Synthesis of Cationic Polyacrylamide by Aqueous Two-Phase Polymerization in Poly(ethylene glycol) Chloride Solution

Zaiman Liu, Yaling Wei, Baiyu Li, Naipu He

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

Correspondence to: Z. Liu (E-mail: liuzm@mail.lzjtu.cn)

ABSTRACT: Aqueous two-phase copolymerization of acrylamide(AM) and acryloyloxyethyl trimethyl ammonium chloride (DAC) was performed in poly(ethylene glycol) (PEG) solution and in PEG chloride(Cl-PEG) solution, respectively. Series of cationic polyacrylamide(CPAM) aqueous dispersion were prepared using potassium persulfate (KPS) as initiator. The effect of total amount of monomers, the dosage of initiator, the content of dispersant, the mass ratio of AM to DAC, and the temperature on the conversion, molecular weight, cationic degree, and stability of aqueous dispersion were studied in detail. It is found that the increase of initiator and reaction temperature resulted in the increase of the final conversion, whereas the increase of DAC and PEG concentration resulted in the decrease of the final conversion. The optimum reaction conditions of synthesis were as follows: (1) PEG-H_2O system: PEG 7.5 g, AM 8 g, DAC 2 g, KPS 0.05 g, H_2O 100 mL, 70°C. In this process conditions, the molecular weight of CPAM was 3.21×10^6, the cationic degree of CPAM was 24.4%, the storage stability of the aqueous dispersion was over 3 months. (2) Cl-PEG-H_2O system: Cl-PEG 7.5 g, AM 8 g, DAC 2 g, KPS 0.05 g, H_2O 100 mL, 65°C. In this process conditions, the molecular weight was 3.68×10^6, the cationic degree was 23.3%, and the storage stability of the aqueous dispersion was over 6 months. In general, the stability of CPAM aqueous dispersion in Cl-PEG system is much better than in PEG system. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

In recent years, aqueous two-phase polymerization of acrylamide (AM) has received great attention as a green and effective approach for the preparation of PAM.[1–11] Through this polymerization process, PAM aqueous dispersion with low viscosity may be prepared. This kind of PAM aqueous dispersion does not contain any organic solvent and could become solution instantaneously on the dilution with water.

Shan et al.[3–5] reported on the phase diagram of PAM-poly(ethylene glycol)(PEG)-water system, polymerization kinetics of AM in aqueous PEG solution and the product viscosity. Recently, Lü et al.[6–9] reported on the droplet formation mechanism, the kinetic model, and the stability of the two-phase polymerization of AM in aqueous PEG solution. They investigated the droplet aggregation behavior and the viscosity evolution during the polymerization. By analyzing the effects of PEG on the stability of this polymerization system, it was found that PEG plays both precipitant and stabilizer role. When PEG concentration ranges from 12 to 24%, increasing its use would promote the droplet

stabilization; however, when PEG concentration exceeds 28%, increasing its use may accelerate the droplet formation that does not further favor the droplet stabilization.[8] Furthermore, the slower the polymerization rate is, the more stable PAM aqueous dispersion will be.

The cationic polyacrylamide (CPAM) prepared by aqueous two-phase polymerization has the following advantages: low apparent viscosity, a quick dissolving in water, aqueous solution without gel, high efficiency and nontoxic, relatively simple field application process, etc.[12–16] Therefore, it is of significant interest to investigate the aqueous two-phase polymerization about CPAM.

The polymerization of AM and cationic monomers was performed in aqueous solution of ammonium sulfate,[17–22] ethanol,[23,24] and chitosan[25] solution. For this dispersion polymerization, the salt concentration not only affected the molecular weight and the particle size but also retarded the polymerization rate.[21] With the increase of the comonomer/AM ratio, the dispersion became less stable during long storage.[17] Because of the

presence of the salt, ionization of the quaternary ammonium groups in the dispersed particles is considered significantly suppressed.

