

Dispersion Copolymerization of Acrylamide and Dimethyl Diallyl Ammonium Chloride in Ethanol-Water Solution

Xiaona Wang, Qinyan Yue, Baoyu Gao, Xiaohui Si, Xun Sun, Shengxiao Zhang

Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Jinan 250100, Shandong, People's Republic of China

Received 7 March 2009; accepted 26 August 2010

DOI 10.1002/app.33288

Published online 29 November 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Poly (acrylamide-dimethyldiallylammonium chloride) (PAM-DMDAAC) particles have been prepared via dispersion polymerizations using poly (vinyl pyrrolidone) (PVP) as a steric stabilizer in ethanol-water media. The monomer reactivity ratios of acrylamide (AM, r_1) and dimethyldiallylammonium chloride (DMDAAC, r_2) were determined as 6.664 and 0.120, respectively, which means that PAM-DMDAAC is a nonideal copolymer. The effects of various polymerization parameters (e.g., concentration of monomer and initiator, medium polarity, the ratio of AM to DMDAAC, initial temperature and ethylene

diamine tetraacetic acid disodium (EDTA)) on the intrinsic viscosity and conversion of copolymer have been investigated. The copolymer was characterized by FTIR and NMR. The optimum operating conditions for preparing PAM-DMDAAC were determined as ethanol content 50%, C_{monomer} (wt %) 40%, $n_{\text{AM}}: n_{\text{DMDAAC}}$ 8 : 2, $C_{\text{initiator}}$ (wt %) 0.04% and initiate temperature 40°C. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1496–1502, 2011

Key words: dimethyldiallylammonium chloride; acrylamide; dispersion polymerization; monomer reactivity ratio

INTRODUCTION

Water-soluble cationic copolymers have been described for various technical and biological applications. The cationic copolymer of acrylamide (AM) and dimethyldiallylammonium chloride (DMDAAC) has the merits of high molecular weight, high charge, good water-solubility, high efficiency, no toxicity, excellent stability of cationic structure, and wide usable pH range. Therefore, it is widely used in the areas of oil exploitation, papermaking, wastewater treatment, mining, printing and dyeing of textiles, daily chemical industry, slurry dehydration, and others.^{1–3} Moreover, it is very cheap. Nowadays the price of PAM-DMDAAC is lower than the price of the other cationic polymers in the international market. Hence, it has good application prospects.⁴

Current synthetic methods to produce PAM-DMDAAC include solution polymerization and inverse emulsion polymerization. The advantages of solution polymerization are simple technology, low cost, safe and convenient operation, and no need to reclaim the solvent.³ However, at the end of the polymerization reaction, the viscosity of the polymer solution is large, and a gel is easily formed. Therefore, it is difficult to produce the polymer with high concentration and high molecular weight.⁵ If the product is turned into a powder, the drying process

will consume more energy. Agglomeration also often happens, and the quality of the product is poor, which is a familiar problem during solution synthesis of polymers. Large amounts of organic solvent and surfactant are used in inverse emulsion polymerization, which is not convenient in practical operations and may cause secondary pollution.

Dispersion polymerization is a unique single step polymerization process, capable of forming monodisperse copolymer microspheres in the range of 0.1–15 μm .^{6–9} During dispersion polymerization, the polymer precipitates out from the initially homogeneous reaction mixture containing monomer, initiator, solvent, and stabilizer. The reaction medium for dispersion polymerization is a good solvent for the monomer and stabilizer, but is a poor solvent for the polymer formed. During the process of dispersion polymerization, stabilizer protects the particles by adsorption, steric, and electrostatic stabilization.^{10–15} Dispersion polymerization has been used to prepare micro or nanoparticles of hydrophobic polymers and core-shell particles using various stabilizers.^{11,12,16–19} It has also been used to prepare finely dispersed submicron size particles from the water-soluble monomer like, acrylamide in ethanol-water media.^{14,20,21} Polymerization of AM and DMDAAC by the method of dispersion polymerization is rarely reported because the dispersion medium often plays a role in chain transfer and leads to a drop in polymerization degree.²²

In this paper, the molar ratio of monomers and reaction conditions were investigated to understand

Correspondence to: Q. Yue (qyyue58@yahoo.com.cn).

their effects on the intrinsic viscosity and conversion of the copolymer, and the optimum operation conditions were gained. FTIR and NMR were used to characterize the copolymer. The monomer reactivity ratios of AM and DMDAAC were calculated using Fineman-Ross equation and manifested the reactive capacity of both monomers in dispersion system.

