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Single Crystal Structure of Form I Syndiotactic Poly(butene-1)

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ABSTRACT: The structures of single crystals of syndiotactic poly(butene-1) in form I, produced by thin-film growth, are studied by transmission electron microscopy and electron diffraction. Bright-field electron microscopy observation shows that the single crystal exhibits a regular rectangular shape with the long axis along its crystallographic *b*-axis. Electron diffraction results indicate an isochiral *C*-centered packing of 2-fold helical chains in an orthorhombic unit cell corresponding to the $C222_1$ space group, according to the model proposed in the literature. The differences with the polymorphic behavior of syndiotactic polypropylene concerning the formation and the stability of the isochiral mode of packing are outlined.

Introduction

While isotactic poly(butene-1) (iPB) was successfully synthesized and extensively studied in the mid-1950s, the synthesis of syndiotactic poly(butene-1) (sPB) was just achieved by the recent discovery of the homogeneous metallocene catalytic systems.[1]

The polymorphic behavior of sPB has been recently described.[2] Two different polymorphic forms, designated as forms I and II, have been found so far.[2−5] sPB crystallizes very slowly, and amorphous samples are generally obtained by cooling the melt to room temperature or precipitation and casting from the polymer solution.[2] However, crystallization in the form I occurs if amorphous samples are maintained at room temperature for several days.[2]

Form I is characterized by chains in the $(T_2G_2)_2$ helical conformation with line repetition symmetry s(2/1)2 and identity period $c = 0.773$ nm.[2−4] The chains are packed in an orthorhombic unit cell with $a = 1.681$ nm, $b = 0.606$ nm, and $c = 0.773$ nm.[3] The space group proposed for the limit-ordered structure is $C222_1$,[3] corresponding to a *C*-centered packing of helical chains having the same chirality.

Form II, which is observed in the oriented sPB fibers drawn at high draw ratios, is characterized by chains in helical conformation of the kind $\approx(T_2G_2)_n$ with s(5/3)2 symmetry and identity period $c = 2.0$ nm.[2,5] The chains are packed in a monoclinic unit cell with parameters $a = 1.545$ nm, $b = 1.436$ nm, $c = 2.0$ nm, and $\gamma = 116°$,[5] according to the space group $P2_1/a$.[5]

It is worth noting that the crystal structure of sPB in the form I is very similar to that of syndiotactic polypropylene (sPP) in the stable helical forms. Systematic structural studies have indicated that sPP presents a very complex polymorphic behavior.[6−14] Two different crystalline forms with chains in the $(T_2G_2)_2$ helical conformation, characterized by a different mode of packing in similar orthorhombic unit cells, have been described.[6,11] The most stable form I of sPP is characterized by an antichiral packing of 2-fold helical chains with a regular alternation of right- and left-handed helices along the axes of the unit cell.[6−9,12,13] The metastable form II of sPP is characterized by a *C*-centered packing of 2-fold helical chains having the same chirality, according to the space group $C222_1$.[10,11,14] The mode of packing in the form II of sPP is therefore similar to that of form I of sPB.

A remarkable difference between form I of sPB and form II of sPP is related to their stability. In the case of sPP the most stable mode of packing is the antichiral one, the isochiral form II of sPP being a metastable modification, which can be obtained only in oriented fibers of sPP.[10,11,14] The antichiral form I of sPP crystallizes in the most common conditions of crystallization, in single crystals and powder samples of sPP,[6−9,11,13] and the isochiral form II has never been observed in single crystals of sPP. In the case of sPB it has been reported that the isochiral mode of packing is stable since the isochiral form I is obtained in powder and fiber samples of sPB.[2,3] A detailed TEM study on the single-crystal structure of sPB can help us to check the stability of the proposed isochiral form I. However, single crystals of sPB and the corresponding electron diffraction pattern have not been reported yet in the literature.

In this paper single crystals of sPB have been obtained for the first time. Bright-field electron microscopy and electron diffraction results are presented in order to check the validity of the proposed isochiral packing model of the form I.

Experimental Section

The sPB sample was supplied by Montell Italy. The sample is highly syndiotactic, the amount of *rrrr* pentads being equal to 93%. The melting temperature is 50 °C.

