Properties of High-Speed Spun High Molecular Weight Poly(ethylene terephthalate) Filaments

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ABSTRACT: High-speed spinning of high molecular weight poly(ethylene terephthalate) (PET) having an intrinsic viscosity of 0.98 dL/g was performed at the take-up velocity range of 2.5–5.5 km/min. The structure of the as-spun filaments was analyzed by density, birefringence, WAXS, DSC, boiling water shrinkage, and tensile properties. Stress-induced crystallization takes place above 3 km/min, which is confirmed by the steep increase in density, the growth of the crystal size, melting point increase, and the decrease in boiling water shrinkage. The plot of crystallinity versus birefringence shows that crystallinity increases drastically after birefringence reaches the value of about 0.075. A comparison with the data of other researchers will clearly present the effects of molecular weight on the properties of PET filaments spun at high speed, for example, the take-up velocity range of the steep increase in density for high molecular weight PET is lower than that for low molecular weight PET by about 1 km/min. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1283–1291, 1999

Key words: high-speed spinning; high molecular weight PET; stress-induced crystallization

INTRODUCTION

Unlike the conventional spin-draw process, which consists of low-speed spinning and subsequent drawing, high-speed spinning adopts a one-step process, producing filaments at high speed. Extensive investigations were performed on the process–structure–property relationships of high-speed spun poly(ethylene terephthalate) (PET) filaments as a function of take-up velocity.[1–8] Above the critical take-up velocity, at which the birefringence of the filament obtained reaches the value of 0.06 or higher, crystallization takes place in the spin line, which leads to the steep increase in filament density.[1–3] Critical take-up velocity varies with other spinning conditions such as a

melt draw ratio[2] and the molecular weight of the polymer used.[9] Crystalline texture improves as the take-up velocity increases.[3,7,10] The molecular orientation in the amorphous region of the high-speed spun filament, on the other hand, is lower than that of the conventional spin-draw filament, which results in lower strength and higher breaking elongation.[8,11] Besides, the radial property difference inside the filament cross section occurs for the ultrahigh-speed spinning above 8 km/min due to a different stress-induced crystallization condition between the sheath and core of the spin line.[12]

In most of the research for high-speed spinning, low molecular weight PET having a low intrinsic viscosity (IV) of about 0.6 dL/g was used, which is for an apparel end use. High molecular weight PET, whose IV is higher than 0.9 dL/g, matches with the filament for a high-performance end use such as tire cord for which a high modu-

lus and dimensional stability are indispensable. Relatively little attention has been paid to the high-speed spinning of high molecular weight PET except for studying the effect of molecular weight on high-speed spinning[9,13] and for achieving improved mechanical properties by modifying threadline dynamics through controlled air quenching[14] or a liquid isothermal bath spinning process.[15,16] This work aimed to characterize the physical structure and properties of PET filaments spun at high speed from high molecular weight PET and to present the effects of molecular weight and processing parameters on the properties of high-speed spun PET filaments in detail by comparing them with the data reported by other researchers.

EXPERIMENTAL

Material and Melt-spinning Process

Tire cord-grade PET supplied by Kolon Ltd. Kumi, South Korea, having an intrinsic viscosity of 0.98 dL/g, measured in 60/40 wt % phenol/tetrachloroethane solvent at 23°C, was used. The viscosity-average molecular weight (M_v) of PET is related to the intrinsic viscosity by the following relation[17]:

$$IV = 2.1 \times 10^{-4} M_v^{0.82} \qquad (1)$$

and thus has the value of 29,800 g/mol. PET chips were dried in a vacuum oven at 140°C for 16 h before extrusion.

