A New Polymerization Method and Kinetics for Acrylamide: Aqueous Two-phase Polymerization

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ABSTRACT: The concept of aqueous two-phase polymerization and a new polymerization method for the preparation of water-soluble polymers are presented. The phase diagram of poly(acrylamide) (PAAm)-poly (ethylene glycol) (PEG)-water two-phase system was measured by the gel permeation chromatography (GPC). The aqueous two-phase of PAAm-PEG-water system can be easily formed. The critical concentration of phase separation was affected by the molecular weight of PEG. The aqueous two-phase polymerization of acrylamide (AAm) has been successfully carried out in the presence of PEG by using ammonium persulfate (APS) as the initiator. The polymerization behaviors with varying concentration of AAm, initiator and PEG, the polymerization temperature, the molecular weight of PEG, and emulsifier types were investigated. The activation energy of aqueous two-phase polymerization of AAm was 132.3 kJ/mol. The relationship of initial polymerization rate (R_{p0}) with APS and AAm concentrations was $R_{p0} \propto$ [APS]$^{0.72}$ [AAm]$^{1.28}$. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1409–1416, 2009

Key words: acrylamide; aqueous two-phase polymerization; kinetics

INTRODUCTION

Water-soluble polymers, such as polyacrylamide (PAAm), are conventionally prepared by homogeneous aqueous solution free-radical polymerization.[1] For homogeneous aqueous solution polymerization, the heat of reaction is difficult to release, because the viscosity of the reaction system increases so drastically that the stirring performance becomes difficult at first, the product is finally jelly-like with sluggish heat transfer. The kinetics of jelly-like polymerization cannot be well controlled, and the properties of the jelly-like product are very difficult to handle. The jelly-like product has to be diluted for a long time before using. The other polymerization methods, such as inverse emulsion polymerization, inverse suspension polymerization and dispersion polymerization, can overcome these shortcomings of homogeneous aqueous solution polymerization. But these polymerization methods need to use some organic solvents, causing problems of pollution and recycling, and consequently restricting the development and application of these polymerization methods.

Mario Ossenbach-Sauter and Riess[2] mixed three kinds of water-soluble polymers, polyoxyethylene, poly(2-vinylpyridinium chloride) and their copolymers, and obtained a relatively stable emulsion. Hosoda et al.[3] investigated the kinetics of sodium acrylate aqueous solution polymerization in the presence of poly(ethylene glycol) (PEG). These processes were categorized as a "water in water" emulsion polymerization. The micrographs, the molecular weights, the viscosity of the reaction system, and the effects used as thickener and flocculant were presented. On the basis of Hosoda's polymerization method, Jin et al.[4] studied the kinetics of acrylamide (AAm) aqueous solution polymerization in the presence of PEG and treated the kinetics as a emulsion polymerization.

However, we think that the mechanism of AAm aqueous solution polymerization in the presence of PEG is different from those of emulsion polymerization, dispersion polymerization, and homogeneous aqueous solution polymerization. The reaction of the emulsion polymerization takes place within the latex particle, and that of dispersion polymerization is in the organic solution phase, and that of homogeneous aqueous solution polymerization is in the homogeneous aqueous solution. In the presence of PEG, however, the polymerization of AAm may take place at the same time in two aqueous phases, PEG

aqueous solution phase, and PAAm aqueous solution phase, and a so-called "aqueous two-phase polymerization" can thus be named according to the mechanism of polymerization.

In this article, the phase diagram of PAAm-PEG-water system and a new polymerization method for AAm in the PEG aqueous solution were studied. The effects of the AAm, initiator and PEG concentration, polymerization temperature, molecular weight of PEG, and emulsifier types on the kinetics of AAm aqueous two-phase polymerization were also investigated.

EXPERIMENTAL

Materials

The water to be used for polymerization in this study was prepared by double distillation. PEGs ($M_W =$ 20,000, 10,000, 6000, and 4000) as the medium polymer were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Acrylamide as the monomer, ammonium persulfate (APS) as the initiator, and sodium dodecylsulfate (SDS) or polyoxyethylene(20)-sorbitan monolaurate (Tween20) used as additional surfactant in some specific experiments were purchased from Acros Organics (NJ). Analytical reagents including sodium thiosulfate, potassium iodide, potassium bromide, potassium bromate, ethanol, and starch indicator were provided by J and K Chemical LTD. All reagents were analytical pure. The water used to make phase diagram was millipore quality. The molecular weight of PAAm used to make phase diagram was about 3×10^6.