The difference of hydrophobicity between dispersion medium and polymer aqueous solution is a key factor for forming stable aqueous dispersion. If PEG solution is replaced by PEG chloride (Cl-PEG) solution, which has a lower polarity, it is expected to enhance the stability of CPAM dispersion. In this article, the aqueous two-phase copolymerization of AM and acryloyl-oxyethyl trimethyl ammonium chloride (DAC) was performed in PEG-water and Cl-PEG-water media as well. The effects of PEG and Cl-PEG on the droplets stability during the aqueous two-phase polymerization were investigated systemically.

EXPERIMENTAL

Materials

AM, potassium persulfate (KPS), PEG (molecular weight 20,000), triethylamine (TEA), and thionyl chloride (SOCl$_2$) were analytical grade. DAC was industrial grade. The water to be used for polymerization in this study was prepared by double distillation.

Preparation of Cl-PEG

Forty grams (2 mmol) PEG was dissolved in 100 mL anhydrous benzene in conical flask, in which 0.56 mL (4 mmol) TEA was added; then the new distilled SOCl$_2$ was slowly added (batch addition) at stirring. The mixture was filtrated after reacting at room temperature for 9 h. The filtrate was precipitated by anhydrous ether, followed by filtration and drying. The crude product was dissolved into benzene, after which the solution was precipitated, filtrated, and dried, finally Cl-PEG obtained.

Polymerization

A certain amount of AM, DAC, dispersant, and water were added into a four-necked bottle equipped with a stirrer, reflux condenser, nitrogen inlet tube, and a constant pressure funnel. The mixture was stirred to form a homogeneous solution, which was purged with nitrogen for 20 min and heated to reach the reaction temperature. The initiator solution was slowly dripped through the funnel to start the polymerization, keeping reaction for 5 h and cooling to room temperature to obtain CPAM aqueous dispersion. After purification treatment of CPAM aqueous dispersion, some solid CPAM was obtained for determination and characterization.

Determination

The intrinsic viscosity of CPAM, [η], was measured according to GB12005.1-89 by Ubbelodhe viscometer in 30°C, using 1 mol/L of NaCl solution as solvent. The relative molecular weight (M_r) of CPAM is given by [η] = $3.684 \times 10^{-2} M_r^{0.646}$.

The overall monomer conversion was calculated from the residual monomers (AM and DAC) content (RM) in copolymer aqueous dispersion measured according to GB12005.3-89:

$$\text{RM} = \frac{(V_1 - V_2) \times c \times 0.03554}{m \cdot s} \times 100$$

where V is the volume of Na$_2$S$_2$O$_3$ standardized solution, with the subscripts 1 and 2 referring to blank test and sample; c is
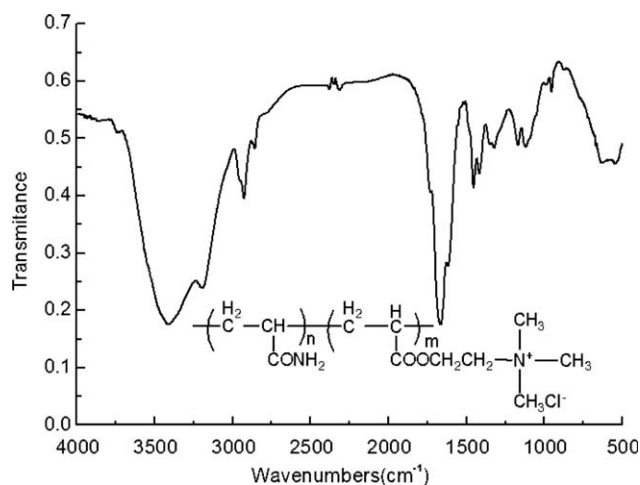

Figure 1. IR spectrum of the CPAM.

concentration of Na$_2$S$_2$O$_3$ standardized solution; m is the weight of sample; and s is the solid content of sample.

