

Effects of Different Coagulation Conditions on Polyacrylonitrile Fibers Wet Spun in a System of Dimethylsulphoxide and Water

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ABSTRACT: Polyacrylonitrile (PAN) precursors were prepared by the wet spinning way. The effects of the coagulation conditions, such as coagulation temperature, coagulation ratio, and coagulation concentration, are discussed in detail. While keeping the coagulation bath concentration constant, as the coagulation bath temperature increased, the cross section deviated less from a circular form, and the as-spun fiber diameter decreased. Measurement to the rate of the boundary movement has been calculated depending on the coagulation rate. While keeping the coagulation bath temperature constant, high coagulation bath concentration can cause more coagulant to diffuse into the

solution to the polymer precipitated consequently, which led to a faster coagulation rate. The as-spun fiber from high coagulation concentration was compacted than those from low concentration. The character of the formed structure reflected the system mobility and capability to crystallize. Improvement in fiber density in the as-spun fiber resulted in improvements in the tensile strength of the as-spun fiber. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3723–3729, 2007

Key words: coagulation conditions; wet spinning; PAN fibers; cross section

INTRODUCTION

In the recent years, there has been a growing interest in the study of making carbon fibers. It can be ascribed to an increase in need for high quality fibers and the aim to produce fibers with high economical efficiency. It is well known that the properties of the final carbon fibers are determined by the nature of the precursor fibers. PAN-based carbon fibers have advantage of lower cost and mature technology, therefore, PAN precursor is presently believed as the most suitable and important precursor for making high performance carbon fibers. Wet spinning is one of the main methods for producing high performance PAN precursors. The mechanism of the PAN fiber formation by wet-spinning technique is quite complex. The spinnability is affected not only by the properties of the spinning solution but also by the coagulation bath conditions.^{1–9} Various factors that influence the coagulation process including the polymer composition, molecular weight, and its distribution of polymer, respectively, were explained by Paul and Mcpeters¹⁰ and Han and

Segal,¹¹ and Takahashi et al.¹² The effect of coagulation bath composition on the structure of as-spun fibers was reported by Knudsen.¹³ Recent investigations that used modeling techniques to understand diffusion processes have been reported by Baojun et al.¹⁴ and Alieva et al.¹⁵ Determination of diffusion coefficient of DMSO in polyacrylonitrile (PAN) fiber formation has been reported by Chen and coworkers.¹⁶ But, an important feature of the coagulation process of solutions is that a distinct moving boundary is associated with the coagulation. The visible boundary separates the coagulation into two regions, one side of the boundary is hard, elastic, coagulating polymer, while the other side is the soft, fluid solution. The boundary begins at the solution surface and moves inward with time until it reaches the center of the solution. The measurement to the rate of the boundary movements was a useful method in the investigation of the coagulation of the coagulation process of spinning dope. Moreover, the growth rate of this boundary was found to be intimately related to the spinnability of polymer solutions and structure of wet spun fibers. In this article, the measurement of the rate of kinetics of this coagulation boundary growth was made under a wide variety of coagulation bath composition, coagulation bath temperature, and minus jet stretch. The effect of these factors on the structure properties of PAN fibers produced by wet spinning was reported.

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EXPERIMENTAL

Materials

Acrylonitrile (AN; Tianjin Chemical Reagent Plant, Tianjin, China) was distilled at 76–78°C before use. Itaconic acid (IA; Lucky, Chuolchome Ueda, Japan) was used as the second monomer, azodiisobutyronitrile (AIBN; Shandong Xueyin Chemical Fiber, Zibo, China) as an initiator, and dimethyl sulfoxide (DMSO; Liaoning Panjin Chemical General Plant, Panjin, China) as solvent.

Preparation of PAN precursors

Free-radical solution copolymerization of IA and AN was carried out in a 50-L pilot-scale stainless reactor with DMSO and AIBN. The resulting 20% (w/w) polymerization solution was deaerated, filtered, and then pumped through a spinneret to a coagulating bath, the intrinsic viscosity $[\eta]$ of the spinning solution was 1.8, the number-average molecular weight M_n of the spinning solution was 160,000. The polymer solution was provided with heat jackets to keep the solution at the desired temperature of 60°C. The spinneret used in this experiment contained 1000 holes of which each diameter is 0.06 mm ($L/D = 1.2$). The distances from hole to hole were very accurately uniform. The length of the coagulation bath was 180 cm and the width and depth of the bath were 20 and 40 cm, respectively.

