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Crystallinity in poly(vinyl alcohol)
2. Computer modelling of crystal structure over a range of tacticities

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In Part 1 of this series, the behaviour of the crystalline phase in atactic poly(vinyl alcohol) was discussed. This paper examines the detail of the crystal structure by use of molecular mechanics modelling, and extends the prediction of crystal structure across the whole range of tacticity, the extremes of which have yet to be synthesised. The variation in the crystal structure with changes in tacticity is modelled in the light of experimentally observed changes in physical properties. As the extremes of stereoregularity are approached, novel crystal structures are considered and extensive comparisons made with existing X-ray diffraction data for the limited tacticity range available experimentally. A crystal structure is proposed for a recently synthesised isotactic rich polymer which was observed to have a distinctly different X-ray powder diffraction trace from the atactic material. Finally, the possibility that water may be incorporated into the atactic crystal structure is discussed and the change in the X-ray diffraction behaviour if water is included is simulated for comparison with experimental data. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(vinyl alcohol); hydrogen bonding; crystal structure)

INTRODUCTION

Commercial poly(vinyl alcohol) (PVOH) is atactic, but nevertheless shows high levels (up to about 50%) of crystallinity. The synthesis of increasingly stereoregular PVOH has led to as-yet unexplained trends in crystallisability and water solubility with tacticity. Provocatively, as the stereoregularity increases, the crystallinity is generally reduced, particularly in the case of isotactic-rich polymers[1].

Bunn[2], in his model of an atactic PVOH crystal, suggested possible intermolecular hydrogen bonding directions within the crystal. No intramolecular hydrogen bonds were indicated, and the positions of the hydrogen atoms were not specifically included. Note that the CH(OH) carbon lies opposite a CH_2 carbon on the adjacent chains. Thus each alcohol hydrogen has hydrogen bonding opportunities with the oxygens on a neighbouring chain both slightly above and slightly below it.

Recent publications (for example Kusanagi and Ishimoto[3] and Sakurada[4]) have discussed two alternative crystal structures for atactic PVOH. One of these is based on the Bunn structure, but, rather than the molecules being placed in the slightly obtuse angle of the monoclinic unit cell, as illustrated in the diagram of Bunn's original publication, the molecules sit in the acute angle‡. The second alternative structure is that proposed by Sakurada *et al.*[5]. The three structures are summarised in *Figure 1*.

The questions remain as to what hydrogen bonding exists within the crystal, and what effect the tacticity has on the hydrogen bonding and the crystal structure in general. Hydrogen bonding influences the crystallisability and the physical and thermomechanical properties of the crystal, as explained in detail in our preceding paper[6]. It also affects the dissolution temperature. In addition, the proposals of alternative structures in the literature would suggest that further validation of the Bunn structure is necessary for its universal acceptance.

Recently, a novel X-ray powder diffraction trace has been published[7] of a highly isotactic PVOH, which suggests a crystal structure distinct from that proposed by Bunn[2].

The advent of crystal structure modelling packages has allowed a detailed study of not only the conformations of the chains within a crystal, but also the hydrogen bonding directions, and it allows a direct and easy comparison of experimental X-ray diffraction traces with those simulated from proposed structures. The modelling work presented here was performed within *Cerius*^{2}§.

ISOLATED CHAINS

In order to incorporate both syndiotactic and isotactic units of PVOH into the proposed atactic crystal structure, both units must take up conformations close to planar zigzag. In particular, the –OH groups, being larger than the hydrogens, should not prevent isotactic units packing in this way. The two tacticities must also be able to pack in this conformation with the same lattice repeat along the chain axis.

The conformations of isotactic and syndiotactic isolated chains were investigated using MOPAC VI:AM1.

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‡ This structure may be constructed from the co-ordinates of the atoms published in Bunn's letter if the origin of the unit cell is set at the obtuse angle

§ Molecular Simulations Inc., San Diego, CA, USA

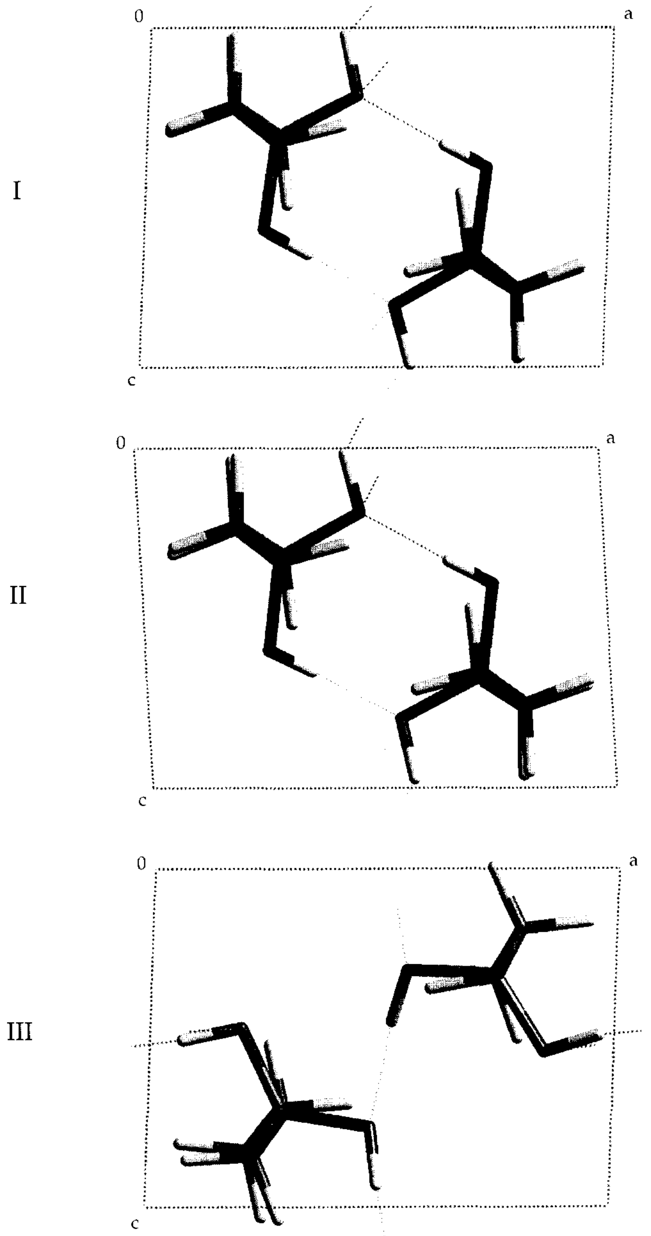


Figure 1 Summary of the three crystal structures for atactic PVOH frequently discussed in published literature. In each case the unit cell is drawn as projected along the molecular axis. I: Bunn structure; II: Bunn structure modified to have molecules sitting in the acute angle of the monoclinic unit cell; III: the alternative crystal structure proposed by Sakurada *et al.*[5]. These are different models from equivalent diffraction data, so the lattice parameters are the same for each (with appropriate transformations of the axes)

