Diffusion Coefficient of DMSO in Polyacrylonitrile Fiber Formation

Liang Ying,[1] Chen Hou,[2] Wang Fei[2]

[1]Office of Science and Technology, Yantai Normal University, Yantai 264025, People's Republic of China
[2]College of Chemistry and Materials Science, Yantai University, Yantai 264025, People's Republic of China

ABSTRACT: A H_2O/dimethyl sulfoxide(DMSO) mixture was used as the coagulation bath for the wet-spun process of acrylonitrile/ammonium itaconate copolymers fibers. Diffusion coefficient of DMSO in the protofibers prepared by acrylonitrile/ammonium itaconate copolymers was determined. It has been found that diffusion coefficient of DMSO outflow of the protofibers prepared by acrylonitrile/ammonium itaconate copolymers synthesized by the solution polymerization is highest compared with those of acrylonitrile/ammonium itaconate copolymers synthesized by H_2O/DMSO mixture suspension polymerization and the aqueous suspension polymerization. With an increase of copolymer concentration in the dope, diffusion coefficient of DMSO decreases continuously. Diffusion coefficient of DMSO increases along with the bath temperature, but the changes of diffusion coefficient values are less prominent as temperature goes beyond 60°C. When DMSO concentration in the coagulation bath was 55 wt %, the value of the diffusion coefficient of DMSO was minimal. Diffusion coefficient of H_2O increases with the jet stretch minus ratio increasing. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4447–4451, 2006

Key words: diffusion; fiber; copolymerization

INTRODUCTION

Wet spinning is one of the main methods of producing polyacrylonitrile precursors.[1,2] The mechanism of the acrylic fiber formation by wet-spinning technique is quite complex and involves a combination of rheological and diffusional phenomena. As the very viscous dope leaves the spinneret to enter the coagulation bath, there are two diffusional motions, which carry solvent out of the protofiber to the bath and coagulate from the bath to the protofiber; when the concentrations of polymer, solvent, and coagulate overcome the phase equilibrium conditions, precipitation of the polymer in fibrillar form takes place.[3] Because of the dependence of subsequent textile properties of the fiber on its structure, particularly on the regularity of the cross-sectional shape, the integrity of the external skin, and the number and size of voids, accurate knowledge of the phenomena regulating these features is of great importance.[4] To our knowledge, earlier studies were just empirical attempts to correlate the actual spinning variables with the final properties of the fibers,[5,6] without any investigation on the dynamics of the phenomenon, and there is almost no reports on diffusion coefficient of solvent in polyacrylonitrile fiber formation process. In this study, H_2O/dimethyl sulfoxide (DMSO) mixture was used as the coagulation bath, acrylonitrile (AN)/ammonium itaconate (AIA) copolymers were used to prepare the spinning dopes. For estimating diffusion coefficient of the solvent, many possible technical designs of wet spinning techniques in fiber formation process were applied. Effect of coagulation variables on the diffusion coefficient of solvent was contrastively studied.

EXPERIMENTAL

Spinning dope and its preparation

AN (Shanghai Chemical Reagents Co., A. R. grade, Shanghai, China) was vacuum distilled from CaH_2, just before polymerization. Comonomer AIA was obtained by neutralization of itaconic acid supplied as extra pure grade by Tianjin Chemical Resin Industry (Tianjin, China) and NH_3. Azobisisobutyronitrile (AIBN; Shanghai Chemical Reagents Co., A. R. grade, Shanghai, China) was used as an initiator and recrystallized from ethanol before use. Polyvinyl alcohol (PVA; Shanghai Chemical Reagents Co., A.R. grade, Shanghai, China) was used as suspending agent. Deionized water (self made) and dimethyl sulfoxide (DMSO) supplied by Tianjin Chemical Resin Industry (Tianjin, China) were adopted as the polymerization medium.

Correspondence to: L. Ying (hettykyc@hotmail.com).

