

Droplet Size and Morphology for the Aqueous Two-Phase Polymerization of Acrylamide in an Aqueous Poly(ethylene glycol) Solution

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ABSTRACT: A kind of polyacrylamide (PAM) latex product dispersed in an aqueous solution was successfully prepared through the aqueous two-phase polymerization of acrylamide in an aqueous solution of poly(ethylene glycol) (PEG). The effects of various polymerization parameters on the size and morphology of droplets rich in PAM were systematically investigated. The droplet size and morphology was significantly influenced by the polymerization rate. The high polymerization rate caused the formation of stripe-shaped droplets because of the aggregation of more droplets rapidly separated from the continuous phase. At the same time, the monomer partition behavior mainly relied on the temperature, and the PEG concentration also dramatically affected the droplet size

and morphology. The increase in PEG concentration not only changed the monomer partition behavior and restrained droplet aggregation but also shortened the critical PAM radical chain length and accelerated the droplet formation. Furthermore, the stirring speed was also recognized as the correlative factor that affected the droplet stability and monomer diffusion rate from the continuous phase into the droplets. The addition of salt and alcohol altered the droplet stability and the final droplet size and morphology. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1747–1758, 2010

Key words: morphology; radical polymerization; water-soluble polymers

INTRODUCTION

Dispersion polymerization is an attractive and promising alternative to other polymerization methods because it affords micrometer-size monodisperse particles in a single-batch process. It can be defined as a special type of precipitation polymerization in which one carries out the polymerization of a monomer in the presence of a suitable polymeric stabilizer soluble in the reaction medium. In the last few decades, the dispersion polymerization of a hydrophobic monomer in an aqueous alcohol solution has been studied by many researchers,^{1–12} and the effect of various experimental parameters on the particle size has been systemically investigated.

Recently, considerable efforts have been devoted to the polymerization of a water-soluble monomer, such as acrylamide (AM), in the aqueous solution

media without the addition of any organic solvent. The aqueous solution as the reaction medium is a good solvent for the monomer but a nonsolvent for the water-soluble polymer obtained in the process of polymerization. It is believed that the newly produced polymers will separate from the continuous phase and form concentrated aqueous droplets of polymer. Polymerization takes place both in continuous phase and in the dispersed phase; this kind of polymerization system could be defined as an *aqueous two-phase polymerization*. The concept of an aqueous two-phase system was presented in the 1950s¹³ and has been applied to the field of biomacromolecule separation. However, studies on the combination of the preparation of water-soluble polymers and aqueous two-phase techniques are still few. In 1980, Hosoda et al.¹⁴ successfully carried out the polymerization of sodium acrylate in the aqueous solution of poly(ethylene glycol) (PEG) and studied the molecular weight of the obtained polymer and the viscosity of the polymerization system. In recent years, Song et al.¹⁵ carried out the polymerization of AM in an aqueous solution of ammonium sulfate (AS) with poly(acryloyloxyethyl trimethylammonium chloride) as the stabilizer and studied the effects of the polymerization conditions on the droplet size. Their results were in conformity with other previous conventional dispersion polymerizations.

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The droplet size increased with increasing monomer and initiator concentrations and with rising temperature and decreasing stabilizer concentration. Moreover, the copolymerization of AM and acryloyloxyethyl dimethylbenzyl ammonium chloride was also studied,¹⁶ and the increase of the cationic monomer fraction led to an increase in droplets. On the basis of the droplet morphology of every stage of the polymerization, Wang and coworkers^{17,18} proposed a distinct droplet formation mechanism for the copolymerization of AM with 2-methylacryloyloxyethyl trimethyl ammonium chloride in an aqueous solution of AS and sodium chloride. They also studied the copolymerization of AM with acrylic acid (AA) in an aqueous AS solution.¹⁹ The effects of the stabilizer's structure, composition, molecular weight, and concentration; AA/AM molar feed fraction; total monomer, initiator, and AS concentrations; and stirring speed on the conversion, droplet size, and distribution were systematically investigated. Wu et al.²⁰ carried out the copolymerization of AM and 2-acrylamido-2-methyl-1-propane sulfonate through the free-radical dispersion polymerization in an aqueous AS solution with poly(2-acrylamido-2-methyl-1-propane sulfonate) as a stabilizer. The average droplet size of the copolymer ranged from 1 to 4 μm and became larger when the solution was diluted with deionized water because of the molecular expansion because of an insufficient salt concentration and weak electrostatic repulsion between droplets. Shan et al.^{21,22} published articles about the polymerization of AM in the presence of an aqueous PEG solution. The phase diagram of a polyacrylamide (PAM)–PEG–water system and the polymerization kinetics of the aqueous two-phase polymerization of AM were systematically investigated.

In a previous study,²³ the droplet formation mechanism for the aqueous two-phase polymerization of AM in an aqueous PEG solution was established, and the growth and aggregation of the aqueous PAM droplets were successfully explained. In this study, we focused on the effects of the principal factors on the droplet size and morphology. The influences of various polymerization conditions, including the polymerization temperature, initiator concentration, initial monomer concentration, PEG concentration, and stirring speed, and the addition of salt and alcohol on the droplet size and morphology of the AM aqueous two-phase polymerization in an aqueous PEG solution were systematically investigated. In all of these studies, the basic recipe given in Table I was used, and one or more parameters were varied as specified and the others were kept the same as given in the recipe.

Transmission electron micrographs were mainly used to qualitatively evaluate the droplet size and morphology. The value of size may not exactly rep-

TABLE I
Standard Recipe for the Aqueous Two-Phase Polymerization of AM

Material	Concentration (wt %)	Amount (g)
AM	2	2
PEG	28	28
APS	0.01	0.01
H ₂ O	70	70

resent the true size of the droplet in a polymerization system because of the loss of water during the transmission electron microscopy (TEM) sample preparation and observation. However, there was a concentrated aqueous solution of PAM in the droplets, which resulted in a large viscosity in their interiors; as a result, the droplets prepared through the aqueous two-phase polymerization were strong enough to retain their original shapes. Thus, the morphologies of the droplets observed by TEM were believable.

EXPERIMENTAL

Materials

AM (99.9%, Acros Organics, USA) was analytical grade and dried *in vacuo* to remove water for 4 h at 45°C. Ammonium persulfate (APS; ARKEMA Changshu, China) as a water-soluble initiator, poly(ethylene glycol) with a molecular weight of 20,000 (PEG20000, Acros Organics), and polyacrylamide with a molecular weight of 500,000 (PAM500000; Acros Organics) were used as received without any purification. Deionized water was used throughout this study.

Polymerization procedure

The aqueous two-phase polymerization of AM in the aqueous PEG solution was performed in a 500-mL glass jacket reactor with a five-necked cover equipped with a motor-driven Teflon stirrer, a reflux condenser, an argon inlet tube, a thermometer, and a sampling tube. PEG, AM, and 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, and the stirring speed was kept at 75 rpm (the temperature and stirring speed of each experiment was kept constant, except as indicated). Then, APS was dissolved in water and introduced to start the polymerization. The reactions were run for 10 h for a high monomer conversion.

