

Rheological Kinetics of Acrylonitrile–Acrylamide Copolymer Solutions in Dimethyl Formamide

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ABSTRACT: Viscosity behavior of dimethyl formamide solutions of acrylonitrile–acrylamide copolymer is discussed. The rheological kinetics of the solutions was studied for contrast. It is shown that the solutions behave the same as Newtonian flow as the rotor speed goes beyond 6 revolutions min^{-1} . With an increase of temperature, the apparent viscosity of acrylonitrile–acrylamide copolymer solutions shows a decreasing trend. The changes of the apparent flow–activation energy of solutions calculated by Arrhenius equation become less prominent along with the changes of the molecular weight of acrylonitrile–acrylamide copolymers. The apparent flow–activation energy of the copolymer

solutions increases continuously with an increase of copolymer concentration. The viscosity of copolymer solutions decreases continuously at concentrations of KCl and NaCl up to 0.02 mol L^{-1} and then increases. The apparent flow–activation energy of acrylonitrile–acrylamide copolymer solutions shows an obvious trend of decrease with addition of alkali salts and the changes of the apparent flow–activation energy of solutions containing NaCl are more prominent than those of solutions containing KCl. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 527–531, 2005

Key words: viscosity; additives; rheology; kinetics (polym.)

INTRODUCTION

In fiber technology, selection of a suitable dope viscosity for spinning of acrylic fibers is an important step.¹ Spinning dopes are usually prepared in temperatures considerably higher than extrusion temperatures and long periods are required for settlement of deaeration. Acrylonitrile (AN) polymer solutions rapidly cooled to the processing temperature tend gradually to the equilibrium state, which is accompanied by variation of viscosity properties.² Increasing the molecular weight of 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 rising of dope viscosity, and is disadvantageous and dangerous for preparation and transportation. Many reagents have been reported in the literature^{3,4} as pretreatments for decreasing the viscosity of AN polymers and moderating the stabilization exotherm. In one case, addition of LiCl to the spinning dope decreases the viscosity of the dopes and moderates the stabilization exotherm of the precursors.⁵ To our knowledge, there are only a few

reports on the viscosity behavior of ordinary AN copolymer dilute solutions, but there are almost no reports on the rheological kinetics of the solutions of high molecular weight AN copolymer with acrylamide (AM) as comonomer. With this view, studies were undertaken on the viscosity behavior of the dimethyl sulfoxide (DMF) solutions of high molecular weight AN–AM copolymer. Rheological kinetics of the solutions was studied for contrast. In this study, different polymerization techniques were used to synthesize AN–AM copolymer. The apparent flow–activation energy of DMF solutions of AN–AM copolymer was calculated and effects of additives on rheological kinetics of AN–AM copolymer solutions were studied for contrast.

EXPERIMENTAL

Materials

Monomer AN was supplied as extra pure grade by Tianjin Chemical Resin Industry (Tianjin, China) and distilled to remove inhibitors before use. DMF was supplied by Shanghai Chemical Resin Industry (Shanghai, China). AM was obtained by neutralization of itaconic acid supplied as extra pure grade by Tianjin Chemical Resin Industry (Tianjin, China) and NH_3 . High molecular weight AN–AM copolymer was pre-

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TABLE I
Comparison of the Viscosity Average Molecular Weight of AN-AM Copolymers

Sample	PAN1	PAN2	PAN3	PAN4
Polymerization technology	DMF solution		Aqueous suspension	
$M_w (\times 10^4)$	8.9	12.4	30.7	41.8

pared by the aqueous suspension polymerization technology. The details of the polymerization technology are given elsewhere.^{6,7} For comparison, ordinary AN-AM copolymer synthesized by DMF solution polymerization⁸ technology was also used. Characteristics of copolymers are given in Table I.

Characterization

The molecular weight (M_w) of AN-AM copolymer was determined by intrinsic viscosity measurements. Intrinsic viscosity $[\eta]$ of AN-AM copolymer was measured at 35°C in dimethyl formamide using an Ubbelohde viscometer,⁹ and the molecular weight was calculated from eq. (1):

$$[\eta] = 2.78 \times 10^{-4} M_w^{0.76} \quad (1)$$

The apparent viscosity of AN-AM copolymer solutions of the same solid content at a constant temperature was measured by using a NDJ-4 rotary viscosimeter, which is an absolute viscosimeter.

