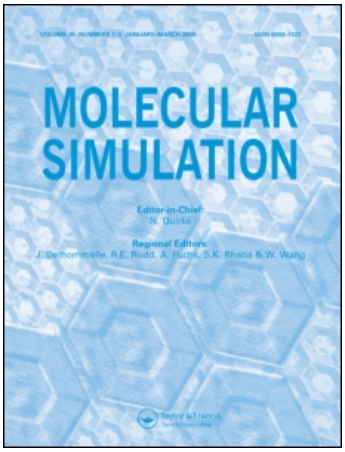

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MODELLING STUDIES OF CRYSTALLINE PEEK

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The x-ray diffraction spectrum of the engineering thermoplastic poly (aryl-ether-ether-ketone), commonly known as PEEK, has been reported in the literature. The unit cell dimensions are consistent with two aryl units per unit cell, while the chemical repeat has three, suggesting that there is not a strict lateral register between chains. The polymer chain packing of crystalline PEEK has been investigated using lattice energy calculations and it is concluded that lateral chain ordering effects are rather unimportant in determining the crystal structure. The crystallographic equivalence of ether and ketone linkages arises due to essentially random chain stacking.

KEY WORDS: Molecular modelling, crystal structure, thermoplastic polymers, PEEK

INTRODUCTION

In recent years there has been considerable interest in studying the structure and morphology of the engineering thermoplastic poly(aryl-ether-ether-ketone), frequently referred to as PEEK. This interest stems largely from the desire to understand at the molecular level the detailed behaviour which gives rise to PEEK's unique thermal and mechanical properties. The hope is that in turn such information will assist in the development of further high performance materials. Central to these studies has been the use of x-ray diffraction techniques to characterise the crystalline regions in a wide range of PEEK samples including mouldings, fibres and films [1–6].

Recent diffraction work [6] has established that the PEEK unit cell has orthorhombic geometry with lattice constants $a = 7.83$Å, $b = 5.94$Å and $c = 9.86$Å. The diffraction pattern is consistent with the crystallographic space group Pbcn in which there are two polymer segments per unit cell related by a 2_1 screw axis. The polymer chains lie in an extended zig-zag conformation and are aligned along the c-axis direction. Refinement of the structure indicates that the oxygen atoms lie in planes parallel to (100) and that the benzene rings are inclined to the latter at angles of approximately $\pm 37°$, alternately down the chain. In addition, the chain geometry at the ether and ketone linkages can be described adequately by a single bond angle of 125°. To illustrate the above descriptions, projections onto the (100), (010) and (100) planes of the PEEK unit cell are shown in Figures 1–3 respectively. The relationship between the chain fragment at the cell centre and those on the edges is of special note.

From the diffraction studies, the nature of the stacking between adjacent polymer

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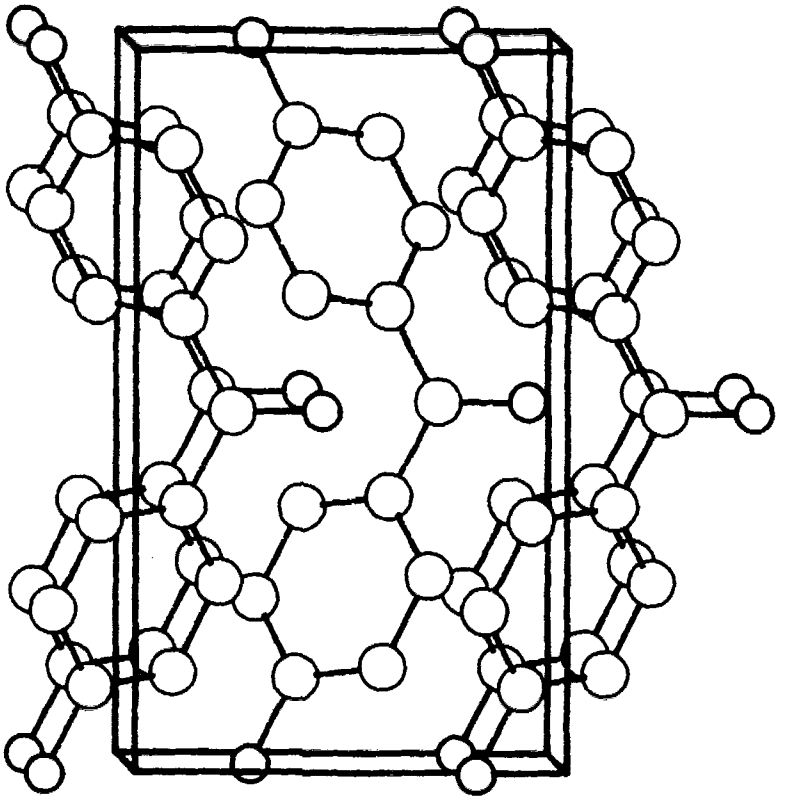