MATERIALS AND METHODS

Chemicals

The monomers AM (40% in water) and DMDAAC (60% in water) were kindly provided by Binzhou chemical Co. Ltd. (Shandong province, China). PVP and *N, N, N', N'*-tetramethyl-ethylenediamine (TMEDA, B.R. Grade) were purchased from Guoyao chemical group Co. Ltd., Shanghai, China and used as received. The other chemicals, such as ethanol, acetone, glycerol, EDTA, sodium chloride (NaCl), potassium persulfate ($K_2S_2O_8$), sodium formate (CHOONa), etc, were purchased from Guangmang Chemical Company, A.R. Grade and were used without further purification. Deionized water was used throughout.

Synthesis of PAM-DMDAAC

Varying quantities of the ingredients were added to a 250-mL four-neck round bottom flask equipped with an anchor-like paddle stirrer, a thermometer and a nitrogen inlet tube. After purging with N_2 for 30 min and controlling the initiation temperature in a water bath, the polymerization was initiated by injecting the initiator solution into the reaction mixture under stirring. The reaction proceeded for 10 h to get high conversion of monomers (the conversion was determined gravimetrically as described later). The data for individual polymers were showed in Table I. Linear PAM-DMDAAC of different DMDAAC feed were synthesized and purified by precipitating samples in acetone. The content of Cl^- in DMDAAC was measured by ion chromatography, and the amounts of monomer units in the copolymers were obtained. In this article, the concentrations of dispersant and initiator are reported as weight percent based on the monomer.

Conversion and intrinsic viscosity measurements

A certain amount of polymerization product was precipitated with ethanol and acetone mixture (volume ratio of 1 : 1), and was washed with acetone. These operations were repeated several times to remove the unreacted monomers. Then the copolymer precipitated was dried to a constant weight at 40 ~ 50°C under vacuum ($\approx 10^{-3}$ Torr). The monomer conversion was calculated by weighing the copoly-

TABLE I
Data for Individual Polymers

Figure	Ethanol content (%)	$n_{AM} : n_{DMDAAC}$	$C_{monomer}$ (%)	$C_{initiator}$ (%)	T (°C)
1	10	8 : 2	40	0.02	40
	20				
	30				
	40				
	50				
2	50	8 : 2	20	0.02	40
			25		
			30		
			35		
			40		
3	50	9 : 1	40	0.02	40
		8 : 2			
		7 : 3			
		6 : 4			
		5 : 5			
4	50	8 : 2	40	0.01	40
				0.02	
				0.04	
				0.06	
				0.08	
5	50	8 : 2	40	0.10	40
				0.02	

mer. The dried sample was used to determine the intrinsic viscosity $[\eta]$ of the copolymer in 1.0 mol/L NaCl solution with an Ubbelohde capillary viscometer (Shanghai Shenli Glass Instrument Co. Ltd., China) at $30 \pm 0.05^\circ C$.

Polymer characterization

For infrared analysis, the dried polymer was mixed with 250 mg KBr, and a pellet was prepared using a press connected to a vacuum pump. Transmission Fourier-Transform Infra Red (FTIR) spectroscopy (AVATAR 370, Thermo Nicolet, USA) was conducted with a Bruker IFS 55 spectrophotometer. The spectra were recorded in the 4000–500 cm^{-1} range with 200 scans collected at 2 cm^{-1} resolution.

The 1H NMR spectrum of the dried copolymer sample was recorded in D_2O using a Bruker (AVANCE 300 MHz, Switz.) spectrometer.

RESULTS AND DISCUSSION

The reactivity ratios of AM and DMDAAC

The initial reactivity ratios of AM and DMDAAC were calculated using Fineman-Ross (FR) equation