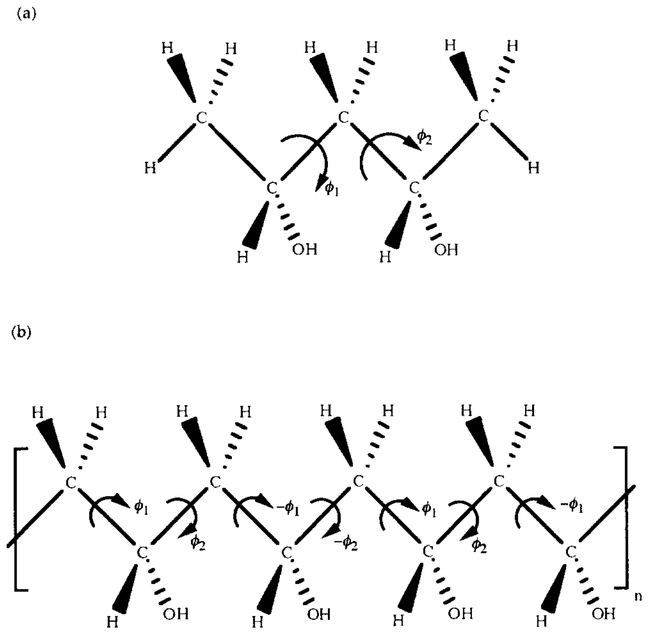


Figure 2 The torsion angles as fixed for MOPAC calculations: (a) torsion angle variables ϕ_1 and ϕ_2 used in mapping conformational space for the 2,4 pentanediol molecules; (b) torsion angles defined for finding the minimum energy close to planar zig-zag for the polymers

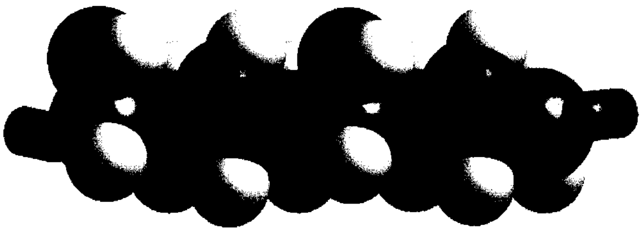


Figure 3 Minimum energy conformation close to planar zig-zag of an isolated isotactic PVOH polymer chain, as calculated by MOPAC

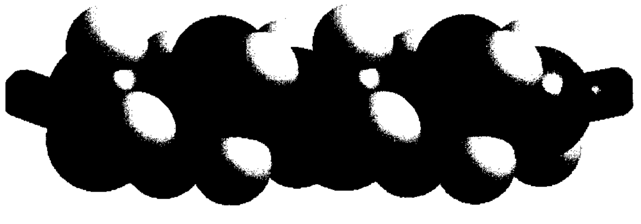


Figure 4 Minimum energy conformation close to planar zig-zag of an isolated syndiotactic PVOH polymer chain with intramolecular hydrogen bonding, as calculated by MOPAC

Conformational energies were first calculated for molecules of 2,4 pentanediol: *meso*-2,4-pentanediol as a model molecule for isotactic PVOH and *racemic*-2,4-pentanediol as a model for syndiotactic PVOH. The heat of formation of a minimised structure in which two torsion angles ϕ_1 and ϕ_2 (as defined in *Figure 2a*) were fixed was calculated for various values of ϕ_1 and ϕ_2 over the complete range (0–360°). Two minima were found for each of the *meso* and *racemic* structures: one close to the planar zig-zag conformation (180°, 180°) and the other close to 180°, 60° (which would indicate the formation of a 3_1 helical structure in the polymer).

To examine the exact torsion angles of the conformational energy minima in the polymer close to the planar zig-zag conformation, a four-monomer repeat unit of a fully isotactic or a fully syndiotactic oligomer with polymerisation links on each end was constructed and placed in a chosen conformation with fixed carbon–carbon torsion angles. The torsion angles were set in the sequence ϕ_1, ϕ_2, $-\phi_1$, $-\phi_2$, as illustrated in *Figure 2b*, to reflect the symmetry of the syndiotactic units, and to allow the conformation to twist away from an exact planar zig-zag while still maintaining an overall straight shape which could pack into a crystal. With these torsion angles fixed, the structure was minimised in MOPAC, recording the final heat of formation of the molecules in this conformation. In this way, by trying different combinations of ϕ_1 and ϕ_2, the exact minimum energy conformation for the polymer close

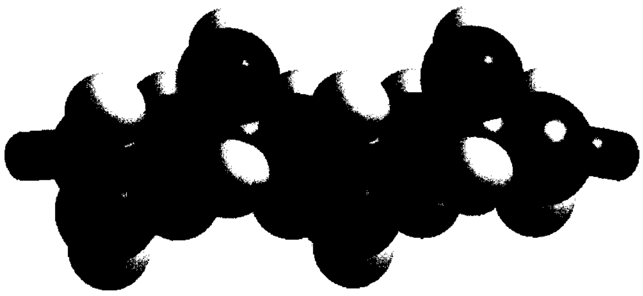
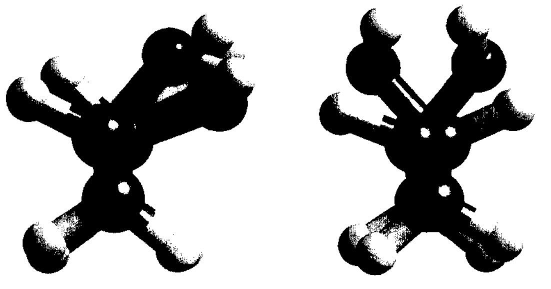
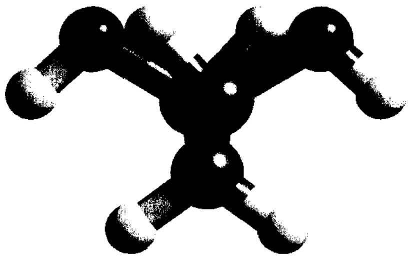


Figure 5 Minimum energy conformation close to planar zig-zag of an isolated syndiotactic PVOH polymer chain without the alcohol hydrogens lying between adjacent oxygens, as calculated by MOPAC



Isotactic
CCCC torsions: 190 170 170 190
HCOH torsions: 40 160 40 160
ΔH=-231.15kCal/mol

