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Conformations in poly(ethylene terephthalate): a molecular modelling study

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Conformations in chains of poly(ethylene terephthalate) (PET) have been studied by using the molecular orbital package, *Mopac*, and the molecular modelling package, *Polygraf*. Both methods reveal two stable structures, namely one where the molecule is planar, and the other in which the CO–O–C–C dihedrals are rotated to $\sim\pm 80°$. These correspond to the well known triclinic crystal structure of PET and a new observed mesophase. Various methods were used to predict the moduli of such chains, both as isolated chains and in a crystal structure. A qualitative agreement with the experimental moduli was found.

(Keywords: poly(ethylene terephthalate); conformation; modulus)

INTRODUCTION

X-ray observations, using $\mathrm{CuK}\alpha$ radiation, have been made on samples of poly(ethylene terephthalate) (PET) fibres (supplied by Hoechst Celanese)[1]. The yarn, with a very low spun orientation, was drawn in one stage on a heated feed roll at 110°C, with a draw ratio of 4 ×. The yarn was cooled rapidly with air jets as it exited the feed roll in order to localize the draw to the roll and inhibit crystallization. The meridional X-ray scan (*Figure 1*) shows a remarkably sharp reflection at 8.6°, as well as reflections at $\sim 26°$ and $\sim 43°$. It is thought that this reflection, which corresponds to a repeat distance of 10.3 Å, is due to a mesophase; the usual triclinic form of PET has a repeat spacing of 10.7 Å[2]. The 26° and 43° reflections that are observed could be the 3rd- and 5th-order reflections from this mesophase, but the triclinic $\bar{1}03$ and $\bar{1}05$ reflections are at similar angles so no positive identification can be made. Such a mesophase has been seen previously by other workers[3,4].

Measurements of the crystal modulus of PET, using X-ray techniques, have been made[5,6], and these show that the moduli of the triclinic form and the mesophase are similar, with the mesophase having a slightly higher modulus. (These moduli are given in *Table 1*, below.)

This paper explores the use of molecular modelling techniques to build and evaluate possible structures for this mesophase, and to attempt to predict the crystal moduli of both phases.

EVALUATION OF SINGLE CHAIN STRUCTURES

The semi-empirical molecular orbital package, *Mopac*[7], running on a Silicon Graphics Indigo R4000 workstation, was used to evaluate possible structures for the PET chains.

Chains were built in two initial conformations (*Figure 2*). In the first case, conformation T_1, the aromatic ring and carbonyl groups were planar, with the ethylene residue fully extended in an all-*trans* conformation. An alternative conformation, T_2, had certain dihedrals rotated (labelled as A in *Figure 3*), so as to give a *cis–trans* conformation. A translation vector was included in the *Mopac* data file to model an infinite polymer chain. Only a single repeat unit was required to give a translation vector greater than 10 Å, as is required by *Mopac*.

The *Mopac* program, using the AM1 Hamiltonian[8], was used to optimize the conformation of these two initial structures. The conformation T_1 showed very little change. When the T_2 conformation was optimized, however, the dihedrals A rotated to $\sim 77°$ (*Figure 4*).

It can be seen, therefore, that there exist two stable conformations of PET, namely the all-*trans* T_1 conformation and the modified T_2 conformation. The repeat lengths calculated for these minimized conformations were 10.84 and 10.60 Å, respectively. The planar conformation T_1 is associated with the triclinic phase, while the modified T_2 conformation is associated with the mesophase. The calculated repeat lengths are slightly higher than the experimental repeat distances (10.75 Å in triclinic PET and 10.3 Å in the mesophase); this difference may be because only an isolated chain is being considered.

Our generated conformation of the mesomorphic form of PET is in agreement with that reported by Auriemma *et al.*[4]. By considering isolated chains, they calculated the minimum energy orientations of the A dihedral to be 180 and $\pm 80°$. Similar types of conformations have also been predicted for poly(butylene terephthalate)[9], in which a phase transformation occurs between the all-*trans* conformation and an alternative conformation in which there has been rotation about the O–C dihedral.