TABLE I
Characterization of AN/AIA Copolymers Prepared by Various Polymerization Technologies

Sample	Polymerization technique	AN/AIA (w/w)	Molecular weight (10^{-4})	Isotacticty (mm)
Poly(AN-AIA)l	DMSO solution		9.89	0.245
Poly(AN-AIA)2	H$_2$O/DMSO mixture suspension	98/2	27.65	0.297
Poly(AN-AIA)3	Aqueous suspension		45.12	0.343

Suspension polymerization, [H$_2$O/DMSO = 70/30 (w/w)] mixture suspension polymerization and DMSO solution polymerization were used to synthesize AN/AIA copolymers.[7,8] After a definite reaction time, the resultant mixture made by suspension polymerization and H$_2$O/DMSO mixture suspension polymerization were poured into a large amount of methanol for precipitation, and washed with methanol several times. The solvent and unreacted monomer in the resultant mixture was removed by the suction pump. Polymers were dried at 60°C under vacuum, and then weighed. Polymers were dissolved in DMSO to get a clear dope. The resulting AN/AIA copolymer solution made by solution polymerization can be directly used as the spinning dope after removal of excess solvent and unreacted monomers by the suction pump at 70°C.

Viscosities of AN/AIA copolymers were measured at 35°C in dimethyl formamide, by using an Ubbelohde viscometer (Shanghai Glass Co., Shanghai, China), and the molecular weight was calculated from the following equation[9]

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

where $[\eta]$ is the intrinsic viscosity of AN/AIA copolymer solution and M_w is the weight average molecular weight of AN/AIA copolymer.

The triad tacticities [(mm), (mr), (rr); m and r mean meso and racemo diad sequences, respectively] of AN/AM copolymers were determined on the basis of the Schaefer's assignment[10] from the ratio of intensities for the three nitrile carbon peaks in the ^{13}C NMR spectra. ^{13}C NMR spectra were recorded on a Bruker-DPX300 spectrometer (Bruker, German) in 2.5 wt % solution in deuterated dimethylsulfoxide (DMSO-d_6) at 80°C under the following operating conditions: complete decoupling mode; pulse delay time, 1.745 s; acquisition time, 0.655 s; pulse width, 5.5 μs (45° pulse); and accumulation, more than 3000 times.

The polymers code and the isotacticty are given in Table I. Tacticity of copolymers discussed here is defined by three monomer units (triad tacticty).

Fiber formation process

The obtained dope was deaerated, filtered, and then pumped through a spinneret (1000 holes, 0.06 mm/

hole, L/D = 1.2) to a coagulation bath. The protofibers were obtained by the complete coagulation. The cross sections of the protofibers were observed under high resolution scanning electron microscope JXA-840 (JEOL, Japan).

Characterization

The trace of DMSO and H$_2$O on the protofibers surface was completely absorbed by the filter paper after spinning process. The residual weight of the protofiber was composed of AN/AIA copolymer weight, solvent DMSO weight, and coagulate H$_2$O weight. AN/AIA copolymer weight was obtained by drying the protofibers in vacuum. The H$_2$O weight was immediately determined by evolved gas analysis (EGA) on a DT40 thermal analyzer (SHIMADZU Corp., Japan). EGA studies were performed at heating rate of 5°C/min in N$_2$, with the highest temperature of 130°C, and then the remainder was the residual weight of DMSO in the protofibers.

Diffusion coefficient (Da) of solvent DMSO was calculated using the Crank's method[11] by calculating DMSO weight outflow of the protofibers with time intervals of t in the coagulation bath. Crank's equation is represented as

$$D_a = \frac{\pi a^2}{16t}\left(\frac{C_t}{C_\infty}\right) \tag{1}$$

where D_a is the diffusion coefficient of DMSO, C_t is outflow weight of DMSO from the protofibers at time t, C_∞ is the equilibrium DMSO outflow weight from the complete coagulated protofibers, a is the radius of the protofiber, and t is the coagulation time.

The density of the precursors was measured according to the floating-sink action of the precursors. The n-heptane and tetrachloromethane were used as the solvent mixture.

