with APS as shown in Figure 7. This result also remarkably suggested that polymerization inside the droplet plays an important role in this system with APS as initiator.

Mechanism of droplets formation and growth

Based on aforementioned results, a new mechanism was proposed for describing the processes for the formation of the droplets in the polymerization system of AM-PEG-H_2O. The schematic representation was shown in Figure 9. The detailed description of the polymerization is as follow. As the reaction starts, primary radicals, generated by decomposition of the initiator, grow in the continuous phase by the addition of monomer units until they reach their critical chain length, as show in Figure 9, reaction I, II. Then these polymer radicals precipitate and aggregate to form nuclei. But the nuclei are not stable,

and they will immediately aggregate with each other to form nanoprimary droplets. The nanoprimary droplets are still unstable, and aggregate sequentially to form more stable small droplets rich in PAM (Fig. 9, reaction III). Then monomer and initiator diffuse into the droplets rapidly, and polymerization takes place in both the continuous phase and the dispersed phase (inside the droplets). In the earlier stage, the PAM droplets are stable and grow mainly by polymerization inside the droplet. Because new smaller droplet generate from continuous phase at the same time, the droplets size distribution becomes wide. However, these small droplets
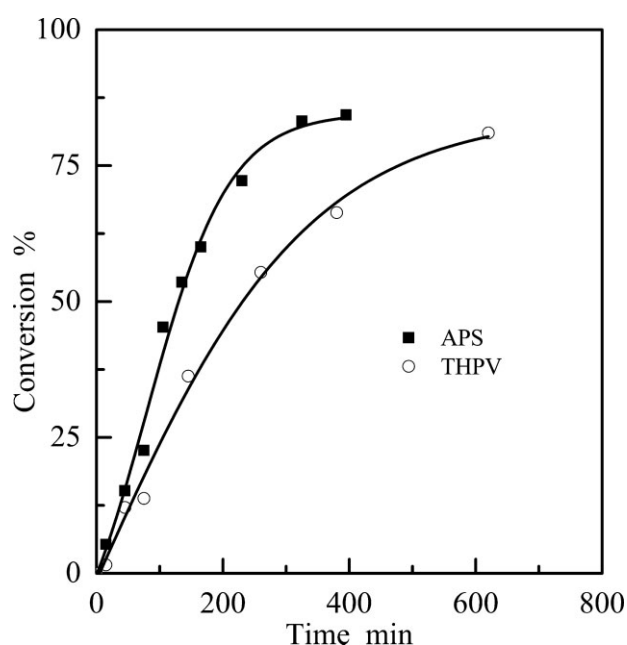

Figure 8 Kinetics of polymerization with APS and THPV as the initiator, respectively, at 60°C (a) APS = 0.01 g, (b) THPV = 0.0089 g (PEG = 28 g, AM = 2 g, H_2O = 70 g).
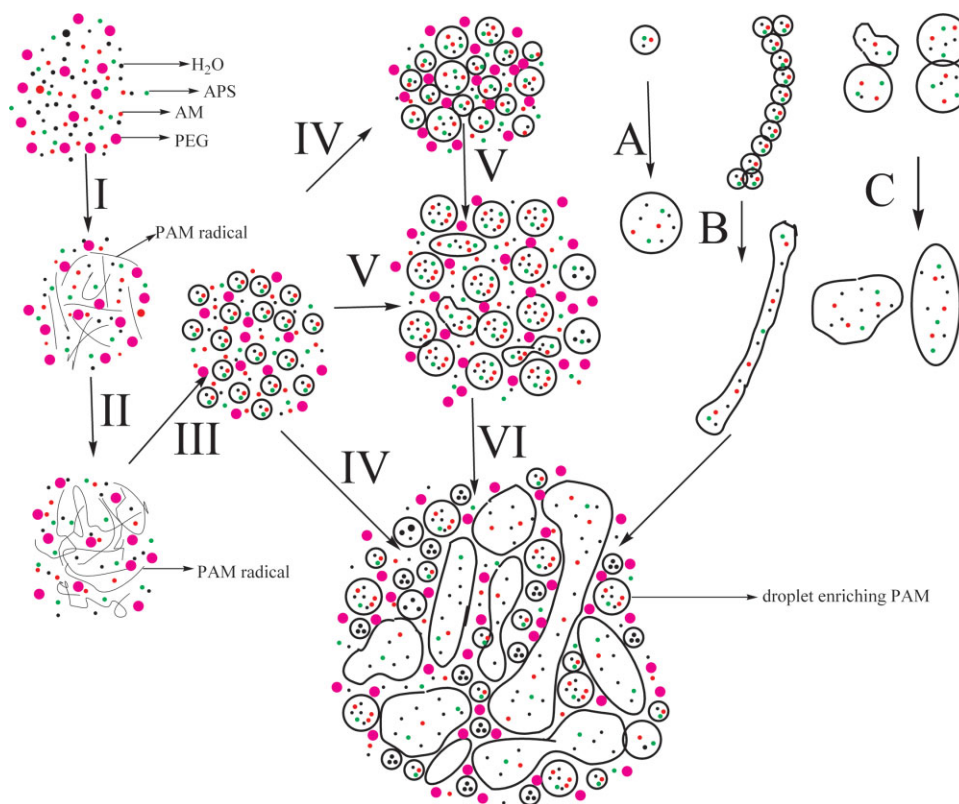
Figure 9 Schematic representation of the mechanism of the formation of droplets in the aqueous two-phase polymerization of AM. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

become unstable with the polymerization and aggregate with each other, make the droplet size distribution narrow (Fig. 9, reaction IV, V). Water molecules ceaselessly shift from continuous phase to dispersed phase with increasing polymer, and as a result, the PEG concentration in continuous phase increase simultaneity leading to the increase of the viscosity of continuous phase which prevents the droplets from aggregation. At the stage of the low conversion, small droplets incline to aggregate quickly forming stripe-shape droplet finally as a result of the high internal viscosity which can prevent the diffusion of polymers among the coalescing droplets (Fig. 9, reaction B). Even at relatively high conversion stage, only a few bigger droplets coagulate to form irregular shape droplets (Fig. 9, reaction C, VI). At the final stage of the polymerization, few coagulation of droplets happen, the growth of the droplets mainly depends on the polymerization inside the droplets (Fig. 9, reaction A). It should be emphasized that the small droplets are formed throughout the whole polymerization (Fig. 9, reaction IV, V, VI).

CONCLUSIONS

A novel polymerization of AM in the aqueous PEG solution with APS as initiator in the absence of any stabilizer was developed. The critical conversion of

phase separation (about 1%) was determined by applying spectrophotometer and improved bromating method. Dynamic light scattering and transmission electron microscopy were used for the investigation of the formation of droplets in the initial stage of polymerization and this stage is believed to be finished at about 3% of conversion. The evolution of PAM droplets size distribution and morphology at every stage were also studied. Various irregular shape droplets suggested much coagulation took place at the relatively low viscosity stage, while few aggregations occurred in high viscosity stage; in addition, the small droplets were produced throughout the whole polymerization, both of which were in conflict with the mechanism of conventional precipitation or dispersion polymerization. According to these phenomena, a new mechanism was proposed to describe the process of the droplets formation and droplets growth in the aqueous two-phase polymerization of AM.

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