Syndiotactic
CCCC torsions: 160 190 200 170
HCOH torsions: 60 -60 60 -60
ΔH=-227.26kCal/mol



Syndiotactic
CCCC torsions: 190 170 170 190
HCOH torsions: 180 180 180 180
ΔH=-228.25kCal/mol

Figure 6 Summary of the three minimum energy conformations predicted by MOPAC. The polymer chains are viewed along the chain axis to show that the -OH groups in the isotactic and non-H-bonded syndiotactic are further apart from one another than for perfect planar zig-zag, but, for the case of the intramolecularly hydrogen bonded syndiotactic molecule, the -OH groups are drawn closer together

to planar zig-zag may be determined. The polymer repeat distance for this unit was fixed at 10.092 Å in all cases. This is the crystal structure repeat for four-monomer units from a unit cell repeat along the chain axis of 2.523 Å. The -OH bond is free to lie along any direction, and this will, naturally, affect the conformational energy, but MOPAC minimisation is unable to rotate the -OH bond fully between local minima to find the direction with an overall minimum conformational energy, and so in each case the minimisation was begun with the -OH bond in each of several starting directions and only the lowest minimum value of the conformational energy was recorded.

The minimum energy conformation found for the isotactic polymer is shown in *Figure 3*. The carbon–carbon torsions are pushed slightly away from 180° in order to leave a little more space between the neighbouring oxygens. The alcohol hydrogens always lie between the neighbouring oxygens to shield the electronegativity and/or to form a hydrogen bond. Two possible minimum energy structures were found for the syndiotactic polymer, each with different directions for the -OH bond. In one structure (*Figure 4*), the -OH bonds tend to lie along the chain axis, falling between the oxygens on neighbouring monomer units. The oxygens are pushed slightly closer together by the twisting of the chain axis slightly away from the planar zig-zag conformation, thus allowing the alcohol hydrogen to sit at a favourable distance from the adjacent oxygen. Alternatively (*Figure 5*), the alcohol hydrogens lie out of the way of interactions with neighbouring oxygens, and consequently, in order to reduce the oxygen–oxygen interaction energy, the oxygen atoms in the minimum structure are pushed further apart than for planar zig-zag by slight changes in the backbone torsion angles. Note that the heat of formation of this structure is slightly lower than for the hydrogen bonded syndiotactic structure, and that the isotactic minimum has a yet lower heat of formation. No minimised structure in which the alcohol hydrogens do not interact with adjacent oxygens was found for the isotactic case.

The three minimum energy structures with the correct molecular repeat distance for the crystal are summarised in *Figure 6*, which shows the view along the chain axis. This highlights the slight differences in conformation to best accommodate oxygen–oxygen or oxygen–hydrogen–oxygen interactions.

In conclusion, an isotactic structure close to the planar zig-zag conformation is favourable because, by pushing the chain slightly away from the planar zig-zag conformation, the oxygen atoms can easily be accommodated and the alcohol hydrogens can fit between neighbouring oxygens, reducing oxygen–oxygen interactions and/or allowing intramolecular hydrogen bonding. Where intramolecular hydrogen bonding is present in a syndiotactic polymer, the oxygen atoms are drawn together to optimise the oxygen–hydrogen–oxygen distances, but a slightly more favourable structure may be achieved by keeping the oxygens further apart and eliminating any intramolecular hydrogen bonding. (N.B. This conformation leaves it possible for the syndiotactic units to hydrogen-bond intermolecularly within a crystal structure.) All of these minimum energy conformations were calculated with the same polymer repeat distance, and could thus fit into the same crystal lattice. The conformational studies of the isolated chains using MOPAC enable a direct comparison to be made with simulations using a range of standard force-field packages used for crystal structure simulations.

In order to model the conformation within a crystal structure, the *Cerius*^{2} molecular mechanics package was used. Initially, crystals were constructed to emulate an isolated chain polymer, for comparison with the results achieved with MOPAC. A section of a single polymer chain (of four monomer units in length) was contained within a unit cell with the molecular axis unit cell repeat distance fixed at 10.092 Å. The repeat distances of the other two axes of the unit cell were fixed to be larger than the non-bonded interaction cut-off distance used for the structure minimisation (20 Å), hence eliminating all interactions between molecules in neighbouring cells perpendicular to the chain axis whilst emulating the one-dimensional polymer repeat as used in MOPAC. Several force fields/charge calculation combinations were tried, as well as several minimisation algorithms and different options settings. The best agreement with the MOPAC results was achieved using the DREIDING II (2.21) force field[8] with the charge

Table 1 Summary of carbon–carbon backbone torsion angles and heats of formation of the conformations of minimum energy as calculated by MOPAC and by molecular mechanics. Data are included for all three minimum energy conformations close to planar zig-zag: one for isotactic PVOH, and two for syndiotactic PVOH with different –OH bond directions. The molecular mechanics data are those from simulations which showed the best overall agreement with MOPAC for all three structures

Sample	MOPAC torsion angles ϕ_1, ϕ_2	MM torsion angles ϕ_1, ϕ_2	MOPAC energy (kcal mol^{-1})	MM energy (kcal mol^{-1})
isotactic	166.6, 169.1	162.0, 164.6	– 231.54	– 83.50
syndiotactic, no H-bonds	168.7, 170.5	171.8, 172.4	– 228.20	– 70.58
syndiotactic with H-bonds	161.0, 170.9	167.8, 172.0	– 227.27	– 58.77

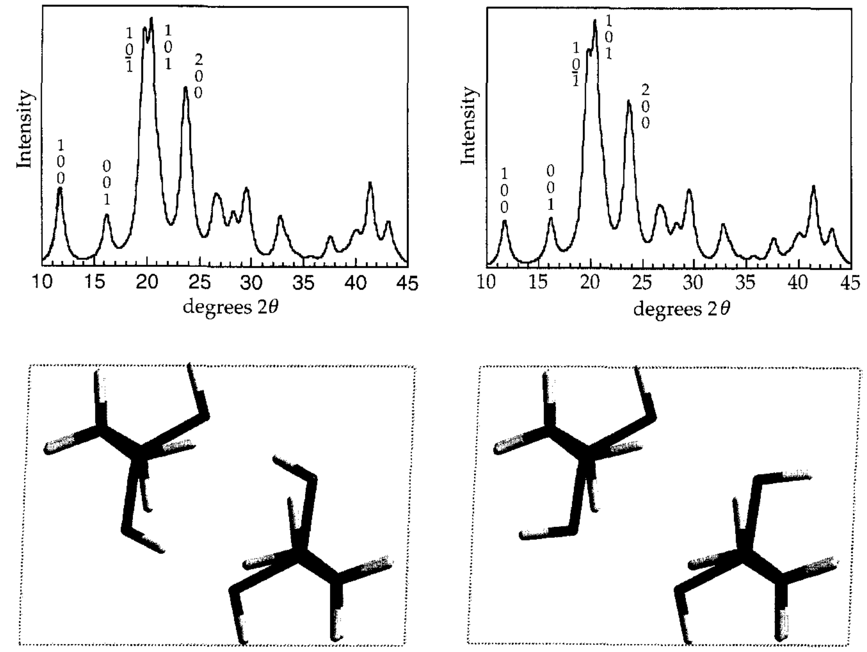


Figure 7 Comparison of X-ray powder diffraction traces of two syndiotactic crystal structures (shown below each) in which only the positions of the hydroxyl hydrogens differ. This is shown to have a marked effect on the relative intensities of the diffraction maxima

