

Kinetics of Diffusion in Polyacrylonitrile Fiber Formation

Chen Hou,¹ Rong-jun Qu,¹ Ying Liang,² Cheng-guo Wang³

¹College of Chemistry and Materials Science, Yantai Normal University, Yantai 264025, China

²Office of Science and Technology, Yantai Normal University, Yantai 264025, China

³Carbon Fiber Center, College of Materials Science and Engineering, Shandong University, Jinan 250061, China

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ABSTRACT: A H₂O/dimethyl sulfoxide (DMSO) mixture was used as the coagulation bath of the wet-spun process for polyacrylonitrile fibers. Diffusion behaviors of coagulate and solvent of the protofibers were studied. Diffusion coefficients of H₂O and DMSO of the protofibers, prepared by acrylonitrile (AN) homopolymers, were also determined. It was found that diffusion coefficients of H₂O and DMSO in the protofibers prepared by AN homopolymers, synthesized by DMSO solution polymerization, are highest compared with those of AN homopolymers synthesized by H₂O/DMSO mixture suspension polymerization and aqueous suspension polymerization. With increasing polyacrylonitrile concentration in the dope, diffusion coefficients of H₂O and DMSO decreased continuously. Diffusion coefficients of

H₂O and DMSO increased concomitantly with increasing bath temperature, but the changes of diffusion coefficient values were less prominent when the temperature increased beyond 60°C. When DMSO concentration in the coagulation bath was 55 wt %, the values of diffusion coefficients of H₂O and DMSO were minimal. Diffusion coefficients increased with increasing jet stretch minus ratio. When the protofiber radius was increased, there was a corresponding increase of diffusion coefficients of H₂O and DMSO. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1529–1533, 2005

Key words: diffusion; polyacrylonitrile; fibers; wet spinning; solution properties

INTRODUCTION

Wet spinning is one of many methods of producing polyacrylonitrile precursors.¹ The mechanism of acrylic fiber formation by the 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 that carry the 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.² Because of the dependency 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.³ To our knowledge, early studies were just empirical attempts to correlate the actual spinning variables with the final properties of the fibers,^{4,5} without any investigation on the dynamics of the phenomena, and there are almost no reports on diffusion coefficients of coagulate and solvent in

the polyacrylonitrile fiber formation process. In this study, a H₂O/dimethyl sulfoxide (DMSO) mixture was used as the coagulation bath of the wet-spun process, and acrylonitrile (AN) homopolymers were used to prepare the spinning dopes. For estimating diffusion coefficients of H₂O and DMSO, many possible technical designs of wet-spinning techniques in the fiber formation process were applied. The effect of the coagulation variables on diffusion coefficients of H₂O and DMSO was also studied.

EXPERIMENTAL

Spinning dope and its preparation

Aqueous suspension polymerization, H₂O/DMSO mixture suspension polymerization, and DMSO solution polymerization were used to synthesize AN homopolymers.⁶ The polymer code and the isotacticity are given in Table I. Tacticity of AN homopolymers discussed here is defined by three monomer units (triad tacticity). Polymers made by aqueous suspension polymerization and H₂O/DMSO mixture suspension polymerization were washed and dissolved in DMSO after drying to obtain a clear dope. The resulting AN polymer solution made by solution polymerization can be directly used as the spinning dope after removal of excess solvent and unreacted monomers.

Correspondence to: C. Hou (chenhou0825@163.net).

TABLE I
Characterization of AN Homopolymer

Sample	Polymerization technique	Molecular weight $\times 10^4$	Isotacticity (mm)
PAN1	DMSO solution	10.32	0.267
PAN2	H ₂ O/DMSO mixture suspension	28.25	0.308
PAN3	Aqueous suspension	41.28	0.351

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. After a definite time, the coagulated protofibers were obtained.

Characterization

The weight of the protofiber was composed of AN polymer weight, coagulate H₂O weight, and solvent DMSO weight. AN polymer weight was obtained by drying the protofibers in vacuum. H₂O weight was determined by thermal gravimetric analysis (TGA) on a DT40 thermal analyzer (Chevrier Instruments, Inc., Quebec, Canada), where the remainder is the residual weight of DMSO in the protofibers.