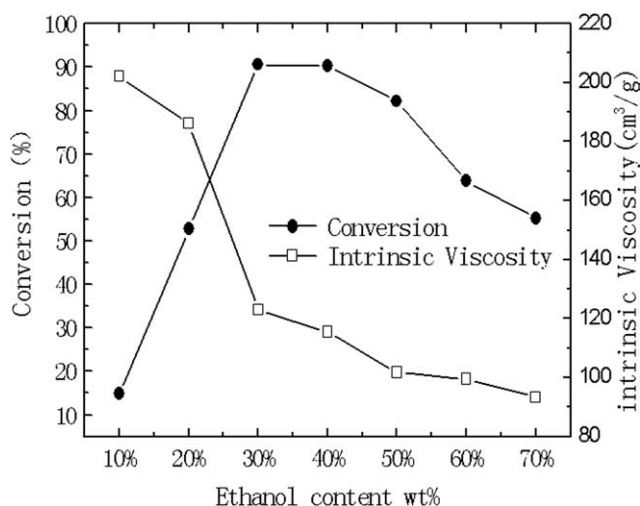


Figure 1 Effect of medium polarity on intrinsic viscosity and conversion ($n_{AM} : n_{DMDAAC} = 8 : 2$; $C_{monomer}$ (wt %) = 40%; $C_{initiator}$ (wt %) = 0.02%; $T = 40^{\circ}\text{C}$).

which showed in eq. (1)²³ and then calculated by curve fitting method to gain the reactivity ratio of AM and DMDAAC (r_1 and r_2), respectively.

$$M_{10}(2 - 1/m_1)/(1 - M_{10}) = r_{10}M_{10}^2(1 - m_1) / [m_1(1 - M_{10})^2] - r_{20} \quad (1)$$

where M_{10} and m_1 are the mole fraction of AM in initial monomers and copolymer, r_{10} and r_{20} represent the initial r_1 and r_2 , respectively.

In ethanol-water solution the reactivity ratios are 6.664 and 0.120 for AM and DMDAAC, respectively. Reactivity ratios r_1 and r_2 are the ratios of the same monomers chain propagation reaction rate constant to the different monomers chain propagation reaction rate constant, whose value can be used to estimate the copolymerization tendency of a pair of monomers. The calculated data show that AM can homopolymerize easier than DMDAAC in ethanol-water solution.

Influence of medium polarity on intrinsic viscosity and conversion

To obtain a stable dispersion polymerization system, the studied ethanol content was limited in the range of 10% ~ 70%. Figure 1 shows that the conversion of monomers first increased and then decreased with the increasing ethanol content. The conversion of monomers reached the maximum 91% when the ethanol content was 30%. However, the intrinsic viscosity of copolymer PAM-DMDAAC decreased with the increasing ethanol content. When ethanol content was low, the reaction environment was close to water; the synthesized polymer could dissolve in

water easily, which resulted in greater system viscosity. When the monomers did not react completely, the conversion would be very low. Hence, the conversion increased gradually with the increasing ethanol content. However, ethanol was a chain transfer agent²⁴; it could hinder the polymerization of monomers markedly when its content increased. Then polymerization rate slowed down, and the conversion was lower. The polymer solubility in the dispersion medium declined and the oligomer would precipitate from the medium because the polarity and solubility parameter of dispersion medium decreased gradually with the increasing ethanol content. Therefore, the final product had smaller molecular weight and lower intrinsic viscosity. When ethanol content was lower than 40%, the products had poor stability and were precipitated easily from the media when they were placed statically for a long time. Therefore, the ethanol content of 50% in this article was selected for further research, then the product obtained could be purified easily, and their conversion and intrinsic viscosity were relatively ideal.

Influence of monomer concentration on intrinsic viscosity and conversion

Figure 2 illustrates the effect of monomer concentration on intrinsic viscosity and conversion. This figure shows that increasing the monomer concentration leads to the increase of conversion and intrinsic viscosity. When the monomer concentration was low, the solvent cage effect²⁵ could lead to the premature termination of the primary radicals of the initiator and lower conversion. Chain transfer agent lowers molecular weight which leads to lower solution viscosity. When the solvent cage effect

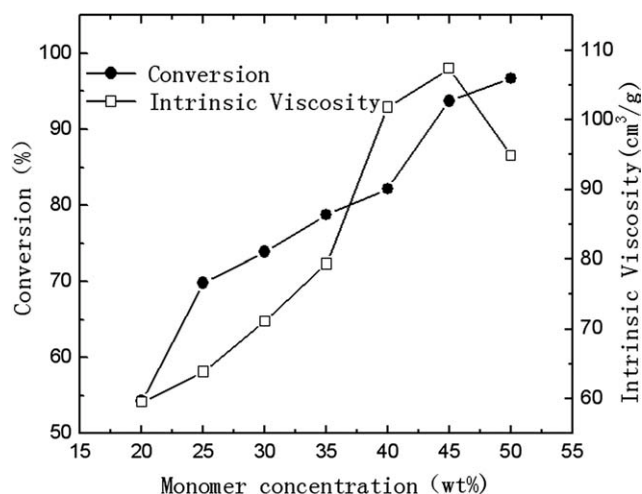


Figure 2 Effect of monomer concentration on intrinsic viscosity and conversion ($n_{AM} : n_{DMDAAC} = 8 : 2$; $C_{initiator}$ (wt %) = 0.02%; ethanol content = 50%; $T = 40^{\circ}\text{C}$).

