

The Effect of Molecular Weight on the Cross Section and Properties of Polyacrylonitrile Precursor and Resulting Carbon Fiber

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SYNOPSIS

In this study, we investigated the effect of molecular weight in the range $1.65\text{--}4.29 \times 10^5$ (\bar{M}_w) on the cross section, surface, thermal, and mechanical properties of polyacrylonitrile (PAN) precursor and its resulting carbon fiber. From the results, it can be seen that the molecular weight, with the same solid content of polymer, changes from 1.65×10^5 to 4.29×10^5 and the cross section of PAN precursor changes from a circular shape with no notable grooves surface to a bean shape with a surface containing deep and straight grooves. PAN precursor with higher molecular weight has a higher onset of exothermic temperature and a higher peak temperature, but has a higher aromatization index (AI value) due to its thin and flat cross section, which causes rapid cyclization during oxidation. An increase in molecular weight results in an increase in crystal size and preferred orientation and a decrease in average pore diameter. This decrease can improve the mechanical properties of PAN precursor and its resulting carbon fiber.

INTRODUCTION

Of all the precursory materials available for making good-quality carbon fibers, PAN is the most useful raw material at the present time.^{1,2} The quality of the ultimate carbon fibers depends largely on the quality of the precursory material.³ The properties of carbon fiber are improved by increasing the molecular weight of PAN precursor.⁴

The number-average molecular weight of PAN has a direct effect on the glass transition properties and results in an increase in T_g .⁵ The DTA result is a strong molecular weight dependence on the exotherm temperatures.⁶ Peak temperature decreases steadily with decreasing molecular weight, and the broadness of the exotherm increases markedly with lower molecular weights. The spinability of PAN fiber increases as the polymer concentration and molecular weight of polymer increase.⁷ The influence

of molecular weight ($4.5 \times 10^4\text{--}1.5 \times 10^5$) on the several structural-mechanical properties (such as tensile strength, elongation, density, porosity, crystal size, and perfection of structure) of PAN fibers has been investigated.^{8,9}

Here, the effect of molecular weight on the cross section and surface shape of PAN precursor and resulting carbon fiber and of molecular weight (\bar{M}_w : $1.65 \times 10^5\text{--}4.29 \times 10^5$) on the cross section, surface, and structural-mechanical properties is presented.

EXPERIMENTAL

The copolymerizations of acrylonitrile (AN) with methyl acrylate and itaconic acid comonomers were carried out in a mixed solvent of acetone and dimethyl sulfoxide at 60°C with α,α' -azobis (isobutyronitrile) as the initiator under an inert atmosphere of nitrogen. The various molecular weights of copolymers were controlled by the concentration of the initiator. The resulting polymerization solution was directly spun through a 10% DMSO coagulation bath at 5°C to form PAN precursor, then stretched in boiling water and dried. PAN precursor

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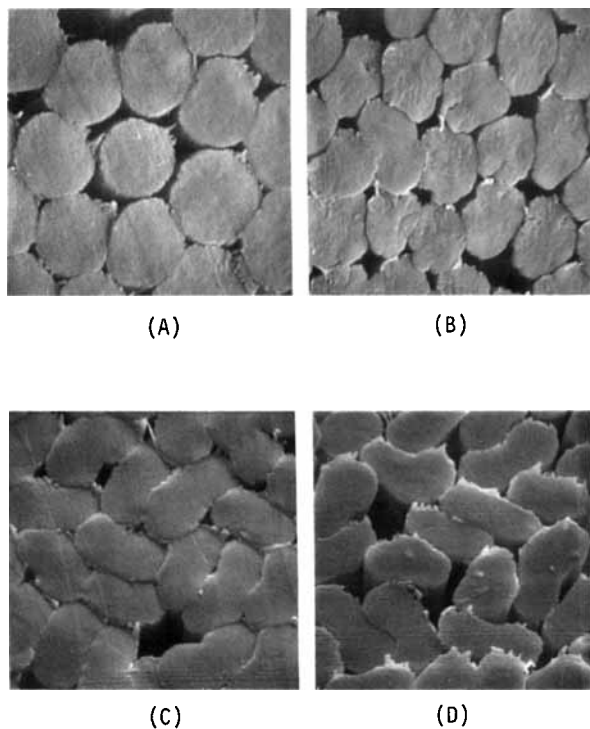
Table I Average Molecular Weight and Dispersity of PAN Precursors

Sample	IV (dL/g)	$\bar{M}_w \times 10^5$	\bar{M}_w/\bar{M}_n
A	0.98	1.65	1.8
B	1.27	2.53	2.5
C	1.67	3.40	2.6
D	1.88	4.29	3.1

was stabilized at 250°C for 30 min, then at 270°C for 1 h in air, under 0.15 g/d tension. The oxidized PAN fiber was carbonized to 1200°C under high-purity nitrogen atmosphere.

