

Polymorphism and Orientation Development in Melt Spinning, Drawing, and Annealing of Nylon-6 Filaments

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Synopsis

A new method has been developed for determining the total crystallinity and relative amounts of α - and γ -phases in nylon-6 samples. The procedure is based on a combination of X-ray and density data and does not require complicated analytical procedures to separate overlapping reflections. The technique has been applied to study the structural changes accompanying the melt spinning, annealing, and drawing of nylon-6 filaments. Higher spin draw ratios result in higher crystallinity, greater relative amounts of γ -phase, and higher orientation. Annealing up to 2 h in boiling water or a 20% aqueous formic acid solution decreases the γ -phase content, increases the α -phase content and total crystallinity, but does not eliminate all of the γ -phase in samples spun with high spin draw ratios. Annealing in vacuum also increases the α -phase content when annealing is carried out at temperatures above 120°C, but there is little effect below this temperature. Drawing of as-spun and conditioned filaments at 90°C also increases the α -phase content and decreases the γ -phase content. The total crystalline content increases with draw ratio for samples with low spin draw ratios, but drawing has little effect on the total crystalline content of samples spun with higher spin draw ratios. Drawing also results in substantial increases in orientation, especially for samples spun with low spin draw ratios. The effects of these changes in structure on the mechanical properties are also described.

INTRODUCTION

Overview and Objectives

Although nylon-6 has been known for approximately half a century^{1,2} and has been used for commercial production of fibers for nearly as long,³ there were, at the beginning of the present research, no broad-based, detailed descriptions of the structure and properties of nylon-6 fibers as a function of processing history in the open literature. Aside from the proprietary nature of the bulk of such research carried out on nylon-6, there are several reasons for the lack of such reported studies. Among them is the fact that nylon-6 is polymorphic and general agreement about the crystalline and/or paracrystalline forms present and their detection has been slow to develop.⁴⁻⁶ In fact, there is still no generally accepted view of the literature on this subject.^{6,7} Furthermore, the nature and properties of nylon-6 filaments and fibers is sensitive to environmental factors such as the presence of moisture (humidity).⁸

Recently, two investigations of structure formation during fiber formation from nylon-6 have appeared. The work of Shimizu et al.⁹ deals with high-speed melt spinning (up to 7000 m/min) while the investigation of Heuvel and Huisman¹⁰ includes melt spinning, drawing, and annealing behavior. While these investigations have established the general trends to be expected, the behavior

of nylon-6 is so complicated that publication of a third study would seem desirable. In addition, a new method has been devised to determine the total crystallinity and the relative amounts of phases present in the samples which is much simpler to apply than the methods used in the above two investigations. The present study thus provides a comparison of results obtained by this new method to the previous literature.

Structural Forms of Nylon-6

Studies on the crystal structure of nylon-6 were first carried out by Brill,¹¹ who reported a monoclinic structure corresponding to what is now universally referred to as the α form. Later researchers, notably Wallner¹² and Holmes et al.,¹³ confirmed the basic characteristics of the α -phase and further refined its structure. The generally accepted prototype of the α -phase is the monoclinic structure of Homes et al.,¹³ for which $a = 9.56 \text{ \AA}$, $b = 17.24 \text{ \AA}$ (chain axis), $c = 8.01 \text{ \AA}$, and $\beta = 67.5^\circ$. The chains are fully extended and occur in antiparallel hydrogen-bonded sheets.

A second well-established crystalline form has been described and studied by Kinoshita¹⁴ and Arimoto.¹⁵ This form, called the γ -phase, is readily formed in nylon-6 by chemical treatment with iodine-potassium iodide solution followed by a de-iodization treatment in sodium thiosulphate solution.^{15,5} The prototype structure for the γ -phase appears to be the monoclinic structure of Arimoto¹⁵ with $a = 9.33 \text{ \AA}$, $b = 16.88 \text{ \AA}$ (chain axis), $c = 4.78 \text{ \AA}$, and $\beta = 121^\circ$. This structure can also be described in terms of a slightly different choice of unit cell (interchange a and c , double c) as monoclinic with $a = 9.56 \text{ \AA}$, $b = 16.88 \text{ \AA}$, $c = 9.33 \text{ \AA}$, and $\beta = 59^\circ$. The latter description is more convenient for comparison with the α -phase. The shortened chain axis crystallographic repeat distance of the γ -form was interpreted by Kinoshita¹⁴ and Arimoto¹⁵ to correspond to a "kinked" or pleated hydrogen-bonded sheet structure in which the hydrogen bonding occurs between parallel rather than antiparallel chains.

In addition to these two well-established phases, the literature contains numerous references to phases that differ in various ways from either the α or γ prototypes described above.

Both Roldan and Kaufman⁴ and Parker and Lindenmeyer⁶ have noted that the unit cell dimensions of the α -phase can vary with processing history. Such forms have been called α -paracrystalline by Roldan and Kaufman, while Parker and Lindenmeyer emphasize that the chain axis repeat distance in all such samples is greater than 17 \AA .

Several authors^{4,13,15-17} have discussed a β form. In some instances the symbol β has been used as a name for a phase that has the shortened chain axis repeat distance of the γ -phase, but has hexagonal or pseudo-hexagonal symmetry. The β form of Roldan and Kaufman⁴ is typical of this group. It seems clear in retrospect that such a phase is not basically different from γ but is slightly less well crystallized than the monoclinic sample of Arimoto.¹⁵ Ziabicki¹⁶ has used the symbol β to describe the pseudo-hexagonal form occurring in melt spun filaments. The chain axis repeat in these filaments is presumably close to 17 \AA (but see the results of the present investigation described later) and would seem more related to the extended chain α -form.

Illers et al.,⁵ in a study utilizing X-ray diffraction, infrared spectroscopy,

density, and calorimetric techniques, cast doubt on the existence of a well-crystallized β -phase that differs substantially from the γ -phase. They showed that the γ -phase formed by iodine treatment cannot be readily transformed to α by dry annealing, but they concluded that a poorly crystallized pseudo-hexagonal form exists in unoriented samples quenched from the melt which can be readily transformed to α by annealing. They called this phase γ^* .

Parker and Lindenmeyer⁶ did an extensive literature review on the crystal structures of nylon-6. Based on this review and their own experience with spun and drawn fibers, they concluded that there are two basic types of structures: (1) extended chain structures with hydrogen bonding primarily between anti-parallel chains (α -type) and structures in which the hydrogen bonding tended to be primarily between parallel chains and the chain axis crystallographic repeat is significantly shortened (γ -type). They interpret the variation of unit cell dimensions within these types as being associated with various imperfections in the idealized prototype structures of the α and γ forms. They emphasize the importance of examining the location of the 0,14,0 reflection to determine chain-axis crystallographic repeat distance and to distinguish between the two structure types.

In a recent paper by Stepaniak et al.,⁷ the authors propose the existence of a "pleated α " structure in filaments that have been melt-spun with low orientation. This phase presumably has hydrogen bonding between antiparallel chains as in the α -phase, but exhibits a shortened repeat distance and pseudo-hexagonal symmetry. The authors argue that such a structure would readily transform to α on annealing or drawing since no breaking of hydrogen bonds between parallel chains and reforming them between antiparallel chains is necessary as in the case of forming α from the γ -phase. These authors suggest that this phase corresponds to the γ^* -phase of Illers et al.⁵ and perhaps also to the β -phase of Ziabicki.¹⁶ They do not, however, provide substantial experimental evidence for the shortened repeat distance, and it is not clear how this phase differs otherwise from a highly imperfect, poorly developed α form.

Based on our view of the literature and our own experimental data to be discussed below, we believe that aside from the amorphous phase there are two basic structure types of nylon-6 as summarized in Table I. There is an "alpha type" structure that possesses hydrogen bonding between antiparallel chains and a

TABLE I
Suggested Notation for Polymorphic Forms of Nylon-6

I. Amorphous (liquid or vitrified liquid)
II. α -Phase type
A. α monoclinic (prototype, stable equilibrium phase of Holmes et al. ¹³)
B. α' monoclinic (paracrystalline α of Roldan and Kauffman ⁴ metastable α forms of Parker and Lindenmeyer ⁶ ; see the latter for additional references)
C. α^* pseudo-hexagonal (same as Illers et al. ⁵ γ^* form, low orientation β form of Ziabicki, ¹⁶ "pleated α " form of Stepaniak et al., ⁷ probably same as γ "nematic" form of Roldan and Kaufman) ^a
III. γ -Phase type
A. γ monoclinic (prototype, stable phase of Kinoshita ¹⁴ and Arimoto, ¹⁵ same as Bradbury ¹⁸ orthorhombic)
B. γ^* pseudo-hexagonal (β form of Roldan and Kaufman, ⁴ γ of Vogelsong, ¹⁹ Ota, ²⁰ high orientation β form of Ziabicki ¹⁶ ^a)

^a See further discussion of the structure of as-spun fiber described in this paper.