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CRYSTAL STRUCTURES

In order to investigate the effect on the chain conformation of other chains in the crystal structure, the molecular simulation package, *Polygraf*[10], was used with the Dreiding force field[11]. This allowed the two initial conformations to be placed in a unit cell which was initially set to a size obtained from the literature[2]. Both the atom positions and unit cell dimensions were allowed to alter as the program found a minimum energy conformation.

After minimization, the two conformations were similar to those produced by *Mopac*. The T_1 conformation remained planar, with a repeat length of 11.01 Å, while for the T_2 conformation the A dihedrals rotated to ~70° and the repeat length was 10.81 Å. Therefore, the two stable conformations that are observed for single chains in the *Mopac* calculations are still stable when the chains are in a crystal lattice. These two minimized unit cells are shown in *Figure 5*.

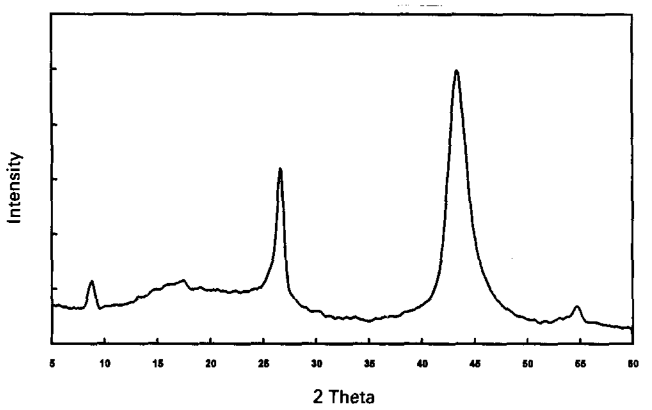

Figure 1 X-ray meridional scan of specially drawn PET fibre (see ref. 1)

Table 1 Experimental and calculated values of PET crystal moduli

	X-ray[a]		Single chain[b] (applied strain)		Unit cell[b]	
Conformation	*ACM*	E_c	*Mopac*	*Polygraf*	Applied strain	Applied stress
T_1	74	110	244	198	192	157
T_2	86	–	115	168	217	182

[a] *ACM* is the apparent crystal modulus determined from X-ray measurements, with E_c the corrected value, taking into account the inhomogeneity of stress in the sample[5]

[b] Applied strain and applied stress refer to methods of calculating the modulus (see text for details)

The repeat lengths, although showing the same trends as the experimental and *Mopac* values, are higher. This is thought to be due to the forcefield parameters that are used. The *Polygraf* program calculates the energy of the structure from a database containing the contributions from various bonded and non-bonded interactions. The equilibrium values and force constants are chosen to best fit the data from a selection of test molecules. However, these parameters are not specifically optimized for PET.

PREDICTION OF MODULI

Experimental calculations of the crystal modulus for the two forms of PET, measured by recording the shift of the X-ray diffraction maxima when a macroscopic stress is imposed on the fibre[12], show that the two forms have similar moduli, with the mesophase having a slightly higher modulus than the triclinic form (see *Table 1*). The apparent crystal modulus (*ACM*) shown in the table is a lower estimate of the true modulus, since it does not take into account any effects due to inhomogeneous stress[5]; a microscopic crystal strain is being related to a macroscopic stress.

The forcefield approach may be used to estimate the crystal moduli of polymer chains. For example, Tashiro *et al.*[13] used a valence forcefield, obtained from vibrational analysis, together with geometry changes from X-ray diffraction measurements, and obtained a modulus of 95 GPa for triclinic PET.