Figure 1 View along the a-axis of the PEEK unit cell.

chains remains unclear. and this provided the impetus behind the present work. As has been pointed out previously [1], the experimentally determined fibre repeat distance (ca 10Å) extends over only two aryl units, whereas the PEEK chemical repeat clearly involves three. If there was strict register between the ether and ketone groups of adjacent chains, a fibre repeat three times greater than inferred (i.e. extending over six aryl residues) would be expected in view of the requirements imposed by the space group Pbcn. Failure to observe strong reflections associated with such a superlattice argues that:

(1) within the precision of the measurements, the ether and ketone linkages are crystallographically equivalent.

(2) the crystallisation process may favour a more disordered, perhaps random, chain stacking in which lateral register is reduced or lost.

In order to investigate further the chain packing in crystalline PEEK, a series of packing energy calculations have been carried out. The chains were modelled by oligomers interacting via a simple atom-pair potential function containing steric and electrostatic terms. These results directly complement those obtained using diffraction methods and illustrate the strengths and limitations of molecular modelling in studying the structure and stability of crystalline polymers.

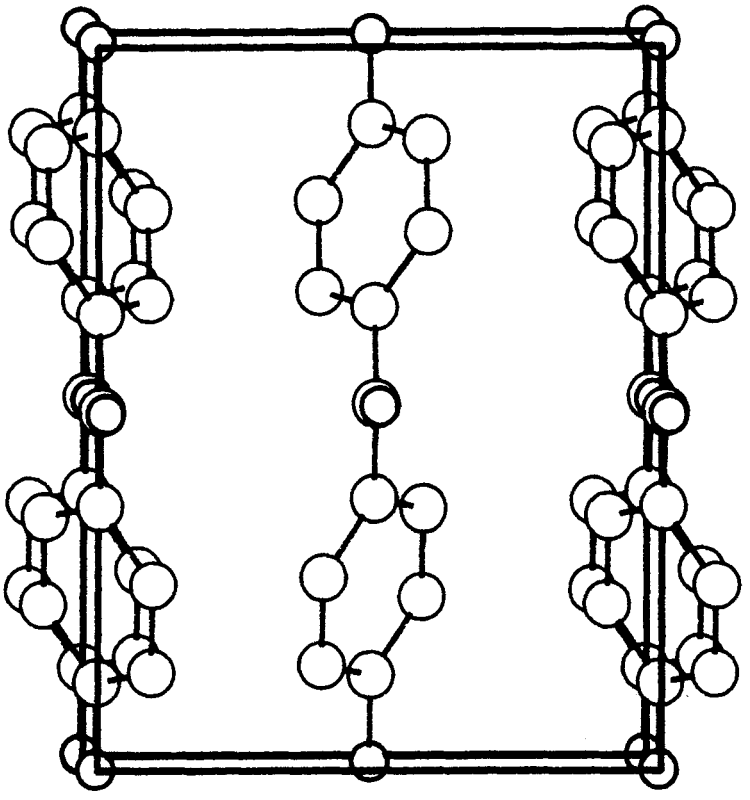

Figure 2 View along the b-axis of the PEEK unit cell.

CRYSTAL MODELS

The smallest array of chain fragments required to model crystal packing in PEEK is determined by two factors:

(i) the size of the PEEK repeat unit and

(ii) the range over which atom-pair interactions must be considered in order to represent the crystal environment correctly.

As discussed above, the smallest chain fragment consistent with both the symmetry requirements of the space group Pbcn and the chemical formula of PEEK contains six aryl units. Accordingly the repeat unit was modelled using the 6-ring structure (X) shown in Figure 4. The crystal packing energy was obtained by positioning this probe fragment centrally in an ordered array of longer chains and calculating its interaction energy with respect to the latter. The precise arrangement of the cluster is governed by the choice of lattice constants and space group Pbcn, with the condition that the ether and ketone linkages are treated as being equivalent.