"gamma type" structure that possesses hydrogen bonding between parallel chains. The gamma type structures generally have a shortened chain axis crystallographic repeat distance as in the prototype γ -phase of Arimoto¹⁵ and are not readily transformed to α on annealing. This view is not substantially different from that of Parker and Lindenmeyer,⁶ although we specifically provide for pseudohexagonal forms of both "alpha type" and "gamma type." At this time we make no further claims about the detailed structure of the pseudohexagonal phase of alpha type.

In accordance with these views, we propose a less confusing nomenclature for the different structures in which all alpha type structures are referred to by the symbol α with or without a modifier. The monoclinic forms with lattice parameters differing substantially from those of Holmes et al.¹³ are called α' while the pseudohexagonal form is called α^* . A similar notation is used for the gamma type structures, but there does not seem to be much need to distinguish a γ' type. An attempt has also been made in Table I to compare the present notation with that in the literature. The idea is not to be all inclusive with respect to the literature but to substantiate the need for the present notation and clarify some of the confusion in the literature concerning the notation and structures which can occur in nylon-6.

Methods of Determining Relative Amounts of Phases

Although numerous investigators have studied the structure and properties of nylon-6, only a few have described methods of obtaining the relative amounts of phases present. All such methods are approximate and depend on the nature of the various approximations made in the analysis. Perhaps the earliest semiquantitative method was that of Roldan, Rahl, and Patterson.²¹ Although there are many good features of their approach, the assumption of separate β and γ phases makes their method obsolete in the context of the present view of the literature as described above.

The method of Kyotani and Mitsuhashi²² is consistent with the present view of the literature. This method involves measurement of the relative intensity of the equatorial γ and α peaks in the range 19–25° 2θ . In addition to the fact this is an inaccurate procedure due to peak overlap, the authors use peak heights rather than integrated intensities. If a wide range of crystal size and perfection is to be encountered, as in the present investigation, the use of peak heights will introduce too much error.

The method of Heuvel, Huisman, and Lind²³ involves computer fitting and weighting of three bell-shaped curves to the equatorial intensity profile in the range 10–34° 2θ . This method is elegant and should find many applications as computer control of diffractometers and analysis of X-ray data become more prevalent. A major drawback in the present application, however, was that they were unable to separate the scattering from the amorphous phase from that from the γ -phase. More recently they have corrected this deficiency¹⁰ by using a five-line model to fit the equatorial profile, but the method still requires considerable computing capacity.

Another recent prior method is that of Stepaniak et al.⁷ This method involved separation of the intensity distribution from a randomized sample in the range 15–30° 2θ into amorphous, γ , and α contributions. The major difficulty of this

technique was the rather arbitrary methods used to perform the separation. These procedures should lead to an overestimate of the amount of γ -phase and an underestimate of the amount of α -phase present in cases for which the 200 and 002, 202 reflections of the α -phase are less well separated than in the Holmes et al.¹³ structure, i.e., as the crystallographic β angle decreases. Very significant errors would be introduced as the α -phase approaches a pseudo-hexagonal structure.

Previous Studies of Melt Spinning and Drawing of Nylon-6

Among the earliest studies of structure development during melt spinning are those of Ziabicki and Kedzierska.^{25,16} They made wide angle X-ray patterns (WAXS) and measured birefringence of spun filaments. As noted above, they described the structure of the spun filaments as pseudo-hexagonal β -phase. They also noted that orientation increases rapidly with draw down. Hamana, Matsui, and Kato,²⁶ Ishibashi, Aoki, and Ishii,²⁷ and Bankar et al.²⁸ made birefringence measurements on a running threadline. For given spinning conditions the birefringence increased with distance from the spinneret as the fiber was drawn down. Increasing draw down caused the maximum birefringence achieved in the spinline to increase, but a further time-dependent increase in birefringence occurred during conditioning of the spun filament in a humid environment. Bankar et al.²⁸ made on-line WAXS patterns which showed that the filaments spun at low speeds into dry or humid air remained amorphous on the spinline, but exhibited the pseudo-hexagonal structure after conditioning. The work of Stepaniak et al.⁷ made a first attempt to determine the relative amounts of phases present in as-spun fibers as a function of spinning conditions. They found that their " γ -index" increases with increasing take-up velocity and draw down. A similar conclusion was reached by both Shimizu et al.⁹ and Heuvel and Huisman.¹⁰

Although numerous investigators (e.g., Refs. 4, 5, 6, 28, 7, 24) have reported that annealing and drawing tend to promote formation of α -phase in nylon-6 fibers, their conditions of spinning and drawing have often not been well defined. Only Stepaniak et al.⁷ and Heuvel and Huisman¹⁰ have attempted to quantify these results and show systematically the effect of spinning and drawing variables.

EXPERIMENTAL DETAILS

Material

The polymer used in this study was a commercial grade of nylon-6 provided by AKZO. The characteristics of this sample are shown in Table II. Prior to spinning, the material was dried by heating at 110°C for 16 h under partial vacuum.

Melt Spinning, Drawing, and Annealing Procedures

Except otherwise noted melt spinning was carried out using a screw extruder with a 25.4-mm diameter screw. The melt was pumped through a single hole spinneret at a rate of 5.0 g/min and a temperature of 262°C. The spinneret hole

TABLE II
 Characteristics of Nylon-6 Sample

Sample	Moisture (%)	Relative viscosity	End groups equivalents (10 ⁶ g)		M_n	M_w	M_w/M_n
			NH ₂	COOH			
Undried	0.34	2.45	54	39	7,600	36,200	4.77
Dried	0.076	2.65	29	49	22,500	46,900	2.08

had a diameter of 0.762 mm and an L/D ratio of 10. The filaments were spun into ambient air at 21°C and were taken up on bobbins with takeup velocities of 160, 480, 960, 1450, 1930, and 2410 m/min. These conditions correspond to spin draw ratios of about 15, 48, 95, 142, 190, and 240.

After conditioning for at least 24 h at 65% relative humidity the filaments were drawn to specified draw ratios. The spun filament was taken from the bobbin by a roll turning at velocity V_1 , passed through a tube heated to 90°C, and then onto a roll turning at velocity V_2 , thus providing a draw ratio V_2/V_1 .

The as-spun or drawn samples were carefully wound onto sample holders for the X-ray measurements described below. Further treatments such as annealing in air, boiling water, or boiling 20% aqueous formic acid were carried out with the fibers wound on these sample holders.

Determination of Approximate Relative Amounts of Phases

The total crystallinity and the relative amounts of polymorphic forms were analyzed by means of a new "γ-index" based on a combination of X-ray diffraction and density data. In establishing the technique, the goals were to find a simple, easy to apply, and reproducible way to determine the relative amounts of crystalline and amorphous material present in the samples and to subdivide the crystalline fraction into a γ-phase type fraction and an α-phase type fraction (see Table I). The method is not designed to distinguish specifically among the α type phases or γ type phases, although this can often be done qualitatively by careful examination of the diffraction pattern.

The technique also utilizes two "standard samples." One of these, the γ standard, is high in γ-phase content but has negligible α content; the other standard, called the α standard, is high in α-phase content but contains negligible γ-phase. Our standard γ sample was obtained by treating a fast spun sample (SDR = 240) in warm potassium iodide solution for 0.5 h, followed by washing in cold sodium thiosulphate solution. This treatment produced a sample with the γ structure of Arimoto.¹⁵ Our standard α sample was produced by hot drawing a slow spun (SDR = 15) sample to 4 × followed by boiling in 20% aqueous solution of formic acid for 0.5 h. The diffraction pattern of this sample indicated that it had the well-developed α structure of Holmes et al.¹³

The diffraction data required are an equatorial scan on which the intense reflections in the range 14–28° 2θ (CuKα radiation) are recorded plus a meridional scan containing the 020 peak at about 11° 2θ and the 0,14,0 peak in the neighborhood of 75–80° 2θ . The 0,14,0 peak is not used in the quantitative phase analysis directly, but it is used in the manner of Parker and Lindenmeyer⁶ to determine the chain axis repeat distance and to qualitatively assess the nature of the phases present.

