

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231698377>

A Structure of Copolymers of Propene and Hexene Isomorphous to Isotactic Poly(1-butene) Form I

ARTICLE *in* MACROMOLECULES · JULY 2006

Impact Factor: 5.8 · DOI: 10.1021/ma052314i

CITATIONS

43

READS

27

8 AUTHORS, INCLUDING:



Giovanni Carlo Alfonso

Università degli Studi di Genova

101 PUBLICATIONS 1,675 CITATIONS

SEE PROFILE



Ewa Piorkowska

Centre of Molecular and Macromolecular Stu...

95 PUBLICATIONS 2,139 CITATIONS

SEE PROFILE

A Structure of Copolymers of Propene and Hexene Isomorphous to Isotactic Poly(1-butene) Form I

B. Lotz,^{*,†} J. Ruan,[†] A. Thierry,[†] G. C. Alfonso,[‡] A. Hiltner,[§] E. Baer,[§] E. Piorkowska,^{||} and A. Galeski^{*,||}

Institut Charles Sadron (CNRS-ULP), 6 rue Boussingault, 67083 Strasbourg, France, Department of Chemistry and Industrial Chemistry, University of Genova, Via Dodecaneso, 31, 16146 Genova, Italy, Department of Macromolecular Science and Center for Applied Polymer Research, Case Western University, Cleveland, Ohio 44106-7202, and Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienciewicza 112, 90363 Łódź, Poland

Received October 27, 2005; Revised Manuscript Received June 21, 2006

ABSTRACT: Isotactic copolymers of 1-propene and 1-hexene that contain over 10% and up to about 25% of hexene units in the chain have been shown to crystallize in an unusual crystal modification that differs significantly from the well-known structures of isotactic polypropylene (α , β , and γ phases) or of isotactic poly(1-hexene) (*Macromolecules* **2005**, 38, 1232). The experimental data obtained by Poon et al. are reinterpreted and analyzed. The new crystal form has a trigonal unit-cell with parameters $a = b = 1.717$ nm, $c = 0.65$ nm, very similar to form I of isotactic poly(1-butene) (iPBu) (trigonal cell with parameters $a = b = 1.770$ nm, $c = 0.65$ nm). The chain conformation is the 3-fold helix of isotactic polypropylene. The side-chain material in the copolymer with the highest hexene content (25%) is about 12% less than in iPBu form I (all ethyl units). These copolymers of propene and hexene adopt a crystal structure isomorphous to that of a third polyolefin (polybutene) that, in terms of overall composition, is close to the average of the two “parent” olefins.

Introduction

In a recent investigation of isotactic random copolymers of propene and hexene (P/H copolymers), a crystal structure that neither resembles those of the well-known α , β , and γ phases of isotactic polypropylene (iPP) nor that of isotactic poly(1-hexene) has been uncovered.¹ It is observed for hexene contents higher than 10% but lower than about 25% and is accompanied by significant modifications of the crystallization process. Whereas incorporation of less than about 10% hexene units in the chain significantly slows down the crystallization rate and reduces the spherulite size, an increase in the crystallization kinetics and concomitant improvement of crystalline morphology (lamellar size, etc.) was observed for higher hexene contents. These observations, together with peculiarities of the melting behavior, suggested that “if the hexene content was less than 10%, comonomer was excluded from the crystal; however, if the comonomer was higher ($>10\%$), the crystallization habit changed so as to accommodate hexene units in the crystal lattice”. The different structure that contains these hexene units was characterized by its powder and fiber X-ray diffraction patterns, mostly on a sample with 22.4% hexene units. A fit with the diffraction data was obtained for a large orthorhombic unit-cell with eight chains. The detailed structural analysis was not, however, completed in the course of this work.

Complementary data and an analysis of this crystal modification are presented in the present article. A reevaluation of the diffraction data indicates that the unit-cell can be reduced to a

smaller trigonal cell that contains six 3-fold helices: the new structure uncovered for this propene-hexene copolymer is actually very similar to the form I of isotactic poly(1-butene).

