Crystalline Phase Orientation in Biaxially Stretched Isotactic Polypropylene Films

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Summary: The different kinds of crystalline orientations which can occur in industrially relevant isotactic polypropylene (i-PP) films are compared with those generally observed for other semicrystalline polymers. The peculiar bimodality typical of the uniplanar-axial orientation which is present in two-step biaxially stretched i-PP films is rationalized in terms of the two alternative stackings on the (0k0) face of bilayers of macromolecules of the monoclinic unit cell.

Introduction

The industrial production of biaxially stretched isotactic polypropylene (i-PP) films is quite relevant due to their easy processing, wide applicability and low cost. Since the physical properties of these films are strongly dependent on molecular orientation, the orientation of the crystalline phase, which is generated by this kind of process, has been thoroughly studied since the late fifties of the last century [1-5]. All these studies have shown a complexity and unicity of the observed crystal phase orientation.

In this paper, the crystalline phase orientation of simultaneous and balanced as well as of two-step and unbalanced biaxially stretched films of i-PP has been deeply characterized and compared with the simpler orientational behaviour, which is observed for other semicrystalline polymers, for similar stretching conditions.

A possible rationalization at molecular level of the peculiar bimodal-axial orientation, which is achieved by two-step biaxial stretching of i-PP, is presented. This bimodal orientation would be associated with two alternative stackings of bilayers of macromolecules of the monoclinic phase.

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Experimental part

The two-step biaxially stretched i-PP films are industrial films produced by Moplefan S.p.A.. The simultaneously biaxially stretched films have been obtained by industrial cast films by drawing at 140°C and constant strain rate of 0.1 sec^{-1} along two mutually perpendicular directions at draw ratios of 4.5 with a Bruckner stretching machine.

Wide-angle X-ray diffraction patterns were obtained with nickel filtered Cu Kα radiation with an automatic Philips diffractometer as well as by using a cylindrical camera (radius=57.3 mm), recorded on a BAS-MS Imaging Plate (FUJIFILM) and processed with a digital imaging reader (FUJIBAS 1800). In particular, in order to recognize the kind of crystalline orientation present in the samples, photographic X-ray diffraction patterns were taken with X-ray beam both perpendicular and parallel to the film surface.

The diffracted intensities *I*(hkl) were obtained by using an AFC7S Rigaku automatic diffractometer (with a monochromatic CuKα radiation), and were collected sending the X-ray beam parallel or perpendicular to the film surface and maintaining an equatorial geometry. Because the collection was performed at constant 2θ values and in the equatorial geometry, the Lorenz and polarization corrections were unnecessary.

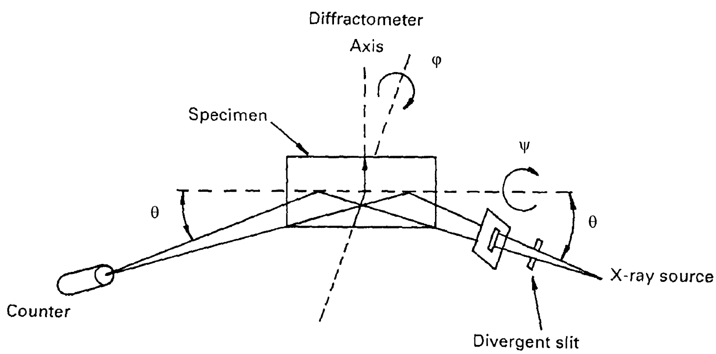

Figure 1: Experimental set up for pole figures analysis in the Schulz geometry.

The study of the preferred orientation of the samples was also carried out using a Philips X-Pert Pro diffractometer. The Schulz back reflection technique [6] was employed to obtain the pole figures of the samples, correcting the data by both the background and the defocusing contributions. In the Schulz reflection method the goniometer is set at the Bragg angle corresponding to the crystallographic planes of interest. A special specimen holder tilted the sample with the horizontal axis (ψ rotation axis), while rotating it in its own plane about an axis normal to its surface (φ rotation axis) (Figure 1). The ψ rotation can be varied from 0° to 90°, whereas the φ rotation can be varied from 0° to 360°. The pole figures are plotted on a polar stereographic projection using linear intensity scale. Iso-intensity lines indicate the relative intensity of the pole related to the maximum diffracted intensity (assumed equal to 10).

Results and discussion

Simultaneous and balanced biaxial stretching

X-ray diffraction photographic patterns, taken with the X-ray beam perpendicular to the film (i.e., along the normal direction, ND) and parallel to the stretching directions (machine direction, MD and transverse direction, TD) for a i-PP film, which has been obtained by a simultaneous biaxial stretching at draw ratios 4.5x4.5, are reported in Figure 2 A, B and C, respectively.