Characterization

The droplet size and size distribution of the product were measured with a laser particle size analyzer (Coulter LS320, USA). The samples were usually

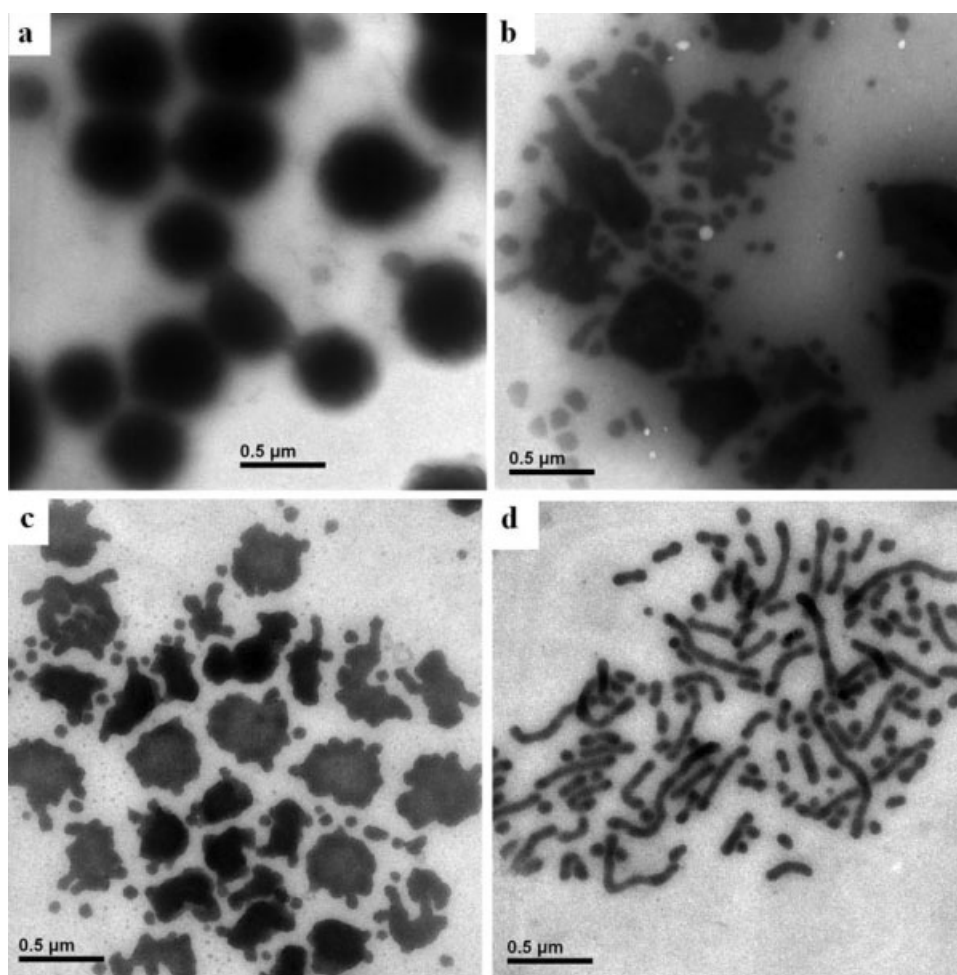


Figure 1 TEM micrographs of the PAM droplets prepared by the aqueous two-phase polymerization of AM in aqueous solutions of PEG with various initiator (APS) amounts: (a) 0.01, (b) 0.015, (c) 0.02, and (d) 0.04% (AM = 2 g, PEG = 28 g, H₂O = 70 g, temperature = 60°C, 75 rpm).

dispersed in methanol. The droplet morphology was observed by TEM (JEOL JSM-1230EXT20, Tokyo, Japan) with diluted redispersions in methanol.

The monomer conversion was determined by a bromating method. About 1.0 g of reactant sample and 100 mL of water were added to an iodine flask. Twenty milliliters of a 0.1 mol/L KBrO₃-KBr aqueous solution (prepared by the dissolution of 3 g of potassium bromate and 25 g of potassium bromide in 1 L of water) was added to the sample solution. After 10 mL of an HCl aqueous solution (5 mol/L) was added, KBrO₃ reacted with KBr to produce Br₂, and then, Br₂ could react with the residual AM in the sample solution for an addition reaction. Ten milliliters of a 20 wt % KI aqueous solution was used to react with the residual Br₂ to produce I₂. By titrating I₂ with a standard solution of Na₂S₂O₃, the total residual contents of AM were determined through the calculation of the consumption of Na₂S₂O₃.

The monomer partitioning was determined by measurement of the AM concentration between the

upper phase, rich in PEG, and the bottom phase, rich in PAM. The aqueous solutions of PEG and PAM were blended in a test tube, and then, AM was introduced into the mixture. The tube was shaken until all of the components were blended equally, and the tube was placed in a flume in which the water temperature remained constant. After the phase separation was complete and maintained for 2 days, we obtained some sample from the upper phase and bottom phase and titrated the AM concentration (the approach was similar to the monomer conversion measurement).

RESULTS AND DISCUSSION

Effect of the APS concentration

To determine the effect of the initiator concentration on the droplet size and morphology, a set of experiments was run in which the initiator concentration was varied from 0.01 to 0.04% and all other parameters, including the temperature, were held constant.

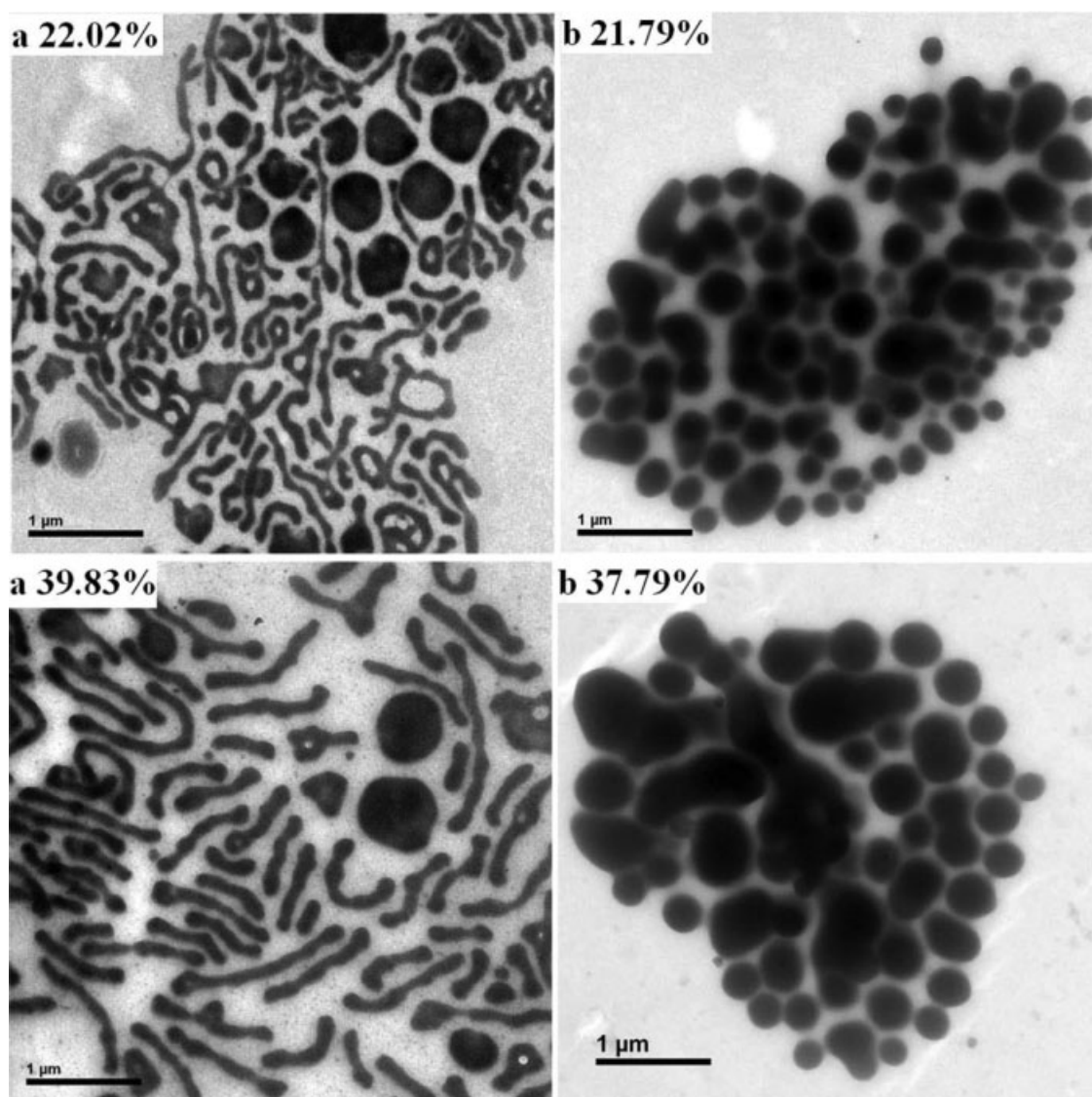


Figure 2 TEM micrographs of the PAM droplets prepared by the aqueous two-phase polymerization of AM in aqueous solutions of PEG with various initiator (APS) amounts: (a) 0.0075 and (b) 0.0025% (AM = 6 g, PEG = 20 g, H₂O = 74 g, temperature = 60°C, 75 rpm).