The diffusion coefficient (D_{H_2O}) of H₂O was calculated using Crank's method by measuring H₂O weight in the protofibers with time intervals of t in the coagulation bath. Crank's equation⁷ is represented as

$$D_{H_2O} = \frac{\pi a^2}{16t} \left(\frac{C_t}{C_\infty} \right) \quad (1)$$

where D_{H_2O} is the diffusion coefficient of H₂O, C_t is the H₂O weight in the protofibers at time t , C_∞ is the equilibrium H₂O weight in the complete coagulated protofiber, a is the radius of the protofiber, and t is the coagulation time.

Diffusion coefficient (D_{DMSO}) of solvent DMSO was also calculated using Crank's method by calculating DMSO weight outflow of the protofibers with time intervals of t in the coagulation bath.

RESULTS AND DISCUSSION

Calculation of diffusion coefficient

A H₂O/DMSO mixture was used as the coagulation bath. The effect of time on H₂O uptake and DMSO residual content in the protofibers was investigated under conditions when DMSO concentration in the coagulation bath was 60 wt %, the coagulation bath temperature was 60°C, and the jet stretch minus ratio was 50%. Concentration of AN homopolymers pre-

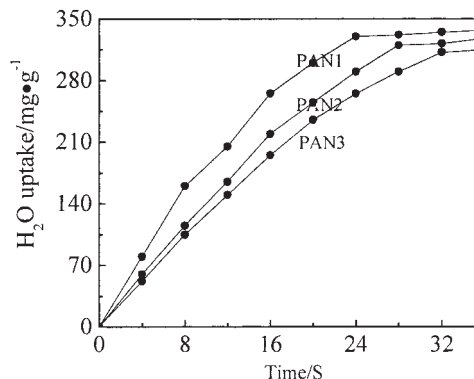


Figure 1 Plot of H₂O uptake versus time.

pared by DMSO solution polymerization, H₂O/DMSO mixture suspension polymerization, and aqueous suspension polymerization in the dope was controlled at 20, 18, 15 wt %, respectively. Figure 1 shows H₂O uptake in the protofibers versus time. Figure 2 shows DMSO residual content in the protofibers versus time. The protofibers prepared by DMSO solution polymerization reached maximum H₂O uptake values within 24 s, whereas the protofibers prepared by H₂O/DMSO mixture suspension polymerization and aqueous suspension polymerization took 28 and 32 s, respectively, to reach equilibrium. The protofibers prepared by DMSO solution polymerization reached equilibrium DMSO residual content values within 8 s, whereas the protofibers prepared by H₂O/DMSO mixture suspension polymerization and aqueous suspension polymerization took 12 and 16 s, respectively, to reach equilibrium.

Diffusion coefficients of H₂O and DMSO were calculated using Crank's method, with a time interval of 8 s in the coagulation bath. Diffusion coefficients of H₂O in the protofibers prepared by PAN1, PAN2, and PAN3 were 0.523×10^{-10} , 0.448×10^{-10} , and $0.392 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, respectively. Diffusion coefficients of DMSO in the protofibers prepared by PAN1, PAN2, PAN3 were 1.57×10^{-10} , 1.05×10^{-10} , and 0.785

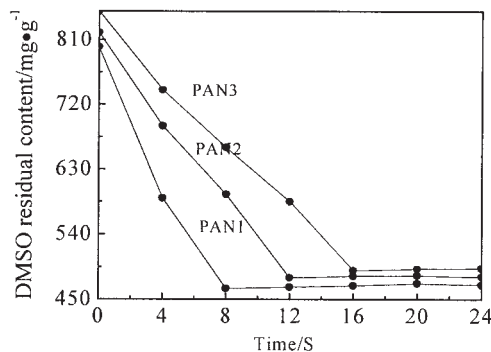


Figure 2 Plot of DMSO residual content versus time.

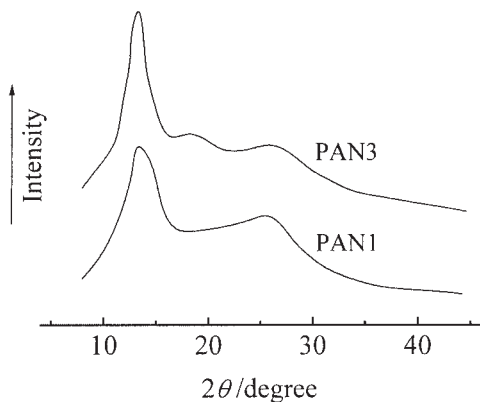


Figure 3 XRD patterns of the protofibers.