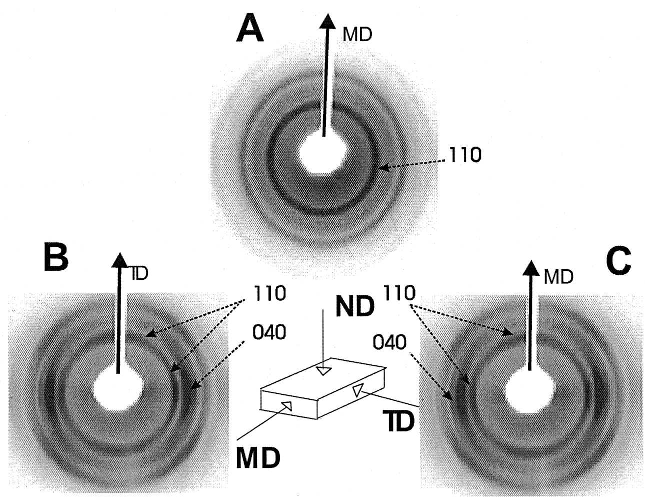

Figure 2: X-ray diffraction photographic patterns, taken with the X-ray beam perpendicular to the film (i.e., along the normal direction, ND) and parallel to the stretching directions (machine direction, MD and transverse direction, TD) for a i-PP film, obtained by a simultaneous biaxial stretching at draw ratios 4.5x4.5.

The reflection rings of the pattern along ND (Figure 2A), as well as the close similarity between the patterns taken with X-ray beam parallel to MD and TD (Figures 2B and 2C), clearly indicate a substantial absence of axial orientation.

The (040) reflection, being intense and equatorial in the X-ray patterns obtained along MD or TD and absent for the pattern obtained along ND, clearly indicates that these planes tend to be parallel to the film and, hence, the *b* axes of the crystallites tend to be parallel to ND, as generally observed for biaxially stretched i-PP films [1-5]. However, as already pointed out by some literature reports [3,5], the observed diffraction patterns cannot be rationalized only in terms of this kind of orientation. For instance the (110) reflection is not only apparent close to the meridian, as expected for *b* parallel to ND, but also on the equator (Figures 1B and C). This is more clearly shown by the azimuthal scan relative to the (110) reflection (at $2\theta = 14.2°$), which presents besides the maximum close to $\psi \approx 75°$ a second maximum at $\psi \approx 0°$ (Figure 3).

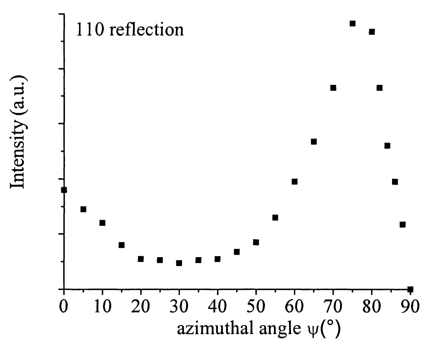

Figure 3: Azimuthal scan relative to the (110) reflection (at $2\theta = 14.2°$), for a X-pattern taken with the X- ray beam parallel to the surface, for a i-PP film obtained by a simultaneous biaxial stretching at draw ratio 4.5x4.5.

Additional information can be achieved by the pole figures relative to the main reflections, which are shown in Figure 4. As already pointed out by a previous reports on biaxially stretched i-PP films [1-5] and indicated by the photographic patterns of Figures 2 and 3, Figure 4A shows that most (0k0) planes are parallel to the film surface. As a consequence, in the (110) and (130) pole figures (Figures 4B and 4C), rings at latitude of 72° and 46° are apparent, respectively. The pole figures of the (110) and

(130) reflections (Figures 4B and 4C) shows a secondary maximum at latitude of 0° which indicate the presence of crystallites with these planes parallel to the film surface, as also described in other literature reports [3,5,7].

The presence, on the diffraction rings of the pole figures 4B and 4C, of intensity maxima along MD clearly indicates some preferential *c*-axis orientation along TD. It is worth noting that this minor axial orientation, which is of course related to a not perfect balancing of draw ratios between the two drawing directions, is not easily detectable from X-ray diffraction photographic patterns (like that one of Figure 2A).