Preparation of PAAm-PEG-water aqueous two-phase system

The aqueous solutions of PAAm and PEG were mixed in a various proportion in a graduated tube. The mixture was shaken vigorously for several minutes and then brought to equilibrium in a thermostatic bath. After 2 days, the mixture was separated into two phases and a distinct interface could be observed between them. However, the equilibrium time was prolonged to 4 days to make sure that complete equilibrium was reached. The upper phase was less viscous and PEG rich, and the lower phase was more viscous and PAAm rich. The samples taken out from each phase were then diluted with pure water and analyzed using the gel permeation chromatography (GPC).[5]

Analysis of phase compositions

The compositions of the diluted samples were determined by Waters 150C GPC equipped with the Ultrahydrogel Columns 2000 and 250. The temperature of the columns was 30°C. The eluent was 0.1 mol/L sodium nitrate solution, and the flow rate was 0.8 mL/min. Calibration curve (peak area ratio versus the ratio of known amount of polymers) were established for PEG and PAAm. The chromatogram of a sample was obtained, and the ratio of the peak area of PEG to PAAm was estimated. The ratio of the amount of PEG to PAAm for the sample was obtained by comparing the estimated peak area ratios to the calibration curves. The chromatogram for the mixture of PAAm and PEG shows that good response and perfect separation of PAAm and PEG can be realized by GPC, and the standard curve with good linear fit for the peak area ratio and mass ratio of PAAm and PEG10000 can be established.

Polymerization

Polymerization was carried out in a 500 mL jacket reactor, equipped with a stirrer, reflux condenser, and a nitrogen inlet tube. AAm, PEG, and distilled water were mixed to form a homogeneous solution. The reagents mixture was heated and purged with nitrogen for 20 min, and at that time, the reaction temperature has reached. The aqueous solution of initiator was introduced to start the polymerization. For the experiment with emulsifier, the emulsifier was dissolved into water with other reactants.

Conversion measurement

Some amount of reaction mixture was withdrawn in a regular time interval and cooled down immediately to stop the reaction to measure the conversion. The residual monomers in the reaction system were analyzed by brominate titration[6,7] to determine the conversion of AAm aqueous two-phase polymerization. In detail, the weighed sample was completely dissolved into 100 mL water, and then 20 mL 0.1 N aqueous solution of bromine prepared by dissolving 3 g potassium bromate and 25 g potassium bromide in 1 L distilled water, and 10 mL HCl aqueous solution (1 : 1 volume ratio of 37% hydrochloric acid aqueous solution : water) were introduced into the aqueous solution of sample. The iodine flask containing the afore-mentioned mixture was put into a dark closet for 30 mins, and then 10 mL aqueous solution of potassium iodide (20 wt %) was added. The iodine was titrated by the aqueous solution of sodium thiosulfate (0.1 mol/L). The residual AAm can be calculated by AAm $= (V_1 - V_2)*c*0.03554$, in which V_1 and V_2 represent the consumed volume of aqueous solution of sodium thiosulfate for the blank and sample titration, respectively. c is the concentration of aqueous solution of sodium thiosulfate. The value of 0.03554 represents the mass of AAm which is consumed by 1 mL aqueous solution of sodium thiosulfate (1 mol/L).
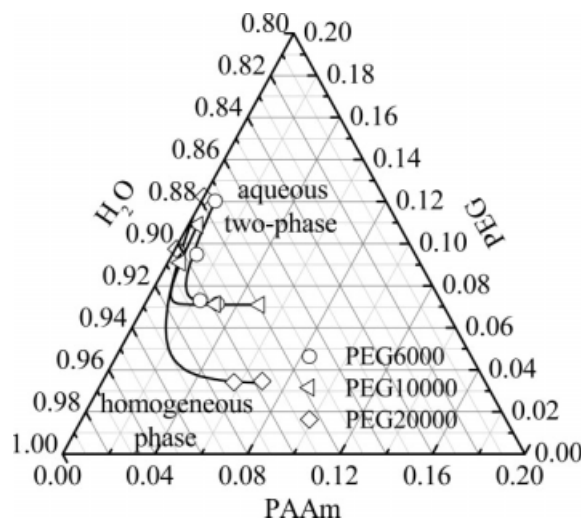
Figure 1 Effect of molecular weight of PEG on the phase diagram of PAAm-PEG-water aqueous two-phase system.