equilibration method (QEq) charges[9], steepest descent algorithm and Ewald cut-off parameters for non-bonded interactions. *Table 1* summarises the backbone torsion angles of the minimum energy conformations calculated with molecular mechanics and those calculated with MOPAC. The molecular mechanics calculations were started from each of the minimum energy conformations calculated by MOPAC. The backbone torsion angles differ between the two methods by a maximum of 6.8°, but the *shape* of the chains (e.g. whether the –OH groups are further apart or closer together than a planar zig-zag conformation) is the same in all cases. In each case, the isotactic chain has the lowest energy and the intramolecularly hydrogen bonded syndiotactic chain has the highest energy[*], although the relative sizes of the energy difference between structures do not show good agreement.

CRYSTAL STRUCTURES

Molecular mechanics calculations were used exclusively to determine the minimum energy crystal structures presented here. The same settings were used as those determined to give the best agreement with MOPAC for isolated chains. The minimisations were made with all atom positions and unit cell parameters free to vary independently. The unit cell parameters from the simulations may be compared with those from diffraction data. The molecular mechanics calculations predict a structure for a crystal at absolute zero, and an estimate may be made of the unit cell parameters at this temperature by extrapolating a fit to data of the parameters measured from fibre diffraction as a function of temperature[10]. The data were measured in the temperature range 20–120°C[†], and all parameters showed a good linear relation to temperature. Assuming no crystal transitions occur below 20°C, therefore, a good estimate may be made of the 0 K cell parameters: $a = 7.54$ Å, $b = 2.52$ Å, $c = 5.47$ Å, $\alpha = \gamma = 90°$, $\beta = 92.2°$.

The structures produced from the molecular mechanics energy minimisations were used to predict X-ray powder diffraction profiles, which enable a rapid comparison with those obtained experimentally, not only a matching of the peak positions with experimental traces but also a detailed comparison of the relative intensities. The first, perhaps surprising, conclusion of these studies was the profound effect the position of the alcohol hydrogen within the unit cell had upon the relative intensities of the low angle peaks.

Figure 7 gives one example of the influence of the hydrogen positions. Two unit cells were constructed with all atoms in identical positions except for the hydrogens attached to the oxygen atoms. These were placed in two

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[*] The energies quoted from the two methods are not directly comparable; for example: that from the molecular mechanics does not include the bond energy, in as much as a bond at its equilibrium length will have zero energy

[†] At around 120°C an abrupt change in the thermal expansion of the unit cell parameters occurs and there is a different, although still linear, change in parameters with temperature, measured up to 200°C, as discussed in the first part of this series of papers

Table 2 The unit cell parameters from the three minimised atactic units with the experimentally determined room temperature and predicted 0 K unit cell parameters

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
atactic (i)	7.87	2.59	5.36	91.6	92.1	90.0
atactic (ii)	7.86	2.60	5.31	90.1	91.9	88.8
atactic (iii)	7.88	2.58	5.36	89.2	90.7	88.2
experimental[2]	7.81	2.52	5.51	90.0	91.7	90.0
0 K predicted[10]	7.54	2.52	5.47			

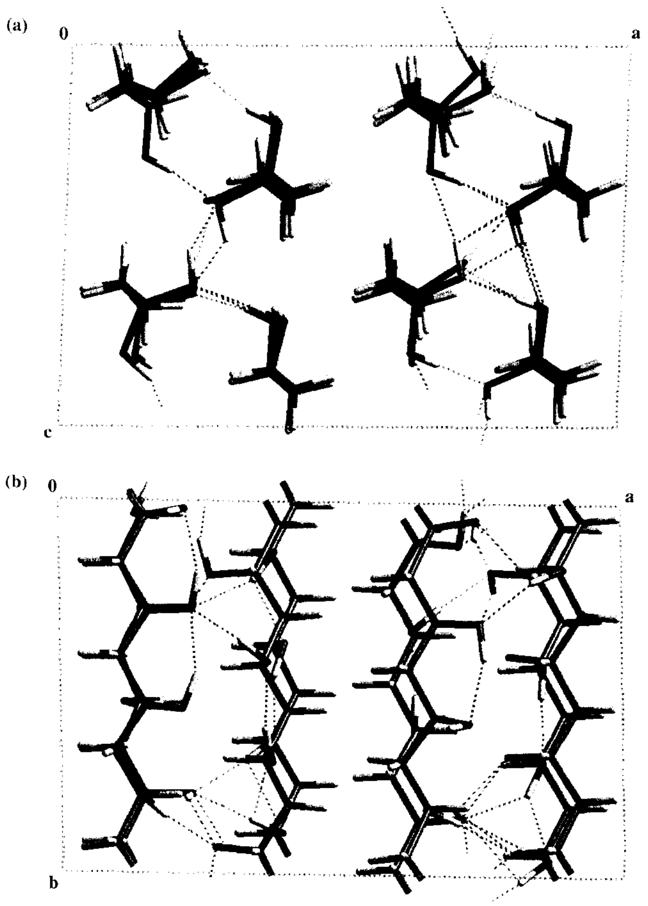

Figure 8 One of the examples of a minimised atactic unit cell (example I): (a) a view along the molecular axis and (b) perpendicular to the polymer chains. In each case the directions of possible hydrogen bonds are indicated

different positions, each forming a reasonable oxygen–hydrogen bond lying in a probable direction within the unit cell. The X-ray diffraction traces show distinct differences in the relative intensities of the lower angle peaks—in particular the 100, $101/10\bar{1}$ and 200 maxima. This unexpected sensitivity of the trace to the direction of the –OH bond can give valuable insight into the direction and nature of the hydrogen bonding within the crystal structure.

