Effect of Inorganic Salts on Viscosity of Acrylonitrile-*N*-Vinylpyrrolidone Copolymer Solutions

Chen Hou, Cheng-Guo Wang, Liang Ying, Hua-Su Cai

Carbon Fiber Center, College of Materials Science and Engineering, Shandong University, Jinan 250061, China

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ABSTRACT: Effects of inorganic salts on viscosities of dimethyl sulphoxide (DMSO) solutions of acrylonitrile(AN)/*N*-vinylpyrrolidone(*N*-VP) copolymer are discussed. Viscosity was determined by the rotary viscosimeter. It was shown that the solution viscosity decreases quickly with addition of KCl and NaCl and the effect of NaCl is more prominent than that of KCl. As concentration of KCl and NaCl went beyond 0.025 mol/L, the viscosity showed a trend of increase. The viscosity increased considerably with addition of $FeCl_3$ and $CuCl_2$. Changes in solution viscosity became less obvious with addition of $ZnCl_2$. As temperature increased, the viscosity of the copolymer solution containing NaCl decreased most quickly and the copolymer solution consisting of $FeCl_3$ showed the slowest decrease. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3492–3495, 2003

Key words: viscosity

INTRODUCTION

Selection of a suitable dope viscosity for spinning of acrylic fibers is an important step. Increasing the molecular weight of acrylonitrile (AN) polymer and the solid content of spinning dope can improve the mechanical properties of precursors and the resulting carbon fiber, which always leads to a rise in dope viscosity, which is a disadvantage and makes the fiber dangerous for transportation. It is feasible to decrease the dope viscosity by increasing the comonomer concentration, but percentage conversion of AN in the polymerization reaction always decreases with the increase in the comonomer content.[1] The effects of inorganic salts on viscosity of AN copolymer solutions have been observed and reported in the literature,[2,3] and addition of LiCl may decrease the viscosity of AN copolymer solutions.[4] To our knowledge, there are only a few reports on effects of inorganic salt ions, that is, Na^+, K^+, Zn^{2+}, Fe^{3+}, Cu^{2+}, Cl^-, SCN^-, on AN copolymer solutions, but there is no report on *N*-vinylpyrrolidone(*N*-VP) as comonomer. In this study, solvent water suspension technique was used to synthesize AN/*N*-VP copolymer. The viscosity was controlled and determined by a NDJ-4 rotary viscosimeter. Effect of different inorganic salts, including NaCl, KCl, $FeCl_3$, $CuCl_2$, $ZnCl_2$, NaSCN, on viscosity of AN/*N*-VP copolymer solutions was contrastively studied.

Correspondence to: C. Hou.

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EXPERIMENTAL

Materials

Monomers AN and *N*-VP were industrial polymerization grade and were distilled to remove inhibitors before use. Azobisisobutyronitrile (AIBN) was used as initiator and was recrystallized from ethanol before use. Poly(vinyl alcohol) (PVA) was used as the suspending agent. Deionized water and dimethyl sulphoxide (DMSO) were adopted as the polymerization medium. NaCl, KCl, $FeCl_3$, $CuCl_2$, $ZnCl_2$, and NaSCN were used as received without further purification.

Polymerization

Required amounts of AN, *N*-VP, PVA, AIBN, and deionized water were placed in a glass flask, which was continuously flushed with ultrapure nitrogen. The flask was wholly immersed in a temperature-controlled water bath and was shaken from time to time. After 2 h, the resultant mixture was poured into a large amount of methanol for precipitation, washed with methanol several times, and dried at 60°C under vacuum until it reached a constant weight. Copolymer samples were then dissolved in DMSO solvent containing different concentrations of inorganic salts to give a 10 wt % solution. The solution was stirred for 2 h until a transparent and viscous complex was obtained and then kept stable at 30°C for 24 h.