In the present investigation the X-ray data were recorded in the transmission geometry using crystal monochromated $\text{CuK}\alpha$ radiation. The fibers were carefully wound parallel to one another on a holder designed for use in the transmission geometry. This holder was mounted in a single crystal orienter which provided the required rotation of 90° in going from the equatorial scan to the meridional scan. The same arrangement provided azimuthal intensity scans needed for the orientation measurements described in a later section. Densities were measured using a density gradient column containing a mixture of carbon tetrachloride and toluene.

The ratio R is defined as the ratio of the integrated intensity of the 020 reflection to the integrated intensity of the equatorial scan in the range $14\text{--}28^\circ 2\theta$:

$$R = \int I_{020} d(2\theta) / \int_{14^\circ}^{28^\circ} I_{\text{eq}} d(2\theta) \quad (1)$$

Both the meridional and equatorial data are corrected for background in the usual manner. Dividing the integrated intensity of the 020 reflection by the integrated intensity of the equatorial reflections normalizes out any variations in irradiated mass from sample to sample and also tends to eliminate any effects of preferred orientation. The latter is true because azimuthal spread in the 020 reflection will be accompanied by azimuthal spread in the equatorial reflections and vice-versa.

Our standard γ sample had a density of 1.1455 g/cm^3 and a ratio $R_\gamma^s = 128.0 \times 10^{-2}$. Assuming the α content of this sample to be negligible, a crystalline fraction of 0.75 was determined using the standard relationship

$$X_\gamma^s = \frac{\rho_\gamma}{\rho} \left(\frac{\rho - \rho_{\text{am}}}{\rho_\gamma - \rho_{\text{am}}} \right) \quad (2)$$

where ρ_γ = theoretical density of γ -phase, ρ_{am} = density of amorphous nylon-6, and ρ = measured density of sample. For an arbitrary sample, we may define "gamma-index" X_γ , the approximate mass fraction of the sample which is γ -phase as

$$X_\gamma = \frac{R - R_\alpha^s}{R_\gamma^s - R_\alpha^s} \cdot X_\gamma^s \quad (3)$$

where $R_\alpha^s = 1.11 \times 10^{-2}$ is the intensity ratio for the standard α sample and R is the intensity ratio for the arbitrary sample. Notice that when $R = R_\alpha^s$, $X_\gamma = 0$, and when $R = R_\gamma^s$, $X_\gamma = X_\gamma^s$. Since

$$X_\gamma + X_\alpha + X_{\text{am}} = 1.0 \quad (4)$$

and

$$\bar{V} = X_\gamma \bar{V}_\gamma + X_\alpha \bar{V}_\alpha + X_{\text{am}} \bar{V}_{\text{am}} \quad (5)$$

where \bar{V} = specific volume of the sample, \bar{V}_γ = specific volume of γ -phase, \bar{V}_α = specific volume of α -phase, and \bar{V}_{am} = specific volume of amorphous phase.

We may combine eqs. (4) and (5) to give

$$X_\alpha = \frac{(\bar{V} - \bar{V}_{\text{am}}) - X_\gamma(\bar{V}_\gamma - \bar{V}_{\text{am}})}{\bar{V}_\alpha - \bar{V}_{\text{am}}} \quad (6)$$

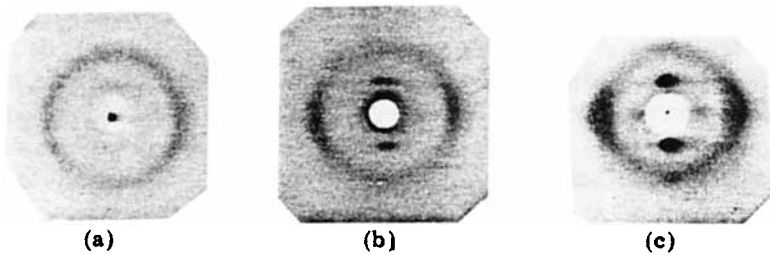


Fig. 1. Typical WAXS patterns of as-spun and conditioned nylon-6 filaments. SDR: (a) 48, (b) 95, (c) 240.

Equations (3), (4), and (6) allow computation of X_γ , X_α , and X_{am} for any sample from a measurement of R and the density (specific volume) of the sample. We must also know the densities of the γ -phase, α -phase, and the amorphous phase. We used the values $\rho_\gamma = 1.17 \text{ g/cm}^3$, $\rho_\alpha = 1.23 \text{ g/cm}^3$, and $\rho_{am} = 1.08 \text{ g/cm}^3$.

Based on the conjecture that the intensity of the 020 reflection may be affected by slippage of the hydrogen-bonded sheets in the γ structure, Stepaniak et al.⁷ have cautioned against using the 020 reflection for determining the relative amount of γ -phase. It is not possible to say that this does not occur at all, but our experience indicates that this effect is less troublesome than the problems associated with separating the equatorial scan into its component reflections.

Orientation Measurements

Orientation changes occurring as a result of spinning, drawing, and annealing treatments were followed by both birefringence and X-ray diffraction techniques. Birefringence is a measure of the anisotropy in the sample averaged over the crystalline and amorphous phases. The X-ray diffraction technique provided the orientation present in the crystalline phases. The data were used to compute crystalline orientation factors by the procedures described by Bankar et al.²⁸ and Stepaniak et al.⁷ The birefringence measurements were carried out by the usual method using a Berek compensator in conjunction with an optical microscope.

Mechanical Properties

A table-model Instron tensile tester was used to measure force vs. elongation curves for the variously treated filaments. The tests were made only after conditioning at 65% relative humidity and 20°C for 24 h. The tests were carried out using initial fiber gage lengths of 12.7 mm and a crosshead speed of 12.7 mm/min.

THE STRUCTURE OF AS-SPUN AND CONDITIONED FILAMENTS

Results

Figure 1 shows WAXS patterns for as-spun and conditioned filaments at different SDR's. All samples show a single broad peak on the equator and increasing orientation with increasing SDR. At higher SDR's, an intense merid-

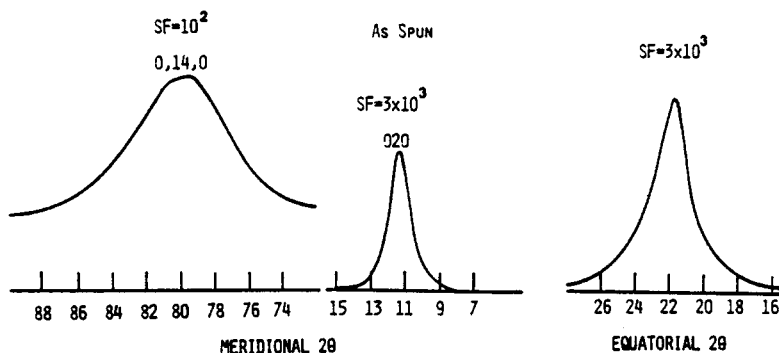


Fig. 2. Meridional and equatorial diffractometer scans for conditioned nylon-6 filament spun with high spin orientation (SDR = 240). The ordinate is intensity in arbitrary units, and SF is the scale factor for the intensity data.

ional 020 reflection is observed. Typical diffractometer scans are presented in Figure 2 for a sample with SDR = 240. The 0,14,0 reflection is very broad and weak but its position can be seen to be near 80°. Figure 3 shows that the 0,14,0 peak tends to shift toward higher diffraction angles with increasing SDR. The effect of SDR on the relative amounts of phases present as computed from the new γ -index method described above is presented in Figure 4. The total crystalline fraction increases slightly with SDR. The γ crystalline fraction goes up with SDR, and the α crystalline fraction is reduced. These results together with the corresponding density data and chain axis orientation factors are summarized for each sample in Table III. The crystalline orientation factors are plotted in Figure 5 and compared to the results of Bankar et al.²⁸

In Figure 6 the results of a special on-line experiment are shown. The birefringence was measured as a function of conditioning time at 60°F (15.6°C) and 55% relative humidity. The data plotted at 0.1 min were actually measured on the running threadline at a point near the takeup bobbin. Each sample was then held in a slack condition for the indicated time and the birefringence remeasured after each holding period. Two characteristics of these results are significant. A rapid increase of birefringence with conditioning time is observed for most samples in the interval between 1 and 10 min after spinning. The rapid increase

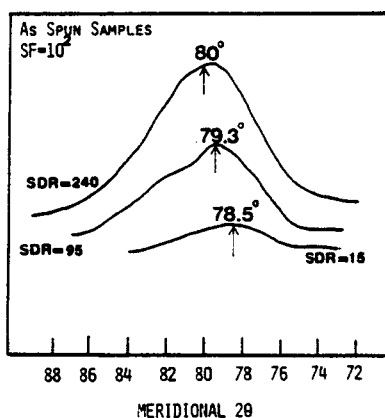


Fig. 3. Diffractometer scans of the 0,14,0 reflection showing the effect of SDR.