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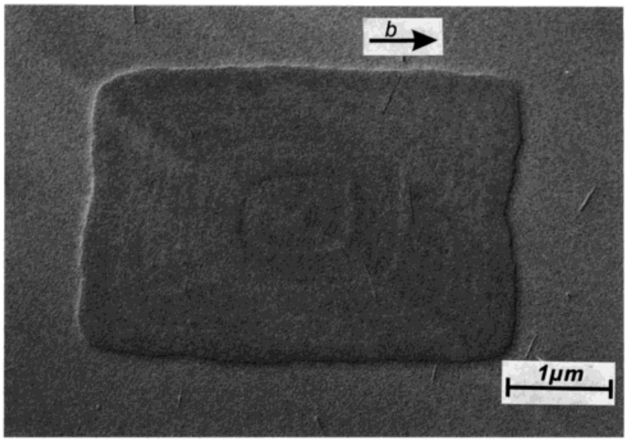

Figure 1. Bright-field electron microscopy image of the single crystal of form I of sPB, shadowed with platinum. The crystallographic *b* axis is along the long dimension of the crystal.

To grow sPB single crystals, thin films of sPB were at first prepared by casting 0.1 wt % xylene solution on carbon-coated copper grids at room temperature. After the evaporation of the solvent, amorphous ultrathin sPB films were obtained. The amorphous thin sPB films were heat-treated at 60 °C for 15 min and then cooled to 30 °C where crystallization occurs after several weeks. For transmission electron microscopy observations, a Philips CM200 TEM operated at 200 kV was used in this study. While bright-field electron micrographs were obtained with platinum shadowed samples, some of the selected area electron diffraction work was done on unshadowed specimens.

Results and Discussion

A bright-field electron micrograph of the sPB single crystal, which has been shadowed with platinum, is reported in Figure 1. It is apparent that the sPB single crystal exhibits a regular rectangular shape with its long axis along the crystallographic *b*-axis, as revealed by the corresponding electron diffraction pattern.

Figure 2a shows the electron diffraction pattern of the obtained sPB single crystals, in which sharp electron reflection spots can be observed. A sketch of the electron diffraction pattern with the indexing of the observed reflections is reported in Figure 2b. It is apparent that all the diffraction spots correspond to equatorial $hk0$ reflections, implying a flat-on structure of the crystal with the molecular chains oriented parallel to the lamellar thickness direction. (The crystals have not been tilted in the electron microscope.) All the reflections are accounted for by the orthorhombic unit cell with axes $a = 1.681$ nm, $b = 0.606$ nm, and $c = 0.773$ nm proposed by De Rosa et al.[3] Moreover, it is noteworthy that only the reflections with $h + k = 2n$ appear on the diffraction pattern. The systematic absence of $h + k = 2n + 1$ indicates a *C*-centered packing of isochiral chains according to the space group $C222_1$. In particular, the presence of the strong 110 reflection and the absence of the 010 reflection is a clear evidence of the centering of the *ab* face of the unit cell. Figure 3 shows a sketch of this packing projected along the chain axis. This result is in agreement with the model of packing proposed by De Rosa et al.[3]

According to the features of the chain packing of Figure 3, a single crystal shape bounded by the densely packed {110} prism faces is expected. Namely, a regular single crystal as sketched in Figure 4 (thick lines) is a more reasonable expected shape of the sPB single crystals. The reason for the formation of the rectangular shaped sPB single crystals is still not clear.

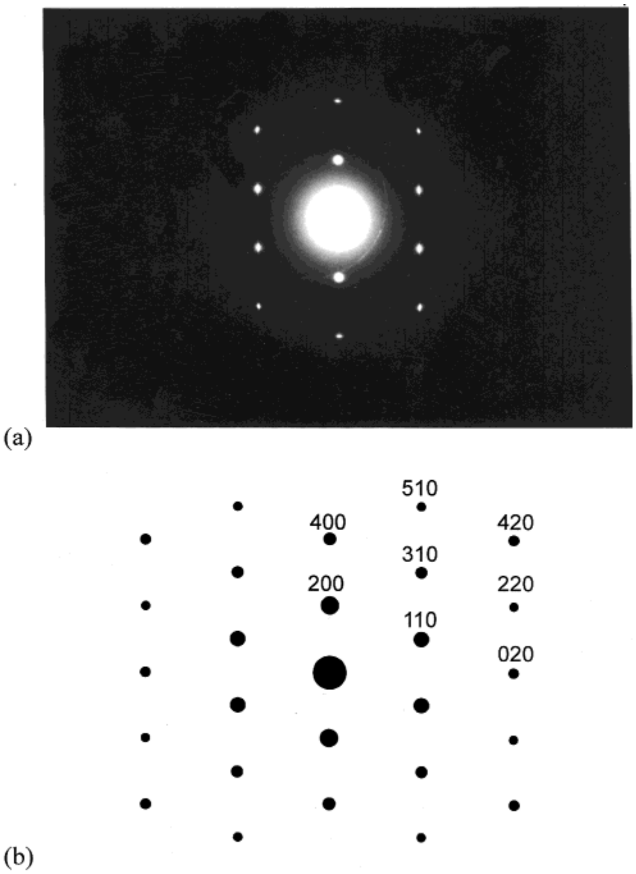

Figure 2. (a) Selected area electron diffraction pattern of the single crystal of form I of sPB and (b) sketch of the electron diffraction pattern with indexing of the observed reflections.