The apparent flow-activation energy of DMF solutions of AN-AM copolymer were calculated by Arrhenius eq. (2).¹⁰

$$\eta = A e^{E_\eta/RT} \quad (2)$$

where η is the apparent viscosity of AN-AM copolymer solutions, E_η is the apparent flow-activation energy of AN-AM copolymer solutions, and A is an equation parameter. The plot of $\ln \eta$ versus T^{-1} gives a straight line.

RESULTS AND DISCUSSION

Flow action of AN-AM copolymer solutions

The apparent viscosity of AN-AM copolymer solutions using an NDJ-4 rotary viscosimeter at the different shearing rate at 35°C was determined. The concentration of AN-AM copolymer in the solutions was kept at 12 wt %. The shearing rate is proportionable to the rotor speed. The shearing rate can be calculated from eq. (3).¹¹

$$\dot{\gamma} = \frac{2 w R^2}{(R^2 - r^2)} \quad (3)$$

where $\dot{\gamma}$ is the shearing rate, w is the rotor speed, and r and R are the radius of the rotor and the beaker, respectively. The experimental results are given in Figure 1. The apparent viscosity of AN-AM copolymer solutions decreases prominently as the rotor speeds up to 6 revolutions min^{-1} and the solutions behave the same as the non-Newtonian flow with the shear force becoming less and less. The changes of viscosity of solutions become less prominent as the rotor speed goes beyond 6 revolutions min^{-1} and it accords with the character of Newtonian flow. Roychen et al.¹² also reported the same result. It may be concluded that AN-AM copolymer solutions show Newtonian flow at high shearing rate and the apparent viscosity is independent of the shearing rate. It is also evident from Figure 1 that effects of the rotor speed on the apparent viscosity of solutions containing ordinary copolymer are less prominent than those of solution containing high molecular weight AN-AM copolymer.

In AN-AM copolymer solutions, two opposite effects of solvent power on the apparent viscosity can be expected. On the one hand, some shrinkage of molecular coils would reduce viscosity. On the other hand, reduction of solvent power leads to an increase of polymer-polymer interactions, promotes aggregation, and generally destabilizes the solution.¹³ Increasing of the rotor speed reduces polymer-polymer interactions continuously, which leads to the decrease of association degree of high molecular chain. Entanglement networks of high molecular chains are destroyed. The high molecular chains partially uncoil and orient themselves at a 45° angle to the flow direction. Slip-pages among the high molecular chains occur easily and the viscosity shows a decreasing trend.

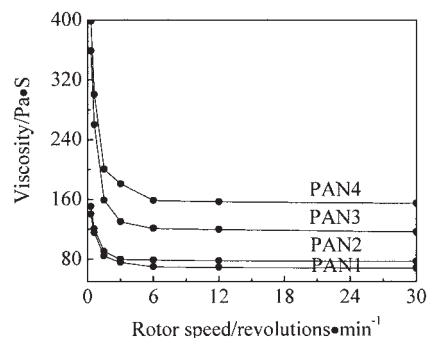


Figure 1 Viscosity curve of AN-AM copolymers.

TABLE II
Effect of Temperature on the Apparent Viscosity of PAN2 Copolymer Solutions

Temperature (°C)	30	35	40	45	50
Apparent viscosity (Pa · s)	93.4	78.9	66.8	56.9	48.7

Effect of temperature on the apparent viscosity of copolymer solutions

The solution containing PAN2 copolymer was used to study the influence of temperature on the apparent viscosity of AN-AM copolymer solutions by varying temperature from 30 to 50°C at a constant rotor speed of 12 revolutions min⁻¹. Table II illustrates effects of temperature on the apparent viscosity of AN-AM copolymer solutions while keeping the concentration of AN-AM copolymer in the solutions at 12 wt %. With an increase of temperature, the apparent viscosity of AN-AM copolymer solutions shows a decreasing trend. The higher the temperature is, the more prominent the solvent power of DMF is. The rate of disentanglement and slippage of the entanglement network is faster. Flow of the high molecular chains occurs easily.

Determination of the apparent flow-activation energy of solutions

According to the results summarized in Table II, the apparent flow-activation energy of PAN2 copolymer solutions with the concentration of AN-AM copolymer at 12 wt % was calculated. Figure 2 is a logarithmic plot of η versus T^{-1} . The apparent flow-activation energy of solutions estimated from the slope is 26.6 kJ mol⁻¹.

