A CATIONIC POLYACRYLAMIDE DISPERSION SYNTHESIS BY DISPERSION POLYMERIZATION IN AQUEOUS SOLUTION

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A cationic polyacrylamide (CPAM) dispersion, the copolymer of acrylamide (AM) and acryloyloxyethyltrimethyl ammonium chloride (DAC), has been synthesized through dispersion polymerization in aqueous ammonium sulfate ($(NH_4)_2SO_4$) solution. The polymerization was initiated by tert-butyl hydroperoxide (TBHP) and ferrisulfas ($FeSO_4$) using poly(dimethyl diallyl ammonium chloride) (PDMDAAC) as the stabilizer. At the optimal reaction conditions, the relative molecular weight of the CPAM dispersion was 4.2×10^6, its charge density was 2.2 $mmol\cdot g^{-1}$, its average particle size was 6.01 μm, and its stability and dissolvability were both excellent. The CPAM dispersion was characterized using Fourier-transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and differential scanning calorimeter (DSC). Results indicated that the copolymerization was successful.

Key words: Cationic polyacrylamide; Synthesis; Characterization; Dispersion polymerization

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INTRODUCTION

In the past several years the production of cationic water-soluble homopolymers and copolymers with acrylamide has grown rapidly, along with their various commercial applications. These polymers are used as retention and drainage aids in papermaking, as flocculants in wastewater treatment, and as stabilizers for emulsion polymerization in cosmetics (Yan 1998). For the same applications, high molecular weight polyacrylamide (PAM) has been widely used because of its effectiveness and low price, but it is nonionic. If a polymer has charged groups on its chain, it will be more effective as a retention aid in papermaking and as a flocculant. Hence, many cationic polymers are prepared by copolymerizing acrylamide (AM) with monomers having cationic charge groups, and this has led to the development of water-soluble cationic polyelectrolytes having marked utility in many applications.

PAM can be prepared through solution polymerization (Tanaka 1986; Okada et al. 1979; Mabire et al. 1984), emulsion polymerization (Chen et al. 1997; Pross et al. 1998), and microemulsion polymerization (Ono and Deng 1997). However, there are some shortcomings in these processes. In order to produce high-molecular-weight polymers with the solution polymerization method, the monomer concentration has to be kept over

10 wt%. This will result in a gelatinous and crosslinked polymer, which is difficult to dissolve in water. The emulsion polymerization could cause environmental pollution problems, because this process needs a large amount of organic solvents. Similar to the emulsion polymerization, microemulsion polymerization also has problems of smelling and safety in the working environment because a mineral oil is used as the dispersion medium. In addition, the inflammability of the product and the wasteful utilization of expensive organic solvents are drawbacks of the water-in-oil emulsion polymerization process.

Dispersion polymerization is a unique polymerization process, capable of forming particles of 0.1 to 10 μm in a single step (Sivakumar 2002; Fong 2005). During dispersion polymerization the polymer precipitates from the originally homogeneous reaction mixture that contains monomer, initiator, solvent, and stabilizer. The reaction medium is selected on the basis of not only its nonsolvent properties for the forming polymer but also its solubility properties for the stabilizer and its miscibility with the monomer. Most research on dispersion polymerization has involved common vinyl monomers such as styrene or (meth)acrylates in polar media (Liu 1998; Winzor 1994). More recently, a dispersion polymerization technique in supercritical carbon dioxide has been developed (Baran et al. 2005; Woods et al. 2005). However, there exist only a few works dealing with dispersion polymerization of water-soluble monomer in aqueous media. Some researchers have carried out the dispersion polymerization of acrylamide (Ray and Mandal 1997, 1999; Guha and Mandal 2004; Ondaral et al. 2010) in aqueous alcohol media. A proper salt added in the water plays a big role on dispersion of polymers, especially for the water-soluble polymers. As the molecular weight of the polymer increases in a highly concentrated salt solution, the polymer precipitates as viscous gel particles. Such a system is obtained when the salt dissolved in the aqueous phase is capable of inducing the salting out (Fong 2005). However, very few study papers have dealt with dispersion polymerization in aqueous without any organic solvent. As far as our information goes, only Song and Ye (2003) have published results concerning the dispersion of acrylamide in aqueous ammonium sulfate solution (see Cho et al. 2002; Song et al. 2003; Ye et al. 2003). In Song's works, a copolymer consisting of acrylamide (AM) and acryloyloxyethyl dimethylbenzyl ammonium chloride (AODBAC) was prepared by dispersion polymerization in an aqueous solution of ammonium sulfate and in the presence of poly(acryloyloxyethyl trimethyl ammonium chloride) (PDAC) as the stabilizer. In Ye's works, a water-soluble cationic copolymer dispersion was prepared by the polymerization of the cationic monomer dimethylaminomethacrylate methyl chloride quaternary (DMC) and acrylamide (AM), and the stabilizer was a copolymer of dimethyl diallyl ammonium chloride and AM (PDMA), a commercially available polymer.

