α−γ Disorder in Isotactic Polypropylene Crystallized under High Pressure

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Introduction

Layer stacking disorder is rather common in metals and in low molecular weight systems. Similar occurrences in polymer structures are both less frequent and less characterized. In the present note, evidence for a unique mode of stacking disorder is presented, involving helix axis directionality, in crystals of isotactic polypropylene. Pressure plays an important role in the crystallization of isotactic polypropylene (iPP). Specifically, about 30 years ago, it was established[1,2] that the ratio between the γ-iPP and the α-iPP polymorphs grows with increasing pressure. More recently,[3] these findings have been shown to apply also to samples of relatively high molecular weight (M_w = 256 000) and high stereoregularity (0.907 isotactic pentads, 1.26% structural irregularities[4]). In practice, with highly stereoregular samples, pure α-iPP is obtained at atmospheric conditions, whereas virtually pure γ-iPP crystallizes at 200 MPa or higher. At intermediate conditions, peaks of both phases are observed in the powder WAXD profiles,[3] and this has also been shown to occur, under even milder pressure, for iPP blended with polycarbonate.[5] It must be stressed however that high-pressure crystallization is not the only way to obtain α-iPP−γ-iPP mixtures. Another possibility, studied for example by Rieger et al.,[6] is that of crystallizing "anisotactic" PP polymerized with homogeneous catalysts. These authors suggested that a connection exists between the amounts of γ-iPP and the frequency of stereochemical inversions present in the polymer fractions separated by solvent extraction. A significant difference is however apparent between the XRD profiles of mixtures of α-iPP and γ-iPP obtained in the two different ways. Crystallization of isotactic PP with large numbers of structural irreguarities gives rise to an XRD profile that appears essentially as the superimposition of the contributions from α-iPP and γ-iPP.[6] In the case of high-pressure crystallized iPP, the copresence of the two phases is also accompanied by a significant change in the intensity ratios of observed peaks as is apparent in Figure 1 of this work and in Figure 3c of ref 5. This is particularly evident in the profiles where the α−γ ratio is close to 0.5, a situation occurring near a crystallization pressure of ca. 75 MPa for the samples in the present study.

In this paper, we investigate the mentioned features of powder XRD profiles observed in samples crystallized under pressure through a model involving coexistence of α-iPP and γ-iPP blocks within individual coherently scattering domains. Since the copresence of α- and γ-iPP within individual crystallites has been previously proposed[3] to account for the small-angle scattering of iPP crystallized under pressure, it appears interesting to evaluate the implications of such a model on WAXD patterns.

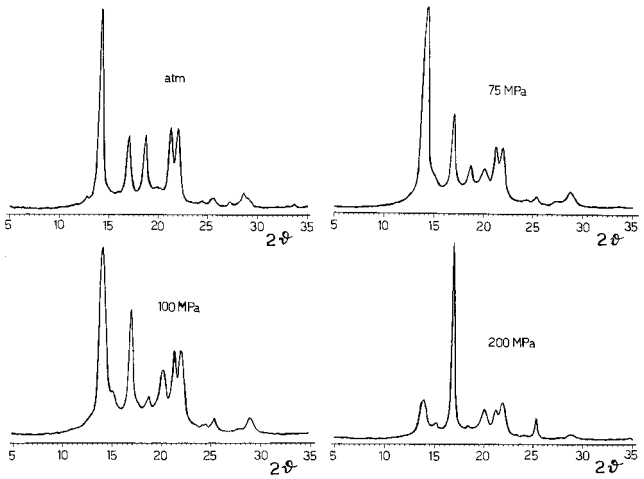

Figure 1. XRD profiles of iPP samples crystallized at 50 °C supercoolings and at the indicated pressures. Note that some preferred orientation is quite probable, at least in the sample crystallized at 200 MPa.

The Structural Model

Both α-iPP and γ-iPP may be described in terms of layered structures characterized by different sequences of the same subunit. This consists of a bilayer of parallel helices.[7] Individual layers within each bilayer are built up with helices of the same chirality, and a configurational inversion occurs between the two monolayers.