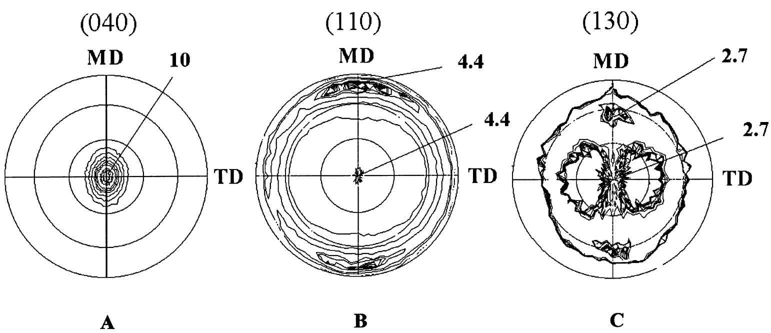

Figure 4: Pole figures relative to the main reflections (040), (110) and (130) for a i-PP film, obtained by a simultaneous biaxial stretching at draw ratios 4.5x4.5.

Two-step and unbalanced biaxial stretching

X-ray diffraction photographic patterns, taken with the X-ray beam perpendicular to the film (i.e., along ND) and parallel to the stretching directions (along MD and TD) for a industrial i-PP film biaxially stretched, in two-steps at draw ratios 8x5, are reported in Figure 5.

The reflection arcs of the pattern along ND (Figure 5A), as well as the substantial differences between the pattern taken with X-ray beam parallel to MD and TD (Figures 5B and 5C), clearly indicate a substantial amount of axial orientation. Moreover, the presence of two maxima (close to the meridian and to the equator) for the (110) reflection, for the pattern taken along ND (Figure 5A), clearly indicate the occurrence of the typical bimodal axial orientation [3,5]. The bimodality of the axial orientation is more clearly shown by the azimuthal scan relative to the (110) reflection (at $2\theta = 14.2°$), obtained by the X-ray beam perpendicular to the film, (Figure 6) which presents besides

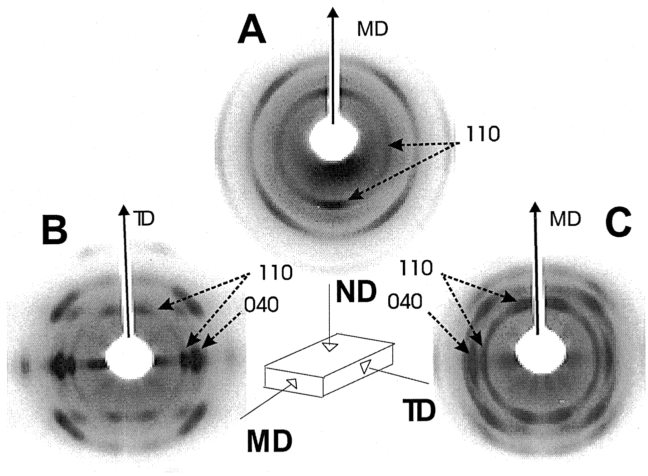

Figure 5: X-ray diffraction photographic patterns, taken with the X-ray beam perpendicular to the film (i.e., along ND) and parallel to the stretching directions (along MD and TD) for a industrial i-PP film biaxially stretched, in two-steps at draw ratios 8x5.

the maximum close to $\varphi \approx 90°$ (corresponding to crystallites presenting the chain axes along TD) a second maximum at $\varphi \approx 0°$ (corresponding to crystallites presenting the chain axes along MD).

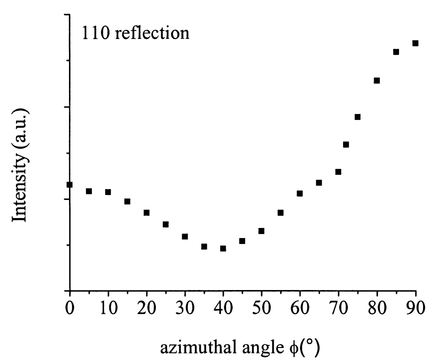

Figure 6: Azimuthal scan relative to the (110) reflection (at $2\theta = 14.2°$), obtained by the X-ray beam perpendicular to the film, for a industrial i-PP film biaxially stretched, in two-steps at draw ratios 8x5.

The (040) reflection, being intense and equatorial for along MD or TD patterns (Figure 5 B and C) and absent for along ND pattern (Figure 5A), again indicates that these planes tend to be parallel to the film and, hence, the *b* axes of the crystallites tend to be parallel to ND. However, the observed diffraction patterns are also more complex of those observed for simultaneous and balanced stretching (Figure 1). For instance the (111) reflection presents three well developed intensity peaks at latitude of nearly 40°, 50° and 80°.

