Macromolecules **2007,** *40,* 8531−8532

Structure of Isotactic Propylene−Pentene Copolymers

Claudio De Rosa,* Finizia Auriemma,
Giovanni Talarico, and Odda Ruiz de Ballesteros

Dipartimento di Chimica "Paolo Corradini", Università di Napoli "Federico II", Complesso Monte S. Angelo, Via Cintia, I-80126 Napoli, Italy

Received September 4, 2007

Revised Manuscript Received October 17, 2007

It has been recently reported that isotactic propylene-hexene copolymers (iPPHe) crystallize in the α form of isotactic polypropylene (iPP) for low hexene concentrations and in the new trigonal form of iPP for hexene contents higher than 10 mol %.[1−3] Hexene units are partially included in both crystals of α form and of the trigonal form,[1,2] but the crystallization of the trigonal form at high hexene concentrations allows a better accommodation of hexene units and the degree of inclusion of comonomers into crystals strongly increase.[1,2]

The inclusion of hexene units in the crystals induces a suitable increase of density that allows crystallization of 3-fold helical chains in the trigonal form, where the helical symmetry of the chains is maintained in the crystal lattice (space group $R\bar{3}c$),[1,2] giving a structure similar to that of form I of isotactic polybutene (iPB).[4] This form has never been observed for iPP homopolymer because, in the absence of bulky side groups, it would have a too low density.[1,2] The structure of propene-hexene copolymers represents the fulfillment of the principles of polymer crystallography[5] and indicates that the packing of polymer molecules is mainly driven by density.[1] We have predicted that copolymers of propene with other olefins, as pentene, may crystallize in the same trigonal form, when the crystal density and the average composition of the copolymer approach those of iPB, provided that the distribution of the comonomer is random.[1,2]

In this communication, we present the case of random propylene−pentene copolymers as the best example for the demonstration of the general principle of *density-driven phase formation in polymers.*

Random propylene−pentene copolymers (iPPe) with concentration of pentene variable in the range 3−60 mol % have been prepared using a C_1-symmetric metallocene catalyst dimethylsilyl(2,4,7-trimethylindenyl)[bis(2-methylthieno)cyclopentadienyl]$ZrCl_2$ (complex **19** of ref 6a), which allows for a truly random distribution of comonomers.[6] The catalyst has been activated with methylaluminoxane (MAO).

All copolymerizations were run at 60 °C in a 250 mL Pyrex reactor, agitated with magnetic stirrer, containing a toluene solution (150 mL) of the catalyst, MAO and liquid pentene. The Al/Zr molar ratio was maintained at about 1000. Propene was bubbled through the liquid phase at pressure of 2 bar and the polymerization was stopped when the propene pressure decreases at 1.8 bar. Under such conditions, total monomer conversions were lower than 10%, ensuring a nearly constant feeding ratio. The copolymers were coagulated with excess methanol acidified with enough HCl (aqueous, concentrated) to prevent the precipitation of alumina from MAO hydrolysis, filtered, washed with further methanol and vacuum-dried. Typical yields were 2−3 g.

The X-ray powder diffraction profiles of as-polymerized samples of iPPe copolymers are reported in Figure 1. All as-polymerized samples have been aged at room temperature for at least 2 months to allow complete crystallization of the samples with high pentene concentration. The profiles of Figure 1 are similar to those of samples crystallized from the melt. It is apparent that the samples crystallize in the α form of iPP up to a concentration of pentene units of nearly 9−10 mol %, as indicated by the presence of typical 110, 040, and 130 reflections of the α form of iPP[7] in the diffraction profiles of Figure 1a−c. For a pentene concentration of 4 mol % an additional reflection at $2\theta \approx 10.5°$ appears (Figure 1b), whose intensity increases with increasing pentene content (Figure 1b−d), and for concentrations higher than 9−10 mol % only reflections at $2\theta \approx 10$, 18, and 21° are present (Figure 1d−g). The diffraction profiles of Figure 1e−g resemble that of form I of iPB,[8] indicating that, as predicted,[1] for these pentene contents the copolymers crystallize into the trigonal form, which is isomorphous to form I of iPB.[4]

The three reflections at $2\theta \approx 10$, 18, and 21° observed in the diffraction profiles of Figure 1d−g are accounted for by a hexagonal unit cell and are indexed with Miller indices 110, 300, and 211 + 220. Chains in 3_1 helical conformation with chain axis of 6.5 Å are packed in a trigonal unit cell with a rhombohedral symmetry according to the space group $R3c$. The values of the Bragg angles of the 110, 300, 220, and 211 reflections in the diffraction profiles of Figure 1d−g decrease with increasing pentene concentration, indicating increase of dimensions of axes of the trigonal unit cell with increasing pentene content, and inclusion of pentene units in the crystals. For the sample iPPe6 with 30 mol % of pentene values of axes $a = b = 17.1$ Å and $c = 6.5$ Å have been found. Assuming that in this sample the pentene units are included in the crystals, the theoretical density of crystals of the trigonal form is $\rho_{cr} = 0.92$ g/cm^3 in agreement with the experimental density of the crystalline phase of 0.91 g/cm^3.