RESULTS AND DISCUSSION

Phase diagram

The phase diagrams of the PEG-PAAm-water system with varied molecular weight of PEG obtained by GPC are shown in Figure 1. In the upper area of each line in Figure 1, the mixture of two polymers aqueous solution is heterogeneous. An aqueous two-phase system can be obtained if the concentration of the system is above the critical concentration line of the phase diagram. From a thermodynamic point of view,[8] phase separation can occur in a system when the second derivative of Gibb's free energy (ΔG_{mix}) with respect to concentration is negative. $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$, where ΔH_{mix} is the enthalpy of mixing, T is the absolute temperature, and ΔS_{mix} is the entropy of mixing. For an obvious reason, the entropy of mixing is always positive, but it has a relatively small value for polymers because it depends on the number of molecules. When the gain in entropy of mixing is not large enough to compensate the positive PAAm-PEG interaction enthalpy, mixing of the two polymers is thermodynamically not favorable and phase separation occurs. In Figure 1, it was found that phase separation occurred even though the concentration of PAAm was very low in the PAAm-PEG20000-water system. It could be speculated that even when the polymerization reached a low degree of conversion, a new phase in which PAAm was rich would separate from the homogeneous aqueous solution phase, and an aqueous two-phase polymerization system was then obtained. Figure 1 also shows that the critical concentration of phase separation is affected by the molecular weight of PEG. When a PEG with a higher molecular weight is used, a two-phase system was formed at a lower concentration. This can be attributed to the

enhancement of the repulsion force between PAAm and PEG with increasing molecular weight of PEG, as the molecular weight increases, the number of end groups of PEG decreases, and the hydrophobicity difference between the PAAm and PEG enlarges, making the phase separation more favorable. Kishida et al.[9,10] investigated the systems of poly(N-vinylalkylamide)-dextran-water and poly(N-vinylacetamide)-dextran-water and got some results similar to this investigation.

Effect of initiator concentration on the kinetics

In a typical free-radical polymerization, the polymerization rate increases as the initiator concentration increases. The effect of initiator concentration on the conversion of aqueous two-phase polymerization of AAm is illustrated in Figure 2. Just as a typical free-radical polymerization, the polymerization rate and the degree of final conversion increase with the increase in the initiator concentration. At the high initiator concentration, the high conversion of about 100% is reached in a short time. On the other hand, the polymerization rate at a lower initiator concentration is slower, and the final conversion only reaches a lower value, and then keeps constant even the polymerization lasts longer because of the complete consumption of the initiator.

The initial polymerization rate, R_{p0}, is described by the slope of the conversion versus time curve in Figure 2 as the polymerization time is zero. The relationship of initial polymerization rate R_{p0} with initiator concentration [APS] can be obtained by plotting ln (R_{p0}) versus ln [APS], and the $R_{p0} \propto$ [APS]$^{0.72}$ is obtained (Fig. 3). It can be concluded from the exponent number of 0.72 that the termination of some
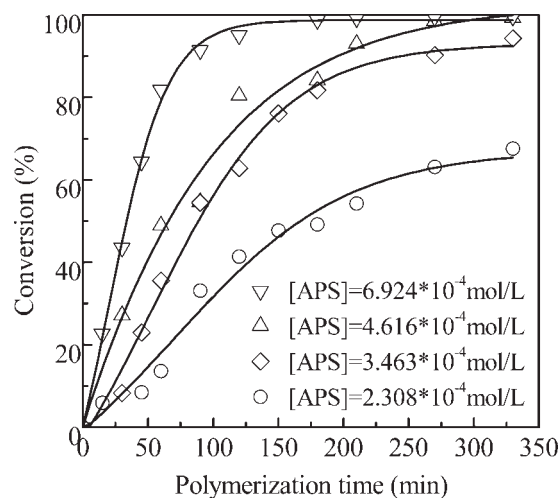

