

Structure Development in the Melt Spinning of Nylon 66 Fibers and Comparison to Nylon 6

MERLIN D. DANFORD, JOSEPH E. SPRUIELL, and JAMES L. WHITE,
*Polymer Engineering, The University of Tennessee,
Knoxville, Tennessee 37916*

Synopsis

The development of crystallinity and orientation during the melt spinning of nylon 66 was investigated. Nylon 66 was found to crystallize in the spinline to form the Bunn-Garner α -triclinic structure. This behavior differs from that of nylon 6. Nylon 66 was found to develop lower crystalline orientation than nylon 6 under comparable spinning conditions.

INTRODUCTION

The aliphatic polyamides nylon 66 and nylon 6 are among the most important commercial fibers. While the dynamics and structure development occurring during the melt spinning of nylon 6 have received substantial study,¹⁻⁸ there have been relatively few published studies for nylon 66. The only investigations of a fundamental character are those of Ziabicki and Kedzierska⁹ and Chappel, Culpin, Gosden, and Tranter,¹⁰ but these are largely qualitative. Hancock, Spruiell, and White¹¹ have made a basic study of structure development during the wet spinning of both nylon 66 and nylon 6. Summaries of nylon 66 technology are given in the treatise edited by Kohan¹² and in the review article by Hopff.¹³

In this paper we present a basic experimental study of structure development of nylon 66 in the spinline and of the structure, orientation, and mechanical properties of the melt-spun fibers. We particularly compare these results with studies of nylon 6 by Bankar, Spruiell, and White⁸ in our laboratories. General reviews of structure development during melt spinning are given in the monograph by Ziabicki¹⁴ and Spruiell and White.¹⁵ This paper continues studies in our laboratory of structure development during fiber formation.^{8,11,15-21}

CRYSTAL STRUCTURES OF NYLON 66

Basic studies of the crystal structure of nylon 66 began with Fuller, Baker, and Pape.²² They determined the chain-axis repeat distance and showed that it corresponded to an extended, planar zigzag chain conformation. Bunn and Garner²³ made a detailed study of the crystal structure of drawn nylon 66. The major phase, denoted α , was shown to consist of extended chains arranged in triclinic unit cells. A second triclinic cell, denoted β , was also observed.

Other polymorphic forms have been described in the literature. Brill,²⁴ Slichter,²⁵ and Starkweather²⁴ describe a high-temperature hexagonal form of nylon 66. Starkweather, Whitney, and Johnson^{26,27} describe a nematic form of nylon 66 induced by quenching. None of these studies nor that of Chappel et al.¹⁰

studies the crystal structure of melt-spun fibers. Reviews of the crystal structures of nylon 66 are given by Clark and Wilson²⁸ and Starkweather.²⁶

Studies of crystalline orientation in nylon 66 are few. Indeed, only Dumbleton, Buchanan, and Bowles²⁹ have reported quantitative orientation measurements. They devised a method for determination of the Hermans orientation factor^{14,15,30-33} and made measurements on drawn nylon 66 fibers.

EXPERIMENTAL

Material

The nylon 66 polymer used was supplied by the Monsanto Textiles Company and was stored in sealed containers until used. It had an intrinsic viscosity $[\eta]$ of 0.85 in 90% formic acid at 25°C. According to Taylor's³¹ $[\eta]$ versus number-average molecular weight relationship, M_n was 10,000. An outside laboratory, however, gave an M_n value of 17,000. Before its addition to the screw extruder, the polymer was further dried in a vacuum oven for 11 hr at 100°C. This reduced the moisture content to 0.02%. The $[\eta]$ was elevated to 0.95 and the Taylor value of M_n , to 12,000.

Laminar shear viscosity measurements were obtained on the dried polymer in an Instron capillary rheometer at 280°C using three dies ($L/D = 9.4, 32.8,$ and $55.7, D = 0.19$ in.). They show a viscosity of 1600 poises at 200 sec^{-1} which decreases with increasing shear rate.