The degree of cationic (DC) of CPAM was determined by silver nitrate titration. Accurately weighed 0.300 g of dried CPAM was completely dissolved in 150 mL of water in beaker flask. After 5 drops of 10 wt % potassium dichromate were added as visual indicator, the solution was titrated using 0.1 mol/L silver nitrate with magnetic stirring, and the visual end point was given by brick red solution, then:

$$DC = M \times N(V - V_0)/W$$

where V and V_0 are the volumes of silver nitrate consumed in sample and blank test, respectively; W is the sample weight; M is the molecular weight of DAC; and N is the concentration of silver nitrate standard solution. A certain amount of the CPAM aqueous dispersion was static stored at room temperature, and after a certain time, the stability could be evaluated with naked eye observation according to the apparent change of the CPAM aqueous dispersion.

Characterization

The polymer was precipitated with acetone and extracted with ethanol, followed by vacuum drying. IR spectrum of the samples was recorded on a VERTEX70 spectrophotometer (BRUKER, German) in KBr pellets. The CPAM aqueous dispersion was directly spread on a microslide, and the microstructure of which was examined using a phase contrast microscope (Ricoh, Japan). The microscopic morphology of CPAM was observed by JEM-1200EX type transmission electron microscope (BRUKER, German).

RESULTS AND DISCUSSION

IR Spectrum of CPAM

IR spectrum of the CPAM is given in Figure 1. It can be found that the band at 1680 cm^{-1} is assigned to amide group; the broad bands at 3412 and 3182 cm^{-1} are related to stretching vibration of N—H; the band at 1453 cm^{-1} is due to bending vibration of —CH$_2$— connecting with N$^+$ of DAC. The results
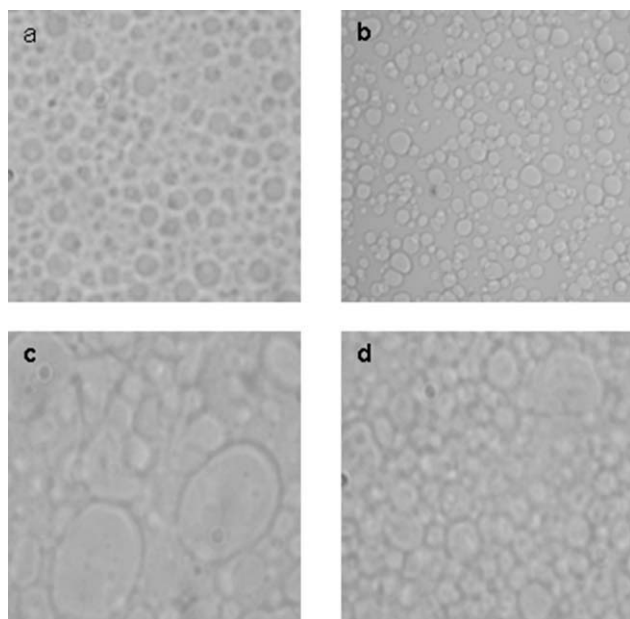
Figure 2. Microstructures of CPAM dispersion in PEG system (a) and Cl-PEG system (b), after static placed 30 days at room temperature in PEG system (c) and Cl-PEG system (d).

indicate the existing of AM and DAC units among the copolymer.

Microstructure of CPAM Aqueous Dispersion

Microstructures of the CPAM aqueous dispersion are shown in Figure 2. It can be seen that the dispersion phase droplets of co-polymer are dispersed homogeneously in the continuous phase of dispersant medium. After 30 days on standing, partial small droplets clustered together forming large droplets in both the copolymer aqueous dispersions, resulting in the decrease of dispersion stability. Moreover, the clustering is more serious in PEG system than in Cl-PEG system, the dispersion stability in Cl-PEG system is better than that in PEG system.