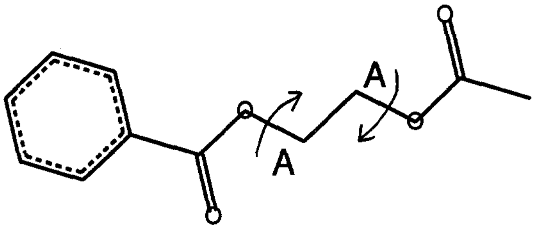

Figure 3 Portion of a PET chain showing the labelled dihedrals A (as referred to in the text)

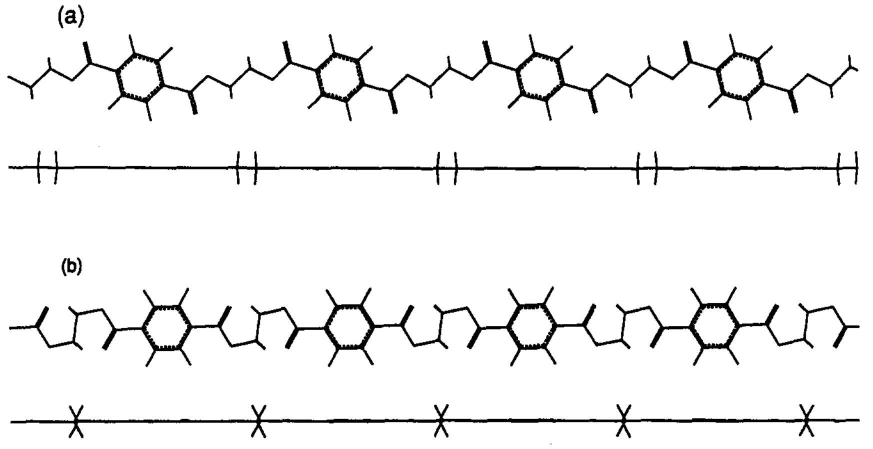

Figure 2 Initial conformations of single PET chains shown from two viewpoints: (a) conformation T_1; (b) conformation T_2

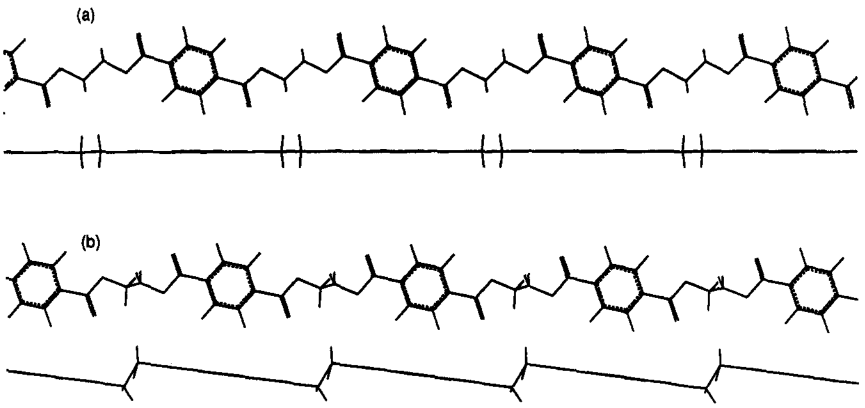

Figure 4 Conformations of single PET chains after minimization by *Mopac*: (a) conformation T_1; (b) conformation T_2

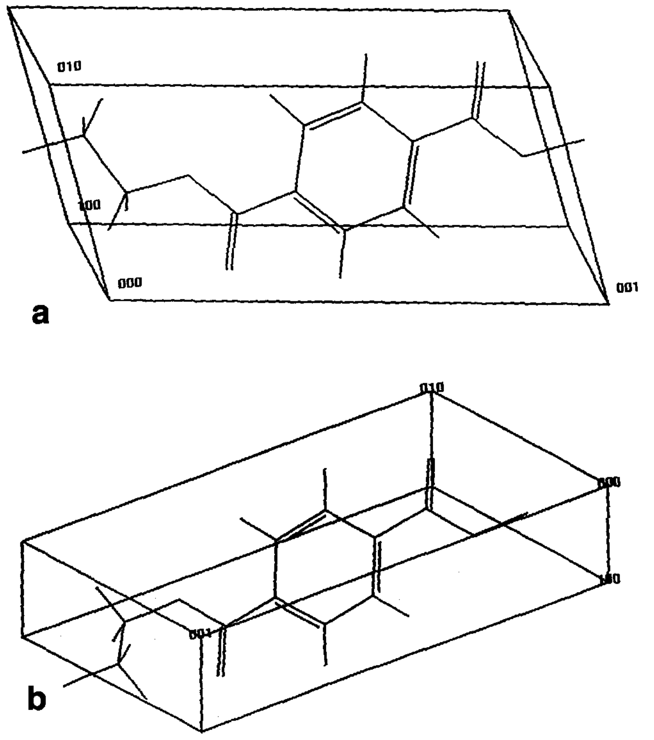

Figure 5 Minimized unit cells for PET, calculated by *Polygraf*: (a) conformation T_1; (b) conformation T_2

