

Viscosity Behavior of Acrylonitrile–Ammonium Itaconate Copolymer Solutions in Dimethyl Sulfoxide

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Received 26 January 2004; accepted 19 April 2004

DOI 10.1002/app.20840

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The viscosity behavior of dimethyl sulfoxide (DMSO) solutions of acrylonitrile–ammonium itaconate copolymer is discussed. The intrinsic viscosity was determined by an Ubbelohde viscometer. It is shown that an increase in the viscosity of acrylonitrile–ammonium itaconate copolymer solutions with time is considerably reduced by mechanical mixing. The viscosity of copolymer solutions with dimethyl formamide as an additive decreases monotonically. The viscosity of copolymer solutions decreases with the addition of H₂O, and as the content of H₂O in DMSO goes beyond 3 wt %, the viscosity shows a trend toward increase. The intrinsic viscosity decreases quickly with the addition of NaCl. As the concentration of NaCl goes beyond 0.015 mol/L, the viscosity increases slowly. The viscosity of co-

polymer solutions containing sodium ethoxide and sodium hydroxide appears to increase after an initial drop. The viscosity of copolymer solutions upon the addition of diethylamine increases continuously with time and changes in viscosity become less prominent after a period of a few hours. The effects of bases on the tacticity of highly isotactic copolymers follow the order of base strength. Diethylamine is more effective for moderating the stabilization exotherm of highly isotactic copolymers compared to sodium ethoxide and sodium hydroxide. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2622–2626, 2004

Key words: viscosity; additive; isotacticity; NMR

INTRODUCTION

In fiber technology, the intrinsic viscosity of spinning dopes for the spinning of acrylic fibers is an important problem.¹ Spinning dopes are usually prepared at temperatures that are considerably higher than extrusion temperatures and long periods are required for the settlement of deaeration. Acrylonitrile (AN) polymer solutions rapidly cooled to the processing temperature tend gradually to the equilibrium state, which is accompanied by a variation of viscosity properties. It is important to select a highly stereoregular acrylonitrile polymer for high-tenacity acrylic fibers. The cationic and anionic polymerization techniques have been successfully used to prepare highly isotactic AN polymers.^{2,3} The dissolution of isotactic acrylonitrile polymer occurs with great difficulty. It is disadvantageous and dangerous for the preparation and transportation of spinning dope. Many reagents were reported in the literature⁴ as pretreatments for decreasing the viscosity of AN polymers and moderating the stabilization exotherm. In one case, the addition of LiCl to the spinning dope decreases the viscosity of

the dopes and moderates the stabilization exotherm of precursors.⁵ To our knowledge, there are only a few reports on ordinary AN copolymer dilute solutions, but there are almost no reports on the solutions of highly isotactic AN copolymer with ammonium itaconate (AIA) as comonomer. With this view, studies were undertaken on the viscosity behavior of highly isotactic AN/AIA copolymer in dimethyl sulfoxide (DMSO) solvent. In this study, different polymerization techniques were used to synthesize the AN/AIA copolymer. The intrinsic viscosity was controlled and determined by an Ubbelohde viscometer. The effects of mechanical mixing and the composition of solvent and additives on the viscosity behavior of AN/AIA copolymer solutions were studied.

EXPERIMENTAL

Materials

AN Monomers were supplied as extra pure grade by Tianjin Chemical Resin Industry (Tianjin, China) and distilled to remove inhibitors before use. DMSO was supplied by Shanghai Chemical Resin Industry (Shanghai, China). AIA was obtained by neutralization of itaconic acid supplied as extra pure grade by Tianjin Chemical Resin Industry and NH₃. Highly isotactic acrylonitrile–ammonium itaconate copoly-

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TABLE I
Important Parameters of AN-AIA Copolymers

Code	Polymerization technology	AN/AIA (w/w)	$[\eta]$	Oxygen in copolymer (wt%)	AIA in copolymer (wt%)	Triad isotacticity
MAP	Matrix-anion	98/2	1.74	0.7881	1.995	0.612
WSP	Water-DMSO suspension	98/2	2.76	0.7897	1.999	0.294

mer (MAP) was prepared by matrix-anion polymerization technology. The details of the polymerization technology are given elsewhere.^{6,7} For comparison, ordinary acrylonitrile-ammonium itaconate copolymer (WSP) synthesized by water-solvent (DMSO) suspension polymerization⁸ was also used. Characteristics of the copolymers are given in Table I.