The results are given in Figure 1, and it can be seen that the droplet morphology changed remarkably with increasing initiator concentration. At a low APS concentration, droplets with a round shape were obtained. However, the droplet morphology turned a popcorn shape when more initiator was used. When we continued to increase the amount of initiator, many stripe-shaped droplets appeared.

To clarify how the droplet shape changed, the droplet morphology at the middle stage of polymerization with different initiator amounts was investigated, as shown in Figure 2, where the initial monomer concentration was 6% and the PEG concentration was 20%. When the initial initiator concentration was 0.0075%, bead string-shaped droplets were observed at a conversion of about 22%. When the initiator concentration decreased to 0.0025%, only oval and round droplets

were found at a similar conversion stage. In the same way, stripe-shaped droplets were formed with greater initiator amounts at a conversion of about 39%; this was not observed with a lower initial initiator amount.

In a conventional dispersion polymerization, a high initial initiator concentration would result in bigger particles. Many researchers^{24,25} have attributed this result to the rapid aggregation of nuclei because of the high polymerization rate. In the aqueous two-phase polymerization, primary radicals generated by the decomposition of initiators grow in the continuous phase by the addition of monomer units until they reach their critical chain length. Then, these polymer radicals precipitate and aggregate to form nuclei. However, the nuclei are not stable, and they immediately aggregate with each other to form small droplets. Thus, if too much initiator is introduced, a great

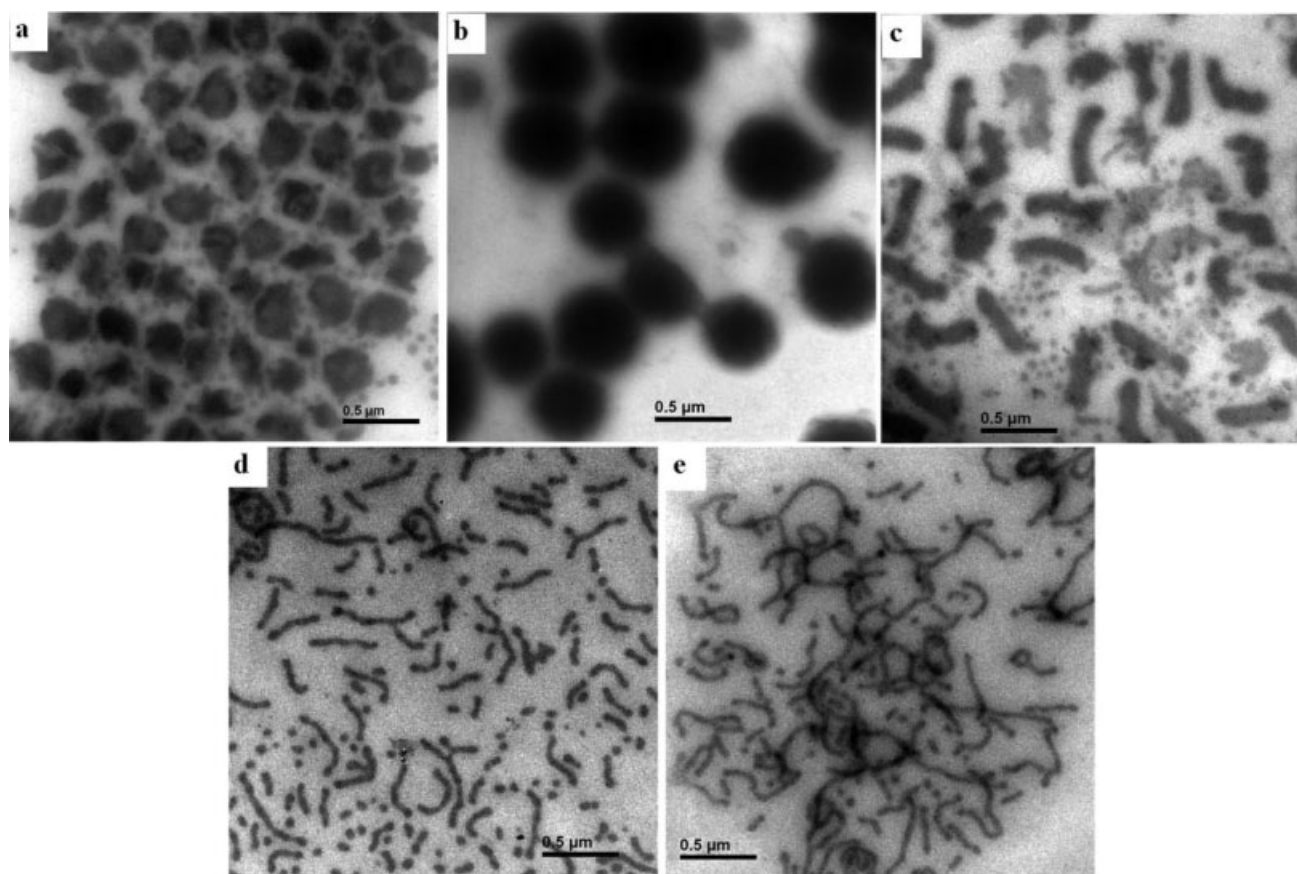


Figure 3 TEM micrographs of the PAM droplets prepared by the aqueous two-phase polymerization of AM in aqueous solutions of PEG at different temperatures: (a) 55, (b) 60, (c) 65, (d) 70, and (e) 75°C (AM = 2 g, PEG = 28 g, H₂O = 70 g, APS = 0.01 g, 75 rpm).

amount of small droplets would be formed instantaneously. In our study, small droplets were generated ceaselessly during the polymerization as explained in previous article.²³ In other words, the high initiator concentration led to a high rate of droplet formation. At the same time, the low viscosity in the earlier stage of polymerization did not prevent the coalescence of small droplets, and the high internal viscosity of the droplets was great enough to prevent the easy diffusion of molecules between the coalescing droplets. Therefore, stripe-shaped droplets were generated in the earlier stage of polymerization. Because more monomer was consumed to generate small droplets because of the high initial initiator concentration, less monomer polymerized inside the droplets. Thus, the stripe-shaped droplets could not become plump. The popcorn-shaped droplets were formed because of the aggregation between bigger droplets and small droplets.

