Melt Spinning of Poly(ethylene Terephthalate)—Structural Transitions in a Range of Spinning Speeds

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Synopsis

The transitions which occur in the structural state of poly(ethylene terephthalate) filaments in the range of spinning speeds, 1600–4500 m/min, have been studied. Thermal annealing of as-spun filaments has been shown to provide useful indirect evidence for the structural states of these filaments. The results have been explained with a simple model of orientation distributions arising from crystallization in an oriented precursor.

INTRODUCTION

The formation of oriented structures in melt spinning of polymers has been discussed widely in the literature. That the spinning variables influenced the fiber structure was recognized as early as 1932 by Carothers and Hill,[1] who found qualitative correlations between tension in melt spinning and X-ray diffraction patterns of polyamide and polyester fibers. They observed clear evidence of molecular orientation. Keller[2,3] provided an extensive qualitative discussion of orientation and crystallinity in melt spun fibers from nylons, polyethylene, and poly(ethylene terephthalate) (PET). In an experimental work to identify the relevant spinning variables, Ziabicki and Kedzierka[4–6] studied molecular orientation developed in melt spinning of nylon-6, PET, and polyethylene filaments. The bulk of the research work since these early studies, however, has been on the evolution of structure in fiber formation from fast crystallizing olefin polymers, especially linear polyethylene and isotactic polypropylene. Little appeared in the literature on PET where detectable crystalline structures are absent when melt-spun at low speeds.[7,8] The recent advent of high speed melt-spinning has led to a renewal of significant interest in structure formation in PET in the process. Notable among the reported studies are those of Liska,[8] Shimizu et al.,[9] and Heuval and Huisman.[10]

Wide-angle X-ray diffraction studies and density measurements indicate that undrawn PET yarn is essentially noncrystalline when the spinning is carried out at low and intermediate speeds (less than ~3000 m/min) and that detectable crystallization occurs in the threadline at speeds of 4000 m/min and higher.[8–10] The primary reason for the absence of significant crystallization at low speeds is the slow rate at which the polymer crystallizes, especially when the orientation in the noncrystalline precursor is low. At high speeds, the increase in the elon-

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gation rate in the molten region of the threadline induces a higher degree of molecular orientation. The consequent increase in the rate of crystallization[11] causes crystallization to occur before the threadline temperature reaches below the glass transition temperature (~75°C).

Several properties of undrawn PET yarns are known to show pronounced changes in a range of winding speeds. For example, the shrinkage of undrawn yarns increases progressively up to winding speeds of ~3000 m/min but then shows a dramatic decrease to low values around 4500 m/min. Quynn[12] has shown that the temperature at which an undrawn PET, when subjected to a small tensile load, undergoes ductile failure is around 145°C for low speed spun yarns, but yarns spun at high speeds fail in such a test only with the onset of melting around 240°C. These and other changes that are observed in the response of undrawn PET filaments produced at increasing winding speeds are well documented in the literature, but clear reasons based on morphological grounds have not been provided.

Relevant quantitative characterization of the transition zone between low speeds (below ~2800 m/min), where there is negligible degree of nucleation and high speeds (~4500 m/min), where there is detectable crystallization in the threadline, is difficult. In this intermediate zone where a network of nuclei is formed without significant growth of crystals, the techniques available currently for morphological characterization are inadequate. Assuming that the critical size of a nucleus is of the order of 1000 Å^3 and that they are spaced approximately 100 Å apart, their volume fraction is only 10^{-3}. Measurements with X-ray diffraction and density fail at such a small fraction of these small crystalline entities. We believe that indirect evidence for the existence of significant nucleation can be obtained by comparing results from heat treatments of these yarns in the presence and in the absence of macroscopic constraints. This aspect will be discussed later in the context of the results from the present study.