Additional information can be achieved by pole figures. The pole figure of the (040) reflection (Figure 7A) shows a strong maximum in ND. Correspondingly, as already discussed for the simultaneously stretched films of the previous section, the (110) and (130) pole figures (Figure 7B and 7C) show rings at latitude 72° and 46°, respectively. These rings present more intense maxima along MD and less intense maxima along TD, which indicate the occurrence of a bimodal axial orientation, with prevailing orientation along TD.

Moreover, the pole figures of Figure 7B and 7C point out the presence of crystallites with (110) and (130) planes parallel to the surface of the sample. Crystallites presenting (110) planes parallel to the film surface, associated with a *c*-axis orientation along TD, can account for the two weak reflections at latitude of 72° along MD, which are present on the (040) pole figure (Figure 7A).

The bimodal axial orientation, associated with a major uniplanar orientation relative to the (0k0) planes and minor uniplanar orientations relative to the (110) and (130) planes, can rationalize all the diffraction peaks which occur in photographic patterns, like those shown in Figure 5B and 5C.

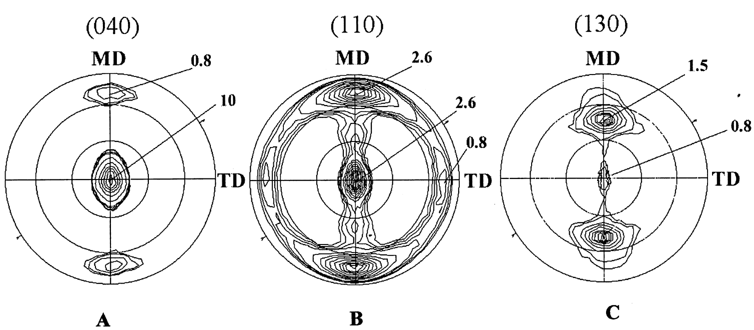

Figure 7: Pole figures relative to the main reflections (040), (110) and (130) for a industrial i-PP film biaxially stretched, in two-steps at draw ratios 8x5.

Crystalline orientation in biaxially stretched films

For semicrystalline polymers, since covalent bonding is stronger than the interchain interactions, the primary slip direction generally is along the chain axis. Hence, as a consequence of uniaxial stretching a *c*-slip mechanism generally occurs, leading to the typical axial orientation. For biaxial stretching, beside the slip direction, also a primary slip plane generally determines the final crystal texture. In fact, the primary slip plane tends to become parallel to the film surface, thus generating the so-called uniplanar and uniplanar-axial orientations [8,9]. In polymers with no specific interactions (such as hydrocarbon polymers), molecular shape and packing density play major roles in determining the slip planes.

For instance, for poly(ethylene-terephtalate) (PET) the slip plane is parallel to the phenyl rings [8,9]. For hydrocarbon polymers, for which the only interchain interactions are of van der Waals type, the primary slip plane generally is that one containing the chain axis and having the highest density. Thus, for instance, for biaxially stretched syndiotactic polystyrene (s-PS) films the highest density planes, being the (010) planes for the δ and clathrate forms, tend to become parallel to the film surface [10].

Also for the monoclinic α form of i-PP [11], it is well established that the primary slip plane is the highest density (0k0) plane, that is the plane defined by the crystallographic *a* and *c* axes [1-5]. It is worth noting that these planes are also those corresponding to minimum energy adjacent re-entry chain folding, as calculated for i-PP crystals [12,13].

Diffraction patterns relative to i-PP films prepared by a balanced and simultaneous biaxial stretching (Figures 2-4), can be rationalized by suggesting that, beside the uniplanar orientation relative to the (0k0) plane, also minor different uniplanar orientations, involving the (110) and (130) planes, would occur [3,5,7].

Beside the above described complication, the orientation of the crystalline phase of biaxially stretched films of i-PP seems to be unique as for the occurrence of a bimodal uniplanar-axial orientation.

In fact, other semicrystalline polymers, like PET and the different crystal forms of s-PS, present a simple uniplanar orientation, both for simultaneous and two-step balanced biaxial stretching. The orientation becomes uniplanar-axial, that is the primary slip planes tend to be parallel to the film plane and the chain axes tend to be aligned along a given direction, as the draw ratio along the two drawing directions becomes unbalanced.

As for i-PP, the uniplanar orientation is observed only for simultaneous biaxial stretching (Figures 2-4) while for two-step stretching *bimodal uniplanar axial* orientation is present, that is an uniplanar orientation associated with a bimodal chain axis orientation with nearly equal populations of chains nearly parallel to the two drawing directions [3]. For biaxial stretching with different draw ratios along MD and TD, i-PP again develops a bimodality into its uniplanar-axial orientation, although of course the ratio between the populations of chains nearly parallel to the two drawing directions are different (Figures 5-7).