Effect of the molecular weight of AN-AM copolymer on the apparent flow-activation energy

Effect of the molecular weight of AN-AM copolymer on the apparent flow-activation energy of so-

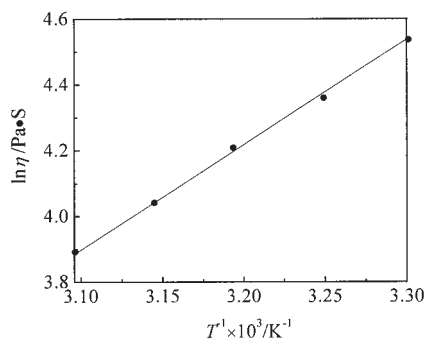


Figure 2 Dependence of the apparent viscosity of PAN2 copolymer solutions on temperature.

TABLE III
Effect of the Molecular Weight of AN-AM Copolymer on the Apparent Flow-Activation Energy of Solutions

Sample	PAN1	PAN2	PAN3	PAN4
$M_w (\times 10^4)$	8.9	12.4	30.7	41.8
E_η (kJ · mol ⁻¹)	26.8	26.6	27.1	26.9

lutions was studied by varying AN-AM copolymers at a constant rotor speed of 12 revolutions min⁻¹. Table III shows the effect of the molecular weight of AN-AM copolymer on the apparent flow-activation energy of solutions while keeping the concentration of AN-AM copolymer in the solutions at 12 wt %. It is evident from Table III that the changes of the apparent flow-activation energy of solutions become less prominent along with the changes of the molecular weight of AN-AM copolymer and the apparent flow-activation energy of solutions is independent of AN-AM copolymer molecular weight, which is in agreement with the literature.¹⁴ It is shown that the flow of the high molecular chain of AN-AM copolymer accords with the character of the stepped block flow.

Effect of AN-AM copolymer concentration on the apparent flow-activation energy

For our initial experiment, influence of AN-AM copolymer concentration on the apparent flow-activation energy of AN-AM copolymer solutions was discussed by varying PAN2 copolymer content from 4 to 20 wt % at a constant rotor speed of 12 revolutions min⁻¹. Figure 3 shows a plot of the apparent flow-activation energy of copolymer solutions as a function of AN-AM copolymer content in DMF. It is evident from Figure 3 that the apparent flow-activation energy of AN-AM copolymer solutions increases continuously along with the increase of AN-AM copolymer concentration. With an increase of AN-AM copolymer concentration, the hydrogen bonding and the

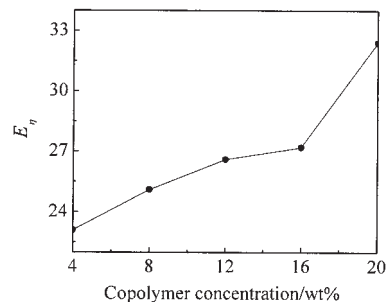


Figure 3 Effect of PAN2 copolymer concentration on the apparent flow-activation energy of solutions.

polymer–polymer interactions in the solutions increase continuously. Flow of the high molecular chains becomes difficult and the apparent flow-activation energy of AN–AM copolymer solutions shows a trend of increase.

Effect of alkali salts on rheological kinetics of copolymer solutions

Effects of alkali salts on the apparent viscosity of PAN2 copolymer solutions was studied by varying concentration of alkali salts from 0 to 0.03 mol L⁻¹ at a constant rotor speed of 12 revolutions min⁻¹ and the mixture was kept at 35°C. The concentration of PAN2 copolymer in the solutions was kept at 12 wt %. Figure 4 shows the changes of viscosity with addition of KCl and NaCl. The apparent viscosity of copolymer solutions decreased continuously at the concentrations of KCl and NaCl up to 0.02 mol L⁻¹ and then increased. The changes of viscosity of solutions containing KCl are less prominent than those of solutions containing NaCl.

The literature¹⁵ reports factors that affect the viscosity of copolymer solutions 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 solutions. There are great salt effects when alkali salts are put in DMF solvent. Alkali salts are decomposed into ions, i.e., Na⁺, K⁺, and Cl⁻. Intermolecular interaction is reduced by Na⁺ and K⁺, which leads to the decrease of association degree of high molecular chains. Entanglement networks of the high molecular chain are destroyed. Disentanglement and slippage of entanglement crosslinks begin to occur. With an increase of alkali salts concentration, the rate of disentanglement and slippage is faster compared to that of entanglement. Entanglement networks of high molecular chains become fewer. The high molecular chains begin to orient toward flow direction. Slippage among the high molecular chains become easier. When alkali

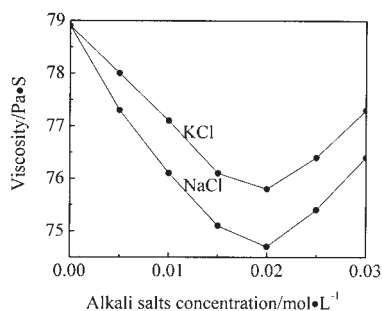


Figure 4 Effect of alkali salts on viscosity of PAN2 copolymer solutions.