Characterization

Elemental analysis of the copolymers was carried out using a PE 2400 elemental analyzer to determine the oxygen content in these copolymers.

The intrinsic viscosity ($[\eta]$) of these copolymers in DMSO was determined using an Ubbelohde viscometer kept vertically in a thermostat bath at the required temperature, $25 \pm 0.05^\circ\text{C}$.

Nuclear magnetic resonance (NMR) measurements were carried out using a Bruker-DPX300 spectrometer (German) operating at 75 MHz. Analysis was made according to the manner of Inoue and the isotacticity discussed here is defined by three monomer units⁶ (triad tacticity).

The exotherm of the AN/AIA copolymer was determined by differential scanning calorimetry (DSC), which was carried out on a Perkin-Elmer Delta thermal analyzer. DSC studies were performed at heating rate of $5^\circ\text{C}/\text{min}$ in oxygen with sample of 2.5 mg, much like the conditions of stabilization of polyacrylonitrile precursors.

RESULTS AND DISCUSSION

Effect of stirring rate on the viscosity of copolymer solutions

An influence of mechanical mixing on the intrinsic viscosity of the copolymers was studied by varying the stirring rate from 0 to 30 revolutions/min. Figure 1 shows the effects of the mechanical mixing, which is the stirring rate, on viscosity-time characteristics of AN/AIA copolymer solutions. The viscosity of copolymer solutions at rest increases continuously with time, but the increase in viscosity is considerably reduced by mechanical mixing. It is shown that the addition of mechanical mixing apparently prevents the formation of aggregates and stabilizes the original structure of the solution.

Effect of solvent composition on the viscosity of copolymer solutions

The composition of the solvent used in the preparation of copolymer solutions can considerably affect their viscosity properties and stability. Dimethyl formamide (DMF) and H_2O are good and poor solvents for AN/AIA copolymers, respectively, and were used as additives. The effect of solvent composition on the viscosity of the copolymer solutions was studied by varying the content of additives in DMSO from 0 to 8 wt %. Figure 2 illustrates the viscosity of copolymer solutions as a function of additive content in DMSO. In the case of DMF used as an additive, the intrinsic viscosity decreases monotonically, as would be expected from the stronger solvent power of DMF than DMSO. In the case of H_2O used as an additive, the viscosity of the copolymer solution decreases continuously as the concentration of H_2O goes to 3 wt % and then increases. Changes of viscosity of MAP copolymers are less prominent compared to those of WSP copolymers. That is to say, the effects of solvent composition on ordinary copolymers are greater compared to the effects of solvent composition on highly isotactic copolymers.

In AN/AIA copolymer solutions two opposite effects of solvent power on viscosity can be expected. On one hand, some shrinkage of the molecular coils

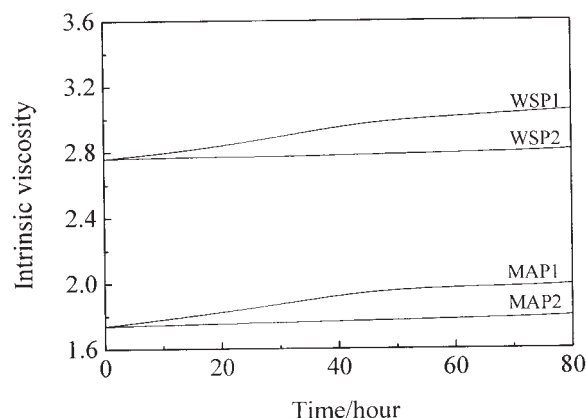


Figure 1 Effect of stirring rate on the viscosity of copolymer solutions. WSP1: WSP copolymers at rest; WSP2: WSP copolymers with a stirring rate of 30 revolutions/min; MAP1: MAP copolymers at rest; MAP2: MAP copolymers with a stirring rate of 30 revolutions/min.