Different laws govern the propagation of this fundamental subunit in α- and γ-iPP, but the substantial identity of its geometrical features in the two structures suggests that stacking faults may occur during the crystallite growth without prohibitive energy requirements. Under this assumption, we studied a model where a unique bilayer is defined by averaging the geometrical features of the two subunits belonging to the α-iPP and γ-iPP structures. This operation involves only minor geometrical adjustments. The structural unit of the bilayer is a subcell containing two trimers belonging respectively to an *L* and an *R* helix; furthermore, each helical fragment coexists with a segment of the same chirality but opposite directionality consistent with the established mode of molecular disorder present in crystalline iPP.[8] This subcell does not coincide necessarily with any of the two crystallographic cells of α-iPP and γ-iPP; it is only defined in order to generate, through bidimensional repetition, the whole bilayer. The subcell parameters are $a = b = 6.55$ Å, $c = 10.49$ Å (the bilayer thickness), and $\gamma = 98.7°$ ($\alpha = \beta = 90°$) and are common to both α-iPP and γ-iPP structures. The bilayer is assumed infinite both along *a* and *b*. This fundamental unit, which we call bilayer A, may give rise to α-iPP and γ-iPP according to the different laws that govern its propagation along the stacking direction. In Figure 2 bilayer A is followed by bilayer B, related to A through a center of inversion. The repetitive action of this element of symmetry generates the sequence ABAB... and, consequently, the α-iPP structure; in particular, if 50% up−down statistics is assumed within each bilayer, space group *C*2/*c* is obtained.

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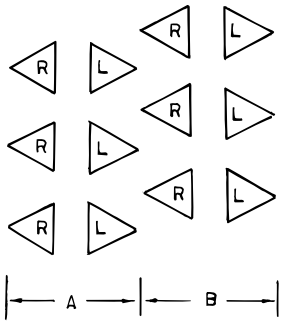

Figure 2. Sequence of bilayers A and B.

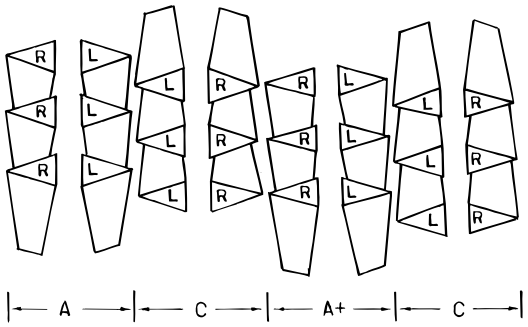

Figure 3. Sequence of bilayers AC(A+)C.

In Figure 3 bilayer A is followed by C, related to A by a 180° rotation around an axis that makes an angle of 40° with the chain axis direction in A. A second 180° rotation applied to C would give A again, but a translation along $0.5a + 0.5b$ must also be applied and we denote this plane as (A+), where the translation is relative to the preceding plane. (A+) is then followed again by C, without any further translation, and this by (A+), which, due to the periodicity of the translation that spans one half of the unit cell, coincides exactly with the original A. The repeated action of these symmetry operations produces the sequence AC(A+)C (A+)..., which coincides with the γ-iPP structure. If, again, 50% up−down statistics is assumed within each bilayer, space group *Fddd* results. By specifying the laws that regulate the transition from one kind of bilayer to the next, it is therefore possible to generate pure α-iPP and γ-iPP structures as well as all kinds of regular or irregular bilayer sequences.