RESULTS AND DISCUSSION

Calculation of diffusion coefficient

H$_2$O/DMSO mixture was used as the coagulation bath. Effect of time on DMSO residual content in the protofibers was discussed when DMSO concentration in the coagulation bath is 60 wt %, the coagulation
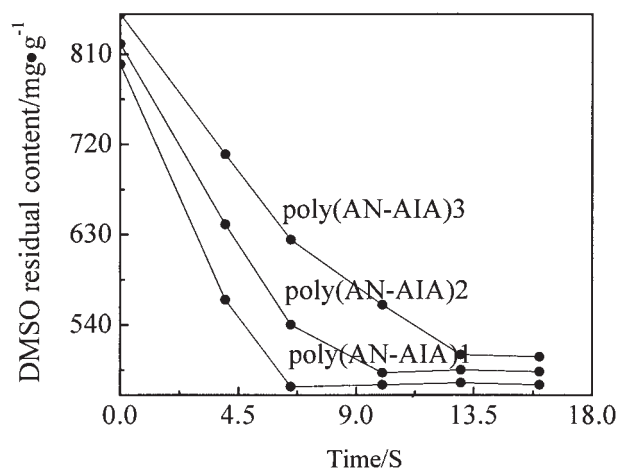
Figure 1 Plot of DMSO residual content in the protofibers versus time.

bath temperature is 60°C, the jet stretch minus ratio is −50%, concentration of AN/AIA copolymers prepared by DMSO solution polymerization, H_2O/DMSO mixture suspension polymerization and aqueous suspension polymerization in the dope are controlled at 20, 18, 15 wt %, respectively. Figure 1 shows DMSO residual content in the protofibers versus time. The protofibers prepared by DMSO solution polymerization reach equilibrium values in 6.5 s, whereas the protofibers prepared by H_2O/DMSO mixture suspension polymerization and aqueous suspension polymerization take 10 and 13 s to reach equilibrium, respectively.

Diffusion coefficients of H_2O and DMSO were calculated using the Crank's method, with a time interval of 8 s in the coagulation bath. Diffusion coefficients of DMSO in the protofibers prepared by poly(AN-AIA)1, poly(AN-AIA)2, and poly(AN-AIA)3 are 1.93×10^{-10}, 1.25×10^{-10}, and 0.965×10^{-10} $m^2 s^{-1}$, respectively. It is reported[12,13] that the diffusion of DMSO out of the protofibers is controlled by the stereo-tacticity and segmental mobility of the polymer chain, and to a considerable extent, by the gel and void structure in the protofibers. From Table I, the fraction value of stereospecific sequence of AN/AIA copolymers prepared by the aqueous suspension polymerization technique can reach 0.343. The fraction value of stereospecific sequence of AN/AIA copolymers prepared by the solution polymerization technique decreases to 0.245. Comparison of SEM images of the cross section of the protofibers prepared by AN/AIA copolymers in Figure 2 shows that there are prominent voids in the protofibers prepared by solution polymerization. It is evident from Table II that the density of the precursors manufactured by the protofibers prepared by the aqueous suspension polymerization is highest. Thus, the protofibers prepared by solution polymerization reach equilibrium faster be-

cause of the presence of the voids and low crystallinity.

Effect of polymer concentration on diffusion coefficient of DMSO

Effect of polymer concentration on diffusion coefficient of DMSO was studied by varying concentration of AN/AIA copolymers prepared by solution polymerization from 19 to 21 wt %, while keeping other factors constant. Figure 3 shows the changes of diffusion coefficient of DMSO as a function of polymer concentration in the dope. Diffusion coefficient of DMSO decreases continuously with an increase of polymer concentration up to 21 wt %. As the polymer concentration increases, the DMSO concentration gradient between the protofibers and the bath decreases, the viscosity of the dope increases quickly and the free volume in the copolymer solution is mostly occupied, so that osmosis of DMSO is more difficult.

Effect of bath temperature and composition on diffusion coefficient of DMSO

Because bath temperature and composition also play an important role in the factors that affect diffusion coefficient of DMSO, it is necessary to study diffusion coefficient of DMSO at the different bath temperature and composition.