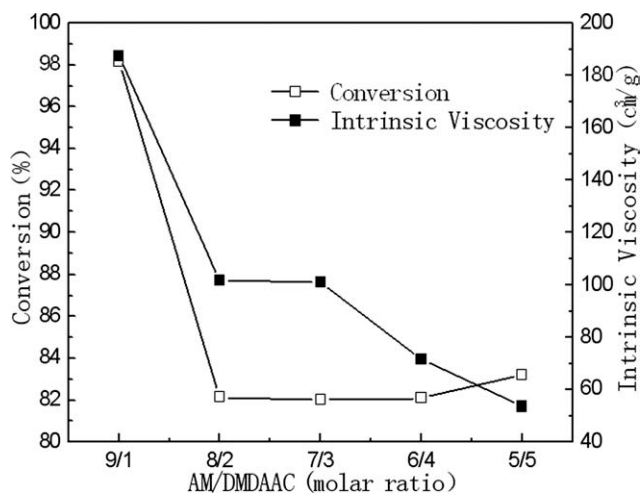


Figure 3 Effect of the molar ratio of AM to DMDAAC on intrinsic viscosity and conversion (C_{monomer} (wt %) = 40%; $C_{\text{initiator}}$ (wt %) = 0.02%; ethanol content = 50%; $T = 40^{\circ}\text{C}$).

decreased with the increasing monomer concentration, the entire chain propagation rate, molecular weight, and intrinsic viscosity increased. Meanwhile, the polymerization rate and the conversion increased. In addition, Figure 2 shows that there is a sharp increase in viscosity between 35 and 45% monomer concentration, in which the solvent cage effect decreases so greatly as to affect the polymerization little. When the monomer concentration was higher than 50%, gel effect often takes place. Thus, the total monomer concentration of 40% is appropriate.

Influence of the molar ratio of AM to DMDAAC on intrinsic viscosity and conversion

When DMDAAC and AM copolymerize, the greater the cationic monomer DMDAAC content is, the better the charge neutralization capacity of PAM-DMDAAC is. This study tried to choose the optimal molar ratio of AM to DMDAAC to synthesize the polymer with higher intrinsic viscosity, cationic degree, and conversion.

Figure 3 shows that the intrinsic viscosity and the conversion decrease with the increasing of DMDAAC content. The value of r_{AM} and r_{DMDAAC} are 6.664 and 0.120, respectively, which indicates the reactivity rate of DMDAAC is much smaller than that of AM. With the decreasing molar ratio of AM to DMDAAC, low active component DMDAAC increased and high active component AM decreased, and then the polymerization rate decreased. In addition, DMDAAC has large steric hindrance and cationic charge, which hampered the spread of monomer to polymer's surface. The chain propagation rate decreased, and the rates of chain transfer and chain termination increased gradually. There-

fore, the conversion and the intrinsic viscosity declined. Furthermore, from Figure 3 it could be seen that the steric hindrance and cationic charge of DMDAAC between 9 : 1 and 8 : 2 of AM : DMDAAC had the most important impact on the polymerization. Considering the cationic degree, intrinsic viscosity and conversion, this study chose the molar ratio of DMDAAC to AM 8 : 2.

Influence of initiator concentration on intrinsic viscosity and conversion

To study the influence of initiator concentration on intrinsic viscosity and conversion, a series of experiments had been carried out with $\text{K}_2\text{S}_2\text{O}_8$ as the initiator. The experimental results were shown in Figure 4.

From Figure 4, it could be seen that the conversion increased and the intrinsic viscosity decreased with the increasing initiator concentration. The initiator was the active center of free radical polymerization reaction.²⁶ The higher the initiator concentration was, the more the active center was. Therefore, when the initiator concentration increased, both the reaction rate and the conversion increased. However, the opportunities of chain transfer and chain termination correspondingly increased, and the polymer's molecular weight was low. When the concentration of $\text{K}_2\text{S}_2\text{O}_8$ was 0.04%, the conversion of monomers could be more than 80%, the intrinsic viscosity of copolymer was 98 cm³/g.