Trial calculations indicate that 15 Å is a reasonable cutoff distance beyond which individual atom-atom contributions to the energy can be neglected. On the basis of the known lattice constants, the crystal model was therefore limited to a lattice of dimensions $4a \times 6b$ (approximately 31 Å by 35 Å) and packed with chains of length

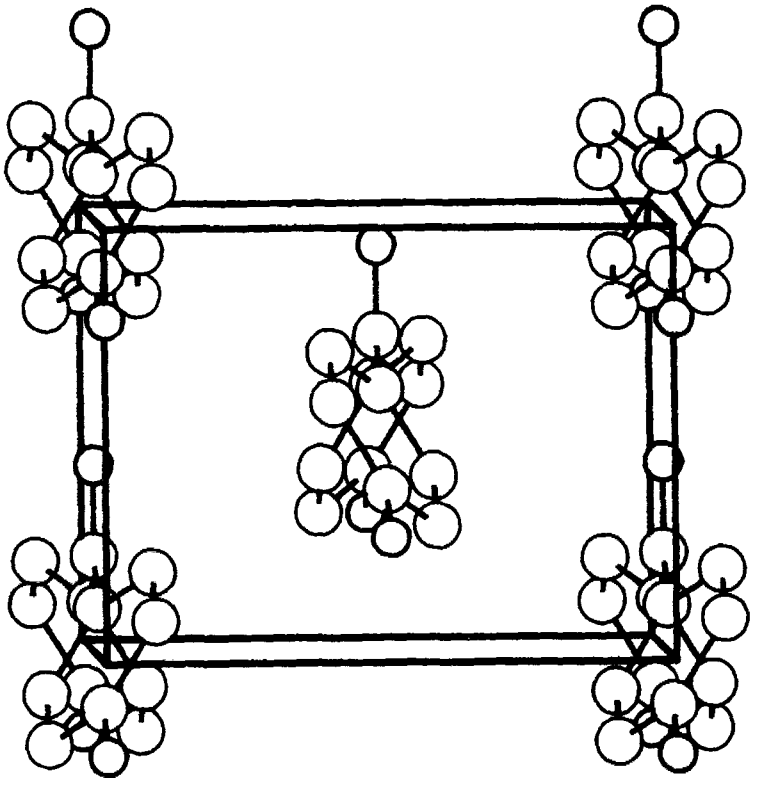

Figure 3 View along the c-axis (fibre axis) of the PEEK unit cell.

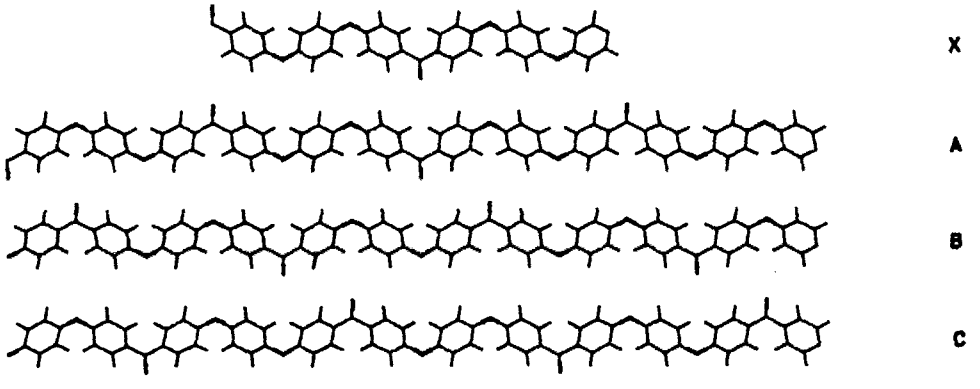

Figure 4 Molecular structures of the PEEK chain fragments (X, A-C) used in the lattice energy calculations.