Computations and Results

DIFFaX is a computer program well suited to deal with the problem of calculating diffraction intensities from crystals that contain coherent planar defects such as twins and stacking faults.[9] We used it in order to compute the powder XRD profiles from model crystals obtained with different bilayer sequences and then compared them with the observed profiles obtained from pressure-crystallized iPP. There are of course many possibilities of interchanging bilayers in order to produce stacking disorder. We first considered the possibility that the transition from α-iPP to γ-iPP, or vice versa, may occur only once every four bilayers with an *a priori* probability that can be varied at will. In other words, α-iPP is present at least with two cells (ABAB), whereas γ-iPP is present at least with one cell (AC-(A+)C). This means that after the first AB or AC pair has been chosen, according to a given a priori probability, the next pair, AB or (A+)C, respectively, follows necessarily.

DIFFaX also allows the treatment of both a single crystal that is infinite along the stacking direction or of an ensemble of crystals with a limited number of bilayers. In the second case, the contribution of each crystal, characterized by a given sequence of bilayers, to the total diffracted intensity is weighted according to the probability pertaining to that stacking sequence.

Results of these calculations for the infinite crystal with different amounts of α-iPP and γ-iPP phases are reported in Figure 4. The most relevant effect concerns the different relative intensities of peaks at 2θ equal to 18.3 and 20°. In this case, the model with 50% α-iPP also shows a significant change in the intensity distribution with a marked increase of the intensity of the peak at 16.9° (040 for α-iPP and 008 for γ-iPP), an effect that may be easily explained considering that both reflections arise from planes perpendicular to the stacking direction and thus are only sensitive to the z coordinate (referred to the bilayer unit cell) of atoms belonging to the different bilayers. More interesting from the point of view of the comparison with experiment is the effect of reducing the crystal thickness to a size involving a small number of bilayers. The results are shown in Figure 5, where all profiles refer to an ensemble of crystals with an average of 50% of α-iPP but with different thicknesses expressed in terms of the total number N of bilayers present along the stacking direction.

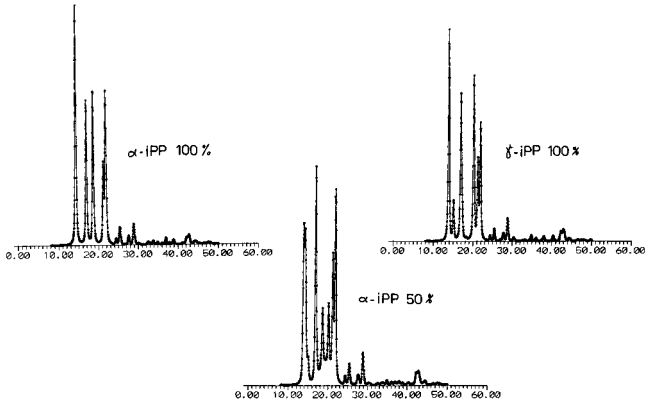

Figure 4. XRD profiles calculated for crystals of infinite thickness composed with different amounts of α-iPP and γ-iPP phases. The $\alpha-\gamma$ transition may occur once every four bilayers.

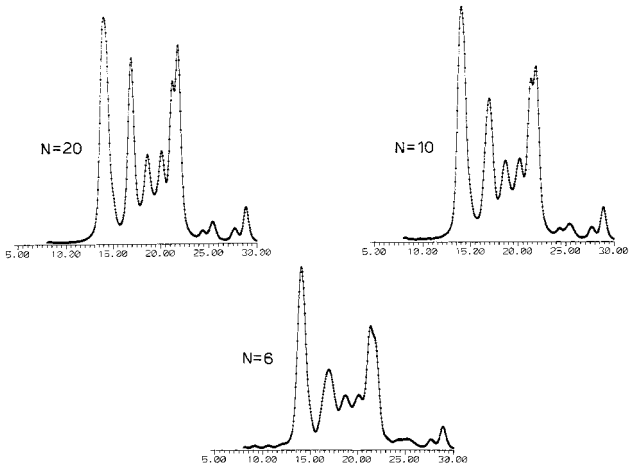

Figure 5. XRD profiles calculated for crystals containing equal amounts of α-iPP and γ-iPP phases but with different thicknesses along the stacking direction expressed with the number N of bilayers. The $\alpha-\gamma$ transition may occur once every four bilayers.