Microstructure of CPAM

The microstructures of CPAM determined by TEM are given in Figure 3. Before taking TEM photographs, the copolymer dispersions were precipitated by acetone. The copolymer particles are 300–500 nm for PEG system and for Cl-PEG system. The nearly regular spherical shape particles are uniformly distributed in both the two dispersions. Because of the less adhesion among particles in Cl-PEG system, the CPAM aqueous dispersion in
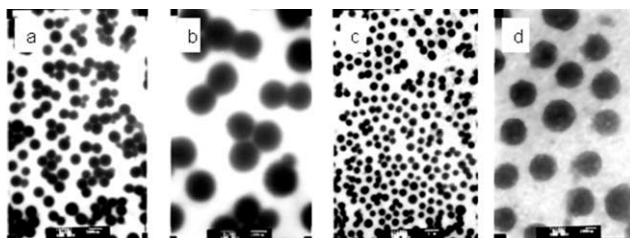

Figure 3. TEM photographs of CPAM prepared in PEG system (a. ×1000; b. ×5000) and in Cl-PEG system (c. ×1000; d. ×5000).
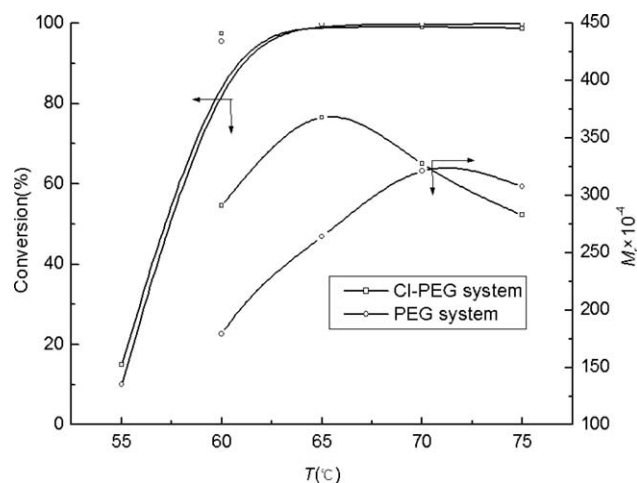

Figure 4. Effect of reaction temperature on molecular weight and conversion.

Cl-PEG system is more stable than in PEG system, which is in agreement with the result in the above paragraph.

Effect of Reaction Temperature

The effect of reaction temperature was investigated while keeping the amount of monomer and dispersant, and the initiator content constant. The amount of monomer was 10 g with mass ratio AM to DAC of 4; the dispersant content was 7.5 g; and the initiator content was 0.05 g.

Figure 4 shows that the molecular weight increases first with increasing the temperature for two systems, then decreases when the temperature reaches 70°C for PEG system and 65°C for Cl-PEG system. This may be because at low temperature, there are few free radicals decomposed from initiators, which can hardly initiate polymerization. The increase of temperature can increase the activity of free radicals and speed up the reaction rate; but when the temperature is too high, the increase of chain transfer rate is far greater than the chain growth rate, making molecular weight reduction. Therefore, to obtain a co-polymer product with relatively high molecular weight, the quite suitable temperature are 70°C and 65°C for PEG system and Cl-PEG system, respectively.

As shown in Figure 4, when the temperature is 55°C, the forming of radical is slow at this low temperature, so the polymerization is far from completion, and the monomer conversion is less than 15% in the two systems. When the temperature is higher than 60°C, the conversion is over 95% in the two systems.

As can be seen in Table I, the DC and the stability of CPAM dispersion increase with the increasing temperature, whereas the stability decreases when the temperature is higher than 70°C. So the optimal temperature can be controlled at 70°C for PEG system and 65°C for Cl-PEG system in terms of DC and stability.

Effect of Monomer Amount

The effect of monomer amount was investigated while keeping the amount of dispersant and the temperature constant. As shown in Table II, the stability of CPAM dispersion decreases

Table I. Effect of Reaction Temperature on Stability of CPAM Dispersion and DC

T (°C)	Stability		DC (%)	
	PEG system	Cl-PEG system	PEG system	Cl-PEG system
55	No reacted	Bottom little clear gel	–	–
60	Layer in 2 weeks	No layer in 6 months	13.8	20.1
65	Layer in 1 month	No layer in 6 months	23.2	23.3
70	No layer in 3 months	Layer in 5 months	24.4	24.8
75	Whole gel	In 2 weeks, partial gel	23.5	24.2

