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Synthesis and rheological behavior of cationic terpolymer of acrylamide

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ABSTRACT

The water-soluble cationic terpolymer of acrylamide was prepared by the aqueous solution polymerization with (2-methacryloyloxyethyl) trimethyl ammonium chloride (DMC) and dimethyldiallylammonium (DMDAAC) as cationic monomers, persulphate/bisulphite and the water-soluble azo-compound as the hybrid initiators. The structure and composition of the cationic terpolymer were characterized by Fourier Transform Infra-Red, ¹H-NMR and Thermogravimetry. Through discussing the effects of terpolymer concentration, shear rate, pH and concentration of added salts on apparent viscosity of terpolymer solution, the rheological properties of terpolymer solution were studied in details. The results indicated that the cationic polymer was P(AM/DMC/DMDAAC) possessing excellent thermal stability. The apparent viscosity of polymer solution increased with increasing terpolymer concentration and was sensitive to pH. However, the apparent viscosity decreased with increasing shear rate, and the shear thinning behavior was obviously irreversible. The terpolymer solution displayed anti-polyelectrolyte characteristics in added salts solution.

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KEYWORDS

Rheology;
Hybrid initiators;
Apparent viscosity;
Shear thinning behaviour;
Anti-polyelectrolyte.

INTRODUCTION

Water-soluble polymers of acrylamide are currently commercialized and widely applied in numerous fields such as the petroleum, paper industries and water treatment^[1]. Polyacrylamides can be divided into four different groups according to their ionic characters. Nonionic polymers are mainly applied in mineral processes. Anionic polymers are mainly used for potable water production or the flocculation of inorganic dispersions. Amphoteric polymers are mainly used in water-treatment processes. Cationic polymers are used

for sludge flocculation and dewatering in wastewater treatment due to the excellent flocculation function originating from synergetic effects of charge neutralization and bridging adsorption^[2-3]. Because the solid suspensions particles are negatively charged in water, flocculant applications are the principal target for cationic polyacrylamides, and they have a high added value from a commercial point of view.

Cationic polyacrylamide can be prepared by the modifications of polyacrylamide or the copolymerization of acrylamide with comonomers having cationic electrolyte groups^[4]. Polyacrylamide is modified by the

Mannich reaction or Hofmann rearrangement to give cationic flocculant with relatively high molecular weight. However, the products from the Mannich reaction have amino groups which are as reactive as to crosslink with each other. In the Hofmann rearrangement, the yield of cationic polymer is very low, and the main chain of polymer is easily hydrolyzed by caustic alkali to give a lower molecular weight polymer^[5]. The other way of obtaining higher molecular weight cationic polymers in a liquid form is to package the polymer in a water-in-oil emulsion^[6,7] or microemulsion^[8]. However, problems arise concerning smell and safety in the working environment because of a mineral oil being used as the dispersion medium. In addition, this type of polymer typically requires more elaborate feeding equipment than that requires for the solution polymers, and this causes a great reluctance among papermakers against using this type of polymer. The inflammability of the products, as well as the wasteful use of expensive organic solvents, is the drawback of the water-in-oil emulsion polymerization process^[9]. Emulsions are thermodynamically unstable and lead to phase separation within a few months. Solution polymerization is a well-known process^[10-12]. In solution polymerization, monomer concentration can be high, and the obtained polymer has suitable and high viscosity.

In this article, we chose DMC and DMDAAC as the cationic monomers, and the new cationic polyacrylamide was synthesized via free-radical aqueous solution polymerization. The new cationic terpolymer possesses high viscosity and thermal stability. The rheological properties of terpolymer solution were also reasonably studied.

EXPERIMENTAL SECTION

Materials

Acrylamide (AM) from Dia-Nitrix Co. Ltd. Japan, was industrial material and used without further purification; (2-methacryloyloxyethyl) trimethylammonium chloride (DMC) (78wt%) was given by Mitsubishi Gas Chemical Company, INC; Dimethyldiallylammonium chloride (DMDAAC) was from Binzhou Chemical Group Company, Shandong; Potassium persulfate (AR) was from Shanghai Plant of Amide; Sodium formaldehyde sulfoxylate dehydrate

(AR) was given by BASF Chemical Co. Ltd. Tianjin; Water-soluble azo-compound was made by ourselves; Deionized water was used throughout this work. Other reagents were AR-grade and used as received.

