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Polymer 47 (2006) 836–840

polymer

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An unusual branching in single crystals of isotactic poly(4-methyl-1-pentene)

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Received 27 October 2005; received in revised form 2 December 2005; accepted 5 December 2005

Available online 27 December 2005

Abstract

Single crystals of low M_w poly(4-methyl-1-pentene) (P4MP1) in its form I display an unusual streaking of their diffraction pattern. The crystals also frequently give rise to composite diffraction patterns made of two patterns rotated by 37°. The streaking indicates a structural disorder, namely a shift of nearby layers along the *a* or *b* axis by one quarter of the unit-cell edge. The daughter crystals, rotated by 37°, are produced on the edges of the parent crystals via an epitaxial growth that is a direct consequence of the structural disorder.

Keywords: Isotactic poly(4-methyl-1-pentene); Structural disorder; Epitaxial branching

1. Introduction

The purpose of this communication is to report on a structural disorder and related epitaxial nucleation that is observed in solution-grown single crystals of a low molecular weight isotactic poly(4-methyl-1-pentene) (P4MP1) in the form I crystal modification (tetragonal unit-cell, 7_2 helix conformation). Similar features have not been observed for higher molecular weight P4MP1. Although the link between the molecular characteristics and the observed phenomena is not yet established, the analysis of the structural disorder and epitaxial crystallization have been completed. In particular, the analysis helps explain a curious 37° in-plane branching of daughter crystals from their parent ones that would appear at first sight very 'un-crystallographic' and would be interpreted as some form of 'non-crystallographic branching'.

2. Experimental

The P4MP1 sample used in the present investigation is of commercial origin (Aldrich). It is a 'low molecular weight' (low M_w) material (melt index 180 g/min (260 °C/5.0 kg, norm ASTM D1238)). The specific molecular characteristics (tacticity?) are probably of importance in the crystallization behavior reported here. For comparison purposes, a high molecular weight material (same origin) was also used.

The P4MP1 sample was dissolved at 75 °C in a cyclohexane solution ($c = 0.1\%$ w/v). Crystallization takes place upon cooling to room temperature after the heating of the oil bath has been turned off (cooling rate in the crystallization range ≈ 0.4 °C/min). The precipitate is deposited on a carbon-coated grid and shadowed with platinum when needed.

Observation of the crystals was performed with Leitz and Zeiss optical microscopes and a Philips CM12 electron microscope operated at 120 kV. The bright fields and diffraction patterns were recorded either on a digital camera (Megaview III, Soft Imaging System) or on photographic plates (Kodak SO163, developed with undiluted D19 for 12 min).

Molecular modeling was performed with the Cerius^2 package developed by Accelrys.

3. Experimental results

3.1. Structural disorder in low M_w P4MP1 single crystals

Single crystals of high M_w P4MP1 crystallized in thin films by slow cooling from high temperature display an *hk*0 diffraction pattern (Fig. 1(a)) characteristic of the P4MP1 form I crystal structure. It was one of the first patterns of polymer single crystals ever recorded, and helped in the first structure determination of this crystal modification [1]. The crystal structure of form I has been refined by Tadokoro

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0032-3861/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2005.12.012