It must be mentioned that, just prior to submission of this paper, we found out that Claudio De Rosa et al., working on similar samples but of different origin, reached independently similar conclusions regarding this crystal structure.²

Experimental Data and Analysis

The fiber pattern of the new crystal modification is reproduced in Figure 1a. In ref 1, it was obtained for a sample that contained 22.4% hexene units. The improved pattern shown in Figure 1a was obtained in the meantime with a sample that contains 25.1% hexene units (samples in this upper composition range display most prominently this new phase and will be used as a reference in the following). As summarized in Table 1, this 25.1% sample fiber pattern displays further reflections at different azimuthal angles (possibly lost on reproduction). The unit-cell dimensions are identical to those obtained for the 22.4% sample.

The 22.4% sample fiber patterns helped Poon et al. to remove an ambiguity in the indexing of the powder pattern. Combining the information of the powder and fiber patterns, an orthorhombic unit-cell with parameters $a = 1.986$ nm, $b = 1.717$ nm, $c = 0.6458$ nm was considered as most probable. In particular, the position of the nonequatorial reflections is consistent with such an indexing.¹

Solving the structure of such a big unit-cell is not an easy task. Indeed, when taking into account the density of the phase, the unit-cell would contain 24 monomers (≈ 18 propene and 6 hexene units), which would imply for example either eight 3-fold helices or six helices with four residues per turn.

Fortunately, the diffraction data can be reevaluated on the basis of a smaller, more tractable unit-cell. An indication that an alternative cell geometry may be considered is provided by the $\sqrt{3}/2$ ratio between the a and b parameters of the

* Corresponding authors. E-mail: lotz@ics.u-strasbg.fr (B.L.); andgal@bilbo.cbmm.lodz.pl (A.G.).

[†] Institut Charles Sadron (CNRS-ULP).

[‡] Department of Chemistry and Industrial Chemistry, University of Genova.

[§] Department of Macromolecular Science and Center for Applied Polymer Research, Case Western University.

^{||} Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences.

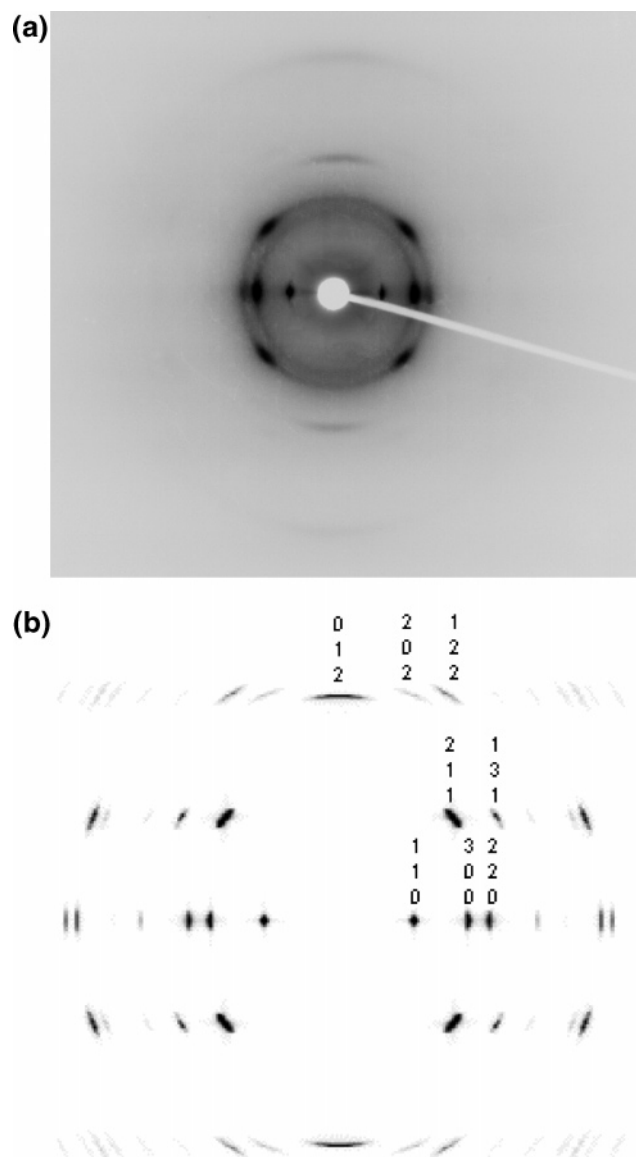


Figure 1. (a) Improved fiber pattern of the crystal modification, obtained with a P/H copolymer with 25.1% hexene units. Its essential features are similar to those of the pattern published in ref 1 (sample with 22.4% hexene units), but it displays additional reflections (probably lost in reproduction, but cf. list and indexing in Table 1). (b) Simulated fiber diffraction pattern of form I of isotactic poly(1-butene) generated with the Cerius² modeling software, using the coordinates given by Natta et al.⁴