Measurements

Given quantities AM, DMC and DMDAAC were dissolved in deionized water in the flask. The pH was adjusted to 6.0 with 0.1M hydrochloric acid. Purified nitrogen was bubbled through the solution at room temperature for about 30min for oxygen removal. The hybrid initiators were added into the solution, and then the sealed flask was put into water bath at 80°C for 4 hours. Afterward, the products were dried, broken and packed.

Characterization

The infrared spectrum of the cationic terpolymer was measured by the 510PFT-IR spectrometer (Nicolet Company of USA); The ¹H-NMR spectrum of the cationic terpolymer was recorded on a DRX-500 instrument (Bruker of Switzerland) with D₂O as solvent. Thermogravimetry of the cationic terpolymer was measured by the TG209 (Netzch of Germany), differential scanning calorimeter at a heating rate of 10°C per minute; The apparent viscosity was measured by the Brookfield Programmable DV-II+ Viscometer (Brookfield Engineering Labs, INC.) at 20°C in deionized water and in several added salts with different concentrations.

RESULTS AND DISCUSSION

Structure characterization of terpolymer

The FTIR spectrum indicated that characteristic

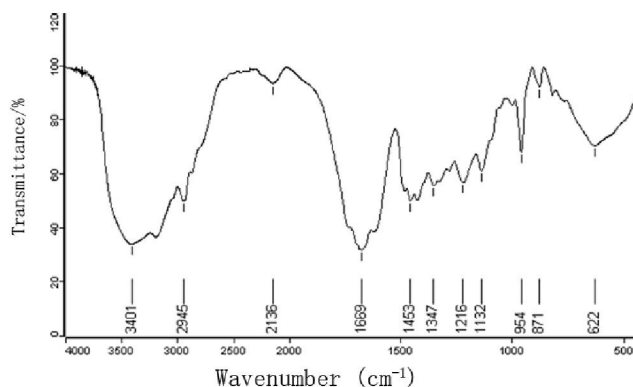


Figure 1 : FTIR spectrum of copolymer

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absorption bands of the sample at 3401 cm^{-1} and 1669 cm^{-1} were assigned to the stretching vibration of $-\text{NH}_2$ and $-\text{C}=\text{O}$ of $-\text{CONH}_2$ groups in AM unit; The characteristic absorption peaks at 1453 cm^{-1} and 945 cm^{-1} arose from $-\text{CH}_2$ and $\text{N}^+(\text{CH}_3)$ stretching vibration of $-\text{CH}_2-\text{N}^+(\text{CH}_3)$ groups in DMC unit; The peak at 1347 cm^{-1} and 1216 cm^{-1} came from the $-\text{CH}_3$ and $-\text{CH}_2$ asymmetry stretching vibration in DMDAAC unit. Since cationic terpolymer had a little coalescent water, there was a broad absorption peak of $-\text{OH}$ over 3000 cm^{-1} (i.e. the overlapping double peaks). The above mentioned characteristic peaks indicated the copolymer was P(AM/DMC/DMDAAC).