Liska, in his excellent study of the response to heat treatment of PET filaments spun at different speeds, has shown qualitatively the role of macroscopic dimensional constraints in structure formation. The range of speeds studied by him was 1450–4000 m/min. In the present study, the influence of dimensional constraints on the transition from the state at low speeds where relaxation of orientation precedes crystallization during annealing to the state at high speeds where crystallization precedes such relaxation is monitored quantitatively. The results are explained on the basis of orientational changes caused by relaxation *as well as* crystallization. The relevance of this analysis to control of melt spinning and subsequent processes is discussed.

EXPERIMENTAL

Materials and Conditions

Undrawn multifilament yarns were supplied by the American Enka Company. The melt spinning conditions are listed in Table I.

Annealing was carried out in an air-circulated oven under the following conditions:

(i) Constant length annealing (CLA): Ten layers were wound with minimum tension on a frame. The frame was placed in the oven previously heated to the

TABLE I
Spinning Conditions

Intrinsic viscosity =	(chips) 0.645 dL/g
	(yarn) 0.615 − 0.63 dL/g
Polymer temperature at the spinneret =	290–295°C
Number of holes in the spinneret =	32
Spinneret hole size =	200 μ diameter
	400 μ length
Blow box air flow rate =	200 ft^3/min

desired temperature, where it remained for the required period of time. On removal from the oven, the fiber was cooled at room temperature before it was removed from the frame. The CLA samples for wide-angle X-ray diffraction (WAXD) were prepared by winding the filament yarns on the X-ray sample holders and annealing this assembly in the oven.

(ii) Free length annealing (FLA): The PET filaments were suspended freely in the oven from a cotton thread.

Morphological Parameters

Flat plate wide-angle X-ray diffraction patterns for the samples (as-spun and annealed) were obtained with a Phillips Norelco X-ray generator. The radiation used was Ni-filtered CuKα (wavelength 1.542 Å). The X-ray unit was operated at 40 kV and 25 MA. The sample to film distance was 7 cm. The fibers were wound on a frame in a parallel alignment and exposed to the X-ray beam which was coming out through a pin hole. The pin hole was 0.015 in. in diameter. The exposure time was 4 h.

Phillips wide-angle X-ray diffractometer was used to obtain the 2θ scan from the as-spun filaments and from the heat treated fibers. The samples were spun in their plane during this scan. A specially designed slit system was used to collimate the X-rays. The diffractometer was also used for azimuthal scans needed for quantitative evaluation of orientation factors.

The orientation of the molecular axis with respect to the fiber axis determines the degree of orientation in a fiber. If a crystal plane can be found, the normal to which lies along the molecular axis, the orientation of this plane with respect to the fiber axis would give the molecular orientation directly. There is no meridional reflection in PET that will give measurable diffraction. However, the plane $(\bar{1}05)$ lies at 9° to the fiber axis and gives easily detected intensity. Azimuthal scans were made on the $(\bar{1}05)$ reflection, at 2θ value between 42.6° and 43.3° giving maximum intensity. There is a small amount of azimuthal overlapping between the $(\bar{1}05)$ and the $(0\bar{2}4)$ planes but it is not serious. The $(\bar{1}05)$ profile was drawn smoothly below the $0\bar{2}4$ reflection to correct for this azimuthal overlapping. The orientation of $(\bar{1}05)$ plane was used as an approximation of crystalline chain orientation. The average crystalline orientation is expressed as the Hermans' orientation function[13] of the $(\bar{1}05)$ plane with respect to the fiber axis.

Zeiss polarized optical microscope with Calcite Ehringhous Compensator, which has an available measuring retardation range of about 32 orders of λ was used for measurement of optical birefringence.

Shrinkage

As-spun PET yarns of 35 cm length were allowed to shrink freely in an air circulated oven at 100°C, 150°C, and 200°C for 2 min and then cooled at room temperature before the length was measured. The shrinkage was calculated as a percentage of the initial length.

