

Stability of Acrylonitrile/Methyl Vinyl Ketone Copolymer Solutions

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ABSTRACT: Methyl vinyl ketone was successfully copolymerized with acrylonitrile for the first time. This was achieved with azobisisobutyronitrile as the initiator. The viscosity behavior of solutions of the acrylonitrile/methyl vinyl ketone copolymers was determined. The solution agreed with the character of Newtonian flow at the lower shearing rate. The addition of mechanical mixing obviously prevented an increase in the viscosity of the copolymer solutions. When dimethylformamide was used as an additive, the solution viscosity decreased monotonically. When H₂O was used as an additive, the viscosity of the copolymer solutions decreased continuously with concentrations of

H₂O up to 4 wt % and then increased. The viscosity of the copolymer solutions decreased continuously with concentrations of KCl and NaCl up to 0.03 mol/L and then increased. Within the first 10 h, there was a great drop in the viscosity of the copolymer solutions containing sodium ethoxide and sodium hydroxide, and then the viscosity appeared to increase. The composition with 12 wt % acetic acid in dimethyl sulfoxide could be considered to be a Θ solvent for the acrylonitrile/methyl vinyl ketone copolymers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3377–3381, 2006

Key words: additives; copolymerization; rheology; viscosity

INTRODUCTION

The stability of spinning dopes for the spinning of acrylic fibers is an important problem.¹ Spinning dopes are usually prepared at temperatures considerably higher than extrusion temperatures, and long periods are required for the settlement of deaeration. In fiber technology, acrylonitrile (AN) polymer solutions that rapidly cool to the processing temperature tend gradually to the equilibrium state, which is accompanied by the variation of the viscosity properties. Concentrated polar AN polymer solutions exhibit intense molecular interactions, and some examples illustrating the aging phenomena of acrylic polymer have been observed and reported in the literature;^{2,3} the addition of additives may vary the viscosity of AN polymer solutions.^{4,5} To our knowledge, there are only a few reports on dilute AN copolymer solutions, but there are almost no reports on concentrated AN copolymer solutions with methyl vinyl ketone (MVK) as a comonomer. With this in mind, we studied the stability of AN/MVK copolymers. In this study, a solvent water suspension technique was used to synthesize a

copolymer. The viscosity was controlled and determined with an NDJ-4 rotary viscosimeter (Shanghai Instruments, Inc., Shanghai, China). The effects of mechanical mixing, composition of the solvent, and additives on the viscosity of AN/MVK copolymer solutions were contrastively studied.

EXPERIMENTAL

Materials

AN (Shanghai Chemical Reagents Co., Shanghai, China; analytical-reagent grade) was vacuum-distilled from CaH₂ just before polymerization. MVK (Shanghai Chemical Reagents; analytical-reagent grade) was used as a comonomer. Azobisisobutyronitrile (AIBN) was used as an initiator and was recrystallized from ethanol before use. Poly(vinyl alcohol) (PVA) was obtained from Shanghai Chemical Resin Industry (Shanghai, China) and used as a suspending agent. Deionized water and dimethyl sulfoxide (DMSO), supplied by Taigu Chemical Plant (Taigu, China), were adopted as the polymerization media.

Copolymerization

A typical example of the general procedure was as follows. Required amounts of AN, MVK, PVA, AIBN, deionized water, and DMSO were placed in a flask, which was continuously flushed with ultrapure nitrogen. The flask was wholly immersed in a temperature-

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TABLE I
Important Parameters of Copolymerization

H ₂ O/DMSO (v/v)	AN/MVK (w/w)	Oxygen concentration in the copolymer (wt %)	MVK concentration in the copolymer (wt %)
90/10	98/2	0.457	1.999

Conditions: [AN] = 4.5 mol/L; [AIBN] = 0.008 mol/L; [PVA] = 0.22g/L; time = 2 h; temperature = 60°C.

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 *in vacuo* until it reached a constant weight. Copolymer samples were obtained.

Characterization

An elemental analysis of the copolymers was carried out with a PE 2400 elemental analyzer (Perkin Elmer, Inc., Shelton, CT) to determine the oxygen content. The viscosity of the copolymers solutions with the same copolymer content was measured with the NDJ-4 rotary viscosimeter under different conditions.

RESULTS AND DISCUSSION

Copolymer composition

The H₂O/DMSO suspension technique was used to synthesize the AN/MVK copolymer. Some important parameters and polymerization conditions of the copolymer are shown in Table I. Pure AN/MVK copolymers were synthesized by this technique. The composition of the AN/MVK copolymers was determined from the oxygen concentration in the copolymers.

