Crystal Structure of Syndiotactic Polypropylene: Clues from Molecular Simulation

Daniel J. Lacks

Department of Chemical Engineering, Tulane University, New Orleans, Louisiana 70118

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The determination of the crystal structures of polymer materials is difficult because the imperfect crystallinity limits the quality of the experimental data. This difficulty has been particularly acute for syndiotactic polypropylene, even though it is one of the simplest polymers. Molecular simulations are presented which suggest that the crystal structure of sPP differs from the previously accepted *Ibca* structure, due to axial displacements of the sheets (the polymer chains in the *b*−*c* plane) from their neighbors along the *a* axis. This result is consistent with an alternative interpretation of existing experimental crystallographic results.

The crystal structure of sPP was originally characterized in the 1960s by the $(ttgg)_n$ chain conformation and chain packing corresponding to the $C222_1$ space group, as shown in Figure 1a.[1] More recently, Lovinger, Lotz, and co-workers have shown that the chains pack differently, with the chains alternating in chirality along both the *a* and *b* axes as shown in Figure 1b, and assigned the *Ibca* space group for sPP.[2−4] This chain packing scheme has been corroborated by other laboratories.[5,6] However, experimental results of Lovinger *et al.* on the most highly annealed and stereoregular sPP samples showed diffraction peaks corresponding to the 111, 311, and 322 reflections, which are forbidden by the *Ibca* space group due to the symmetry along the *c* axis.[7] These diffraction peaks were attributed to defects since they disappeared under weak electronic irradiation. The purpose of this paper is to suggest, instead, that these diffraction peaks arise from the true crystal structure of sPP differing slightly from *Ibca*.

Molecular mechanics calculations are carried out for crystalline sPP with modifications of the empirical force fields of Sorensen *et al.*[8] and Karasawa *et al.*,[9] designated by SLKB* and KDG*. The modifications are described elsewhere,[10] and these force fields have been shown to give accurate results in simulations of isotactic polypropylene.[10,11] The results of the present calculations are very similar for the SLKB* and KDG* force fields, suggesting that the conclusions are not artifacts of the approximate force fields.

The resulting minimum energy structures include axial displacements of the sheets, of 1.65 Å, from *Ibca* symmetry. These sheet displacements can be realized with either an orthorhombic or monoclinic structure for a four-chain (two-sheet) unit cell. For the orthorhombic structure, the sheet displacements alternate between up and down (Figure 2b). The decrease in energy accompanying the sheet displacement from *Ibca* symmetry is very significant (approximately 5% of the total binding energy), as shown in Figure 3. For the monoclinic structure, the sheet displacements increase along the *a* axis (Figure 2c); the monoclinic angle $\beta = 107°$ leads to equal sheet displacements along the *a* axis. The orthorhombic structure is found to be lower in energy than the monoclinic structure (by 0.015 and 0.009 kcal/mol per unit cell with the SLKB* and KDG* force fields, respectively), in agreement with the experimental result that the structure is orthorhombic. A previously reported sPP calculation found only the monoclinic structure because the calculation was carried out for the primitive two-chain unit cell,[12] and the orthorhombic structure requires four chains per unit cell. It is noted that similar axial sheet displacements occur in nylon crystals, and both orthorhombic and monoclinic structures similar to those described here occur in crystals of various nylons.[13]

The reason why the axial displacements occur can be understood in terms of the interchain methyl−methyl interactions. The sPP crystal structures are based on

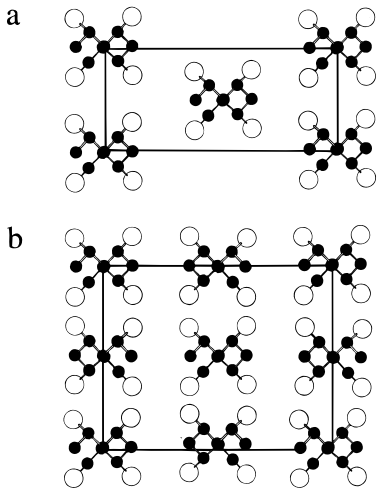

Figure 1. Proposed crystal structures of sPP: (a) $C222_1$; (b) *Ibca* or distorted *Ibca*. For the *Ibca* structure, the polymer chains at $x = 0.5$ have the *z* coordinate $z = 0.5$ (the chains are shifted up by half a repeat unit), whereas for the distorted *Ibca* structure these chains have the coordinate $z = 0.29$.The filled symbols are framework carbon atoms, and the open symbols are the pendent methyl groups. The *a* axes are horizontal, the *b* axes are vertical, and the *c* axes come out of the page.

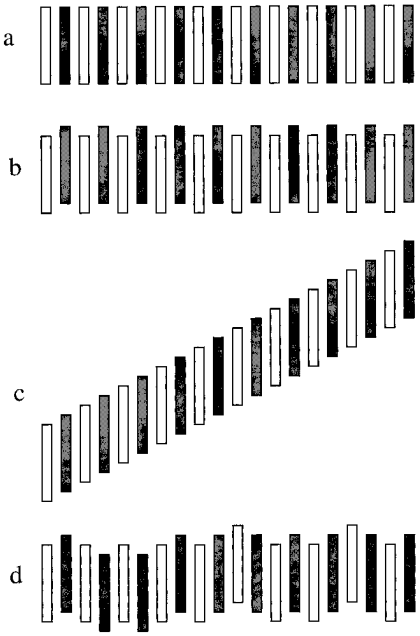

Figure 2. Schematic diagrams of axial displacements of the sheets from their neighbors along the *a* axis. Each rectangle represents a sheet, one unit cell in length along the *c* axis. The *a* axes are horizontal and the *c* axes are vertical. (a) *Ibca* structure (no displacements); (b) orthorhombic structure; (c) monoclinic structure; (d) random displacements.