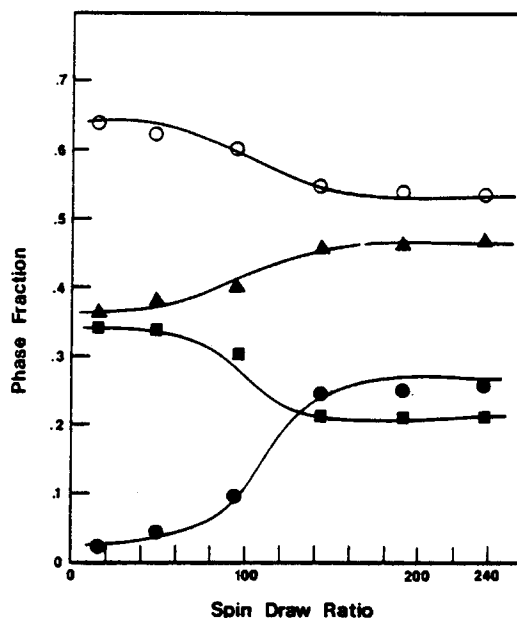


Fig. 4. Phase fractions of conditioned nylon-6 filaments as a function of SDR: (O) amorphous fraction; (▲) crystalline fraction ($\alpha + \gamma$); (●) γ fraction; (■) α fraction.

in birefringence occurs earlier as the SDR increases. At the higher spin draw ratios the on-line birefringence (0.1 min) is quite substantial, indicating that some crystallization may be occurring on the running threadline under these conditions.

Interpretation and Discussion

The spun and conditioned filaments exhibit very broad diffraction peaks. The peaks are sufficiently well-defined to indicate that the samples are no longer entirely amorphous but are partially crystalline. Based on the work of Hamana et al.,²⁶ Ishibashi et al.,²⁷ and Bankar et al.²⁸ and on the data in Figure 6, it would appear that much of the crystallinity is developed by cold crystallization during conditioning. An analysis of the data shown in Figure 6 given elsewhere²⁹ shows that both primary and secondary crystallization processes are occurring. The primary crystallization obeys Avrami kinetics with an Avrami exponent between 1 and 2, which would suggest fibrillar growth from preexisting nuclei. These

TABLE III
Characteristics of As-Spun and Conditioned Filaments of Nylon-6

Spin draw Ratio (SDR)	γ fraction	α fraction	Crystalline fraction	Amorphous fraction	Density	Chain axis orientation
15	0.022	0.341	0.363	0.637	1.1288	0.07
48	0.043	0.337	0.380	0.620	1.1301	0.20
95	0.093	0.307	0.400	0.600	1.1303	0.50
142	0.245	0.211	0.456	0.544	1.1303	0.66
190	0.251	0.212	0.463	0.537	1.1310	0.69
240	0.254	0.213	0.467	0.533	1.1315	0.71

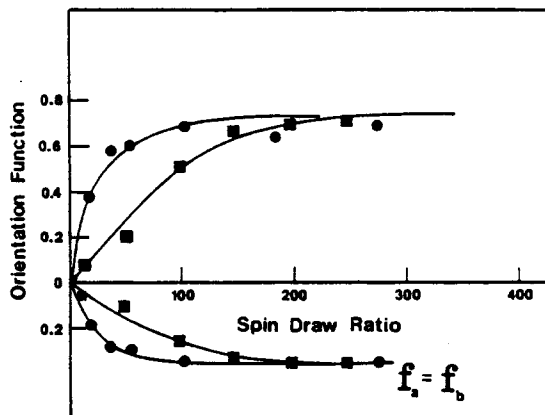


Fig. 5. Orientation function of spun and conditioned nylon-6 filaments as a function of SDR: (●) Bankar et al.; (■) present results.

results are qualitatively in agreement with the results of Shimizu et al.,⁹ who also measured birefringence as a function of conditioning time.

At very high SDR's, corresponding to very high spinning speeds, it would appear that strain-induced crystallization can occur on the running threadline. This conclusion is based on both the present data and those of Shimizu et al.⁹ and Heuvel and Huisman¹⁰ since the present data do not extend to high enough spinning speeds to investigate thoroughly this process.

In the range of conditions studied in the present research, both the strain-induced crystals and those that form during the subsequent cold crystallization process must be very small and/or paracrystalline in order to account for the breadth of the diffraction peaks. The diffractometer scans indicate that in this rather imperfect form the crystals exhibit pseudohexagonal symmetry in agreement with the interpretations of previous investigators.^{17,25-28,30,5,7}

The measurements on the 0,14,0 reflection show that the peak occurs at about 78.5° 2θ at the lowest SDR and shifts to higher 2θ with increasing SDR. Based on the interpretation of the 0,14,0 reflection provided by Parker and Lindemeyer⁶ and making due allowance for the breadth of the peaks, this would seem to result from an increased tendency for γ-phase formation. This is qualitatively

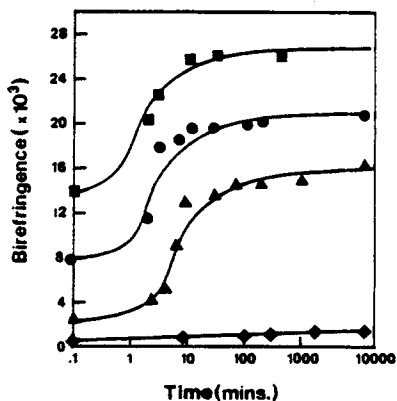


Fig. 6. Birefringence of melt spun nylon-6 as a function of time at 55% RH and 60°F. SDR: (■) 45; (●) 25; (▲) 12; (◆) 5.

similar to the variation obtained by application of the γ -index method as presented in Figure 4. The latter provides a more quantitative characterization of this change. This technique also shows that at low SDR's there is a significant α -phase fraction which decreases with increasing SDR. This α -phase is very poorly developed, paracrystalline, and pseudo-hexagonal. It presumably corresponds to the α^* form of Table I. As noted in Table I, this form also corresponds to the γ^* form of Illers et al.⁵ and to the so-called pleated α form of Stepaniak et al.⁷ The observation of the 0,14,0 reflection at about $78.5^\circ 2\theta$ does not substantiate the idea of a pleated α structure, however. Both the position of the 0,14,0 reflection and the relative intensity of the 020 meridional peak do indicate that a very imperfect paracrystalline α -phase predominates at low SDR's, and this is the interpretation used here.

Since increasing SDR tends to increase the amount of γ -type phase at the expense of α -type phase, it would appear that the strain-induced crystallization occurring from the oriented melt under dry conditions gives the γ -type phase. The phase forming by cold crystallization during conditioning would seem to be the α -type phase (α^* , Table I).

The slightly slower increase of chain axis orientation factor with SDR exhibited by the present results as compared to the results of Bankar et al.²⁸ (Fig. 5) would seem to stem from small variations in other spinning conditions. It has been demonstrated in several instances³¹⁻³⁴ that the orientation developed in spun filaments correlates directly with the spinline stress. Although SDR affects spinline stress, other factors, such as extrusion temperature, extrusion rate, cooling rate, polymer molecular weight, etc., can effect the spinline stress and hence the orientation developed. Unfortunately, the spinline stress itself was not measured during the spinning of the present filaments. It would appear that it developed somewhat less slowly with SDR for the present filaments than in the case of Bankar et al.²⁸

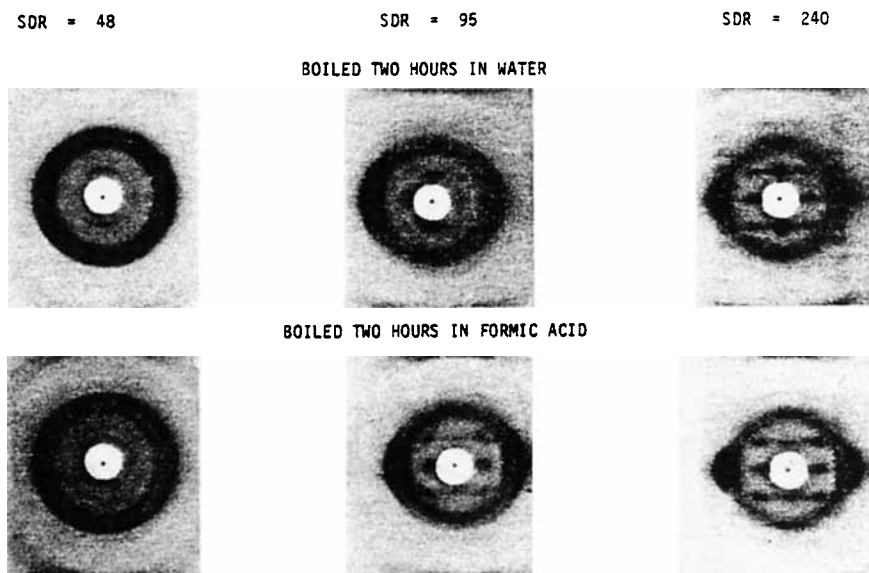


Fig. 7. Typical WAXS patterns of nylon-6 filaments after annealing. Top row: boiled 2 h in water. Bottom row: boiled 2 h in aqueous 20% formic acid solution.