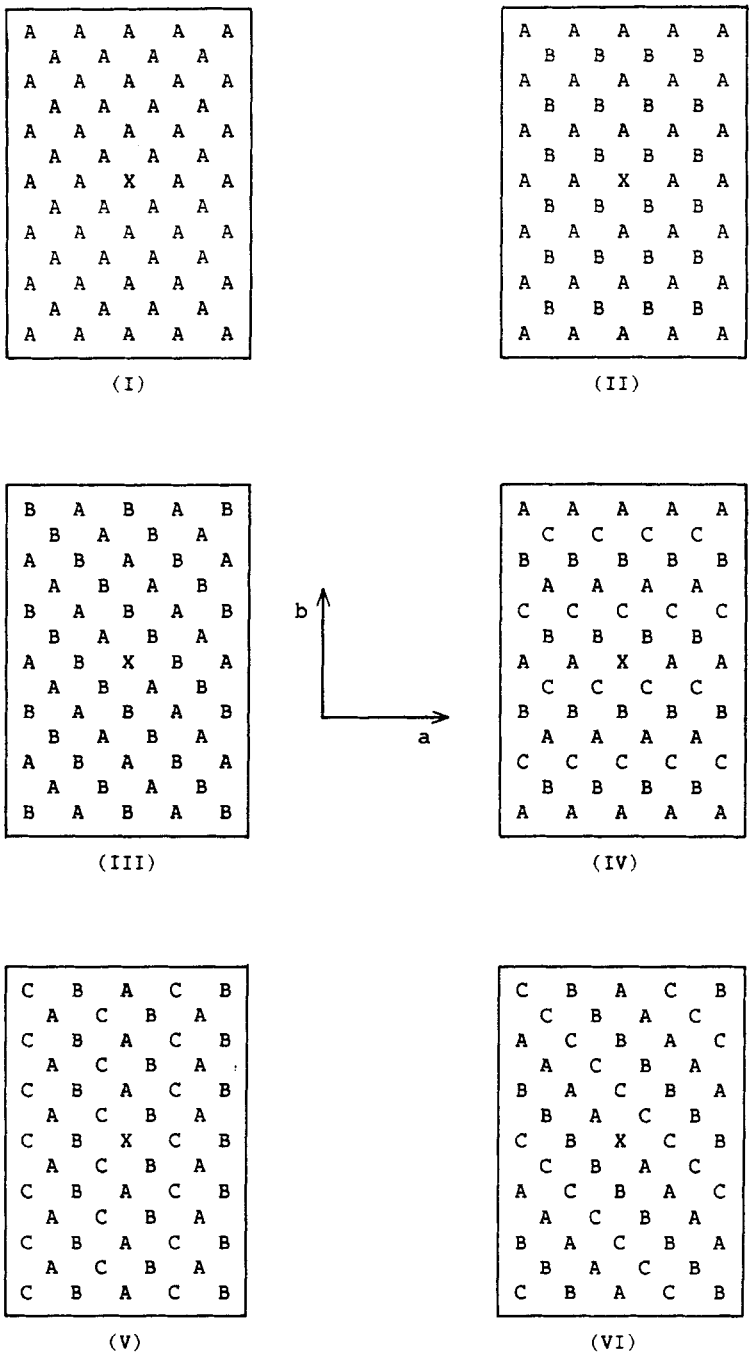

Figure 5 Schematic representations of the six chain packing arrangements considered (I-VI) viewed parallel to the c-axis. The labels X and A-C refer to the structures shown in Figure 4.

of approximately 60 Å, 12 aryl units per chain.

In order to model the possible ordered lateral packing arrangements of PEEK, three 12-ring structures are required (structures A-C, Figure 4). The sequence A-C is generated by systematically shifting the chain register. The chosen probe unit, X, maps symmetrically onto structure A.

In this study, six different cases of ordered lateral chain packing have been considered. The corresponding model structures are shown in Figure 5 and may be classified as follows:

I Perfect ordering

II Register parallel to the a- and b-axes

III Diagonal register with pattern repeat at every second chain along the *a*- and *b*-axes

IV Register parallel to the *a*-axis only

V Register parallel to the *b*-axis only

I Diagonal register with pattern repeat at every third chain along the *a*- and *b*-axes

In the above context, the term 'register' refers to the matching of ketone groups of adjacent chains in planes parallel to (001).

COMPUTATIONAL DETAILS

All lattice energy computations reported here were carried out with the Chem-X suite of programs [7] on a MicroVax II computer on an array of chains illustrated in Figure 6. The molecular models A-C and X were constructed using the geometry given by Fratini et al [6] and summarised in Table 1. The terminal atom vacancies in each chain were left unfilled in order to facilitate the calculation of strictly per-monomer energies and the correct representation of atomic charges. The atomic charges themselves were obtained by performing MOPAC calculations on the model compounds *M* and *N* shown in Figure 7, and mapping the resulting charges onto the chemical repeat unit. Only minor adjustments (less than 0.01 electron) were needed to achieve charge neutrality; the working values used in this paper are shown in Figure 8.

