

Bimodal Crystalline Orientation in Polypropylene: Mechanism of Formation

A. SAKTHIVEL and A. S. ABHIRAMAN,* *Georgia Institute of
Technology, Atlanta, Georgia 30332*

Synopsis

Melt-spun polypropylene fibers have two sets of crystallites, each with a different preferred orientation. A probable kinetic mechanism of nucleation and growth of the two sets of crystallites, based on an analysis of crystallization in oriented polymers, is proposed. Experimental data on the fractions of these two sets of crystallites in as-spun fibers and the effect of subsequent drawing or thermal annealing on the relative amounts of these two sets are presented.

INTRODUCTION

Isotactic polypropylene, when crystallized subsequent to the development of extensional flow-induced orientation, contains two sets of monoclinic crystallites, each with a different preferred orientation.¹⁻⁵ One set has the *c*-axis preferentially oriented along the flow direction (axially oriented crystallites) while the other set has the *a** axis in the reciprocal space oriented preferentially along this direction (laterally oriented crystallites). The occurrence of such bimodal distribution in isotactic polypropylene was reported initially by Compostella et al.,¹ Awaya and Zasshi,³ and Ishizuka et al.⁴ and it is seen clearly in the x-ray diffraction fiber patterns (Fig. 1) We present here experimental data on the fractions of these two sets of crystallites in melt-spun polypropylene fibers, and the effect of subsequent drawing or thermal annealing on this bimodal distribution. A probable kinetic mechanism of nucleation and growth of the two sets of crystallites, based on an analysis of crystallization in oriented polymers,⁶ is proposed.

EXPERIMENTAL DETAILS AND RESULTS

Fibers were spun at three different speeds, 500, 1000, and 2000 m/min from commercial polypropylene (Hercules Profax 6301). The number average molecular weight (\bar{M}_n) and the ratio of weight to number average molecular weights (\bar{M}_w/\bar{M}_n) were, after spinning, 32,000 g/mol and 4, respectively. The melt throughput during spinning was adjusted to give a constant linear density of fibers at all the spinning speeds. The melt spun fibers were drawn at two different draw ratios, viz., at 1.5 and at 80% of the maximum possible draw ratio.[†] The spinning conditions are listed in Table I. The drawing was carried with the feed roll at 100 m/min and with

* To whom all correspondence should be addressed.

† It is taken to be the maximum draw ratio at which the filaments can be continuously drawn for fifteen minutes without filament breakage.