Using the optimisation parameters for the molecular mechanics minimisation which gave the best match to the MOPAC results for the isolated chain, the crystal structure of atactic PVOH was modelled. To simulate a section of atactic crystal, a large unit cell was created containing eight polymer chains each of four monomer units in length. The tacticity along each of the chains was chosen such that the sequences of isotactic and syndiotactic units had propagated in a Bernoullian manner (i.e. there was no 'blockiness' in the tacticity). The minimisation was started from a Bunn crystal structure and all the atom positions and charges and the unit cell parameters were free to vary during the minimisation. The –OH bonds can lie in several possible orientations and, because the minimisation process cannot always allow the bonds to change direction between the various possibilities, the –OH bond directions were periodically tested during the minimisation process to find the lowest minimum energy position.

Figure 8 shows the minimum energy structure of one of the examples of an atactic unit cell as modelled. It strongly resembles the model proposed by Bunn, with the carbon backbone torsion angles close to planar zig-zag. The directions of the –OH bonds are largely determined by the opportunities for the proton to hydrogen-bond with adjacent oxygens. This, in turn, has an influence on the local carbon backbone torsion angles. In general, the oxygens seem to bond intermolecularly, unless no, or only poor, intermolecular bonding opportunities are available. Murahashi *et al.*[11] suggested that intramolecular hydrogen bonding was possible from their i.r. examination of isotactic rich polymer; however, they were not able to distinguish contributions from the amorphous and crystalline phases in their low crystallinity samples. In this case, intramolecular bonds are seen to be formed in the crystal. As the simulation was restricted to quite a small area of atactic crystal, three examples of atactic crystals were simulated, in each case ensuring Bernoullian statistics for the tacticity. For each example a similar structure was produced. *Table 2* summarises the unit cell parameters of each of the atactic minimised structures, along with the experimentally determined room temperature parameters and those predicted for 0 K by extrapolation of experimental data. The agreement between modelled and experimental results is quite good; however, if the –OH bonds are left to lie along alternative directions (i.e. not being rotated into the lowest energy position, but stuck in an alternative minimum), the shape of the minimum unit cell is generally radically altered, becoming triclinic and very large, such that adjacent chains do not interact greatly.

The X-ray diffraction traces were simulated from each of the three minimum energy atactic structures modelled. The simulated traces and a published experimental trace[7] are given in *Figure 9*. The agreement with room temperature experimental traces is good, especially in the light of the intensity variations which can result from different positions of the hydroxyl hydrogens alone, as demonstrated in *Figure 7*.

Although the modelled structure is like that proposed by Bunn (molecules set in the obtuse angles of the monoclinic unit cell), we may briefly consider the other two descriptions of the atactic form of PVOH. *Figure 10* shows the X-ray diffraction traces corresponding to each of the structures shown in *Figure 1*. In each case, the hydrogen atoms were placed in those positions deemed most likely. Although the different structures show different relative intensities in the diffraction trace, it is not possible to compare these directly with experimental data, as the directions of the –OH bonds

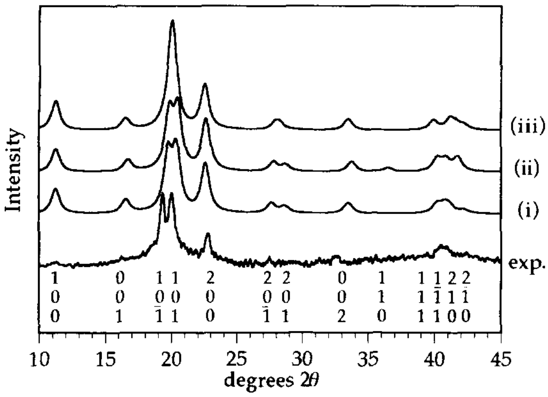

Figure 9 X-ray diffraction traces from the three examples of atactic unit cells, each containing 32 monomer units. In each case the structure is that of minimum energy found by modelling. An experimental powder diffraction trace from an atactic sample is shown for comparison

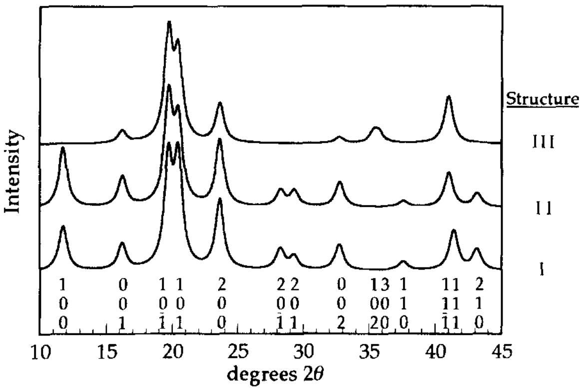

Figure 10 Simulated X-ray powder diffraction traces from the three crystal structures shown in *Figure 1*. The indexing is taken from structures I and III. The monoclinic angle is acute for structure II and so, for example, indices 101 and 10$\bar{1}$ should be reversed

and hence the positions of the alcohol hydrogens within the models are not known, particularly for an imperfect crystal at room temperature. However, on minimisation of the atom positions and unit cell parameters of the two alternative structures, structure (b) (similar to Bunn) rapidly returns to a Bunn structure, with the monoclinic angle returning to greater than 90°. Structure (c) (as proposed by Sakurada *et al.*[5]) did not form a stable structure close to the starting position; rather, the unit cell elongated and became triclinic, reducing inter-chain interactions. The weight of the modelling evidence is thus to support the original Bunn structure and to discount the alternative structures described by other authors[3–5].

SYNDIOTACTIC CRYSTAL STRUCTURES

The energy-minimised structure for a purely syndiotactic crystal is shown in *Figure 11*. The structure is broadly that predicted by Bunn and the minimised atactic structures, although it incorporates only syndiotactic units. The backbone torsion angles of the chains are around 175°, i.e. the conformation is closer to planar zig-zag than predicted for the isolated chains. The hydrogen bonding within the crystal is as suggested by Bunn, and 100% intermolecular. The minimised unit cell parameters were: a = 7.79 Å, b = 2.58 Å, c = 5.23 Å, α = 90.3°, β = 93.4°, γ = 90.0°. The minimisation was started from several different unit cells; in particular, the initial direction of the –OH bond was varied, as the minimisation process was sometimes unable to rotate this bond from one local energy minimum to another. The final structure was not only that of the lowest energy, but also showed the best agreement with the estimated unit cell parameters and with the simulated diffraction trace (discussed below). Where the –OH bond lay in a less favourable direction, this would frequently have a drastic effect on the unit cell parameters, pushing the chains a long way apart and forming a large, triclinic unit cell.