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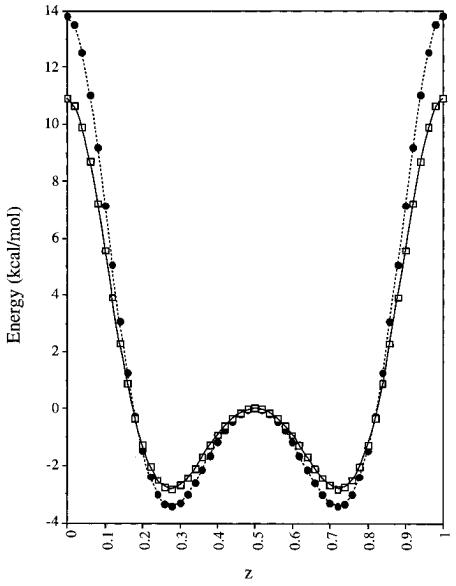

Figure 3. Potential energy of the sPP crystal for the distorted *Ibca* structure as a function of the magnitude of the axial sheet displacement from *Ibca* symmetry. Squares are the SLKB* calculation, and circles are the KDG* calculation.

the interdigitation of the methyl groups on neighboring chains along the *a* and *b* axes. Along the *a* axis, the symmetric *Ibca* structure leads to equal interchain methyl−methyl distances of approximately 5 Å, as shown in Figure 4a. The symmetric structure minimizes the repulsive interactions between methyl groups, but also minimizes the attractive interactions. Since the van der Waals diameter of a methyl group is approximately 4 Å,[14] repulsive effects are less important than attractive effects, and the total methyl−methyl interaction energy is lowered by axial displacements which lead to one shorter interaction (approximately 4 Å) and one longer interaction (approximately 6 Å), as shown in Figure 4b. In contrast, the symmetry along the *b* axis is not broken because the neighboring chains are closer in this direction, and the interchain methyl−methyl distances are already near the van der Waals diameter for the equilibrium structure.

The orthorhombic and monoclinic structures have the same nearest-neighbor sheet−sheet interactions and differ only in the next-nearest-neighbor sheet−sheet interactions. Consequently, the energy difference between these two structures is very small (as shown above), and there is not a large energy penalty for defect crystals which mix the two structures—i.e., structures which include random up or down displacements of subsequent sheets, as shown in Figure 2d. However, the barrier to moving a sheet between energy minima is large (approximately 3 kcal/mol per unit cell), and therefore the motion of sheets between minima is expected to be small at room temperature (i.e., the structure in Figure 2d is a static rather than a dynamic structure). The small energy penalty for random sheet displacements combined with the large energy barrier for sheet motion between minima suggests that kinetic effects during crystal growth would lead to the incorporation of defects of this type in real sPP crystals. Also, annealing at higher temperatures would be expected to decrease the extent of these defects by providing more energy for the sheets to move between energy minima (the mechanism for this sheet motion is likey to be complex and is beyond the scope of these calculations).

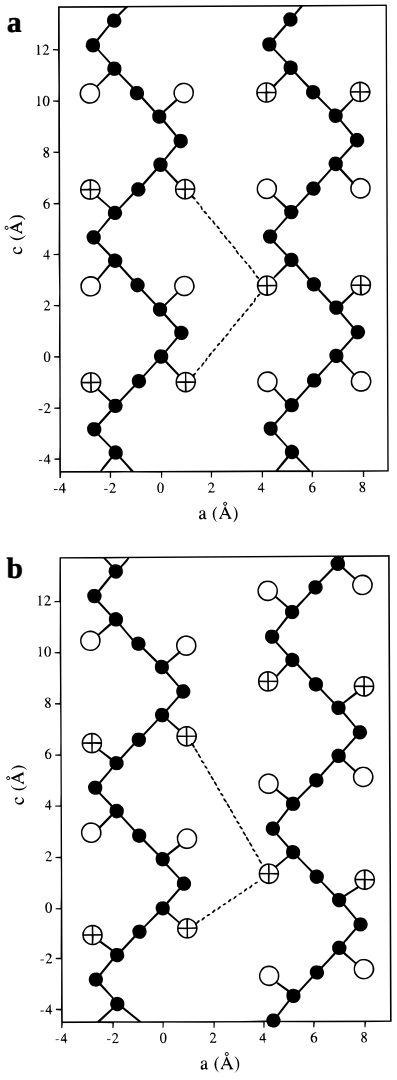

Figure 4. Intersheet interactions sPP: (a) *Ibca* structure; (b) distorted *Ibca* structure. Filled symbols are framework carbon atoms, and open symbols are the pendent methyl groups. The open symbols without crosses are at $b = 0$, and those with crosses are at $b = 3.7$ Å.

The results of the present calculations are consistent with existing experimental results and give an alternative explanation for the experimental observation by Lovinger *et al.* of the 111, 311, and 322 diffraction peaks.[7] The initial experimental observation of these diffraction peaks is accounted for by the structure presently proposed for sPP. These peaks disappear upon electron irradiation because the radiation induces movement of the sheets in the crystal from one local axial minimum to another, which randomizes the axial displacements and leads to broadening and weakening of the 111, 311, and 322 reflections until they are no longer detectable (similar radiation effects have been found in polyethylene[15]). Also, less highly annealed or stereoregular structures may also contain enough random sheet displacements so as to render the 111, 311, and 322 reflections undetectable, explaining why these diffraction peaks have not been observed in such samples.

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