Melt Spinning

The fibers were melt spun from a Fourné Associates extruder with a 1.3-cm-diameter screw. A 0.381-cm-diameter single-hole spinneret with L/D of 5 was used. The fibers were spun through air and taken up on a Leesona 959 SCR winder. This apparatus is the same as that used by Bankar et al.^{7,8} in melt-spinning nylon 6 and, with the exception of the take-up device, that of Dees and Spruiell¹⁷ and Nadella et al.²⁰ Fibers were spun at extrusion rates of 2.6 and 5.2 g/min metered by a gear pump. Take-up velocities ranged up to 2400 m/min.

On-Line Measurements

On-line measurements of fiber diameter and birefringence as a function of position were carried out. Fiber diameter was determined photographically and the birefringence, with an Olympus polarizing microscope with a Berek compensator. Spinline tensions were measured in the lower part of the spinline with a Rothschild tensiometer. The procedures are similar to those used in studies by Bankar et al.⁸ and Nadella et al.²⁰

Structural Characterization of Fibers

Melt-spun fibers were studied using wide-angle x-ray diffraction (WAXS), small-angle x-ray scattering (SAXS), birefringence, and density techniques. Crystallinities were determined in the usual way from densities obtained in a gradient density column. The general procedures and apparatus used are the same as in our earlier papers.^{8,11,16-20}

Crystalline Orientation Factors

The WAXS patterns were used to determine Hermans orientation factors f_c ^{14,15,30-33,35-37}:

$$f_c = \frac{\overline{3 \cos^2 \Phi_{c,z}} - 1}{2} \quad (1)$$

where $\Phi_{c,z}$ is the angle between the fiber axis z and the chain axis c . Only two reflections, the 100 and combined 010-110, were sufficiently intense to make quantitative measurements feasible. Various approximate methods were used to obtain f_c .

In the simplest we considered the idea of a pseudo-orthorhombic unit cell. The (100) was used to determine an $f_{a'}$. The (010-110) angular intensity variations were taken equivalent to those of (010) alone and used to obtain $f_{b'}$. f_c was obtained from Stein's relation³⁵

$$f_c = -(f_{a'} + f_{b'}) \quad (2)$$

This relationship is not strictly valid, since the angle between the normal to the (100) plane and the normal to the (010) plane is not 90° but 114°.

Other procedures involved using the methods of Wilchinsky^{36,37} who devised procedures for obtaining orientation factors in triclinic unit cells. Specifically, Wilchinsky showed that

$$\overline{\cos^2 \Phi_{hko,z}} = e^2 \overline{\cos^2 \Phi_{u,z}} + f^2 \overline{\cos^2 \Phi_{v,z}} + 2ef \overline{\cos \Phi_{u,z} \cos \Phi_{v,z}} \quad (3)$$

where e and f are the directional cosines of the unit vector perpendicular to the hkl plane with respect to the orthogonal u and v axes, respectively. In addition,

$$\overline{\cos^2 \Phi_{u,z}} + \overline{\cos^2 \Phi_{v,z}} + \overline{\cos^2 \Phi_{c,z}} = 1 \quad (4)$$

To determine $\overline{\cos^2 \Phi_{c,z}}$, we need three hko reflections. Taking the angle between the (100) and (010) planes of the triclinic cell as 114.03° and that between the (100) and (110) as 61.17°, we may write

$$\overline{\cos^2 \Phi_{100,z}} = \overline{\cos^2 \Phi_{v,z}} \quad (5a)$$

$$\overline{\cos^2 \Phi_{010,z}} = 0.834 \overline{\cos^2 \Phi_{u,z}} + 0.166 \overline{\cos^2 \Phi_{100,z}} - 0.372 \overline{\cos \Phi_{u,z} \cos \Phi_{v,z}} \quad (5b)$$

$$\overline{\cos^2 \Phi_{110,z}} = 0.767 \overline{\cos^2 \Phi_{u,z}} + 0.233 \overline{\cos^2 \Phi_{v,z}} + 0.845 \overline{\cos \Phi_{u,z} \cos \Phi_{v,z}} \quad (5c)$$

As we cannot determine $\overline{\cos^2 \Phi_{100,z}}$ independently of $\overline{\cos^2 \Phi_{010,z}}$, some additional assumption must be used.

