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

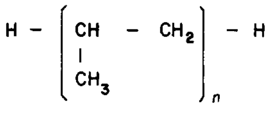
Isotactic polypropylene (iPP) is a commercially important polymer which has been studied extensively over the course of the last three decades. Early X-ray powder spectra[1] indicated amorphous, smectic (pseudo-hexagonal), and crystalline phases for iPP. Further experiments have given evidence for three 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



$$H-\left[\begin{array}{l}CH - CH_2\\ \;|\\ CH_3\end{array}\right]_n-H$$

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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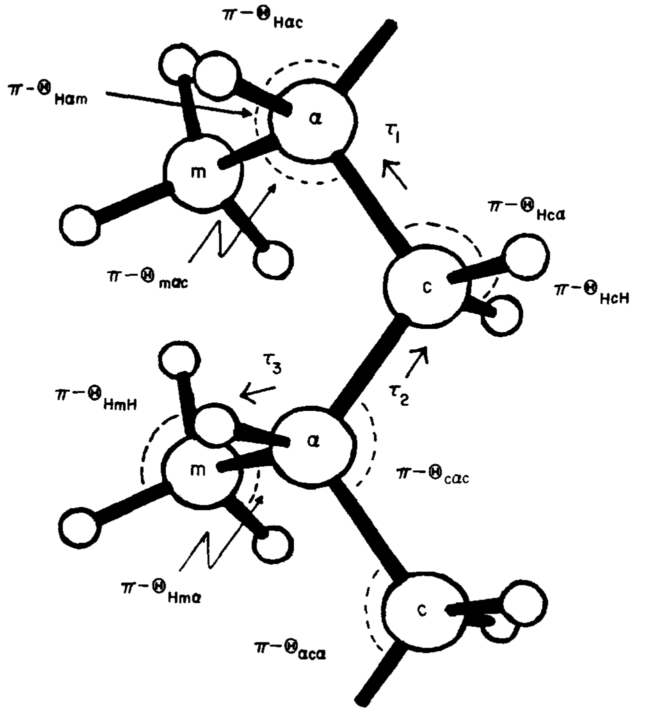

Figure 1 Configurational and conformational parameters of isotactic polypropylene

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 $H–m_n–\alpha_n–c_n = -32°$.

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 $c–\alpha–c = \alpha–c–\alpha = 114°$, 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