Effect of the temperature

Figure 3 shows the TEM photographs of the PAM droplets prepared at different polymerization temperatures from 55 to 75°C. The differences in the

droplet morphology seem to be more remarkable compared to that due to the increase in the initial initiator amount. At 55°C, the droplet shape was

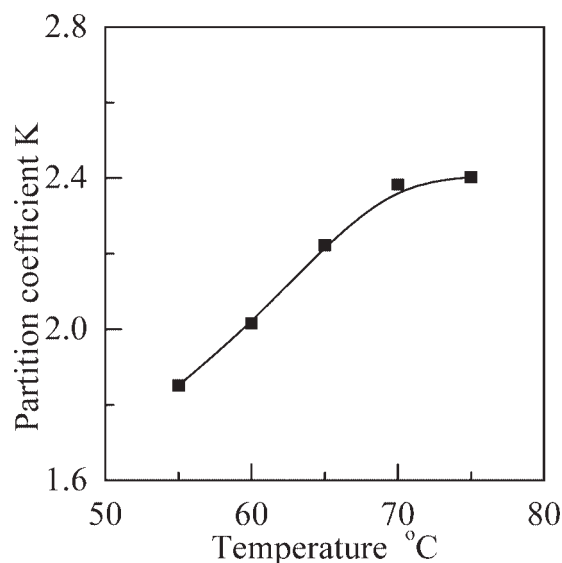


Figure 4 Effect of the temperature on the partition coefficient of AM in the PAM-PEG-water system (PAM500000 = 10%, AM = 5%, PEG20000 = 28%).

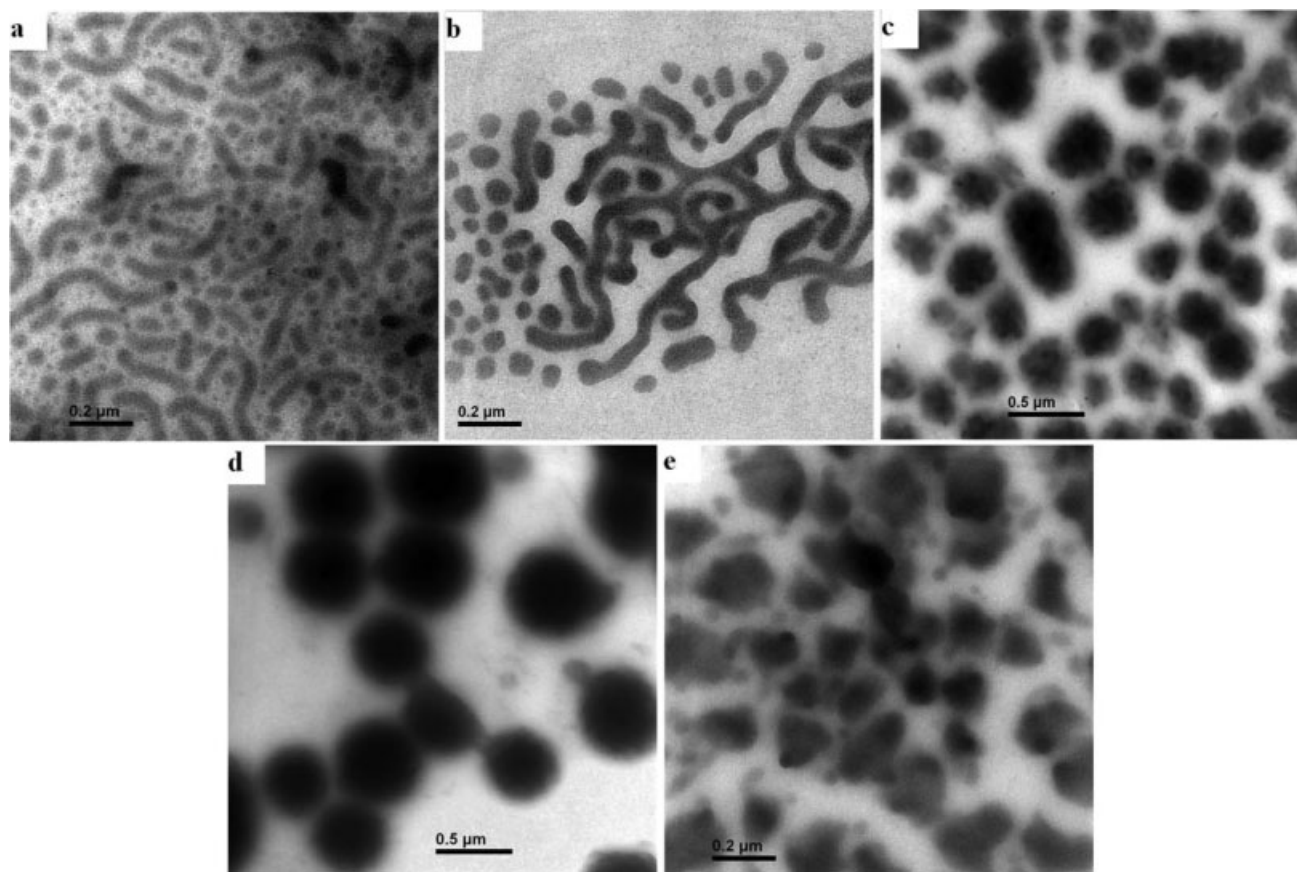


Figure 5 TEM micrographs of the PAM droplets prepared by the aqueous two-phase polymerization of AM with various concentrations of aqueous solutions of PEG: (a) 16, (b) 20, (c) 24, (d) 28, and (e) 32% (AM = 2 g, PEG + H₂O = 98 g, APS = 0.01 g, temperature = 60°C, 75 rpm).

irregular. However, spherical droplets were formed at 60°C. When the temperature was increased to 65°C, the droplet morphology turned to a thicker stripe shape. When the temperature was increased to 70 and 75°C, the stripe-shaped droplets became thinner and longer.

First, the polymerization rate sharply accelerated with rising temperature. Second, the rising temperature also altered the *monomer partition coefficient*, defined as the ratio of AM concentration in the continuous phase to that in the dispersion phase. A change in the monomer partition with rising temperature was also observed in the dispersion polymerization of styrene in ethanol or ethanol/water media.^{26,27} As shown in Figure 4, the partition coefficient increased with rising temperature in the aqueous two-phase system, which suggested that more monomer polymerized in the continuous phase. Therefore, more small droplets were generated and aggregated to form the striped-shaped droplets finally. Thus, both the increase in the polymerization rate and the increase in the monomer partition coefficient due to rising temperature led to the generation of more striped-shaped droplets. To our surprise, round droplets could not be prepared at 55°C

[Fig. 3(a)] with the low polymerization rate and partition coefficient. This may have been due to the lower solubility of PAM in the aqueous PEG solution at 55°C according to the study of the phase

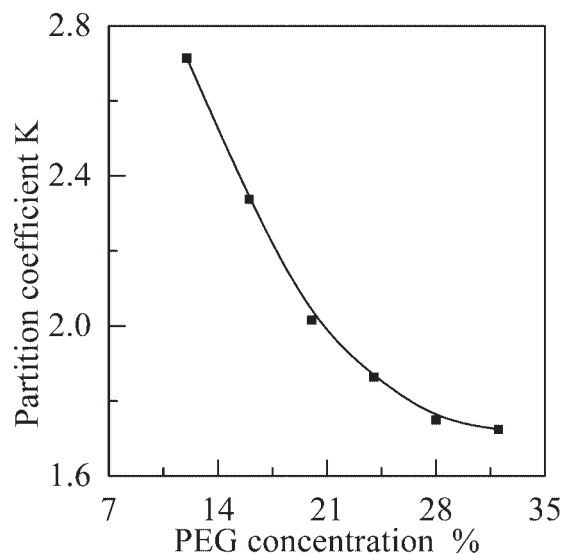


Figure 6 Effect of the PEG20000 concentration on the partition coefficient of AM in the PAM-PEG-water system (PAM500000 = 10%, AM = 5%, temperature = 60°C).