Influence of initial temperature on intrinsic viscosity

To synthesize the polymer the initial temperature is one of the most important parameters. Figure 5

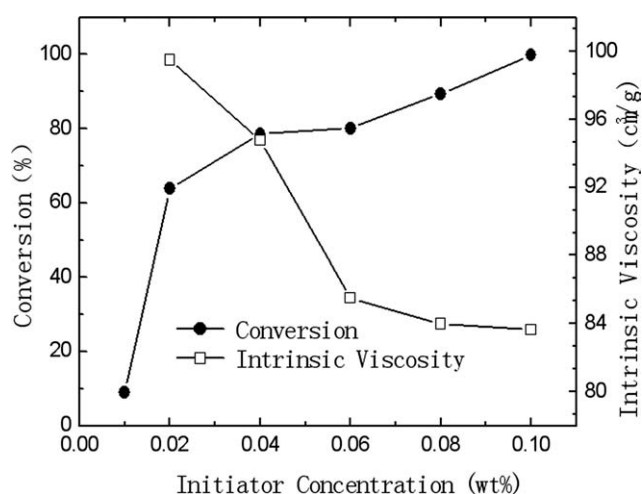


Figure 4 Effect of the initiator concentration on intrinsic viscosity and conversion ($n_{\text{AM}} : n_{\text{DMDAAC}} = 8 : 2$; C_{monomer} (wt %) = 40%; ethanol content = 50%; $T = 40^{\circ}\text{C}$).

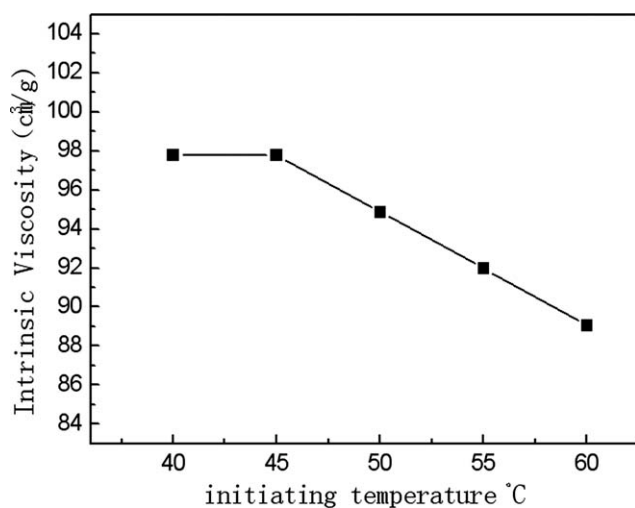


Figure 5 Effect of initiating temperature on intrinsic viscosity ($n_{AM} : n_{DMDAAC} = 8 : 2$; $C_{monomer}$ (wt %) = 40%; $C_{initiator}$ (wt %) = 0.04%; ethanol content = 50%).

illustrates the influence of initial temperature on intrinsic viscosity. The copolymer's intrinsic viscosity decreased with the increasing initial temperature. When the initial temperature was low, the free radical was less, the chain propagation dominated, the chain termination opportunity was few, and the copolymer's molecular weight was higher. When the initial temperature was increased, the free radical increased. Meanwhile, the chain termination opportunity correspondingly increased because of the frequent collision of free radicals. Hence, the copolymer's intrinsic viscosity and molecular weight declined.⁵ When the initial temperature was high, the reaction rate was very large, the quantity of heat of polymerization could not fall apart easily, and gel would appear. The temperatures lower than 40°C also was considered, at which the free radical was little, the chain termination rate was higher than that of chain propagation. Then the final conversion was very low after a very long reaction time. Considering the reaction rate and intrinsic viscosity, the best initial temperature was 40°C.

Influence of EDTA on intrinsic viscosity and conversion

EDTA has the chelation and is capable of chelating metal ions. In the polymerization, it can be used as additives²⁷ to eliminate the interference of metal ions on free radical polymerization and facilitate the polymerization. The influence of EDTA on intrinsic viscosity and conversion was shown in Figure 6.