A tire cord melt-spinning apparatus was used, which was equipped with a large-scale extruder and a gear pump to yield a high total mass flow rate. Multifilament melt spinning was performed at the extrusion temperature of 295°C with a die having 192 holes and each having a diameter of 0.6 mm. The holes are distributed in the form of three concentric circles at the outer part of the die. By fixing the rpm of the gear pump, the mass flow rate was adjusted at 2.4 g min^{-1} hole^{-1}. Below the die assembly, a shroud heater and a radial flow quenching chamber were placed in a row (Fig. 1). The shroud heater having a height of 12 cm was located 15 cm below the spinneret, and its temperature was set to 300°C (with no air flow). The room between the die and the shroud was sealed with steam. The radial flow quenching chamber was placed 39 cm below the spinneret with an insulation plate being inserted between

Figure 1 Schematic diagram of a shroud heater and a radial-flow quenching chamber. Arrows indicate directions of air flow and the centimeters in parentheses are the distances from the spinneret.

the shroud and the quenching chamber. Quenching air had a temperature of 25°C with a radial velocity of 36 m/min. It passes through a cylindrical air filter which is 90 cm long and has the inside diameter of 32 cm, through the filament layer from outside to inside, and then goes out. Filaments that passed through them were taken-up at the winder via godet roller. Take-up velocity was increased by 0.5 km/min from 2.5 up to 5.5 km/min.

Characterization

Density

Density was measured on small loops of filaments with a density gradient column at 23°C, which had the liquid system of n-heptane/tetrachloromethane. Volume fraction crystallinity (X) was calculated from the measured filament density (ρ) using the following equation:

$$X = \frac{\rho - \rho_a}{\rho_c - \rho_a} \qquad (2)$$

where ρ_a and ρ_c are densities of fully amorphous and crystalline samples, respectively. For PET, ρ_a of 1.335 g/cm^3 and ρ_c of 1.455 g/cm^3 were used.[18]

Birefringence

Birefringence measurements were performed using a Zeiss Axiophot polarizing microscope with

an Ehringhaus compensator. The diameter of the filament was measured with the help of an eyepiece micrometer. An average of five different measurements was reported.

X-ray Diffraction

Wide-angle X-ray scattering (WAXS) analyses of filament samples were performed with a Rigaku Denki RU200B X-ray diffractometer. WAXS intensity curves for equatorial and azimuthal scans were obtained using nickel-filtered CuKα radiation. Apparent crystal sizes (L_{hkl}) were estimated using the Scherrer equation[19] with a correction factor (K) of 0.9 for lattice distortion:

$$L_{hkl} = \frac{K\lambda}{\beta \cos \theta} \qquad (3)$$

where λ is the wavelength of the X-ray beam; β, the half-width of a pure equatorial reflection profile in radians; and θ, the Bragg angle. The pure reflection profile for the (hkl) plane was obtained by resolving the equatorial scattering curve into three Pearson VII functions.[20] An interplanar spacing (d) was calculated from the equation of $n\lambda = 2d \sin \theta$ with n of 1 and the number of repeating units as L_{hkl}/d. The crystalline orientation factor was determined from averaging two crystalline orientation factors of (010) and (100) planes. The crystalline orientation factor of each plane was obtained from the resolved azimuthal reflection profile using the half-width method. The amorphous orientation factor (f_a) was calculated from the measured birefringence (Δn), crystallinity, and crystalline orientation factor (f_c) by the equation proposed by Stein and Norris[21]:

$$\Delta n = \Delta n_c X f_c + \Delta n_a (1 - X) f_a \qquad (4)$$

where Δn_c and Δn_a are intrinsic birefringences of crystalline and amorphous phases, respectively. Following Dumbleton,[22] Δn_c of 0.220 and Δn_a of 0.275 were used.

DSC

Thermal characteristics were analyzed with a Perkin–Elmer DSC-7 differential scanning calorimeter. Filament samples, knotted together to have the weight of about 10 mg, were used in each run. The first heating DSC thermograms were obtained at a heating rate of 10°C/min.

Boiling Water Shrinkage

A loop of filaments whose initial length (l_0) was 137 cm, as measured under a slight tension which did not cause deformation, was immersed in boiling water for 30 min and the length after shrinkage (l_s) was measured under the same tension after 24 h. Percentage shrinkage was determined using the following equation:

$$\text{Percentage shrinkage (\%)} = \frac{l_0 - l_s}{l_0} \times 100 \qquad (5)$$

Tensile Property

Tensile tests were done on an Instron at room temperature. A gauge length of 50 mm and constant crosshead speed of 30 mm/min were used. An average of seven individual tests was obtained.