It is worth noting that the value of $a = b$ axes approaches the value of the unit cell of iPB[4] ($a = b = 17.7$ Å) for higher pentene concentrations, for instance for the sample iPPe7 with 55 mol % Pe, when the average composition of iPPe copolymers approaches that of iPB. Therefore, when propene and pentene units are randomly blended along the same macromolecules and the average overall composition of the two comonomers approaches that of 1-butene ($\approx$50% C_3H_6 + $\approx$50% C_5H_{10} = C_4H_8), copolymer chains behave as poly(butene) macromolecules and crystallize into the stable form I of iPB. The inclusion of pentene comonomeric units in the crystal lattice produces an increase of density that allows crystallization of the trigonal form where the helical symmetry of the chains is maintained in the crystal lattice, as predicted by principles of polymer crystallography.[1,2,5]

The best positioning of chains inside the unit cell has been found by packing energy calculations and from the best agreement between calculated and experimental diffraction patterns. A model of packing for the space group $R3c$ (or $R\bar{3}c$ if statistical disorder in the positioning of up and down chains is considered) is shown in Figure 2. The structure contains high degree of disorder due to the constitutional disorder of the random copolymer chains that produces disorder in the position-

---

* To whom correspondence should be addressed. Telephone: ++39 081 674346. Fax ++39 081 674090. E-mail: claudio.derosa@unina.it.

10.1021/ma701985m CCC: $37.00

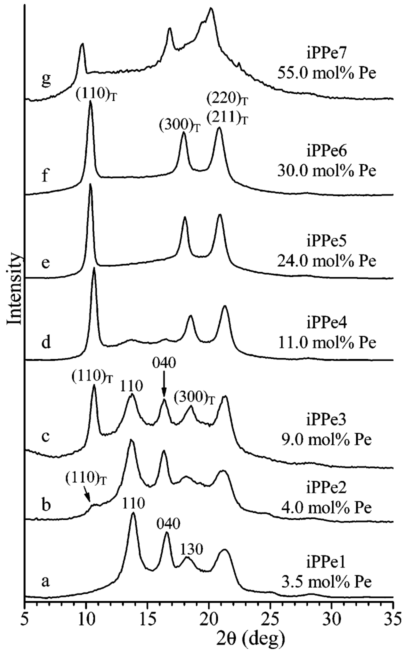

Figure 1. X-ray powder diffraction profiles of iPPe copolymer samples with the indicated concentration of pentene units (Pe). The 110, 040, and 130 reflections of α form and the $(110)_T$, $(300)_T$, $(220)_T$, and $(211)_T$ reflections of the trigonal form are also indicated.

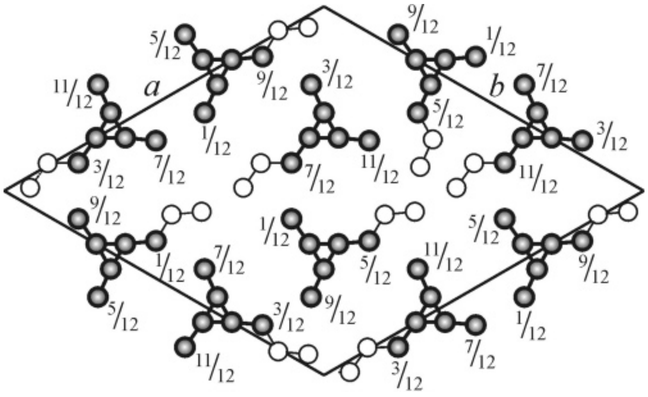

Figure 2. Model of the crystal structure of the trigonal form of iPP in the space groups $R3c$ found in propylene−pentene copolymers. The atoms of ethyl side groups of the pentene comonomeric units, randomly distributed along each iPP chain, are shown as thin lines. The height of the propylene methyl groups are indicated in $c/12$ units ($c = 6.5$ Å).

ing of the lateral groups in the unit cell. In the model of Figure 2, only one of the possible low-energy positions of ethyl pendant groups is shown. Because of the statistical distribution of pentene units along the chains, each chain containing 30−50 mol % of pentene units bears on average nearly 1.5 pentene unit in a turn of the helix included in the chain axis and the structure can be described with a fractional occupancy of the outer ethyl portion of the side chain. A disorder in the orientation of chains around the chain axes may also be present. A good agreement between calculated structure factors and experimental intensities of reflections observed in the powder diffraction profiles (Figure 3) has been obtained for a disordered model containing statistical up−down disorder, corresponding to the statistical space group $R\bar{3}c$, and introducing a slight rotational disorder, corresponding to rotations of the chains of about ±20° around the chain axes with respect to the average positions of chains shown in the model of Figure 2. The fractional coordinates of the atom of the asymmetric unit of the model of Figure 2 for the space group $R\bar{3}c$, are reported in Table 1.