For each lattice, the interaction energy between the probe fragment *X* and all other chains was calculated using the following expression, summed over all atom pairs:

$$V = A \exp(-Br)/r^{D} - C/r^{6} + Kq_1q_2/\varepsilon r$$

In this equation, A, B, C and D are potential constants, K is a conversion factor, ε is the dielectric constant (and is fixed to 1.0) and q_1 and q_2 are atomic charges as determined above. In order to minimise end-chain effects and to make the results directly comparable, only terms in the range $0 < r < 15$ Å were included. The lattice energy per mole-of-monomer (for rigid chains) is obtained by dividing the summation by a factor of four. Initially, the crystal models were set up using the a and b values reported by Fratini *et al.* [6]. However, in order to test the sensitivity of the results and the energy parameterisation implemented with Chem-X, an alternative geometry was also used. The latter was obtained by constructing a closest-packed Pbcn array consisting of nine *X* chain fragments and by minimising the total interfragment energy as a function of displacements in the ab plane. This procedure is essentially equivalent

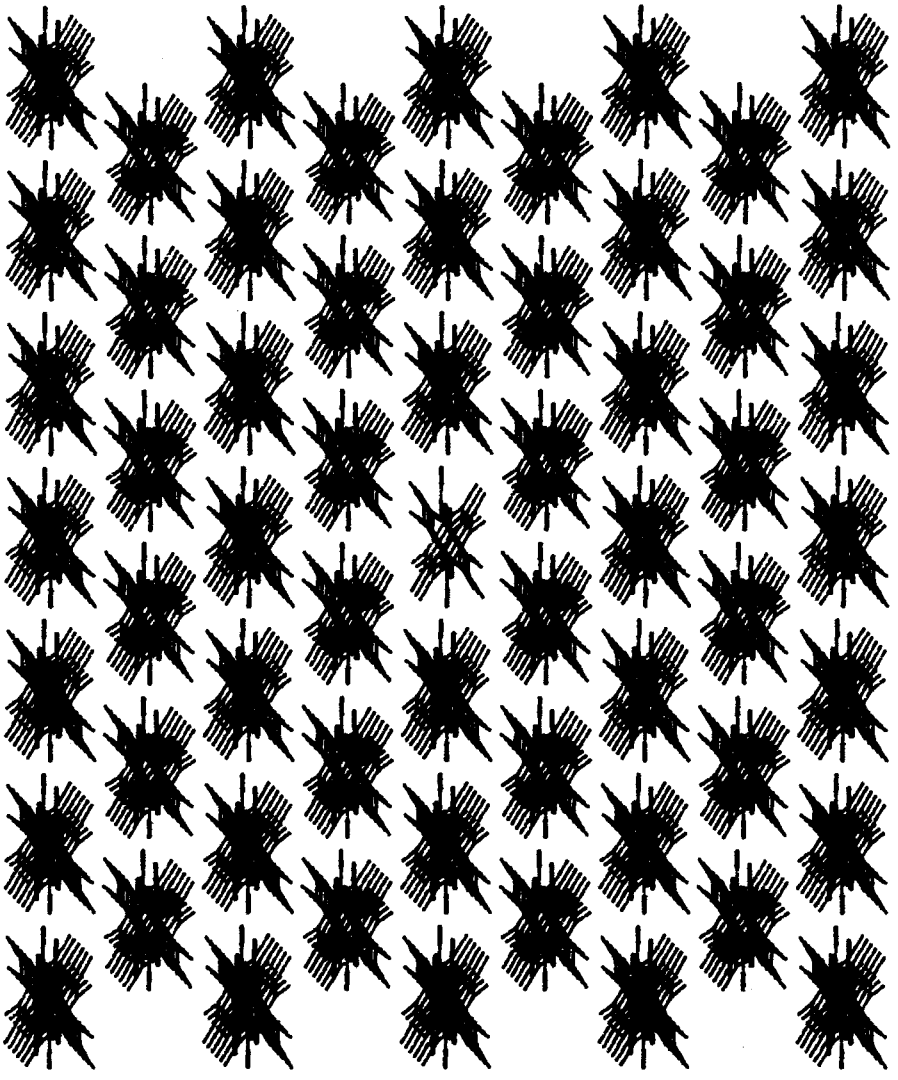

Figure 6 View of the central portion of Lattice I showing the embedded position of the probe fragment X.

to optimising the geometry of lattice I. From the final chain separations, the values $a = 7.94$Å and $b = 5.63$Å (which compare with the experimental values 7.83Å and 5.94Å) were inferred. As expected, the latter were found to be rather insensitive to the exact charge distribution used.

