Dominant interactions in the conformation of isotactic polypropylene: 1. Intrachain energy

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A calculation is presented of the intrachain component of the conformational energy of isotactic polypropylene. Multiple minima are found for the energy as a function of the three torsional angles, with a strong dependence noted on the rotation of the methyl group. A comparison is made between the energies of ordered and disordered chain conformations constructed to produce the experimentally observed 3_1 helix.

(Keywords: polypropylene; conformation; commensurability; energy calculations)

INTRODUCTION

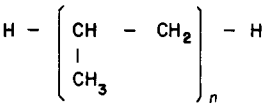
Isotactic polypropylene (iPP) is a commercially important polymer which has been studied extensively over the course of the last three decades. Early X-ray powder spectra[1] indicated amorphous, smectic (pseudo-hexagonal), and crystalline phases for iPP. Further experiments have given evidence for three different crystalline structures[2,3] a monoclinic α-form, a hexagonal β-form and a triclinic γ-form. In spite of the difference in three-dimensional orientation, infra-red spectra[1,4] and n.m.r.[5] experiments indicate that the chain conformation is a 3_1 helix in all phases. In the monoclinic α-form, left- and right-handed 3_1 helices are paired, with two pairs per unit cell. The triclinic γ-form is a solid state deformation from the monoclinic α[3,6]. The hexagonal β-form is thought[2,3] to consist of chains of one handedness.

Various calculations have attempted to reproduce these experimental results in order to test our knowledge of the determining forces, and an approximate 3_1 helix has indeed been calculated to be the conformation of minimum potential energy[7-15]. It appears in two forms, the right-handed (tg) helix, and the left-handed ($g't$). Crystal packing calculations[16,17] have been applied to the unit cell for the α and γ forms to compare the packing energy of structures differing in the placement of *up* and *down* chains. A chain is classified as up or down according to the angle the methyl carbon makes with a plane perpendicular to the vertical chain axis. The up–down order of the chains has been considered to determine the point group symmetry of the α-form, from the ordered $P2_1/c$ to the disordered C2/c. It has been assumed that one can exchange up and down chains without affecting the interchain spacing, but that exchange of left- and right-handed chains would require a change in the unit cell dimensions[18].

We have been interested in the role of the side group in determining the packing of the different crystalline phases of iPP. In this paper we examine the role of the methyl side group in determining the intrachain conformational energy, describe the molecular parameters determining the configuration of iPP, outline the potential energy functions used to determine the interaction energy between atoms, and compare the results with previous work. The conclusion explores the implications of the results for crystal packing, and indicates the direction of future efforts.

PARAMETERS

Polypropylene has the polymer formula



A chain segment consisting of two monomeric units of iPP is shown in *Figure 1* in the planar zig-zag conformation. In this isotactic configuration the methyl side groups are attached to the left backbone carbon atoms, pointing behind the plane of the backbone. Addink and Beintema[2] pointed out the necessity of considering the other isotactic configuration which has all the methyl side groups pointing in front of the plane of the backbone. One configuration can be obtained from the other through a 180° rotation about a horizontal axis through the plane of the figure. The type of configuration determines whether a chain forms the up or the down structure when it is conformationally altered to the form of a 3_1 helix. The configuration shown in the figure forms right-down and left-up 3_1 helices, while the other forms right-up and left-down when the appropriate torsional rotations are made.

The unique bond angles and torsional rotational angles of iPP are indicated in *Figure 1*. Using the labelling of m for the methyl carbon, α for the methine carbon, c for the methylene carbon, and capital C to represent all carbon atoms, we find the unique bond lengths to be $\overline{\alpha c}$, $\overline{\alpha m}$, and $3\overline{HC}$. The nine angles given are not all independent. As shown by Flory and Suter[13], dependences at each atom reduce the nine independent bond angles in each propylene monomer to six; for example the carbon bond angles α–c–α, c–α–c, m–α–c and the hydrogen bond angles H–m–H, H–c–H and H–α–m.