Time of as-spun fibers in coagulation bath

The time of as-spun fibers in coagulation bath can be attained as follows: the sign can be marked carefully with the ink inside drip pipe without circulating the aqueous solution of the coagulation bath when the spinning solution emerges from the spinneret hole, and then the time can be measured by stopwatch when the formed filaments marked leave the hole to the first roller. The coagulated filaments were drawn in four steps in bath water of different concentration, followed by lubrication with heat-resistant amine silicone oil. The resulting filaments were dried to collapse, further drawn in pressure steam set followed by soakage, then thermoformed in a heating oven, and wounded to obtain PAN precursors.

Measurement

Coagulation rate

To exhibit the effects of coagulation variables on the coagulation of the polymer solution, on the assumption that the diameter of the as-spun fiber is the same as that of the spinneret hole, the relationship between the spinning conditions and the minimum

coagulation rate $\xi/t^{1/2}$ required for complete coagulation of the spinning solution in the coagulation bath has been shown by Liu et al.^{17–19} as follows:

$$\xi/t^{1/2} = 0.7(D/2)(\langle V \rangle/L)^{1/2}$$

where ξ is the depth of penetration of the nonsolvent in the polymer solution during coagulation as a function of time t , D is the diameter of the spinneret orifice hole, L and $\langle V \rangle$ are the immersion distance and the average velocity of the as-spun fiber, respectively. $\langle V \rangle$ is the average solution velocity in the spinneret hole and is calculated without considering the familiar Barus effect as follows: $\langle V \rangle = 4Q/(\pi D^2 \times 1000)$, where Q is the rate of pumping in cubic centimeters per minute. So

$$\begin{aligned} \xi/t^{1/2} &= 0.7(D/2)((4Q/\pi D^2 \times 1000)/L)^{1/2} \\ &= 1.25 \times 10^{-2}(Q/L)^{1/2} \end{aligned}$$

Jet stretch minus ratio

The jet stretch minus ratio was generally accepted as a comprehensive index of the hydrodynamic process of wet spinning the as-spun fibers. It is defined as the ratio of the linear take up rate at which as-spun fibers are taken out of the coagulation bath subtracts the linear rate at which spinning dope is extruded through the spinneret holes to the linear rate at which spinning dope.

SEM observation of precursors

The resulting polymers were examined with a scanning electron microscope (SEM), Hitachi Model 8010 (Tokyo, Japan), at 25 kV accelerating potential. To observe the cross section of the obtained as-spun fiber, the coagulated fiber samples were directly immersed into liquid and subjected to lyophilization. The specimens were sputtered with Au to get a better image to avoid electron charging effects by using a metal evaporating apparatus (fine-coat ion sputter JFC-1100, Jeol, Tokyo, Japan).

Mechanical properties

The liner densities of the as-spun fiber or different stretch stages fiber were determined as the weight of 1-m long sections in milligrams, it could be weighed in the physical scale balance. Bulk density of the fibers was determined by means of a density gradient column maintained at 25°C, the columns were prepared in the 250-mL graduated cylinders, carbon tetrachloride with a density of 1.57 g/cm³ and xylene with a density of 0.90 g/cm³. The fiber samples for density determination were prepared by

tying knots in the filaments and placing them in the column, the fibers first sunk and then came to rest at the position corresponding to their density.

The titer was measured by XD-1 fiber fineness machine, all the fibers were measured by a XQ-1 testing machine (both XD-1 and XQ-1 were made in Donghua University, Shanghai, China) at a cross-head speed of 0.5 mm/min with a testing length of 20 mm and load cell of 15 g. In each case, at least 30 sample filaments were tested, and taken for the average of 30 filaments in each experiment.