In the present work, A cationic polyacrylamide (PAM) emulsion was synthesized from acrylamide (AM) and a cationic monomer, acryloyloxyethyltrimethyl ammonium chloride (DAC), using the dispersion polymerization method in aqueous ammonium sulfate ($(NH_4)_2SO_4$) solution. The polymerization was initiated by tert-butyl hydroperoxide (TBHP) and ferrisulfas ($FeSO_4$), using poly(dimethyl diallyl ammonium chloride) (PDMDAAC) as the stabilizer. DAC and DMDAAC were chosen because they are cheap and easy to get, and have not appeared in academic research. The formed cationic acrylamide copolymer (CPAM) was characterized using Fourier-transform infrared

(FTIR), ^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy, and differential scanning calorimeter (DSC).

EXPERIMENTAL

Materials

Acrylamide (AM) was obtained as an industrial product, in white powder form, from Shandong Sangong chemistry industry group (China). Acryloyloxyethyltrimethyl ammonium chloride (DAC), having the formula CH_2=CH-COO$(CH_2)_2$-N$(CH_3)_3$Cl, was obtained as an industrial product, a colourless transparent liquid having a concentration of 80%, from Shandong Sangong chemistry industry group (China). Dimethyl diallyl ammonium chloride (DMDAAC), having the formula $(CH_2$=CH-$CH_2)_2$N$(CH_3)_2$Cl, was obtained as an industrial product, a faint yellow liquid having a concentration of 80%, from Shandong Sangong chemistry industry group (China). Ammonium sulfate, tert-butyl hydroperoxide (TBHP) and ferrisulfas ($FeSO_4$), AR grade, were obtained from Tianjin Tianyi chemical reagents company (China).

Experimental Methods

The synthesis of stabilizer

The polymeric stabilizer poly(dimethyldiallylammonium chloride) (PDMDAAC) was synthesized in this laboratory by polymerizing DMDAAC in a 20 wt% aqueous solution under nitrogen atmosphere using 0.03 wt% (based on the monomer) tert-butyl hydroperoxide (TBHP) and ferrisulfas ($FeSO_4$) as the initiator at 20 ^{o}C. As a stabilizer, the relative molecular weight of PDMDAAC was about 5.0×10^5 when calculated according to China national standards, GB 12005.1-1989 and GB 12005.10-1992. The chemical structure of PDMDAAC is shown in Fig. 1.

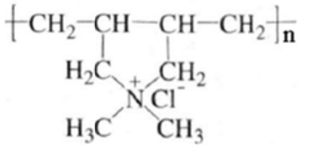

Fig. 1. Chemical structure of stabilizer PDMDAAC

The synthesis of CPAM dispersion

Varying quantities of monomers (AM and DAC), PDMDAAC, and the aqueous solution of ammonium sulfate were added to a 500-mL four-neck separable flask equipped with an anchor-like paddle stirrer, a thermometer, a feeder, and a nitrogen inlet tube. After purging with N_2 (purity>99.99%) for 30 min and controlling the temperature at 20 ^{o}C in a water bath, the polymerization was initiated by injecting the initiator (TBHP and $FeSO_4$) solution into the reaction mixture under stirring. The agitation speed was fixed at 300 revolutions per minute in all experiments. The reactions were conducted for 6 h to get a CPAM dispersion (Ni and Kawaguchi 2004; Ye et al. 2002). The chemical structure of CPAM dispersion is shown in Fig. 2.