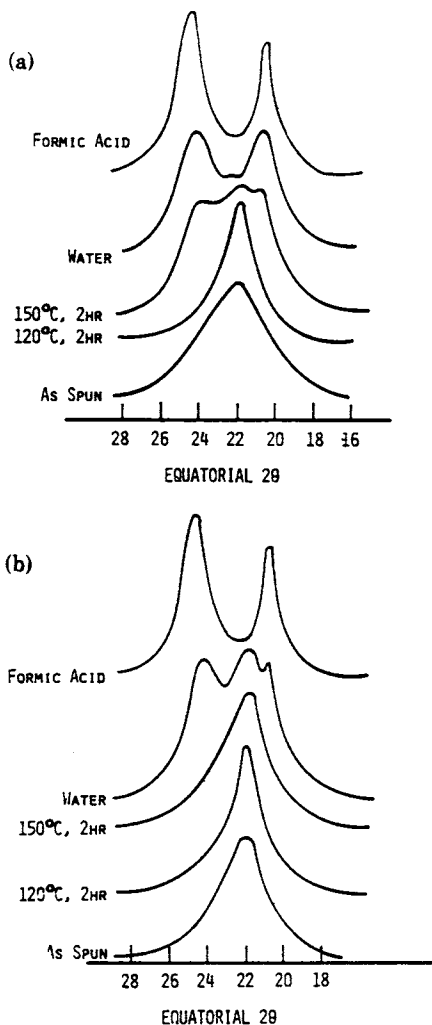


Fig. 8. Equatorial diffractometer scans of samples annealed in various ways: (a) initial samples spun with SDR = 15; (b) initial samples spun with SDR = 240.

ANNEALING OF CONDITIONED FILAMENTS

Results and Interpretation

The effect of annealing the spun and conditioned filaments is described in this section. Figure 7 presents WAXS patterns of samples that have been annealed by boiling for 2 h in either water or a 20% aqueous formic acid solution. These may be compared to Figure 1 which showed similar patterns for the as-spun and conditioned samples. For SDR's below about 48 the samples readily anneal to the monoclinic α -phase in either water or formic acid solution as indicated by the observation of the characteristic 200 and 002, 202 reflections of the monoclinic α form. At higher SDR's there appears to be considerable γ -phase in the samples annealed in water, although it is largely removed by annealing in formic acid solution.

Figure 8 shows a comparison of equatorial diffractometer scans of samples spun with low and high SDR's which have been annealed in various ways. It is

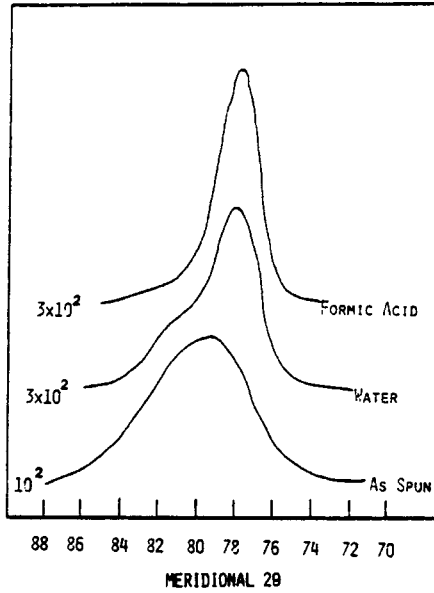


Fig. 9. Diffractometer scans showing the effect of annealing on the 0140 reflection of samples spun with SDR = 240.

also clear from these data that the low SDR samples anneal to the α form more readily than the high SDR samples; compare especially the curves for a 2-h vacuum anneal at 150°C and also the curves for annealing in water.

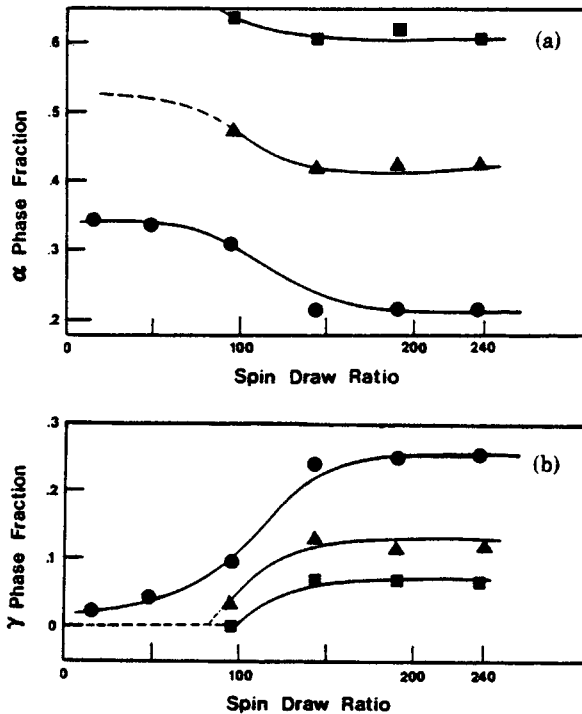


Fig. 10. The effect of annealing on: (a) α -phase fraction; (b) γ -phase fraction as a function of SDR; (●) as spun; (▲) boiling water; (■) 20% formic acid.

Figure 9 shows the changes in the 0, 14, 0 reflection observed on annealing the high SDR ratio material under various conditions. The striking feature of these results is the occurrence of resolved doublets for some samples indicating the presence of both γ and α forms. With increasing severity of the annealing treatment the amount of α form increases, but, qualitatively, the relative amount of γ in the sample does not appear to change much except on annealing in formic acid solution. It is also clear from these data that dry annealing must be carried out above 120°C for appreciable formation of the α form.

The application of the new γ -index method to annealing is shown in Figure 10. These results show that there is a substantial increase in the crystalline fraction due to annealing, especially when carried out in formic acid solution. The bulk of the observed change is associated with an increase in the amount of α -phase present, but there is also a decrease in the amount of γ -phase.

Figure 11 shows the measured chain axis crystalline orientation factors for annealed samples compared to the as-spun and conditioned filaments. Although there are some measurable differences of orientation, the differences are not great and tend toward increasing orientation with increasing severity of annealing. In view of the large increase in the amount of α -phase present, this can only mean that the new α crystals grow epitaxially on existing crystals or from oriented nuclei.

Discussion

The general trend is that the spun fibers initially exhibiting a pseudo-hexagonal structure develop an appreciable fraction of the monoclinic α -phase if annealed in boiling water or 20% aqueous formic acid. Formic acid solution is much more effective than water in producing the monoclinic α form, and water is more effective than annealing dry (in vacuum). The effect of the annealing medium is presumably related to its role in helping to temporarily breakup hydrogen bonding, thus allowing the chain rearrangement needed to form the α -phase. This effect is further illustrated in the behavior of the γ -phase fraction. In samples having an appreciable fraction of γ -phase initially (high SDR's), there was a tendency to retain this γ -phase in all but the most severe annealing con-

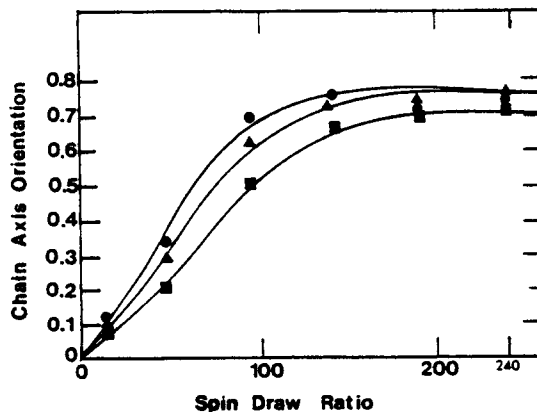


Fig. 11. The effect of annealing on chain axis orientation function of spun nylon-6 filaments: (●) as spun; (▲) boiling water; (■) 20% formic acid.