RESULTS AND DISCUSSION

PET fibers spun at low speeds have been found in the present study, as in others, to be essentially amorphous [Figs. 1(A) and 1(D)]. The tendency for

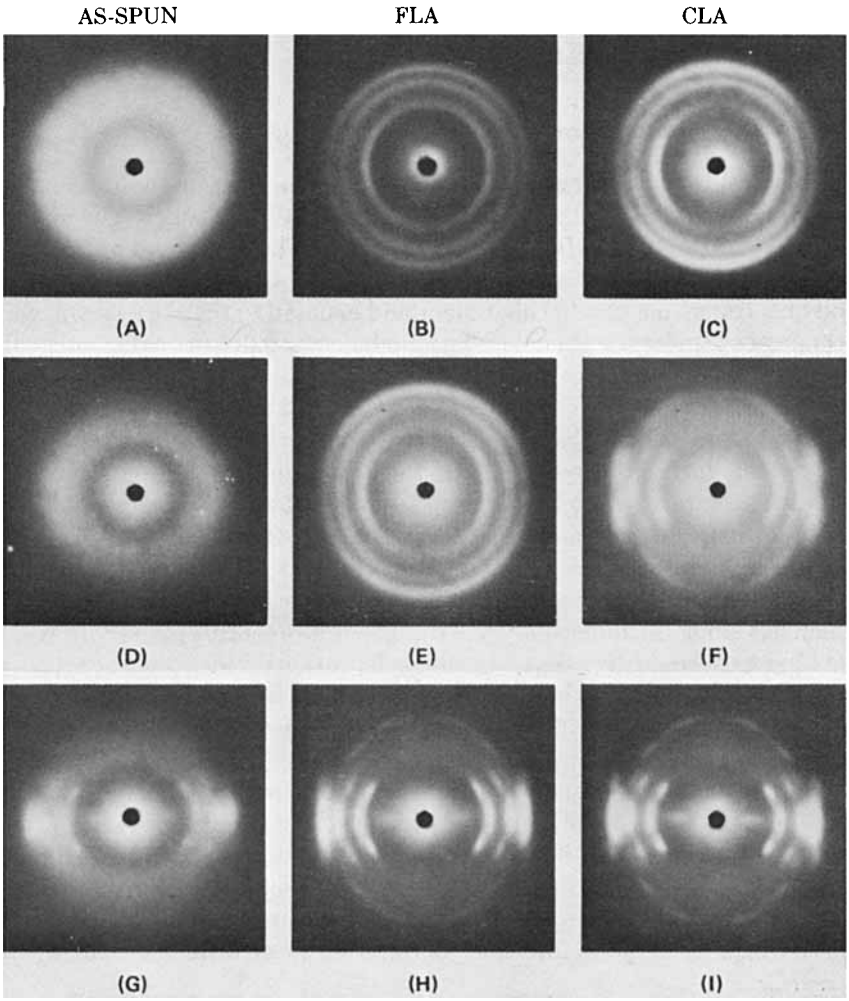

Fig. 1. Flat plate WAXS photographs: annealing temperature = 150°C, annealing time = 2 min; FLA = free length annealing; CLA = constant length annealing. (A)–(C), 1600 m/min; (D)–(F), 2800 m/min; (G)–(I), 4500 m/min.

crystallization to occur increases with the spinning speed. The initiation of crystallization is observed in the fibers spun at 4500 m/min [Fig. 1(G)]. Also, the orientation of the as-spun filaments increases monotonically with the winding speed (Fig. 2).

Before examining the results from the annealing experiments, we present a discussion of the consequences of crystallization in an oriented uncrystallized polymer. (A mathematical framework for this analysis is given in Ref. [14].) Such an analysis is relevant in understanding the nature of orientational changes accompanying crystallization in a melt spinning threadline.[15] As we will see later in this section, it can also be helpful in studying the nature of apparently amorphous filaments by their response to heat treatments. ("Uncrystallized" and "amorphous" are used interchangeably in this paper.)

Crystallization and Orientation Distributions

Figure 3(A) shows an arbitrary orientation distribution of chain segments in a fully amorphous precursor that is about to undergo crystallization. Here, the orientation angle represents the inclination of chain segments with respect to the preferred direction, which is, for example, the fiber axis in a melt-spun fiber.