Table III. Effect of Monomer Amount on Molecular Weight, Conversion, and DC

Monomer (g)	$M_r \times 10^{-4}$		Conversion (%)		DC (%)	
	PEG	Cl-PEG	PEG	Cl-PEG	PEG	Cl-PEG
10.0	321	368	99.74	99.02	24.4	23.3
12.5	334	372	99.50	99.30	23.9	24.2
15.0	342	381	98.91	98.81	24.5	23.9

The mass ratio of AM to DAC in monomer is 4.

with increasing the monomer amount. When the monomer amount is 20 g, the clear gels without fluidity are formed in both the two systems, which is because the higher the monomer amount, the faster the polymerization rate. As a consequence, the copolymers forming rate is far higher than the dispersion rate, and the dispersant quantity is not sufficient to reach the critical phase separation concentration; so the small droplets agglomerate into large droplets, even into gel instead of dispersing in time, resulting in the stability decreased.

As shown in Table III, the molecular weight increases with increasing the monomer amount, and the conversions are kept high in the two systems, whereas the DC remains unchanged. This is because the mass ratio of AM to DAC is unchanged, and so is the reactivity ratios of AM and DAC.

Effect of Initiator Content

The effect of initiator content was investigated while keeping the amount of monomer, dispersant, and the temperature constant. The amount of monomer was 10 g with mass ratio AM to DAC of 4, the dispersant content was 7.5 g. The temperatures were 70°C and 65°C for PEG system and Cl-PEG system, respectively.

As shown in Figure 5 the initiator content has strong effect on molecular weight. If the initiator content is too little, few free radicals are generated, then the monomers can hardly polymerize, resulting in a relatively low molecular weight. As the initiator content increases, the free radical concentration increases consequently, and the polymerization rate is accelerated; at the

Table II. Effect of Monomer Amount on Stability of CPAM Dispersion

Monomer (g)	PEG system	Cl-PEG system
10.0	No layer in 3 months	No layer in 6 months
12.5	Layer in 1 months	Layer in 6 months
15.0	Layer in 1 months	Layer in 3 months
17.5	Whole gel	In a week, pasted
20.0	Whole gel	Whole gel

The mass ratio of AM to DAC in monomer is 4.

same time, the termination rate of activity chains also increases, thus the final polymer molecular weight reduces when the initiator content is beyond 0.05 g, with the crosslink possibly to occur. When the initiator content is above 0.05 g, the conversions are high nearly to 100%.

As shown in Table IV, the DC of CPAM in both the systems is down first and up later with increasing the initiator content. The reactivity ratio of DAC is smaller than that of AM, so as the initiator increases, the homopolymerization of AM occupies the main status, corresponding to cationic degree reduces. When the initiator content is more than 0.07 g, the free radical concentration increases with increasing the initiator content, and the collision probability between macroradicals and DAC also increases; thereby the polymerization rate accelerated, and the DC increased accordingly.

Table IV shows that the stability decreases with increasing initiator content. This is because as the initiator increases, there is an increase in the polymerization rate which makes the increase of termination rate; thus the adsorbed rate of dispersant molecules on the droplets of dispersion phase is generally slower than a new surface generation rate, leading to a speed up of the particles aggregation rate and the stability of the system decreasing. As a whole, in the same initiator content, the stability of CPAM dispersion in Cl-PEG system is higher than the other one. Considering the conversion, molecular weight, DC, and stability, the appropriate initiator content is about 0.05 g.
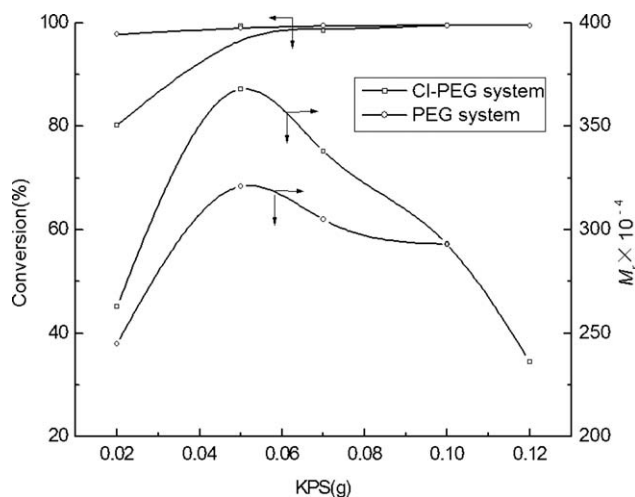

Figure 5. Effect of initiator content on molecular weight and conversion.