RESULTS AND DISCUSSION

The calculated lattice energies for each of the six chain stacking arrangements con-

Table 1 Molecular geometry used for constructing the PEEK chain model

Parameter	*Value*
$R(C\text{-}O)$	1.36 Å
$R(C=O)$	1.23 Å
$R(C\text{-}CO)$	1.47 Å
$R(C\text{-}C)$	1.395 Å
$R(C\text{-}H)$	1.05 Å
$\theta(C\text{-}O\text{-}C)$	125°
$\theta(C\text{-}CO\text{-}C)$	125°
$\phi(C\text{-}C\text{-}O\text{-}C)$	±37°
$\phi(C\text{-}C\text{-}CO\text{-}C)$	±37°

sidered are listed in Table 2. Also given are the non-bonded (steric) and electrostatic contributions to the energies, E_{nb} and E_{elec} respectively. The values in columns 1–3 were obtained using the experimental geometry (G1) whereas those in columns 4–6 refer to the optimised cell geometry (G2).

Several points are apparent from these results. First, for given lattice spacings, the total energy does not vary markedly on passing from one stacking arrangement to another. For both G1 and G2, the variations amount to about 2kJ/mole, or less than 2% of the mean lattice energies. Secondly, the G2 lattices are calculated to be about 4 kJ/mole more stable than those constructed using the experimental geometry, G1. The agreement is encouraging in view of the crude nature of the potential function used, as is the fact that the calculated and observed lattice constants differ by only about 0.1 and −0.3Å in the a and b directions respectively. Finally, it is found that electrostatic interactions account for about 9% of the total lattice energies. Note that the calculated E_{elec} values represent upper limits for the set of charges used since the dielectric constant, ε in Equation (1), was taken as unity.

Detailed analysis of the results reveals further trends in the data. For example, the G2 non-bonded energies for lattices I, II and V are greater than those for II, IV and

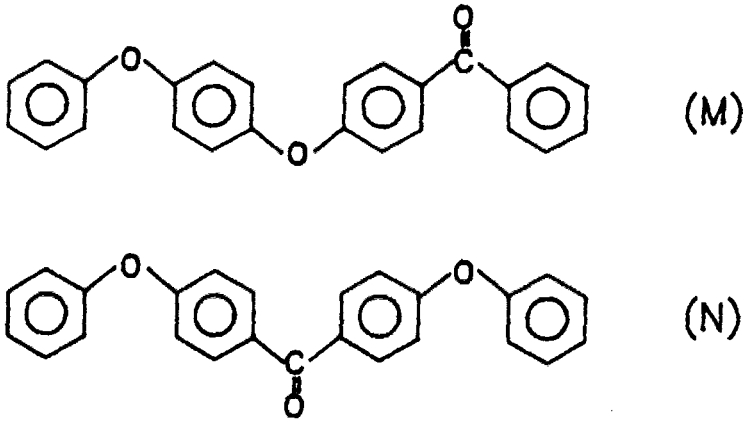

Figure 7 Model molecules used in MNDO calculation.

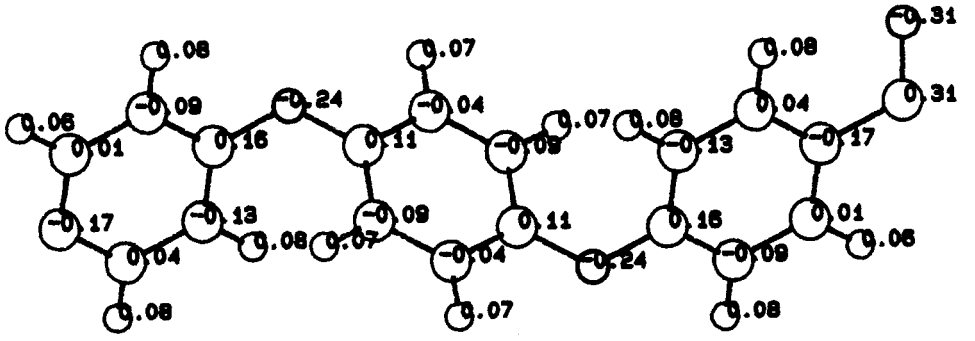

Figure 8 PEEK atomic charges used in the energy calculations and obtained from MNDO calculations.