Characterization

Elemental analysis of the copolymers was carried out using a PE 2400 elemental analyzer to determine the

TABLE 1
Important Parameters of Copolymerization

H_2O/DMSO/(v/v)	AN/N-VP/(w/w)	$Mn \times 10^{-4}$	Oxygen concentration in copolymer/wt %	N-VP concentration in copolymer/wt %
90/10	98/2	39.8	0.262	1.82

Condition: |AN| = 4.15 mol/l; |AIBN| = 0.008mol/l; |PVA| = 0.22 g/l; time 2 h; temperature 60°C.

oxygen in these copolymers. Viscosities of the copolymers were measured at 30°C in DMF by using an Ubbelohde viscometer, and the number-average molecular weights (*Mn*) of the purified copolymers were calculated from the following equation[5]:

$$[\eta] = 3.92 \times 10^{-1}\, Mn^{0.75} \quad (1)$$

where $[\eta]$ is intrinsic viscosity, and *Mn* is the number-average molecular weight.

Viscosity of the copolymer solutions of the same solid content was measured using the NDJ-4 rotary viscosimeter at a constant temperature. The range of concentration of inorganic salts in copolymer solution was from 0–0.035 mol/L.

RESULTS AND DISCUSSION

Copolymer composition

H_2O/DMSO suspension technique was used to synthesize AN/*N*-VP copolymer. Some important parameters and polymerization conditions of the copolymer are shown in Table I. It shows that pure AN/*N*-VP copolymer can be synthesized by this technique. The composition of AN/*N*-VP copolymers was determined from the oxygen concentration in the copolymer.

Flow action of copolymer solutions

Viscosity of AN/*N*-VP copolymer solutions without inorganic salts using the different shearing rates at 30°C was determined using a NDJ-4 rotary viscosimeter. The concentration of AN/*N*-VP copolymer in the solutions was kept at 10 wt %. The shearing rate is proportional to the rotor speed. The shearing rate can be calculated from the following equation[6]:

$$\gamma = 2wR^2/(R^2\ r^2) \quad (2)$$

TABLE II
Effect of Rotor Speed on Viscosity of Copolymer Solution

Rotor speed/(circle/min)	1.5	3	6	12
Viscosity/Pa S	376.6	373.2	378.4	374.5

where γ is the shearing rate, w is the rotor speed, and r, R are the radius of the rotor and the beaker, respectively. The experimental results are given in Table II. Changes in viscosity become less prominent with an increase of rotor speed. This accords with the character of Newtonian flow. Roychen et al.[7] also reported the same result. It may be concluded that copolymer solutions show Newtonian flow at lower shearing rate and the viscosity is independent of shearing rate.

An influence of alkali salts on the viscosity of the copolymer solutions was studied by varying concentration of alkali salts from 0 to 0.035 mol/L at a constant rotor speed of 6 circle/min and keeping the mixture at 30°C. The concentration of AN/*N*-VP copolymer in the solutions was kept at 10 wt %. Figure 1 shows the changes of viscosity with addition of KCl and NaCl. The viscosity of the copolymer solution decreases continuously as the concentrations of KCl and NaCl rise to 0.025 mol/L, then increases. The changes in viscosity of solution containing KCl are less prominent than those of solution containing NaCl.

The literature[8] reports factors that affect the viscosity of copolymer solution at a constant shearing rate; these factors can be divided into two different groups. The first includes the extent of high molecular entanglement. The second is the free volume in the copolymer solution. There are great salt effects when alkali salts are put into DMSO solvent. Alkali salts are decomposed into ions because of solvation effect, that is, Na^+, K^+, Cl^-. Intermolecular interaction is reduced by Na^+ and K^+, which leads to the decrease of associa-

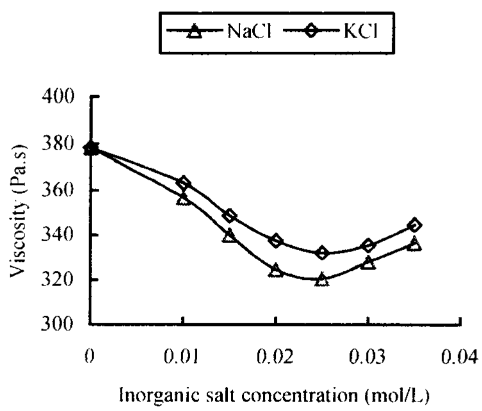

Figure 1 Effect of alkali salts on viscosity of copolymer solution.