Table IV. Effect of Initiator Content on Stability of CPAM Dispersion and DC

	Stability		DC (%)	
KPS (g)	PEG system	Cl-PEG system	PEG system	Cl-PEG system
0.02	Layer in 3 months	No layer in 6 months	24.4	29.27
0.05	No layer in 3 months	No layer in 6 months	23.9	22.75
0.07	No layer in 3 months	Layer slightly in 4 months	18.5	16.53
0.10	Layer in 1 month	Layer slightly in 4 months	20.2	19.62
0.12	Layer in 2 weeks	Layer in 4 months	23.4	20.13

Table V. Effect of DAC Amount on Stability of CPAM Dispersion and DC

	Stability		DC (%)	
DAC (g)	PEG system	Cl-PEG system	PEG system	Cl-PEG system
2	No layer in 3 months	No layer in 6 months	24.4	23.3
3	No layer in 3 months	No layer in 6 months	27.9	28.2
4	Layer in 2 months	Layer in 3 months	35.5	33.9
5	Whole clear gels	Layer in 1 month	44.3	46.8

The mass of AM is 8 g.

Effect of DAC Amount

As shown in Figure 6, the molecular weight of CPAM obviously decreases with increasing the DAC amount. This is because as cationic monomer dosage increases, the positive charge density increases whereas the diffusion rate of monomers to particles decreases, leading to a chain growth rate decreasing and chain termination rate increasing, and finally the molecular weight decreases. The conversion decreases with increasing the DAC amount in both the two systems. This is because the electrostatic repulsion effect and steric effect of DAC restrain the collisions between monomers and macroradicals, resulting in a reduction in reaction probability.

As shown in Table V, the DC obviously increases with increasing the DAC amount. Commonly, the DC of cationic coagulant is more than 20%, so when m(AM): m(DAC) is 8 : 2–8 : 3, i.e., the DAC amount is 2–3 g, these products with DC of 23.3–28.2% can basically meet the need in commercial. Additionally, the stability of CPAM dispersion decreases with increasing the DAC amount. Because of the increase of DAC concentration, the adsorption of dispersant on surface of precipitate copoly-
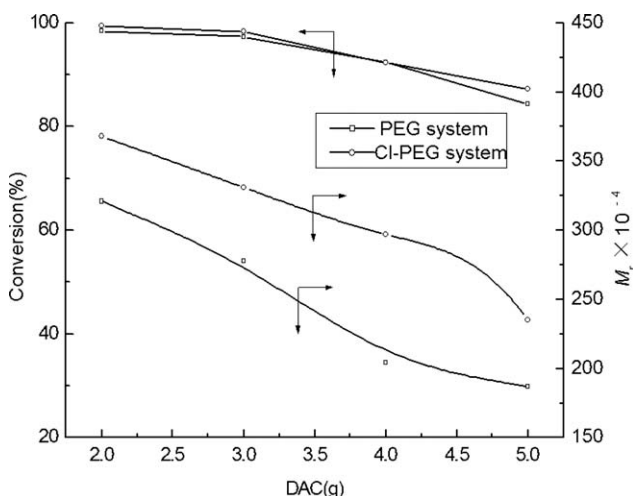
mers is restrained, resulting in the agglomeration of copolymers.

