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Crystal Structure of the Trigonal Form of Isotactic Polypropylene as an Example of Density-Driven Polymer Structure

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When Natta and Corradini in the 1950s resolved the crystal structure of all the isotactic polymers produced soon after the discovery of Ziegler−Natta catalysts, the basic principles of *Polymer Crystallography* were set.[1] Since no strong electrostatic interactions are present, polymer crystals follow the *Principle of Close Packing*: *macromolecules tend to achieve the closest distance between nonbonded neighboring atoms; this distance is, however, never lower than the sum of their van der Waals radii*. Moreover, since the crystal structure of a molecule must correspond to one of the minima of the free energy surface, the close packing principle implies that the *free energy* minima are close to the minima of *internal* energy and, hence, to the minima of the specific volume surface.[1]

Entropy also determines the mode of packing of molecules. *A molecule in a crystal tends to maintain part of its symmetry elements, provided that this does not cause a serious loss of density*. In a more symmetric position, a molecule has a greater freedom of vibration, that is, the structure corresponds to a wider energy minimum.[1]

On the basis of these principles, it was established and experimentally found that isotactic poly(α-olefins) synthesized with Ziegler−Natta catalysts, having macromolecular chains in 3-fold helical conformation, crystallize in trigonal lattices, where the local 3-fold helical axes of the single molecule coincide with the crystallographic 3-fold axes. This is, for instance, the case of isotactic polystyrene (iPS),[2] polybutene (iPB),[3] poly(*o*-fluorostyrene),[4] and 1,2-poly(1,3-butadiene).[5] The crystal structure of form I of iPB, a prototype of this class of polymer crystals, is shown in Figure 1A. Chains in 3/1 helical conformation are packed in a trigonal unit cell with axes $a = b = 17.7$ Å and $c = 6.5$ Å, according to the space group $R3c$ or $R\bar{3}c$.[3] The unit cell houses six chains, each 3/1 right-handed helical chain is surrounded by three left-handed helical chains. The density of crystals is high, $\rho_c = 0.95$ g/cm^3, due to the close packing of helices bearing bulky lateral groups.

It is also well-known that the famous crystal structure of the stable form of isotactic polypropylene (iPP), found by Natta and Corradini,[6] does not comply with the possible rule of maintaining the 3-fold helical symmetry of the chains in the crystal lattice. In fact, chains of iPP assume the stable 3/1 helical conformation, but they are not packed in trigonal unit cells, maintaining the crystallographic 3-fold symmetry, because this would produce a crystal lattice with very low density due to the too small side groups, compared with the ethyl or phenyl groups in iPB or iPS, respectively. The 3-fold helical chains are instead packed in a monoclinic unit cell, according to the space group $C2/c$ or $P2_1/c$,[6,7] so that the local symmetry of the chain conformation is lost in the lattice, allowing for a denser packing (Figure 1B, $\rho_c = 0.936$ g/cm^3).[6]

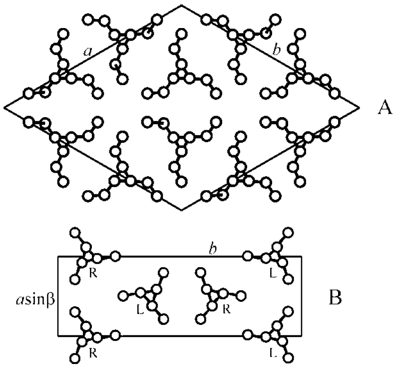

Figure 1. Structures of form I of iPB (A)[3] and the α form of iPP (B).[6]

In this communication, we show that, if iPP macromolecules are modified, for instance, by incorporating bulky hexene comonomeric units, such as to be included in the crystals of α form, when the amount of included comonomer achieves a particular value, the sample crystallizes in a new form characterized by a trigonal unit cell, so that the 3-fold helical symmetry of the chains may be maintained in the lattice. This occurs because the crystal density becomes as high as that of crystals of iPB, due to the inclusion of the bulky hexene comonomer.

Random propylene−hexene copolymers (iPPHe) with concentration of hexene variable in the range of 2−26 mol % have been prepared using a metallocene catalyst. The X-ray powder diffraction profiles of some samples of iPPHe copolymers are reported in Figure 2 and are compared with those of samples of iPP and iPB prepared with the same catalyst. The samples crystallize in the α form of iPP up to a hexene concentration of nearly 10% (Figure 2b,c). The Bragg distances of 110 and 040 reflections slightly increase with increasing hexene concentration, indicating increase of a and b axes of unit cell and inclusion of hexene units in the crystals of α form.

At 9 mol % of hexene, an additional reflection at $2\theta = 10.2°$ appears, and for hexene contents higher than 18 mol %, the X-ray diffraction profile totally changes, the main reflections being at $2\theta = 10.2$, 17.5, and 20.6° (Figure 2d−e). This indicates that these copolymer samples crystallize in a new crystalline form.

The X-ray fiber diffraction pattern of fibers of the sample iPPHe4 shows the same reflections at $2\theta = 10.2$, 17.5, and 20.3° on the equator and a strong reflection at $2\theta = 20.6°$ on the first layer line. From the fiber pattern, a chain axis periodicity $c = 6.5$ Å has been evaluated. This indicates that in this new crystalline form the iPP chains keep the 3/1 helical conformation.