TABLE III
Effect of Transition-Metal Salts on Viscosity of Copolymer Solution

Inorganic salts	Viscosity/Pa S	Inorganic salt concentration(mol/L)						
		0	0.01	0.015	0.02	0.025	0.03	0.035
$FeCl_3$	η	378.4	401.3	419.4	435.6	470.2	498.5	534.6
$CuCl_2$	η	378.4	394.3	408.3	423.5	445.7	473.4	506.8
$ZnCl_2$	η	378.4	382.3	389.9	392.1	398.1	408.7	419.8

tion degree of high molecular. Entanglement networks of high molecular chain are destroyed. Disentanglement and slippage of entanglement crosslink begin to occur. With an increase of alkali salt concentration, the rate of disentanglement and slippage is faster compared to that of entanglement, and entanglement networks of high molecular chain are becoming less and less. The high molecular chains begin to orient towards flow direction gradually as a departure from the balance. Slippage among the high moleculars becomes easily. The introduction of alkali salts KCl and NaCl produces a decrease in the viscosity of the copolymer solution. When alkali salt concentration is above 0.025 mol/L, the free volume in the copolymer solution is mostly occupied. Free area in which high moleculars relatively move becomes less. The viscosity of copolymer solution rises slowly.

Effect of transition-metal salts on viscosity of copolymer solution

Transition-metal salts $FeCl_3$ and $CuCl_2$ are difficult to dissolve in DMSO solvent. Saturated solutions consisting of $FeCl_3$ and $CuCl_2$ were firstly obtained. The saturated solutions were then appended to DMSO solvent, and solutions containing different concentrations of inorganic salts were attained. Transition-metal salt $ZnCl_2$ is easily dissolved in DMSO. In order to study the effect of transition-metal salts on the viscosity of AN/*N*-VP copolymer solution, the rotor speed was controlled at 6 circle/min and the mixture was kept at 30°C. The concentration of AN/*N*-VP copolymer in the solutions was kept at 10 wt %. The main changes of viscosity are presented in Table III. As the transition-metal salt concentration was increased from 0 to 0.035 mol/L, the viscosity of copolymer solutions showed an prominent increase, except for the fact that the increase in viscosity of copolymer solution containing $ZnCl_2$ was less obvious, which shows disagreement with the values reported.[9] It is chemical interaction that induces the viscosity of copolymer solutions consisting of $FeCl_3$ and $CuCl_2$ to increase with the increase of concentration of transition-metal salts. The presence of transition-metal ions, particularly those of iron or copper in AN copolymer solutions, is considered as an important factor for yellowing of acrylic fibers. These metal ions form colored complexes or salts with the nitrile copolymers and give darkening and gelation effect to the acrylic copolymer solutions.[10] Disentanglement and slippage of entanglement crosslink relatively easily occurs because of better dissolvability of $ZnCl_2$. On the other hand, the coordinated complexation ability of Zn^{2+} is great. Zn^{2+} may form salts with the nitrile radical of the two polyacrylonitrile molecules bordering on each other. The changes in viscosity of copolymer solution are less prominent by adding $ZnCl_2$.

Effect of anions on viscosity of copolymer solution

The effects of anions on the viscosity of AN/*N*-VP copolymer solutions are also discussed. Alkali salts NaCl and NaSCN were selected to study effects of anions Cl^{1-} and SCN^{1-} on viscosity of solution. Anion concentration was varied from 0 to 0.035 mol/L, and other experimental parameters were kept constant. It is evident from Table IV that the viscosity of the copolymer solution containing Cl^{-} drops more considerably than that of SCN^{-} with an increase in anion concentration.