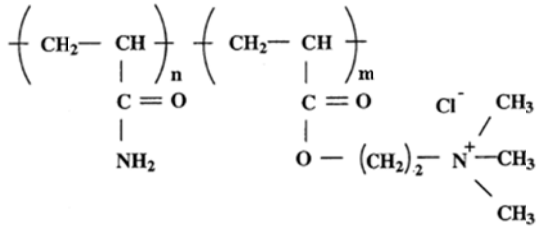

Fig. 2. Chemical structure of CPAM emulsion

In this paper, the concentrations of monomers (AM and DAC), PDMDAAC, and ammonium sulfate are weight percent based on total aqueous solution. The monomers (AM and DAC) concentration was kept at 12 wt%, and the molar ratio of AM to DAC was 90/10. The PDMDAAC concentration was kept at 1.0 wt%. The ammonium sulfate concentration was 30 wt%. The concentration of initiator was weight percent based on monomers, and the initiator concentration was kept at 0.04 wt%.

The characterization of CPAM dispersion

After reaction, the polymerization product was removed from the glass vessel and the copolymer was purified using the following procedures: the copolymer was precipitated by pouring the polymer solution into a large quantity of ethanol and washed with acetone. These operations were repeated several times to remove the inorganic salts and unreacted monomers. Then the copolymer precipitated was dried to a constant weight at 40 ^{o}C under vacuum. The dried sample was used to determine the characterizations.

The molecular weight of the CPAM dispersion samples was measured according to China national standards, GB 12005.1-1989 and GB 12005.10-1992. The charge density was measured by colloidal titration.

The particle size was measured with a laser particle size distribution analyzer (model: GSL-101BI). Infra-red spectra of the dried CPAM sample was measured by Bio-Rad FTS 135 Fourier infra-red spectrometer using a potassium bromide disc technique.

The ^{1}H NMR spectrum of the dried CPAM sample was obtained in deuterium oxide (D_2O) with a Bruker (300MHz 1H) NMR spectrometer.

Differential scanning calorimetry (DSC) curves of the dried CPAM samples were obtained at a heating rate of 10 ^{o}C/min and a scanning range of 20 ^{o}C to 300 ^{o}C with a differential scanning calorimeter.

RESULTS AND DISCUSSION

The Characterization of CPAM Dispersion

Physical properties

Under the optimal reaction conditions, we prepared CPAM dispersion with high molecular weight, high charge density, excellent stability, and easy dissolvability. For the physical properties of the CPAM dispersion see Table 1.

Table 1. Physical Properties of CPAM Dispersion

Items	Testing result
Appearance	Ivory-white liquid
Solids content (%)	40
Dissolvability	Dissolve quickly in tap water
Apparent viscosity (mPa·s)	12
Relative molecular weight（$\times 10^4$ gmole^{-1})	420
Charge density (m mol·g^{-1})	2.2
pH value	6.7
Average particle size (μm)	6.01
Stability	No change in 6 months

Particle size analysis of CPAM dispersion

In theory, monodisperse polymer microspheres with particle size in the range 0.1 to 10 μm can be obtained by dispersion polymerization. The particle size distribution of the CPAM dispersion is shown in Fig. 3. As shown, the particle size of the laboratory-produced CPAM dispersion was mainly in the range 2 to 10 μm, and the average particle size was 6.01μm. The particle size distribution was narrow and relatively uniform. The stability and dissolvability of the CPAM dispersion were excellent. These results show that the dispersion polymerization in the preparation of CPAM microsphere can be successful.

