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Energetics Analysis of Syndiotactic Polypropylene Crystal Structure

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The interpretation of diffraction patterns of crystalline syndiotactic polypropylene (sPP) has undergone important changes since the early proposal by Corradini et al.[1] from fiber X-ray patterns that the sPP structure is based on an orthorhombic unit cell with two isochiral (ttgg)$_2$ helical chains, $a = 14.50$ Å, $b = 5.60$ Å, c(fiber axis) = 7.40 Å, and C-centered to give space group $C222_1$. Electron diffraction patterns of single crystals obtained by Lotz, Lovinger, and Cais[2] indicated, on the basis of extra reflections, that the b-axis is doubled (to 11.20 Å), suggesting an alternation of right-handed (R) and left-handed (L) helices along this direction. Steric packing considerations suggested an alternation of R and L helices along the a-axis, leading to a unit cell with four chains and space group *Ibca*. Streaking of some of the reflections implied an intermolecular lattice disorder, which was interpreted in terms of the coexistence of both types of packing arrangements.

Subsequent studies elaborated on the *Ibca* proposal: X-ray studies of thick films and bulk specimens were said to support this structure;[3] a simulation of packing defects, viz., relative b-axis displacements of adjacent bc sheets, was found to explain the diffraction streaks if a small amount of packing defects along the c-axis is included;[4] and atomic force microscopy studies demonstrated the alternation of R and L chains in the bc plane.[5] Further examinations of this question[6,7] concluded that various kinds of statistical disorder can exist, with the $C222_1$ and *Ibca* representing "limit-ordered" structures. Disorder was also indicated by solid-state NMR studies.[8,9]

In the analysis of the diffraction results, steric packing considerations played an important role in determining possible unit cell chain arrangements. A chain packing energy calculation had been done,[10] but this was based on a simplified model of one a-axis chain adjacent to four bc chains, and it utilized an early energy function.[11] A more recent molecular mechanics (MM) calculation with empirical force fields[12] examined the unit cell energy as a function of c-axis displacements between the two adjacent bc sheets. This study found that the minimum energy is not at the *Ibca* structure (which we designate as $\Delta c = 0$) but at $\Delta c = 0.223$ (c) (or equally at $\Delta c = -0.223$). It was supposed that the extra diffraction peaks were due to this departure from an *Ibca* structure.[12]

We have done three MM calculations to investigate the energetics of the sPP unit cell structure. In the first, we obtained the complete energy surface as a function of Δb and Δc, subject only to the constraints in the minimization that the R and L chains in the b-axis repeat are related by the center of inversion of the *Ibca* structure and that the unit cell is orthorhombic. In the second, we examined the positions and energies of the minima when the unit cell angles are also allowed to vary. In the third calculation, we obtained the energy surface under the constraint of an orthorhombic unit cell with room temperature a and b dimensions, viz., $a = 14.50$ Å, $b = 11.20$ Å (c was allowed to vary).

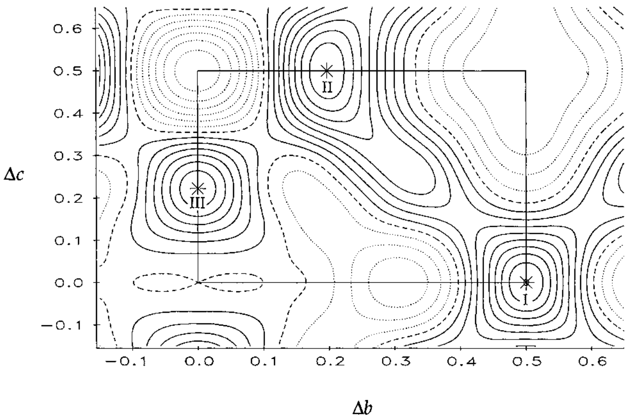

Figure 1. Energy surface for an orthorhombic cell as a function of fractional unit cell displacements in the b-axis (Δb) and c-axis (Δc) directions of bc sheets of chains in the *Ibca* structure. The *Ibca* structure is at the origin and is represented as zero energy. Energy contours are at 0.5 (kcal/mol)/unit cell, with negative energies being shown by solid lines, zero energy by a broken line, and positive energies by dotted lines.

