Synthesis and Characterization of Polyacrylonitrile Copolymers Containing Amine Groups

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Abstract—Polyacrylonitrile copolymers containing amine groups (Poly(AN-VA-DEMA) copolymers) were synthesized by the aqueous precipitation copolymerization of acrylonitrile (AN), vinyl acetate (VA) and methacrylic acid 2-dimethylaminoethyl ester (DEMA) with a $Na_2S_2O_5$-$NaClO_3$ redox initiating system. The influences of monomer concentration, temperature, pH value of the medium, initiator concentration and additive amount of DEMA on the yield and viscosity-average molecular weight (M_η) of the Poly(AN-VA-DEMA) copolymer were systemically investigated. The composition of Poly(AN-VA-DEMA) copolymer were characterized by FTIR and NMR.

Keywords- polyacrylonitrile; methacrylic acid 2-dimethylaminoethyl ester; amine groups; aqueous precipitation copolymerization; polymerization parameters

I. INTRODUCTION

Polyacrylonitrile (PAN) fiber is one of the major synthetic fibers which has been widely used in apparel, home furnishings and industrial fabrics because of its outstanding physical and chemical properties [1]. In order to endow PAN fiber with different functions like hydrophilicity, dyeability, antibacterial property, and flame-retardency many efforts have been made to modify PAN fibers by various methods, including copolymerization of functional monomers [2-6].

In recent years, much work has been carried out on methacrylic acid 2-dimethylaminoethyl ester (DEMA) [7]. The homopolymer of DEMA is a weak cationic polyelectrolyte in aqueous solutions, exhibiting high pH and thermal sensitivity which has applied as hydrogel, brush and nanofiltration membranes [8]. There also have been many studies on functional materials based on acrylonitrile and DEMA copolymer which has large potential applications on CO_2 and dye adsorption, ion exchange, ultrafiltration and pH-responsive materials [9-11]. However, DEMA contains basic tertiary amine groups which has great influence on the polymerization process of PAN and the properties of end products. Previous reports hadn't paid much attention on the synthesis process of this copolymers. In this paper, Poly(AN-VA-DEMA) copolymer was synthesized by the aqueous precipitation copolymerization. The influences of polymerization parameters were investigated. The composition of the copolymer were characterized. parentheses, following the example.

II. EXPERIMENTAL

A. Materials

Acrylonitrile (AN) was purchased from China Petroleum & Chemical Corporation (Shanghai, China), and was distilled before use. Vinyl acetate (VA), sodium pyrosulfite ($Na_2S_2O_5$), sodium chlorate ($NaClO_3$) and 2-mercaptoethanol were of analytical grade and purchased from Sinopharm Chemical Reagent (Shanghai, China). Methacrylic acid 2-dimethylaminoethyl ester was purchased from Xinyu Chemical Co., Ltd. (Jiangsu, China).

B. Synthesis of the Poly(AN-VA-DEMA) Copolymer

In the typical experiment, required amounts of AN, VA, DEMA, $Na_2S_2O_5$, $NaClO_3$ and deionized water were placed in a flask with nitrogen atmosphere. The reaction mixture was stirred continuously at 60°C for 1 h, then terminated by 5 wt% NaOH aqueous. The resultant mixture was washed thoroughly and filtered several times, dried at 60°C in vacuum for 12h and then weighed. The viscosity-average molecular weight of various samples in

DMF at 25°C were determined via a dilution method with an Ubbelohde viscometer [12].

C. Characterization

The FTIR spectra were recorded on a Nicolet 6700 FTIR spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker av400 NMR spectrometer and DMSO-d6 was used as solvents.

III. Results and Discussion

A. Synthesis of the Poly(AN-VA-DEMA) Copolymer

Poly(AN-VA-DEMA) copolymer was synthesized by the aqueous precipitation copolymerization of AN, VA and DEMA with a $Na_2S_2O_5$-$NaClO_3$ redox initiating system. The influences of monomer concentration, temperature, pH value of the medium, initiator concentration and additive amount of DEMA on the yield and M_η of the Poly(AN-VA-DEMA) copolymer were investigated to obtain optimum reaction conditions.