RESULTS AND DISCUSSION

Effect of coagulation rate

In general, the coagulation rate is more informative than the coagulation strength for understanding the morphological characteristics of wet-spun filament. Inside the coagulation bath, removal of solvent from the coagulating filament, and the solidification of dissolved polymer take place simultaneously. Many researchers^{17,20,21} have argued that a sharp boundary line is associated with the diffusion of coagulant into polymer solutions. The solidification boundary begins at the solution surface and moves inward with time until it reaches the center of the coagulating fiber. Measurement of the rate of this boundary movement has been known and recognized as a very useful tool in the examination of the coagulation process of polymer solutions. Furthermore, the growth rate of this boundary was found to be strongly related to the spinnability of the dope solution²⁰ and the structure of wet-spun filaments.²² The theory and diffusion models related to this boundary movement were well surveyed.²³ When the spinning solution is

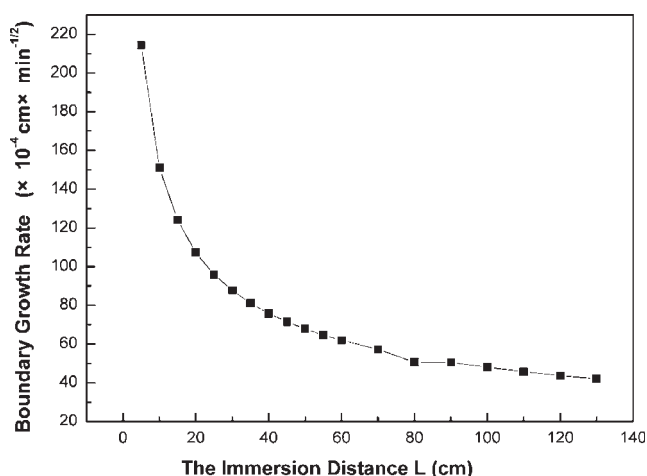


Figure 1 Relationship between the coagulation rate and the immersion distance: coagulation bath temperature = 40°C, DMSO/H₂O = 60/40 (wt/wt), jet stretch minus ratio = -30%.

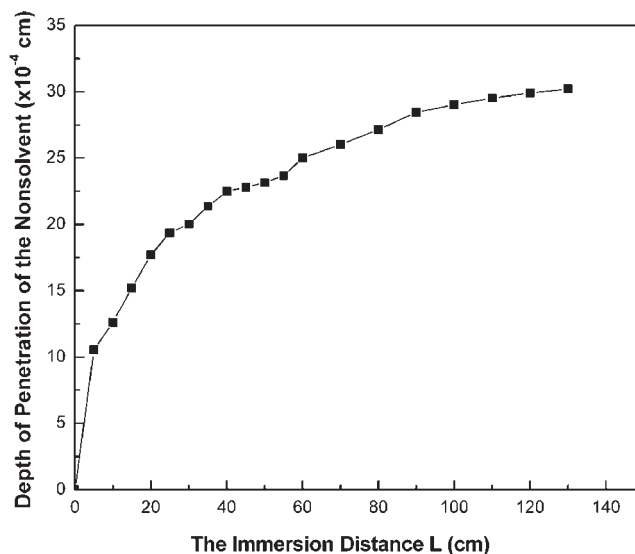


Figure 2 Relationship between the penetration and the immersion distance: coagulation bath temperature = 40°C, DMSO/H₂O = 60/40 (wt/wt), jet stretch minus ratio = -30%.

extruded into the coagulation bath, the diffusion interchange occurs between the two phase, one is solvent as DMSO, the other is insolvent as water, a very distinct moving boundary turns out, one side of the boundary is hard, while the other side is the soft original gel. This boundary begins at the surface and moves inward to the center. In our laboratory, the feeding rate of pumping meter that is linked with the spinneret is 1.2 cc in cubic centimeters per minute, so that the boundary moving was attained by controlled time when changing the position of a gelled rod immersed in the coagulant bath, the time that the as-spun fiber runs in the coagulation can be got by using the second watch. The depth of penetration, ξ , along the periphery of the cross section was calculated as follows:

$$\begin{aligned} \xi &= 1.25 \times 10^{-2} \times (1.2/L)^{1/2} \times t^{1/2} \\ &= 1.37 \times 10^{-2} \times (t/L)^{1/2} \text{ cm} \end{aligned}$$

Figure 1 shows us the relationship between the coagulation rate and the immersion distance in coagulation bath, when the distance between the as-spun fiber and spinneret orifice increases, the minimum coagulation rate decreases. After immersion, the distance is about 1 m and the minimum coagulation rate does not decrease. It demonstrates that no more exchange takes place and a state of equilibrium is achieved between the two phases. Figure 2 testifies that the above result is right, but with regard to the nature of the polymer, it is not a really true thermodynamic equilibrium and the final state may depend on the path to an extent. If given spinning solution,