Effect of the bath temperature on diffusion coefficient of DMSO out of the protofibers prepared by AN/AIA copolymers synthesized by solution polymerization while keeping other experimental parameters constant was discussed by varying temperature in the range of 45–70°C. As shown in Figure 4, diffusion coefficient of DMSO increases continuously with an increase of temperature, but the changes of diffusion coefficient values are less prominent at temperature beyond 60°C, which show a few disagreements with the values reported.[14]

In wet-spun process, values of diffusion coefficients of solvent always vary with changes of bath concentration. Effect of bath composition on diffusion coefficient of DMSO out of the protofibers prepared by
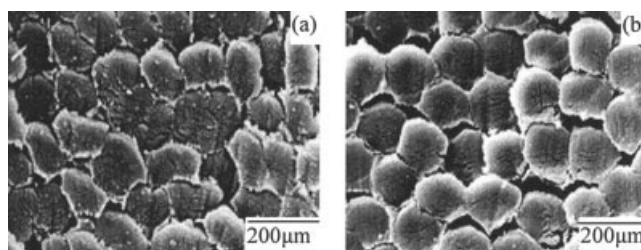
Figure 2 Comparison of SEM images of the protofibers prepared by different polymerizations (a) DMSO solution polymerization; (b) the aqueous suspension polymerization.

TABLE II
Comparison of the Protofibers Prepared by Various Polymerization Technologies

Sample	Polymerization technique	Density of the precursors (g/cm^3)	Number of voids
Poly(AN-AIA)1	DMSO solution	1.135	Few
Poly(AN-AIA)2	H$_2$O/DMSO mixture suspension	1.140	—
Poly(AN-AIA)3	Aqueous suspension	1.143	Least

AN/AIA copolymers synthesized by solution polymerization while keeping other experimental parameters constant was studied. It is evident from Figure 4 that there is a great drop in diffusion coefficient of DMSO as the bath concentration of DMSO up to 55 wt %, and then the coefficient appears to increase. The bath concentration of DMSO at which the values of diffusion coefficient of DMSO is minimal is governed by the gel formed in the protofibers.[15] With an increase of DMSO concentration in the bath, the gel density becomes higher, which makes the osmosis of DMSO more difficult. At DMSO concentration beyond 55 wt %, the gel becomes swollen and its density becomes lower, the diffusion of DMSO outflow of the protofibers becomes easy.

Effect of jet stretch minus ratio on diffusion coefficient of DMSO

The ease of fiber formation under continuous spinning conditions is decided by jet stretch minus ratio. The jet stretch ratio is generally accepted as a comprehensive index of the rheology and hydrodynamic process of wet spinning.[16] This term is defined as the ratio of the linear take-up rate at which protofibers are taken out of the coagulation bath to the linear rate at which spinning dope is extruded through the spinnerette holes. According to Han and Segal, the jet stretch ratio can be expressed as:

$$\phi = \frac{V_1 - V_2}{V_2} \tag{2}$$

Where ϕ is the jet stretch ratio, V1 is the linear velocity of the spinning dope in the spinnerette hole, V2 is the linear velocity of the filament at the take-up roller.

Effect of jet stretch minus ratio on diffusion coefficient of DMSO out of the protofibers prepared by AN/AIA copolymers synthesized by solution polymerization while keeping other experimental parameters constant was studied. Figure 5 shows that diffusion coefficient of DMSO increases from 1.83×10^{-10} to 2.07×10^{-10} when jet stretch minus ratio rises from -70 to -30%. According to the literature reported,[17] decreasing the values of jet stretch minus ratio is accompanied by decreasing bulk density and increasing numbers of voids. Increasing numbers of voids in the protofibers ease DMSO diffusion, and diffusion coefficient of DMSO shows a trend of increase.

CONCLUSIONS

Laboratory studies of the fiber formation process have shown that diffusion coefficient of DMSO out of the protofibers prepared by AN/AIA copolymers synthesized by solution polymerization is highest compared with those of AN/AIA copolymers synthesized by H$_2$O/DMSO mixture suspension polymerization and
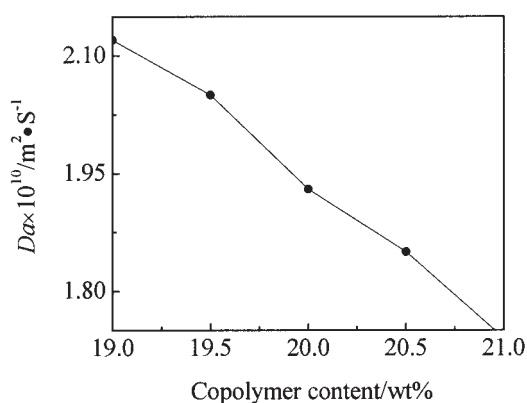