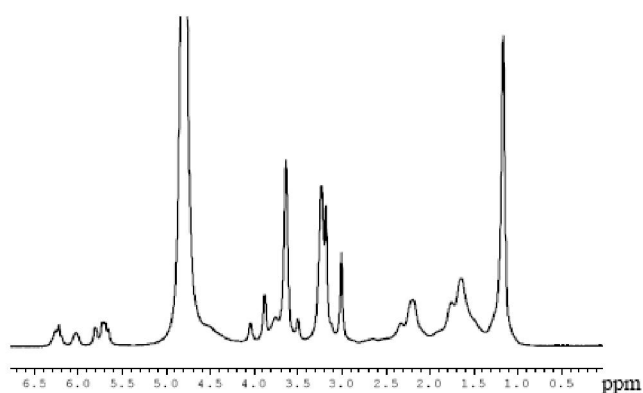


Figure 2 : ^1H -NMR spectrum of copolymer

The ^1H -NMR spectrum indicated that the peaks at 1.165 ppm was ascribed to the protons of the $-\text{CH}_3$ in the DMC unit. The peaks at the ranges of $1.641\sim 1.755\text{ ppm}$ and $2.19\sim 2.33\text{ ppm}$ assigned to the protons of $-\text{CH}_2-$ and $-\text{CH}-$ in AM unit, respectively. The peak at 5.712 ppm was the proton of $-\text{NH}_2$ of $-\text{CONH}_2$ group. The peaks at $3.005\sim 3.234\text{ ppm}$ corresponded to the three protons of $-\text{CH}_3$ group bonded with N atom in the molecule chains of DMC/DMDAAC. The results proved that the copolymer was P(AM/DMC/DMDAAC).

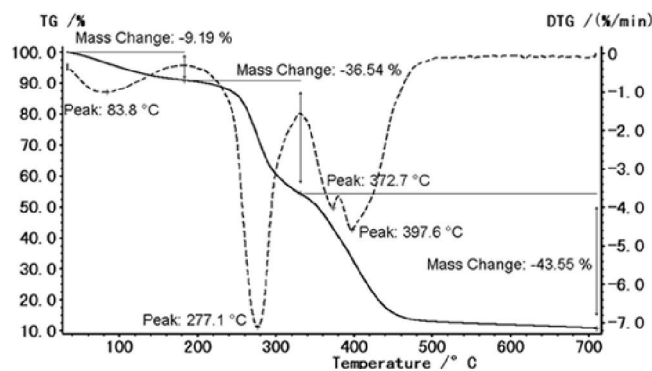


Figure 3 : Thermogravimetry cure of copolymer

The thermal decomposition processes were divided into three stages. The first stage began at about 100°C , which was physical losses process. Polyacrylamide could be cross-linked by imide formation. The weight ratio of thermal losses was about 9.19 percent, due to the volatilization of some water and reagents. The second stage started at about 180°C , and ended at about 330°C . Because the imidic reaction released ammonia gas, the weight ratio of thermal losses was 36.54 percent (the theoretical weight ratio of thermal losses was 36.84 percent). There was an inflexion at 265°C . It could be concluded that it was the glass transition temperature of the terpolymer, at which the micro-Brownian movements of the molecular chain segments became significant. The curve rapidly decreased between 277.1°C and 330°C , indicating that the chemical reaction take place and methyl group escape from quaternary ammonium. The third stage began at about 330°C . The decomposition rate reached maximum at about 440°C . The breakdown of imide groups released nitrile, and the polymer backbone gradually ruptured^[13]. The weight of the sample became constant at about 490°C . Since any responses of the material to a particular chemical and physical environment mainly occurred at or above the glass transition temperature, so the higher the glass transition temperature, the better the chemical and physical resistance. The results displayed that the cationic terpolymer had thermal stability.

Effect of the terpolymer concentration

As shown in Figure 4, the apparent viscosities decreased first and then increased with increasing terpolymer concentrations. At the high dilute, the apparent viscosities increased with decreasing terpolymer concentration, which showed the polyelectrolyte effect^[14,15]. Because the electrostatic repulsions of the same charges became strong on the chains, the macromolecular chains adopted extended conformations and possessed large hydrodynamic volumes^[16], resulting in the falling of the electrolytes shield function. However, when the terpolymer concentration increased, the counterions could not escape from the macromolecular chains. The ionization induced the obvious change of