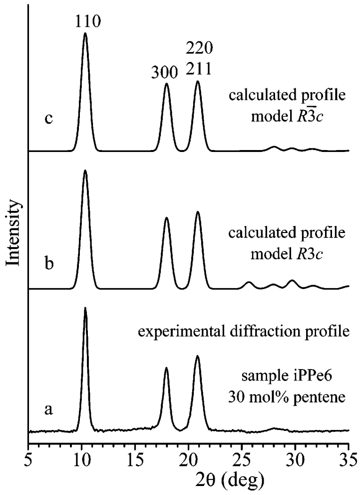

Figure 3. Comparison between the experimental X-ray powder diffraction profile of the sample iPPe6 with 30 mol % of pentene units (Figure 1f), after the subtraction of the amorphous halo (curve a) and the calculated X-ray powder diffraction profiles for the model of crystal structure of Figure 2, with unit cell axes $a = b = 17.1$ Å and $c = 6.5$ Å and space group $R3c$ (curve b), and for the limit disordered model containing up−down disorder, corresponding to the statistical space group $R\bar{3}c$ (curve c). Both models $R3c$ and $R\bar{3}c$ present a slight disorder in the orientation of the chains around the chain axes corresponding to rotations of chains of ±20° around the chain axes with respect to the average positions of chains shown in the model of Figure 2.

Table 1. Fractional Coordinates of the Carbon Atoms of the Asymmetric Unit in the Average Model of Figure 2 of the Crystal Structure of the Trigonal Form of Copolymers iPPe in the Space Group $R\bar{3}c$[a]

atom	x/c	y/c	z/c	occupancy factor
C1	0.287	0.287	−0.065	0.500
C2	0.287	0.287	0.170	0.500
C3	0.230	0.189	0.250	0.500
C4	0.131	0.138	0.170	0.150
C5	0.075	0.042	0.251	0.150

[a] The atoms C4−C5 correspond to the lateral ethyl group of the pentene comonomeric unit, which is present with a concentration of 30 mol %. The coordinate corresponding to the disordered model that gives the best agreement of Figure 3 can be obtained by introducing disorder in the rotations of the chains of about ±20° around the chain axes with respect to the average position.

Acknowledgment. Financial support from Basell Polyolefins, Ferrara, Italy, is gratefully acknowledged. We thank Patrizia Oliva of University of Salerno for the NMR analysis.

References and Notes

(1) De Rosa, C.; Auriemma, F.; Corradini, P.; Tarallo, O.; Dello Iacono, S.; Ciaccia, E.; Resconi, L. *J. Am. Chem. Soc.* **2006**, *128*, 80.
(2) De Rosa, C.; Dello Iacono, S.; Auriemma, F.; Ciaccia, E.; Resconi, L. *Macromolecules* **2006**, *39*, 6098.
(3) Poon, B.; Rogunova, M.; Hiltner, A.; Baer, E.; Chum, S. P.; Galeski, A.; Piorkowska, E. *Macromolecules* **2005**, *38*, 1232. Lotz, B.; Ruan, J.; Thierry, A.; Alfonso, G. C.; Hiltner, A.; Baer, E.; Piorkowska, E.; Galeski, A. *Macromolecules* **2006**, *39*, 5777.
(4) Natta, G.; Corradini, P.; Bassi, I. W. *Nuovo Cimento, Suppl.* **1960**, *15*, 52.
(5) Natta, G.; Corradini, P. *Nuovo Cimento, Suppl.* **1960**, *15*, 9. Natta, G.; Corradini, P. *J. Polym. Sci. Polym. Phys Ed.* **1959**, *29*, 29. De Rosa, C. *Top. Stereochem.* **2003**, *24*, 71.
(6) (a) Resconi, L.; Guidotti, S.; Camurati, I.; Frabetti, R.; Focante, F.; Nifant'ev, I. E.; Laishevtsev, I. P. *Macromol. Chem. Phys.* **2005**, *206*, 1405. (b) De Rosa, C.; Auriemma, F.; Ruiz de Ballesteros, O.; Resconi, L.; Camurati, I. *Macromolecules* **2007**, *40*, 6600.
(7) Natta, G.; Corradini, P. *Nuovo Cimento, Suppl.* **1960**, *15*, 40.
(8) Kaszonyiova, M.; Rybnikar, F.; Geil, P. H. *J. Macromol. Sci. Phys.* **2005**, *44*, 377.

MA701985M