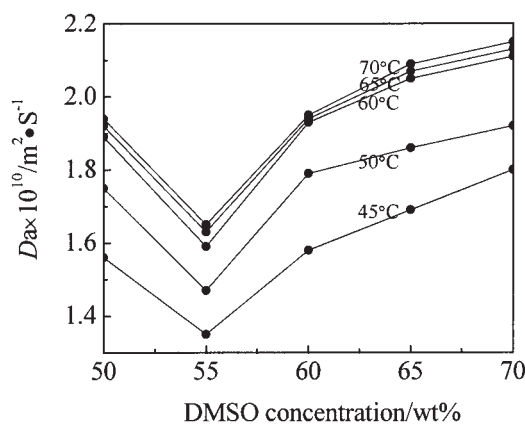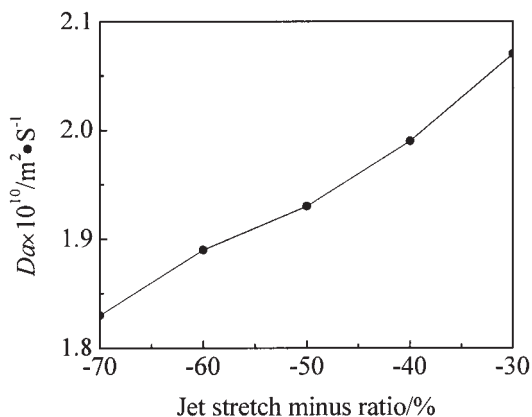**Figure 3** Relationship between of AN/AIA copolymer concentration and diffusion coefficient of DMSO.

Figure 4 Effect of the coagulation bath composition and temperature on the diffusion coefficient of DMSO.

Figure 5 Relationship between diffusion coefficient of DMSO and jet stretch minus ratio.

aqueous suspension polymerization. Diffusion coefficient of DMSO decreases continuously with an increase of polymer concentration in the dope. Diffusion coefficient of DMSO increases continuously with an increase of the bath temperature, but the changes of diffusion coefficient values are less prominent at temperature beyond 60°C. There is a great drop in diffusion coefficient of DMSO as the concentration of DMSO in the bath up to 55 wt %, and then the coefficient appears to increase. As the jet stretch minus ratio was progressively increased, there is a corresponding increase of diffusion coefficient of DMSO.

References

1. Datye, K. V. Synth Fibers 1996, 4, 11.
2. Andrej, Z. Fundamentals of Fiber Formation: The Science of Fiber Spinning and Drawing; Wiley: New York, 1976.
3. Thorne, D. J. J Appl Polym Sci 1970, 14, 103.
4. Rende, A. J Appl Polym Sci 1972, 16, 585.
5. Hersh, S. P.; Higgins, T.; Krause, D. H. W. J Appl Polym Sci 1963, 7, 411.
6. Chen, H.; Wang, C.; Liang, Y.; Cai, H. Chin J Chem Eng 2003, 11, 166.
7. Roychen, J.; Surekha, D.; Animesh, K. R. Polym Int 1991, 26, 89.
8. Kashyap, A. K.; Kalpagam, V. J Polym Sci 1979, 17, 225.
9. Bajaj, P.; Surya Kumari, M. Text Res J 1990, 113.
10. Schaefer, J. Macromolecules 1971, 4, 105.
11. Paul, D. R. J Appl Polym Sci 1969, 13, 817.
12. Chen, H.; Cheng-Guo, W.; Liang, Y.; Hua-Su, C. J Appl Polym Sci 2003, 90, 2752.
13. Qian, B.; Qin, J.; Zhou, Z. Text Asia 1989, 40.
14. Li, Q.; Shen, X.; Meng, Q.; Feng, Y. The Manufacture Process of Acrylic Fibers; Chinese Textile Press: Beijing, 2000.
15. Dong, J.; Luo, H.; Wang, Q.; Cao, Z. Manufacture Process of Synthesized Fibers; Beijing Textile Industry Press: Beijing, 1993.
16. Prasad, G. Synth Fibers 1985, 6.
17. Knudsen, J. P. Text Res J 1963, 33, 13.