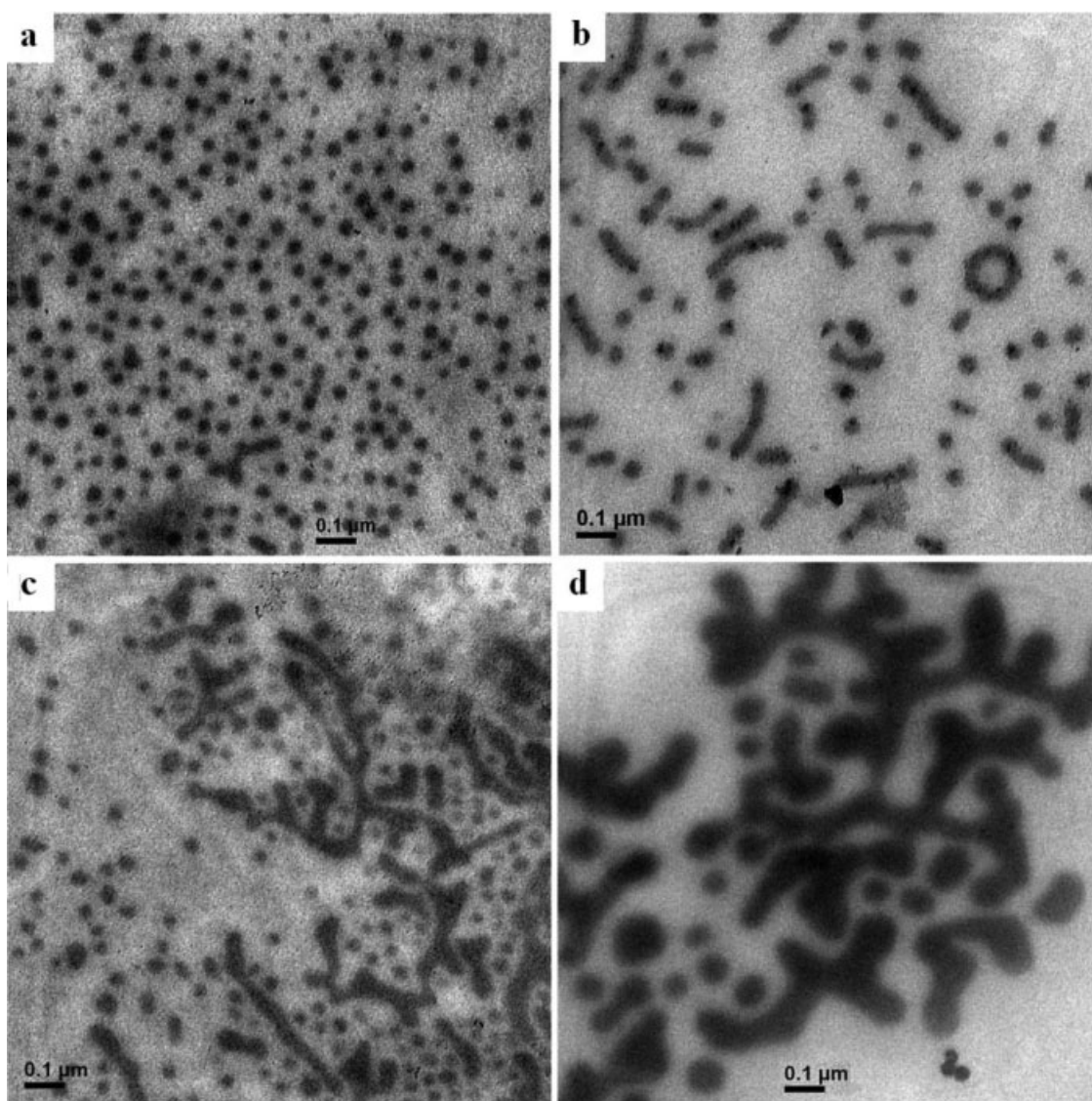


Figure 7 TEM micrographs of the PAM droplets prepared by the aqueous two-phase polymerization of AM in aqueous solutions of PEG with different initial monomer concentrations: (a) 1, (b) 1.5, (c) 2, and (d) 3.5% (PEG = 20 g, AM + H₂O = 80 g, APS = 0.01 g, temperature = 60°C, 75 rpm).

diagram of the PAM-PEG-water system.²² This indicated that the critical length of PAM chains for phase separation was shortened at 55°C; this accelerated droplet formation. Therefore, the aggregation of small droplets occurred again. This finding appears to favor the suggestion that the droplet formation velocity depended not only on the polymerization rate but also on the critical chain length. At higher temperatures, the droplet formation velocity was not slowed because of the high polymerization rate, although the critical chain length was longer.

Effect of the PEG concentration

Stabilizers such as homopolymers and amphipathic and graft copolymers are recognized to play a crucial role in dispersion polymerization.²⁸ Normally,

an increase in stabilizer concentration results in a decrease in particle size.

PEG acted as the dispersion media in the aqueous two-phase system and not only played a phase-separation role but also acted as a stabilizer for the dispersed PAM droplets. Two phenomena were observed with increasing PEG concentration from 16 to 28%, as shown in Figure 5: the morphology tended to be spherical, and the size became larger. This seemed to partially contradict the conventional dispersion polymerization.

These results may have been due to two factors. The increase in the PEG concentration reduced the coalescence of the droplets and also decreased the monomer partition coefficient, as shown in Figure 6. The latter indicated that more monomer was distributed in the dispersion phase and polymerized inside

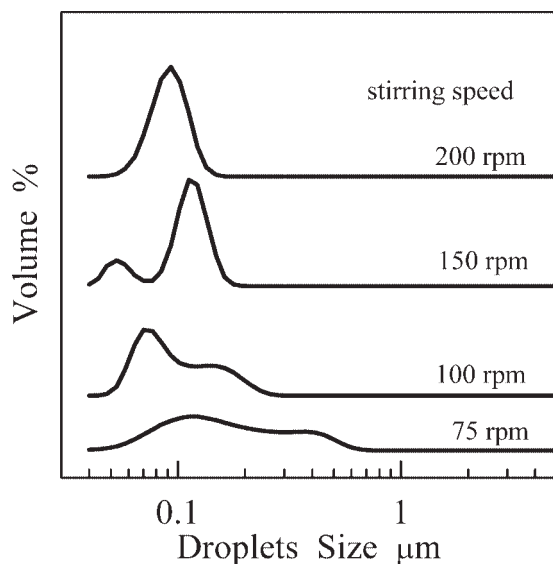


Figure 8 Droplet size distribution of the aqueous two-phase polymerization in aqueous solutions of PEG at different stirring speeds (AM = 2 g, PEG = 28 g, H₂O = 70 g, APS = 0.01 g, temperature = 60°C).

the droplets, which caused the droplet size to become larger. However, when the PEG concentration was increased sequentially to 32%, the droplets became irregular and small. This was because increasing the PEG concentration sequentially to 32% did not reduce the partition coefficient significantly, but the critical chain length was shortened, which led to the acceleration of droplet formation. At the same time, the increasing PEG concentration could not prevent the coalescence of droplets separated rapidly from the continuous phase. This result corresponded with the phenomenon observed at the polymerization temperature of 55°C, discussed previously, and gave direct verification that the critical length of PAM radical really influenced the velocity of droplet formation. Wang et al.¹⁷ also observed irregular droplets when a high AS concentration was used. They attributed this to rapid droplet formation and the poor ability to protect the droplets from coalescence resulting from the low solubility of the stabilizer in the concentrated aqueous AS solution.

Effect of the AM concentration

The effect of the monomer concentration on the particle development in free-radical dispersion polymerization has been studied previously, where it was found that an increase in monomer concentration generally produces larger particles.

In this set of experiments, the monomer concentration was varied from 1 to 3.5%, and the other components were the same as those listed in Table I. The microstructures of the products prepared with

various initial monomer concentrations are presented in Figure 7. Few striped-shaped droplets were observed at the 1% monomer concentration; however, many striped-shaped droplets turned up at the 1.5% monomer concentration. When the monomer concentration was increased sequentially, the morphology did not change significantly, but the size increased.