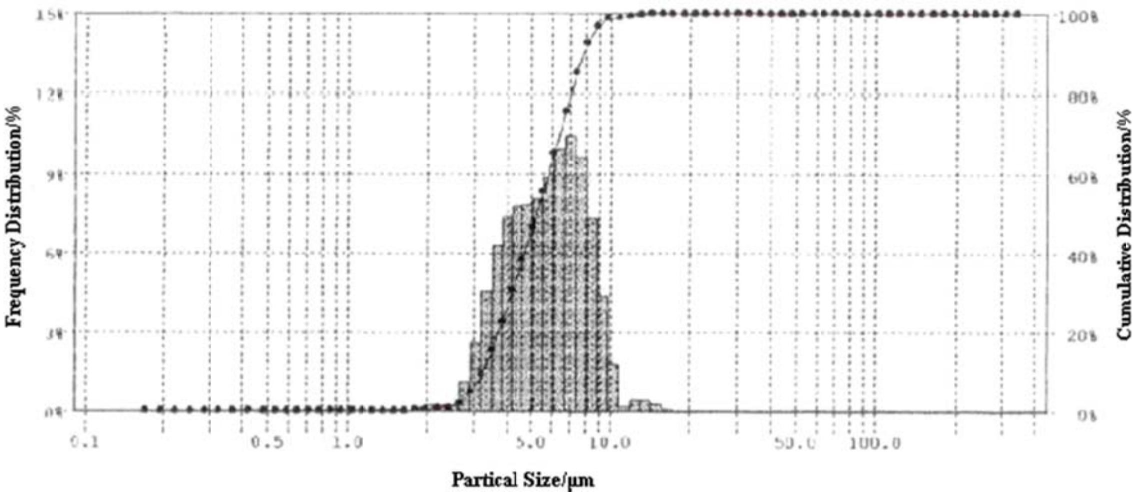

Fig. 3. Particle size distribution of CPAM dispersion

FTIR spectrum of CPAM dispersion

The FTIR spectrum of the laboratory-produced CPAM dispersion is shown in Fig. 4. The peak at 1651.47 cm^{-1} is attributed to the carbonyl(C＝O) of the amide group, the peak at 1733.48 cm^{-1} is due to the carbonyl(C＝O) of the ester, and the peak at 1419 cm^{-1} is due to the N-CH_3 bond of the DAC unit. The IR spectra of CPAM dispersion shows the product contained both an AM unit and a DAC unit, indicating that the copolymerization of the two monomers was successful.

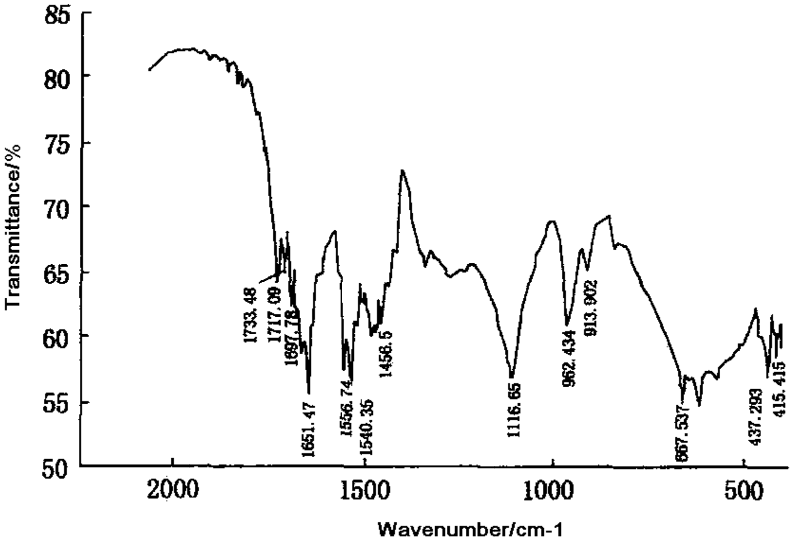

Fig. 2. IR spectrum of CPAM product

^{1}H NMR spectrum of CPAM dispersion

The ^{1}H NMR spectrum of the dried CPAM sample in D_2O is shown in Fig. 5. From the spectrum, the approximate composition of the copolymer is calculated. The ^{1}H NMR spectrum shows a sharp singlet at 3.31 ppm (g), which was assigned to the three equivalent methyl groups of ammonium. 1H signals were from the -CH_2- and -CH- of AM and in the ranges of 1.78 – 1.22 ppm (a) and 2.36 – 2.08 ppm (b), respectively. The analytical results of the ^{1}H NMR spectrum provide further support for the formation of the copolymer of AM and DAC.