The no. 1 experiment was carried out without EDTA and the no. 2 was done with EDTA that accounted for 0.03% of the total mass. From the graph, it could be seen that both conversion and intrinsic viscosity were significantly improved after

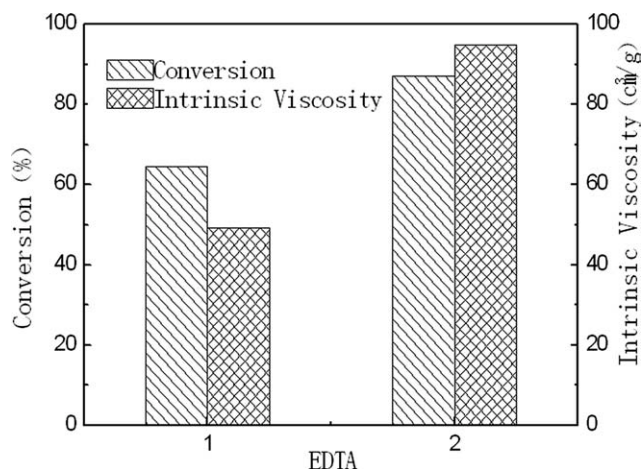


Figure 6 Effect of EDTA on intrinsic viscosity and conversion ($n_{AM} : n_{DMDAAC} = 8 : 2$; $C_{monomer}$ (wt %) = 40%; $C_{initiator}$ (wt %) = 0.04%; ethanol content = 50%; $T = 40^\circ\text{C}$; 1 and 2 correspond to the experiments without and with EDTA, respectively).

adding EDTA. Some impurities existed in reaction system, which could transfer the active center, induce chain termination and disturb the polymerization badly. However, EDTA had the ability to chelate metal ions in reaction system and reduced impurities' interference. During the experiment, it could be seen obviously that reaction rate increased, and the solution became white latex quickly after adding EDTA. Furthermore, EDTA could work as a buffer and maintain the reaction system at a suitable pH within the scope of (5.5–6.5), which also facilitated the polymerization.

FTIR analysis

To investigate the interaction between AM and DMDAAC, FTIR of PAM, PDMDAAC, and PAM-

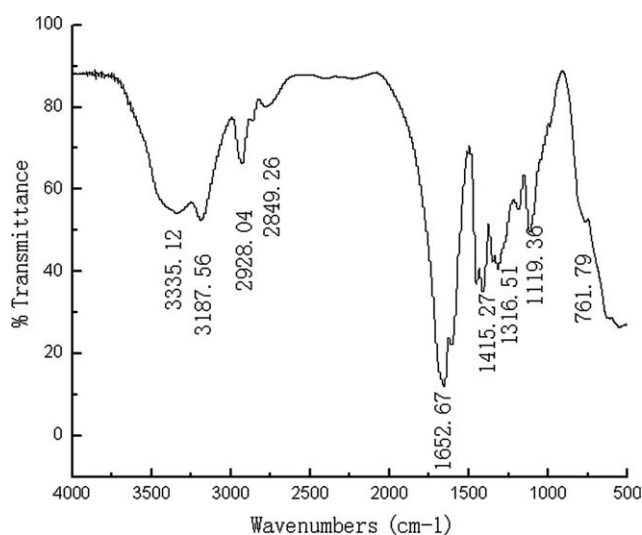


Figure 7 IR spectra of PAM.

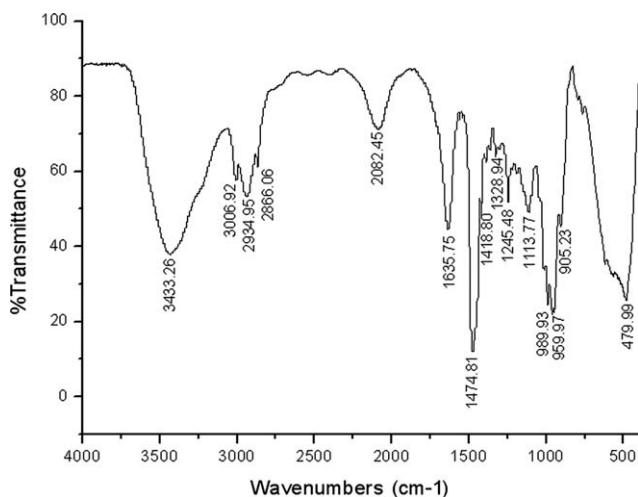


Figure 8 IR spectra of PDMDAAC.