Crystallization involves forming a small but stable nucleus between a critical number of chain segments to which segments are added until the growth process is terminated due to one reason or another. Formation of a stable nucleus in a given direction is an event dictated by the change that the necessary critical number of segments within a small volume are aligned essentially in the same direction.[16] This requirement increases significantly the likelihood of forming

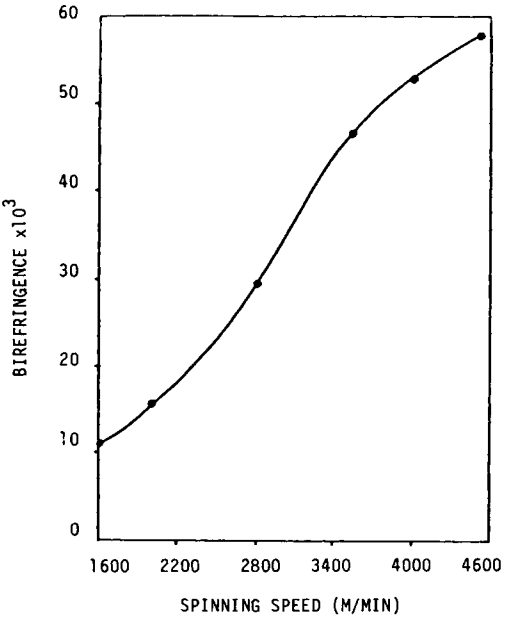

Fig. 2. Birefringence of as-spun PET filaments as a function of spinning speed (visual fit of data is shown).

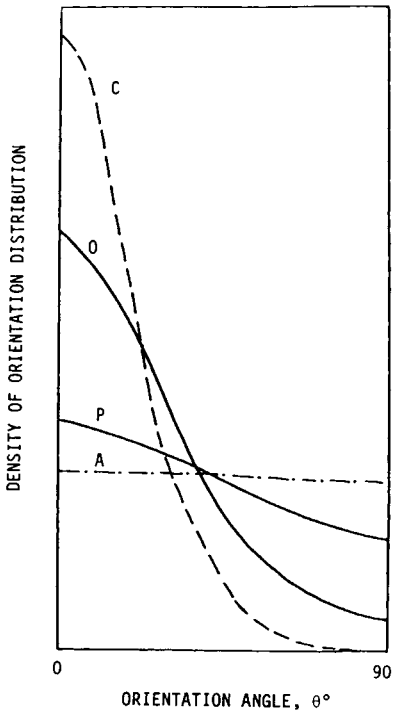

Fig. 3. Schematic representation of orientation distributions resulting from crystallization [orientation distributions of all the segments prior to crystallization (P), crystallized segments (C), and uncrystallized segments (A); the weighted combination of C and A is the orientation distribution of all the segments following crystallization (0)].

a nucleus with the chain direction close to the preferred direction. Thus, crystallization in an anisotropic amorphous precursor would lead to a greater degree of anisotropy in the orientation distribution of crystals than that of the precursor [Fig. 3(B)]. In many instances, it is more important you know the orientation of the segments which have been left uncrystallized. If we consider two precursor segments around a growing crystal, the one that is less inclined with respect to the segments in the crystal is more likely to be incorporated in the crystal than the other. In a system where an increasing number of crystals are growing closer to the preferred direction, the inference is that those precursor segments which are closer to the preferred direction are more likely to crystallize when compared to segments at high inclination to that direction. Thus the orientation distribution of the amorphous segments remaining after crystallization would show a significantly smaller fraction along the preferred direction when compared to the initial amorphous precursor [Fig. 3(C)].

In summary, when an oriented uncrystallized polymer crystallizes without relaxation in a process, the crystals formed would be more oriented than the precursor and the fraction that is left uncrystallized would be much less oriented.

Response of Undrawn PET Filaments to Thermal Annealing

When an oriented, apparently amorphous, undrawn PET fiber is subjected to annealing above T_g, orientational relaxation as well as crystallization can occur.

