Rheological Kinetics of Acrylonitrile/Amino Ethyl-2-Methyl Propenoate Copolymer Solutions in Dimethyl Sulfoxide

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ABSTRACT: Viscosity behavior of dimethyl sulfoxide solutions of acrylonitrile (AN)/amino ethyl-2-methyl propenoate (AEMP) copolymer was discussed. Rheological kinetics of the solutions was studied in contrast. It is shown that the solutions behave the same as Newtonian flow as the rotor speed goes beyond 12 rpm. With an increase of temperature, the apparent viscosity of AN/AEMP copolymer solutions shows a trend of decrease. 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 AN/AEMP 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 as the concentrations of KCl and NaCl up to 0.02 mol L^{-1}, and then it increases. the apparent flow-activation energy of AN/AEMP 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. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2972–2976, 2006

Key words: viscosity; additives; rheological kinetics

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 it 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] Various carboxylic acids are used as comonomers to copolymerize with AN to obtain speciality fibers for various applications.[6,7,8] Considerable information exists in the literature on the use of comonomers other than carboxylic acids for the preparation of polyacrylonirile precursor fibers.[9] In the case of amino ethyl-2-methyl propenoate (AEMP), a lowering of the time of stabilization, a reduction in the thermal degradation, and a better control of heat flux during oxidative cyclization have been reported. To our knowledge, there are only few reports on the viscosity behavior of ordinary AN copolymer dilute solutions, but there is almost no report on rheological kinetics of the solutions of high molecular weight AN copolymer with AEMP as comonomer. With this view, studies were undertaken on the viscosity behavior of the dimethyl sulfoxide (DMSO) solutions of high molecular weight AN/AEMP copolymer. Rheological kinetics of the solutions was studied for contrast. In this study, different polymerization techniques were used to synthesize AN/AEMP copolymer. The apparent flow-activation energy of DMSO solutions of AN/AEMP copolymer was calculated and effects of additives on rheological kinetics of AN/AEMP copolymer solutions were studied in contrast.

MATERIALS AND METHODS

Materials

AN (Shanghai Chemical Reagents, A.R. grade) was vacuum-distilled from CaH_2 just before polymeriza-

Sample	M_w (10^4)	$M_{w\text{-standard}}$ (10^4)
DMSO solution		
Poly(AN/AEMP)1	9.64	10.1
Poly(AN/AEMP)2	12.6	13.1
Aqueous suspension		
Poly(AN/AEMP)3	36.2	37.2
Poly(AN/AEMP)4	48.9	49.2

tion. AEMP (Shanghai Chemical Reagents, A.R. grade) was used as a comonomer. Azobisisobutyronitrile (AIBN) was used as an initiator and recrystallized from ethanol before use. Polyvinyl alcohol (PVA) was used as a suspending agent. Deionized water and DMSO were adopted as the polymerization medium. High molecular weight AN/AEMP copolymer was prepared by the aqueous suspension polymerization technology. The details of the polymerization technology are given elsewhere.[10,11] For comparison, ordinary AN/AEMP copolymer synthesized by DMSO solution polymerization technology was also used.

Characterization

Conversion and the rate of polymerization were calculated from the weight of polymer obtained. The molecular weight (M_w) of the purified polymers was determined by viscosity measurements. Intrinsic viscosity [η] of the polymers were measured at 35°C in dimethyl formamide using an Ubbelohde viscometer[12] and the molecular weight was calculated from

$$[\eta] = 2.78 \times 10^{-4} \, M_w^{0.76} \tag{1}$$

To compare with the above measurements of M_w, the molecular weights ($M_{w\text{-standard}}$) were also measured by gel permeation chromatography (GPC) using a Waters 515 GPC instrument (Milford, MA), all samples were run in DMSO with a column temperature of 30°C.