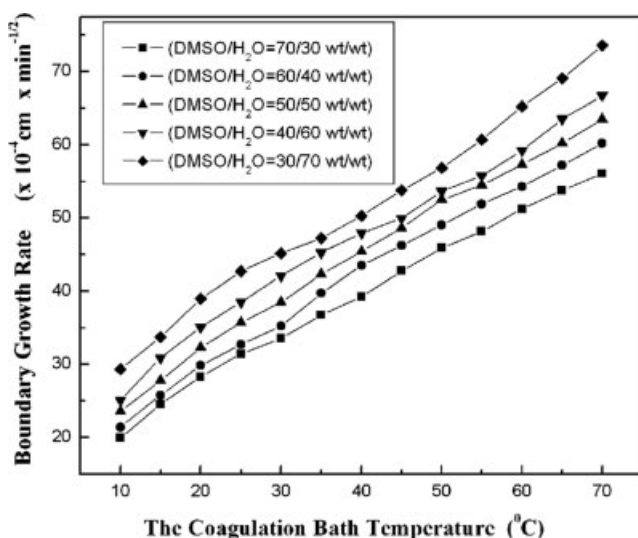


Figure 3 Effect of the coagulation bath temperature and composition on the coagulation rate (jet stretch minus ratio = -30%).

however, the final state should be adequately described by the composition of the coagulation and the temperature at which coagulation occurs.

On the basis of upper analysis, to examine the effect of coagulation, bath temperature, and composition on the coagulation rate, the distance between the spinneret orifice and the first roller-up is kept constant, and the experimental values of the coagulation rates are shown in Figure 3 by changing the temperature from 10 to 70°C and by changing coagulation DMSO composition from 30 to 70% (wt %). When the coagulation bath composition and jet stretch minus ratio are fixed, the coagulation rate almost linearly increases with the coagulation bath temperature increase; it is due to the fact that the mobility of a coagulant molecule increases with temperature increase. If the coagulation bath temperature is fixed, and the same is the coagulation bath composition, we think that the coagulation bath temperature and composition are key factors affecting the fiber structure and consequently the fibers properties; the coagulation rate data do provide

information relating to the extent and effect of the coagulation variables on the solidification process of spinning solution.

It is well-known that the mechanical properties of resultant product are strongly affected by change in the temperature of the bath. The cross section of wet-spun fibers becomes more circular at a higher bath temperature^{13,24} with a higher solid content in the dope²⁵ and with a higher solvent content in the coagulation bath.²⁶ As the bath temperature was progressively decreased, as shown in Table I, there was a corresponding improvement in fiber bulk density, an increase in internal surface area, and a reduction in the number of the large voids per filament cross section, a reduction for elongation at break and its tenacity. It can be explained in terms of fiber structure, at lower coagulation rate, that the outward diffusion of the solvent predominates, and there is more scope for internal adjustment of osmotic stresses. The fiber had well defined membranes, better structural uniformity, and a larger number of micropores than fibers produced at higher coagulation rate. It implies that a fiber spun into the bath with a lower temperature can attain a higher degree of orientation of the molecular chains. As the bath temperature decreases, the jet-swell ratio increases, so does the tension of the spun fiber, and the molecular chains tend to align more effectively together along the spinning line, thus causing the coagulated fiber to attain a softer and a more flexible structure. The cross-section of the filament spun at 55°C or above was round, and it became more bean-shaped as the temperature of coagulation bath was progressively decreased, as shown in Figure 4. According to Arrhenius equation and eq. (1), the coagulation rate increased with the increase in the temperature of the coagulation bath, which resulted in thicker and denser membranes that made osmosis of water difficult. At the same time, increasing coagulation rate could affect the microstructure of as-spun fiber; the titer attained from different bath temperature decreased with the decrease in temperature. A possible explanation for the size effect is as follows: the higher surface-to-volume ratio of smaller

TABLE I
Effect of Coagulation Bath Temperature on As-Spun Fiber

Coagulation temperature (°C)	Spinning pressure (MPa)	Cross-section	Protofiber bulk density (g/cm ³)	Elongation at break (%)	Titre (dtex)	Tenacity (cN/dtex)
60	1.38	Round	0.37	139.6	5.67	0.570
57	1.40	Round	0.41	138.4	5.58	0.585
54	1.42	Bean	0.45	132.9	5.43	0.609
50	1.50	Bean	0.48	127.6	4.98	0.677
40	1.68	Bean	0.53	122.4	4.66	0.564
30	2.75	Bean	0.57	116.8	4.12	0.428

Coagulation bath concentration = 60%, jet stretch minus ratio = -30%.