The additional methods of determining $\overline{\cos^2 \Phi_{c,z}}$ and f_c through eq. (5) were (1) presuming

$$\overline{\cos^2 \Phi_{110,z}} = \overline{\cos^2 \Phi_{010,z}} \quad (6a)$$

and (2) neglecting the cross term, i.e.,

$$\overline{\cos^2 \Phi_{u,z} \cos \Phi_{v,z}} = 0 \quad (6b)$$

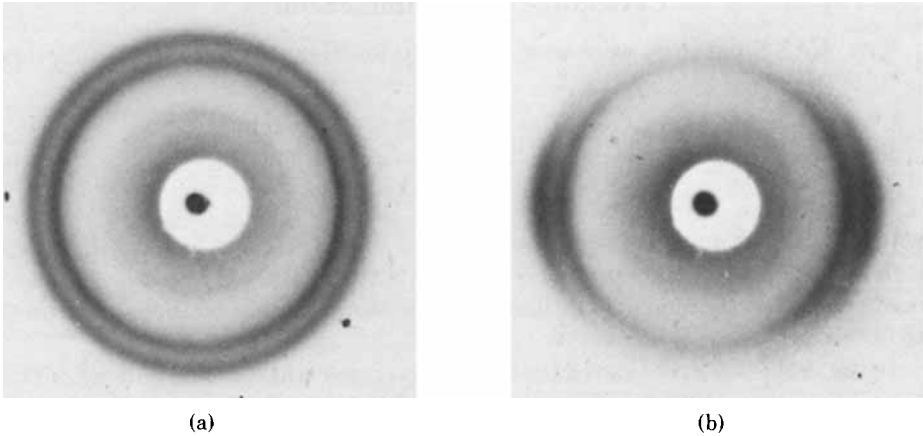


Fig. 1. WAXS patterns for melt-spun nylon 66 fibers spun at 2.6 g/min: (a) 100 m/min; (b) 750 m/min.

Amorphous and Average Orientation

One may define an orientation factor f_a for the amorphous phase as well. The birefringence may be expressed as

$$\Delta n = Xf_c \Delta_c^0 + (1 - X)f_a \Delta_a^0 \quad (7)$$

where X is the fraction of crystalline material and Δ_c^0 and Δ_a^0 are the intrinsic polarizabilities. Values of Δ_c^0 and Δ_a^0 for nylon 66 are given by Culpin and Kemp³⁸ and Matsumoto.³⁹ As these numbers are close to each other, we may define an average orientation factor

$$\Delta n = f_{av} \Delta^0 \quad (8)$$

with

$$f_{av} = Xf_c + (1 - X)f_a$$

Mechanical Properties of Spun Fibers

Stress-strain curves were obtained on melt-spun fibers using a table model Instron tensile testing machine. The apparatus and procedures were essentially those used in our earlier study on nylon 6.⁸

TABLE I
Observed Interplanar Spacing for Nylon 66 Melt-Spun Fiber

Melt-spun fiber <i>d</i> -spacing	Reflection <i>hkl</i>	Corresponding interplanar spacings computed from α unit cell of Bunn and Garner, Å
6.45	(002)	6.43
4.36	(100)	4.36
3.66	(010, 110)	3.67
2.37	(210, 110, 017, 127)	2.35
2.13	(120, 117, 027)	2.12

RESULTS

Polymorphic Form and Crystallinity

WAXS patterns of melt-spun fibers are shown in Figure 1. The repeat distances of the major reflections from these patterns are shown in Table I where they are compared to the "d" spacings computed from Bunn and Garner's²³ α -triclinic unit cell. This clearly indicates that our melt-spun fibers have the α -structure.