The apparent viscosity of AN/AEMP 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. These measurements were carried out 20 times and the average value with regard to the above results is obtained. The apparent viscosities of AN/AEMP copolymer solutions discussed in the following are all the average values. The apparent flow-activation energy of DMSO solutions of AN/AEMP copolymer were calculated by Arrhenius equation[13]

$$\eta = A \, e^{\frac{E_\eta}{RT}} \tag{2}$$

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

RESULTS AND DISCUSSION

Flow action of AN-AEMP copolymer solutions

Characteristics of copolymers are given in Table I. It is evident that the molecular weights calculated from the intrinsic viscosity agree with those determined with GPC characterization.

The apparent viscosity of AN/AEMP copolymer solutions using NDJ-4 rotary viscosimeter at the different shearing rate at 35°C was determined. The concentration of AN/AEMP 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 the following equation[14]

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

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/AEMP copolymer solutions decreases prominently as the rotor speed up to 12 rpm 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 12 rpm and it accords with the character of Newtonian flow. Roychen et al.[15] and Wu et al.[16] also reported the same result. It may be concluded that AN/AEMP copolymer solutions show Newtonian
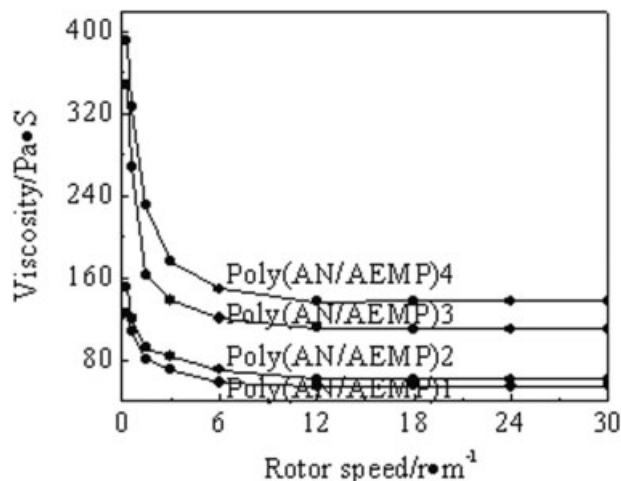

Figure 1 Viscosity curve of AN/AEMP copolymers.

TABLE II
Effect of Temperature on the Apparent Viscosity of
Poly(AN/AEMP)2 Copolymer Solutions

Temperature (°C)	Apparent viscosity (Pa s)
30	72.8
35	61.2
40	51.6
45	44.4
50	36.6

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/AEMP copolymer.

In AN/AEMP 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 increased polymer-polymer interactions, promotes aggregation, and generally destabilizes the solution.[17,18] The increasing of the rotor speed reduces polymer-polymer interactions and increases the solvent power continuously, which leads to the decrease of association degree of high molecules. Entanglement networks of high molecular chain are destroyed. The rate of disentanglement and slippage is faster compared to that of entanglement, and the high molecular chains begin to orient towards flow direction gradually as a departure from the balance. Slippage among the high molecular chains becomes easily.

Effect of temperature on the apparent viscosity of copolymer solutions

The solution containing Poly(AN/AEMP)2 copolymer was used to study the influence of temperature on the apparent viscosity of AN/AEMP copolymer solutions by varying temperature from 30 to 50°C at a constant rotor speed of 12 rpm. Table II illustrates effects of temperature on the apparent viscosity of AN/AEMP copolymer solutions while keeping the concentration of AN/AEMP copolymer in the solutions at 12 wt %. With an increase of temperature, the apparent viscosity of AN/AEMP copolymer solutions shows a trend of decrease. The higher the temperature is, the more prominent is the solvent power of DMSO. The rate of disentanglement and slippage of entanglement network and crosslink is faster. Flow of the high molecular chains occurs easily.
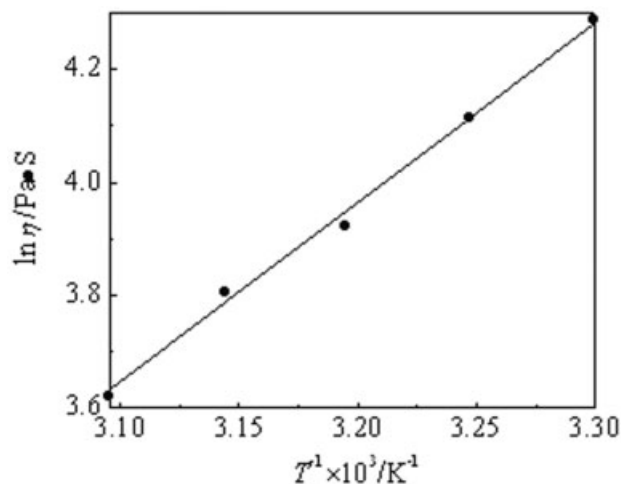