RESULTS AND DISCUSSION

High-speed melt spinning of high molecular weight PET (IV of 0.98 dL/g) was done at various take-up velocities of 2.5–5.5 km/min. Under the spinning conditions described above, PET showed good spinnability up to 5.5 km/min, whereas the breakage in the spin line occurred occasionally above 5.5 km/min. The fixed mass flow rate corresponds to the calculated extrusion velocity of 7.0 m/min by considering the density of extrudate as a linear decreasing function of the spinning temperature.[2] The melt draw ratio calculated as the ratio of take-up to extrusion velocity varies from 358 (2.5 km/min) to 787 (5.5 km/min). The linear density of filaments obtained ranged from 750 to 1625 denier/192 filaments depending on take-up velocity.

Focusing on the quenching conditions, the shroud heater located just below the spinneret is similar to the on-line zone heating chamber used in the study of Hotter et al.[14] They set a zone heating chamber at a high temperature close to the spinneret and found that the retarded air quench due to a heating chamber grants improved stability to the spinning at very high take-up velocities and yields a continued development in orientation beyond the take-up velocity range where a decline is usually observed. With the shroud heater, it is confirmed that the air quenching does not take place before filaments reach the quenching chamber. Thus, it provides a

Figure 2 Density and volume fraction crystallinity of PET filaments spun at various take-up velocities. The result of this study is shown by filled circles. Reference numbers and intrinsic viscosities of the other researchers are indicated.

similar retarded air-quench condition and is expected to have similar influence on the threadline dynamics. But the stabilizing effect of the shroud heater on the spinning at high take-up velocities was not appreciable above 5.5 km/min. In general, maximum take-up velocity without spin line breakage for high molecular weight PET is lower than that for low molecular weight PET. Reported maximum take-up velocities for high molecular weight PET are 6–6.5 km/min without any quench modifications[9,13] and 7 km/min with the zone heating chamber.[14] A relatively low take-up velocity limit in this study, regardless of the use of the shroud heater, is believed to be due to the notably higher melt draw ratio. Chen et al.[13] reported that in the monofilament spinning radial-flow quench completely eliminates the crimping behavior and produces a symmetrical fringe pattern in an interference photomicrograph when compared with a cross-flow quench. Although the radial-flow quench used in this study is not expected to have exactly the same effect as for monofilament spinning, no crimp was observed in this study either.

Figure 2 shows the density and the calculated volume fraction crystallinity of PET filaments as a function of take-up velocity. The result of this study is shown by filled circles and some data of other researchers available in the literature are also included in discussing the effects of molecular weight and spinning conditions. Of those researches, some adopted the melt spinning at a constant take-up denier[3,6,13] and others including this study at a constant mass flow rate.[9] Filled and empty symbols, respectively, represent high

and low molecular weight PET and the notation in Figure 2 is also used for Figures 3, 4, and 7.

As seen in Figure 2, the overall tendency is that the density and thus the crystallinity of PET filaments increase steeply above certain take-up velocity and then level off or decrease. The steep increase originates from the fact that chain segments highly oriented by draw down behave as nucleation sites for crystallization when orientation reaches a critical value.[2,23] Although precise spinning conditions are different from each other, the take-up velocity range of the steep increase in

Figure 3 Birefringence of PET filaments spun at various take-up velocities. Symbols are the same as those in Figure 2.