VI by about 1 kJ/mole. This behaviour appears to be correlated with the presence or absence of chain register parallel to the b axis, i.e. in the direction of the carbonyl bonds. (See Figure 5.). However, in view of the smallness of the energy differences, and the fact that G2 is probably biassed towards lattice *I*, too much weight should not be attached to such observations.

An important question which remains is the significance of these results in terms of understanding the structure of crystalline PEEK. The problem of predicting polymer crystal structures on the basis of chain packing energy calculations is well known [8] and is hindered by the fact that statistical and kinetic effects may dominate. The approach taken here has been to make use of the well-known Regime I model for secondary nucleation kinetics [9] which has been used successfully to analyse spherulite growth in a number of systems including PEEK [10]. At constant temperature, the model predicts that the crystal growth rate G is given by

$$G = K \exp\left[-4b\sigma\sigma_e T_m^{02}/\Delta H_f \varrho k\, \Delta T\, T^2\right] \quad (2)$$

where b is the step height of the growth face, σ_e is the planar surface free energy of lamellar crystals, σ is the side surface energy, T_m^0 is the ideal crystal melting point, T is the crystallisation temperature, ΔH_f is the heat of fusion, ϱ is the crystal density, k is Boltzmann's constant, $\Delta T = T_m^0 - T$ and k is a proportionality constant. The relevant parameter values for PEEK (taken from reference [10]) are shown in Table 3.

Table 2 Calculated lattice energies for various chain stacking arrangements of PEEK. Individual contributions from the non-bonded and electrostatic terms are also given. All values in kJ/mol-monomer.

	Geometry 1[a]			*Geometry 2*[b]		
Lattice	E_{tot}	E_{nb}	E_{elec}	E_{tot}	E_{nb}	E_{elec}
I	117.0	108.2	8.8	121.6	112.1	9.5
II	116.3	107.5	8.8	121.1	111.8	9.3
III	116.1	107.6	8.5	119.6	110.7	8.9
IV	117.1	107.5	9.6	121.2	110.9	10.3
V	116.6	107.5	9.1	121.3	111.9	9.4
VI	117.9	107.7	10.2	121.9	111.1	10.8

[a] a = 7.83 Å, b = 5.94 Å (Reference 6)
[b] a = 7.94 Å, b = 5.63 Å (calculated)

Table 3 Experimental lamellar crystal parameters, taken from reference 10, used in the calculation of relative crystallisation rates

ΔH_f	130	J g^{-1}
σ	37	erg cm^{-2}
σ_e	49	erg cm^{-2}
T_m^0	668	K
b	4.68	Å
ϱ	1.40	g cm^{-3}

Table 4 Calculated ΔH_f values and relative rates of crystallisation for the six chain stacking arrangements considered.

Lattice	ΔH_f(J g^{-1})	*rel. rate*
I	130	1
II	128.3	0.8
III	123.1	0.4
IV	128.6	0.8
V	128.9	0.9
VI	131.1	1.2

In order to make use of the current data, the following assumptions have been made:

(1) the surface energies σ and σ_e are independent of the degree of lateral chain ordering, so the same values can be used throughout.

(2) the differences in calculated *G2* lattice energies are equal to the differences in heats of fusion for the six molecular stacking arrangements considered. Differences in entropies are neglected with such an assumption.

Setting ΔH_f for lattice *I* equal to the experimentally observed value (130 kJ/mole) and assuming a crystallisation temperature of 300 C, the relative crystallisation rates of lattices I-VI in Geometry 2 were calculated using Equation (2). The results are summarised in Table 4. On the basis of these numbers it seems clear that no single chain stacking arrangement is likely to dominate the crystal morphology. The calculated growth rates all lie within a factor of three of one another. It is therefore likely that lateral chain ordering effects are rather unimportant in determining the crystal structure of PEEK and that the crystallographic equivalence of the ether and ketone linkages arises due to essentially random chain stacking.

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