Flow action of the copolymer solutions

The viscosity of the AN/MVK copolymer solutions at different shearing rates at 40°C was determined with the NDJ-4 rotary viscosimeter. The AN/MVK copolymer was dissolved in the solvent DMSO, and this yielded a 15 wt % solution. The solution was stirred for 2 h at 40°C until a transparent and viscous complex was obtained. The shearing rate was proportional to the rotor speed. The shearing rate was calculated as follows:⁶

$$\gamma = \frac{2wR^2}{(R^2 - r^2)} \quad (1)$$

where γ is the shearing rate; w is the rotor speed; and r and R are the radii of the rotor and beaker, respec-

TABLE II
Effect of the Shearing Rate on the Viscosity
of the Copolymer Solutions

Viscosity (Pas)	Shearing rate (s ⁻¹)			
	19	38	76	152
	369.6	373.2	367.4	371.5

tively. The experimental results are given in Table II. There was no effect of the shearing rate on the apparent viscosity of the solutions with an increase in the shearing rate. This agreed with the character of Newtonian flow. Roychen et al.⁷ reported the same result. It may be concluded that the copolymer solutions showed Newtonian flow at the lower shearing rate and that the viscosity was independent of the shearing rate.

Effect of the stirring rate on the viscosity of the copolymer solutions

The influence of the mechanical mixing on the viscosity of the copolymer solutions was studied through variations in the stirring rate from 0 to 510 s⁻¹, and the copolymer solutions were kept at 40°C. The viscosity of the AN/MVK copolymer solutions was determined with a concentration of 15 wt % at a constant shearing rate of 76 s⁻¹. Figure 1 illustrates the effect of the stirring rate on the viscosity-time characteristics for the AN/MVK copolymer solutions. The viscosity of the copolymer solutions at rest increased continuously with time, but the increase in the viscosity of the copolymer solutions was considerably reduced by the mechanical mixing. The changes in the viscosity of the solutions with a stirring rate of 510 s⁻¹ were less prominent than those of solutions with a stirring rate of 255 s⁻¹. The addition of the mechanical mixing apparently led to the depolymerization of the AN/

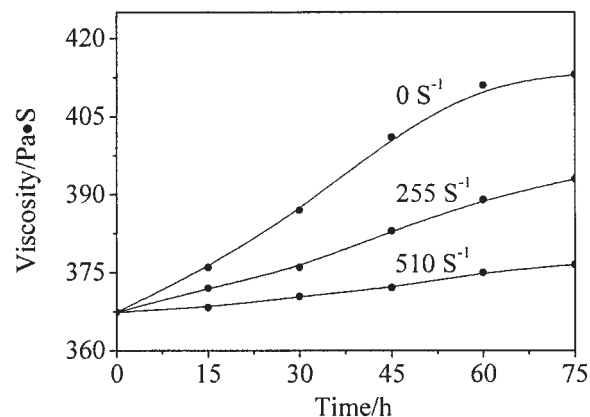


Figure 1 Effect of the stirring rate on the viscosity of the copolymer solutions.

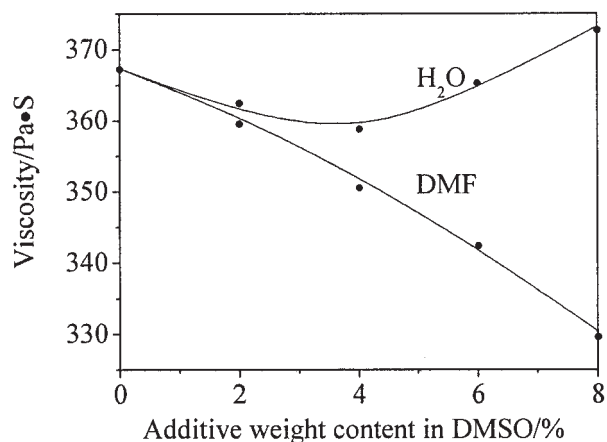


Figure 2 Effect of the additives on the viscosity of the copolymer solutions.

MVK copolymers, prevented the formation of aggregates, and stabilized the original structures of the solutions.