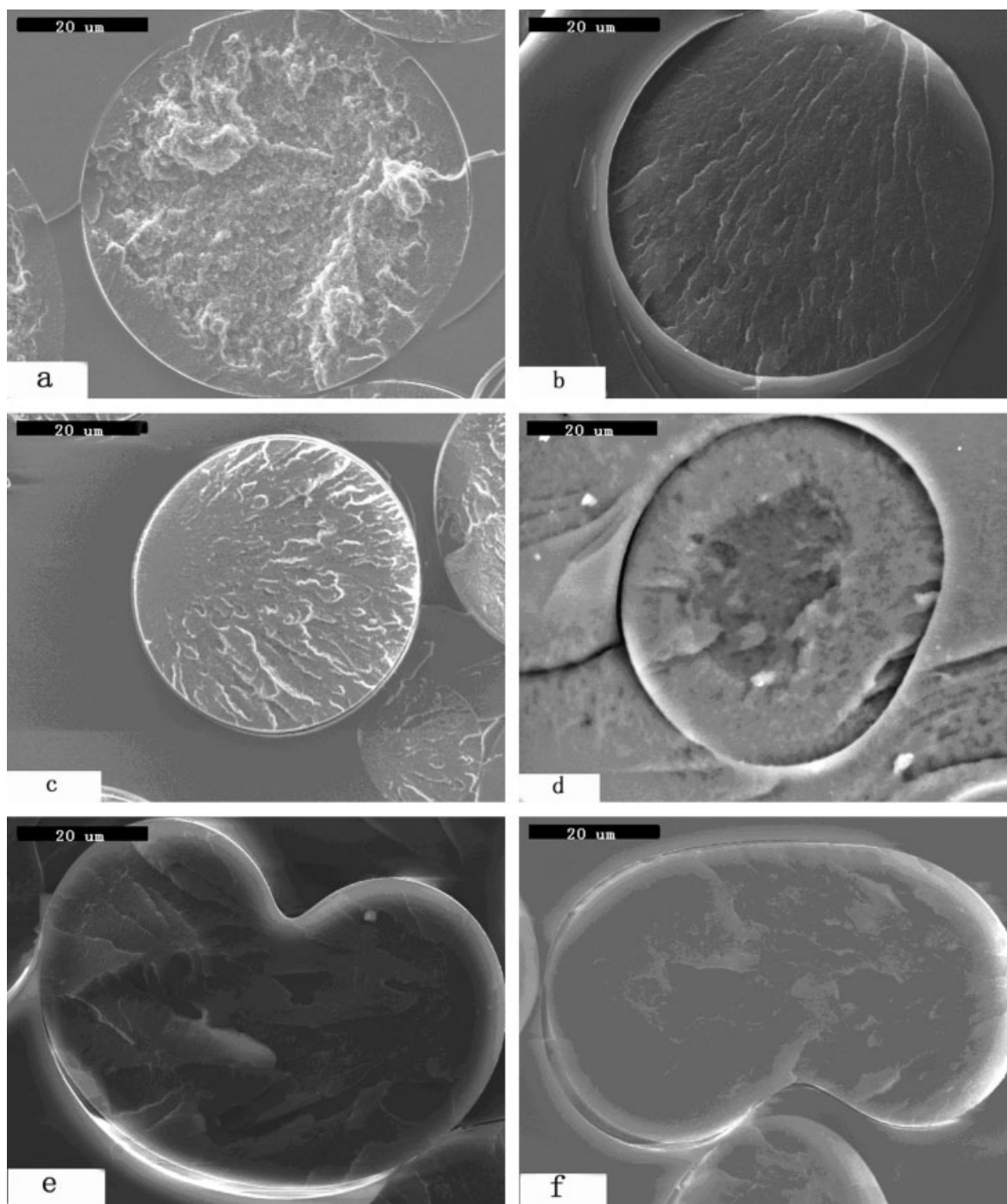


Figure 4 Effect of coagulation bath temperature on the morphology of as-spun fiber (coagulation bath concentration = 60%, jet stretch minus ratio = -30%). (a) 60°C, (b) 57°C, (c) 54°C, (d) 50°C, (e) 40°C, and (f) 30°C.

filaments reduces the time required for coagulation and thereby shortens the zone where not-coagulated solution exists in the filament. Figure 4 also testifies when the as-spun fiber is completely coagulated, the diameter of cross section is almost 60 μm .