TABLE I. Effect of monomer concentration on the aqueous precipitation copolymerization of AN, VA and DEMA

Monomer concentration (%)	M_η (10^4)	Yield (%)
15	7.82	70.9
20	6.76	82.5
25	6.15	85.1
28	5.98	84.8

Other reaction conditions: temperature=60 °C, pH=2.0, initiator concentration=0.6%, $NaClO_3/NaS_2O_{5\,(mol)}$=1/3, chain transfer concentration=0.3%, DEMA addition=2.5%.

The yield and M_η of the copolymers prepared with different monomer concentration were shown in Table 1. As the monomer concentration increased, the yield increased, and M_η of the copolymer decreased. The initiator concentration increased with monomer concentration, as the ratio of initiator/monomer was fixed. But the solubility of the initiator is much more than monomer, these changes could be explained by the increase of the radical concentration in the reaction system.

TABLE II. Effect of temperature on the aqueous precipitation copolymerization of AN, VA and DEMA

Reaction Temperature (°C)	M_η(10^4)	Yield (%)
45	7.29	73.4
50	6.85	75.8
55	6.78	82
60	6.76	82.5
65	6.59	84.2

Other reaction conditions: monomer concentration=15%, pH=2.0, initiator concentration=0.6%, $NaClO_3/NaS_2O_{5\,(mol)}$=1/3, chain transfer concentration=0.3%, DEMA addition=2.5%.

The yield and M_η of the copolymers prepared at different temperature were shown in Table 2. As the reaction temperature increased, the yield increased, and M_η of the copolymer decreased. The initiator decomposition rate and free radical concentration increased as the reaction temperature increased, resulted in the acceleration of reaction rate which caused the raise of the yield. Meanwhile, the rate of chain transfer and termination also increased which resulted in the decrease of M_η. As excessively high temperature cause a tendency to implode, to ensure polymerization process steady, 60 oC was the proper temperature.

TABLE III. Effect of the pH value of reaction medium on the aqueous precipitation copolymerization of AN, VA and DEMA

pH value of reaction medium	M_η (10^4)	Yield (%)
1.5	6.35	74.5
2	6.76	82.5
3	6.88	80.8
3.5	7.09	78.3

Other reaction conditions: temperature=60°C, monomer concentration=15%, initiator concentration=0.6%, $NaClO_3/NaS_2O_{5\,(mol)}$=1/3, chain transfer concentration=0.3%, DEMA addition=2.5%.

The yield and M_η of the copolymers prepared at different pH values of reaction medium were shown in Table 3. As pH increased, M_η of the copolymer increased. The yield increased as pH decreased, but when pH decreased to 1 the yield was the minimum. The effect of pH is mainly related to the mechanism of redox initiating system. In the $Na_2S_2O_5$-$NaClO_3$ initiating system, component which really generates free radical is H_2SO_3. The mechanism are as follows:

$$ClO_3^- + H_2SO_3 \xrightarrow{k} ClO_2^- + HSO_3^{\bullet -} + HO^\bullet \quad (1)$$

$$HSO_3^{\bullet -} + HO^\bullet \longrightarrow SO_4^{2-} + 2H^+ \quad (2)$$

TABLE IV. The ionization equilibrium of H_2SO_3, HSO_3- and SO_{32}- under different pH value [13]

pH value	1	2	3	4
SO_3^{2-} (mol%)	0.0000074	0.00031	0.0047	0.047
HSO_3^- (mol%)	0.15	0.63	0.94	0.95
H_2SO_3 (mol%)	0.85	0.37	0.055	0.005

As can be seen in Table 4, the ionization equilibrium concentration of H_2SO_3 decreased as pH increased which meant free radical concentration deceased. The effect of pH is also reflected in the electric potential of the polymerization system. Low pH which caused low potential between polymer particles which would make the system unsteady and result in the decrease of the yield and M_η.