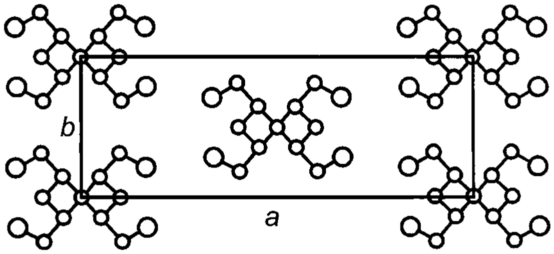

Figure 3. Model of the isochiral *C*-centered packing of the 2-fold helical chains of sPB in the orthorhombic unit cell according to the space group $C222_1$.[3]

Electron microscopy observations have therefore confirmed that for sPB the isochiral mode of packing of 2-fold helical chains is stable and occurs not only in powder and fiber samples but also in single crystals. We recall that, as already discussed in the Introduction, in the case of sPP the isochiral form II, which presents a structure similar to that of form I of sPB, has been observed only in oriented fibers of sPP.[10,11,14] In particular, for high stereoregular sPP samples, form II can be obtained only from stretched fibers initially in the trans planar form III of sPP when the tension is removed.[14,15] A crystal-to-crystal transition from the trans planar form III to the isochiral helical form II occurs in the stretched fibers of sPP upon the release of the tension.[14,15] This transition from an all-trans

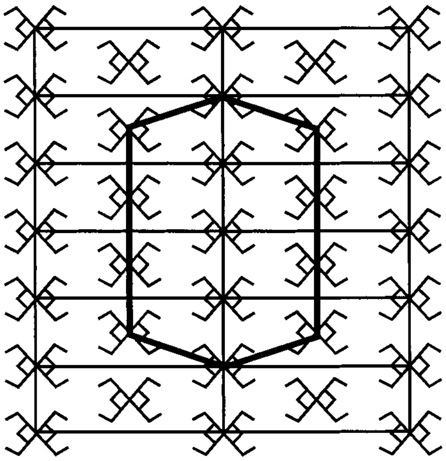

Figure 4. Sketch of the expected shape of the sPB single crystals bounded by the densely packed {110} prism faces (thick lines).

planar conformation into the helical conformation is a cooperative process, imposed by steric constraints, which involves the formation of helical chains having the same chirality.[16] This cooperativity leads to the formation of an isochiral structure (form II of sPP) even though the fully antichiral structure (form I of sPP) is more stable.[16] It has been recently shown that in sPP, when the formation of the trans planar conformation is prevented, like for instance in copolymers of sPP with small amounts of 1-butene, the isochiral form II of sPP does not form any more,[17] confirming the need of the cooperative process in sPP for the formation of the isochiral structure.

Since no polymorphic form with chains in trans planar conformation has been observed for sPB, the formation of a stable isochiral structure in sPB is related to different mechanisms compared to sPP. The key feature is probably the conformation assumed by the bulky ethyl lateral groups in the 2-fold helical chain of sPB. An unusual “bouble gauche” conformation of the lateral groups, for which the methyl carbons of the ethyl groups are in gauche arrangement to both neighboring methylene carbons, has been proposed on the basis of conformational energy calculations.[2] This conformational assignment has been confirmed by the resolution of the crystal structure of form I[3] and by the analysis of the solid-state ^{13}C NMR CPMAS spectra of form I of sPB.[4] The positioning of the methyl carbons in the sPB chains makes the isochiral *C*-centered packing energetically favored because a hypothetical antichiral structure with right- and left-handed helices alternating along the *a* and *b* axes would present too short distances between the methyl carbons of neighboring chains along the *a* axis.

Conclusions

Single crystals of sPB in the form I were produced by thin-film growth and studied by transmission electron microscopy and electron diffraction. Bright-field electron microscopy observation shows that the sPB single crystal exhibits a regular rectangular shape with its long axis along the crystallographic *b*-axis. The electron diffraction pattern clearly indicates an isochiral *C*-centered packing of the 2-fold helical chains of s-PB in the orthorhombic unit cell according to the space group $C222_1$. These results confirm that the isochiral packing of helical chains is the stable mode of packing in sPB.

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