Figure 4 Plot of crystallinity versus birefringence of PET filaments spun at various take-up velocities. Symbols are the same as those in Figure 2. Solid lines present regressions from the data of this study.

crystallinity is 4–5.5 km/min for low molecular weight PET, while that for high molecular weight PET is lower by about 1 km/min and ranges between 3 and 4.5 km/min. The result of this study is identical with the trend of high molecular weight PET. The melt from higher molecular weight PET contains physical crosslinks of higher density and thus gives higher elongational viscosity. Through the simple constitutive equation in which spinning stress is obtained by the product of elongational viscosity and the velocity gradient, it leads to higher spinning stress which produces molecules of a higher level of orientation capable of stress-induced crystallization. Conclusively, higher spinning stress encountered at the same take-up velocity for high molecular weight PET explains the crystallization in the lower take-up velocity range. In this way, a speed gap in the crystalline development occurs depending on molecular weight. In addition, the lower take-up velocity limit for high molecular weight PET mentioned above is also explained in this way, that is, higher spinning stress leads to a rupture in the spin line at lower take-up velocity.

Comparing this study with the high molecular weight data of Shimizu et al.[9] (both have IVs of 0.98 dL/g) may reveal the effect of the melt draw ratio. The mass flow rate in the study of Shimizu et al.[9] (5.54–5.77 g min^{-1} hole^{-1}) is about twice as large as that of this study. The melt draw ratio

varies over the range of about 40–280 (1–6.5 km/min) and is much lower than that of this study at the same take-up velocity. While the starting and the saturation values for crystallinity of both studies are situated at the same level, the crystallinity of this study is the higher of the two by about 10% at 4 km/min. Therefore, the steep increase portion of the change in crystallinity for this study is located at a slightly lower take-up velocity range. This effect of melt draw ratio is explained by the different cooling conditions.[2] The higher melt draw ratio increases cooling intensity, which gives higher elongational viscosity through the relation in which elongational viscosity is given as an exponentially decreasing function of temperature.[24] Higher spinning stress generated due to a higher melt draw ratio results in a lower shift as does the molecular weight effect. But the effect of the melt draw ratio is thought to be minor compared to that of the molecular weight as the extent of the shift due to a different melt draw ratio is smaller. It is somewhat hard to compare it with the study of Chen et al.[13] adopting constant denier spinning.

Ziabicki[25] suggested a qualitative regularity that crystallinity does not level off but passes through a maximum and then decreases. It is based on the fact that the product of the maximum crystallization rate and the crystallization time, a rough estimate of crystallinity, shows a maximum of which the value and the position depend on the polymer viscosity, filament radius, and cooling intensity. In Figure 2, low molecular weight PET exhibits maximum crystallinity, while the high molecular weight PET including this study usually levels off. The value of the maximum crystallinity is higher for low molecular weight PET. The position of maximum crystallinity is located at lower take-up velocity for high molecular weight PET, which is explained in a similar way as to the speed gap. Unless there is limited spinnability for high molecular weight PET, it will also show a maximum.

Figure 3 shows the change in birefringence of PET filaments with take-up velocity. The birefringence of this study increases rapidly from a relatively low take-up velocity of 2.5 km/min and then levels off at around 5 km/min. The relatively high value of birefringence obtained in this study is basically related to the high melt draw ratio and is consistent with the result of Hotter et al.[14] who modified the air quench with the heating chamber to give a retarded air quench and, hence, improved the orientation.

Birefringence develops nearly in a linear fashion especially at low take-up velocity range, which differs from the evolution shape of crystallinity. The less pronounced sigmoidal feature implies that at a low take-up velocity range overall orientation increases linearly with the imposed draw down. On the other hand, crystallinity develops in a nonlinear manner with take-up velocity, that is, it increases steeply when the produced birefringence or the spinning stress has a critical value. For instance, George et al.[4] reported that crystallization takes place when the spinning stress is above 0.08 g/den. Above the critical take-up velocity, the necklike deformation related to the crystallization in the spin line predominates in the threadline dynamics.[26] Therefore, at a high take-up velocity range, the effect of the melt draw down becomes less significant[2] and birefringence develops not in a linear fashion but in the form of leveling off or showing a maximum with increasing take-up velocity, which follows the tendency of crystallinity.

