polymer reports

Possible models for the polyethylene hexagonal phase

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The high-pressure, high-temperature phase of polyethylene (PE) crystallizes in a hexagonal (or trigonal) lattice with $a = b = 4.8_8$ Å[1]. The specific volume increase of 0.08_5 ml g^{-1}, observed passing from the orthorhombic to the hexagonal phase[2], requires a c spacing for the ethylene unit of 2.45 Å. As Bassett, Block and Piermarini have pointed out[1] such a low value, compared to ~2.53 Å of the orthorhombic phase[3], is unlikely to be accounted for by a reduction of the $C\hat{C}C$ bond angle to ~106°, assuming a $\overline{CC}$ bond distance of 1.53 Å. Therefore these authors, on the basis of geometrical and energetical criteria, proposed a possible disordered helical conformation, formed mainly by *trans* bonds and with a small proportion of *gauche* bonds.

The aim of this paper is to show the occurrence of PE two-atom helices, with internal rotation angles near 180°, which can satisfy the known parameters and the packing requirements of the hexagonal phase without invoking disordered models. In a previous paper[4] it was found by means of potential energy calculations that PE, treated as a two-atom chain, presents a large flat minimum region around the transplanar conformation. As an example, the energy of the helix with both the dihedral angles equal to 170° differs from that of the zigzag planar structure by less than 0.1 kcal, although the semi-empirical potentials used were markedly hard. Moreover, by putting the $C\hat{C}C$ bond angles equal to 110° and the two internal rotation angles ψ_1 and ψ_2 equal to 165.3°, PE is arranged nearly as polytetrafluoroethylene[5,6], giving rise to a monomer repeat on the helical axis, Z, of 2.50 Å and to a three-fold screw axis. This aixs can be retained , Z decreased and R, the radius of the helix formed by the carbon atoms increased, if ψ_1 and ψ_2 vary little in an opposite sense near to 165° in such a way as to keep the angle of rotation φ about the helical axis constant and equal to 24° on passing from the ith atom to the $(i+Z)$th atom.

Furthermore, helices with a six-fold screw axis and φ equal to 20° or 15° can be generated in the same zone of ψ_1 and ψ_2 values. *Table* 1 collects some examples and lists the lowest H... H intermolecular contact resulting if these helices are packed in the unit cell of the PE hexagonal phase. *Figure* 1 shows the values assumed by ψ_1 and ψ_2 within the range 160°–174° for φ equal to 24°, 20° and 15°. The broken lines join helices with $Z = 2.45$ Å. All the calculations were performed by assuming $\overline{CC} = 1.53$ Å, $\overline{CH} = 1.08$ Å, $C\hat{C}C = 110°$ and $H\hat{C}C = 109.47°$.

Table 1 Some geometrical parameters of PE helices with three- and six-fold screw axis and shortest H . . . H intermolecular distances in the PE hexagonal cell

ψ_1 (degrees)	ψ_2 (degrees)	r (Å)	Z (Å)	ϕ (degrees)	d_m (H . . . H) (Å)
165.3	165.3	0.44	2.50	24	2.48
166.7	164.0	0.59	2.49	24	2.35
167.0	163.8	0.64	2.49	24	2.33
167.5	163.3	0.74	2.49	24	2.29
168.0	162.9	0.85	2.48	24	2.26
168.5	162.5	0.97	2.47	24	2.22
169.0	162.1	1.08	2.47	24	2.19
169.5	161.7	1.20	2.46	24	2.16
170.0	161.3	1.32	2.45	24	2.13
170.3	165.5	1.08	2.48	20	2.25
170.9	165.0	1.30	2.47	20	2.20
171.6	164.5	1.52	2.45	20	2.14
173.0	168.9	1.56	2.47	15	2.23
173.5	168.5	1.88	2.46	15	2.15
174.0	168.2	2.19	2.44	15	2.12