Effect of the solvent composition on the viscosity of the copolymer solutions

The composition of the solvent used in the preparation of the copolymer solutions considerably affected the viscosity properties and stability of the copolymer solutions. Dimethylformamide (DMF) and H₂O were good and poor solvents, respectively, for the AN/MVK copolymer, and they were used as additives. The effect of the solvent composition on the viscosity of the copolymer solutions was studied through variations in the contents of the additives in DMSO (from 0 to 8 wt %) at a constant shearing rate of 76 s⁻¹, and the mixture was kept at 40°C. The concentration of the AN/MVK copolymer in the solutions was kept at 15 wt %. Figure 2 illustrates the viscosity of the copolymer solutions as a function of the additive content in DMSO. When DMF was used as an additive, the solution viscosity decreased monotonically, as would be expected from the stronger solvent power of DMF (with respect to DMSO). When H₂O was used as an additive, the viscosity of the copolymer solution decreased continuously with the concentrations of H₂O up to 4 wt % and then increased. In concentrated copolymer solutions, two opposite effects of the solvent power on the viscosity were expected. On the one hand, some shrinkage of molecular coils reduced the viscosity. On the other hand, the reduction of the solvent power led to increased polymer-polymer interactions, promoted aggregation, and generally destabilized the solutions.⁸ The addition of increasing amounts of H₂O to DMSO reduced the solvent power continuously, and the viscosity minima reflected the

competition between chain-coiling and polymer-interaction effects. At a high concentration of H₂O, the solution formed solid and elastic gels.

Effect of the alkali salts on the viscosity of the copolymer solutions

The influence of the alkali salts on the viscosity of the AN/MVK copolymer solutions was studied through variations in the concentration of the alkali salts from 0 to 0.04 mol/L at a constant shearing rate of 76 s⁻¹, and the mixture was kept at 40°C. The concentration of the AN/MVK copolymer in the solutions was kept at 15 wt %. Figure 3 shows changes in the viscosity with the addition of KCl and NaCl. The viscosity of the copolymer solutions decreased continuously as the concentrations of KCl and NaCl increased to 0.03 mol/L and then increased. The changes in the viscosity of the solutions containing KCl were less prominent than those of solutions containing NaCl.

In the literature,⁹ factors have been reported 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 were great salt effects when alkali salts were placed in a DMSO solvent. Alkali salts were decomposed into ions because of a solvation effect (i.e., Na⁺, K⁺, and Cl⁻). Intermolecular interactions were reduced by Na⁺ and K⁺, and this led to a reduction of the association degree of high molecular chains. Entanglement networks of high molecular chains were destroyed. With an increase in the alkali salt concentration, the rate of disentanglement and slippage was faster than that of entanglement. The introduction of alkali salts KCl and NaCl produced a decrease in the viscosity of the copolymer solutions. When the alkali salt concentration

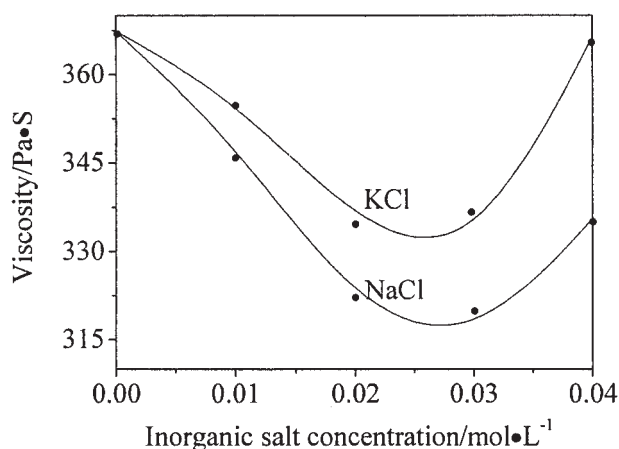


Figure 3 Effect of the alkali salts on the viscosity of the copolymer solutions.

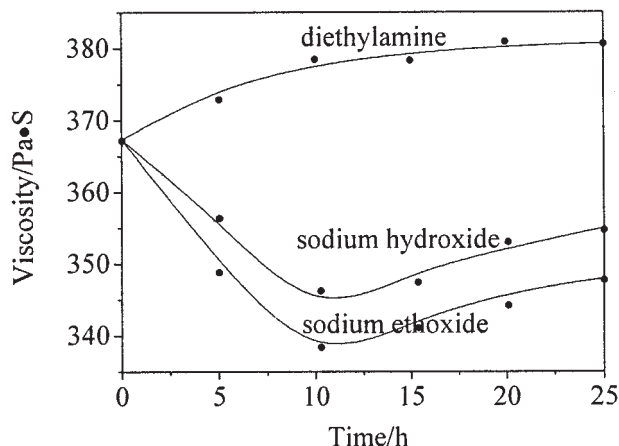


Figure 4 Effect of the base on the viscosity of the copolymer solutions.

went beyond 0.03 mol/L, the free volume in the copolymer solutions was mostly occupied. The viscosity of the copolymer solutions rose slowly.