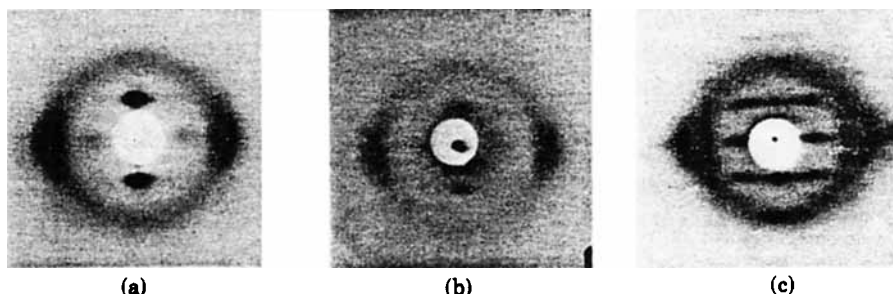


Fig. 12. Typical WAXS patterns of drawn nylon-6 samples. Draw temperature 90°C; SDR = 142; DR: (a) 1; (b) 2; (c) 4.

ditions. This would appear to be related to the stability of the hydrogen bonds in the γ -phase structure and the need to break these bonds in order to transform γ to α . This behavior is consistent with Illers' ⁵ observation that γ -phase formed by treatment in KI solution cannot be transformed to α by annealing in air or steam unless heated to a temperature high enough to melt it. Generally, the amorphous regions are more accessible to small molecules and so even in the case of annealing in water the major effect appears to be the transformation of the amorphous regions to monoclinic α -phase. At low SDR's there is very little γ -phase initially, but there is pseudohexagonal α -phase present (α^*). As noted by Illers⁵ and others,^{7,28} there is no difficulty in transforming this paracrystalline pseudohexagonal α to the monoclinic α form.

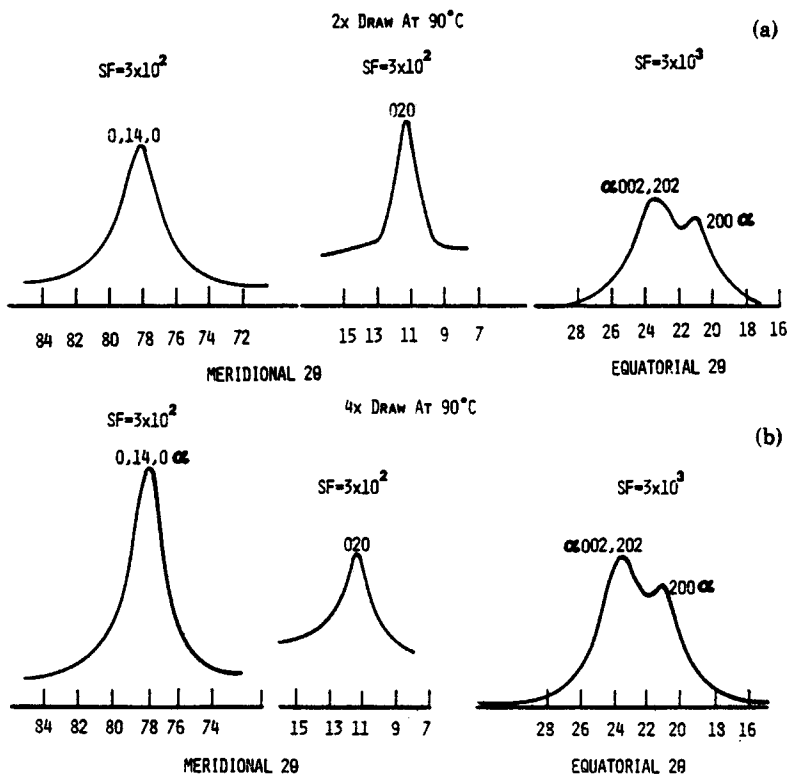


Fig. 13. Diffractometer scans of drawn nylon-6 samples. Draw temperature 90°C; SDR = 240; DR: (a) 2; (b) 4.

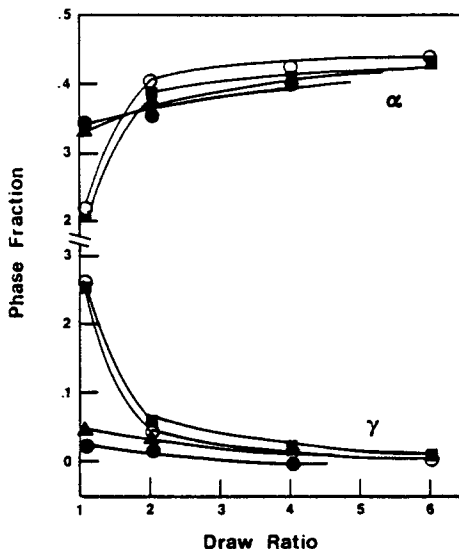


Fig. 14. The fraction of α -phase and γ -phase as a function of draw ratio for samples spun with differing SDR's: (●) 15; (▲) 48; (■) 142; (○) 240.

An important effect of annealing is the perfection of the crystals, resulting in a less paracrystalline structure and a larger crystal size. The α form produced by annealing in boiling formic acid solution is essentially the prototypic monoclinic form of Holmes et al.¹³ The α form produced by annealing in vacuum, air, or water was relatively imperfect. This form has been called "paracrystalline α form" by Roldan and Kaufman,⁴ and it is designated α' in Table I. With sufficient annealing this form is monoclinic. The d -spacings of this monoclinic α' form are not sharply defined; they vary with the annealing treatment as discussed by Parker and Lindenmeyer.⁶ One extreme of this variability appears to be the pseudohexagonal α which led Parker and Lindenmeyer⁶ to conclude that a single strong equatorial reflection and a strong 020 meridional peak is not

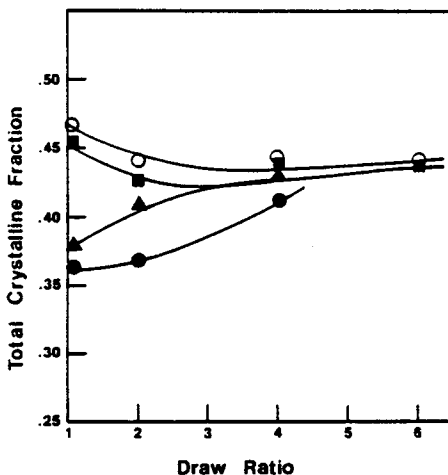


Fig. 15. Total crystalline fraction vs. draw ratio for samples spun with differing SDR's: (●) 15; (▲) 48; (■) 142; (○) 240.

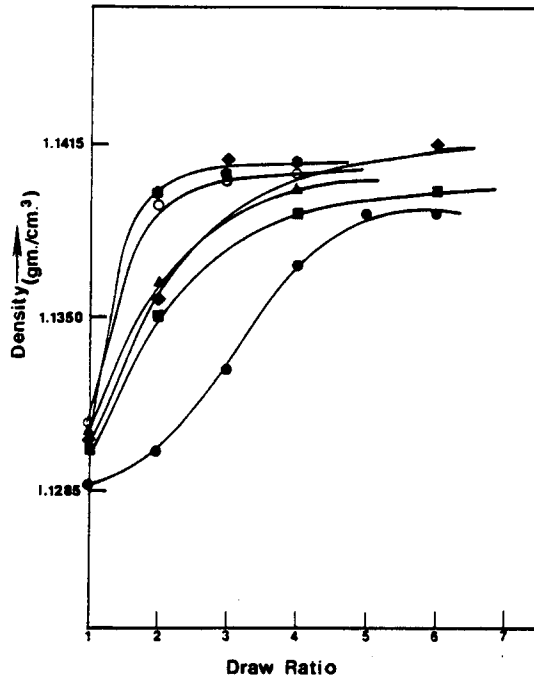


Fig. 16. Density of nylon-6 filaments as a function of draw ratio for samples spun with differing SDR's: (●) 15; (■) 48; (◆) 95; (▲) 142; (●) 190; (○) 240.