Figure 2 Effect of initiator concentration on the conversion of aqueous two-phase polymerization of AAm ([AAm] = 1.48 mol/L, [PEG] = 4.77 mol/L).
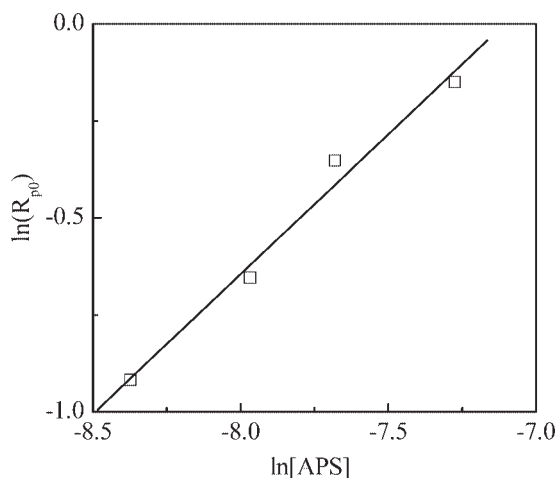
Figure 3 Relationship between initial polymerization rate and ln [APS] of aqueous two-phase polymerization of AAm.

Figure 4 Effect of initiator concentration on the polymerization rate of aqueous two-phase polymerization of AAm.

macroradicals was realized through a bimolecular termination reaction,[11] but some others were terminated through unimolecular termination. As polymerization proceeded, the PAAm concentration exceeded the critical PAAm concentration of phase separation, phase separation took place. A new phase enriched in PAAm was formed out of the PEG20000 aqueous solution during the phase separation. The initiator would be distributed in both phases, now initiating the polymerization of the monomers in the two phases. Some macroradicals were separated from the continuous phase and could also be captured by the dispersed droplets. The high viscosity of the dispersed phase made the diffusion of macroradical difficult. As the termination of macroradical was controlled by diffusion, the probability of the bimolecular macroradical reaction was reduced leading to some radicals be terminated through unimolecular termination and deviating the initiator concentration dependency from 0.5 to 0.72. However, in the homogeneous aqueous solution polymerization of AAm,[7,12] the termination was dominated by the bimolecular disproportionation termination.

The effect of initiator concentration on the polymerization rate R_p of the aqueous two-phase polymerization of AAm is shown as R_p versus polymerization time in Figure 4. The polymerization rate change with time can be divided into two stages, namely increase and attenuation stages. As the aqueous two-phase polymerization proceeded, PAAm-rich phase would be separated from the PEG20000 continuous phase and formed a PAAm-rich dispersed droplets. Macroradicals were distributed in the dispersed droplets with high viscosity, and the probability of termination of these macroradicals became lower than conventional aqueous
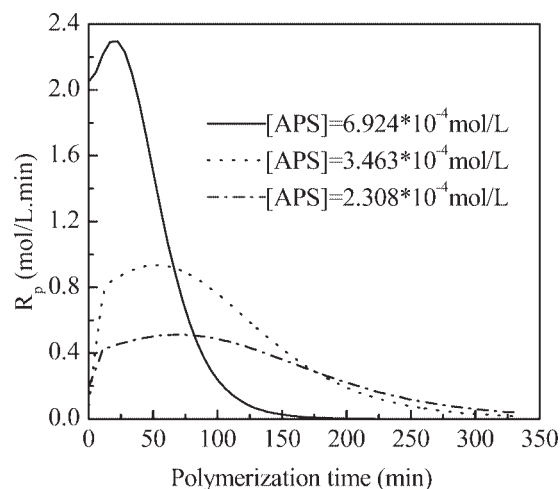
solution polymerization. The macroradical concentration accumulated in the reaction system, the polymerization rate increased drastically forming the increase stage of the polymerization rate. At the same time, the monomer concentration in both continuous and dispersed phases decreased, making the polymerization rate decrease. These two factors affected the polymerization rate in opposite directions. When the balance between the monomer consumption and macroradical accumulation was reached, the polymerization rate would reach its maximum. The peak of polymerization rate occurred earlier as the initiator concentration is higher (Fig. 4). As the polymerization rate at high initiator concentration was faster than that of the low initiator concentration, the monomers were consumed more
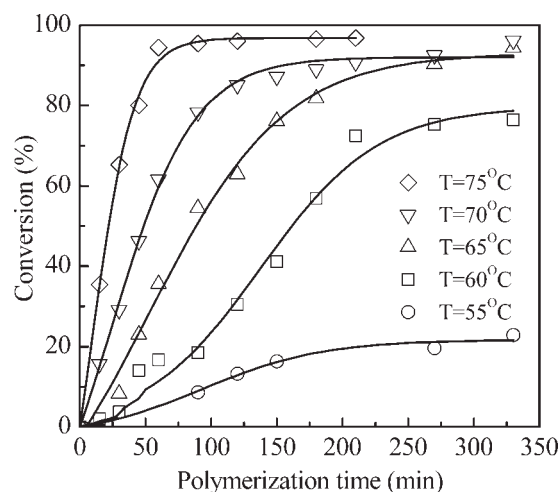