orthorhombic cell; this ratio suggests that some form of hexagonal or trigonal cell geometry is involved. Indeed, the

diffraction data can be interpreted equally well on the basis of a trigonal unit-cell with parameters $a = b = 1.717$ nm. Determination of the c axis parameter rests mostly on the new near-meridional reflection measured on the third layer line and indexed as 113 in the trigonal unit-cell because the c axis parameter features most prominently in its spacing. It yields a c axis parameter of 0.65 nm, which is a standard repeat distance for helical polyolefins, with either 3- or 4-fold helical symmetry. Indexing of all the reflections on the basis of a trigonal unit-cell with parameters $a = b = 1.717$ nm and $c = 0.65$ nm is presented in the calculated diffraction pattern shown in Figure 1b, which uses a structural model developed now.

The unit-cell derived above provides an immediate clue about the underlying crystal structure of this P/H copolymer. It corresponds very nearly to one of the three crystalline forms of the next member of the polyolefin family, namely isotactic poly(1-butene) (iPBu).³ The form I of iPBu has a trigonal unit-cell with parameters $a = b = 1.770$ nm, $c = 0.65$ nm.⁴ It houses six 3-fold helices in which each helix of a given hand is surrounded by three helices of opposite hand (cf. Figure 2d).⁵ The space group for this crystal modification of iPBu1 is $R3c$ (if all helices are isocline) or, more probably, $R\bar{3}c$ (if anticline helices can be found statistically at any chain site). The calculated diffraction pattern of this crystal modification of iPBu is illustrated in Figure 1b. Comparison with Figure 1a suggests that the crystal modification of the P/H copolymer is similar to that of iPBu form I in its major features if not, of course, in its details. The exact space group cannot be determined from the systematic absences of the diffraction pattern. Indeed, the extinction rules for the two space groups are very similar, and the reflections present in the experimental pattern are not discriminative. It is reasonable to consider the statistical $R\bar{3}c$ space group as the most likely candidate, in line with earlier analyses of the iPBu1 crystal structure.

Further details of this structure might conceivably be accessible by conformational and packing energy analysis. Modeling of a unit-cell with statistical substitution of side chains is, however, a complex procedure. By definition, the outer parts of the flexible hexene side chains take conformations that depend on the local environment, namely the presence of hexene units in the next strands of the same helix or in neighbor helices. These side-chain conformations cannot be determined by packing energy analysis because "fractional" presence of atoms is not manageable by packing analysis. Extended hexene side chains (i.e., all-trans conformations) seem to be unlikely because they would stretch and impinge in the nearby helices. It appears reasonable, therefore, to assume the existence of gauche bonds in the hexene side chains. A few hints about the side-chain conformations are actually provided by a more detailed analysis

Table 1. Summary of Diffraction Data for the P/H 22.4 and P/H 25.1 Copolymers^a

	observed D spacing (nm), (obs rel intensities (%))	calculated D spacing (nm), (calcd rel intensities, %)	indices	P/H 25.1, (P/H 22.4)	
				2θ (deg)	azimuthal angle (deg)
equator	0.859 (70)	0.858 (9)	110	10.3 (10.3)	0
	0.503 (100)	0.496 (100)	300	17.65 (17.65)	0
	0.431 (50)	0.429 (38)	220	20.6 (20.6)	0
first layer	0.429 (8)	0.425 (62)	211	20.8 (20.7)	42 (42)
	0.255 (weak, ≈ 0)	0.247 (15)	511	35.2 (n.o.)	24 (n.o.)
second layer	0.313 (9)	0.317 (7)	012	28.1 (28.5)	86.5 (86.5)
	0.283 (2.3)	0.281 (4)	122	31.8 (31.6)	64 (62)
third layer	0.211 (8.2)	0.210 (49)	113	42.8 (n.o.)	86.5 (n.o.)