DMDAAC were measured and the results were shown in Figures 7–9. From spectra of PAM and PAM-DMDAAC, it can be seen that the amino $-\text{NH}_2$ stretching vibration absorption peak appears around 3400 cm^{-1} , $-\text{OH}$ characteristic absorption peak appears near 3187 cm^{-1} , which shows that both PAM and PAM-DMDAAC have strong hydroscopic property. In Figure 8 $-\text{OH}$ characteristic absorption peak around 3433 cm^{-1} also shows the strong hydroscopic property of PDMDAAC. The band at 3008 cm^{-1} in Figures 8 and 9 is the characteristic peak of methylene bonding with $-\text{N}^+$. The peaks around 2928 cm^{-1} should be assigned the stretching vibration of methyl and methylene, the band at 1660 cm^{-1} for the characteristic absorption peak of carboxyl $\text{C}=\text{O}$ in amido group. Except for the above-mentioned characteristic peaks in Figure 9, it also can be seen that 1457.07 cm^{-1} is the characteristic peak of dual methyls bonding with

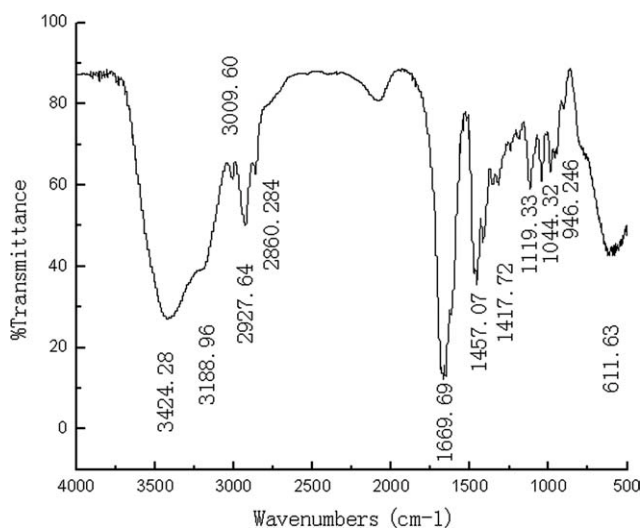


Figure 9 IR spectra of PAM-DMDAAC.

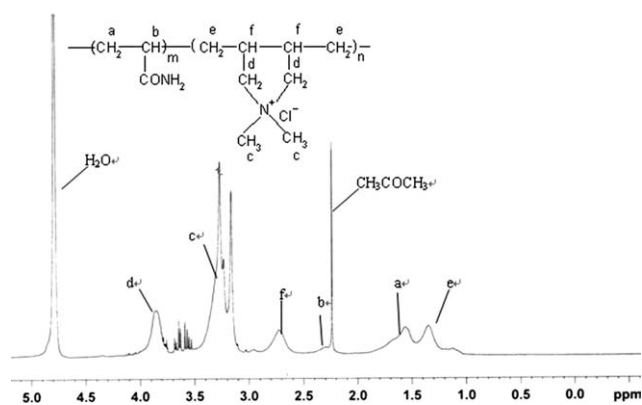


Figure 10 ^1H NMR spectrum of dispersion copolymer.

$-\text{N}^+$, 946.25 cm^{-1} for the characteristic absorption peak of quaternary amino $-(\text{CH}_2)_2\text{N}^+(\text{CH}_3)_2$,²⁸ which manifests that the pentatomic ring with nitrogen exists in PAM-DMDAAC. It can be concluded that the two monomers are copolymerized.

NMR analysis

Figure 10 shows the ^1H -NMR spectrum of the copolymer. According to Ref. 29 each proton is distinguished from the resonance peaks of the copolymer resulted from the dispersion polymerization, as shown in Figure 10. According to the integral area of the resonance peaks of a and e proton (CH_2 of AM and CH_2 of DMDAAC, respectively), the approximate composition of the copolymer could be calculated. The molar ratio of AM to DMDAAC in the copolymer is about 80/20, which is almost the same in the feed.

CONCLUSIONS

In ethanol-water solution the reactivity ratios are 6.664 and 0.120 for AM and DMDAAC, respectively. The data show that AM can homopolymerize easier than DMDAAC in ethanol-water solution.

The optimum operation conditions for preparing PAM-DMDAAC with $\text{K}_2\text{S}_2\text{O}_8$ as the initiator were determined as $n_{\text{AM}} : n_{\text{DMDAAC}} = 8 : 2$, C_{monomer} (wt %) = 40%, $C_{\text{initiator}}$ (wt %) = 0.04%, ethanol content = 50% and initial temperature = 40°C . On these conditions, the synthesized copolymer with the intrinsic viscosity of $98\text{ cm}^3/\text{g}$ could be separated, purified, and dissolved easily.