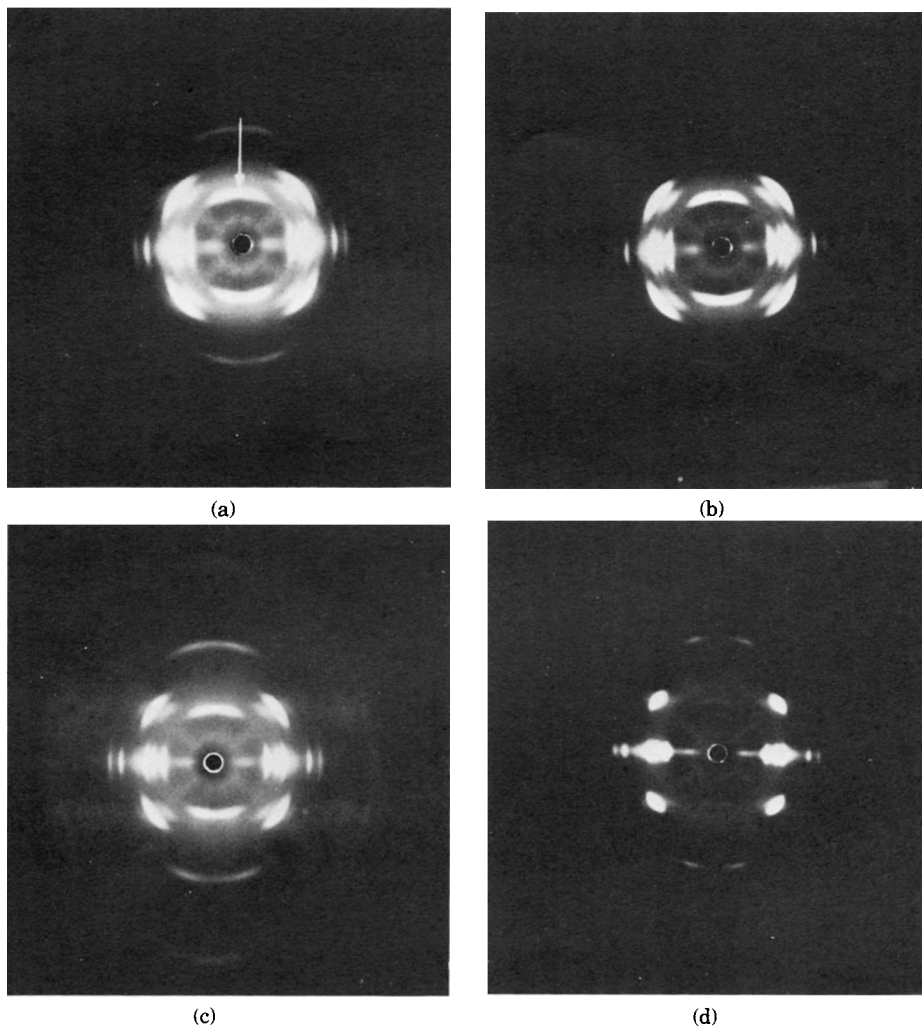


Fig. 1. Cylindrical WAXS photographs of as-spun and drawn polypropylene fibers [radius of the camera = 3 cm; arrow points to the (110) reflection from laterally oriented crystals]; Spinning speed (m/min): (a) 2000 (undrawn); (b) 500 (undrawn); (c) 500 (drawn 1.5 \times); (d) 500 (drawn 4.0 \times).

both the feed and draw rolls at 100°C. Thermal annealing was carried out at 150°C for 2 min in an air-circulating oven with the fiber being free to change in length.

As shown in Figure 1, the (110) reflection at $2\theta = 14.14^\circ$ consists of an

TABLE I
Details of Melt Spinning

Polymer temperature at the spinneret = 250°C
Spinneret hole size = 400 μm (diam) \times 1600 μm (length)
Temperature of quench air = 20°C
Velocity of quench air = 100 ft/min.
Spinning velocities = 500, 1000, 2000 m/min.
Denier per undrawn filament \approx 8.5
Total denier of undrawn yarn \approx 1200

equatorial component and a component close to the meridian. A North American x-ray diffraction unit (Type 12045) equipped with a geiger counter and a strip-chart recorder was used to make the azimuthal scans at $2\theta = 14.14^\circ$, corresponding to the (110) crystalline diffraction peak. Nickel filtered CuK_α radiation (wavelength = 1.54 \AA) was used. The azimuthal scans were made at constant scattering angle with the sample, a planar array of the filaments, being rotated in its plane at $12^\circ/\text{min}$. All the intensity measurements were made in the transmission mode. Typical scans from the different fibers are shown in Figures 2 and 3 and the fractions of laterally and axially oriented crystallites were estimated from these scans as described below. Fraction of laterally oriented crystals are equal to

$$\frac{\int_0^{\pi/4} I_{110}(\phi) \sin \phi d\phi}{\int_0^{\pi/2} I_{110}(\phi) \sin \phi d\phi} \quad (1)$$

Fraction of axially oriented crystals = $1 -$ fraction of laterally oriented crystals, where

$\phi =$ azimuthal angle

$I_{110}(\phi) =$ intensity at angle ϕ , corrected for background scattering

The fractions of laterally oriented crystallites estimated from x-ray diffraction data are given in Table II for the unannealed and annealed fibers.