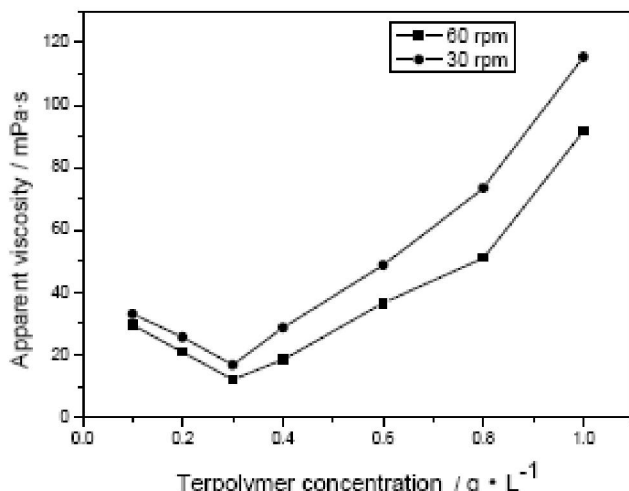


Figure 4 : Effect of terpolymer concentration on the apparent viscosity of terpolymer

macromolecular conformation. The apparent viscosities didn't only depend on the charge densities, but also on inter and intramolecular interaction. The polyelectrolyte effect was restrained. Therefore, the apparent viscosities increased with increasing terpolymer concentration.

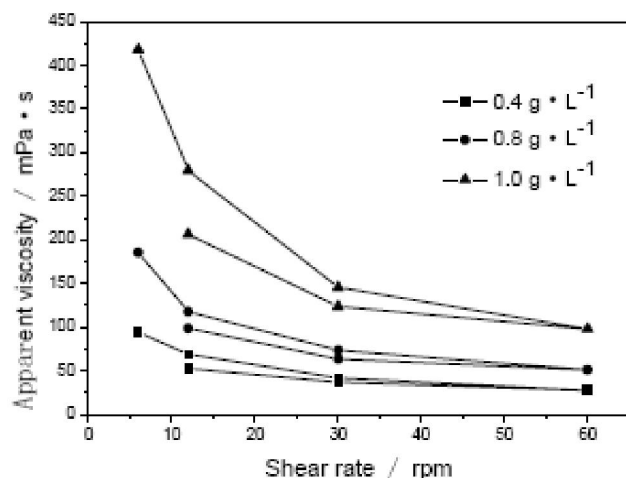


Figure 5 : Effect of shear rate on the apparent viscosity of terpolymer

Effect of shear rate

As shown in Figure 5, apparent viscosities decreased with increasing shear rate, which exhibited pseudoplastic behavior^[13]. It was reasonable to consider that shearing force made the chains ruptured and macromolecules decomposed. When the shear rate decreased again, the apparent viscosities could not recover. Macroscopically, the apparent viscosities decreased.