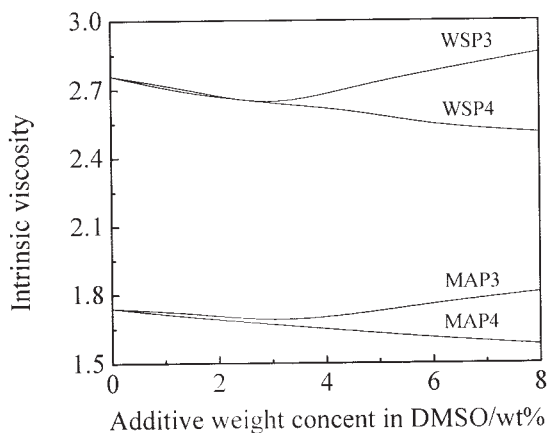


Figure 2 Effect of additives on the viscosity of copolymer solutions. WSP3: WSP copolymers with H₂O as an additive; WSP4: WSP copolymers with DMF as an additive; MAP3: MAP copolymers with H₂O as an additive; MAP4: MAP copolymers with DMF as an additive.

would reduce viscosity; on the other hand, the reduction of solvent power leads to increased polymer-polymer interactions, promotes aggregation, and generally destabilizes the solution.⁹ The addition of increasing amounts of H₂O to DMSO reduces the solvent power continuously; minima of viscosity reflect the competition between chain-coiling and polymer interaction effects. At high concentrations of H₂O, the solution forms solid and elastic gels.

Effect of alkali salts on the viscosity of copolymer solutions

The influence of alkali salts on the intrinsic viscosity of AN/AIA copolymer solutions was studied by varying the concentration of alkali salts from 0 to 0.030 mol/L. Figure 3 shows the changes in intrinsic viscosity of copolymers with the addition of NaCl. The viscosity of both MAP and WSP copolymers decreases continuously as the concentrations of NaCl rises to 0.015 mol/L and then increases.

There are great salt effects when alkali salts are added to DMSO solutions of AN/AIA.¹⁰ Alkali salts decompose into ions, i.e., Na⁺, Cl⁻. Intermolecular interactions of AN/AIA copolymer chains in DMSO solvent are reduced by Na⁺, which leads to a decrease in the entanglement of AN/AIA copolymer chains. Disentanglement and slippage of the entanglement networks of AN/AIA copolymer chains shows an obvious trend of increase. With an increase in the alkali salts concentration, the rate of disentanglement and slippage is faster compared to that of entanglement, so that the introduction of alkali salts such as NaCl produces a decrease in the viscosity of AN/AIA copolymer solutions. When the alkali salt concentration is above 0.015 mol/L, the free volume in the solutions is

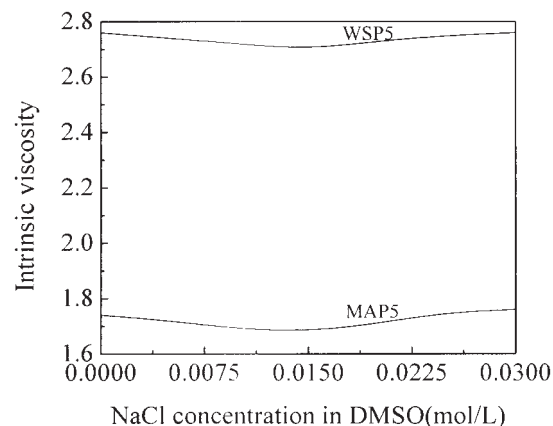


Figure 3 Effect of alkali salts on the viscosity of copolymer solutions. WSP5: WSP copolymers treated with NaCl; MAP5: MAP copolymers treated with NaCl.

mostly occupied and the free area in which AN/AIA copolymer relatively move becomes smaller. The intrinsic viscosity of the copolymer starts to rise slowly.

Effect of base on the viscosity of copolymer solutions

For our initial experiment, two strong bases, such as sodium ethoxide and sodium hydroxide, and a weak base, diethylamine, were used. As soon as the AN/AIA copolymer was added to the DMSO-base mixture, the copolymer dissolved, and coloration occurred simultaneously. The solution containing diethylamine did not turn as dark as the solution containing sodium ethoxide and sodium hydroxide.