$\times 10^{-10} \text{ m}^2 \cdot \text{S}^{-1}$, respectively. Identical results were also reported in the literature.⁸ It is reported^{9,10} that the diffusion of H_2O into the protofibers and the diffusion of DMSO out of the protofibers is controlled by the stereotacticity and segmental mobility of the polymer chain, and to a considerable extent the crystallinity, the gel, and void structure in the protofibers. From Table I, the fraction value of the stereospecific sequence of AN homopolymers, prepared by the aqueous suspension polymerization technique, can reach 0.351. With increasing DMSO concentration in the H_2O /DMSO mixture, the extent of stereospecific sequence of AN homopolymers decreases. The fraction value of the stereospecific sequence of AN homopolymers, prepared by the solution polymerization technique, is minimal. Comparison of the crystallinity of the protofibers prepared by AN homopolymers in Figure 3 shows that there is a marked decrease in crystallinity in the protofibers prepared by solution polymerization. Osmosis of H_2O and DMSO in the protofibers prepared by solution polymerization becomes more facile, and H_2O uptake and DMSO outflow of the protofibers are the first to reach equilibrium.

Effect of polymer concentration in the bath on diffusion coefficient

The effect of polymer concentration in the bath on diffusion coefficients of H_2O and DMSO was studied by varying the concentration of AN homopolymers prepared by solution polymerization, from 19 to 21 wt %, while keeping other factors constant. Diffusion coefficients of H_2O and DMSO were calculated with time intervals of 8 s in the coagulation bath. Figure 4 shows the changes of diffusion coefficients of H_2O and DMSO as a function of polymer concentration in the dope. Diffusion coefficients of H_2O and DMSO decrease continuously with increasing polymer concentration up to 21 wt %. As the polymer concentration increases, the viscosity of the dope increases quickly,

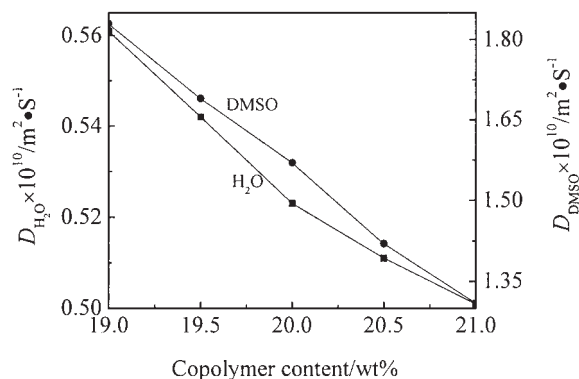


Figure 4 Relationship between AN homopolymer concentration and diffusion coefficient.

the free volume in the homopolymer solution is mostly occupied, and osmosis of H_2O and DMSO becomes more difficult. Diffusion coefficients of H_2O and DMSO show a decreasing trend.

Effect of bath temperature and composition on diffusion coefficient

Because the bath temperature and composition also play an important role in the factors that affect diffusion coefficients of H_2O and DMSO, it is necessary to study diffusion coefficients of H_2O and DMSO at different bath temperatures and compositions.

The effect of the bath temperature on diffusion coefficients of H_2O and DMSO in the protofibers prepared by AN homopolymers, synthesized by solution polymerization while keeping other experimental parameters constant, was evaluated by varying the temperature in the range of 45–70°C. Diffusion coefficients of H_2O and DMSO were calculated with time intervals of 8 s in the coagulation bath. As shown in Figure 5, the diffusion coefficient of H_2O increases continuously with increasing temperature, although the changes of diffusion coefficient values are less prominent at tem-

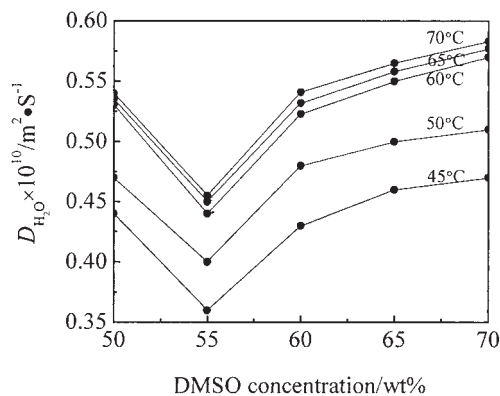


Figure 5 Effect of coagulation bath composition and temperature on diffusion coefficient of H_2O .