Crystallinity, determined from density, is plotted as a function of spinning stress in Figure 2. The crystallinity values are of the order of 34% and are observed to decrease very slightly with increasing take-up stress.

Orientation Measurements

The WAXS patterns show increasing crystalline orientation with increasing take-up velocity and drawdown. The crystalline orientation has been reduced to the Hermans orientation factors by the three methods described in the previous section. These results are summarized in Figure 3(a). Within the errors of the scale of the plot, the orientation factors are independent of method of calculation. The data for the two extrusion rates are plotted as a function of spinline stress which combines it into a single curve. This method of plotting was suggested by the results of Nadella et al.²⁰ and Oda et al.²¹

We plot birefringence as a function of spinline stress in Figure 4. It is an increasing function of spinline stress independent of extrusion rate over the range of variables studied.

The birefringence measurements may be used with the crystallinity values to compute amorphous orientation factors. These values are plotted in Figure 3(b) as a function of spinline stress. The variation of amorphous orientation is approximately linear with spinline stress in the range investigated.

SAXS Measurements

The SAXS patterns exhibited a weak maximum whose 2θ position and azimuthal intensity distribution varied with the spinline stress. At a spinline stress of 1.8×10^6 dynes/cm² (100 m/min, 2.6 g/min), the maximum was a complete

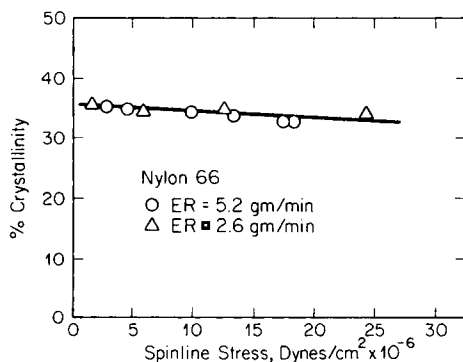
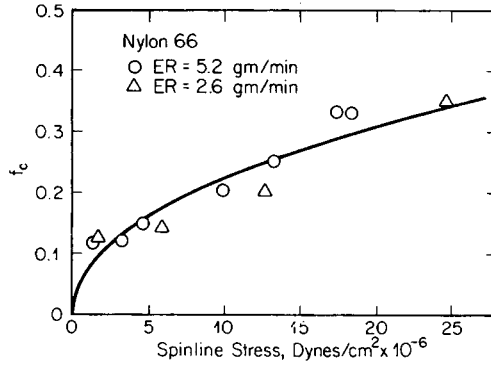
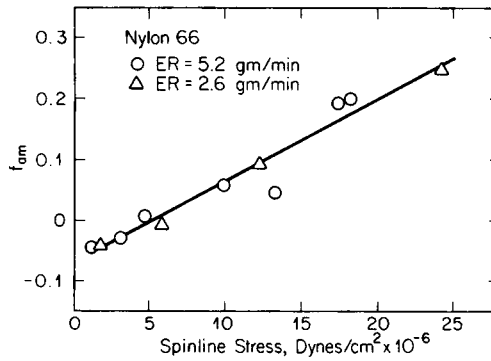


Fig. 2. Crystallinity as function of spinline stress for melt-spun fibers: (O) ER = 5.2 g/min; (Δ) ER = 2.6 g/min.



(a)



(b)

Fig. 3. Hermans orientation factors of nylon 66 fibers: (a) crystalline orientation factor (*c*-axis); (b) amorphous orientation factor; (○) ER = 5.2 g/min; (△) ER = 2.6 g/min.