^a Observed D spacings and observed relative intensities measured on the fiber pattern (flat plate) of sample P/H 25.1%. Calculated spacings are for a trigonal unit-cell with parameters $a = b = 1.717$ nm, $c = 0.65$ nm. The space group is assumed to be $R3c$ (statistical presence of up- and down-pointing helices at each site). The calculated relative intensities are for a fiber pattern (same flat plate geometry) of model (b) in Figure 2. 2θ and azimuthal setting values for the P/H 25.1 sample and in parentheses for the P/H 22.4 sample (n.o.: not observed).

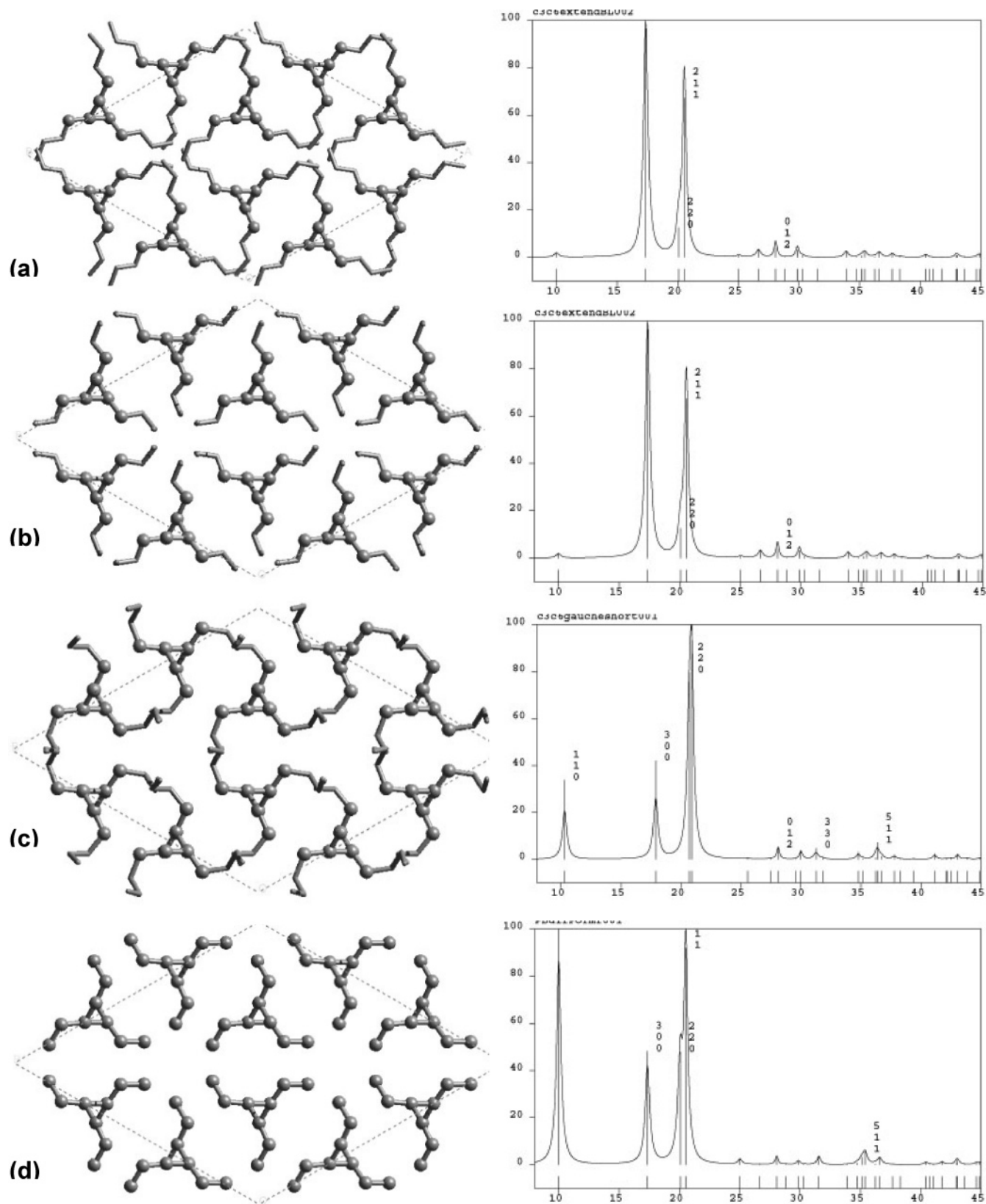


Figure 2. Comparison of expected powder diffraction patterns for a 25% P/H copolymer with different conformations of the hexene side chains (a, b, c) and iPBu1 (d). The outer carbons of the side chains have 0.25 occupancy factors (shown as cylinders). The backbone and alpha carbons of the side chains are shared by P and H units, and thus have a 1.0 occupancy factor. Note that the drawings assume, for clarity, $R3c$ cell symmetry, i.e., show a single helix at any chain site location, but the patterns correspond to a more realistic $R3c$ cell symmetry with statistical up–down substitution. In the patterns, note the variation of the 110/300 intensity ratio (peaks at $\approx 10^\circ$ and $\approx 18^\circ$, respectively) resulting from the introduction of hexene units, and also as functions of the hexene side-chain conformation. The side-chain conformations are defined by the following torsional angles (in deg), in the sequence C(H) (main chain)–C α , C α –C β , C β –C γ : model (a): $-166.6, 176.5, -179.8$; model (b): $-166.6, 176.5, -59.8$; model (c): $155.3, -73.2, -77.3$. In iPBu1 form I (model (d)), the C(H) (main chain)–C α torsional angle is 175.5° .

of the relative intensities of some critical reflections in the copolymers' X-ray diffraction patterns, as examined now.

Figure 2 summarizes the essential ingredients of the reasoning. It displays the iPBu1 cell as well as the propene–hexene chain in the iPBu1 form I packing mode. The carbon atoms with an occupancy factor of 1 are shown as balls, and the carbon atoms with an occupancy factor of 0.25 are shown as cylinders (thus corresponding to the pattern expected