This bimodal uniplanar-axial orientations of i-PP could be in principle simply attributed to the tendency of the chain axes to be oriented along both machine directions. However, this interpretation is not able to rationalize the different behaviour of most polymers that in similar processing conditions lead only to uniplanar or uniplanar-axial orientation, without any bimodality.

Stackings of bilayers of macromolecules of the monoclinic unit cell

In this section, a molecular rationalization of this bimodal uniplanar-axial orientation is proposed. It is based on the peculiar ability of the monoclinic structure of i-PP to give rise to defective stackings on the (0k0) face of bilayers of macromolecules.

Let us recall the molecular organization into the monoclinic α-form [11]. Bilayers of macromolecules are stacked one on the other, along the direction perpendicular to the *ac* plane (that is to the (0k0) plane), in such a way that the top layer on one bilayer and the bottom layer of the bilayer in contact are made up of helices which are enantiomorphous (Figure 8a,b). It is however worth noting that a favorable interdigitation of the methyl groups occurs also when the next bilayer brings in contact a layer of the same chirality, but only if a tilting of the chain axes of nearly 81° occurs (Figure 8a,c).

This alternative stacking of bilayers of macromolecules is the molecular origin of the well known phenomenon of lamellar branching [14-17] which frequently occurs in solution crystallization as well as for bulk crystallization of spherulites which have positive birefringence [15,16].

It is also interesting to note that the γ form of i-PP, which is unique in presenting non parallel chain axes [18], is built up by regular sequences of bilayers like those of Figure 8a,c.

The occurrence of two alternative stackings of bilayers of macromolecules has been also invocked to rationalize [17,19] the existence of a bimodal crystal orientation in some melt-spun fibers of i-PP, which contain chains of the crystalline phase oriented parallel to the flow direction, but also a significant population of chains of the crystalline phase which are oriented nearly perpendicular to the flow direction [19-21].

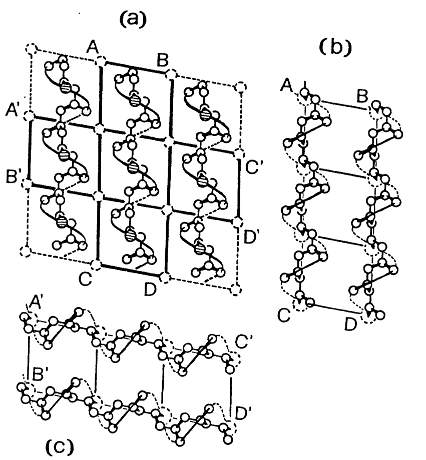

Figure 8: Possible chain axes orientations in the crystal packing of i-PP: (a) A layer of left-handed helices parallel to the (0k0) face of the monoclinic α-form. The methyl groups which project out of the mean plane toward the reader are shaded, while broken line circles indicate the available space for the methyl groups of the next layer. (b) Next coming layer built up with helices of opposite chirality (right-handed): a parallel arrangement of the chain axes allows for a favorable packing. (c) Next coming layer built up with helices of the same chirality (left-handed): a tilting of the chain axes of 81° is required for a favorable interdigitation of methyl groups to occur.

We suggest that the occurrence of two alternative stackings of bilayers of macromolecules can also constitute the molecular origin of the peculiar *bimodal uniplanar axial orientation*, which characterize two-step biaxially stretched i-PP films.

Conclusions

The X-ray diffraction patterns of isotactic polypropylene biaxially stretched films can be interpreted by assuming that beside the uniplanar orientation relative to the (0k0) plane minor uniplanar orientations relative to (110) and (130) planes can contribute to the crystal texture.

Moeover, the X-ray diffraction patterns of i-PP films, which have been biaxially stretched in two steps, show the presence of *bimodal uniplanar axial* orientation, that is an uniplanar orientation associated with a bimodal chain axis orientation with populations of chains nearly parallel to the two drawing directions.

This peculiar bimodality typical of the uniplanar-axial orientation, which is present in two-step biaxially stretched i-PP films, has been rationalized in terms of the two alternative stackings on the (0k0) face of bilayers of macromolecules of the monoclinic unit cell.

It is also worth noting that the presence of the described bimodality of the orientation in i-PP biaxially stretched films is beneficial to the balancing of the mechanical properties along different directions in the film plane. This can perhaps help to understand why industrial plants relative to other polymers like PET are conducted with nearly identical draw ratios in machine and transverse directions, while for i-PP large differences between the two draw ratios are allowed.

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