Each propylene monomer has three torsional angles. These are indicated in *Figure 1*, where, starting at the top

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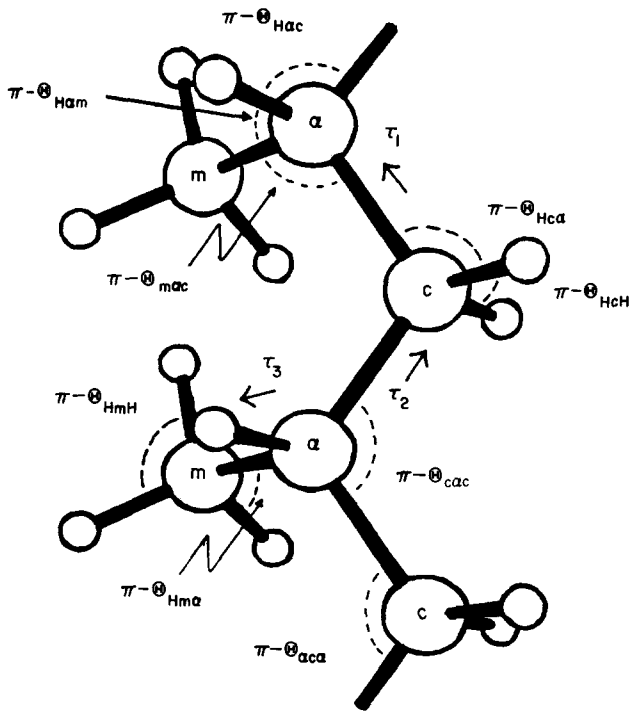

Figure 1 Configurational and conformational parameters of isotactic polypropylene

of the figure, the backbone α–c bonds form one set, represented by τ_1, and the c–α bonds form a second set τ_2. The third set of bond rotations, τ_3, are the m–α bonds. In *Figure 1* these are represented by arrows pointing in the direction of the right handed torsional rotation. The zero of rotation for τ_1 and τ_2 was chosen to be the all *trans* conformation. The zero of rotation for the set of bonds τ_3 was arbitrarily taken at the torsional angle $H\text{–}m_n\text{–}\alpha_n\text{–}c_n = -32°$.

The helical pitch can be related to the torsional rotations of bond sets one and two, the backbone bonds. The pitch K_l is the number of monomers, K, in the helix that must be travelled to achieve a rotation of $2\pi l$ about the chain axis. For a chain of two inequivalent atoms, Hughes and Lauer[19] developed an expression for the angle of rotation between the projection of two equivalent backbone atoms in the plane perpendicular to the chain axis. Their equation can be inverted to find the backbone torsional rotations that produce a specific helical pitch.

To simulate a long chain, a polymer was constructed in which all geometrically equivalent bonds were given identical orientations. Each monomer then has the same values for the three bond lengths, the six independent bond angles, and the three torsional rotation angles. The fixed lengths and angles were chosen in accordance with the crystallographic data of Mencik[20]. The backbone bond lengths were $\overline{\alpha c} = 1.54$ Å. The $\overline{m\alpha}$ bond length varied from 1.54 Å up to 1.56 Å in Mencik's fit, so both extreme lengths were considered. The backbone angles were $c\text{–}\alpha\text{–}c = \alpha\text{–}c\text{–}\alpha = 114°$, the angle that places a helix precisely in the unit cell length $c = 6.5$ Å. The methyl side group angle was $< m\alpha c = 107.5°$. For this analysis, hydrogens were added to the crystallographic carbon positions at tetrahedral angles, i.e. $< HmH = < HcH = < H\alpha m = 109.5°$, at a distance of $\overline{CH} = 1.10$ Å. Conformational results were independent of the number of repeat units above $n = 6$, in agreement with the results of Ajo *et al.*[15], so the calculations were performed for $n = 6$. The polypropylene macromolecule segment was thus replaced by a molecule of the oligomer 1,3,5,7,9,11-hexamethyldodecane, with the above fixed values for bond lengths and angles, with variable torsional rotations.

POTENTIAL ENERGY FUNCTIONS

A detailed understanding of the structure and stability of the various phases of iPP will obviously require consideration of both intrachain and interchain forces. However, the fact that a 3_1 helical conformation is observed in all the recorded phases of this material suggests that intrachain forces may play a dominant role. Interchain forces will necessarily have to be invoked to explain the formation of an exactly commensurate helix, since the repeat unit of iPP is not sufficiently symmetric for an isolated chain to adopt such a conformation. It is, however, of interest to ask initially whether the conformational potential energy of a polypropylene chain subject to intrachain forces alone will dictate a structure close to the 3_1 helix.