TABLE V. Effect of the initiator concentration on the aqueous precipitation copolymerization of AN, VA and DEMA

Initiator concentration (%)	M_η (10^4)	Yield (%)
0.3	7.58	78.7
0.5	6.89	80.6
0.6	6.76	82.5
0.7	6.49	85.2

Other reaction conditions: temperature=60°C, monomer concentration=15%, pH=2.0, $NaClO_3/NaS_2O_{5\,(mol)}$=1/3, chain transfer concentration=0.3%, DEMA addition=2.5%.

The yield and M_η of the copolymers prepared with different Initiator concentration were shown in Table 5. As initiator concentration increased, the yield increased and M_η decreased which were caused by the increase of free radical concentration.

TABLE VI. EFFECT OF DEMA ON THE AQUEOUS PRECIPITATION COPOLYMERIZATION OF AN, VA AND DEMA

DEMA addition (%)	M_η (10^4)	Yield (%)
0.5	7.54	78.5
1.0	7.12	81.2
1.5	6.8	83
2.0	6.72	83.2
2.5	6.59	84.1

Other reaction conditions: temperature=60°C, monomer concentration=15%, pH=2.0, initiator concentration=0.6%, $NaClO_3/NaS_2O_5$ $_{(mol)}$=1/3, chain transfer concentration=0.3%, DEMA addtion=2.5%.

The yield and M_η of the copolymers prepared with different amount of DEMA were shown in Table 6. As DEMA addition increased, the yield increased and M_η decreased. When DEMA addition was above 1.5%, the yield and M_η nearly remained unchanged. These were caused by the increase of system viscosity after addition of DEMA.

On the basis of the above results and the balance between yield and the spinnability, which was determined by the M_η of the copolymer, the optimum reaction conditions were as follows: temperature=60°C, monomer concentration=15%, pH=2.0, initiator concentration=0.6%, $NaClO_3/Na_2S_2O_5$ $_{(mol)}$=1/3, chain transfer concentration=0.3% and DEMA addition=2.5%

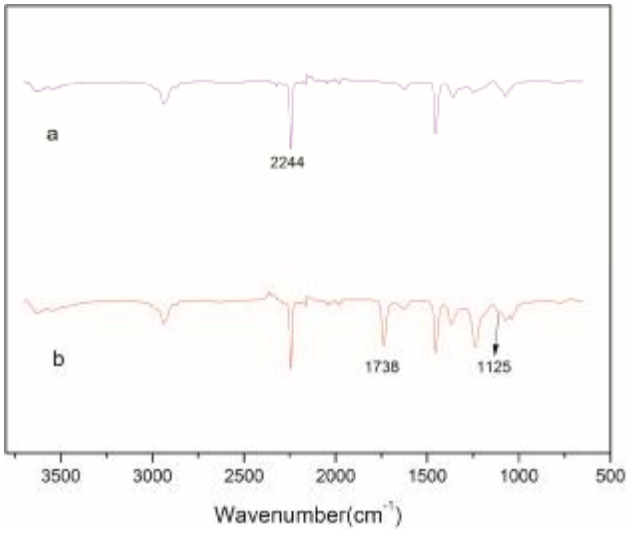

Figure 1. FTIR spectrum of (a) PAN and (b) Poly(AN-VA-DEMA)

Fig. 2 shows ^{1}H-NMR spectrum of PAN homopolymer and Poly(AN-VA-DEMA). In Fig. 2, Peak 1 and Peak 4 are the peaks βH^1 and $\alpha H^1$of in AN group. Peak 2 and Peak 3 are the peaks of CH_3 bonded to amino and ester. It was noticed that Peak 5 and Peak 6 are weak and even level to the base line. Those are the peaks of CH_2 bonded to ester groups in DEMA and VA. The ^{1}H-