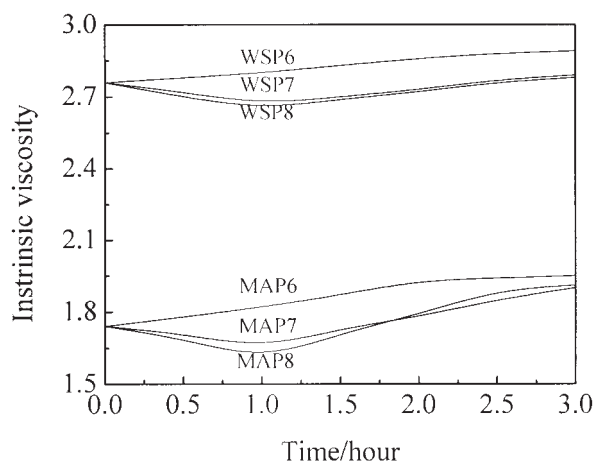


Figure 4 Effect of base on the viscosity of copolymer solution. WSP6: WSP copolymers treated with diethylamine; WSP7: WSP copolymers treated with sodium hydroxide; WSP8: WSP copolymers treated with sodium ethoxide; MAP6: MAP copolymers treated with diethylamine; MAP7: MAP copolymers treated with sodium hydroxide; MAP8: MAP copolymers treated with sodium ethoxide.

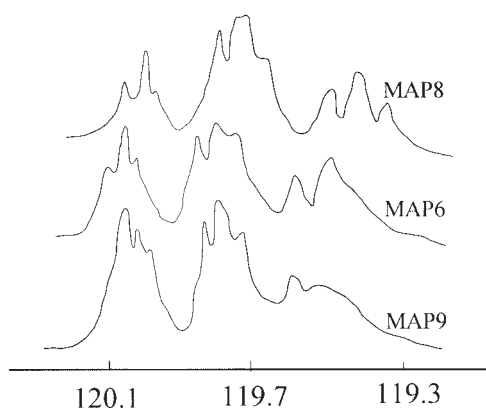


Figure 5 Expansion of NMR spectrum of MAP copolymers. MAP6: MAP copolymers treated with diethylamine; MAP8: MAP copolymers treated with sodium ethoxide; MAP9: untreated MAP copolymers.

The influence of bases on the viscosity of AN/AIA copolymer solutions was studied by keeping the concentration of the base at 0.02 mol/L. Figure 4 shows a plot of viscosity against time. Changes in the viscosity of MAP copolymers are more prominent compared to those of WSP copolymers. That is to say, the effects of a base on highly isotactic copolymers are greater compared with those of ordinary copolymers.

It is evident from Figure 4 that within the first hour there is a great drop in viscosity of the copolymer solutions containing a strong base, and then the viscosity appears to increase. Batty and Guthrie¹¹ indicated that the rapid viscosity drop is due to random chain scission and the polymer chains would coil tightly. Bashir et al.¹² also reported an increase in viscosity with sodium hydroxide after an initial drop. The viscosity increase is probably due to a limited amount of crosslinking. It is important to note that gelation was observed and a dark red-black gel was formed 15 h later.

The viscosity of copolymer solutions containing a weak base does not decrease but increases with time. The changes of viscosity become less prominent after

a period of a few hours, which is in agreement with the literature.¹³

Triad tacticity of nitrile group of AN/AIA copolymers was determined using a Bruker-DPX300 spectrometer. The comparison of triad tacticity of MAP copolymers treated with a base with that of untreated MAP copolymers in Figure 5 shows that the addition of base causes an obvious change in the tacticity of MAP copolymers. There is a simultaneous increase in syndiotactic triads along with a remarkable drop in isotactic triads; a certain proportion of isotactic sequences is converted to syndiotactic sequences, which is in agreement with the literature.¹⁴ This shows that the strong base abstracts the methine proton from the isotactic triads and the nitrile group rearranges to a syndiotactic configuration.

Table II shows the changes in tacticity for the copolymers treated with bases. As shown in Table II, the weak bases behave the same as strong ones, but changes in the tacticity of copolymers are less prominent. The effects of alkalis on the tacticity of polymers follow the order of base strength: sodium ethoxide > sodium hydroxide > diethylamine. The effects of bases on the tacticity of WSP copolymers are less obvious.