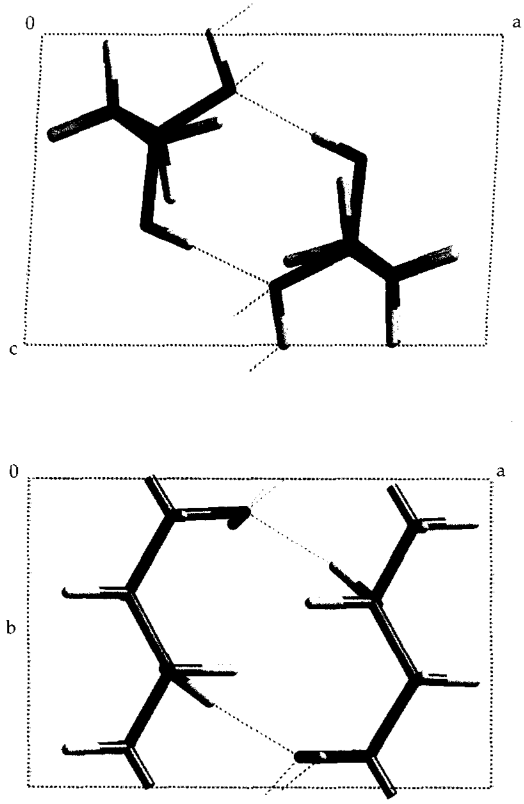

Figure 11 The minimised syndiotactic crystal structure similar to that found for the atactic cases: (a) view along and (b) perpendicular to the molecular axis

An alternative crystal structure, distinct from that proposed by Bunn, was found, which resulted from minimisation from certain starting conditions. The structure is shown in *Figure 12*. The unit cell parameters of the minimised structure are: a = 7.82 Å, b = 2.58 Å, c = 5.34 Å, α = 90.1°, β = 84.3°, γ = 90.0°. It has a slightly lower energy than that shown in *Figure 11*. There is a third direction for the intermolecular hydrogen bonding in this structure (in the centre of the unit cell as shown in *Figure 12*, running approximately along [0*VW*]), which has the result of pulling the monoclinic angle to less than 90°.

The simulated diffraction patterns of the two syndiotactic structures are shown in *Figure 13* along with the trace measured from atactic PVOH at room temperature for comparison. However, in the absence, to date, of the successful synthesis of a very highly syndiotactic sample from which to measure the diffraction profile, these simulations cannot be used to determine which structure occurs. It is a characteristic of such molecular mechanics simulations that more than one alternative minimum structure is predicted, although they may not all be observed experimentally.

Once even a small proportion of isotactic units is

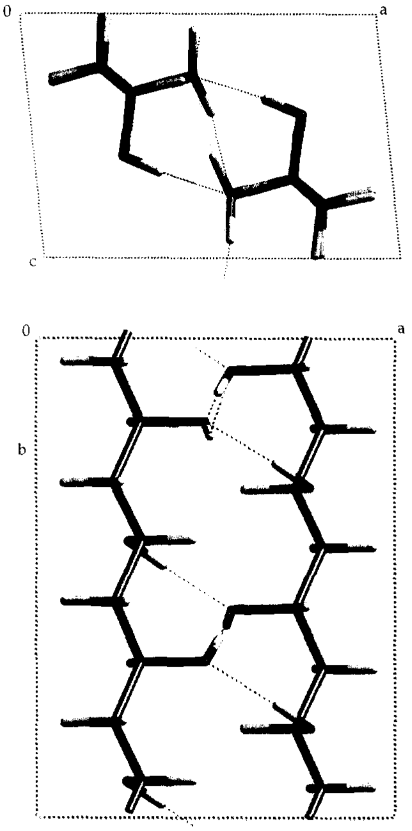

Figure 12 An alternative syndiotactic crystal structure with a novel hydrogen bonding direction: (a) view along and (b) perpendicular to the molecular axis

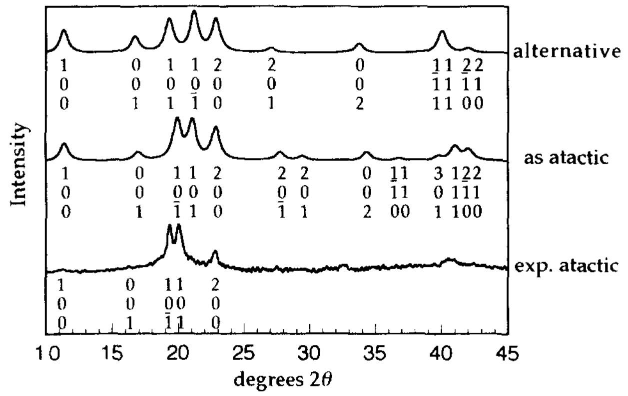

Figure 13 Simulated X-ray powder diffraction traces from the two minimised syndiotactic structures shown in *Figures 11* and *12*, and that determined experimentally from an atactic sample

incorporated into the structure, the lower energy syndiotactic structure (*Figure 12*) is no longer stable, reverting once more to the structure as modelled for atactic crystals. This is because there is an insufficient number of the novel intermolecular hydrogen bonds possible to sustain an acute monoclinic angle. Thus, this second structure hinted at by the modelling is only potentially applicable to polymers at or close to pure syndiotactic. Such molecules have not yet been synthesised.

TOWARDS ISOTACTIC

As more isotactic units are incorporated into the modelled atactic structure, the proportion of intramolecular hydrogen bonding increases, and so the Bunn structure becomes energetically less favourable. There is a decreasing level of bonding between the 'paired' molecules across the unit cell.

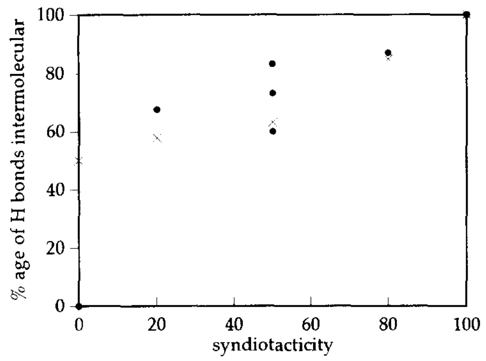

Figure 14 The proportion of the hydrogen bonding that is intermolecular as a function of tacticity from modelling results presented here (•) and (×) by Kusanagi and Ishimoto[3]. For purely isotactic, the • point refers to the novel isotactic structure discussed in the next section

The crystal structure of PVOH across a range of tacticities has been modelled by Kusanagi and Ishimoto[3] using a polymer molecular mechanics model. The simulations were all started from a Bunn-type structure with an acute monoclinic angle (*Figure 1b*). The simulations were performed over the complete range of tacticities, but did not appear to find structures much different from the starting conditions. The unit cell parameters were tabulated as a function of tacticity, with no discernible trends, but it is perhaps noteworthy that the monoclinic angle varied either side of 90° across the tacticity series, and at 50% syndiotacticity (atactic) the angle was determined to be 90°. The intermolecular hydrogen bonding directions were slightly different than for Bunn or the modelling work presented here, and the third direction for intermolecular hydrogen bonding found here for syndiotactic crystals was not considered. The proportion of hydrogen bonding that is intermolecular (rather than intramolecular) is plotted as a function of syndiotacticity in *Figure 14*, showing decreasing intermolecular hydrogen bonding towards the isotactic end. The modelling work presented here, which gives a superior fit to the Bunn model, predicts the same trend over much of the tacticity range, although the proportion of intermolecular bonding is slightly higher than that found by Kusanagi and Ishimoto[3]. As discussed by these authors, the intermolecular hydrogens are generally the stronger, so an increase in melting point with increasing syndiotacticity can be predicted. In a similar way, as isotactic-rich crystals contain lower levels of intermolecular bonding, the crystallinity is expected to be lower, as is observed.