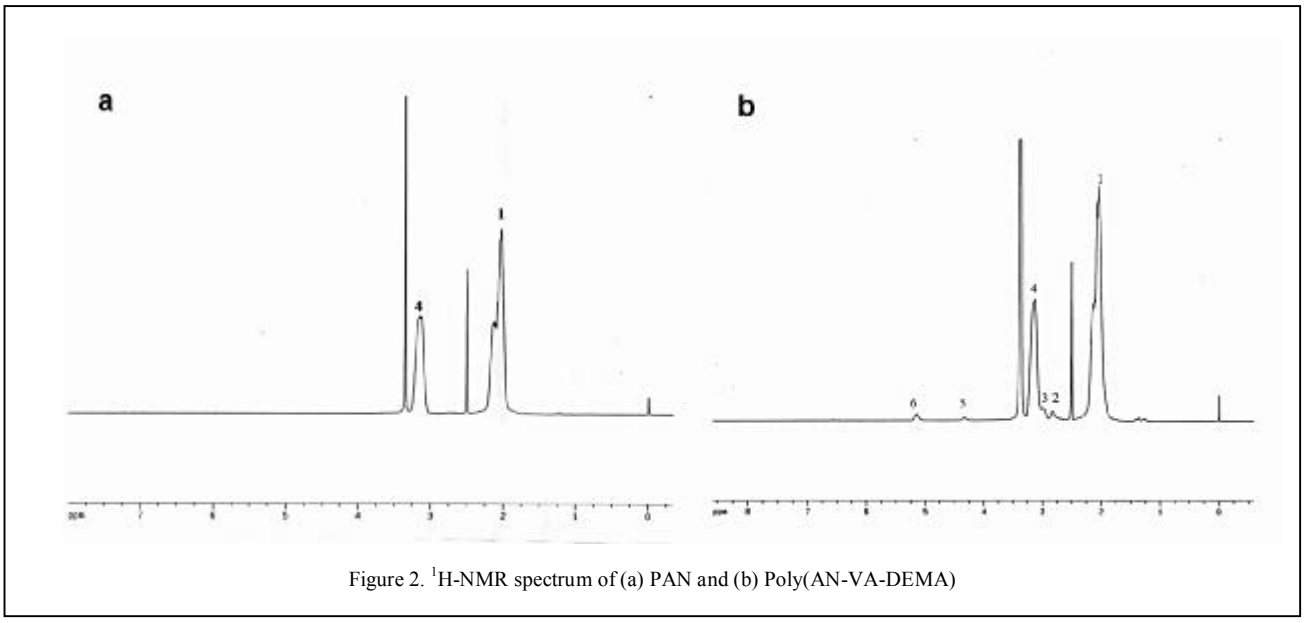

Figure 2. ^{1}H-NMR spectrum of (a) PAN and (b) Poly(AN-VA-DEMA)

B. Characterization of Poly(AN-VA-DEMA) Copolymer

Fig. 1 shows the FTIR spectra of PAN homopolymer and Poly(AN-VA-DEMA). As demonstrated in Fig. 1, the typical absorption peaks of PAN homopolymer are as follows: stretching of CH_2 at 2940 cm^{-1}, stretching of C≡N at 2240 cm^{-1}, bending of CH_2 at 1454 cm^{-1} and rocking of CH_2 at 1366 cm^{-1}. For Poly(AN-VA-DEMA), in addition to the characteristic peaks above, the spectrum exhibited a peak of υC=O at 1738 cm^{-1} and an peak at 1125 cm^{-1} from C-N stretching of -$N(CH_3)_2$ groups. It is obvious that amine groups was successfully copolymerized on the polymer chain after the polymerization.

NMR spectrum confirmed that amine groups were existed in the polymer chain.

IV. CONCLUSIONS

Various Poly(AN-VA-DEMA) copolymers containing amino groups were synthesized by the aqueous precipitation copolymerization of AN, VA and DEMA. The yield of copolymerization increased with the increase of monomer concentration, temperature, initiator concentration, DEMA addition and the decrease of pH. The decrease of monomer concentration, temperature, initiator concentration and DEMA addition caused a

increase in M_η of the copolymers. The optimum reaction conditions of the copolymerization were as follows: temperature=60°C, monomer concentration=15%, pH=2.0, initiator concentration=0.6%, $NaClO_3/Na_2S_2O_{5\ (mol)}$=1/3, chain transfer concentration=0.3% and DEMA addition=2.5%. The chemical composition were characterized by FTIR and NMR which indicated that amino groups were existed on the polymer chain.

ACKNOWLEDGMENT

This work is financially supported Shanghai Leading Academic Discipline Project (No. B603) and the Program of Introducing Talents of Discipline to Universities (No.111-2-04).

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