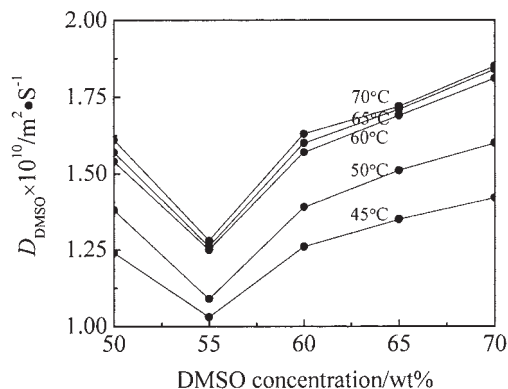


Figure 6 Effect of coagulation bath composition and temperature on diffusion coefficient of DMSO.

temperatures exceeding 60°C. It is also evident from Figure 6 that changes of the diffusion coefficient of DMSO were generally identical to those of the diffusion coefficient of H₂O with increasing temperature, showing only a few discrepancies with the values reported.¹¹ This can be explained by taking into account the glass-transition temperatures of these protofibers. The values of glass-transition temperature of AN homopolymers dissolved into DMSO solvent substantially decrease, presumably because of a reduction in dipole interaction arising from the irregularly disposed pendant groups. As the bath temperature increases to 60°C, the lower glass-transition temperature eases H₂O and DMSO diffusion and provides more sites. At temperatures exceeding 60°C, there are no obvious factors that favor diffusions of H₂O and DMSO molecules and an increase of diffusion coefficient values is less obvious.

In the wet-spun process, the value of diffusion coefficient of coagulate always varies with changes in bath composition. The effect of the bath composition on diffusion coefficient of the protofibers, prepared by AN homopolymers synthesized by solution polymerization while keeping other experimental parameters constant, was studied. It is evident from Figure 5 and Figure 6 that there is a substantial decrease in the diffusion coefficients of H₂O and DMSO at concentrations of DMSO up to 55 wt %, and then the coefficient appears to increase. The bath concentration at which the values of diffusion coefficient of coagulate are minimal is governed by the gel formed in the protofibers.¹² With increasing DMSO concentration, the gel density becomes higher, thus hindering the osmosis of H₂O and DMSO. As the DMSO concentration exceeds 55 wt %, the gel becomes swollen and its density becomes lower, thus once again promoting easier diffusion of H₂O and DMSO.

Effect of jet stretch minus ratio on diffusion coefficient

The ease of fiber formation under continuous spinning conditions is determined by the jet stretch minus ratio.

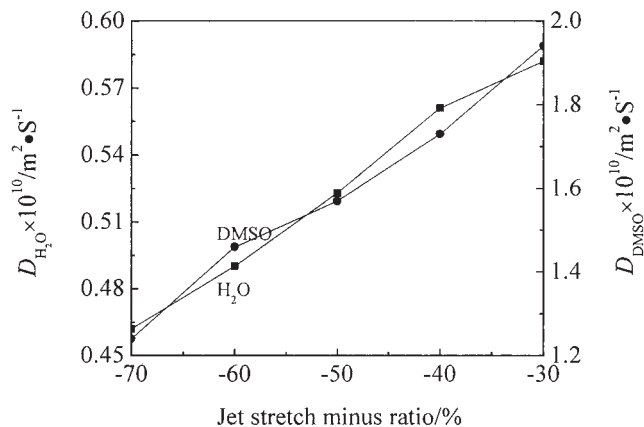


Figure 7 Relationship between diffusion coefficient and jet stretch minus ratio.

The effect of jet stretch minus ratio on diffusion coefficients of H₂O and DMSO of the protofibers, prepared by AN homopolymers synthesized by solution polymerization while keeping other experimental parameters constant, was studied. Diffusion coefficients of H₂O and DMSO were calculated with time intervals of 8 s in the coagulation bath. Figure 7 shows that diffusion coefficients of H₂O and DMSO increase when the jet stretch minus ratio increases from -70 to -30%. According to Knudsen,¹³ decreasing values of the jet stretch minus ratio are accompanied by decreasing bulk density and increasing number of voids. Increasing the number of voids in the protofibers facilitates H₂O and DMSO diffusion and diffusion coefficients of H₂O and DMSO show an increasing trend.