Table 1. Energy-Minimized Syndiotactic Polypropylene Crystal Structures

minimum^a	a^b	b^b	c^b	α^c	β^c	γ^c	Δb^d	Δc^d	ΔE^e
				Orthorhombic Unit Cell					
I	13.73	10.69	7.69	90.0	90.0	90.0	0.5	0.0	−4.51
II	13.70	10.62	7.68	90.0	90.0	90.0	0.196	0.5	−4.45
III	13.80	10.64	7.64	90.0	90.0	90.0	0.0	0.222	−3.43
				Unconstrained Unit Cell					
I	13.77	10.94	7.67	87.8	89.2	89.2	0.5	0.0	−7.29
II	13.64	10.90	7.67	87.6	89.7	89.5	0.196	0.5	−7.72
III	13.73	10.93	7.63	87.7	88.0	88.1	0.0	0.222	−7.13
				Room Temperature a and b, Orthorhombic Unit Cell					
I	14.50	11.20	7.40	90.0	90.0	90.0	0.5	0.0	−2.64
II	14.50	11.20	7.40	90.0	90.0	90.0	0.185	0.5	−2.26
III	14.50	11.20	7.40	90.0	90.0	90.0	0.0	0.222	−1.89

^{a} See Figure 1. ^{b} In angstroms. ^{c} In degrees. ^{d} In fractions of unit cell lengths. ^{e} In (kcal/mol)/unit cell with respect to $E(Ibca) = 0$.

The potential energy function is based on our development of a spectroscopically determined force field (SDFF),[13] which we had implemented for linear saturated hydrocarbons[14] and have now extended to branched saturated hydrocarbons.[15] The physical accuracy of this SDFF is illustrated by its ability to reproduce the observed chain elastic modulus of polyethylene to ~1%.[16] The energy calculations, performed with our SPEAR program,[17] of course allowed full optimization of the internal chain geometry (no internal coordinates were constrained) and involved a sufficient number of unit cells so that summations of nonbonded interactions extended to ~30 Å from atoms in the central unit cell. Our calculations reproduce the recently detected minimum,[12] but we also find two additional minima of even lower energy. A slight departure from orthorhombic symmetry is found for the fully optimized (i.e., 0 K) structure, although this result must be tempered by the lack of inclusion of the zero-point vibrations.[18] We also cannot be sure that this departure persists at room temperature since we have not done the necessary statistical mechanical calculation.[18]

In Figure 1 we present the energy surface for the fully optimized orthorhombic unit cell as a function of Δb and Δc, and in Table 1 we give various characteristics of the structures at the minima. In Figure 2 we show schematically the nature of the three minimum energy structures.

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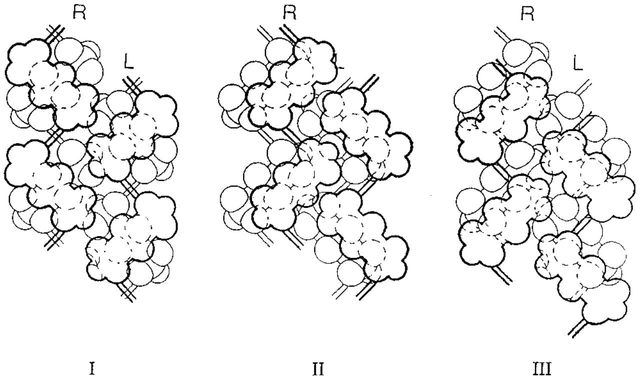

Figure 2. Schematic diagram of the three minimum-energy structures of Figure 1. The view is along the *a*-axis, with the *c*-axis vertical and the *b*-axis horizontal. The top surfaces of chains in a *bc* plane are represented by light lines, with right-handed and left-handed helices alternating along the *b*-axis. The bottom surfaces of chains on an adjacent *bc* sheet (along the *a*-axis) are represented by heavy lines, and similarly alternate R and L. The "sticks" connecting the outlined "pentane units" represent such units on the opposite sides of each chain.[2] The optimized torsion angles are within a few degrees of the canonical values, viz., ±60 and 180°.