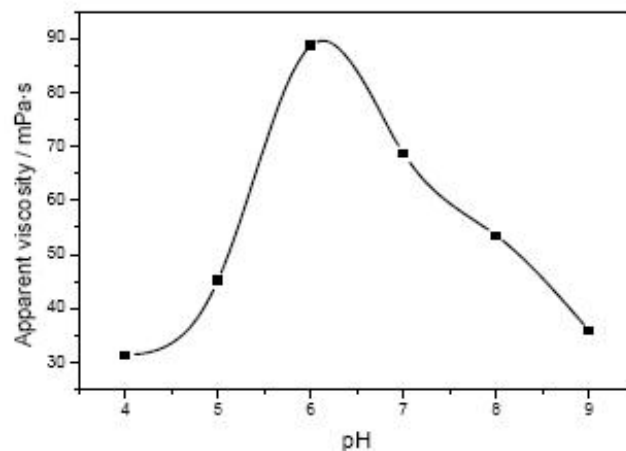


Figure 6 : Effect of pH on the apparent viscosity of terpolymer

Effect of pH

To study effect of pH on the apparent viscosity, several experiments were conducted with pH varied from 4.0 to 9.0. It indicated that terpolymer solution was obviously pH-responsive. The pH determined the charge density and molecular conformation^[17]. When hydrochloric acid was added into the solution, H^+ neutralized the counter ion OH^- . The densities of free-charge became higher on the chains, and the electrostatic repulsion of the cations became stronger. The apparent viscosity reached peak at $pH=6.0$. However, at the region of $pH < 6.0$, the redundant H^+ formed ion-atmosphere of the strong electric field, restricting the electrostatic repulsions of the cation, and the chains coiled to contract, leading to the apparent viscosity decreasing. When ammonia was added into the solution, much OH^- diffused inter and intramolecules. Polymer chains carried many negative charges, making the electrostatic field balanced and electrostatic repulsions weak. In addition, the polyacrylamide could form NTP in the high pH solution, and NTP was the chain-translated reagent. Consequently, the apparent viscosity decreased and solution became turbid and phases separated at the region of $pH > 9.0$.

Effect of the concentration of added salts

The apparent viscosities increased with increasing concentration of added salts. At the same concentration of added salts, the apparent viscosities in NaCl solution were higher than in $CaCl_2$ or Na_2SO_4 solution. Under the same concentration of anion Cl^- , the thickening effect of Na^+ was better than Ca^{2+} , and under the same cation

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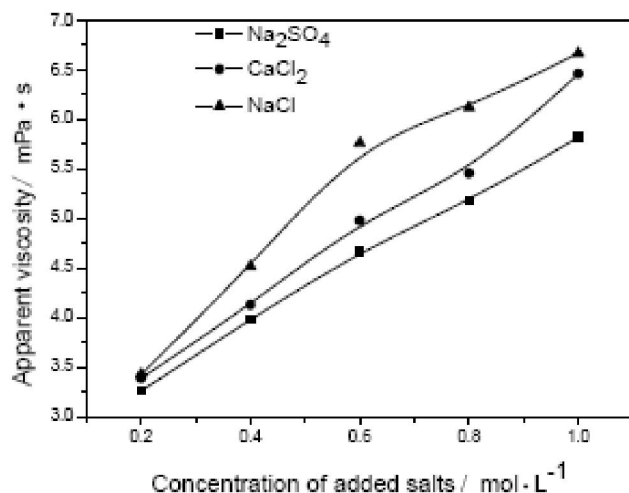


Figure 7 : Effect of the concentration of added salts on the apparent viscosity of terpolymer

Na⁺, the thickening effect of Cl⁻ was better than SO₄²⁻. When the low-molecular-weight electrolytes were added to polymer solution, the salt-ions made amount of free-water translate into water of hydration of salt-ions, which enhanced the polarity of solution and destroyed the hydrogen bonds between polymer molecules and water molecules. The chains associated with each other, and the hydrodynamic volumes became large. As a result, the apparent viscosities increased with rising concentration of added salts.

According to the soft-hard acid-base theory, Cl⁻ was the hard anion, and easily combined with hard cationic Na⁺[18]. The bondage degree of Cl⁻ on quaternary ammonium decreased, and the high molecular chains tended to extend, which led the apparent viscosity increase. However, under the same concentration of added salts, the apparent viscosity in the Na₂SO₄ was lower than in CaCl₂ and NaCl. Because the charge of SO₄²⁻ was notably higher than Cl⁻, the effect of electrostatic screening on polymer molecules was more effective, and the solvating action of Na₂SO₄ was also weaker than both CaCl₂ and NaCl.

CONCLUSION

The cationic terpolymer P(AM/DMC/DMDAAC) was prepared by aqueous solution polymerization of acrylamide (AM), (2-methacryloyloxyethyl) trimethylammonium chloride (DMC) and dimethyldiallylammonium chloride (DMDAAC) as the

raw materials. The FTIR, ¹H-NMR and Thermogravimetry of copolymer indicated that the new cationic polymer was P(AM/DMC/DMDAAC) having better thermal stability and its glass transition temperature was 265°C. The apparent viscosity of terpolymer decreased first and then increased with increasing terpolymer concentration, and decreased with increasing shear rate. The terpolymer aqueous solution was pH-responsive, and phases separated at the region of pH>9.0. The terpolymer solution showed anti-polyelectrolyte effect in different added salts solution.

ACKNOWLEDGEMENTS

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