The three reflections at $2\theta = 10.2$, 17.5, and 20.6° observed in the powder and fiber diffraction patterns are accounted for by a

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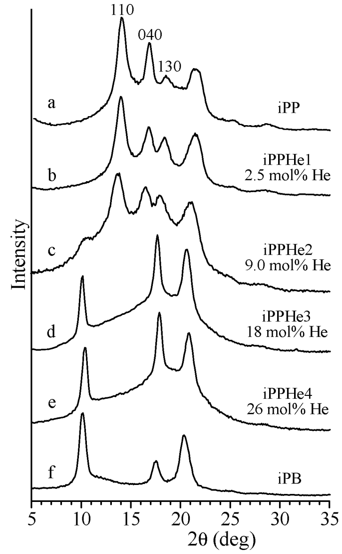

Figure 2. X-ray powder diffraction profiles of iPPHe copolymer samples with the indicated concentration of hexene units (He) in comparison with those of the α form of iPP (a) and form I of iPB (f).

hexagonal unit cell with axes $a = b = 17.5$ Å and $c = 6.5$ Å. Assuming that in the sample iPPHe4 with 26 mol % of hexene, the hexene units are included in the crystals, the theoretical density of crystals of the new form is $\rho_{cr} = 0.91$ g/cm^3 for six chains of iPP in 3/1 helical conformation in the unit cell. This is in agreement with the experimental density $\rho = 0.86$ g/cm^3 of the sample iPPHe4 having a crystallinity of 17% (Figure 2e) and a density of the crystalline phase $\rho_{cr} = 0.90$ g/cm^3 (the density of amorphous iPP being $\rho_a = 0.854$ g/cm^3). It is worth noting that similar diffraction data have been reported in a recent paper, but a different structure has been proposed.[8]

The four most intense reflections at $2\theta = 10.2$, 17.5, 20.3, and 20.6° are indexed with Miller indices 110, 300, 220, and 211 of the hexagonal unit cell. This suggests that the 3/1 helical chains are packed in a trigonal lattice with a rhombohedral symmetry according to the space group $R3c$, as in the case of iPB (Figure 1A)[3] or iPS.[2] The X-ray powder and fiber diffraction patterns of the new form of iPP are, indeed, very similar to that of form I of iPB (Figure 2f).[3] The similar structures of form I of iPB and of the new form of iPP have been confirmed by resorting to the method of direct reconstruction of electronic density distribution by using only equatorial reflections (see Supporting Information).

A model of the crystal structure of the new trigonal form, with disorder in the positioning of the lateral groups, according to the space group $R3c$, is shown in Figure 3. The 3/1 helical symmetry of the chains is maintained in the lattice, and the chain axes coincide with the crystallographic 3-fold axes. The orientation of the chains around the 3-fold axes has been found by packing energy calculations and from the best agreement between calculated and experimental diffraction patterns. A better agreement has been obtained by introducing disorder in the up/down position of the chains (see Supporting Information). This means that in each site of the lattice up or down chains, having the same chirality, can be found with the same probability. A limit-disordered model, containing statistical up/down disorder, can be described by the statistical space group $R\bar{3}c$. Disorder in the orientation of chains around the 3-fold axes and in the conformation of the lateral groups, along with the constitutional disorder, may be also present.

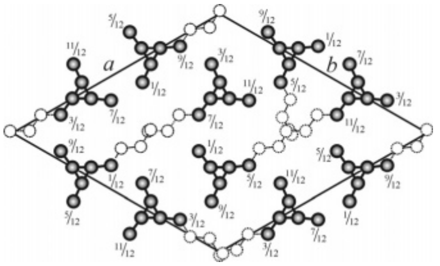

Figure 3. Model of the crystal structure of the trigonal form of iPP in the space groups $R3c$ found in propene–hexene copolymers. The atoms of propyl side groups of the hexene comonomeric units, randomly distributed along each iPP chain, are shown as thin dotted lines.

It must be mentioned that, parallel to our analysis, Bernard Lotz et al.[9] have reevaluated the original diffraction data of ref 8 and reached independently similar conclusions.

The inclusion of hexene comonomeric units in the crystal lattice produces an increase of mass, and crystals in the trigonal form achieve a density as high as that of form I of iPB. In conclusion, the suitable increase of density allows crystallization of 3-fold helical chains of iPP in a new form characterized by a trigonal unit cell, where the helical symmetry of the chains is maintained in the crystal lattice, as predicted by principles of polymer crystallography. This form does not crystallize and has never been observed so far for the iPP homopolymer because, in the absence of bulky side groups, it would have too low density. Almost 50 years after the resolution of the crystal structure of the α form of iPP[6] and the enunciation of general principles of polymer crystallography,[1] we have shown that iPP is no longer an exception, but the structure of propene–hexene copolymers represents the fulfillment of these principles and indicates that the packing of polymer molecules is mainly driven by density. The principle of density (entropy)-driven phase formation suggests that copolymers of propene with other olefins may crystallize in the same trigonal form when the crystal density and the average composition of copolymer approach those of iPB, provided that the distribution of the comonomer is random. We can predict that the crystallization of the trigonal form occurs at higher comonomer concentrations in the case of a smaller comonomer, such as, for instance, pentene.

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Supporting Information Available: Experimental part, X-ray diffraction calculation, and Fourier synthesis. This material is available free of charge via the Internet at http://pubs.acs.org.

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