NOVEL ISOTACTIC STRUCTURE

In the previous section the inclusion of increasing numbers of isotactic units into a Bunn-type crystal structure was discussed. A novel X-ray diffraction trace from a sample with a high level of isotacticity (88%) has been published[7], suggesting an alternative crystal structure. The apparent absence of a low angle peak at around 12° suggests that the unit cell may no longer contain two polymer chains. Unit cells with a single polymer chain were minimised using *Cerius*^{2} molecular mechanics, and two minima, both with unit cells close to hexagonal, were found independently, which minimised to form structures with very similar unit

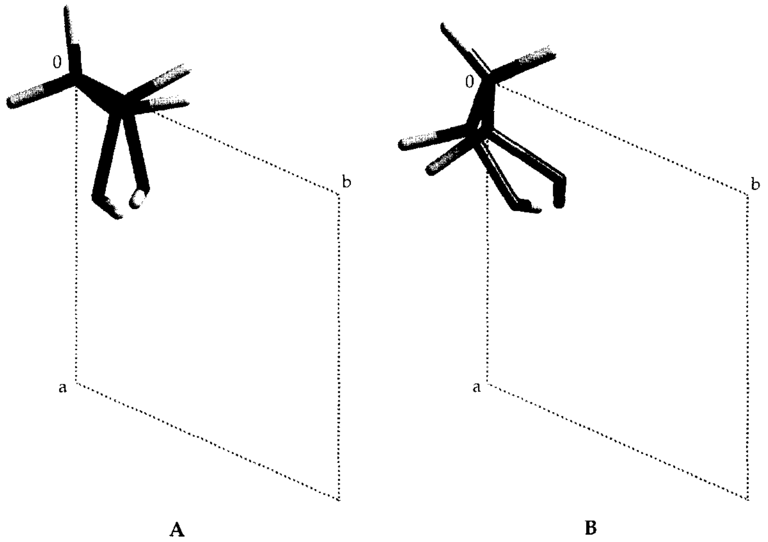

Figure 15 The two minimum energy motifs of the isotactic unit cell as viewed along the molecular axis. The two structures A and B are distinct

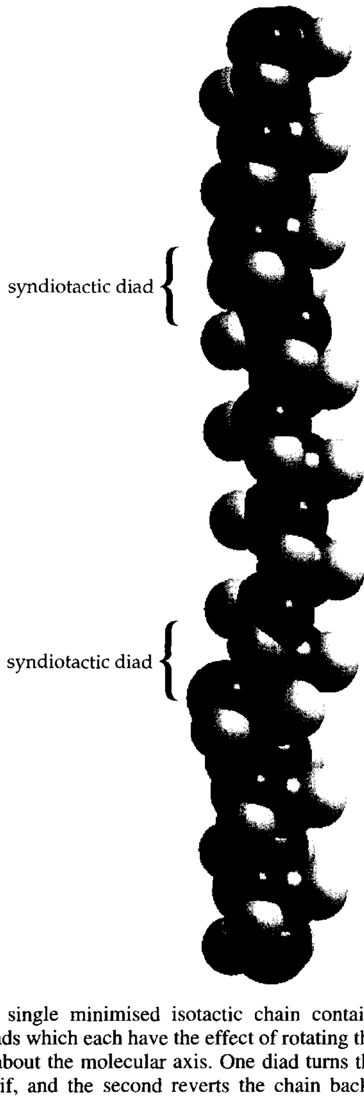

Figure 16 A single minimised isotactic chain containing two single syndiotactic diads which each have the effect of rotating the polymer chain through ~60° about the molecular axis. One diad turns the chain into the alternative motif, and the second reverts the chain back to the original orientation

cell parameters but with a different lattice motif. The two unit cells both had α and β parameters close to, but either side of 90°. When the minimisation was performed with $\alpha = \beta = 90°$ fixed, commensurate with a co-crystallisation of the two motifs, both structures remained stable to minimisation, with practically identical parameters. The two structures, shown in *Figure 15*, are distinct from one another in motif but both have unit cell parameters $a = 4.87$ Å, $b = 4.6$ Å, $c = 2.64$ Å, $\alpha = 90°$, $\beta = 90°$ and $\gamma = 66°$. The two structures were minimised from different starting conditions. Structure A is of lower energy than B, as is expected from the slight elongation of the unit cell along one axis, but both structures are stable to minimisation. Structure A minimised to an enthalpy of -36.471 kcal per mole of monomer and B to -36.465 kcal per mole of monomer.

Because the unit cell does not contain bi-layers of intermolecularly bonded molecules, the hydrogen bonding is exclusively intramolecular. A single molecule can progress from one of these motifs to another by the incorporation of a single syndiotactic unit into an isotactic chain. The syndiotactic unit has the effect of rotating the molecule through approximately 60° about the molecular axis. Two examples of such rotations are shown in the molecule in *Figure 16*. Where a syndiotactic unit is incorporated into a predominantly isotactic chain (as marked), the chain is rotated about the molecular axis through such an angle as would comfortably change the structure from one motif to another and, at the second syndiotactic unit, it is rotated back again. This molecule, as an isolated chain, was found to be stable in this conformation both to minimisation in *Cerius*^{2} molecular mechanics and the lowest energy conformation of many tried MOPACs. The chain was also successfully minimised in *Cerius*^{2} molecular mechanics within a fixed repeating unit cell with parameters as found for the two purely isotactic units. Thus, only a very small proportion of syndiotactic units incorporated into the crystal allows the two motifs to co-crystallise.

The best fit of the simulated X-ray trace to the experimental data is from a combination of the two structures shown in *Figure 15*. To achieve the best ratio of the primary peaks 100 and 010, a mixture of the two motifs in the ratio 3:1 (the lower energy structure being more prolific) is suggested. The experimental and the best-fit simulated traces are shown, for comparison, in *Figure 17*. The widest angle peaks are more broadened experimentally, as expected, for example by thermal vibrations.