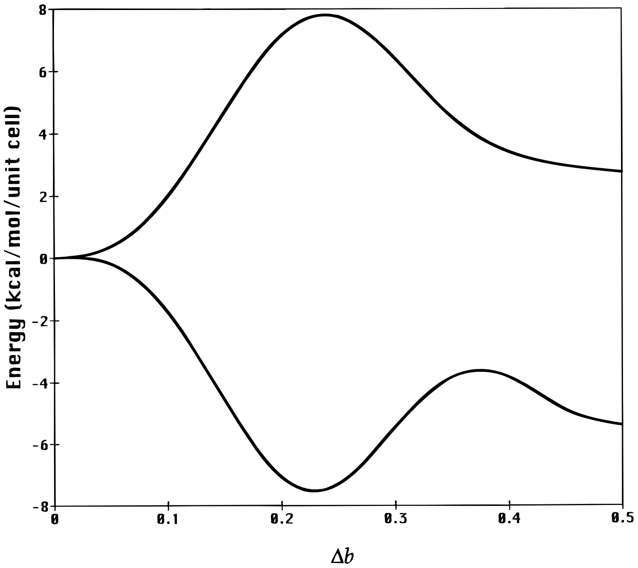

Figure 3. Variations in lattice repulsive, $\Delta E_{\mathrm{l,r}}$ (upper curve), and attractive, $\Delta E_{\mathrm{l,a}}$ (lower curve), energies as Δb is varied (at $\Delta c = 0$) from the *Ibca* structure.

In the case of the orthorhombic symmetry, the unit cell dimensions at all three minima are essentially the same (the variation in all is less than 0.28%). With respect to the *Ibca* structure, we find a minimum similar to that recently obtained[12] when Δc is varied at $\Delta b = 0$, i.e., structure III at $\Delta c = 0.222$ and $\Delta E = -3.43$ (kcal/mol)/unit cell. However, variation of Δb shows that two other minima exist (structures I and II), with comparable energies that are ~2 (kcal/mol)/unit cell lower than that of structure III. It may seem strange that, for example, structure I is at such a low-energy minimum when it would seem from steric packing considerations (as seen in Figure 2) that this might in fact be a high-energy structure. However, when one examines the variation in energy components with Δb, it is clear that it is necessary to probe beyond the apparent steric interactions to a quantitative knowledge of the energetics. In Figure 3 we show the lattice repulsive, $\Delta E_{\mathrm{l,r}}$, and attractive, $\Delta E_{\mathrm{l,a}}$, energies as a function of Δb at $\Delta c = 0$ (the changes in bonded and electrostatic energies are much smaller and are not shown in the figure). We see that, while the change in $\Delta E_{\mathrm{l,r}} + \Delta E_{\mathrm{l,a}}$ is small for $\Delta b < 0.35$, for $\Delta b > 0.4$ both $\Delta E_{\mathrm{l,a}}$ and $\Delta E_{\mathrm{l,r}}$ decrease as Δb approaches 0.5. Thus, although it may seem that the steric packing arrangement for structure I should be unfavorable (cf. Figure 2), this structure actually permits favorable attractive interactions to increase even as repulsive interactions decrease. Similar details of the quantitative balance between these main energy contributions account for the presence of the other minima.

When the restriction of orthorhombic symmetry is removed, the cell relaxes slightly (the angles departing by no more than 2° from orthogonality) and the minima are closer in energy (although structure II is now lower in energy than structure I). The unit cell dimensions remain about the same for all structures (the variation is less than 0.35%).

The calculation involving an orthorhombic unit cell with room temperature dimensions, although it neglects the contributions of the chain and lattice vibrations at non-zero temperature,[18] indicates that the same three minima are likely to pertain for the structure of room temperature crystalline sPP, and probably in the energetic order of the 0 K calculations.

What implications do these results have with respect to the determination of the sPP structure from the diffraction patterns? Calculations of the expected diffraction patterns show that none of these three individual minimum energy structures can fully reproduce the observed pattern.[19] It is possible that a mixture of these three pure structures, each present in coherent "blocks", may be able to better explain the observed results. On the other hand, it may be necessary to introduce, in the manner of defects,[4] a more localized statistical mixing of these structures. The influence of chain folds in determining unit cell chain packing may also have to be considered. It is clear that the detailed nature of the crystal structure of sPP is still an open question.

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