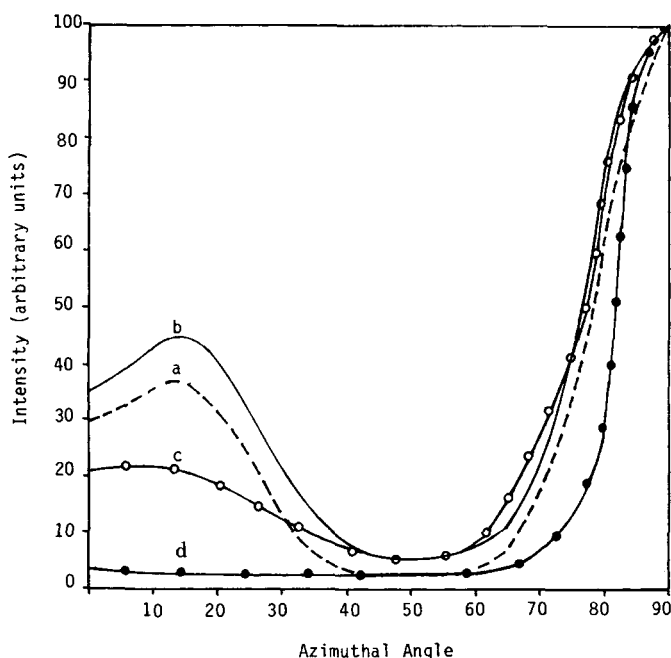


Fig. 2. Diffraction intensity (in arbitrary units) vs. azimuthal angle of as-spun and drawn fibers: Spinning speed 0 (m/min): (a) 2000 (undrawn); (b) 500 (undrawn); (c) 500 (drawn $1.5\times$); (d) 500 (drawn $4.0\times$).

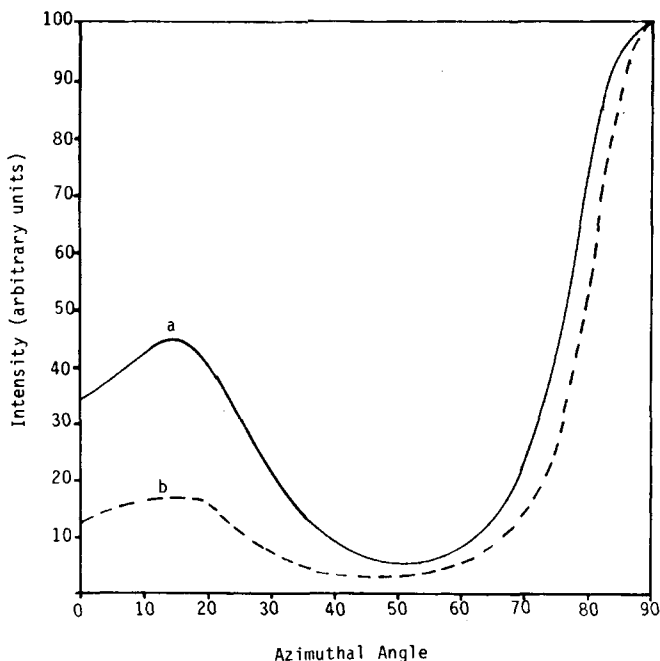


Fig. 3. Diffraction intensity (in arbitrary units) vs. azimuthal angle: Spinning speed (m/min): (a) 500 (undrawn, unannealed); (b) 500 (undrawn, annealed at 150°C for 2 min.)

MECHANISM OF FORMATION OF BIMODAL ORIENTATION DISTRIBUTION

An excellent discussion of the observations regarding bimodal crystal orientation distribution in polypropylene has been provided by Clark and Spruiell.⁷ We summarize below the relevant evidence cited by them.

- (i) The *c*-axis of the unit cell is normal to the crystalline lamella surface.⁸
- (ii) The growth axis of the crystalline lamella is parallel to the a^* -axis of the reciprocal space.
- (iii) Crystallization transforms selectively some of the molecular segments while rejecting the others.
- (iv) It is seen clearly from the "on-line" x-ray diffraction observations of Katayama et al.² that the laterally oriented crystallites appear subsequent to the formation of the axially oriented crystallites (Fig. 4). The smaller size, lower melting point, and the greater solubility of laterally oriented

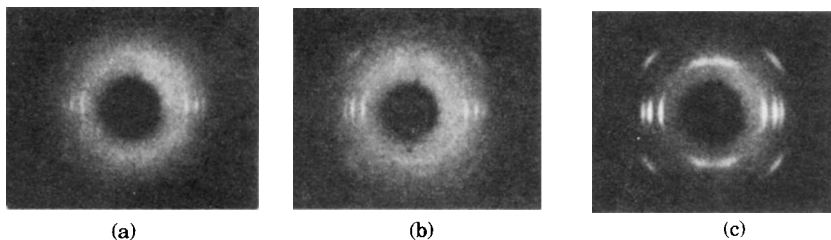


Fig. 4. X-ray diffraction photographs of running thread of polypropylene at various distances from spinneret (from Ref. 2): (a) 24 cm; (b) 30 cm; (c) 100 cm.

crystallites when compared with those of axially oriented ones are consistent with such an observation.