If the rate of crystallization is such that significant crystallization can take place before relaxation of the orientation, the result will be a fiber which possesses a degree of crystalline orientation that is much higher than that of the precursor. If, on the other hand, complete orientational relaxation precedes crystallization, the product will have an essentially isotropic distribution of crystals.

When one anneals PET filaments which are essentially amorphous but oriented to different degrees, the following can be expected. Since the rates of crystal nucleation and growth increase with increasing precursor orientation,[17-19] the extent of orientational relaxation preceding crystallization should decrease with increase in precursor orientation. When undrawn PET filaments produced at different winding speeds are annealed, the average crystalline orientation and the birefringence obtained are as shown in Figures 4 and 5. Almost complete relaxation of orientation takes place in the low-speed spun material while the high rate of crystallization in material spun at higher speeds causes highly oriented crystallization to occur before significant relaxation of the precursor orientation.

If orientational relaxation of a molecule in a system requires cooperative relaxation of the other molecules, then it can take place only if the necessarily consequent macroscopic shrinkage is permitted. As discussed before, nucleation and crystal growth during melt spinning increase with increasing winding speed. This implies increasing extents of intermolecular connectivity in the material

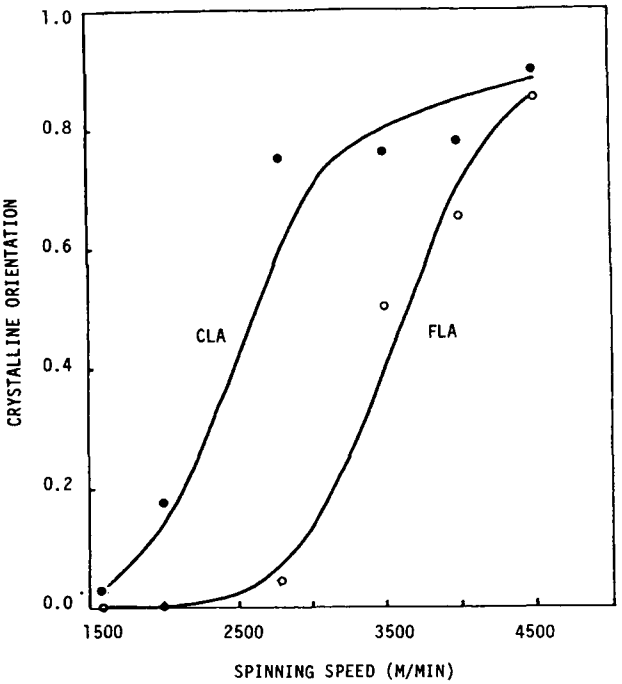

Fig. 4. Hermans' crystalline orientation of PET yarns (annealed for 2 min at 150°C) as a function of spinning speed (CLA = constant length; FLA = free length; visual fit of data is shown). Accuracy of measurements with low orientations suffered because of overlapping $\bar{1}05$ and $\bar{0}24$ reflections. The WAXS photographs in Figure 1 suggest a slight lateral orientation in the annealed low speed yarns.