for the copolymer with 25% hexene units). Different side-chain conformations for the hexene side chains are modeled, that either “stretch out” away from the main-chain helix, or are packed closer to this helix by introducing gauche bonds at various locations of this side chain. The side-chain conformations are first minimized for a single chain (i.e., in the absence of the crystal environment, although it may be difficult to reach energy minimization convergence criteria in this process) and are introduced in the unit-cell without further conformational minimization or adjustment. The corresponding calculated powder diffraction patterns are represented together with the models. They display a striking variation of the relative intensities of the 110 and 300 reflections (at $\approx 10^\circ$ and $\approx 18^\circ$, respectively). In essence, the 110 reflection becomes weaker and weaker as the side chains are more extended, virtually vanishing for the model with the most stretched out side chains. This variation is easily understandable when examining the corresponding model. Indeed, stretched out chains even out the electron density distribution along the (110) planes, and thus reduce the intensity of this reflection. On the contrary, the “pure” iPBu1 model concentrates the carbon atoms near the helix axis, which results in a stronger 110 reflection.

The relative intensity of the $hk0$ reflections and, in particular, the ratio of 110 and 300 intensities, becomes therefore an indicator of the side-chain conformation. This ratio has been determined on powder patterns of iPBu1 form I and different P/H copolymers (the next peak is the overlapping of 220 and 211, which cannot be deconvoluted in powder patterns and, therefore, is not taken into account in this analysis). The following values were obtained (peak heights expressed in arbitrary units (a.u.), pattern of iPBu1 as published in Figure 3 of the paper by Gohil et al.⁶): Isotactic PBu1 form I: 110, 17.98 a.u.; 300, 8.53 a.u.; ratio 110/300: 2.1. 13.9 P/H copolymer: 110, 9.04 a.u.; 300, 8.26 a.u.; ratio 110/300: 1.09. 22.4 P/H copolymer: 110, 12.19 a.u.; 300, 17.83 a.u.; ratio 110/300: 0.68. 25.2 P/H copolymer: 110, 33.11 a.u.; 300, 36.19 a.u.; ratio 110/300: 0.91.