Rules for determining the conformation of an isolated polymer were listed qualitatively by Liquori[21], and Natta and Corradini[18]; equivalent bond lengths and bond angles should be equal, single bonds should be rotated so that pendant atoms should be staggered (the principle of staggered bonds), and the van der Waals distances between non-bonded atoms should be sufficient to permit unstrained packing. If the above rules could not be satisfied simultaneously, they suggested the deformation of bond angles to values exceeding the normal values (i.e. more than 110° for the C–C–C angle), slight deviations from the principle of staggered bonds, and shortening of interatomic distances to less than the sum of their van der Waals radii. Since our interest is in the contribution of side-group repulsion in modelling the experimental results, the lengths and angles were considered to be fixed at the experimental values.

The remaining rules concerning the principle of staggered bonds are placed upon a more quantitative footing through the use of potential energy functions that depend upon atomic coordinates. It is clearly impossible to perform a detailed quantum mechanical analysis of the electronic ground state of a macromolecule. Accordingly semi-empirical methods are extrapolated from smaller molecules as reasonable approximations of the interatomic forces found in polymers. The potentials depend only upon the centre-to-centre separation between non-bonded atoms.

Scott and Scheraga[22,23] systematized the procedure for calculating the potential energy coefficients between different atoms. In their later papers[23] they selected the 6–12 potential

$$\Phi(r) = Br^{-12} - Ar^{-6} \qquad (1)$$

as the most appropriate. The coefficients A are determined from a modified Slater–Kirkwood equation, and the coefficients B are chosen to minimize the potential at the contact distance, the sum of the van der Waals radii. We chose to use the coefficients selected by Hopfinger[24], as listed in *Table 1*. Other sets of coefficients were also tested, but it was found to be unnecessary to repeat the complete calculation using these alternative coefficients

Table 1 Non-bonded 6–12 potential energy parameters

	A (kcal Å^6 mol^{-1})	B (kcal Å^{12} mol^{-1})
HH	70.38	6286
CH	161.9	44650
CC	327.5	285800

because the qualitative features of the conformational energy were left essentially unchanged by this substitution.

In some contexts it has been found that use of only two-body potentials is inadequate. In studies of the barrier to rotations about the $\overline{CC}$ bond in an ethane molecule, for example, Mason and Kreevoy[25] were only able to account for half the barrier height between staggered and eclipsed conformations when using only the two-body potential energy functions described above. A torsional potential energy term of the form

$$\Phi(\omega)=\tfrac{1}{2}\Phi_0(1+\cos(n\omega+\alpha_0)) \qquad (2)$$

was then proposed to model the remaining barrier energy. This added term was assumed to take some account of hybridization with *d* and *f* orbitals. Fortunately, it is not necessary to invoke this type of interaction in our calculation for iPP because the two-body forces hindering rotation are very much larger than is the case for ethane. The strong two-body intrachain forces acting to restrict rotation about both $\overline{c\alpha}$ and $\overline{m\alpha}$ bonds then make the neglect of any additional forces an acceptable approximation.

Conformational calculations were performed using the molecular design package[26] CHEMLAB-II, originally developed at Case Western Reserve University by A. J. Hopfinger[27]. The program PSCAN was used to rotate the three sets of torsional bonds. The conformational energy, as a function of the rotation angles of the two backbone carbons, was calculated using the rotation of the m–α bond that minimized the energy. All three sets of bonds were rotated at 5° intervals over most of their range, but a finer grid of 1° intervals was used near local minima. The results were plotted by the contour subroutine of the NCAR graphics package, which calculated the true contour lines by interpolating between data points.

RESULTS

The conformational energy associated with a single repeat unit is plotted in *Figure 2* as a function of the backbone carbon bond rotations, τ_1 and τ_2, after minimizing at each point with respect to the rotation angle τ_3 of the methyl group. Contours are drawn at intervals of 1.0 kcal mole^{-1} of monomers; this energy is obtained by dividing the conformational energy of the oligomer by six. We first note the expected symmetry under interchange of τ_1 and $-\tau_2$, corresponding to a transformation from left- to right-handed helices. The states in the upper right, above the $\tau_1=-\tau_2$ line, correspond to right-handed states, while those in the lower left are left-handed. Departures from perfect mirror symmetry about this diagonal in *Figure 2* originate in the sensitivity of the computation to roundoff errors. The energy along $\tau_1=-\tau_2$ is a line of local maxima, which restricts the conversion between left- and right-handed chains. In terms of the configuration drawn in *Figure 1*, the state where $(\tau_2,\tau_1)=(120°,0°)$ is a right-handed, down, 3_1 helix, while the $(0°,-120°)$ state is a left-handed, up, 3_1 helix. The contours for the alternate $\overline{m\alpha}=1.56$ Å distance were qualitatively similar to those for $\overline{m\alpha}=1.54$ Å, so only the latter have been presented. The smooth curve in *Figure 2* is the locus of all values (τ_2,τ_1) having a 120° rotation about the chain axis between monomeric units, and hence describes the possible 3_1 helices.