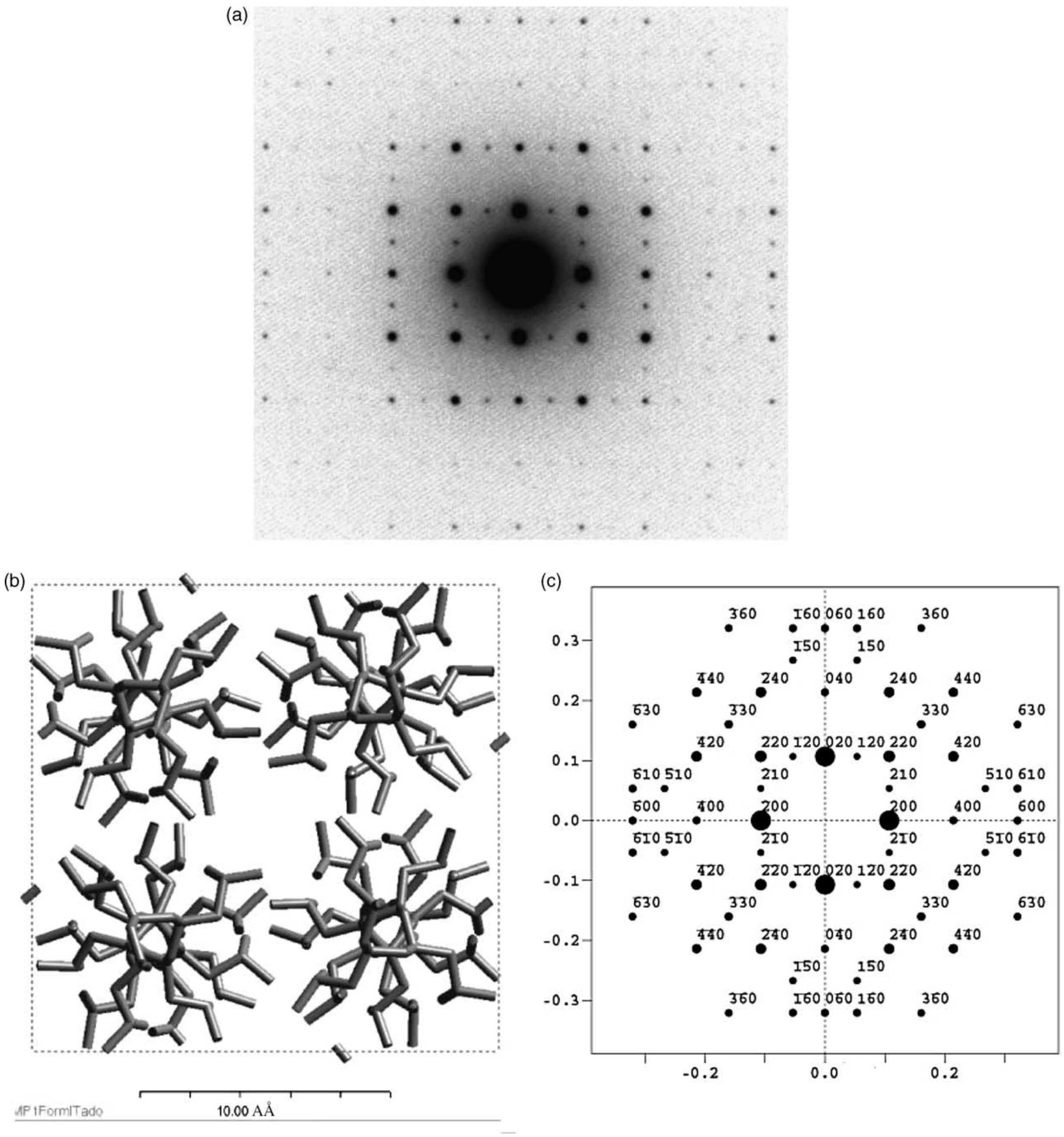

Fig. 1. (a) *hk*0 Electron diffraction pattern of a single crystal of high M_w P4MP1. (b) The crystal structure of form I of isotactic P4MP1, after reference [2]. (c) Simulated *hk*0 electron diffraction pattern of the P4MP1 crystal structure.

and coworkers [2]. It has a tetragonal unit-cell with parameters $a=b=18.88$ Å, $c=13.8$ Å. The cell contains four 7_2 helices, two right handed and two left handed ones (Fig. 1(b); simulated pattern and indexing of the reflections in Fig. 1(c)). Further crystal modifications are known for P4MP1. They rest on different helix geometries [3,4]: four-fold [5], two-fold with four residues per turn [6,7], three-fold [8] but they do not feature in the present report.

The crystals of low M_w P4MP1 obtained by crystallization in cyclohexane solution have an overall rounded square shape and display some overgrowths and screw dislocations that indicate a tetragonal cell projection (Fig. 2(a)). Their diffraction pattern (Fig. 2(b)) has an original feature, not observed in crystals of the high M_w material. It displays a significant streaking on the layer lines indexed as *h*20 and 2*k*0. On these layer lines, reflections with *h* or *k* odd, respectively, and more specifically 120 or 210 have nearly vanished and become streaked, whereas they are very sharp in Fig. 1(a) (cf. indexing in Fig. 1(c)). This streaking is best revealed when displaying the intensities of the diffraction pattern in logarithmic scale, which highlights the weaker reflections.