The most probable mechanism of formation of the bimodal crystal orientation distribution that is consistent with the above-mentioned observations appears to be the epitaxial, second stage growth of laterally oriented crystals on axially oriented, first stage crystals of polypropylene.^{7,9,10} Clark and Spruiell have indicated that epitaxial matching may be obtained when the a^* -axis in the reciprocal space of the crystals formed in the second stage is normal to the chain folded lamella of the first stage. With the b -axis of the two sets of crystals coinciding with each other, a good match is obtained between the fold repeat distance along the a^* -axis direction of the first stage crystals (13.1 Å) and the 13 Å spacing between alternate turns along the c -axis direction in the helical conformation (α form) of the second stage crystals. A rigorous test for a true epitaxial relationship between these two crystal populations, however, has not been made.

Epitaxial matching of the kind described by Clark and Spruiell⁷ may provide a driving force for the formation of the unique bimodal crystal orientation distribution in polypropylene. It should be recognized, however, that unless other kinetic factors play a part in the process, a chain segment would tend to attach itself to a growing crystal in the same sense as the other segments in the crystal. We describe, in the following, a kinetic mechanism by which the nature of orientation distribution of chain segments rejected by the first-stage axially oriented crystals could tend to generate in a set of second-stage crystals an orientation normal to that of the former.

The occurrence of two sets of crystals with distinctly different orientation distributions can be explained qualitatively with a model of crystallization in a precursor subsequent to the development of deformation induced orientation along a preferred direction (PD1). A quantitative framework for such a model is given in Ref. 6.

Crystallization involves forming a small but stable nucleus from a critical number of segments,¹¹ to which chain segments are added until the growth process terminates. Polymers rarely crystallize completely. Constraints such as chain entanglements prevent complete crystallization. Nucleation theory of polymers requires that a certain number of segments within a certain volume be aligned for nucleation to occur.¹¹ This requirement increases the probability that the nuclei are more oriented along the PD1 direction than the molecular chains in the uncrystallized polymer.

The rate at which segments in the precursor are incorporated in a growing crystal is likely to decrease with increased inclination of a precursor segment with respect to the crystal because, with increasing inclination of a precursor segment with respect to the crystal, the degree of reorientation necessary for crystallization increases. With a highly anisotropic distribution of growing crystals, the inference is that those precursor segments that are oriented close to the flow orientation direction are likely to crystallize faster than those that are at a higher inclination to that direction.

The final orientations of the crystals and the uncrystallized segments will depend on the following two factors:

(a) The degree of preferential attachment of the segments that are oriented close to the preferred direction of the primary crystalline nuclei, viz., the direction of flow orientation (PD1).

(b) The extent to which crystallization has occurred.

Preferential initial transformation to crystals of precursor segments that are closer to the flow orientation (PD1) can lead to an orientation distribution of uncrystallized segments with a preferred direction that is normal to PD1. If additional crystalline nuclei are formed at this stage, this orientation distribution is also likely to be anisotropic but with the preferred direction of these (PD2) being normal to PD1.

The model described above is shown schematically in Figure 5. Crystallization in a precursor with anisotropic orientation distribution, f_p , produces an initial crystal orientation distribution, f_{c1} , which shows a higher orientation of crystals along the preferred direction than the precursor. Such preferential growth of crystals leaves untransformed segments which are predominantly inclined at large angles to the growing crystals, as indicated by their orientation distribution, f_{a1} . If, at this stage, additional primary crystalline nuclei appear and grow, then orientation distribution f_{c2} would be dictated by f_{a1} , thus exhibiting a preferential orientation lateral to that of f_{c1} . The net orientation distribution of all the crystals, f_c , is then a combination of f_{c1} and f_{c2} , weighted appropriately by their respective mass fractions.