The overall minimum occurs at (127°,5°)—and therefore also at (−5°,−127°)—near the (120°,0°) rotations of the experimentally reported 3_1 helix. Previous calculations, some of which are noted in *Table 2*, have resulted in minima in the same neighbourhood in τ_1–τ_2 space, but the present calculation suggests slightly larger values for both τ_1 and τ_2 than previously suggested. All show minima near the range of values necessary to describe an exact 3_1 helix, a result that, as expected, appears largely independent of the magnitude of the torsional potential, and of the form of the non-bonded potential function. The absolute minimum must therefore reside in a shallow well determined predominantly by side group repulsions.

Allegra *et al.*[12] were the first to point out the presence of several local minima in addition to the absolute minimum near the 3_1 helix position. They noted ten minima, corresponding to five sets of left- and right-handed orientations. Our calculation indicates the presence of the six sets of local minima listed in *Table 3*; these are marked with the corresponding letter in *Figure 2*. The presence of these other minima suggests additional conformational states available to an isolated chain of iPP at a modest cost in energy. It should be noted that a proper treatment of the torsional potential should shift the relative energies of these minima by a small amount. The local minima for the bond length $\overline{m\alpha}=1.56$ Å are located at precisely the same rotations, but at a slightly lower energy.

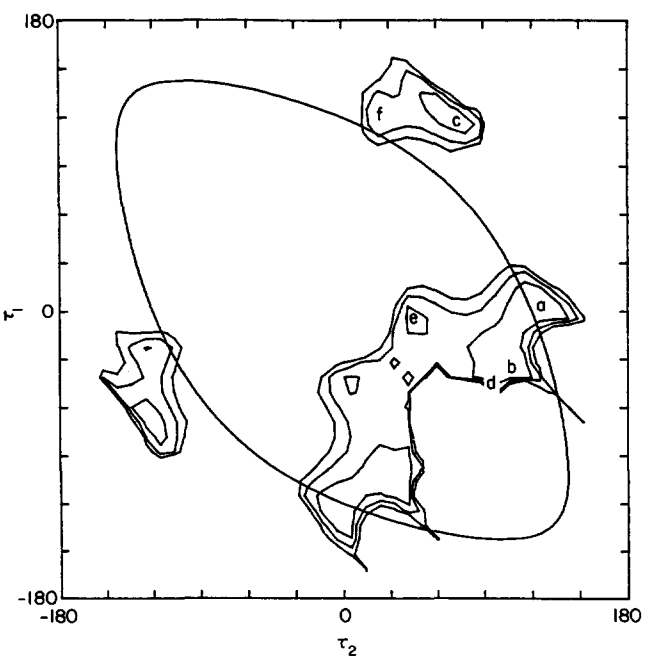

Figure 2 Contour plot of the conformational energy as a function of the torsional rotations τ_1 and τ_2. Contours are drawn at 1.0 kcal mol^{-1} intervals up to a maximum of 3 kcal mole^{-1} above the absolute minimum. Six local minima are labelled according to the order in *Table 3*. The smooth line is the locus in τ_1–τ_2 space of a 3_1 helix

Table 2 Comparison of assumptions and results of several conformational energy calculations. The quantities listed are defined in the text. (A) and (B) Borsova *et al.*[8], (C) DeSantis *et al.*[9], (D) Tadokoro *et al.*[11], (E) Corradini *et al.*[14], (F) this paper

	A	B	C	D	E	F
θ_{CxC}	114	109.5	114	114	116	114
P.E.	mix	mix	mix	6–12	6–12	6–12
Φ_0	3.0	3.0	0.0	2.0	2.8	0.0
n	3	3	2	20	2	6
$\{\tau_1,\tau_2\}$	0, 120	−20, 100	−3, 118	−1, 124	4, 120.5	5, 127
K_1	3	3.8	3.1	2.91	2.95	2.79

Table 3 Local minima in the conformational calculation, energy in kcal mol^{-1} per monomer, and the number of monomers, K_1, in a 2π rotation of the helix