A similar streaking in *hk*0 diffraction patterns has been observed and analyzed recently in this laboratory while investigating the structure of isotactic polyvinylcyclohexane

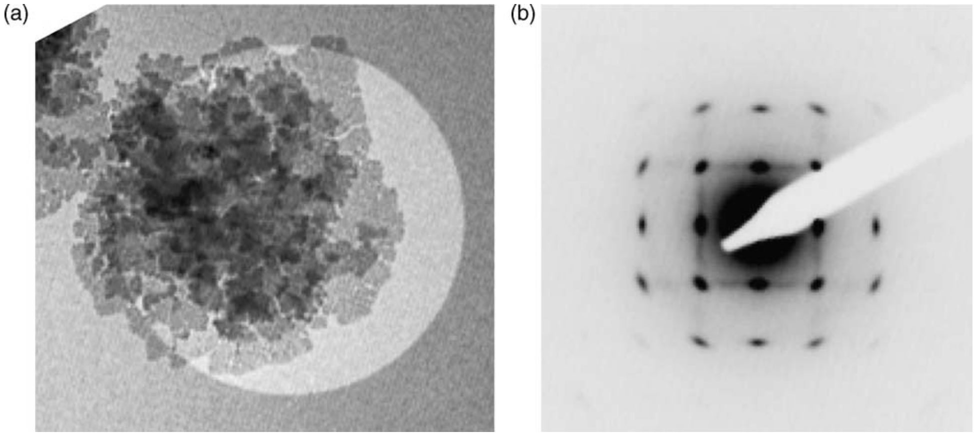

Fig. 2. (a) Single crystal of low M_w P4MP1 obtained from a cyclohexane solution by slow cooling to room temperature. (b) Diffraction pattern of a single crystal as in part (a) in proper relative orientation. Note the streaking of reflections with either *h* or *k* odd.

(PVCH) [9]. As in the present case, it indicates a structural disorder that affects the position (in *c* axis projection) of the helices in the lattice—specifically that some helices are shifted by half a helix diameter (or one quarter of a cell edge) relative to their 'normal' position in the lattice. The streaking does not result from, e.g. disorder in the up-down orientation of helices linked, for example, with chain folding. This disorder would not modify the position of the stems in the unit-cell, whereas the present streaking is definitely linked with a positional disorder. In the present context, the streaks are only taken as an indication that a certain amount of positional disorder exists; the disorder may involve very small patches of helices, or longer strings of helices, or even whole layers of helices. Actually, establishing the existence of a structural disorder based on shifts of helices by *a*/4 or *b*/4 is only a preliminary step in the analysis of a more original feature observed in these single crystals, as examined now.

3.2. Non-crystallographic branching or twinning in low M_w P4MP1 single crystals

A second, more original observation was made while investigating the structure of these low M_w P4MP1 single crystals. A significant proportion of these crystals display a diffraction pattern more complex than those analyzed so far (Fig. 3(a)). The pattern is made of two overlapped *hk*0 patterns as in Fig. 2(b), but rotated relative to each other. The two patterns have different intensities, which suggests that crystals giving rise to the weaker pattern evolved some time during growth of the 'parent' crystal. Strikingly, the rotation (around the *c* axis) of the two patterns has a constant value of ≈37°. This constancy is essential in the present context, since it demonstrates that we are dealing with some specific form of crystallographic or epitaxial relationship between the two crystals rather than some disordered aggregation of crystals

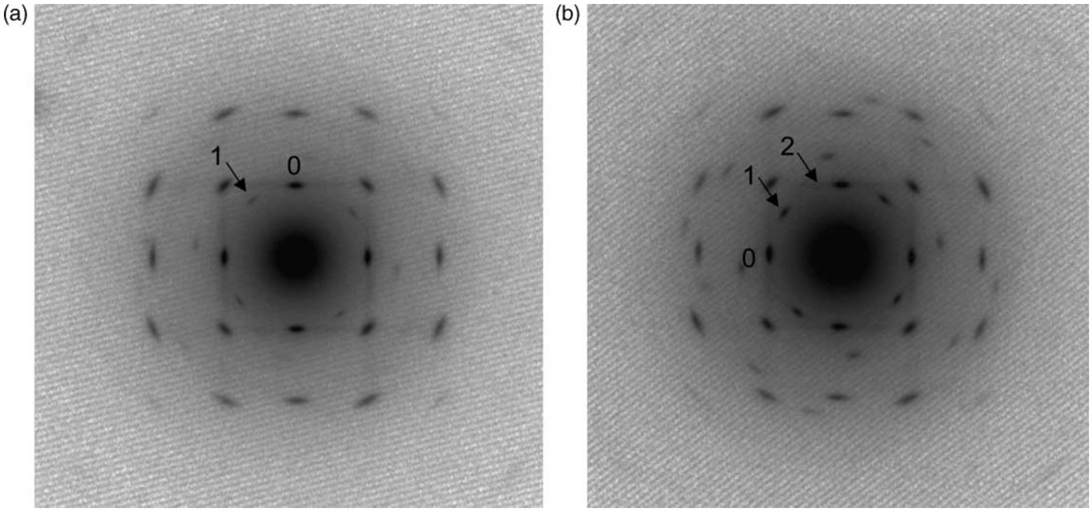

Fig. 3. (a) Diffraction pattern of crystals similar to those shown in Fig. 2(b) but that display two orientations of the cell axes rotated by 37°. (b) Diffraction pattern as in part (a) but showing two successive rotations of the cell by 37°. The successive generations of crystals are noted 0, 1 and 2.