The effect of molecular weight on the development of birefringence is similar to that in crystallinity and can be seen between the data of the same authors, that is, Shimizu et al.[9] and Chen et al.[13] But, on the whole, it is less noticeable than in crystallinity. Besides, the reversal in the birefringence value between high and low molecular weight PET usually takes place at a high take-up velocity above 6 km/min due to different spinnability.

The above discussion about the crystalline development is clearly shown in the plot of crystallinity versus birefringence given in Figure 4. As pointed out by Shimizu et al.,[2] such a plot has an inflection point above which crystallinity increases drastically, and the birefringence value giving such a conversion is 0.06 or higher. The result of this study agrees with the discussion and exhibits the inflection point at the birefringence of about 0.075, as can be seen from the two regression lines, one of which in the low birefringence region is adjusted to pass through the origin. All data cited here show a rather good correspondence irrespective of molecular weight and spinning conditions, which suggests that such a phenomenon is an intrinsic one.

Equatorial WAXS diffraction patterns in Figure 5 show that three major peaks of the PET crystal start to develop above 3 km/min, which is in accordance with the crystallinity change in Figure 2. As take-up velocity increases, more sharp and resolved peaks are obtained, indicating the

Figure 5 Equatorial WAXS patterns of PET filaments spun at various take-up velocities. Take-up velocities (km/min) are indicated in the figure.

formation of much more perfect crystalline structures. Apparent crystal sizes in the lateral direction calculated from the resolved three Pearson VII functions are shown in Table I. Crystal sizes increase rapidly in the take-up velocity range of 3–4 km/min and then tend to increase slowly. Of the three lateral directions, the crystal size of the (100) plane normal shows a continued increase with take-up velocity. The number of repeating units per crystal has the same trend, and, therefore, the overall change of crystal size in the lateral direction is identical with the result of the volume fraction crystallinity. Crystalline and amorphous orientation factors are also shown in Table I. Along with the enlargement of the crystal size, the crystalline orientation factor increases rapidly at 3–4 km/min and is over 0.9 at 4 km/min. The amorphous orientation factor increases but slowly with increasing take-up velocity, which implies that crystalline-phase evolution predominates in the development of birefringence.

Figure 6 presents DSC thermograms of PET filaments. The cold crystallization peak shifts to a lower temperature and its area decreases with increasing take-up velocity, just as the general trend goes.[3] As the crystallization peak is located at a low temperature close to the glass transition, it is difficult to clearly distinguish between the glass transition and the crystallization exotherm even at a low take-up velocity of 2.5 km/min. This

Table I   Crystal Structure and Orientation Factors of PET Filaments

Take-up Velocity (km/min)	Crystal Size (Å)			Interplanar Spacing (Å)			Repeat Units (per Crystal)			Orientation Factors	
	010	$\bar{1}10$	100	010	$\bar{1}10$	100	010	$\bar{1}10$	100	f_c	f_a
2.5	—	—	—	—	—	—	—	—	—	—	—
3	16.8	17.0	31.2	4.95	3.92	3.44	3.4	4.3	9.1	0.825	0.214
3.5	33.0	25.8	40.0	5.01	3.93	3.43	6.6	6.6	11.6	0.873	0.266
4	55.1	42.3	44.4	5.03	3.94	3.43	11.0	10.7	12.9	0.914	0.291
4.5	57.6	45.5	48.7	5.00	3.93	3.42	11.5	11.6	14.2	0.926	0.308
5	56.8	51.6	51.4	5.00	3.94	3.42	11.4	13.1	15.0	0.941	0.314
5.5	57.1	48.8	53.8	5.00	3.94	3.42	11.4	12.4	15.8	0.946	0.313

appearance may be another feature of PET filaments spun from high molecular weight PET, that is, higher spinning stress causes higher molecular orientation, and as a result, it increases the ability to start thermally induced crystallization at a lower temperature than in the case of low molecular weight PET. In the DTA diagrams of Heuvel and Huisman[3] using the PET of 0.63