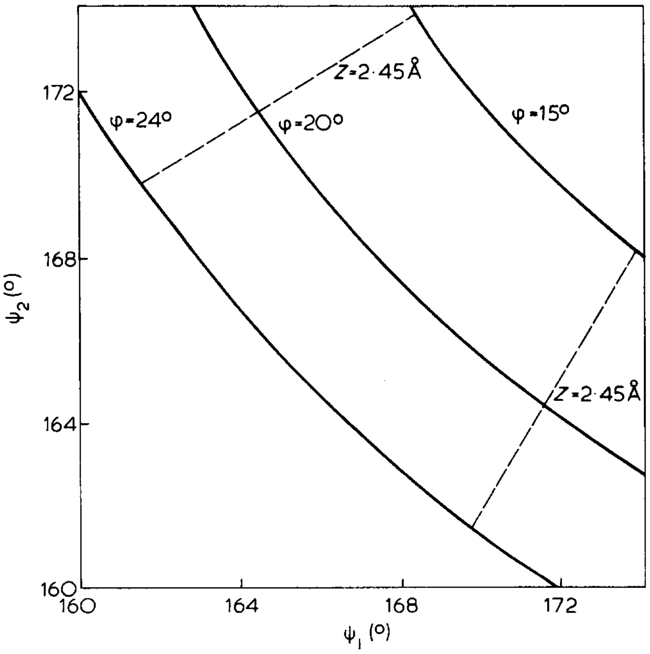

Figure 1 Helices with ϕ equal to 24°, 20° and 15° (full lines) as a function of ψ_1 and ψ_2. The helices with Z = 2.45 Å lie on the broken lines

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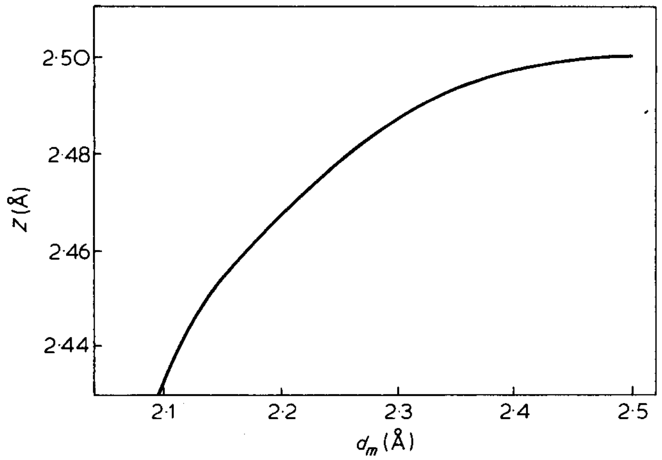

Figure 2 Plot of Z as a function of d_m (H . . . H) for the helices of *Table 1*

Conformations having six-fold screw axis with φ other than 24°, 20° and 15° (for example 12° or 10°) were not considered owing to their unsatisfactory Z and d_m(H... H) values.

Van der Waals energy calculations were carried out in order to verify if it were possible to determine which helices of those reported in *Table* 1 produce efficient packings. Potentials proposed by Bartell[7], Brant, Miller and Flory[8], Kitaigorodskii[9], Parsonage and Pemberton[10], Williams[11], Hopfinger[12] and Scott and Scheraga[13] were employed. Chains composed of 30 CH_2 groups were rotated by the same angle in the hexagonal cell. Unfortunately the energy generally decreases with r in the range investigated when the H...H potential presents an interatomic distance at the energy minimum, R_m, equal to or greater than 2.60 Å. Only the Hoppinger and Scott–Scheraga potentials have r_m less than 2.60 Å and in these cases the energy decrease is accompanied by the rise in r. Inspection of the results clearly showed the inadequacy of the potential energy calculations in establishing the most stable packings, since the energy minima strongly depend on the shape, hardness and r_m of the potentials. Therefore we resorted to the 'close contacts') criterion in order to judge the lattice stability of the hexagonal PE. By fixing the least allowed H...H intermolecular distance at 2.2Å it can be inferred that helices with Z in the range 2.46–2.47 Å (in reasonable agreement with the derived value of 2.45 Å) are possible (see *Table* 1). The behaviour of Z vs. d_m (H...H) for the data of *Table* 1 is represented by the curve, computed by least-squares fitting, shown in *Figure* 2.

However, greater Z and d_m (H...H) values cannot be excluded owing to the precision of at least 1% obtained in the measurements of the a axis[1]. As an example, for a equal to 4.85 Å Z becomes 2.48 Å if the volume of the ethylene unit is kept constant.

Finally it should be emphasized that the model of a transplanar conformation with a small percentage of *gauche* bonds seems to be unlikely since the planar zigzag chains in the hexagonal cell give rise to a d_m (H... H) of 2.8 Å, too large for efficient packing.

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