The important drop of the ratio for the 13.9 P/H copolymer compared to iPBu demonstrates a significant spread of electron density over the (110) planes for these relatively low hexene concentrations. As expected also, presence of more and more side-chain material results in a decrease of the 110/300 intensity ratio. Although the 110/300 ratio determined for the 25.2 copolymer does not follow the trend set by the 13.9 and 22.4 copolymers, the ratios for both the 22.4 and the 25.2 copolymers are significantly higher than would be expected if the side chains were extended (compare with Figure 2a and b). On the basis of diffraction evidence, therefore, it appears highly likely that for the higher hexene contents, the side chains “fold” more or less along the helix axis rather than stretch out as they would in, say, the crystal structure of the hexene homopolymers. The variation of the ratio 110/300 suggests that this “folding” probably results from introduction of gauche bonds near the main-chain atoms. In model (c) of Figure 2, the gauche bond is introduced at the $C\alpha-C\beta$ bond of the side chain, i.e., the first “extra” atom of the hexene unit has the same location as the last side-chain carbon in the iPBu1 structure. However, it

involves two “unnatural” successive gauche bonds in the outer part of the side chains (cf. legend to Figure 2). At the same time, this conformation generates only a single short van der Waals contact between main and side chain (a perfectly admissible H–H distance of 0.208 nm). This model reproduces reasonably well the experimental relative intensity of 110 and 300 reflections, but the 220 intensity appears excessive. Finally, it should be noted that the “folding” of the side chain results in a helix that is “jacketed”, which may reduce the c axis position correlation between neighbor chains implicit in the trigonal space group. A relaxation of this c axis correlation is indeed suggested by the weaker than expected intensity of all nonequatorial reflections in the copolymers powder and fiber patterns.

Discussion

Copolymers of propylene and hexene adopt, in a limited composition range, a crystal structure that borrows the helix organization and packing mode of another polyolefin, namely poly(1-butene). The switch from crystal modifications typical of isotactic polypropylene, and most notably its γ modification, frequently observed in polypropylene copolymers,⁷ to this different packing mode appears, however, reasonable. Indeed: The chain conformation is the 3-fold helix characteristic of all crystal modifications of polypropylene and is maintained for the polypropylene copolymers. For higher members of the polyolefin family, however, the chain conformation is more variable: three different chain conformations for isotactic PBu (3₁, 11₃, and 4₁), at least four for isotactic poly(4-methyl-1-pentene) (2₁, 3₁, 7₂, 4₁). The chain conformation of the propylene copolymers remains dominated by their high propylene content. The packing of the side chains is, expectedly, strongly influenced by the bulkiness of the side-chain butyl groups of the hexene units. They are too bulky to be incorporated in a propylene-type chain packing that is designed to accommodate methyl groups only (cf. the dense array of methyl groups in the ac face of the α phase or the structurally equivalent ab face of the γ phase).^{8,9} Indeed, Poon et al. have shown that they are rejected from the iPP type crystal lattice for low hexene contents.¹ The PBu1 form I type structure adopted by the copolymer is actually an elegant compromise between the requirements of main-chain conformation (3-fold helix) and the need to provide more room for the side chains.

Evaluation of the side-chain content in the samples that display this different crystal modification is of interest and can be based on simple density considerations. The sample with 22.4% hexene units has a unit-cell slightly contracted in the ab plane compared to that of iPBu form I: 1.717 nm versus 1.770 nm. The cell volume is, therefore, 94% of that of iPBu, or 6% contraction. The material in the cell can be partitioned between main chains and side chains. Because the main-chain conformations are identical, the helical backbone contribution to the overall volume must be similar for the copolymer and iPBu. The increase (or decrease) in cell volume primarily depends on the side-chain material. For iPBu, the six chains (18 residues) have ethyl side chains, i.e., 36 carbon atoms, distributed evenly in the cell. The copolymer side chains are methyl and butyl groups. Compared to iPBu1, the deficit of material in the copolymer side chains for copolymers with 22.4% and 25.1% hexene units is 16.4% and 12.5%, respectively. Remembering that this evaluation does not include about half of the material in the cell (the helix backbones), it appears that the deficit in side-chain material is mostly responsible for the observed cell contraction.

The packing of the side chains suggests that the cell may accommodate hexene units only up to a certain limit. It is

reasonable to assume that this upper limit is not far removed from the iPBu1 crystal structure itself. For the P/H copolymers, this limit corresponds to 33% hexene units because it has on average two side-chain carbon atoms $((0.33 \times 4) + (0.66 \times 1))$ per monomer, as does iPBu1. A somewhat reduced upper limit may be more realistic, and is actually observed. For example, a copolymer with 25% hexene units would have one hexene unit every fourth residue if they were evenly distributed along the chain. In the 3-fold helix, this would imply that any hexene side chain has as neighbors, in the helix axis direction (that is, on the nearby turns of the helix), only less-bulky methyl groups of the propylene units, which would favor the packing of the bulkier hexene side chains parallel to the helix axis. This hypothesis is supported by the analysis of the relative intensity of 110 and 300 reflections of the copolymers that does not support stretched out and favors “folded” conformations of the hexene side chains.