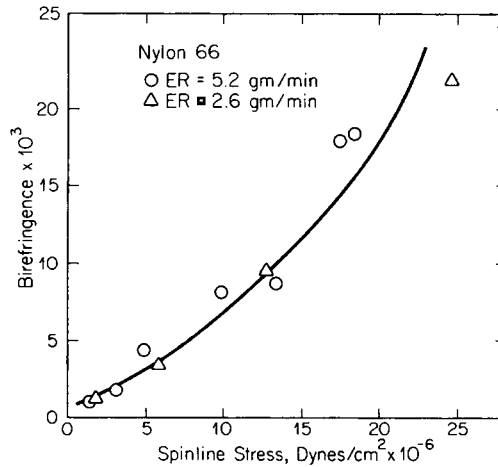


Fig. 4. Birefringence as a function of take-up stress for melt-spun nylon 66 fibers: (○) ER = 5.2 g/min; (△) ER = 2.6 g/min.

ring with only slightly higher intensity on the meridian than elsewhere. The position of the maximum corresponded to a long period of 86 Å. At a spline stress of 24.6×10^6 dynes/cm², the intensity was much stronger on the meridian than on the equator, although it could hardly be described as a well-defined

“two-point” pattern. The position of the maximum corresponded to a long period of 72 Å.

On-Line Measurements

Measurements of fiber diameter and birefringence as a function of spinline position were obtained. Birefringence is plotted as a function of spinline position in Figure 5. Generally, birefringence continues to increase along the spinline. At large distances from the spinneret, it appears to approach the values for spun and equilibrated fibers (see the comparisons listed in Table II). The fraction of the equilibrated birefringence reached in the observable portion of the spinline decreases with increasing take-up velocity.

Mechanical Properties

Engineering stress is plotted as a function of superficial infinitesimal strain for typical cases in Figure 6. As one goes to higher drawdowns and spinline stresses, there is an increase in modulus, yield strength, and tensile strength. Elongation to break decreases as the drawdown of the fiber is increased.

DISCUSSION AND COMPARISON TO NYLON 6

Crystallization

Our spinline studies suggest that nylon 66 crystallizes in the spinline to form the Bunn-Garner α -triclinic structure. This is very much unlike the behavior of nylon 6, which generally does not crystallize in the spinline but rather on the bobbin into a poorly defined γ -pseudohexagonal structure. This is most characteristically seen by comparing Bankar et al.'s⁸ study of nylon 6 birefringence variation along the spinline and spun fiber data with the present results. Bankar et al.'s spinline birefringences are much lower than our own, and their values are more than an order of magnitude lower than those of equilibrated nylon 6 fibers.

The crystallization of nylon 66 but not nylon 6 in the spinline should not be

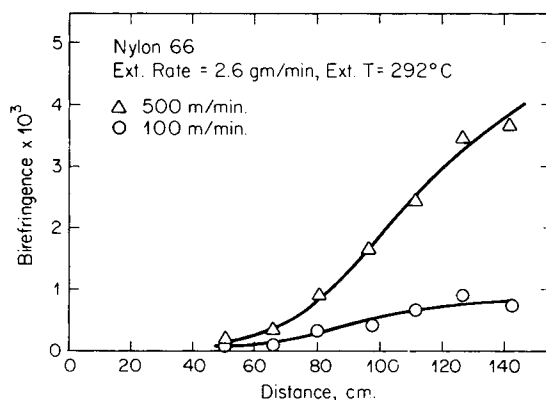


Fig. 5. Birefringence variation with position along the length of the spinline; ER = 2.6 g/min; extension temp. = 292°C: (Δ) 500 m/min; (○) 100 m/min.

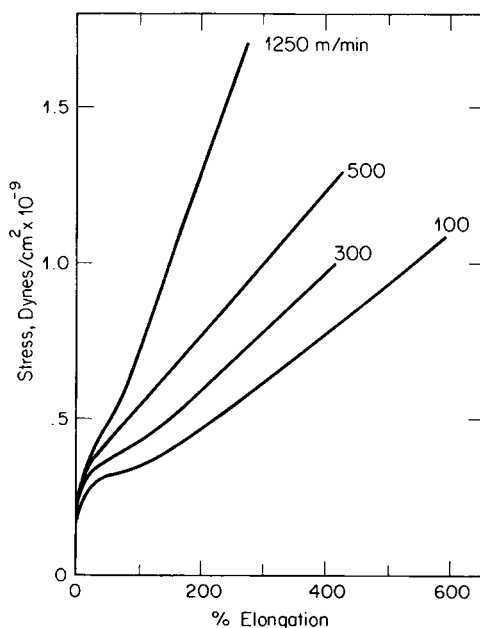


Fig. 6. Engineering stress-superficial infinitesimal strain plots for nylon 66 fibers as function of spinning conditions.