Effect of the base on the viscosity of the copolymer solutions

Two strong bases, such as sodium ethoxide and sodium hydroxide, and a weak base, diethylamine, were used in this experiment. As soon as the AN/MVK copolymer was added to the DMSO–base mixture, the copolymer dissolved, and coloration occurred simultaneously. The solution containing diethylamine did not become as dark as the solution containing sodium ethoxide and sodium hydroxide. The influence of the alkali salts on the viscosity of the AN/MVK copolymer solutions was studied with a base concentration of 0.02 mol/L and a constant shearing rate of 76 s^{-1} ; the mixture was kept at 40°C . The concentration of the AN/MVK copolymer in the solutions was kept at 15 wt %. Figure 4 shows a plot of the viscosity against time. Within the first 10 h, there was a great drop in the viscosity of the copolymer solutions containing the strong base, and then the viscosity appeared to increase. As soon as the strong base was added to the polymer solutions, the intermolecular interactions of the polymer chains were reduced, and this led to a decrease in the association degree of high molecular chains. Entanglement networks of high molecular chains were destroyed. Thus, the addition of sodium ethoxide and sodium hydroxide produced a decrease in the viscosity of the copolymer solutions. Batty and Guthrie¹⁰ indicated that the rapid viscosity drop was due to random chain scission and the polymer chains being coiled tightly. Bashir et al.¹¹ also reported an increase in the viscosity with sodium hydroxide after

an initial drop. The viscosity increase was probably due to a limited amount of crosslinking.

The viscosity of the copolymer solutions containing the weak base did not drop but instead increased in the first 10 h. After a period of 10 h, changes in the solution viscosity became less prominent, and this agreed with the literature.^{11,12}

Effect of acetic acid on the viscosity of the copolymer solutions

As an extension of viscometric studies, the effect of acetic acid on the viscosity of the copolymer solutions was studied. For this work, the copolymer was dissolved in DMSO, and the acetic acid was carefully added to give the required composition of the mixed solvent. The effect of the solvent composition on the viscosity of the copolymer solutions was studied through variations in the contents of the additive in DMSO from 0 to 18 wt % at a constant shearing rate of 76 s^{-1} , and the mixture was kept at 40°C . The concentration of the AN/MVK copolymer in the solutions was kept at 15 wt %. The results are given in Figure 5. The values of the viscosity of the copolymer solutions suddenly dropped at 12 wt % acetic acid in DMSO. The composition with 12 wt % acetic acid in DMSO could be considered a Θ solvent¹³ for the AN/MVK copolymer.

CONCLUSIONS

Laboratory studies of the viscosity behavior of DMSO solutions of AN/MVK copolymers showed no effect of the shearing rate on the apparent viscosity of the solutions with an increase in the shearing rate at lower shearing rates, and this accorded with the character of Newtonian flow. The increase

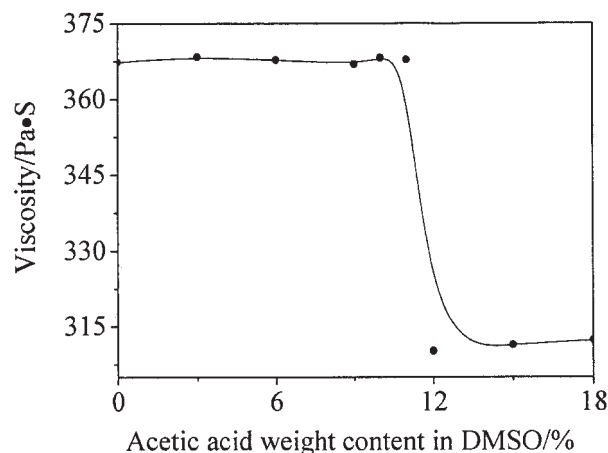


Figure 5 Effect of acetic acid on the viscosity of the copolymer solutions.

in the viscosity of the copolymer solutions was considerably reduced by the mechanical mixing. When DMF was used as an additive, the solution viscosity decreased monotonically. When H₂O was used as an additive, the viscosity of the copolymer solution decreased continuously with concentrations of H₂O up to 4 wt % and then increased. The viscosity of the copolymer solutions decreased continuously with the concentrations of KCl and NaCl up to 0.03 mol/L and then increased. The changes in the viscosity of the solutions containing KCl became less prominent than those of solutions containing NaCl. Within the first 10 h, there was a great drop in the viscosity of the copolymer solutions containing sodium ethoxide and sodium hydroxide, and then the viscosity appeared to increase. The composition with 12 wt % acetic acid in DMSO could be considered a Θ solvent for the AN/MVK copolymer.

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