Two approaches were used to calculate the modulus of the two structures found above. In the first method, the repeat spacing (*Mopac* translation vector or *Polygraf* c-axis length) was systematically changed by ±1% from its equilibrium value, and at each stage the energy of the structure re-evaluated. By fitting a quadratic expression to the energy E as a function of the repeat spacing x ($(E-E_0)=\frac{1}{2}k(x-x_0)^2$) a value for the stiffness k can be found and, together with an assumed cross-sectional area, a modulus may be estimated.

Using the above method, with reported values of the undeformed unit cell dimensions, *Mopac* can be used to find the modulus for a single chain. With *Polygraf*, the minimized unit cell can be similarly used to obtain a value for the crystal cell modulus. In this calculation, the other cell parameters (a, b, α, β and γ) were also fixed, since although an option to allow them to alter was available, it did not work correctly. Thus, a stiffness was in fact calculated in this case, rather than a modulus, which would require the remaining cell parameters to be allowed to alter as the c-axis length is changed.

It was also possible in *Polygraf* to calculate a modulus for a single chain, thus allowing a comparison with the *Mopac* values. This was achieved by setting the a and b dimensions of the cell to a value larger than the range of non-bonded interactions (say 20 Å) so as to remove the effect of adjacent chains in the calculations.

An alternative method to obtain the modulus of a unit cell in *Polygraf* is to modify the energy expression to include external stresses and optimize the dimensions of the unit cell, as well as the positions of the atoms. From the change in the length of the c-axis with applied stress, a crystal modulus can be evaluated. The results from all of these calculations are given in *Table 1*.

The calculations on single chains show the T_1 conformation to have a higher modulus than the T_2 conformation, which is what would be expected since the T_1 conformation has no rotatable dihedrals. This does not agree with the experimental observations. The results for the unit cells, however, show the two conformations to have similar moduli, with T_2 higher than T_1, i.e. in agreement with experiment.

All of the calculated values are much higher than the X-ray data. A partial explanation is that the X-ray experiment gives a lower bound to the modulus[5]; however, we have only considered here a single repeat unit (and periodic boundary conditions) and so have modelled a perfect crystal whose modulus would represent an upper bound on the modulus of a real material. There are also problems with the suitability of the forcefield parameters used in the *Polygraf* program for PET.

CONCLUSIONS

Using molecular modelling techniques, it has proved possible to generate two stable structures for PET. In one structure the PET chains are fully extended, corresponding to the usual triclinic form, while in the other form the A dihedrals (see *Figure 3*) are rotated to ~ ±80°. This latter structure is assigned to the mesomorphic form of PET that has been observed in specially drawn fibres. The relative repeat lengths of the two calculated structures are in agreement with the experimental data, but the absolute lengths, however, are too high.

Two different methods were used to predict the crystal modulus of both the triclinic and the mesophase form of PET, either by imposing a strain on the system and calculating the change in energy, or by imposing an external stress and then calculating the strain. This was performed on both single chains and for a crystal structure. For single chains the fully extended conformation has the higher modulus, while in a crystal structure the rotated *cis*-form has a higher modulus, which is more in agreement with experimental observations. However, the calculated moduli are generally higher than the experimental values.

Forcefield approaches to modelling are much faster than quantum mechanical approaches, but the value of the results depends crucially on the quality of the parameterization of the forcefield. For good results, particularly for properties other than simple equilibrium geometries, some modification of the supplied forcefields appears necessary. Work is in progress to calculate better forcefield parameters using *ab initio* calculations.

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