sufficient evidence for the existence of γ -phase. They suggest examination of the 0,14,0 reflection for this distinction as previously discussed. Our examination of the 0,14,0 reflection is consistent with the existence of the pseudohexagonal

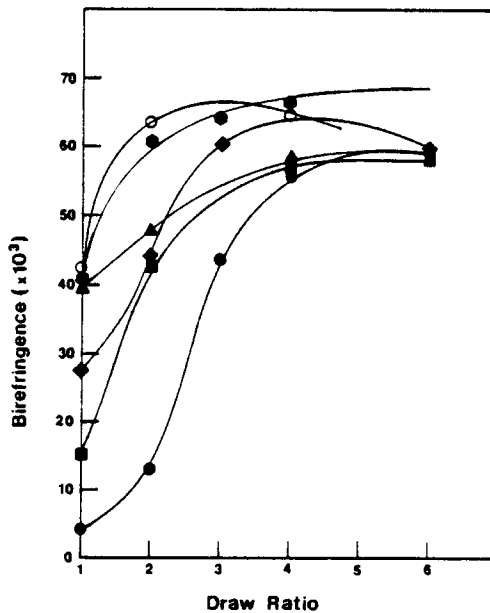


Fig. 17. Birefringence of nylon-6 filaments as a function of draw ratio; SDR: (●) 15; (■) 48; (◆) 95; (▲) 142; (●) 190; (○) 240.

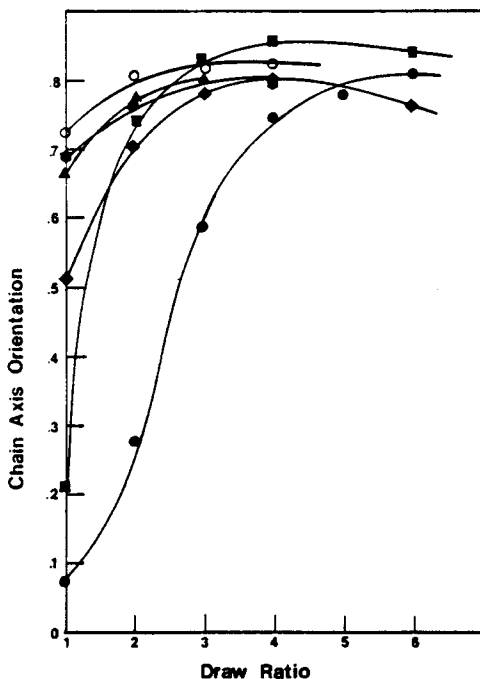


Fig. 18. Crystalline orientation function of nylon-6 filaments as a function of draw ratio; SDR: (●) 15; (■) 48; (◆) 95; (▲) 142; (○) 190; (○) 240.

α , but does not rule out the possibility that samples exhibiting strong 020 meridional reflections also contain an appreciable fraction of γ -phase. This would be the interpretation used in the new γ -index analysis.

STRUCTURE CHANGES DUE TO DRAWING

Results and Interpretation

It is well known that drawing tends to promote the formation of α -phase in nylon-6, and the data in Figures 12–14 document this fact for the samples prepared in the present investigation. Both the flat plate WAXS patterns of Figure 12 and the diffractometer scans of Figure 13 show that the 020 meridional intensity is decreasing. The diffractometer scans show more clearly that the single equatorial reflection of the spun filaments is splitting into two peaks (the α 200 and 002,202 reflections) and the 0,14,0 reflection is growing and sharpening in the neighborhood of $78^\circ 2\theta$ while decreasing in the neighborhood of $80^\circ 2\theta$. It is also clear from these data that the amount of γ -phase present in the samples is decreasing as a result of the drawing. All these features are clearly shown in the γ -index analysis as shown in Figure 14. These results also illustrate the difference in behavior of the low-SDR samples and the high-SDR samples. The former have little or no γ -phase initially and drawing merely results in a slight increase in α fraction together with a tendency for formation of the monoclinic α' from the pseudohexagonal α^* . This effect is also shown in terms of the total crystalline fraction in Figure 15.

It is interesting that Figure 15 indicates that there is little change in the total crystalline content of the high SDR samples during drawing at 90°C . At first

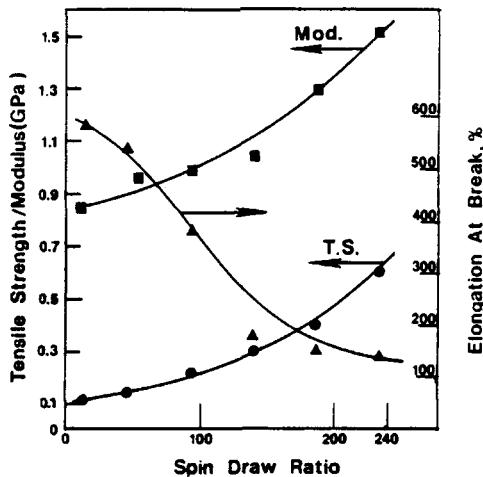


Fig. 19. Tensile properties of as-spun and conditioned nylon-6 filaments.

thought, this seems to contrast with the large increases in density observed due to drawing as shown in Figure 16. However, it must be remembered that α -phase has a much higher density than γ -phase. Consequently, all the data are consistent with the hypothesis that drawing is transforming γ -phase into α -phase in the high-SDR samples.

The changes in birefringence and chain-axis crystalline orientation factor as a function of draw ratio are shown in Figures 17 and 18, respectively. These two plots show a very similar dependence on draw ratio, and it is clear that the major factor contributing to the birefringence changes is the change in crystalline orientation. It is also clear that the orientation changes are much greater for the low-SDR samples than for the high-SDR samples. This, of course, is a direct result of the high spin orientation present in the high-SDR samples.

Discussion

Perhaps the most striking feature of the drawing results is the observation that the total crystalline content of the high-SDR samples remains nearly constant while the amount of α -phase is increasing.

This behavior is quite different than in the case of annealing in air or vacuum and, to some extent, even water and formic acid solution. As discussed previously, annealing produces α primarily from the noncrystalline amorphous contribution rather than from the γ -phase. The stresses applied during drawing appear to be more effective than thermal activation for breaking the hydrogen bonds in the γ -phase fraction and eliminating the kink in the nylon-6 chain which is present in the γ form. In this respect the data of Figure 14 indicate that most of the γ -phase is removed by a draw ratio of about $2x$. This is consistent with the results of Heuvel and Huisman¹⁰ for drawing of high-speed spun yarns. For their samples drawing was carried out at 180°C, a much higher temperature than for the present samples (90°C). This would seem to imply that draw ratio is a more important variable than draw temperature in controlling the deformation induced transformation of γ -phase to α -phase.

Finally, it should be noted that the effect of post-annealing of drawn filaments was not investigated in the present research. However, this has been given

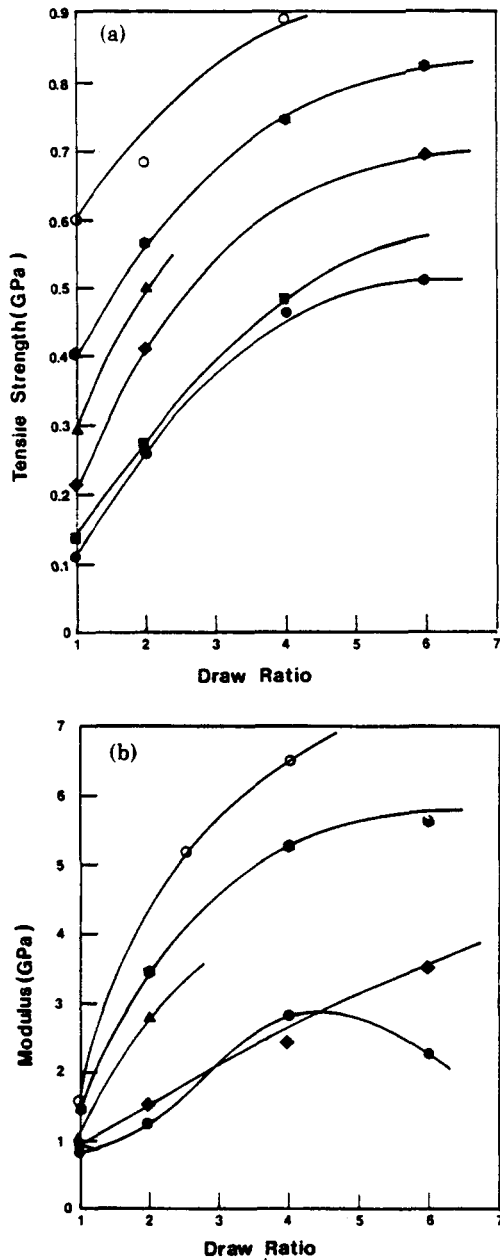


Fig. 20. Tensile properties of nylon-6 filaments as a function of draw ratio: (a) tensile strength; (b) Young's modulus; (c) elongation to break. SDR: (●) 15; (■) 48; (◆) 95; (▲) 142; (●) 190; (○) 240.

relatively complete treatment by Parker and Lindenmeyer⁶ for one set of spinning and drawing conditions corresponding to production conditions for carpet yarn. Starting with this material which was slightly monoclinic (nearly pseudohexagonal) α' , they found that annealing tended to give a structure which approached the monoclinic α structure of Holmes et al.¹³ more as the annealing temperature was increased from 55°C to 205°C.