Figure 5 Effects of temperature on the conversion of aqueous two-phase polymerization of AAm ([AAm] = 1.42 mol/L, [PEG] = 4.77 mol/L, [APS] = 3.463 × 10⁻⁴ mol/L).
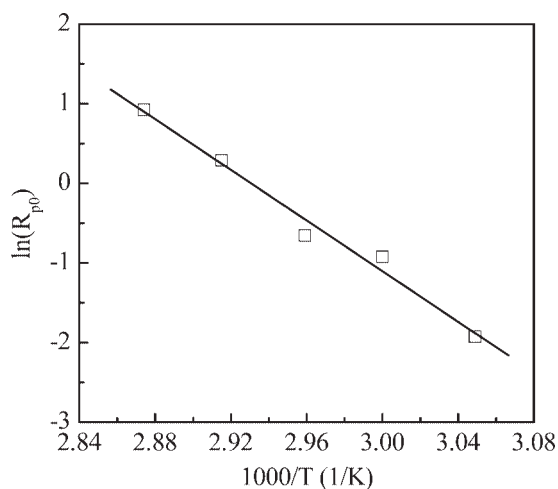
Figure 6 Relationship between initial polymerization rate and temperature of aqueous two-phase polymerization of AAm.

quickly, and the balance could be obtained in a shorter time.

Effect of polymerization temperature on the kinetics

Figure 5 shows the conversion versus polymerization time of the system at different polymerization temperatures from 55 to 75°C. The polymerization rate increases as the polymerization temperature increases. At the low polymerization temperature, the polymerization rate is very slow. The final conversion is less than 20% at 55°C as the polymerization time is 5 h, but over 90% in 50 min at 75°C. The polymerization temperature had significant effect on the polymerization rate of aqueous two-phase polymerization of AAm initiated by APS. Figure 6 demonstrates the Arrhenius dependency of the initiating rate of polymerization over the temperature range 55–75°C. The slope of the plot yields the activation energy of the aqueous two-phase polymerization of AAm of 132.3 kJ/mol. But the activation energy of homogeneous aqueous solution polymerization of AAm initiated by persulfate was only 70 kJ/mol.[12] Other investigators[13] also reported that the activation energy was 70–125 kJ/mol. The activation energy of aqueous two-phase polymerization of AAm is much larger than that of homogeneous aqueous solution polymerization of AAm. Again this can be explained by the phase separation. As the PAAm concentration exceeded the critical PAAm concentration of phase separation during the polymerization, PAAm-rich solution droplets separated from the PEG20000 aqueous solution. The monomers would diffuse into the dispersed droplets for further polymerization, which needed extra energy so that the overall activation energy of the

system should be larger and the initiating rate of the aqueous two-phase polymerization of AAm was more sensitive to the polymerization temperature than that of homogeneous aqueous solution polymerization of AAm.

Effect of monomer concentration on the kinetics

The influence of AAm concentration on the aqueous two-phase polymerization rate was studied by changing the concentration from 0.738 to 2.215 mol/L. The result is showed in Figure 7. The polymerization rate and the final degree of conversion increase with increasing monomer concentration, which complies with the theory for typical free-radical polymerization. The relationship between the initial polymerization rate R_{p0} and monomer concentration [AAm] is illustrated in Figure 8, in which a linear relationship between ln R_{p0} and ln [AAm], i.e., $R_{p0} \propto$ [AAm]$^{1.28}$, is obtained. The exponent number greater than 1.0 has been found by many researchers over the past few decades[12,14–17]. Riggs and Rodriguez[12] interpreted the high exponent number as an evidence of the monomer influence on the initiating rate. Hunkeler[16] considered that the association of monomer and initiator leaded to a donor–acceptor interaction between amide and persulfate. The decomposition of this charge transfer complex leaded to a secondary initiation reaction, which proceeded in competition with or, more often, even in preference to the thermal bond rupture of the peroxide. It would accelerate the polymerization and make the dependency of the polymerization rate on the monomer concentration stronger, higher than a first-order reaction. From the hybrid cage and complex mechanism[16], $R_p \propto [M]$ when the thermal
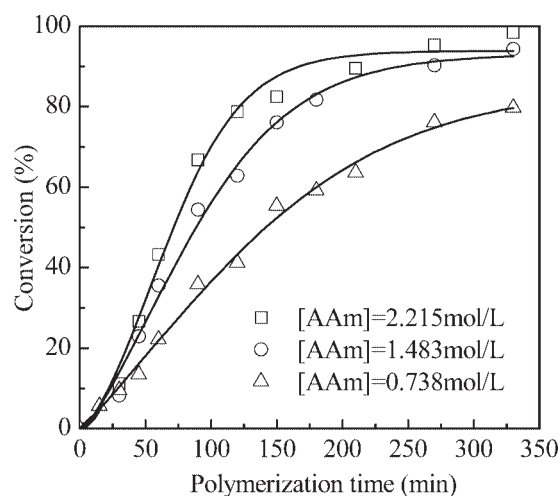