The average molecular weight and distribution (\bar{M}_w/\bar{M}_n) were determined by a Waters model 440 gel-permeation chromatograph (eluting solvent: DMF containing 0.5 LiBr wt %; column: μ -Bondagel E-Linear). The molecular weight data of various PAN precursors are shown in Table I.

Intrinsic viscosity (I.V.) measurements of PAN fibers were carried out in DMF with 0.5 LiBr wt % at 30°C by an Schott-Gerate AVS 300 viscometer, equipped with an Ubbelohde solution viscometer.

**Figure 1** Effect of molecular weight on the cross sections of PAN precursors ($\times 1550$): (A)–(D) are the samples.**Table II** Effect of Molecular Weight on Viscosity of Polymer Solution

	Sample			
	A	B	C	D
Bulk viscosity ^a (cps)	2000	2560	3040	4250

^a Bulk viscosity of polymer solution with 22% of solid content at 60°C.

The bulk viscosity of polymer solution was measured by a Brookfield LVF.

Scanning electron microscopes (SEM), Cambridge S4-10, were used to examine the cross section and longitudinal surface of PAN precursor. Thermograms of PAN precursor were obtained using Perkin-Elmer system 7/4 differential scanning calorimeter. Samples were heated under air purge at a rate of 20°C/min.

A Rigaku X-ray diffractometer, using Ni-filtered $\text{CuK}\alpha$ radiation, was used to measure the crystalline-related properties of the sample. Crystal size L_c was calculated by using the following equation:

$$L_c = K\lambda/B \cos \theta$$

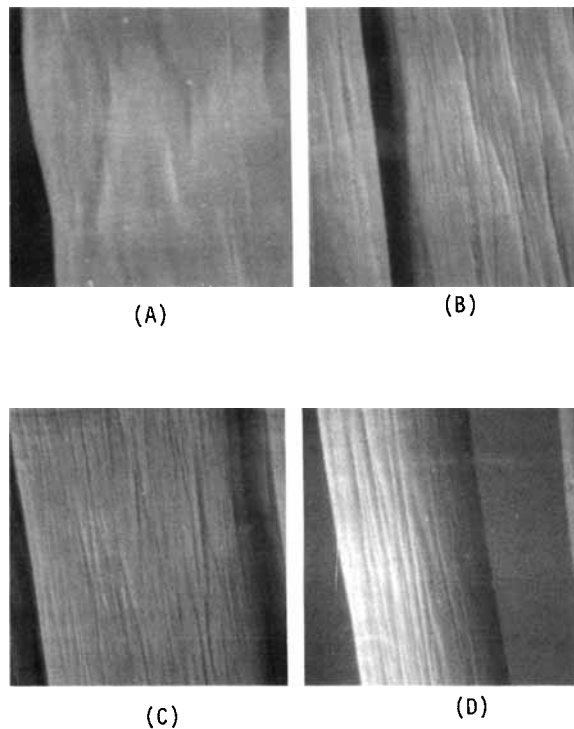
**Figure 2** Scanning electron micrograph of the surface of PAN precursors with different molecular weight ($\times 4500$): (A)–(D) are the samples.

Table III The Mechanical Properties of PAN Precursors

Sample	Crystal Size L_c (Å)	Orientation (%)	Tensile Strength (g/d)	Elongation
A	29.15	75	3.53	23.4
B	30.15	76	3.48	21.2
C	32.37	78	4.25	19.3
D	33.32	80	4.75	19.2

in which $\lambda = 1.54$, K is the apparatus constant (0.89), and B is the half-value width in the radian of the X-ray diffraction intensity (I) vs. 2θ curve.

The preferred orientation of the fibers was determined by an X-ray diffractometer with a fiber specimen attachment. The precursors and carbon fibers were located at approximately 17° (2θ) and 24° – 25° , respectively, and the 360° azimuthal circle was used to permit the fiber axis to be rotated 360° about the vertical. Orientation was calculated by the following equation:

$$O\% = [(360 - H)/360] \times 100\%$$

where H is the half-value width in degrees of the curve of intensity (I) vs. azimuthal angle.