Figure 2 Dependence of the apparent viscosity of poly(AN/AEMP)2 copolymer solutions on temperature.

Determination of the apparent flow-activation energy of solutions

According to the results summarized in Table II, the apparent flow-activation energy of poly(AN/AEMP)2 copolymer solutions with the concentration of AN/AEMP 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-AEMP copolymer on the apparent flow-activation energy

Effect of the molecular weight of AN/AEMP copolymer on the apparent flow-activation energy of solutions was studied by varying AN/AEMP copolymers at a constant rotor speed of 12 rpm. Table III shows effect of the molecular weight of AN/AEMP copolymer on the apparent flow-activation energy of solutions while keeping the concentration of AN/AEMP copolymer in the solutions at 12 wt %. It is evident from the 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/AEMP copolymer; the apparent flow-activation energy of solutions is independent of AN/AEMP

TABLE III
Effect of the Molecular Weight of AN/AEMP
Copolymer on E_η of Solutions

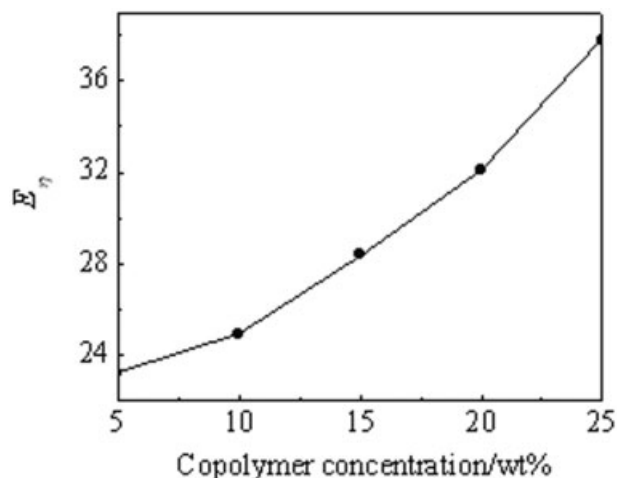| Sample	M_w (10^4)	E_η (kJ mol^{-1})
Poly(AN/AEMP)1	9.64	27.3
Poly(AN/AEMP)2	12.6	26.6
Poly(AN/AEMP)3	36.2	26.4
Poly(AN/AEMP)4	48.9	27.1

Figure 3 Effect of poly(AN/AEMP)2 copolymer concentration on E_η of solutions.

copolymer molecular weight, which is in agreement with the literature.[19] It is shown that the flow of the high molecules of AN/AEMP copolymer accords with the character of the stepped block flow.

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

For our initial experiment, influence of AN/AEMP copolymer concentration on the apparent flow-activation energy of AN/AEMP copolymer solutions was discussed by varying poly(AN/AEMP)2 copolymer content from 5 to 25 wt % at a constant rotor speed of 12 rpm. Figure 3 shows a plot of the apparent flow-activation energy of copolymer solutions as a function of AN/AEMP copolymer content in DMSO. It is evident from Figure 3 that the apparent flow-activation energy of AN/AEMP copolymer solutions increases continuously along with the increase of AN/AEMP copolymer concentration. With an increase of AN/AEMP copolymer concentration, the hydrogen bonding and the polymer-polymer interactions in the solutions increase continuously. Flow of the high molecular chains becomes difficult and the apparent flow-activation energy of AN/AEMP copolymer solutions increases.