The above reasoning also suggests that copolymers of propene with olefins different from hexene may possibly crystallize in a similar form-I-type poly(1-butene) crystal structure when the average side-chain material approaches that of poly(1-butene). This may shift the range of compositions to, e.g., higher comonomer contents in case the side chain is shorter (e.g., pentene). To our knowledge, experimental support for (or against!) this assumption is not yet available.

Conclusion

The copolymers of propylene and hexene adopt in a limited composition range ($\approx 10\%$ to $\approx 25\%$ hexene units) a crystal packing mode that is different from those known for both isotactic polypropylene and isotactic poly(1-hexene).¹ The analysis developed in this article indicates that this structure is very similar, and is actually isomorphous to, that of isotactic poly(1-butene) in its form I. This form shares with isotactic polypropylene the 3-fold helix conformation, whereas the different arrangement of and wider distance between helices allows for incorporation of a certain proportion of larger side

chains. This proportion cannot exceed some limiting value, in the 25–30% range for hexene units. The limits of the composition window in which this form is observed are thus accounted for. The lower limit (10%) corresponds to a composition above which the hexene units are too numerous and can no longer be excluded from the iPP-type crystal lattice; their incorporation in the crystal generates an iPBu form-I-type lattice that preserves the polypropylene 3-fold helix conformation and provides more room for the side chains. The observed upper limit probably approaches or corresponds to the maximum admissible load of longer hexene side chains that the more expanded iPBu lattice can accommodate.

References and Notes

- (1) Poon, B.; Rogunova, M.; Hiltner, A.; Baer, E.; Chum, S. P.; Galeski, A.; Piorkowska, E. *Macromolecules* **2005**, *38*, 1232.
- (2) De Rosa, C.; Auremma, F.; Corradini, P.; Tarallo, O.; Dello Iacono, S.; Ciaccia, E.; Resconi, L. *J. Am. Chem. Soc.* **2006**, *128*, 80.
- (3) Holland, V. F.; Miller, R. L. *J. Appl. Phys.* **1964**, *35*, 3241.
- (4) Natta, G.; Corradini, P.; Bassi, I. W. *Nuovo Cimento, Suppl.* **1960**, *15*, 52.
- (5) It should be noted that a similar crystal structure is observed for stereocomplexes formed by racemic blends of chiral molecules (e.g., poly(lactic acid)) that can crystallize in 3-fold helical conformations. The large six-chain trigonal unit-cell of this stereocomplex has been described on the basis of a smaller triclinic unit-cell with two chains only, one right-handed helix and one left-handed helix (Okihara, T. et al. *J. Macromol. Sci. Phys.* **1991**, *B30*, 119). Whereas this is indeed the smallest possible unit-cell, it does not take advantage of the symmetry elements (3-fold screw axes) that exist in the larger trigonal cell. The trigonal cell is actually the logical unit-cell, and has been used since the early analyses of polyolefin structure analysis: isotactic poly(1-Butene) form I, isotactic polystyrene, etc (cf. for example: Natta, G.; Corradini, P.; Bassi, I. W. *Nuovo Cimento, Suppl.* **1960**, *15*, 69).
- (6) Gohil, R. M.; Petermann, J. *J. Macromol. Sci., Phys.* **1980**, *B18*, 217.
- (7) Busse, M.; Kressler, J.; Maier, R.-D.; Scherble, J. *Macromolecules* **2000**, *33*, 8775; Hosier, I. L.; Alamo, R. G.; Estes, P.; Isasi, J. R.; Mandelkern, L. *Macromolecules* **2003**, *36*, 5623.
- (8) Lotz, B.; Wittmann, J. C.; Lovinger, A. *J. Polymer* **1996**, *37*, 4979.
- (9) Brückner, S.; Meille, S. V. *Nature* **1989**, *340*, 455; Meille, S. V.; Brückner, S.; Porzio, W. *Macromolecules* **1990**, *23*, 4114.

MA052314I