Figure 7 Effects of monomer concentration on the conversion of aqueous two-phase polymerization of AAm ([PEG] = 4.77 mol/L, [APS] = 3.463 × 10^{-4} mol/L).
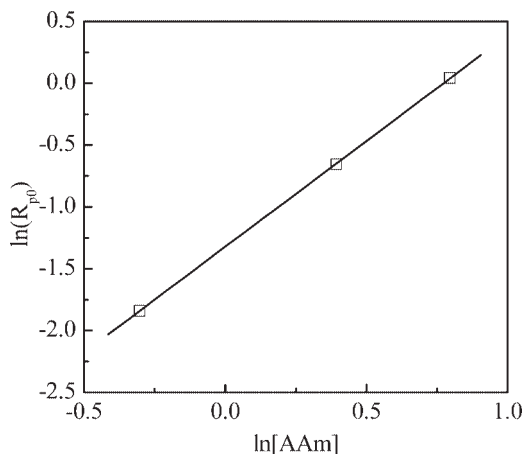
Figure 8 Relationship between initial polymerization rate and ln [AAm] of aqueous two-phase polymerization of AAm.

decomposition dominated, and $R_p \propto [M]^{3/2}$ while the monomer-enhanced decomposition dominated. In the case that the two initiation processes proceeded at the same time, the dependency of the polymerization rate on the monomer concentration would be $R_p \propto [M]^{1 \sim 1.5}$.

Effect of PEG's molecular weight on the kinetics

The effects of PEGs with different molecular weight on the kinetics of aqueous two-phase polymerization of AAm are shown in Figure 9. From Figure 9, the conversion versus polymerization time curve had a little difference among the PEGs with various molecular weights. At the low conversion stage, the curves even overlap each other. It is easy to understand that the PAAm concentration was lower than the critical PAAm concentration of phase separation at
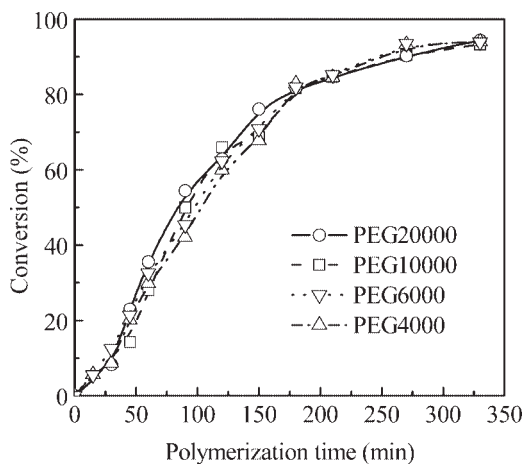

Figure 9 Effects of dispersed medium types on the conversion of aqueous two-phase polymerization of AAm ([AAm] = 1.42 mol/L, [PEG] = 4.77 mol/L, [APS] = 3.463 × 10^{-4} mol/L).
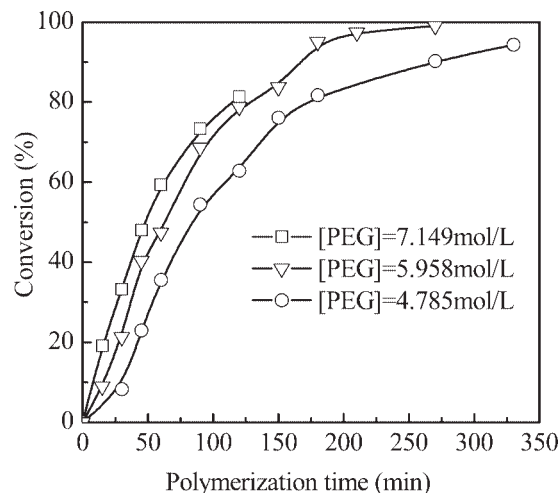
Figure 10 Effects of PEG20000 concentration on the conversion of aqueous two-phase polymerization of AAm ([AAm] = 1.42 mol/L, [APS] = 3.463 × 10^{-4} mol/L).