The "aromatization index" (AI) value, described by Uchida et al.,¹⁰ was calculated from the following equation:

$$AI = I_a / (I_p + I_a)$$

in which I_a is the diffraction intensity of the aromatic structure at $2\theta = 24^\circ$ – 25° and I_p is the diffraction intensity of the PAN crystal at $2\theta = 17^\circ$.

The mechanical properties of the fibers were determined using a Hung Ta Microcomputer Universal Type 8104 with a crosshead speed of 10 mm/min and 0.5 mm/min for PAN precursor and carbon fiber, respectively, and load cell of 30 g and 2 cm of testing gauge. Pore diameter of fiber was measured with a Micromeritics Autopore II 9220 using pressure from 0 to 55,000 psia.

RESULTS AND DISCUSSION

Cross Section and Longitudinal Surface

With the same solid content of polymer solution, the molecular weight ranging 1.65×10^5 – 4.29×10^5 greatly affects the cross section of PAN precursor, which is shown in Figure 1. PAN precursor has the

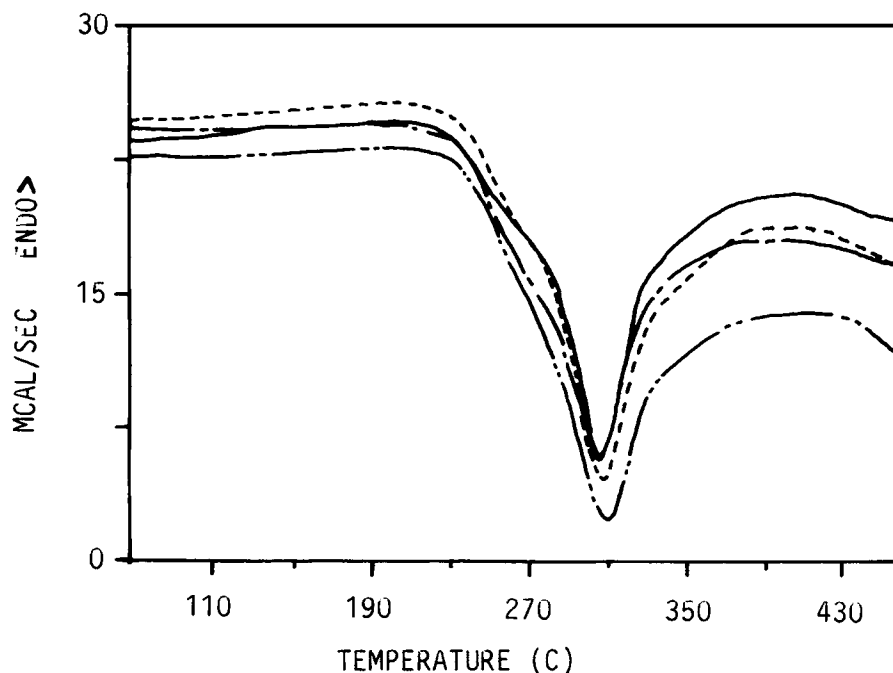


Figure 3 DSC curves of PAN precursors: sample A (—); sample B (---); sample C (— · —); sample D (----).

Table IV DSC Characterization of PAN Precursors

Sample	Onset of Exothermic Temperature (°C)	Peak Temperature (°C)	Exothermic Heat (cal/g)
A	218	305	-419
B	221	307	-487
C	217	304	-398
D	224	311	-486

circular cross section at weight-average molecular weight 1.65×10^5 and exhibits the bean cross section as molecular weight increases. The viscosity significantly increases with polymer concentration, average molecular weight, and inverse temperature.¹¹ Hence, the bulk viscosity of polymer solution at the same solid content increases with molecular weight, as shown in Table II. The diffusion coefficient, which can affect the cross section of wet-spun fiber, of solvent and nonsolvent changes depending on the viscosity of polymer solution. In terms of other technical spinning variables, cross sections of wet-spun fibers become more circular at higher bath temperatures,^{12,13} higher polymer contents in the spinning dope,¹²⁻¹⁴ and higher solvent contents in the coagulation baths.¹²⁻¹⁶

Figure 2 shows the longitudinal surfaces of PAN precursors exhibit no notable grooves at molecular weight 1.65×10^5 and straighter and deeper grooves as molecular weight increases. Figure 2 seems to indicate the relationship between the parallel degree of grooves and molecular orientation (Table III). An increase in orientation results in an increase in the parallel degree of grooves.