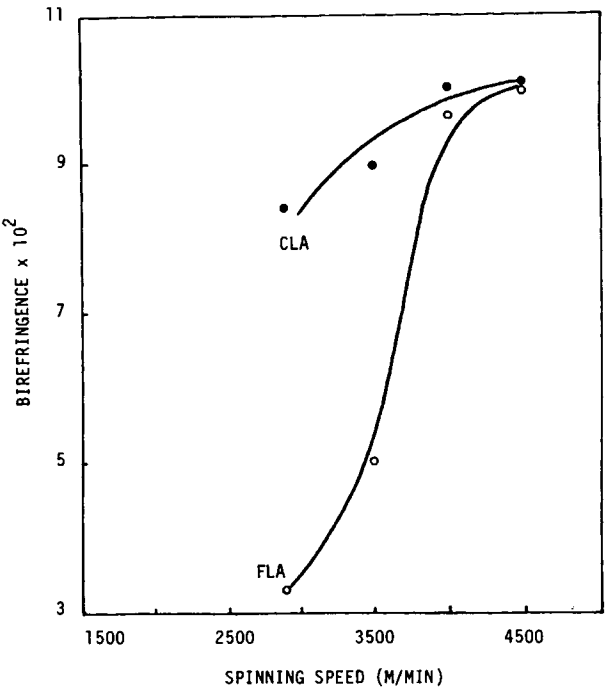

Fig. 5. Birefringence of PET yarns (annealed for 2 min at 150°C) as a function of spinning speed (CLA = constant length; FLA = free length; visual fit of data is shown). Measurements on yarns spun at low speeds were not possible because voids developed during annealing.

produced at higher speeds. This, by itself, would cause the differences in crystalline orientations developed in subsequent constant length and free length annealings to increase with spinning speed. If crystallization precedes orientation relaxation under free conditions, there is preferential transformation of oriented precursor segments, thus diminishing the retractive orientational relaxation in the material. Since both nucleation induced intermolecular connection and the rate of crystal growth in the threadline and during annealing (influenced by precursor orientation) increase with winding speed, the difference between the crystalline orientations in the constant length and free length annealings should be small at low as well as high speeds, with a maximum in between. Such is indeed observed experimentally as shown in Figure 6.

The pattern observed in the data presented so far can also be seen qualitatively in the WAXD flat plat photographs shown in Figure 1(A)–1(I).

Shrinkage Behavior

One of the consequences of the structural response to thermal annealing is in the shrinkage behavior of as-spun PET yarns (Fig. 7). One sees clearly the influence of the extent to which crystallization takes place before orientational relaxation. A comparison of the data on crystalline orientation of free and constant length annealed filaments (Fig. 4) indicates that a network of connected nuclei is formed in the threadline at speeds of ~2800 m/min. The consequence of crystallization in the as-spun material and any additional crystallization prior

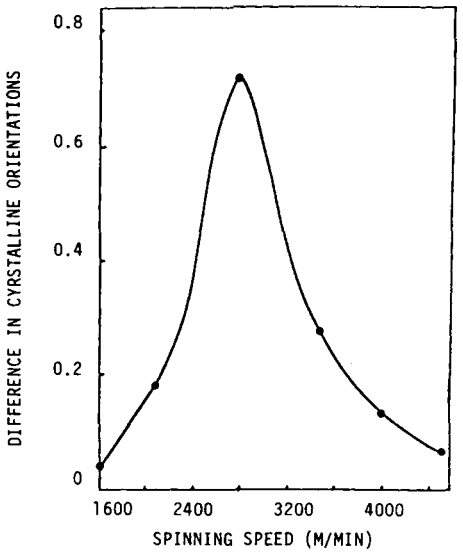

Fig. 6. Difference between Hermans' crystalline orientation developed in constant length and in free annealing as a function of spinning speed (visual fit of data is shown).

to total relaxation of amorphous orientation in uncrystallized segments during free annealing is to deplete preferentially the more oriented precursor segments. Thus one would expect the relative roles of orientation relaxation and crystallization to cause a maximum in the shrinkage under the same conditions, where the difference between crystalline orientation of the constrained and free an-

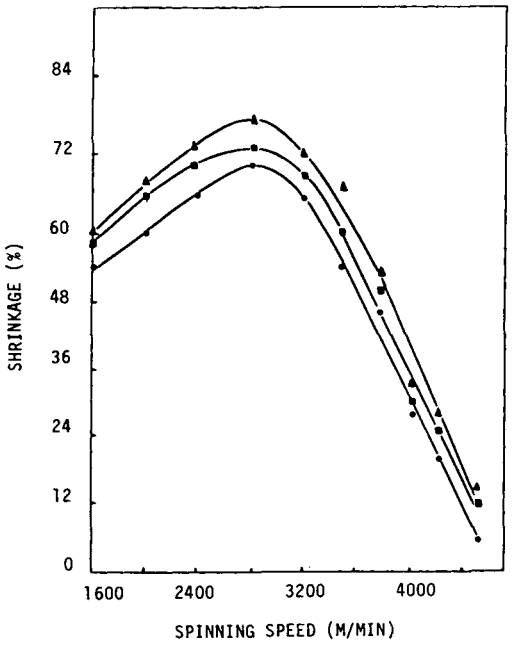

Fig. 7. Shrinkage of as-spun yarns as a function of spinning speed: (▲) 200°C; (■) 150°C; (●) 100°C.

nealed samples is also a maximum. This contention is clearly supported by the shrinkage behavior of the as-spun yarns in a wide range of temperatures (Figs. 6 and 7).