Effect of the protofiber radius on diffusion coefficient

Effects of the protofiber radius on diffusion coefficients of H₂O and DMSO are shown in Figure 8. As

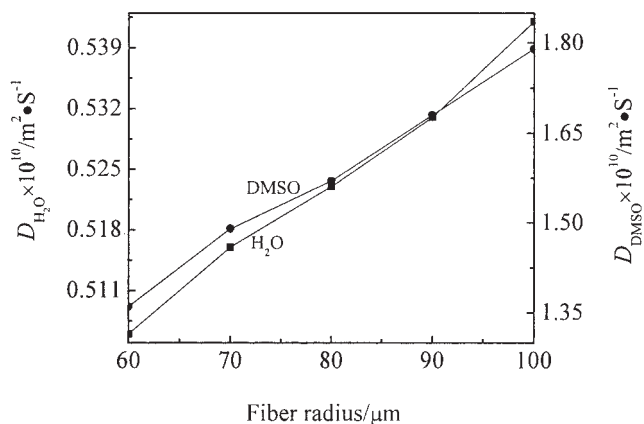


Figure 8 Relationship between diffusion coefficient and the protofiber radius.

shown in the figure, when the protofiber radius is progressively increased, there is a corresponding increase of diffusion coefficients of H₂O and DMSO. At the very outlet from the spinneret, a sudden desolvation of the outer layer of the protofiber occurs, so that a skin of coagulated polymer builds up. This skin has properties different from those of the inner core of the fiber. Diffusion coefficients of H₂O and DMSO depend on the thickness and denseness of this skin.¹⁴ With increasing protofiber radius, the relative percentage of the skin becomes less and the skin becomes thin and sparse, the osmosis of H₂O and DMSO becomes easier, and diffusion coefficients of H₂O and DMSO increase.

CONCLUSIONS

Laboratory studies of the fiber formation process have shown that diffusion coefficients of H₂O and DMSO of the protofibers prepared by AN homopolymers, synthesized by DMSO solution polymerization, are highest compared with those of AN homopolymers synthesized by H₂O/DMSO mixture suspension polymerization and aqueous suspension polymerization. Diffusion coefficients of H₂O and DMSO decrease continuously with increasing polymer concentration in the dope. Diffusion coefficients of H₂O and DMSO increase continuously concomitantly with increasing bath temperature, but the changes of diffusion coefficient values are less prominent when the temperature

exceeds 60°C. There is a substantial decrease in diffusion coefficients of H₂O and DMSO up to 55 wt % concentration of DMSO in the bath, after which the coefficients appear to increase. Diffusion coefficients of H₂O and DMSO increase coordinately with increasing jet stretch minus ratio. As the protofiber radius is progressively increased, there is a corresponding increase of diffusion coefficients of H₂O and DMSO.

References

1. Keshav, V. D. *Synth Fibers* 1996, 4, 11.
2. Ziabicki, A. *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. Hou, C.; Wang, C.-G.; Liang, Y.; Cai, H. *Chin J Chem Eng* 2003, 11, 166.
7. Bajaj, P.; Surya, K.; Munukutla, S. *Text Res J* 1990, 113.
8. Dong, J.; Luo, H.-L.; Wang, Q.-R.; Cao, Z.-L. *Manufacture Process of Synthesized Fibers*; Beijing Textile Industry Press: Beijing, China, 1993.
9. Hou, C.; Wang, C.-G.; Liang, Y.; Cai, H.-S. *J Appl Polym Sci* 2003, 90, 2752.
10. Qian, B.-J.; Qin, J.; Zhou, Z.-L. *Textile Asia* 1989, 40.
11. Prasad, G. *Synth Fibers* 1985, 6.
12. Paul, D. R. *J Appl Polym Sci* 1969, 13, 817.
13. Knudsen, J. P. *Text Res J* 1963, 33, 13.
14. Li, Q.-S.; Shen, X.-Y.; Meng, Q.-C.; Feng, Y.-S. *The Manufacture Process of Acrylic Fibers*; Chinese Textile Press: Beijing, China, 2000.