These results can be explained as follows. Although initial monomer concentration was increased, the polymerization rate was accelerated, the small droplets separated rapidly from the continuous phase; this caused the small droplets to aggregate easily. Thus, the striped-shaped droplets were obtained and became longer and plumpish with increasing initial monomer concentration. It was evident that the evolution trend of the droplet size and morphology observed with various monomer concentrations conformed with that observed at different conversion stages in one run. This appears to give additional support to the droplet formation mechanism proposed before.²³

Effect of the stirring speed

Kawaguchi et al.⁷ reported that the diameter of microspheres decreased with increasing stirring rate in the polymerization of AM/methyl acrylic acid (MAA)/N,N'-methylene bisacrylamide (MBAM) in isopropyl alcohol. Wang et al.¹⁹ obtained similar results for the copolymerization of AM and acrylic acid in aqueous AS solution. They concluded that the high stirring speed reduced the aggregation of nuclei and increased the droplet stability. Yasuda et al.²⁹ systemically studied the particle formation stage in the dispersion polymerization of styrene. It was found that the polymerization rate in the ethanol phase was about 30- to 40-fold greater than that in particles at high stirring speeds. It was thought that the high monomer concentration in the ethanol phase at the high stirring speed was caused by the low radical absorption rate of the particle from the continuous phase. Thus, the higher the stirring speed was, the smaller the particles were.

In this study, apparent decreases in the polymerization rate and droplet size were found, as shown in Figures 8–10, when the stirring rate was increased from 75 to 200 rpm in the aqueous two-phase polymerization of AM. The oval or striped-shaped droplets shown in Figure 9(a–c) suggested some coalescence of the droplets when the stirring speed was 75, 100, and 150 rpm, respectively. However, when the stirring speed was increased to 200 rpm, little aggregation of the droplets was observed, as shown in Figure 9(d).

As described previously, with increasing stirring speed, more polymerization took place in the

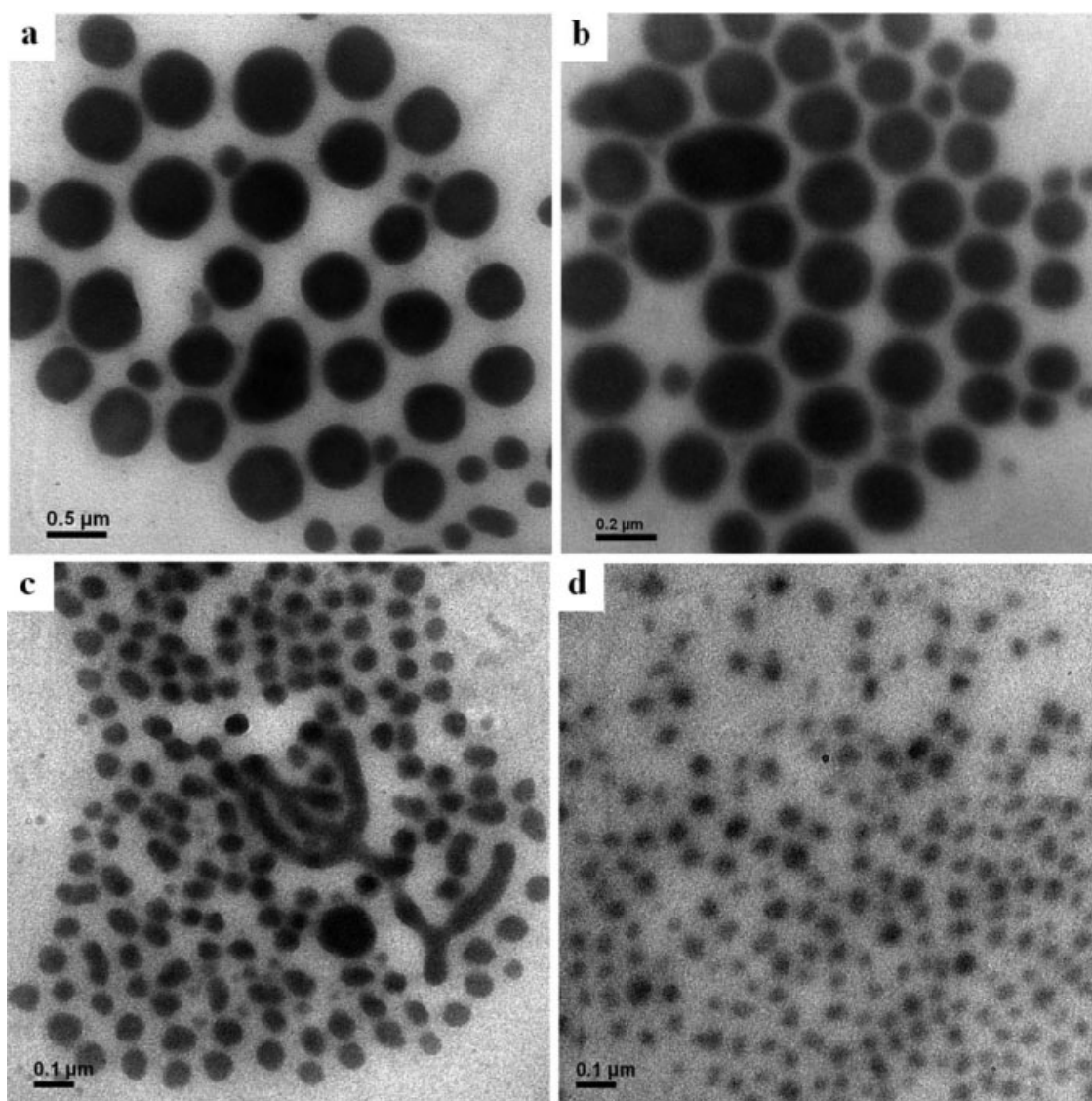


Figure 9 TEM micrographs of the PAM droplets prepared by the aqueous two-phase polymerization of AM in aqueous solutions of PEG at different stirring speeds: (a) 75, (b) 100, (c) 150, and (d) 200 rpm (AM = 2 g, PEG = 28 g, H₂O = 70 g, APS = 0.01 g, temperature = 60°C).

continuous phase; this led to a decrease in the droplet size. This suggestion was verified by the decreasing polymerization rate due to increasing stirring speed, as shown in Figure 10. As we all know, the aqueous two-phase polymerization took place in both the continuous and dispersion phases. Because the higher viscosity inside the droplets reduced the termination rate coefficient, the polymerization rate in the dispersion phase was higher than that in the continuous phase. Thus, if fewer polymer radicals were transferred into the droplets, the polymerization rate decreased. The reverse result was obtained by Yasuda et al.;²⁹ they found that the polymerization rate increased with increasing stirring speed for the dispersion polymerization of styrene in an ethanol medium. They attributed it to the wonderful compatibility between styrene and ethanol, which

led to a low monomer concentration in the particles. However, the swelling ratio of the particles increased dramatically when some water was introduced into ethanol.²⁷ As a result, they believed that the kinetics of polymerization were slowed with increasing stirring speed for the dispersion polymerization of styrene in an aqueous ethanol solution. Furthermore, the increasing stirring speed also restrained the coalescence between the droplets, which made the droplet morphology become round.