Figure 6 DSC thermograms of PET filaments spun at various take-up velocities. Take-up velocities (km/min) are indicated in the figure.

dL/g, this overlap is found at 4–5 km/min. The crystallization peak vanishes almost entirely above 5 km/min. In addition, the melting point was increased from 255°C at 3 km/min to 280°C at 5.5 km/min, which indicates the formation of more thermally stable crystals. This substantial increase above a relatively low take-up velocity of 3 km/min is also characteristic of high molecular weight PET, which is related to the crystalline structure development in Figure 2 and Table I. Above 4 km/min, a shoulder appears in the melting peak. The position of the shoulder coincides with the melting point of filaments spun at low take-up velocity, which is attributed to the melting of the ordered region produced by annealing during the DSC test.

Figure 7 shows boiling water shrinkage except for the dry shrinkage data from Yasuda.[5] The data of Heuvel and Huisman are obtained from another reference.[27] At a low take-up velocity range, shrinkage increases with increasing take-up velocity because higher molecular orientation yields a higher entropic retractive force and ordered molecules can actually shrink without any obstacles such as crystals. Above the critical take-up velocity, crystals generated hinder the shrinkage of molecules in the amorphous region, and thus shrinkage decreases rapidly with increasing crystallinity. From this discussion, the shrinkage change as a function of take-up velocity is directly predicted from the crystallinity change in Figure 2. The boiling water shrinkage of this study decreases drastically at 3–4 km/min where the crystallinity in Figure 2 increases steeply, and above 4 km/min, it has a value below 5%. Besides, the effect of molecular weight is also manifested in that the range of the steep decrease

Figure 7   Boiling water shrinkage of PET filaments spun at various take-up velocities. Note that the data of Yasuda[5] are from a dry shrinkage test. Symbols are the same as those in Figure 2 except for the data of Heuvel and Huisman.[27]

in shrinkage for high molecular weight PET is lower than that for low molecular weight PET by more than 1 km/min.

Tensile tests showed that a natural draw zone diminishes with increasing take-up velocity and disappears at 5.5 km/min. Tensile properties are shown in Figure 8. Yield stress and tenacity increase, while yield strain and breaking elongation decrease with increasing take-up velocity. While tensile strengths of PET filaments high-speed spun from low molecular weight PET usually show a maximum and a decrease, those of this study do not show a maximum. Instead, the rate

of increase in yield stress decreases markedly above 5 km/min where the natural draw zone starts to disappear, and the rate of increase in tenacity gradually decreases at higher take-up velocities, which is thought to be related to the saturation in the structural developments such as the changes in crystallinity and birefringence. High molecular weight PET exhibits higher strength values than does low molecular weight PET below the take-up velocity where the reversal of birefringence takes place.[13] Besides, tensile properties obtained in this study follow the general trend, that is, high-speed spun filaments show lower strengths and higher breaking elongation than those of the conventional spin-draw filaments.[11]

CONCLUSIONS

High-speed spinning of high molecular weight PET and structural characterizations of the PET filaments obtained were performed. Density increases steeply at take-up velocities of 3–4.5 km/min due to a stress-induced crystallization. Birefringence increases linearly with take-up velocity and then levels off. WAXS diffraction patterns and the crystal-size enlargement accord with the result of density. Crystalline and amorphous orientation factors increase rapidly at 3–4 km/min. Cold crystallization peaks occur at lower temperatures near the glass transition, and the melting point starts to increase above 3 km/min. Boiling water shrinkage decreases drastically at the same take-up velocity range as that of the steep increase in crystallinity. Tensile properties vary depending on the structural developments. Such

(a)

(b)

Figure 8   Tensile properties of PET filaments spun at various take-up velocities: (a) yield stress and yield strain; (b) tenacity and breaking elongation.

an aspect that crystallization in the spin line takes place at a lower take-up velocity range for high molecular weight PET (speed lead) can be seen definitely by comparing it with the data of other researchers for high and low molecular weight PET. In this study, crystallinity increases drastically after birefringence reaches the value of about 0.075. From the plot of crystallinity versus birefringence, such an inflection of crystallinity could be regarded as an intrinsic phenomenon notwithstanding molecular weight and spinning conditions.