Under normal conditions for making carbon fiber, the cross section and longitudinal surface of carbon fiber can be determined by the cross section and surface of its PAN precursor. The cross section and longitudinal surface of carbon fiber are almost similar to those of its PAN precursor.¹⁷ The surface roughness of carbon fiber can improve the mechanical properties of composite material reinforced with carbon fiber.¹⁸

Thermal Properties

Figure 3 shows the DSC curves of various PAN precursors with different molecular weights. In Table IV it is shown that peak temperature increases as molecular weight increases and that the onset of exothermic temperature has the same tendency.

Plots of loss tangent as a function of temperature curves shown in Figure 4 are distinguished by two

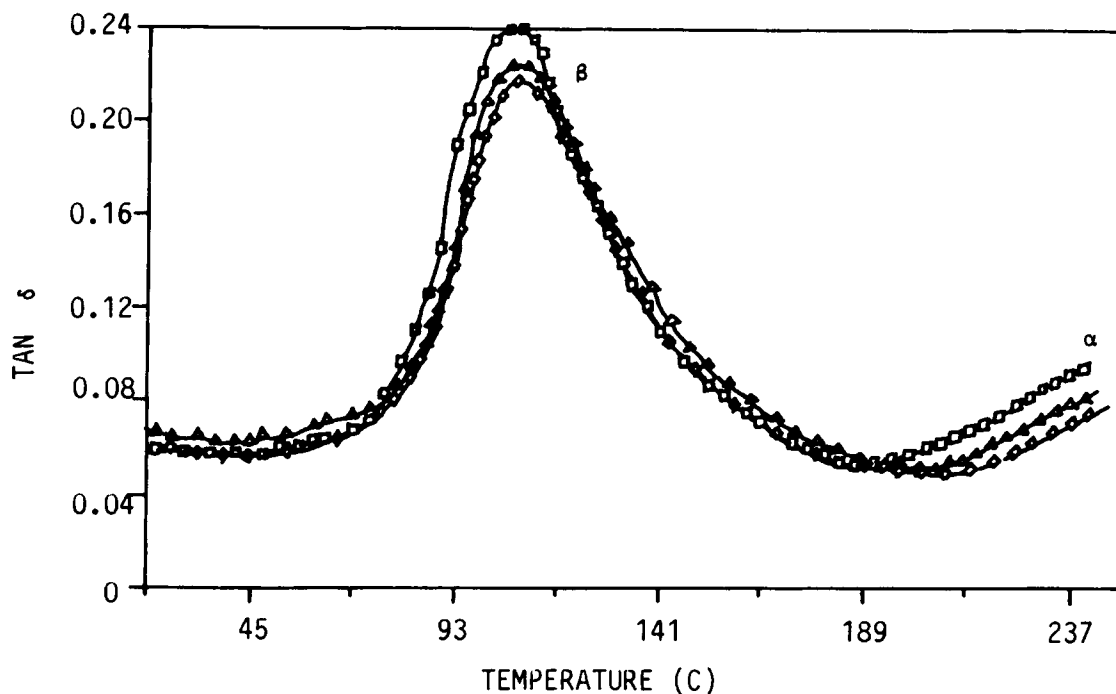


Figure 4 Temperature dependence of loss tangent for PAN precursors: (□) sample A; (△) sample C; (◇) sample D.

Table V Mechanical Properties of Resulting Carbon Fiber

Sample	Crystal Size L_c (Å)	Orientation (%)	Tensile Strength (g/d)	Elongation (%)	Average Pore Diameter (μm)
A	10.07	71.9	10.6	0.65	0.0667
B	11.06	74.1	13.5	0.81	0.0440
C	11.61	75	13.6	0.92	0.0349
D	12.19	76.2	15.2	1.11	0.0303

defined peaks at approximately 110°C (beta) and approximately 240°C (alpha). The beta peak was attributed to molecular motion. The alpha peak was believed to be caused by some type of chemical reaction such as cyclization, cross-linking, or degradation, during the stabilization process. Sample A, with lower molecular weight, has a lower onset of alpha peak, which indicates a lower cyclization temperature, which is the same as those of its DSC characterization.