The occurrence of bimodal crystal orientation distribution is seen most clearly in melt spun polypropylene fibers (Figs. 1 and 2; Table II). For ease of comparison, the scattering intensity distributions have been normalized to give a maximum intensity of 100 (in arbitrary units) in each case. Drawing these fibers leads to a significant reduction in the fraction of laterally oriented crystallites. Since this occurs with a slight reduction in the extent

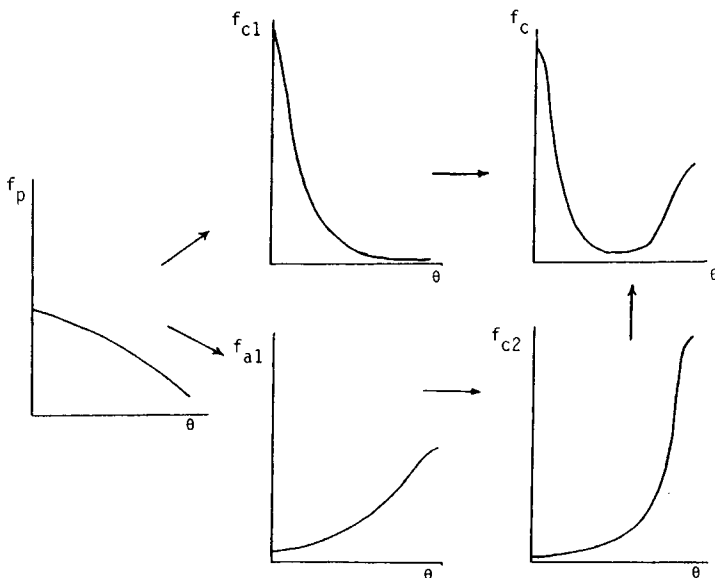


Fig. 5. Illustration of the development of two sets of crystals in melt spinning with preferred axial and lateral orientations: f_p , orientation distribution function (ODF) of precursor; f_{c1} , ODF of crystals appearing initially in the process; f_{a1} , ODF of segments remaining uncrystallized at an intermediate stage; f_{c2} , ODF of crystals appearing at later stages; f_c , ODF of all the crystals at the completion of the crystallization process (from Ref. 6).

TABLE II
Fraction of Laterally Oriented Crystals and Birefringence

Spinning speed	Draw ratio	Fraction of laterally oriented crystallites		Birefringence	
		As-spun and drawn	Annealed	As-spun and drawn	Annealed
500	Undrawn	0.20	0.10	0.015	0.024
500	1.5	0.12	0.07	0.020	0.024
500	4.0	0.04	0.04	0.030	0.029
1000	Undrawn	0.17	0.07	0.016	0.024
1000	1.5	0.11	0.04	0.019	0.026
1000	3.0	0.03	0.03	0.029	0.030
2000	Undrawn	0.17	0.07	0.017	0.023
2000	1.5	0.09	0.04	0.021	0.027
2000	2.9	0.05	0.05	0.031	0.028

of crystallization, it must be presumed that the laterally oriented chain-folded crystals are destroyed during the drawing process, probably by a simple unravelling of the chains from these crystals. Thermal annealing of the as-spun fibers which increases the extent of crystallization also leads to a preferential increase in the fraction of axially oriented crystallites (Fig. 3) and in the overall orientation as measured by birefringence (Table II). As crystallization proceeds in fibers in which a bimodal orientation of crystals exists, the relative growths of the two sets of crystals will be dictated by the relative growth surface areas and by the preferred direction of uncrystallized segments which would oscillate between the two directions. With a monotonically decreasing fraction of uncrystallized segments, the changes in the relative fractions of the two sets of crystals are likely to be small at the later stages of crystallization.

CONCLUDING REMARKS

Preferential initial crystallization of segments that are aligned close to the flow direction which can lead to the development of laterally oriented distribution of subsequently crystallizing segments, coupled with possible epitaxial matching of two sets of crystals proposed by Clark and Spruiell,⁷ appears to be the mechanism by which the bimodal orientation distribution develops in polypropylene. The special combination of requirements in extent of crystallization, degree of preferential attachment of segments to growing crystals, the minimum density of segments necessary for the formation of primary nuclei along the different directions, and possible epitaxial matching of crystals formed in the first and second stages appear to make it a highly selective process. Although the qualitative mechanism is clear, a quantitative theory of crystallization with experimentally identifiable parameters that takes into account all of the above-mentioned factors is still to be developed. It should be recognized that the structures formed in most fiber formation structures are far from equilibrium structures and that the prevailing kinetics of molecular rearrangement dictate the kind of structures formed in these processes.

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