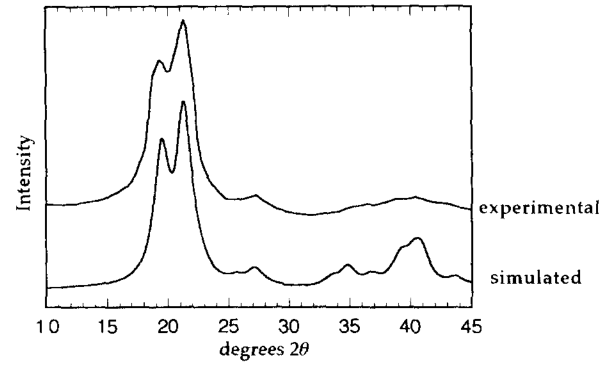

Figure 17 The X-ray powder diffraction trace simulated from a 3:1 ratio of the two motifs shown in *Figure 15*, and the diffraction trace determined experimentally from the polymer containing 88% isotactic diads[7]

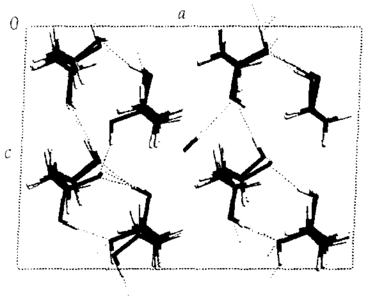

Figure 18 An example of a section of a model of atactic PVOH crystal viewed along the molecular axis. The model contains 32 monomer units and one water molecule in the site of minimum steric hindrance. Hydrogen bonds are shown as dashed lines

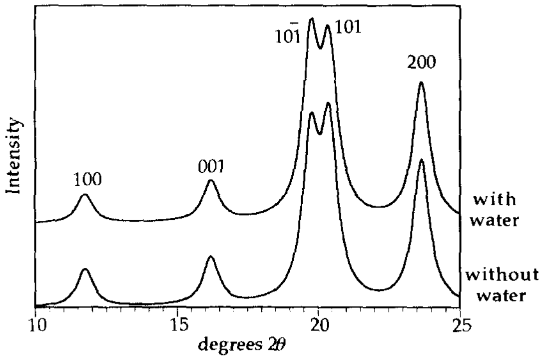

Figure 19 X-ray powder diffraction traces simulated from the model shown in *Figure 18* with and without the water molecule included. The relative intensities of the 10$\bar{1}$ and 101 peaks are reversed, as is observed experimentally[6]

No minimisations of the isotactic chains packed into a mixed crystal have been performed at this stage since, in order to achieve a good mix of the two types with the incorporation of syndiotactic 'defects' down the chain, this task would involve a large structure to be calculated.

INCLUSION OF WATER

Simulations of the X-ray diffraction traces from models of the Bunn atactic crystal structure indicated that the relative intensities of the diffraction peaks were highly sensitive to the direction of the hydrogen bonds in the structure and also to the presence of water molecules. Experimental evidence discussed in the first paper of the series raises the possibility that water molecules could be included within the atactic structure. An investigation was made as to the possible positioning of a water molecule within the crystal. The most likely position of a water molecule was found on purely steric grounds (shown in *Figure 18*); the model was not energy minimised with the water molecule present. Although the positioning of the water molecule in the site of maximum free volume means that it is close to the hydrophobic faces of its neighbouring polymer molecules, the water is in a good position to be able to form several possible hydrogen bonds with the neighbouring polymer chains. Any water–polymer hydrogen bonds formed would have the effect of decreasing the polymer–polymer hydrogen bonding, so the incorporation of water into the crystal structure would be expected to decrease the dissolution temperature. Simulations of the X-ray diffraction profiles (*Figure 19*) from a section of atactic polymer with and without water incorporated into the structure in the position of least apparent steric hindrance show the same swapping of the relative intensities of the 10$\bar{1}$ and 101 peaks observed experimentally[6]. As in the experiments, the other diffraction peaks remain largely unaffected. The decrease in size of the unit cell observed experimentally could be a result of the water molecule forming a 'bridge' of hydrogen bonding between polymer molecules, drawing them closer together. Such bonding would form a hydrogen bond 'tie' across the part of the cell formally linked only by van der Waals interactions. Water incorporated into the crystal in this way would not be removed below temperatures considerably above that at which free water is released.

CONCLUSIONS

Modelling of isolated chains of all isotactic or all syndiotactic units using MOPAC AM1 revealed local minima in energy at conformations close to planar zig-zag in both cases, suggesting that an atactic crystal, where syndiotactic and isotactic units are incorporated into a single crystal lattice, can be stabilised.

Molecular mechanics simulations using DREIDING II (2.21) forcefield in *Cerius*[2] gave similar minimum energy structures for isolated chains to MOPAC, so this forcefield was used to extend the modelling to crystal structures.

The direction of the –OH bond in the crystal structure has a profound effect upon the relative intensities of the X-ray diffraction peaks as simulated from a series of models, because the carbon and oxygen atoms are situated close to the systematically absent positions for the low-angle peaks. Hence, these peak intensities are sensitive to the direction and nature of hydrogen bonding in the crystal.

A series of atactic unit cells were minimised with a structure similar to that proposed by Bunn, with a reasonable agreement of the unit cell parameters with experiment. The alternative crystal structures discussed were not able to be stabilised.

A purely syndiotactic crystal structure was able to be predicted by the model which is very similar to Bunn, and also a slightly different structure was found which is predicted to be stable only for crystals very close to being fully syndiotactic. In both cases the bonding is entirely intermolecular.

Minimised structures were found to have an increasing proportion of intramolecular hydrogen bonds with decreasing syndiotacticity.

An alternative crystal structure has been proposed for crystals composed of a very high proportion of isotactic units, which is consistent with an experimentally determined X-ray diffraction trace. The structure is stabilised by the favourable intramolecular hydrogen bonding predicted here for chains of isotactic units, and is distinct from that for the atactic crystals. Two motifs were found to be stable to energy minimisation within the same unit cell. A single chain of polymer could change between one motif and another by the incorporation of a single syndiotactic diad into the chain, forcing a rotation of the molecule of approximately 60° about the chain axis.

The structural change observed in the crystals formed with water present could be explained by the incorporation of water molecules into the crystal structure. Molecular modelling reveals that there is little steric hindrance to water and that there exists good hydrogen bonding opportunities which will result in a decrease in the polymer–polymer intermolecular hydrogen bonding. Simulations of the X-ray diffraction profiles from crystal structure with and without water included reproduces the reversal in the relative intensities of the $10\bar{1}$ and 101 peaks observed experimentally.

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