Effect of the addition of salts and alcohols

Figure 11(a) represents the morphology of the PAM droplets prepared with 28% PEG, 2% AM, and 0.01% APS, and spherical droplets were observed in the product. On the basis of this recipe, 0.1% kalium sulfate was introduced to this polymerization

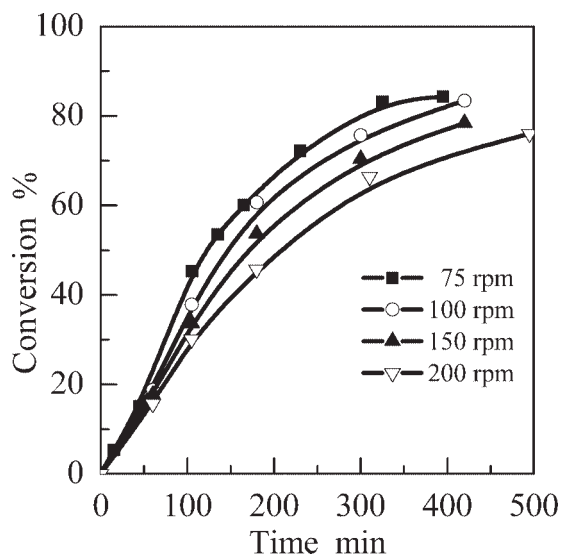


Figure 10 Kinetics of the aqueous two-phase polymerization in aqueous solutions of PEG at different stirring speeds (AM = 2 g, PEG = 28 g, H₂O = 70 g, APS = 0.01 g, temperature = 60°C).

system. As shown in Figure 11(b), some irregular-shaped droplets were observed compared to the droplet morphology prepared without kalium sulfate addition. This was because the addition of electrolyte screened the surface charge due to the decomposition of $S_2O_8^{2-}$ as the initiator and decreased the contribution of electrostatic stabilization. Although an oil-soluble initiator was used, the polymerization rate was slowed, and many striped-shaped droplets were observed.²³ The droplets lost the electrostatic stabilization from initiator fragments, and more initiator decomposed in the contin-

uous phase and generated more droplets; this resulted in droplet aggregation.

As shown in Figure 12, the addition of *tert*-butyl alcohol (TBA) not only decreased the size of droplets but also destroyed the droplet stabilization and led to the formation of many stripe droplets with increasing TBA amount. Contrarily, the addition of glycol increased the droplet stability and decreased the droplet size, just as shown in Figure 13(a,b). The droplet morphology shifted from an irregular shape to round as with increasing amount of glycol when the monomer, dispersant, and initiator concentrations were kept constant at 2, 28, and 0.015%, respectively.

As we all know, TBA is a nonsolvent for PAM; the addition of TBA to an aqueous solution of PEG would make the solvent increasingly poor for PAM. Hence, the critical chain length would be shortened, and less PAM would be soluble in the continuous phase. In other words, small droplets would be rapidly separated from the continuous phase, and the viscosity of the continuous phase would be lower, both of which would lead to a greater coalescence of droplets. Thus, irregular and even striped-shaped droplets were formed with increasing TBA content, just as shown in Figure 12(a,b). This result seems to confirm the suggestion that the droplet formation velocity was assuredly affected by the critical chain length once again. Glycol is also a relatively poor solvent for PAM compared to water; however, the addition of glycol had a distinct effect on the droplet morphology. Because of the relatively high viscosity of glycol, the addition of glycol increased the viscosity of the continuous phase and constrained the

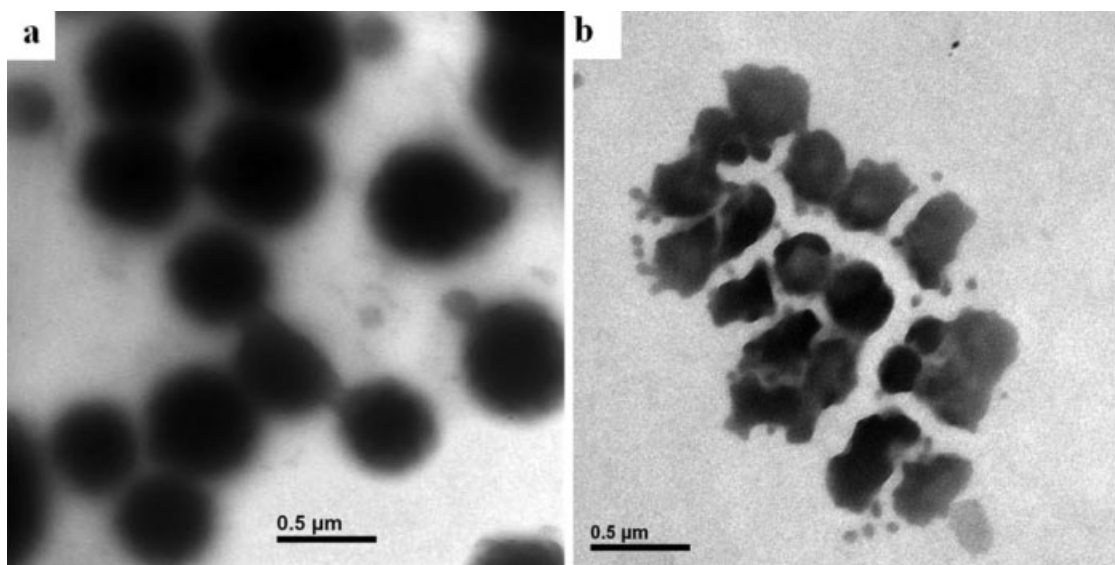


Figure 11 TEM micrographs of the PAM droplets prepared by the aqueous two-phase polymerization of AM in aqueous solutions of PEG: (a) no addition and (b) 0.1% K₂SO₄ addition (AM = 2 g, PEG = 28 g, H₂O = 70 g, APS 0.01 g, temperature = 60°C).

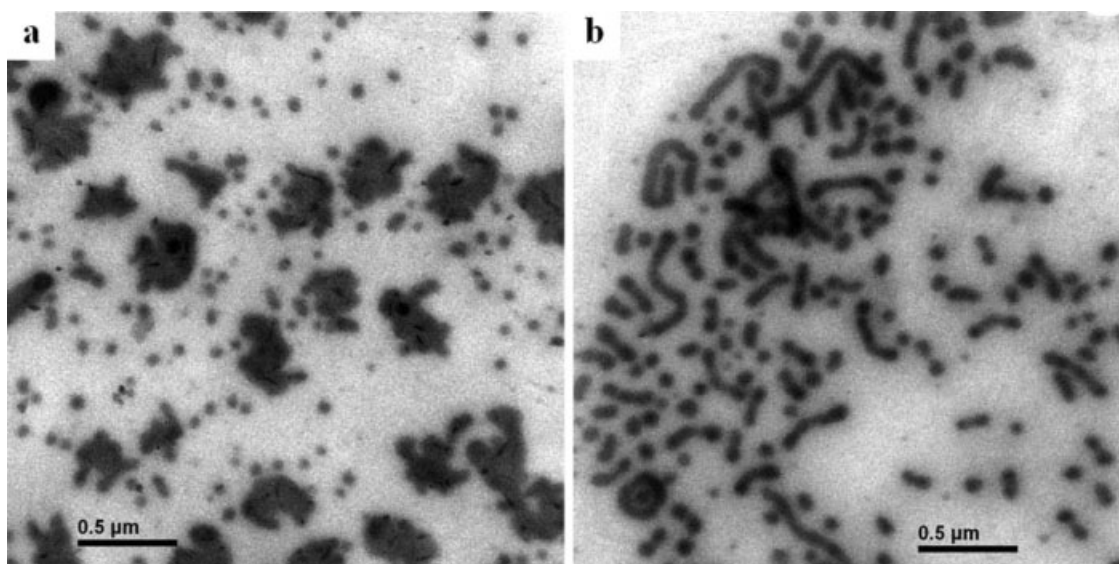


Figure 12 TEM micrographs of the PAM droplets prepared by the aqueous two-phase polymerization of AM in aqueous solutions of PEG: (a) 5 and (b) 10% TBA addition (AM = 2 g, PEG = 28 g, TBA + H₂O = 70 g, APS = 0.01 g, temperature = 60°C).

aggregation of droplets. Furthermore, both TBA and glycol decreased the solubility of PAM in the aqueous solution and interacted with AM through hydrogen bonding. Consequently, less monomer and water diffused into the PAM droplets, and less polymerization took place inside the droplets, which resulted in a decrease in the droplet size. Thus, the monomer partitioning behavior played a rather important role in the droplet size and morphology for the aqueous two-phase polymerization of AM in the aqueous PEG solution.