TABLE II
Comparison of Maximum On-Line Birefringence to That of Equilibrated Fibers

Take-up velocity, m/min	Extrusion rate, g/min	Maximum on-line birefringence	Equilibrated birefringence
100	2.6	0.85×10^{-3}	1.12×10^{-3}
500	2.6	4.0×10^{-3}	9.71×10^{-3}

completely unexpected. Studies of quiescent crystallization kinetics of these polymers indicate that nylon 66 crystallizes more rapidly by about an order of magnitude.^{40,41}

Orientation

Observations of WAXS patterns for nylon 66 and nylon 6 spun under similar conditions (equivalent spinline stress levels) indicate that the crystalline orientation of nylon 66 is much lower than that of nylon 6. This is shown in terms of crystalline orientation factors in Figure 7. There would seem to be no obvious reason for this. This figure also shows high-density polyethylene¹⁷ and polypropylene²⁰ data. These data are similar in character to the nylon 6 data. The SAXS results are also consistent with the low crystalline orientation of nylon 66. The reason for the peculiar behavior of nylon 66 must somehow relate to its morphology. Perhaps this low orientation merely indicates that nylon 66 crystallizes primarily in a spherulitic mode and has little tendency to form row nucleated or "cylindritic" structures.

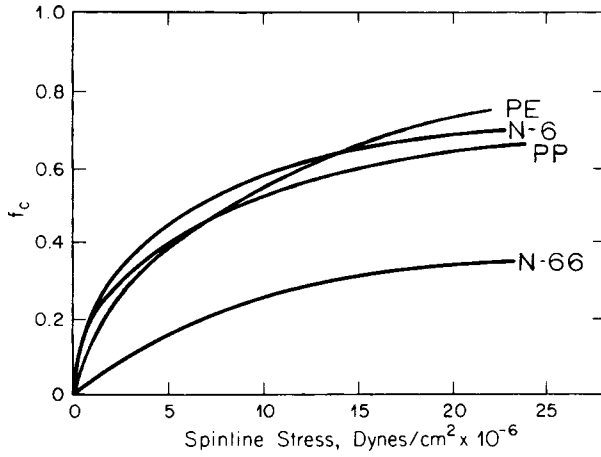
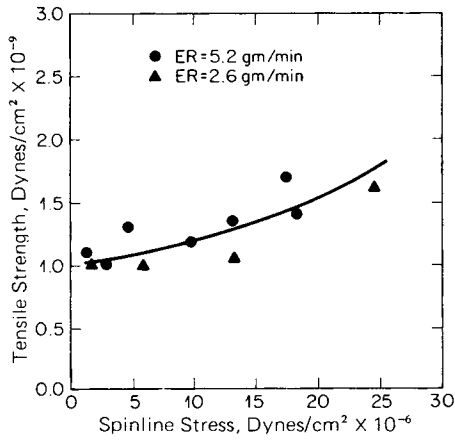
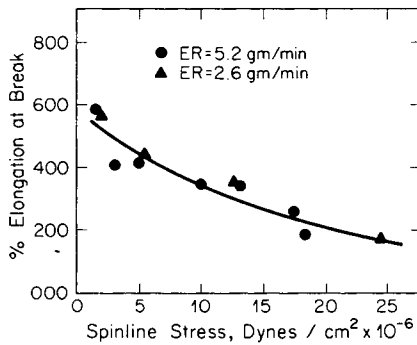


Fig. 7. Crystalline Hermans orientation factors for nylon 66, nylon 6, high-density polyethylene, and polypropylene as function of spinline stress: (●) ER = 5.2 g/min; (▲) ER = 2.6 g/min.