The study on the effect of bath temperature had concluded that slower solidification process is better than rapid solidification process. Increasing coagulation bath concentration may also help getting slower

solidification. Effect of coagulation bath concentration on the as-spun fibers was studied while keeping other experimental parameters constant and was discussed by changing concentration from 30 to 70% in weight percent of DMSO. It was showed that with the concentration increase, the cross section shape varied from bean shape to round shape. The tensile strength and as-spun fiber bulk density of as-spun fiber improved, but its elongation at break and

TABLE II
Effect of Coagulation Bath Concentration on As-Spun Fiber

Concentration (%)	Cross-section shape	Protofiber bulk density (g/cm ³)	Tenacity (cN/dtex)	Elongation at break (%)	Liner density (g/cm ³)
30	Bean	0.33	0.49	142.6	1.145
40	Bean	0.37	0.57	137.4	1.144
50	Bean	0.41	0.67	132.4	1.136
55	Bean	0.44	0.67	126.3	1.132
60	Round	0.51	0.68	124.8	1.130
70	Round	0.62	0.72	112.5	1.125

Coagulation bath temperature = 50°C, jet stretch minus ratio = -30%.

average amounts of voids per fiber cross section decreased, as showed in Table II. It also can be rationalized based on the information obtained from fiber structure studies. At higher coagulation bath concentration, more coagulant was required to diffuse into the solution to precipitate the polymer consequently, which led to a faster coagulation rate. It had no enough time to adjust to the internal stresses that caused expansion of the polymer network and made the structure round. The as-spun fiber from high coagulation concentration seemed to be denser than those from low concentration. It was that high concentration solutions were in the liquid phase⁹ with molecules more aligned upon at faster rates. The molecules did not get the opportunity to completely relax to result in the denser structure. So the linear density was lower, in fact, it suggests that the composition of the respective coagulated layer as well as the coagulated filament at the end of the coagulation bath is dominated solely by the mass transfer rate difference between solidification solvent.

Effect of jet minus stretch ratio

The ease of fiber formation under continuous spinning conditions is decided by jet stretch minus ratio. The effect of apparent minus stretch on the property of as-spun fiber was presented in Table III. The shape of cross section for as-spun fiber changed from the dumb-bell shape to the oval shape, but the cross section of the as-spun fiber apparently gave no evidence of a clear pore structure. Its tensile strength

increased from 0.541 to 0.592 cN/dtex, and also its density from 1.130 to 1.144 g/cm³ with the jet stretch minus rate decreasing from -20 to -55%. It demonstrated that when the as-spun fiber extruded from the spinneret, the initial phase of stretching involved deformation of the fibrillar with concurrent orientation of the fibrils; in other words, it appears that improvement in fiber density in the as-spun fiber also resulted in improvements in the tensile strength of the as-spun fiber.

It is evident that in the fiber formation process during solidification, especially during the drawing stage, the macromolecules change their spatial configuration, and the grafted chains change their position in the direction of drawing forces. With the time that the as-spun fiber stayed the coagulation bath prolonged, the coiled chains are flattened, the secondary bonds can be formed between CN groups of the grafted PAN chains. The character of the formed structure depends on the extent of deformation applied as well as on the conditions of fiber drawing affecting the system mobility and capability to crystallize. Thus, the properties of fibers depend not only on the number and length of chains but also on the conditions of deformation processes, which consequently affect quantitatively the formation of secondary bonds.