Effect of Dispersant Amount

The dispersant amount is very important to the stability, which mainly decide the viscosity of continuous phase and the stability of dispersion in nucleation stage. It can be seen from Figure 7 that, in both the two systems, the conversion decreases with the increase of dispersant amount, whereas the molecular weight increases first and then decreases. This is because when the amount of dispersant is too small, the surface of the particles is
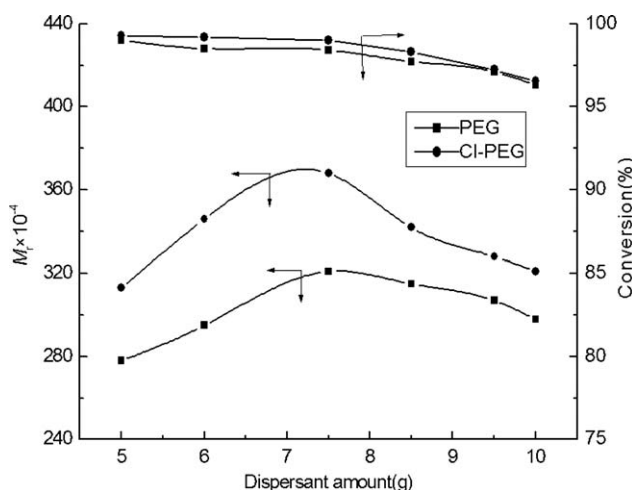

Figure 7. Effect of dispersant amount on molecular weight and conversion.

Table VI. Effect of dispersant amount on stability of CPAM dispersion

Dispersant (g)	PEG system	Cl-PEG system
5	Whole clear gels	Layer in a day
6	Layer in 2 weeks	Layer in 6 months
7.5	No layer in 3 months	No layer in 6 months
9	Layer in 3 weeks	Layer in 3 months
10	Whole clear gels	Layer in 2 weeks

Figure 6. Effect of DAC amount on molecular weight and conversion (AM 8 g).

insufficiently covered by dispersant molecules, so the dispersion stability is poor, and the polymer molecular weight distribution is not uniform. The amount of dispersant increasing, the shielding effect of the dispersant solution on free radical is enhanced, and the viscosity increases, which is not conducive to the monomer diffusion to the polymer particles. Therefore, the conversion decreases.

With increasing the amount of dispersant, the viscosity increases, which hinders the forming of core and the growth of polymer particles; hence the proportion of polymerization in the continuous phase will rise and tend to forming more oligomers, so that the polymerization rate declines and the molecular weight decreases.

When the amount of PEG is 5–10 g, the DC of CPAM is 23.8–24.5% in PEG system; and when the amount of Cl-PEG is 4–12 g, the DC of CPAM is 23.2–24.3% in Cl-PEG system. In both the two systems, the DC has no significant change with increasing the dispersant amount.

Table VI shows that there are significant influences on the stability in the two systems. When the dispersant content is too low, the coalescence among polymer molecules is easy to occur, i.e., the small particles of dispersion phase tend to coagulate into large particles, even forming gel. With increasing the dispersant content, there are more reaction sites, and the adsorption rate of dispersant on polymer particles is much faster; the polymer molecules is covered by dispersants when the particle size is small and particles can be further stability. But when the dispersant amount is too large, the viscosity increases, and the bridging effect of the excess dispersant would result in a large particle generation, which will separate from continuous phase to form a gel. The stability of CPAM dispersion in Cl-PEG system is better than that in PEG system at varying dispersant amount. The optimum amount of dispersant is about 7.5 g.

CONCLUSIONS

Two-phase copolymerization of AM and DAC in aqueous PEG solution and aqueous Cl-PEG solution as well was successfully performed with KPS as the initiator, and the stable conditions for these copolymerization systems were investigated systemically. The stability of CPAM dispersion decreased with increasing the monomer and initiator content. The reaction temperature and dispersant amount had important influence on the stability of CPAM dispersion, too. In general, the stability of CPAM aqueous dispersion in Cl-PEG system is much better than in PEG system. This might be because the polarity of Cl-PEG is lower than that of PEG, the difference of hydrophobicity between Cl-PEG and CPAM could be enhanced. The optimum reaction conditions in Cl-PEG solution were as follows: Cl-PEG 7.5 g, AM 8 g, DAC 2 g, KPS 0.05 g, H_2O 100 mL, and 65°C. In this process conditions, the molecular weight of CPAM was 3.68×10^6, the cationic degree was 23.3%, and the storage stability of the aqueous dispersion was over 6 months.