(a)



(b)

Fig. 8. (a) Tensile strength and (b) elongation to break of nylon 66 filaments as function of spinning stress: (●) ER = 5.2 g/min; (▲) ER = 2.6 g/min.

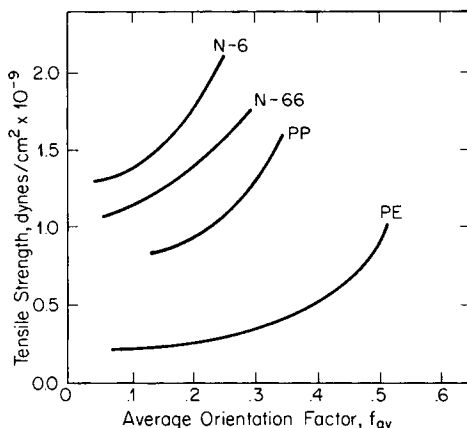


Fig. 9. Tensile strength of nylon 66, nylon 6, high-density polyethylene, and polypropylene as function of average orientation factor.

Mechanical Properties

Tensile modulus, yield strength, tensile strength, and elongation to break generally correlate with increasing levels of spinline stress or orientation. Correlations with modulus are the poorest, and tensile strength and elongation to break are generally the best. The correlation of tensile strength and elongation to break with spinline stress is illustrated in Figure 8. These plots are of special interest because of the correlations of mechanical properties developed by Nadella et al.^{20,42} with these quantities.

In Figure 9 we plot tensile strength as a function of average orientation. We plot not only nylon 66 data but also nylon 6, high-density polyethylene,¹⁷ and polypropylene²⁰ data. Figure 9 is of special interest in its comparison of polyamides with polyolefins. The higher strength properties of the polyamides and the inferior properties of polyethylene are clear.

The authors wish to thank the Monsanto Textiles Company (Pensacola, Florida) for providing the nylon 66 used in this study. J. B. McKoy of Monsanto provided helpful information and criticisms throughout the course of this study.

References

1. A. Ziabicki and Kedzierska, *J. Appl. Polym. Sci.*, **2**, 14 (1959).
2. I. Hamana, M. Matsui, and S. Kato, *Melli and Textilber.*, **4**, 382 (1969).
3. T. Ishibashi, K. Aoki, and T. Ishii, *J. Appl. Polym. Sci.*, **14**, 1597 (1970).
4. N. M. Pasika, A. C. West, and E. L. Thurston, *J. Polym. Sci., Polym. Phys. Ed.*, **10**, 2313 (1972).
5. T. Ishibashi and T. Ishii, *J. Appl. Polym. Sci.*, **20**, 335 (1976).
6. T. Ishibashi and J. Furukawa, *J. Appl. Polym. Sci.*, **20**, 1421 (1976).
7. V. G. Bankar, J. E. Spruiell, and J. L. White, *J. Appl. Polym. Sci.*, **21**, 2135 (1977).
8. V. G. Bankar, J. E. Spruiell, and J. L. White, *J. Appl. Polym. Sci.*, **21**, 2341 (1977).
9. A. Ziabicki and K. Kedzierska, *J. Appl. Polym. Sci.*, **6**, 111 (1962).
10. F. P. Chappel, M. F. Culpin, R. C. Gosden, and T. C. Tranter, *J. Appl. Chem.*, **14**, 12 (1964).
11. T. A. Hancock, J. E. Spruiell, and J. L. White, *J. Appl. Polym. Sci.*, **21**, 1227 (1977).