	τ_1	τ_2	τ_3	Energy	K_1
(a)	5	127	105	0.00	2.79
(b)	−35	108	85	0.35	3.69
(c)	118	75	81	0.35	2.29
(d)	−47	95	86	0.50	4.25
(e)	−4	44	99	0.75	8.47
(f)	122	24	61	0.92	2.71

Finally we compute the effect of the methyl rotations upon the energy of each of these local minima. In *Figure 3* we plot the energy of each local minimum as a function of τ_3, the rotational angle of the m–α bond. The dependence is close to sinusoidal within the 0° to 120° range of the C_{3v} symmetric methyl group, as would be expected, except for curve (e), which exhibits a slight inflection.

The most striking aspect of these results is the large size of the barrier to rotation of the methyl group in comparison to the variation in energy as one passes from one local minimum in τ_1–τ_2–τ_3 space to another. This is particularly pronounced for the minima (c) and (f), in the upper part of *Figure 2*. Even for the minimum at (b) in *Figure 2*, for which the rotational barrier is the lowest shown in *Figure 3*, the energy to rotate the methyl group is several times larger than the energy that would be gained by a transition from (b) to (a). These results remain qualitatively the same for a choice of the bond length $\bar{m}\bar{\alpha} = 1.56$ Å, although the amplitude of the energy variation is slightly reduced.

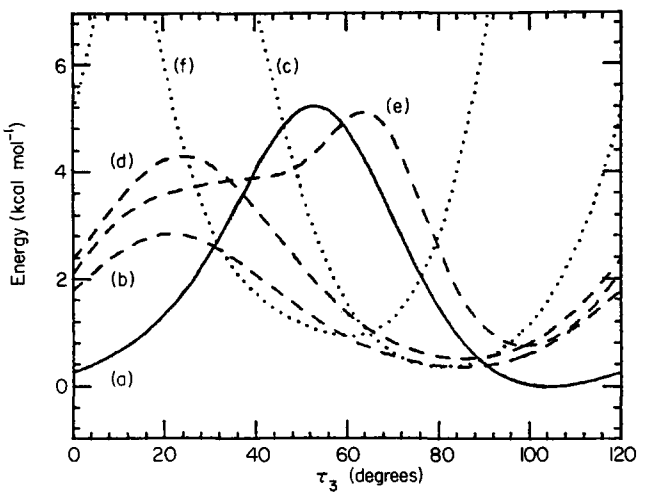

Figure 3 Energy of conformational local minima as a function of the rotational angle τ_3 of the methyl group. The curves correspond to the minima labelled in *Figure 2* and *Table 3*

DISCUSSION

The immediate conclusion to be drawn from this calculation is the fact that the conformational energy of iPP is dominated by the orientation of the methyl side groups. While such a phenomenon is clearly to be expected for polymers with bulky side groups, it is not an obvious result for the relatively small methyl. We further note that a calculation based solely upon non-bonded potentials yields a map of conformational energies that does not differ in any substantial way from those produced by previous calculations that have included torsional potentials. The importance of the location of the hydrogen atoms of the methyl groups, however, indicates the need for further study of the forms of the semi-empirical interatomic potentials. These improved potentials may be necessary to obtain accurate predictions of such experimental quantities as heats of formation, molecular geometry and vibrational frequencies.

It is only in the very simplest of polymers that the monomeric repeat unit has sufficient symmetry to make a commensurate structure the stable conformation of an isolated chain. In the case of iPP, the symmetry-breaking effect of the methyl side group removes any possibility that intrachain forces alone could yield a precise 3_1 helix. This is reflected in the results shown in *Figure 2*, in which the absolute minimum at (a) lies close to, but not on, the line defining the 3_1 helix.

This raises the question of the response of the chain to the interchain forces that will tend to constrain a three-dimensional crystal to be commensurate. If, at least on average, the chain rotates by 120° for each propylene repeat, then one of two possibilities must occur. Either the chain must be distorted to a pure helical structure that does not correspond to any minimum of the intrachain energy, or else the chain must take on a form that has short-range disorder but which allows each chain segment to lie in one of the local minima in the intrachain energy.

In the first case, the ordered structure will be formed as an exact 3_1 helix of minimum intrachain energy by seeking the minimum energy along the line in τ_1–τ_2 space that defines such a structure. We calculate the increase in intrachain energy above the absolute minimum to be 0.2 kcal mole^{-1} for this possibility. This is illustrated in *Figure 4*, which shows the potential energy along a line drawn from *a* to *b* in *Figure 2*. The periodic 3_1 helix has an energy represented by the solid curve at the point marked as 3_1 on the abscissa.