Effect of temperature on viscosity of copolymer solution

Because temperature also plays an important role in the factors that affect viscosity of AN/*N*-VP copolymer solution,[11] it is necessary to study the viscosity of copolymer solution at different temperatures. The ef-

TABLE IV
Effect of Anions on Viscosity of Copolymer Solution

Inorganic salts	Viscosity/Pa S	Inorganic salt concentration (mol/L)						
		0	0.01	0.015	0.02	0.025	0.03	0.035
NaCl	η	378.4	356.7	340.2	324.6	320.5	328.2	336.7
NaSCN	η	378.4	367.2	354.6	345.5	334.8	343.6	356.9

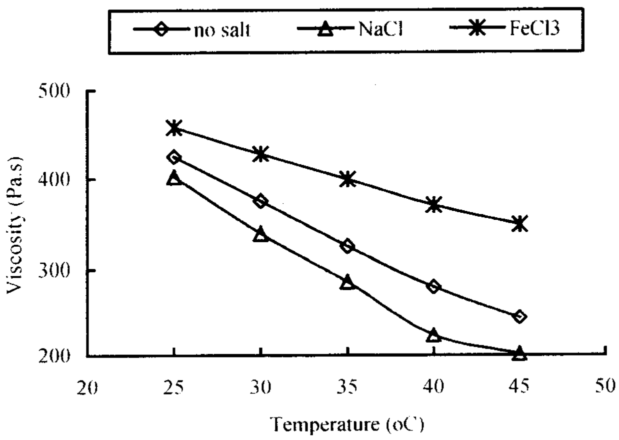

Figure 2 Effect of temperature on viscosity of copolymer solution.

fect of temperature on viscosity was studied by varying temperature in the range of 25–45°C while keeping the salts of NaCl and $FeCl_3$ at the constant concentration of 0.01 mol/L and other experimental parameters constant.

By comparing the values in Figure 2, it is possible to divide the results into three groups. The first is copolymer solution containing alkali salt NaCl, the viscosity of which decreases most quickly with an increase of temperature. The higher the temperature is, the more prominent the solvation effect of DMSO and the salt effect of NaCl are. The rate of disentanglement and slippage of entanglement network and crosslink are faster. Flow of the high molecular chains occurs easily. The copolymer solution consisting of $FeCl_3$ belongs to the second group. When the temperature increases from 25 to 45°C, the copolymer solution shows the slowest decrease of viscosity. This could be related to the increase in the chemical reaction and gelation effect at higher temperature. The last group includes the copolymer solution without salts. The rate of decrease of viscosity of the copolymer solution is intermediate.

CONCLUSIONS

Laboratory studies of viscosity of AN/*N*-VP copolymer solutions have shown that copolymer solutions show Newtonian flow at lower concentration and shearing rate. The viscosity of copolymer solution decreases quickly with addition of alkali salts and the effect of NaCl is more prominent than that of KCl. When the concentration of alkali salts is beyond 0.025 mol/L, the viscosity shows a trend of increase. The viscosity increases considerably when transition-metal salts $FeCl_3$ and $CuCl_2$ are appended to the copolymer solution. Changes of solution viscosity become less obvious with addition of $ZnCl_2$. When temperature increases from 25 to 45°C, the viscosity of the copolymer solution containing NaCl drops most considerably and the copolymer solution consisting of $FeCl_3$ shows the slowest decrease.

References

1. Dong, J.-Z.; Zhao, Y.-M.; Chen, X.-Y. Process of Synthetic Fiber; China Textile Press: Beijing, 1996.
2. Gargallo, L.; Games, C. L.; Radic, D. Eur Polym J 1984, 20, 483.
3. Ogawa, E.; Shima, M. Polymer J 1986, 13, 443.
4. Prasad, G. Man Made Textile 1985, 57.
5. Onyon, R. F. J Polym Sci 1956, 22E.
6. Lan, L.-W. Polymer Physics; Northwestern Polytechnical University Press: Xian, 1989.
7. Roychen, J.; Surekha, D.; Animesh, K. R. Polym Int 1991, 26, 89.
8. He, M.-J.; Chen, W.-X.; Dong, X.-X. High Polymer Physics; Fudan University Press: Shanghai, 2000.
9. Jin, L.-C. Synth Fiber Indus 1991, 14, 30.
10. Datye, K. V.; Gupta, D. C. Synth Fibers 1984, 6.
11. Pan, Z.-R. Polymer Chemistry; Chinese Chemical Industry Press: Beijing, 1997.