The process of structure development during annealing of as-spun PET filaments can be summarized as shown in Table II.

TABLE II
Summary of PET Structural Response to Heat Treatment

Winding speed	Annealing conditions	Structural response
1600 m/min	Constant length	Relaxation → Crystallization
	Free length	Relaxation → Crystallization
2800 m/min	Constant length	CRYSTALLIZATION and Relaxation
	Free length	RELAXATION and Crystallization
4500 m/min	Constant length	Crystallization
	Free length	Crystallization

Other Experiments

Additional experiments were conducted at long annealing times as well as with the combination of short time constant length annealing and short time free annealing. The latter was conducted to determine if a significant potential for structural and dimensional changes existed at the end of a short-time constant-length annealing. The results from these studies are given in Tables III and IV. These results are compatible with the preceding discussions. Only small additional changes are observed when the time of annealing is increased. Also, irrespective of the relative roles of relaxation and crystallization rates, one finds only insignificant changes during free annealing of a material which has undergone a prior constant length annealing at the same temperature.

SUMMARY OF INFERENCES

(1) The qualitative predictions from the simple scheme of analysis of orientation development in melt spinning are consistent with the birefringence of undrawn PET yarns produced at different winding speeds.

(2) The increased orientation in the melt zone obtained at increasing winding

TABLE III
Birefringence and Crystalline Orientation of PET Fibers Annealed For 30 Min

Spinning speed (m/min)	Birefringence		Crystalline orientation	
	Free annealing	Constant length annealing	Free annealing	Constant length annealing
1600	—[a]	—[a]	—[a]	0.03_8
2000	—[a]	—[a]	—[a]	0.18_6
3000	0.0407	0.0978	0.08_7	0.78_2
3500	0.0577	0.1100	0.50_7	0.86_7
4000	0.1008	0.1132	0.67_1	0.89_4
4500	0.1053	0.1163	0.91_5	0.93_7

[a] These measurements could not be made because of excessive voids in the fibers.

TABLE IV
Results from the Combination Annealing Experiments

Spinning speed (m/min)	Birefringence	Crystalline orientation	Residual shrinkage (%)
1600	—[a]	0.034_2	1
2000	—[a]	0.107_3	1
2800	0.0886	0.703_7	1.5
3500	0.1004	0.721_2	0
4000	0.1011	0.761_2	0
4500	0.1166	0.872_1	0

[a] These measurements could not be made because of excessive voids in the fibers.

speeds also causes the likelihood of nucleation in the crystallization zone to increase and thus introduces a higher degree of intermolecular connection.

(3) When low-speed spun PET filaments are thermally annealed, almost total relaxation of orientation takes place prior to crystallization, irrespective of the constraint imposed on the length.

(4) When high-speed spun PET fibers are annealed, crystallization takes place with little relaxation of precursor orientation, in both free and constant length annealing conditions.

(5) The transition between the different behaviors in the low- and high-speed spun PET yarns is in a range of winding speeds, which depends on the constraint imposed during the post-spinning crystallization process.

(6) The drastic changes that take place in the structural response in the intermediate range of winding speeds, especially in the range defined by constant length annealing, are critical. This range would be shifted by factors which influence the orientation introduced in the melt zone. The process variables that influence this orientation have been discussed by Ziabicki[20] and Hagler.[21] Fluctuations in process conditions here would have a greater effect in the response of the fiber in any subsequent high temperature process when compared with fibers produced outside this range.

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