(or of some form, necessarily less specific, of interaction through the fold surfaces). The rotation of the daughter pattern relative to the parent one may be clockwise or anticlockwise. This is not unexpected, since for any one crystal, the rotation sense is reversed when observing the crystal from the $+c$ or $-c$ directions. Occasionally, the diffraction pattern indicates superposition of three single *hk*0 diffraction patterns (Fig. 3(b)). The relative intensity decreases as the different patterns are rotated, a feature that is again consistent with successive 'filiations' during the course of crystal growth.

As indicated, this 37° 'in-plane branching' of the growth is observed, in our hands, mostly for low M_w samples. Searching for evidence of such branching, we note that Fig. 6 in the paper by Frank et al. [1] displays two superposed P4MP1crystals that seem to derive from each other and are also rotated by the tale-telling 37°. Although purely indicative, this observation may suggest that the branching reported here might be more frequent in P4MP1 crystal growth than we originally thought.

4. Discussion

4.1. Origin of the 37° in-plane branching

The origin of the 37° rotation between two P4MP1 lattices can be correlated directly with the existence of the structural disorder revealed by the streaked diffraction patterns (Fig. 2(b)). It indicates indeed a structural relationship between the two lattices involved—but a highly unusual one indeed.

Consider the local structure of an *ac* growth face on which a new layer (top layer in Fig. 4) is growing and is shifted by half a helix diameter (i.e. *a*/4) with respect to the substrate one (bottom layer in Fig. 4). The position of the end stem of this new layer is quite unique. Its position is such that its distance to the 'reference' helix of the substrate (black shading, marked A) is close to the *a* parameter of the unit-cell. Actually, three different locations of this stem may be considered. They are shown as circles in Fig. 4 and named 1–3. In position 1, the distance with the neighbor substrate stems (marked B and C) is equal to that observed in the tetragonal crystal lattice (i.e. *a*/2 or 9.44 Å), which amounts to considering a local hexagonal packing of the form I helices. The distance from the reference substrate stem A is then 16.35 Å, and the angle is of course 30°. In position 2, the inter-sheet distance between substrate and deposit layers is maintained at *a*/2 (i.e. 9.44 Å), as in the tetragonal lattice. The distance of stem 2 with the reference stem A is 17.01 Å, and the angle between the two lattices is 33°6. Position 3 corresponds to the 37° angle measured in the diffraction patterns. The distance with stem A is 17.73 Å.

This simple analysis suggests a plausible origin of the daughter crystal, and links it directly with the existence of the structural disorder indicated by the streaked diffraction pattern. In the present case, a nucleation event that takes as a substrate the two helices 17.73 Å apart (i.e. stems marked A and 3) generates a new tetragonal lattice oriented 37° away from the parent lattice. Analysis in terms of local epitaxial relationship seems appropriate at this stage. Indeed, the distance between the two helices is only slightly less than in the crystal lattice. The dimensional mismatch between the deposit and the local substrate amounts to: [(17.73 − 18.88 Å)/18.88 Å] = −6.09%. This is a standard value for epitaxial interactions, and suggests even that the 37° angle measured in these P4MP1 crystals (i.e. also the shift to position 3 in Fig. 4 rather than, e.g. positions 2 or 1) is reached to optimize—or, more simply, to allow—the epitaxial interaction.