CONCLUSIONS

The distance between as-spun fiber and spinneret orifice increases, the coagulation rate decreases, after immersion the distance is about 1 m, and the mini-

TABLE III
Effect of Apparent Minus Stretch on the Property of As-Spun Fiber

Jet stretch minus ratio (%)	Shape of cross-section for protofiber	Tensile strength (cN/dtex)	Density (g/cm ³)
-55	Dumbbell-shaped	0.592	1.144
-50	Bean-shaped	0.586	1.142
-40	Oval-shaped	0.566	1.139
-30	Round	0.543	1.133
-20	Round	0.541	1.130

Coagulation bath concentration = 60%, Coagulation bath temperature = 60°C.

mum coagulation rate does not decrease. The coagulation rate measurement showed that the most significant variable affecting the coagulation process is the nature of the coagulant. When the coagulation bath composition and jet stretch minus ratio are fixed, the coagulation rate almost linearly increases with the coagulation bath temperature increasing. The cross section of the filament spun at 55°C or above was round, and it became bean-shaped as the temperature of coagulation bath was progressively decreased. When the as-spun fiber is completely coagulated, the diameter of cross section is almost 60 μm. Keeping other experimental parameters constant by changing concentration from 30 to 70%, with the concentration increases, the cross section shape varied from bean shape to round shape, the tensile strength, and as-spun fiber bulk density of as-spun fiber improved, but its elongation at break and average amounts of voids per fiber cross section decreased. Keeping other experimental parameters constant by changing the jet stretch minus rate decreasing from -20 to -55%, the shape of cross section for as-spun fiber changed from the dumb-bell shape to the oval shape; the cross section of the as-spun fiber apparently gave no evidence of a clear pore structure.

References

1. Paul, D. R. *J Appl Polym Sci* 1969, 13, 817.
2. Stoyanov, A. I. *J Appl Polym Sci* 1982, 27, 235.
3. Stoyanov, A. I. *J Appl Polym Sci* 1979, 23, 3123.
4. Rakas, M. A.; Farris, R. J. *J Appl Polym Sci* 1990, 40, 823.
5. White, J. L.; Hancock, T. A. *J Appl Polym Sci* 1981, 26, 3157.
6. Stoyanov, A. I. *J Appl Polym Sci* 1981, 26, 1813.
7. Takaku, A.; Hashimoto, T.; Mtyoshi, T. *J Appl Polym Sci* 1985, 30, 1565.
8. Dorogy, W. E., Jr.; St. Clair, A. K. *J Appl Polym Sci* 1991, 43, 501.
9. Dave, V.; Glasser, W. G.; Wilkes, G. L. *J Polym Sci Part B: Polym Phys* 1993, 27, 1145.
10. Paul, D. R.; Mcpeters, A. L. *J Appl Polym Sci* 1973, 21, 1669.
11. Han, C. D.; Segal, L. *J Appl Polym Sci* 1970, 14, 2973.
12. Takahashi, M.; Nukushina, Y.; Kosugi, S. *Textile Res J* 1964, 34, 87.
13. Knudsen J. P. *Textile Res J* 1963, 33, 13.
14. Baojun, G.; Ding P.; Zhenquin W. *Adv Polym Technol* 1986, 6, 509.
15. Alieva, E. R.; Kozhernikov, Y. P.; Medvedev, V. A.; Serkov, A. T. *Khim Volokna* 1990, 5, 6.
16. Liang, Y.; Chen, H.; Wang, F. *J Appl Polym Sci* 2006, 100, 4447.
17. Liu, C. K.; Cuculo, J. A.; Smith, B. *J Polym Sci Part B: Polym Phys* 1989, 27, 2493.
18. Liu, C. K.; Cuculo, J. A.; Smith, B. *J Polym Sci Part B: Polym Phys* 1990, 28, 449.
19. Cho, J. J.; Hudson, S. H.; Cuculo, J. A. *J Polym Sci Part B: Polym Phys* 1989, 27, 1699.
20. Paul, D. R. *J Appl Polym Sci* 1968, 12, 2273.
21. Knaul, J. Z.; Creber, K. A. M. *J Appl Polym Sci* 1997, 66, 117.
22. Ford, R. W.; Tlavsky, J. D. *J Appl Polym Sci* 1968, 12, 2299.
23. Han, C. D.; Segal, L. *J Appl Polym Sci* 1970, 14, 2999.
24. Paul, D. R. *J Appl Polym Sci* 1967, 11, 439.
25. Zwick, M. M.; Van Bochove, C. *Textile Res J* 34: 417 1964.
26. Paul, D. R.; Armstrong, A. A. *J Appl Polym Sci* 1973, 17, 1269.