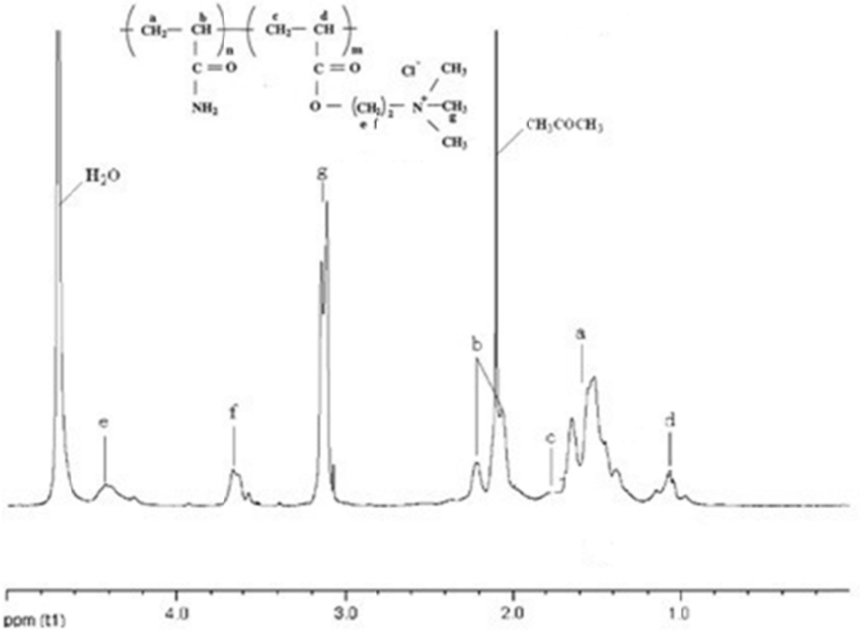

Fig. 5. ^{1}H NMR spectrum of CPAM product

DSC curve of CPAM dispersion

The DSC curve of the purified CPAM product is shown in Fig.6. Only one glass transition point is apparent in the plot. This indicates that there was only one polymer in the CPAM dispersion. The glass transition temperature (T_g) of PAM, the homopolymer of acrylamide, is 165.0 ^oC (Zhang and Liu 2000), whereas the T_g of the newly made CPAM dispersion product was 145.67 ^oC. This implies that the product was the copolymer of two monomers, not a mixture of homopolymers from each monomer. The T_g of the laboratory-produced CPAM was less than the T_g of PAM, which could be attributed to the flexible ester groups of DAC molecular chains increasing the free volume, making the polymer structure looser (Zhang and Liu 2000).

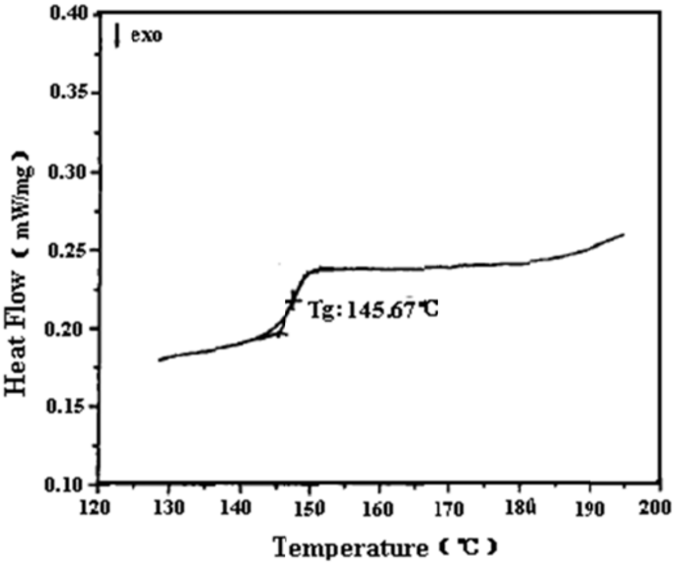

Fig. 6. DSC curve of CPAM product

CONCLUSIONS

1. A cationic polyacrylamide (CPAM) product was successfully synthesized as an aqueous dispersion with acrylamide (AM) and acryloyloxyethyltrimethyl ammonium chloride through dispersion polymerization in aqueous solution of ammonium sulfate. At the optimal reaction conditions, the relative molecular weight of the laboratory-produced CPAM dispersion was 4.2×10^6, its charge density was 2.2 mmol·g-1, its average particle size was 6.01 μm, and its stability and dissolvability were both excellent.
2. The CPAM dispersion was characterized by Fourier-transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and differential scanning calorimetry (DSC). The FTIR and ^1H NMR spectra of the product showed the existence of copolymerization between the cationic group DAC and AM. Its DSC curve indicated that the product was a copolymer of two monomers, not a mixture of homopolymers of each monomer. The copolymerization was judged to be successful.

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