12. M. I. Kohan, Ed., *Nylon Plastics*, Wiley-Interscience, New York, 1973.
13. H. Hopff, in *Man-Made Fibers*, Vol. 2, H. Mark, S. M. Atlas, and E. Cernia, Eds., Wiley, New York, 1968.
14. A. Ziabicki, *Fundamentals of Fibre Formation*, Wiley-Interscience, New York, 1976.
15. J. E. Spruiell and J. L. White, in *Fiber and Yarn Processing*, J. L. White, Ed., *Appl. Polym. Symp.*, **27**, 121 (1975).
16. L. E. Abbott and J. L. White, in *U.S.-Japan Seminar on Polymer Processing and Rheology*, D. C. Bogue, M. Yamamoto, and J. L. White, Eds., *Appl. Polym. Symp.*, **20**, 247 (1973).
17. J. R. Dees and J. E. Spruiell, *J. Appl. Polym. Sci.*, **18**, 1053 (1974).
18. J. L. White, K. C. Dharod, and E. S. Clark, *J. Appl. Polym. Sci.*, **18**, 2539 (1974).
19. J. E. Spruiell and J. L. White, *Polym. Eng. Sci.*, **15**, 660 (1975).
20. H. P. Nadella, H. M. Henson, J. E. Spruiell, and J. L. White, *J. Appl. Polym. Sci.*, **21**, 3003 (1977).
21. K. Oda, J. L. White, and E. S. Clark, *Polym. Eng. Sci.*, **18**, 53 (1978).
22. C. S. Fuller, N. O. Baker, and N. R. Paper, *J. Am. Chem. Soc.*, **62**, 3275 (1940).
23. C. W. Bunn, and E. V. Garner, *Proc. R. Soc.*, **A189**, 39 (1947).
24. R. Brill, *J. Prakt. Chem.*, **161**, 49 (1943).
25. W. P. Slichter, *J. Polym. Sci.*, **35**, 77 (1958).
26. H. W. Starkweather, in *Nylon Plastics*, M. I. Kohan, Ed., Wiley, New York, 1973.
27. H. W. Starkweather, J. F. Whitney, and D. R. Johnson, *J. Polym. Sci.*, **A1**, 715 (1963).
28. E. S. Clark and F. Wilson, in *Nylon Plastics*, M. I. Kohan, Ed., Wiley, New York, 1973.
29. J. H. Dumbleton, D. R. Buchanan, and B. B. Bowles, *J. Appl. Polym. Sci.*, **12**, 2067 (1968).
30. J. J. Hermans, P. H. Hermans, D. Vermaas, and A. Weidinger, *Recl. Trav. Chim. Pays-Bas*, **65**, 427 (1946).
31. P. H. Hermans, J. J. Hermans, D. Vermaas, and A. Weidinger, *J. Polym. Sci.*, **3**, 1 (1948).
32. R. S. Stein and F. H. Norris, *J. Polym. Sci.*, **21**, 381 (1956).
33. A. Ziabicki, *J. Appl. Polym. Sci.*, **2**, 24 (1959).
34. G. B. Taylor, *J. Am. Chem. Soc.*, **69**, 635 (1947).
35. R. S. Stein, *J. Polym. Sci.*, **31**, 327 (1958).
36. Z. Wilchinsky, *J. Appl. Phys.*, **30**, 792 (1959).
37. Z. Wilchinsky, *Adv. X-Ray Anal.*, **6**, 231 (1963).
38. M. F. Culpin and K. N. Kemp, *Proc. Phys. Soc.*, **69**, 1301 (1957).
39. K. Matsumoto, *Sen-i-Gakkaishi*, **32**, T-365 (1976).
40. J. H. Magill, *Polymer*, **3**, 655 (1962).
41. J. V. McLaren, *Polymer*, **4**, 175 (1963).
42. H. P. Nadella, J. E. Spruiell, and J. L. White, Drawing and Annealing of Polypropylene Fibers: Structural Changes and Mechanical Properties, University of Tennessee Polymer Science and Engineering Report No. 91, April 1977. *J. Appl. Polym. Sci.* (to appear).

Received July 1, 1977

Revised September 14, 1977