the initial stage of the reaction, polymerization processed in the homogeneous aqueous solution, the conversion versus polymerization time curves of different molecular weights were almost the same. As the polymerization proceeded to a higher conversion, the polymerization rate of the system of PEG20000 was a little higher than the other systems. Because of large molecular weight of PEG in this system, PAAm-rich phase was easier to separate from the continuous phase (PEG20000) as shown in Figure 1, and the probability of bimolecular termination became small which made the free-radical concentration increase and the polymerization rate enhance. Although the kinetics of the low molecular weight PEG system was similar to that of the PEG20000 system, the stability of final product of low molecular weight PEG was worse than that of the PEG20000 system. When the low molecular weight PEG was used, coagulation developed in the polymerization process, and the final reaction product contained the jelly-like gel. When high molecular weight PEG, e.g., PEG20000, was used, the reaction product retained a microdispersion system, the viscosity of the system (about 1.7 Pa s) was much lower than the product of homogeneous aqueous solution polymerization (about 100 Pa s).

Effect of PEG concentration on the kinetics

Figure 10 compares the conversion versus polymerization time curves of the system with PEG20000 but varied concentration from 4.79 to 7.15 mol/L. The polymerization rate increases with the increase of the PEG20000 concentration. These results can be actually predicted on the basis of the PAAm-PEG-water phase diagram in the Figure 1. As the PEG20000 concentration increases, the critical PAAm
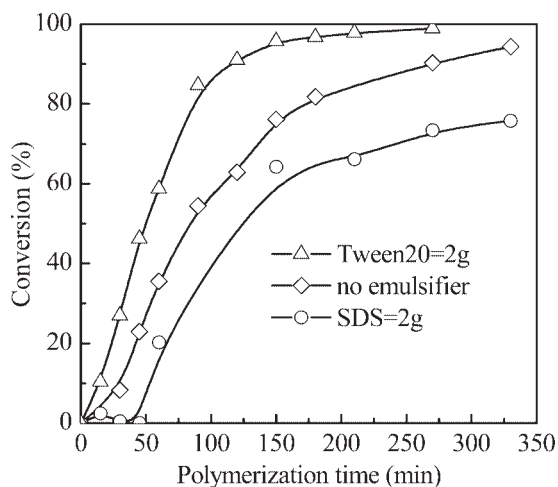
Figure 11 Effects of emulsifiers types on the conversion of aqueous two-phase polymerization of AAm.

concentration of phase separation decreases. The PAAm was more inclined to separate from the PEG continuous phase in the high PEG20000 concentration polymerization system. Once the free radical separated from the continuous phase to form a dispersed phase, as a consequence, it would diminish the recombination probability, prolong the lifetime of free radical, and increase the free-radical concentration in the polymerization system and the polymerization rate at the same time. However, the viscosity of the system increased with the increase of the PEG20000 concentration up to 50%. High concentration of PEG was inclined to separate from the aqueous solution and cling to the wall of the jacket tank, making the stability of the system decrease.

Effect of emulsifier type on the kinetics

The effect of emulsifier type on the kinetics of aqueous two-phase polymerization of AAm is summarized in the Figure 11. A longer induction period, lower polymerization rate, and lower final conversion can be found for the system using sodium dodecylsulfate (SDS) (HLB = 40) as the emulsifier. SDS was a strong hydrophilic emulsifier, and the sulfate group of SDS molecule was inclined to diffuse into the dispersed phase. However, the alkyl group of SDS would impede the entrance of the SDS molecules into the dispersed phase. Therefore, SDS molecules were apt to distribute on the surface of dispersed droplets so that the surface structure of droplets changed. The diffusion of monomer became more difficult, and the rate of polymerization with the addition of SDS decreased.