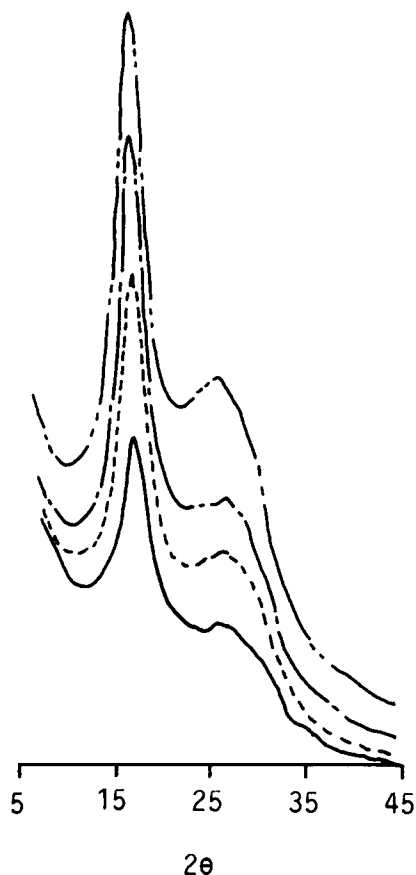


Figure 5 X-ray diffraction patterns of oxidized PAN precursor: AI value 20.6% for sample A (—), 25% for sample B (---), 25.4% for sample C (-·-·-); 28.4% for sample D (·····).

From previous investigation,¹⁹ the PAN precursor with the lowest onset of exothermic temperature, which is regarded as the cyclization temperature, had the largest AI value. Here, it is interesting that the PAN precursor with higher molecular weight and higher onset of exothermic temperature has a higher AI value (Fig. 5). This is attributed to that the time required for oxygen to attack the AN units of the cross-section center for the bean cross section during oxidation to form the ladder polymer is less than that for the circular cross section.

Mechanical Properties

The increase in molecular weight leads to a positive influence on the tenacity of PAN precursor (Table III) and its resulting carbon fiber (Table V) because of the perfection of crystal, preferred orientation, and smaller average pore diameter.

CONCLUSIONS

PAN precursor exhibits the circular cross section in the molecular weight 1.65×10^5 , and the bean cross section with straighter and deeper grooves in its longitudinal surface, in the higher molecular weight 3.4×10^5 . PAN precursor has a higher onset of exothermic temperature, peak temperature, and higher AI value as the molecular weight increases. The increase of molecular weight can improve the properties of PAN precursor and its resulting carbon fiber.

REFERENCES

1. W. Watt, *Carbon*, **10**, 121 (1972).
2. O. P. Bahl and L. M. Manocha, *Carbon*, **12**, 417 (1974).
3. O. P. Bahl, R. B. Mathur, and K. D. Kundra, *Fibre Sci. Tech.*, **15**, 147 (1981).
4. G. Henrici Olive and S. Olive, *Adv. Polym. Sci.*, **51**, 48 (1983).

5. R. B. Beevers, *J. Polym. Sci. A*, **2**, 5257 (1964).
6. Edward V. Thompson, *J. Polym. Sci. B*, **4**, 361 (1966).
7. S. Uchiyama, *Sen-I Gakkaishi*, **22**, 421 (1966).
8. A. I. Stoyanov, *J. Appl. Polym. Sci.*, **24**, 583 (1979).
9. A. Takaku and N. Kishi, *Sen-I Gakkaishi*, **22**, 103 (1966).
10. T. Uchida, I. Shinoyama, Y. Ito, and K. Nukuda, in *Proceedings of the 10th Biennial Conference on Carbon*, Bethlehem, PA, 1971, p. 31.
11. A. Ziabicki, *Fundamentals of Fibre Formation*, Wiley, New York, 1976, p. 252.
12. J. P. Knudsen, *Text. Res. J.*, **33**, 13 (1963).
13. M. Takahashi and M. Watanabe, *Sen-I Gakkaishi*, **15**, 951 (1959).
14. M. M. Zwick and C. Van Bochove, *Text. Res. J.*, **34**, 417 (1964).
15. M. Takahashi and M. Watanabe, *Sen-I Gakkaishi*, **17**, 249 (1961).
16. Z. K. Walczak, *Formation of Synthetic Fibre*, Gordon & Breach, New York, 1977, p. 244.
17. J.-S. Tsai, *Polyacrylonitrile Precursory Fibre for Carbon Fibre*, CRC/CTCI Report No. 064, 1986, p. 85.
18. A. Shindo, private communication.
19. J.-S. Tsai and C.-H. Lin, *J. Appl. Polym. Sci.*, to appear.

Received November 13, 1989

Accepted October 12, 1990