The molar ratio of AM to DMDAAC has a great impact on the intrinsic viscosity and cationic degree of the product. The greater the proportion of AM is, the larger the intrinsic viscosity of the product is. On the contrary, the greater the proportion of DMDAAC is, the higher the cationic degree of the product is. To get the copolymer with a suitable

cationic degree and intrinsic viscosity, the molar ratio of AM to DMDAAC should be adjusted flexibly according to actual need.

Adding EDTA can accelerate reaction rate and increase conversion and intrinsic viscosity (molecular weight). IR spectrum and $^1\text{H-NMR}$ spectrum manifest that the monomers DMDAAC and AM turn into the copolymer PAM-DMDAAC.

References

1. Xu, X. *Chinese J Synthetic Chem* 2003, 11, 509.
2. Ma, X.; Wang, A.; Hu, X.; Chen, Y. *Polym Mater Sci Eng* 1997, 13, 26.
3. Zhang, Y.; Gu, X. *Fine Chem* 2002, 19, 521.
4. Ma, Q. *Flocculation Chemistry and Flocculants*, China Environmental Sci Press: Beijing, 1988.
5. Yue, Q.; Li, Y.; Gao, B.; Yang, Z.; Zou, X. *J Shandong Univ (Nat Sci)* 2004, 39, 86.
6. Sairam, M.; Babu, V. R.; Naidu, B. V. K.; Aminabhavi, T. M. *J Pharmaceutics* 2006, 320, 131.
7. Wang, W.; Liu, L.; Huang, Z.; Yang, W. *RadTech Asia* 2005, 703.
8. Shim, S. E.; Jung, H.; Lee, K.; Lee, J. M.; Choe, S. *J Colloid Interface Sci* 2004, 279, 464.
9. Cho, M. S.; Yoon, K. J.; Song, B. K. *J Appl Polym Sci* 2002, 83, 1397.
10. Tseng, C. M.; Lu, Y. Y.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Part A: Polym Chem* 1986, 24, 2995.
11. Paine, A. J. *Macromol* 1990, 23, 3109.
12. Paine, A. J. *J Colloid Interface Sci* 1990, 138, 157.
13. Paine, A. J.; Luymes, W.; McNulty, J. *Macromol* 1990, 23, 3104.
14. Guha, S.; Mandal, B. M. *J Colloid Interface Sci* 2004, 271, 55.
15. Chen, D.; Liu, X.; Yue, Y.; Zhang, W.; Wang, P. *Eur Polym J* 2006, 42, 1284.
16. Sparnacci, K.; Laus, M.; Tondelli, L.; Magnani, L.; Bernardi, C. *Macromol Chem Phys* 2006, 203, 1364.
17. Ober, C. K.; Lok, K. P. *Macromol* 1987, 20, 268.
18. Takahashi, K.; Miyamori, S.; Uyama, H.; Kobayashi, S. *J Polym Sci Part A: Polym Chem* 1996, 34, 175.
19. Corner, T. *Colloids Surf* 1981, 3, 119.
20. Ray, B.; Mandal, B. M. *Langmuir* 1997, 13, 2191.
21. Ray, B.; Mandal, B. M. *J Polym Sci Part A: Polym Chem* 1999, 37, 493.
22. Lu, J.; Liang, H. *Polymer Chemistry*; Chem Industry Press: Beijing, 2005, p 93.
23. Hagiopol, C. *Copolymerization Toward a Systematic Approach*; Plenum Publishers, Kluwer Academic: New York, 1999.
24. Wang, J. *High Polymer Chemistry*; Harbin Institute of Technol Press: Harbin, 2004.
25. Zhang, W.; Qiao, X.; Chen, J.; Li, M. *Chinese J Appl Chem* 2005, 22, 749.
26. Boguslavsky, L.; Baruch, S.; Margel, S. *J Colloid Interface Sci* 2005, 289, 71.
27. Zhao, H.; Yue, Q.; Gao, B. *Chinese J Industrial Water Treatment* 1999, 19, 1.
28. Li, B.; Yu, H.; Shao, X. *Chinese J Analysis Lab* 2002, 21, 41.
29. Vu, C.; Cabestany, J. *J Appl Polym Sci* 1991, 42, 2587.