On the contrary, with the addition of polyoxyethylene(20)sorbitan monolaurate (Tween20) (HLB = 16.7) as the emulsifier, the polymerization rate of the system increases, the final conversion is also higher

than that of the other systems. The hydrophilic group of Tween20 is EO chain segment, the hydrophilicity of which is similar to PEG. However, some hydrophobic groups are also in the Tween20 molecule, and the hydrophobicity of Tween20 is stronger than that of PEG. In the system of aqueous two-phase polymerization, the dispersed phase was the aqueous solution of PAAm which had stronger hydrophilicity than that of PEG, the molecules of Tween20 were more inclined to in the aqueous solution of PEG. The hydrophobic group of Tween20 made the difference of hydrophobicity between the continuous phase and PAAm rich phase increase and influenced the phase diagram by lowering the critical concentration of phase separation. As the critical concentration of phase separation was lowered, the PAAm and its free radicals would more easily separate from the PEG solution. In the dispersed phase, the lifetime of the free radical prolonged, the aggregate of free radicals increased, and the polymerization rate added Tween20 increased.

CONCLUSIONS

The phase diagram of the PAAm-PEG-water system with varied molecular weight of PEG was obtained by GPC. From the results of the phase diagram, it could be concluded that the phase separation took place even though the concentration of PAAm was very low. The PAAm-PEG-water aqueous two-phase system was easily obtained. The critical concentration of phase separation was affected by the molecular weight of PEG, which decreased with increasing molecular weight of PEG. The effects of polymerization affecting factors on the kinetics of aqueous two-phase polymerization of AAm in the presence of PEG were also investigated. The increase of initiator, monomer, and PEG concentration resulted in the increase of the polymerization rate and final conversion. The molecular weight of PEG was not shown to obviously affect the kinetics of aqueous two-phase polymerization but significantly affect the stability of the polymerization system. The higher molecular weight of PEG was used, the more stability of system could be obtained. The activation energy of aqueous two-phase polymerization of AAm was 132.3 kJ/mol. The initial polymerization rate, R_{p0}, was obtained from the slope of conversion versus polymerization time curve. The form $R_{p0} \propto [APS]^{0.72} [AAm]^{1.28}$ could be obtained. The dependency of initial polymerization rate on APS concentration was 0.72. It meant that the termination occurred through the unimolecular and bimolecular macroradical reaction at the same time. The polymerization rate was greater than first order in monomer concentration because the thermal decomposition and monomer-enhanced decomposition occurred simultaneously.

References

1. Yan, R. X. Water Soluble Polymer; Chem Industrial Press: Beijing, 1998. p 84.
2. Mario Ossenbach-Sauter, M. M.; Riess, G. C R Acad Sci Paris Ser C 1976, 283, 269.
3. Hosoda, Y.; Ueshima, T.; Ishihara, S.; Imamura, K. In Contemporary Topics in Polymer Science; Bailey, W. J., Tsurta, T., Eds.; Plenum Press: New York, 1980; Vol. 4, p 575.
4. Jin, Z. Z.; Zhu, Y.; Hu, Y. D. Chem J Chinese Univ 1991, 12, 942.
5. Stenekes, R. J. H.; Franssen, O.; Van Bommel, E. M. G.; Crommelin, D. J. A.; Hennink, W. E. Pharm Res 1998, 15, 557.
6. Misra, G. S.; Bajpai, U. D. N. J Macromol Sci Chem 1979, A13, 1135.
7. Misra, G. S.; Narain, H. Makromol Chem 1968, 113, 85.
8. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1953.
9. Kishida, A.; Nakano, S.; Kikunaga, Y.; Akashi, M. J Appl Polym Sci 1998, 67, 255.
10. Kishida, A.; Kikunaga, Y.; Akashi, M. J Appl Polym Sci 1999, 73, 2545.
11. Odian, G. Principle of Polymerization, 2nd ed.; Wiley: New York, 1981.
12. Riggs, J. P.; Rodriguez, F. J Polym Sci Part A-1: Polym Chem 1967, 5, 3151.
13. Thomson, R. A. M. In Chemistry and Technology of Water-Soluble Polymer; Finch, C. A., Ed.; Plenum Press: New York, 1983; p 41.
14. Hunkeler, D.; Hamielec, A. E. Polym Prepr (Am Chem Soc Div Polym Chem) 1989, 30, 346.
15. Lin, H. R. Eur Polym Mater 2001, 37, 1507.
16. Hunkeler, D. Macromolecules 1991, 24, 2160.
17. Hunkeler, D.; Hamielec, A. E.; Baade, W. Polymer 1989, 30, 127.