Effect of bases on the stabilization exotherm of MAP copolymers

It is reported in the literature¹⁵ that ammonium and amine were used as comonomers in polymerization to moderate the stabilization exotherm of polyacrylonitrile. In this study, the effect of bases on the stabilization exotherm of copolymers was also studied. The experimental results are given in Table III. It is obvious that diethylamine is more effective for moderating the stabilization exotherm of polymers compared to sodium ethoxide and sodium hydroxide. The obtained DSC curves of MAP treated with alkalis are shown in Figure 6. For untreated MAP, there is only one exothermic peak; but for MAP treated with diethylamine, there are two separated peaks. Comparing the DSC

TABLE II
Effect of Alkalis on Tacticity of AN-AIA Copolymers

Sample	Triad tacticity		
	Isotacticity	Syndiotacticity	Disordered structure
Untreated MAP	0.612	0.286	0.102
MAP treated with sodium ethoxide	0.419	0.298	0.283
MAP treated with sodium hydroxide	0.483	0.294	0.223
MAP treated with diethylamine	0.578	0.291	0.131
Untreated WSP	0.294	0.512	0.217
WSP treated with sodium ethoxide	0.236	0.521	0.243
WSP treated with sodium hydroxide	0.258	0.518	0.224
WSP treated with diethylamine	0.273	0.526	0.201

curves, MAP treated with diethylamine has the lower start exothermal reaction temperature. The two separated peaks and lower start temperature make the exothermic reaction temperature of MAP wider than one sharply concentrated temperature zone, alleviate the exothermic reaction, and moderate the stabilization exotherm of polyacrylonitrile; as a result, to some extent the fusion of polymers is avoided. Heating MAP polymers in an oxidizing atmosphere causes formation of a cyclic structure consisting of naphthyridine rings and crosslinking. The ammonia or amine groups in diethylamine are believed to act as catalysts in the cyclization reaction.

CONCLUSION

Laboratory studies of the intrinsic viscosity of acrylonitrile–ammonium itaconate copolymer showed that the increase in viscosity, which is very strong in copolymer solutions at rest, is considerably reduced by mechanical mixing. Effects of solvent composition on ordinary copolymers are greater compared to the effects on highly isotactic copolymers. The viscosity of copolymer solutions with DMF as an additive decreases monotonically. The viscosity of copolymer solutions decreases continuously with the addition of H₂O, and when the content of H₂O in DMSO goes beyond 3 wt %, the viscosity shows a trend of increase. The viscosity of copolymer solutions decreases quickly with the addition of NaCl. When the concentration of alkali salts goes beyond 0.015 mol/L, the viscosity shows a trend of increase. There is a great drop in viscosity of copolymer solutions containing sodium ethoxide and sodium hydroxide within the first hour, and then the viscosity appears to increase. The viscosity of copolymer solutions containing diethylamine does not drop but increases in the first hour, and the changes in solution viscosity become less prominent after a period of a few hours. The effects of bases on the tacticity of ordinary copolymers are less obvious and the effects of bases on the tacticity of

TABLE III
Effect of Alkalis on Stabilization Exotherm of MAP Copolymers

Sample	T_i (°C)	T_f (°C)	ΔQ (mJ · mg ⁻¹)
Untreated MAP	261.7	304.6	564.3
MAP treated with sodium ethoxide	248.1	298.7	538.7
MAP treated with diethylamine	218.3	278.8	504.3

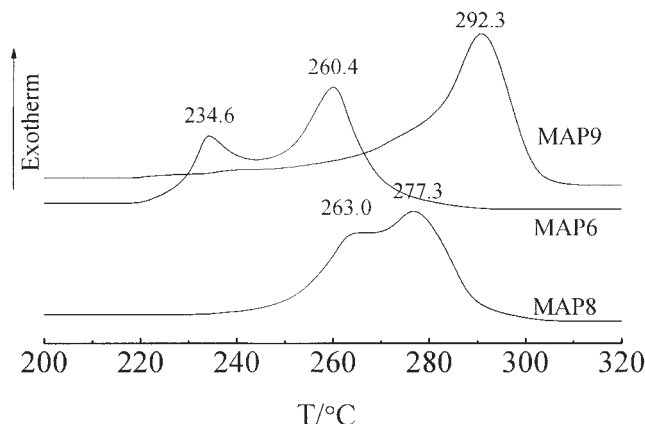


Figure 6 DSC curves of MAP copolymers. MAP6: MAP copolymers treated with diethylamine; MAP8: MAP copolymers treated with sodium ethoxide; MAP9: untreated MAP copolymers.

highly isotactic copolymers follow the order of base strength. Diethylamine is more effective for moderating the stabilization exotherm of AN/AIA copolymers prepared by matrix-anion polymerization technology than sodium ethoxide and sodium hydroxide.

The authors thank the National 863 Project (Contract No.2002AA304130) for providing financial assistance.

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