REFERENCES

1. Shimizu, J.; Toriumi, K.; Tamai, K. Sen-I Gakkaishi 1977, 33, T208.
2. Shimizu, J.; Okui, N.; Kaneko, A.; Toriumi, K. Sen-I Gakkaishi 1978, 34, T64.
3. Heuvel, H. M.; Huisman, R. J Appl Polym Sci 1978, 22, 2229.
4. George, H. H.; Holt, A.; Buckley, A. Polym Eng Sci 1983, 23, 95.
5. Yasuda, H. In High-Speed Fiber Spinning; Ziabicki, A.; Kawai, H. Eds.; Wiley: New York, 1985; Chapter 13.
6. Vassilatos, G.; Knox, B. H.; Frankfort, H. R. E. In High-Speed Fiber Spinning; Ziabicki, A.; Kawai, H., Eds.; Wiley: New York, 1985; Chapter 14.
7. Fujimoto, K.; Iohara, K.; Ohwaki, S.; Murase, Y. J Appl Polym Sci 1991, 42, 1509.
8. Kiang, C. T.; Cuculo, J. A. J Appl Polym Sci 1992, 46, 83.
9. Shimizu, J.; Okui, N.; Kikutani, T.; Toriumi, K. Sen-I Gakkaishi 1978, 34, T93.
10. Shimizu, J.; Kikutani, T.; Takaku, A.; Okui, N. Sen-I Gakkaishi 1984, 40, T177.
11. Kawaguchi, T. In High-Speed Fiber Spinning; Ziabicki, A.; Kawai, H., Eds.; Wiley: New York, 1985; Chapter 1.
12. Shimizu, J.; Okui, N.; Kikutani, T. Sen-I Gakkaishi 1981, 37, T135.
13. Chen, G. Y.; Cuculo, J. A.; Tucker, P. A. J Appl Polym Sci 1992, 44, 447.
14. Hotter, J. F.; Cuculo, J. A.; Tucker, P. A. J Appl Polym Sci 1991, 43, 1511.
15. Wu, G.; Zhou, Q.; Chen, J. Y.; Hotter, J. F.; Tucker, P. A.; Cuculo, J. A. J Appl Polym Sci 1995, 55, 1275.
16. Zhou, Q.; Wu, G.; Tucker, P. A.; Cuculo, J. A. J Polym Sci Polym Phys Ed 1995, 33, 909.
17. Conix, A. Makromol Chem 1958, 26, 226.
18. Daubeny, R. P.; Bunn, C. W.; Brown, C. J. Proc R Soc A 1954, 226, 531.
19. Alexander, L. E. X-Ray Diffraction Methods in Polymer Science; Wiley: New York, 1969.
20. Heuvel, H. M.; Huisman, R.; Lind, K. C. J. B. J Polym Sci Polym Phys Ed 1976, 14, 921.
21. Stein, R. S.; Norris, F. H. J Polym Sci 1956, 21, 381.
22. Dumbleton, J. H. J Polym Sci A-2 1968, 6, 795.
23. Schultz, J. M. Polym Eng Sci 1991, 31, 661.
24. Kase, S. In High-Speed Fiber Spinning; Ziabicki, A.; Kawai, H., Eds.; Wiley: New York, 1985; Chapter 3.
25. Ziabicki, A. In High-Speed Fiber Spinning; Ziabicki, A.; Kawai, H., Eds.; Wiley: New York, 1985; Chapter 2.
26. Shimizu, J.; Okui, N.; Kikutani, T. In High-Speed Fiber Spinning; Ziabicki, A.; Kawai, H., Eds.; Wiley: New York, 1985; Chapter 7.
27. Heuvel, H. M.; Huisman, R. In High-Speed Fiber Spinning, Ziabicki, A.; Kawai, H. Eds.; Wiley: New York, 1985; Chapter 11.