CONCLUSIONS

The aqueous two-phase polymerization of AM was carried out in the aqueous solution of PEG with APS

as the initiator. The effect of various polymerization conditions on the droplet size and morphology were systematically studied.

The size and morphology of the droplets were significantly dependent on the kinetics of the polymerization. Thus, the initiator and monomer concentration and the polymerization temperature remarkably affected the morphology of the droplets. The morphology of the droplets was inclined to become stripe-shaped with increasing initiator concentration, monomer concentration, and polymerization temperature. Moreover, the monomer partitioning between the continuous phase and the dispersion phase also significantly influenced the morphology of the droplets because the monomer partition behavior changed the proportion of the polymerization in the

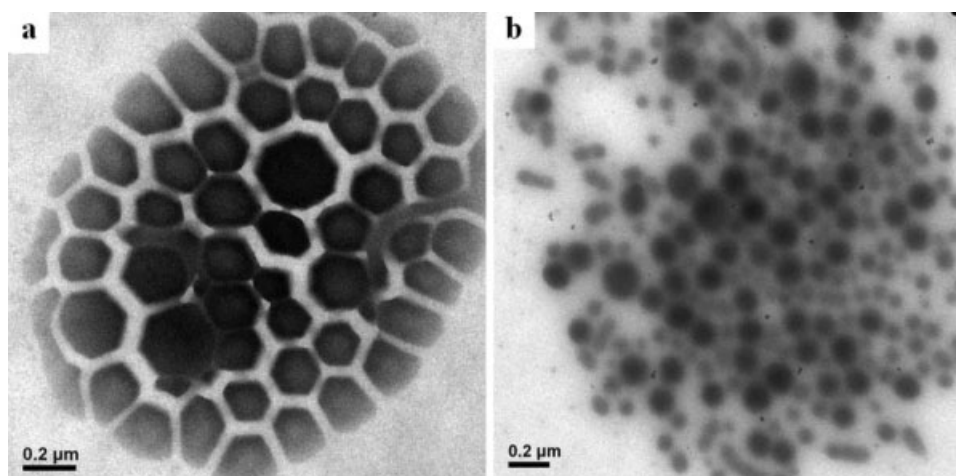


Figure 13 TEM micrographs of the PAM droplets prepared by the aqueous two-phase polymerization of AM in aqueous solutions of PEG: (a) 5 and (b) 10% glycol addition (AM = 2 g, PEG = 28 g, glycol + H₂O = 70 g, APS = 0.015 g, temperature = 60°C).

continuous phase and inside the droplets. The monomer partition increased with decreasing PEG concentration and rising temperature. In addition, increasing PEG concentration not only restrained the aggregation of the droplets but also shortened the critical length of the PAM radical chain. Consequently, the increase in the PEG concentration tended to generate bigger and round droplets at first and then smaller and irregular droplets. The rise in the temperature from 60 to 75°C tended to generate longer and thinner striped-shaped droplets. With increasing stirring speed, the droplet size decreased. On one hand, the increasing stirring speed decreased the adsorption rate of polymer radicals into the droplets, which was confirmed by the decreasing polymerization rate with increasing stirring speed; on the other hand, the high stirring speed also restrained the aggregation of the droplets and resulted in round droplets. The addition of salt decreased the droplet stability and led to the generation of some striped-shaped droplets. When TBA and glycol was introduced into the polymerization system, both decreased the droplet size. The former caused lots of aggregation and formed many striped-shaped droplets. However, the latter made the droplets become more stable.

In conclusion, droplet aggregation and stabilization were a crucial course in the aqueous two-phase polymerization of AM in the aqueous PEG solution. The final determinative factors affecting the droplet size and morphology can be summarized as the velocity of the droplet formation, polymerization inside the droplets, and viscosity of the continuous phase.

References

1. Ray, B.; Mandal, B. M. *Langmuir* 1997, 13, 2191.
2. Guha, S.; Mandal, B. M. *J Colloid Interface Sci* 2004, 271, 55.
3. Guha, S.; Ray, B.; Mandal, B. M. *J Polym Sci Part A: Polym Chem* 2001, 39, 3434.
4. Baade, W.; Reichert, K. H. *Eur Polym J* 1984, 20, 505.
5. Wang, W.; Liu, L. Y.; Huang, Z. H.; Yang, W. T. *Acta Polym Sinica* 2005, 320.
6. Ni, H. M.; Kawaguchi, H. *J Polym Sci Part A: Polym Chem* 2004, 42, 2823.
7. Ni, H. M.; Kawaguchi, H. *J Polym Sci Part A: Polym Chem* 2004, 42, 2833.
8. Ye, Q.; Zhang, Z. C.; Jia, H. T.; He, W. D.; Ge, X. W. *J Colloid Interface Sci* 2002, 253, 279.
9. Okaya, T.; Kikuchi, K.; Suzukl, A.; Ikeda, N. *Polym Int* 2005, 54, 143.
10. Paine, A. J. *Macromolecules* 1990, 23, 3109.
11. Paine, A. J.; Luymes, W.; McNulty, J. *Macromolecules* 1990, 23, 3104.
12. Kim, J.; Jeong, S. Y.; Kim, K. U.; Ahn, Y. H.; Quirk, R. P. *J Polym Sci Part A: Polym Chem* 1996, 34, 3277.
13. Albertsson, P. A. *Partition of Cell Particles and Macromolecules: Distribution and Fractionation of Cells, Viruses, Microsomes, Proteins, Nucleic Acids, and Antigen-Antibody Complexes in Aqueous Polymer Two-Phase Systems*; Wiley: New York, 1960.
14. Hosoda, Y.; Ueshima, T.; Ishihara, S.; Imamura, K. In *Contemporary Topics in Polymer Science*; Bailey, W. J.; Tsuruta, T., Eds.; Plenum: New York, 1980; Vol. 4, p 575.
15. Cho, M. S.; Yoon, K. J.; Song, B. K. *J Appl Polym Sci* 2002, 83, 1397.
16. Song, B. K.; Cho, M. S.; Yoon, K. J.; Lee, D. C. *J Appl Polym Sci* 2003, 87, 1101.
17. Chen, D. N.; Liu, X. G.; Yue, Y. M.; Zhang, W. D.; Wang, P. X. *Eur Polym J* 2006, 42, 1284.
18. Liu, X. G.; Chen, D. N.; Yue, Y. M.; Zhang, W. D.; Wang, P. X. *J Appl Polym Sci* 2006, 102, 3685.
19. Liu, X. G.; Xiang, S.; Yue, Y. M.; Su, X. F.; Zhang, W. D.; Song, C. L.; Wang, P. X. *Colloids Surf A* 2007, 311, 131.
20. Wu, Y. M.; Wang, Y. P.; Yu, Y. Q.; Xu, J.; Chen, Q. F. *J Appl Polym Sci* 2006, 102, 2379.
21. Shan, G. R.; Cao, Z. H. *J Appl Polym Sci* 2009, 111, 1409.
22. Shan, G. R.; Cao, Z. H.; Huang, Z. M.; Weng, Z. X. *Chem J Chin Univ* 2005, 26, 1348.
23. Lü, T.; Shan, G. R. *J Appl Polym Sci* 2009, 112, 2859.
24. Shen, S.; Sudol, E. D.; El-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 1993, 31, 1393.
25. Shen, S.; Sudol, E. D.; El-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 1994, 32, 1087.
26. Lu, Y. Y.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Part B: Polym Phys* 1988, 26, 1187.
27. Lacroix-Desmazes, P.; Guillot, J. *J Polym Sci Part B: Polym Phys* 1998, 36, 325.
28. Paine, A. J. *J Colloid Interface Sci* 1990, 138, 157.
29. Yasuda, M.; Seki, H.; Ypkpyama, H.; Ogino, H.; Ishimi, K.; Ishikawa, H. *Macromolecules* 2001, 34, 3261.