The alternative structure consists of a disordered sequence of chain segments possessing the exact long-range order of a 3_1 helix, but which has the short-range disorder of a mixture of segments from the minima at (a)

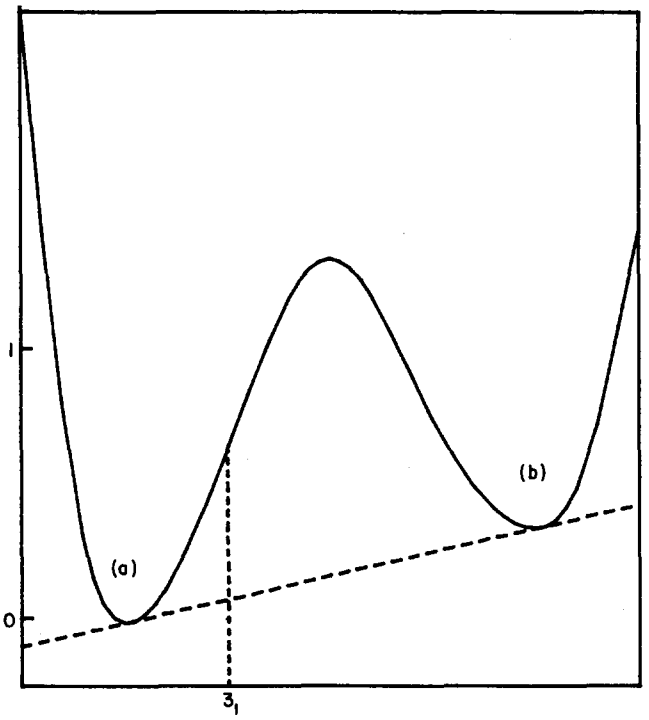

Figure 4 Conformational potential energy along the line in *Figure 2* from state (a) to state (b). The broken curve represents the estimated energy for a disordered state constructed as a combination of states (a) and (b)

and (b) in *Figure 2*. While we cannot calculate the conformational energy for each possible disordered array, we can make a rough estimate of the free energy difference between such a state and the all-(a) conformation. The helix at (a) yields a structure whose pitch differs from the pure 3_1 helix by 7.5%. The helix at (b), on the other hand, differs by -19%. An admixture of (a) and (b) segments in the ratio of roughly five to two will then approximate the correct pitch. The energy of such a system is hard to estimate, but is likely to be greater than that of a pure (a) by an amount somewhat larger than 2/7 of the energy difference between (b) and (a), namely 0.1 kcal mole^{-1}. This construction is shown as the broken line in *Figure 4*, and is seen to pass through the 3_1 pitch at a lower energy than the solid line. From this must be subtracted the effects of the entropy of disorder which will be $-0.59\,kT$ for a completely random structure, and smaller for a helix sufficiently ordered to maintain closeness to a regular 3_1 structure. For a chain in which two (b) segments are constrained to be present in every consecutive sequence of 7 monomer units, the entropy term would reduce the free energy by $0.43\,kT$. The disorder would then contribute -0.25 kcal mole^{-1} at room temperature, and lower the free energy of the incommensurate structure below that of the commensurate one.

The uncertainties involved in this estimate and the comparatively small difference between the energies of these two types of structure make it difficult to state definitively that the second type will be preferred in equilibrium; interchain forces could contribute an energy sufficient to drive the system towards the more ordered conformation. This is an example of a Frenkel–Kontorova process, and has been described in the context of such other helical polymers as poly(tetrafluoroethylene)[28].

The structure of *Figure 3* suggests a number of other questions related to the dynamics of the iPP chain. The presence of the 'mountain ridge' along the line $\tau_1 + \tau_2 = 0$ shows that there is a barrier to conversion between left- and right-handed chains. How, then, does the pairing of left- and right-handed helices occur in the formation of α-iPP? Is the handedness of a chain fixed at solidification from the melt? If so, then pairing must require an exchange of chains between different lattice sites. If, on the other hand, a left-to-right defect can be formed and propagate along a chain, then pairing can occur without lateral motion of a chain. The answers to these questions require the calculation of energies of structures that are not regular helices, and will be the subject of the following paper in this series.

ACKNOWLEDGEMENT

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