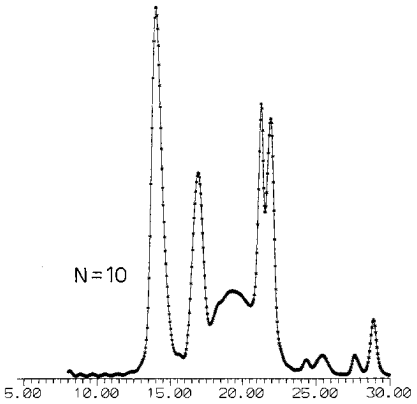

Figure 6. XRD profile calculated for crystals 10 bilayers thick. The $\alpha-\gamma$ transition may occur once every two bilayers.

As the number of bilayers forming the crystals is lowered from 20 to 6 (i.e., the coherently scattering crystallite dimension in the stacking direction is lowered from ca. 200 to ca. 60 Å), a progressive increase of the intensity of the peak at 14°, relative to all other intensities, is observed so that it rapidly becomes the most intense peak in the profile, in semiquantitative agreement with the iPP profiles in Figure 1. Similar domain size effects will also apply to samples with different α/γ proportions. For a quantitative comparison between calculated and observed spectra, preferred orientation should also be considered. The evaluation of the relative weight of the two mentioned factors is however beyond the scope of this preliminary note.

At this point, further disorder was introduced by allowing structural $\alpha-\gamma$ inversions to occur every two bilayers instead of four. An (A+) plane can be followed by a B plane without involving any new contact relative to the AB sequence so that an (A+)C sequence may be substituted, with a given a priori probability, by an (A+)B one and vice versa an AB sequence may be substituted by an AC one. These substitutions however break down the regularity of the resulting crystal lattice in the *a* and *b* directions; in fact, now the translation within the bilayer may also affect α-iPP blocks and not only γ-iPP and therefore substantial disorder results also in the direction of *a* and *b*. As may be seen in Figure 6, where the (A+)B, (A+)C, AC, and AB sequences are considered equiprobable, this is reflected in the coalescence between peaks at 18.3 and 20°, a feature that is not present in the observed profile.

Concluding Remarks

The present analysis suggests that limited intracrystalline disorder that locally preserves the structural features of α-iPP and γ-iPP is compatible with available diffraction patterns of samples where the two phases coexist. On the contrary, fully disordered (statistical) $\alpha-\gamma$ layer sequences do not appear to be consistent with published experimental data. Our results can be summarized as follows. (1) Infinite crystals (i.e., practically larger than 200 Å in the stacking direction) built with statistical sequences of blocks of each polymorph at least four bilayers wide (40 Å) give rise to profiles that are close to the superimposition of the pure α and γ contributions. (2) The presence of blocks made of only two bilayers is ruled out by the features of the corresponding calculated profile in which the 130 (α) and 117 (γ) peaks fuse in a single broad maximum. Such an event was never observed experimentally. (3) The coherent domain dimensions along the stacking direction are likely to be about 100 Å (i.e., ca. 10 bilayers). This value is consistent with typical coherent domain dimensions in polymers and specifically in iPP. Note that coherently scattering domains may be substantially smaller than individual crystals.

The copresence of α- and γ-iPP in the same crystallite in pressure-crystallized samples[3] appears to be thus fully acceptable. It is reasonable to suggest however that stacking disorder is limited by small but probably nonnegligible strain energy where the two lattices of α-iPP and γ-iPP are forced to match within a common crystal. In fact, the small crystal thickness, in addition to relatively long block sequences characteristic of the two pure phases, allows for minimizing the intracrystalline interaction between α and γ blocks. According to the present model, coherent domains contain, on average, only one $\alpha-\gamma$ transition. This may well be consistent with the finding, published in a recent paper,[10] that only $\alpha-\gamma$ branching occurs while the reverse is prohibited, at least in low molecular weight iPP samples.

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References and Notes

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