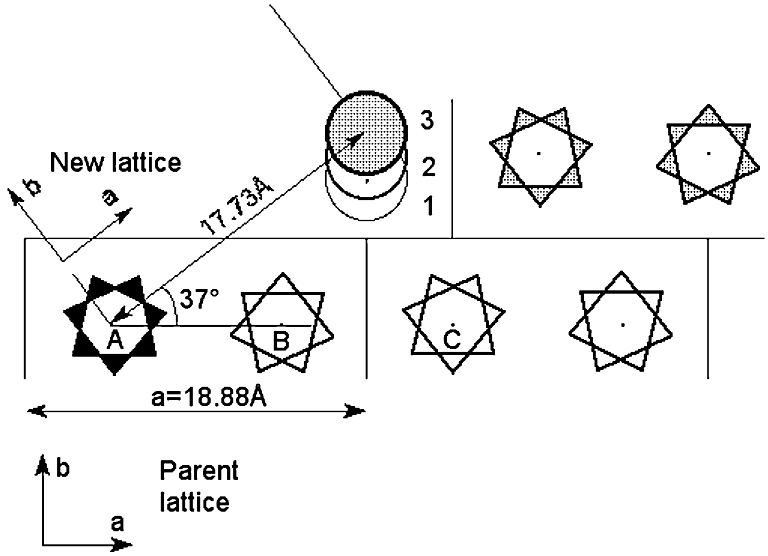

Fig. 4. Probable origin of the daughter crystals rotated by 37° relative to the parent ones. The drawing illustrates two *ac* layers of helices, the top one shifted by one quarter of a unit-cell edge. The end (left-hand side) helix of this layer (shaded) is nearly one *a* parameter away from the substrate (parent) reference helix marked A (black shading). Three positions are considered: position 1 assumes that the inter-helix distance with the substrate stems B and C is *a*/2 of the tetragonal lattice. Position 2 assumes that the inter-layer distance of the tetragonal lattice is maintained across the contact plane. Position 3 corresponds to the actual rotation of the two lattices (37°), and assumes that the helix is on the mediatrix of the two substrate helices B and C, i.e. not allowing for probable local positional adjustments. The distances between helices 1–2 and 2–3 are 1.27 and 1.23 Å, respectively. The distance between the helix in position 3 and the substrate helix A is fully compatible with an epitaxial relationship that generates a new lattice orientation (indicated).

Should this relationship be described as a case of twinning or as a case of epitaxial crystallization? The rotation of the two lattices is at a defined and constant angle, but it does not correspond to any standard reflection or rotation twin. Geometrically, the contact plane is close to ($\bar{2}30$) (or better to ($\bar{3}40$)) for the parent lattice, and (010) for the daughter lattice.

Description of the whole process as a twin relationship might be possible if one abandons the narrow sense of twinning and considers multicomponent twins. In this extended acceptation of the word, the shift of layers described earlier may also be described as a translation twin (with translation by a fractional part of the lattice spacing) [10]. The structural relationship that gives rise to the 37° 'rotational misfit' generates a row of 'twinning dislocations' and 'epitaxial dislocations' that is parallel to the bisector of the 37° angle, that is, roughly parallel to ($\bar{1}30$).

4.2. *'Non-crystallographic' branching in polymer crystallization*

Polymer spherulite crystallization is characterized by a fanning out of lamellae from the nucleation center. This fanning out implies also multiplication of lamellae in order to fill in a diverging space. Two mechanisms have been invoked or observed so far that account for this fanning out and lamellar multiplication: screw dislocations and 'non-crystallographic' lamellar branching. The development of screw dislocations is well documented and by far the most effective means to multiply the number of lamellae. The screw dislocations are characterized by Burgers vectors parallel to the chain axis and generate new lamellae that are out of the plane of the parent lamella (above and below), but maintain the orientation of the crystal unit-cell (except for a possible splaying of lamellae). The 'non-crystallographic' lamellar branching is comparatively more mysterious and has not received much attention thus far. Contrary to screw dislocations, the non-crystallographic branching takes place within the plane of the parent crystal ('in-plane'): if described as crystallographic features, the Burgers vector of these defects is normal to the chain axis. However, no clear experimental data are available, not to mention the variability of, e.g. angles involved in non-crystallographic lamellar branching.

The observations reported here may well represent a first analysis of an in-plane lamellar branching with the Burgers vector normal to the chain axis. As indicated, it would be considered as 'non-crystallographic', since it does not correspond to any 'familiar' twin. However, the specificity of the branching angle indicates that it is by no means representative of lamellar branching in general. The underlying principles may however have wider impact in crystal growth.

The analysis illustrated in Fig. 4 is tailored for a tetragonal unit-cell, and is therefore susceptible to take place in other polymers with similar cell symmetry. However, this type of structural defect can take place in any growth process—and, possibly, induce an 'epitaxial' growth with a different in-plane unit-cell orientation.

5. Conclusion

P4MP1 crystallized from solution may produce single crystals of form I (tetragonal unit-cell, 7_2 helices) that display two connected structural features: a disorder characterized by an *a*/4 shift of *ac* layers, and the original formation of daughter crystals that are rotated by a specific angle (37°) relative to the parent crystal in the plane of the crystal. The shift, although rare, is not unusual in polymer crystallography (it has been observed in PVCH [9], syndiotactic polypropylene [11] and syndiotactic polystyrene [12]). The structural relationship between daughter and parent crystals is best described as an epitaxial, rather than a twin, relationship. The epitaxial growth starts from a site (Fig. 4) that, in the parent crystal, combines a 'normal' and a shifted layer, which accounts for the link between layer shifts and generation of these rotated daughter crystals.

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