TABLE IV
Effect of Alkali Salts on the Apparent Flow-Activation Energy of PAN2 Copolymer Solutions

Additive	None	NaCl	KCl
E_{η} (kJ · mol ⁻¹)	26.6	23.9	24.7

salts concentration is above 0.02 mol L⁻¹, the free volume in the copolymer solutions is mostly occupied. The free area in which high molecular chains move becomes less. The viscosity of copolymer solutions rises slowly.

To study the effect of alkali salts on the apparent flow-activation energy of AN–AM copolymer solutions, the alkali salts concentration was kept at 0.02 mol L⁻¹ at a constant rotor speed of 12 revolutions min⁻¹ and the concentration of PAN2 copolymer in the solutions at 12 wt %. Table IV illustrates the effect of alkali salts on the apparent flow-activation energy of PAN2 copolymer solutions. The values of the apparent flow-activation energy of AN–AM copolymer solutions show an obvious decreasing trend with addition of alkali salts and the changes of solution containing NaCl are more prominent than those of solution containing KCl.

CONCLUSIONS

Laboratory studies of viscosity behavior of dimethyl formamide solutions of acrylonitrile–acrylamide copolymer have shown that the apparent viscosity of AN–AM copolymer solutions decreases prominently at the rotor speeds up to 6 revolutions min⁻¹. The changes of viscosity of solutions become less prominent as the rotor speed goes beyond 6 revolutions min⁻¹ and accord with the character of Newtonian flow. With an increase of temperature, the apparent viscosity of AN–AM copolymer solutions shows a decreasing trend. The changes of the apparent flow-activation energy of solutions calculated by Arrhenius equation become less prominent along with the changes of the molecular weight of the AN–AM copolymer. The apparent flow-activation energy of AN–AM copolymer solutions increases continuously with an increase of AN–AM copolymer concentration. The apparent viscosity of copolymer solutions decreases quickly with the addition of KCl and NaCl. When the concentration of alkali salts goes beyond 0.02 mol L⁻¹, the viscosity shows an increasing trend. The apparent flow-activation energy of AN–AM copolymer solutions shows an obvious trend of decrease with addition of alkali salts and the changes of the apparent flow-activation energy of solution containing NaCl are more prominent than those of solutions containing KCl.

References

1. Gargallo, L.; Games, C. L.; Radic, D. *Eur Polym J* 1984, 20, 483.
2. Masson, J. C. *Acrylic Fiber Technology and Application*; Marcel Dekker: New York, 1995.
3. Winters, R. D. U.S. Pat. 4, 279, 612 (1981).
4. Lewin, M.; Guttman, H.; Naor, Y. *J Macromol Sci-Chem* 1988, A25, 1367.
5. Hou, C.; Wang, C.-G.; Ying, L.; Cai, H.-S. *J Appl Polym Sci* 2003, 89, 3492.
6. Hou, C.; Chenguo, W.; Ying, L.; Cai, H. *Chinese J Chem Eng* 2003, 11, 166.
7. Chen, H.; Zhang, W.-X.; Wang, C.-G.; Cai, H.-S. *Polym Mater Sci Eng* 2003, 19, 79.
8. Bajaj, P.; Paliwal, D. K.; Gupta, A. K. *J Appl Polym Sci* 1993, 49, 823.
9. Kashyap, A. K.; Kalpagam, V. *J Polym Sci* 1979, 17, 225.
10. Dong, J.-Z.; Zhao, Y.-M.; Chen, X.-Y. *Process of Synthetic Fiber*; China Textile Press: Beijing, 1996.
11. Lan, L.-W. *Polymer Physics*; Northwestern Polytechnical University Press: Xian, 1989.
12. Roychen, J.; Surekha, D.; Animesh, K. R. *Polym Int* 1991, 26, 89.
13. Jain, M. K.; Abhiraman, A. S. *J Mater Sci* 1987, 22, 278.
14. He, M.-J.; Chen, W.-X.; Dong, X.-X. *High Polymer Physics*; Fudan University Press: Shanghai, 2000.
15. Bajaj, P.; Paliwal, D. K.; Gupta, A. K. *J Appl Polym Sci* 1998, 67, 1647.