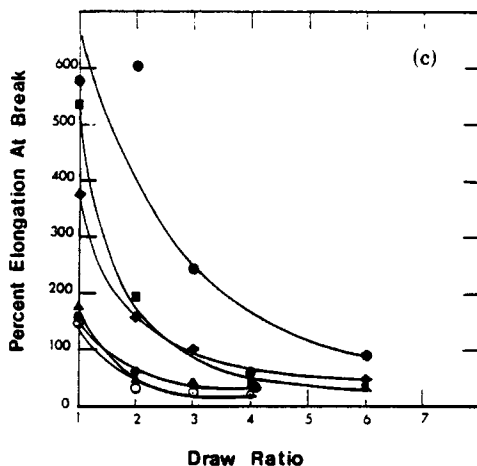


Fig. 20. (Continued from previous page.)

TENSILE PROPERTIES OF NYLON-6 FILAMENTS

Results

The tensile properties of the as-spun and conditioned filaments are presented in Figure 19. These results and the individual stress vs. elongation curves are very similar to the previous results of Bankar et al.²⁸ Data for drawn fibers are presented in Figure 20.

Discussion

There seems to be no satisfactory method of deciding with certainty what effect the relative amounts of α - and γ -phases have on the tensile properties of as-spun filaments. This is true because other factors such as orientation and total crystalline content change with SDR as well as the relative amounts of α - and γ -phases. It is true that orientation rises rapidly with SDR (Fig. 5) while the tensile strength and modulus do not change much until the orientation has almost leveled off. On this basis it is tempting to conclude that the relative amounts of α and γ have a significant effect on the tensile properties. However, the same trend with orientation is observed in polymers such as isotactic polypropylene and nylon-66,^{32,34,35} where there is no transition to a different crystal form with changing SDR. It seems more reasonable that the changes in the orientation, number of tie molecules, and other details of the fiber morphology may be more significant in determining the tensile properties than are the relative amounts of α - and γ -phases. It does appear that the degree of orientation present is an important factor in determining the mechanical properties of either spun or drawn filaments as may be demonstrated by plotting tensile strength, modulus, or elongation to break versus the fiber birefringence, as shown in Figure 21. Although there is a reasonably broad scatterband present, it is clear that tensile properties correlate reasonably well with birefringence (and hence average orientation) independent of the method of preparation of the sample. Similar behavior has also been reported for isotactic polypropylene.³⁵

It should be realized by the reader that the comments we have made with re-

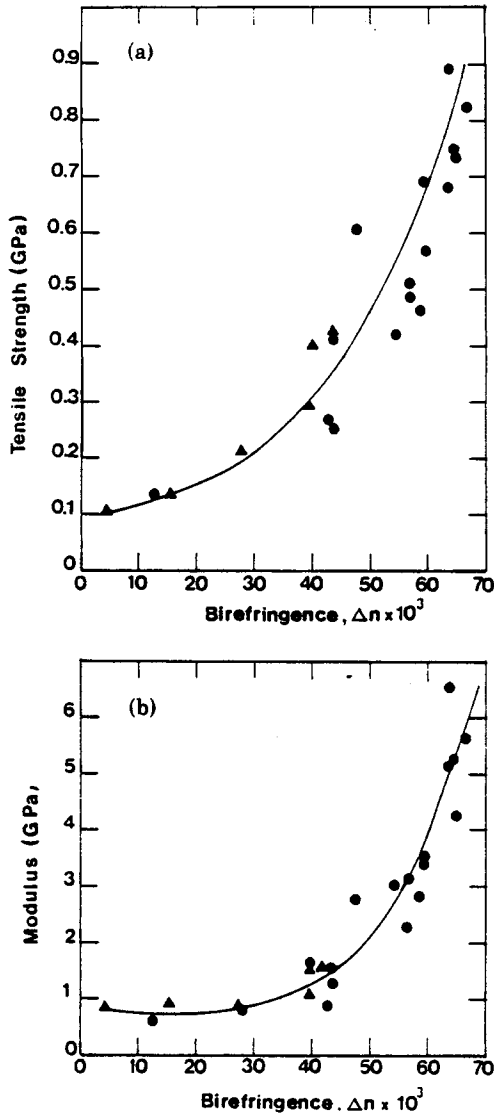


Fig. 21. Tensile properties of nylon-6 filaments as a function of birefringence: (a) tensile strength; (b) Young's modulus; (c) elongation to break. (▲) As spun; (●) drawn.

spect to the role of the relative amount of α - and γ -phases pertains only to the tensile properties which were investigated in this research. There are many other physical characteristics such as dyeability, dimensional stability, etc., which may be important in a commercial fiber which were not considered in this research.

CONCLUSIONS

A new method has been developed for estimating the relative amounts of phases in nylon-6. The method subdivides the sample into an α fraction, a γ fraction, and a noncrystalline, amorphous fraction. Based on the current literature, these distinctions appear to be the most significant. Further distinctions

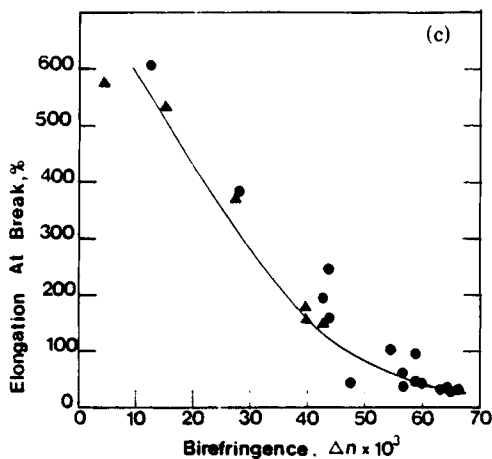


Fig. 21. (Continued from previous page.)

concerning the relative perfection of the α and γ fractions can also be made in a qualitative sense.

Based on these procedures, it was demonstrated that the relative amount of phases in as-spun and conditioned filaments of nylon-6 depends on the molecular orientation (SDR) developed by spinning. Low orientation samples contain higher amorphous and α -phase fractions and lower γ -phase fractions than samples having higher spin orientation (high SDR's). Both the α and γ fractions exhibit a poorly developed pseudo-hexagonal structure.

Annealing tends to increase the amount of α -phase mainly at the expense of the amorphous contribution. The nature of the α -phases changes; it becomes monoclinic and increases in perfection as the severity of annealing increases. In the high-SDR samples containing appreciable γ -phase, there is a decrease in the relative amount of γ -phase on annealing, but γ -phase is not eliminated by the most severe annealing treatment investigated (2 h in boiling aqueous 20% formic acid solution). The low-SDR samples anneal more readily to the α -phase.

Drawing of as-spun and conditioned filaments also increases the relative amount of α -phase. The perfection of this phase undoubtedly depends on the draw temperature. Under the drawing conditions used (90°C, in air), the γ -phase is converted to monoclinic paracrystalline α -phase with increasing draw ratio. Most of the transformation occurs between a draw ratio of 1 and 2. There does not appear to be much change in amorphous fraction in samples which had high spin orientation (high SDR's), but the amorphous fraction decreased as the α -fraction increased and became more perfect in the samples which had low spin orientation.

The results obtained using the new method of estimating the relative amounts of phases present in nylon-6 are qualitatively consistent with the more elaborate method used by Heuvel and Huisman.¹⁰ It would be useful to perform experiments on the same series of samples by the two techniques in order to allow quantitative comparison.

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