REFERENCES

1. Jin, Z. Z.; Zhu, Y.; Hu, Y. D. *Chem. J. Chin. Univ.* **1991,** *12,* 942.
2. Shan, G. R.; Cao, Z. H.; Huang, Z. M.; Weng, Z. X. *Acta Polym. Sin.* **2005,** *5,* 769.
3. Shan, G. R.; Cao, Z. H. *J. Appl. Polym. Sci.* **2009,** *111,* 1409.
4. Shan, G. R.; Cao, Z. H.; Huang, Z. M.; Weng, Z. X. *Acta Polym. Sin.* **2003,** *6,* 784.
5. Shan, G. R.; Cao, Z. H.; Huang, Z. M.; Weng, Z. X. *Chem. J. Chin. Univ.* **2005,** *26,* 1348.
6. Lü, T.; Shan, G. R. *J. Appl. Polym. Sci.* **2010,** *116,* 1747.
7. Lü, T.; Shan, G. R. *J. Appl. Polym. Sci.* **2009,** *112,* 2859.
8. Lü, T.; Shan, G. R.; Shang, S. M. *J. Appl. Polym. Sci.* **2011,** *122,* 1121.
9. Lü, T.; Shan, G. R. *AIChE J.* **2011,** *57,* 2493.
10. Cho, M. S.; Yoon, K. J.; Song, B. K. *J. Appl. Polym. Sci.* **2002,** *83,* 1397.
11. Liu, X. G.; Chen, D. N.; Yue, Y. M.; Zhang, W. D.; Wang, P. X. *J. Appl. Polym. Sci.* **2006,** *102,* 3685.
12. Pan, M.; Chen, D. J. *Acta Petrol. Sin. (Petroleum Processing Section)* **2007,** *23,* 51.
13. Ding, W.; Yu, T.; Qu, G. M.; Zhang, Y. Q. *Chin. J. Appl. Chem.* **2009,** *26,* 392.
14. 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.
15. Lü, T.; Shan, G. R.; Shang, S. M. *J. Appl. Polym. Sci.* **2010,** *118,* 2572.
16. Zhao, L.; Shan, G. R.; Weng, Z. X. *Acta Polym. Sin.* **2006,** *8,* 944.
17. Song, B. K.; Cho, M. S.; Yoon, K. J.; Lee, D. C. *J. Appl. Polym. Sci.* **2003,** *87,* 1101.
18. Chen, D. N.; Liu, X. G.; Yue, Y. M.; Zhang, W. D.; Wang, P. X. *Eur. Polym. Mater.* **2006,** *42,* 1284.
19. Wu, Y. M.; Chen, Q. F.; Xu, J.; Bi, J. M. *J. Appl. Polym. Sci.* **2006,** *102,* 2379.
20. Wu, X. J.; Zhao, W. P.; Wang, C. X.; Wu, Y. M. *Express Polym. Lett.* **2010,** *4,* 275.
21. Wu, Y. M.; Chen, Q. F.; Xu, J.; Bi, J. M. *J. Appl. Polym. Sci.* **2008,** *108,* 134.
22. Wu, Y. M.; Wang, C. X.; Xu, J. J. *Appl. Polym. Sci.* **2010,** *115,* 1131.
23. Wang, X.; Yue, Q. Y.; Gao, B. Y.; Si, X. H.; Sun, X.; Zhang, S. X. *J. Appl. Polym. Sci.* **2011,** *120,* 1496.
24. Liu, X. G.; Chen, Q.; Xu, K.; Zhang, W. D.; Wang, P. X. *J. Appl. Polym. Sci.* **2009,** *113,* 2693.
25. Liu, J.; Wang, C. X.; Wu, Y.M. *Iran. Polym. J.* **2011,** *20,* 887.