Effect of alkali salts on rheological kinetics of copolymer solutions

Effects of alkali salts on the apparent viscosity of poly(AN/AEMP)2 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 rpm and the mixture was kept at 35°C. The concentration of poly(AN/AEMP)2 copolymer in the solutions was kept at 12 wt %. Figure 4 shows the changes of vis-

cosity with the addition of KCl and NaCl. The apparent viscosity of copolymer solutions decreases continuously as the concentrations of KCl and NaCl up to 0.02 mol L^{-1}, and then it increases. The changes of viscosity of solutions containing KCl are less prominent than those of solutions containing NaCl.

The literature[20] 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 DMSO 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 molecules. Entanglement networks of high molecular chain are destroyed. Disentanglement and slippage of entanglement crosslink 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 are becoming less and less. The high molecular chains begin to orient toward flow direction gradually as a departure from the balance. Slippage among the high molecular chains become easily. When alkali salts concentration is above 0.02 mol L^{-1}, the free volume in the copolymer solutions is mostly occupied. Free area in which high molecular chains relatively 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/AEMP copolymer solutions, the alkali salts concentration was kept at 0.02 mol L^{-1} at a constant rotor speed of 12 rpm and the concentration of poly(AN/AEMP)2 copolymer in the solutions at 12 wt %. Table IV illustrates effect of alkali
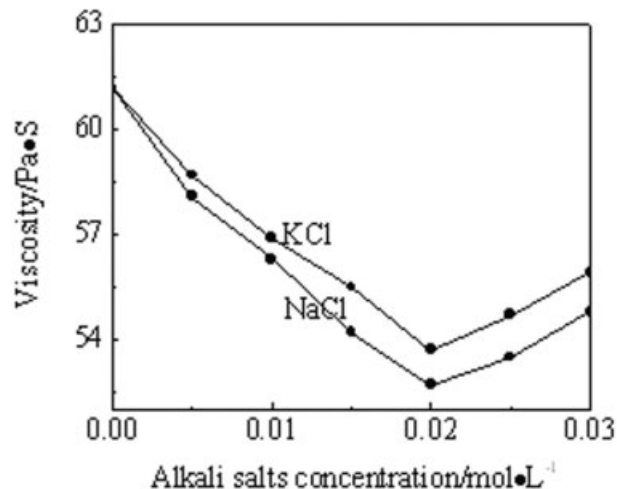

Figure 4 Effect of alkali salts on viscosity of poly(AN/AEMP)2 copolymer solutions.

TABLE IV
Effect of Alkali Salts on E_η of Poly(AN/AEMP)2
Copolymer Solutions

Additive	E_η (kJ mol^{-1})
No	26.6
NaCl	22.4
KCl	23.4

salts on the apparent flow-activation energy of poly(AN/AEMP)2 copolymer solutions. The values of the apparent flow-activation energy of AN/AEMP copolymer solutions shows an obvious trend of decrease 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 the viscosity behavior of DMSO solutions of AN-AEMP copolymer have shown that the apparent viscosity of AN/AEMP copolymer solutions decreases prominently as the rotor speed up to 12 rpm. The changes of viscosity of solutions become less prominent as the rotor speed goes beyond 12 rpm and it accords with the character of Newtonian flow. With an increase of temperature, the apparent viscosity of AN/AEMP copolymer solutions shows a trend of decrease. 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 AN/AEMP copolymer. The apparent flow-activation energy of AN/AEMP copolymer solutions increases continuously with an increase of AN/AEMP copolymer concentration. The apparent viscosity of copolymer solutions decreases quickly with addition of KCl and NaCl. When the concentration of alkali salts goes beyond 0.02 mol L^{-1},

the viscosity shows a trend of increase. the apparent flow-activation energy of AN/AEMP 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.

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