

## **Polymer crystal silverware: a fast method for the prediction of polymer crystal structures**

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Received: 11 December 1995/Revised version: 29 January 1996/Accepted: 2 February 1996

### Summary

A method is presented for the fast prediction of polymer crystal structures. From a stable helical conformation of the polymer chain well packed three dimensional periodic starting structures are generated using an adapted version of M. Blanco's Molecular Silverware algorithm. These structures are then energy-minimised using classical molecular mechanics methods. The method only requires a rough estimate of the crystalline density. No information about crystal class, space group or cell parameters is necessary. Using this method, possible crystal structures of poly(ethylene ketone), Nylon-6,6 and poly(ethylene terephthalate) are calculated. Both the  $\alpha$ - and  $\beta$ -structures of poly(ethylene ketone) are correctly predicted. For Nylon-6,6 the lowest-energy structure obtained corresponds to the experimental  $\alpha$ -structure. For poly(ethylene terephthalate) a large number of structures are generated using the algorithm. Besides the experimental structure four structures are found with a lower energy than the experimental structure.

### Introduction

The prediction of the crystal structure of a crystalline polymer is of utmost importance for the development of new crystalline high-performance polymers. When it is possible to predict the crystal structure of a polymer, the ultimate mechanical properties can be calculated, and this even before the polymer has been synthesised, and/or shaped into a highly crystalline fiber.

Although prediction of polymer crystal structures has been attempted by some researchers (1-5), no general and automated method exists as yet. We hereby present a simple and fast method for the generation of polymer crystal structures, based on packing considerations only. Polymer chains in a crystalline environment can be described as helices. Excellent molecular modelling methods already exist for the generation of stable helical structures of polymer chains and for calculating their relative stabilities. These methods can be used to select the most stable helical conformations as a starting point for packing trials in order to obtain stable crystal structures. We have now developed a method which does this packing automatically starting from the geometry of the helical repeat unit. The method does not require any knowledge of the crystal class, space group or cell parameters. Only a rough estimate of the density is required. The latter can be obtained from group contribution methods or just from common sense.

The method is applied in order to find all possible crystal structures of poly(ethylene ketone), Nylon-6,6, and poly(ethylene terephthalate).

### Method

We will explain the method assuming two polymer chains per unit cell. An analogous method can be used when four polymer chains per unit cell are assumed. The latter case will be elaborated in a following, more extensive publication (6). Initial packings with two or four monomer units in the unit cell, after energy-minimisation, can lead to crystal structures that can be reduced to structures with one polymer chain per unit cell, as will be demonstrated for Nylon-6,6 and for poly(ethylene terephthalate).

When the conformation of the polymer chain is known the unit cell length (c-axis length) can be obtained from simple molecular modelling methods. It is then decided how many chains will be placed in the unit cell (in this case 2). A rectangular unit cell is then constructed with  $a=b$ , or with some  $b/a$  ratio, so that the unit cell volume corresponds to a reasonable density for the crystalline polymer. One can of course also start from an hexagonal or any other (e.g. skew) unit cell.

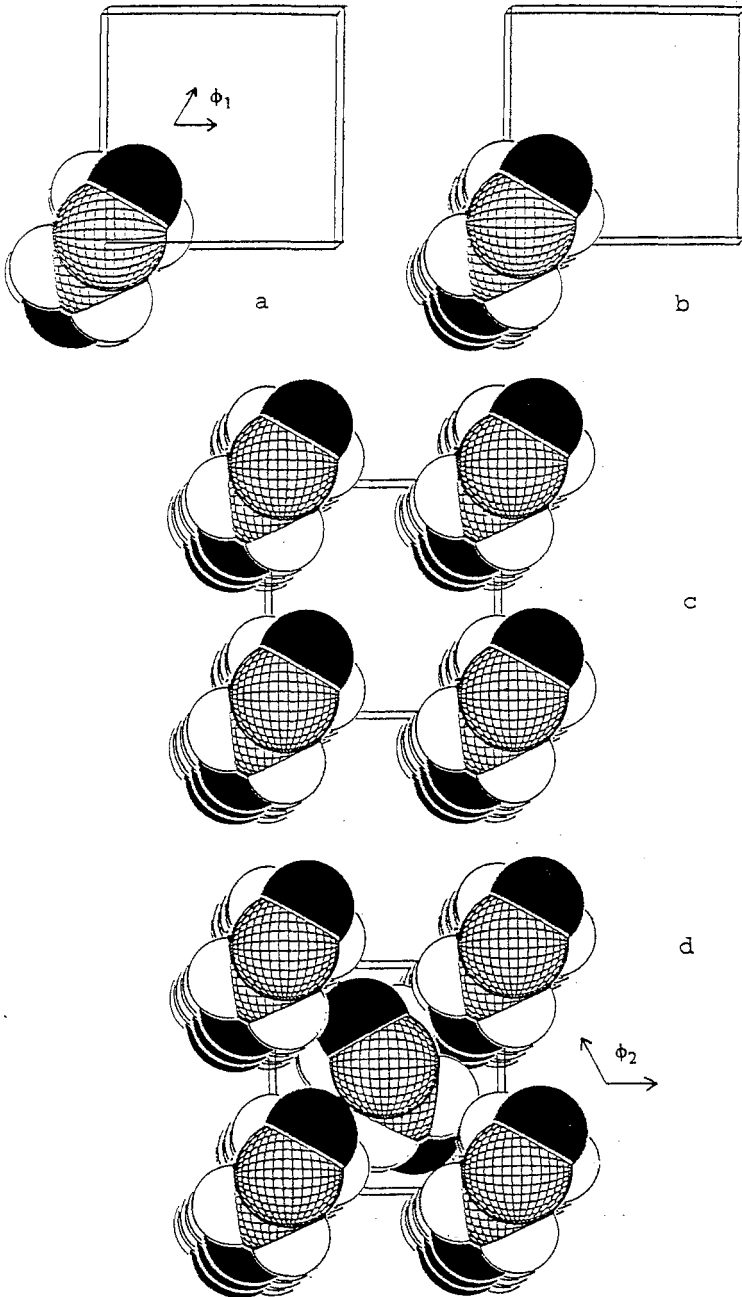
A first polymer helical repeat unit is placed on the corner of the unit cell with the helical axis coinciding with the c-axis of the unit cell (fractional coordinates  $0,0,z$ ) (fig.1a) with setting angle  $\phi_1$  and replicas are constructed along the +c and -c axis (fig.1b). Also replicas of this "trimer" are constructed at the three other corners of the unit cell (fig.1c). Then it is checked whether these chains overlap on basis of their Van der Waals radii. If this is so,  $\phi_1$  is increased by an amount  $\delta\phi_1$  and the process is repeated. If no overlap is found a second helical repeat unit is placed in the centre of the unit cell (fractional coordinates  $0.5,0.5,z$ ) with a setting angle  $\phi_2$  and a z-offset (displacement along the c-axis) of  $0\text{\AA}$  (fig.1d). The setting angle  $\phi_2$  can be a random angle or can be altered stepwise. In our method we prefer to use a random angle. Once the setting angle  $\phi_2$  chosen, the z-offset is calculated for which the central helical repeat unit is just touching one of the corner chains (based on the Van der Waals radii) with no other Van der Waals overlap with any of the other chains. So the new helical repeat unit just fits in the "gap" created by the trimers on the corners of the unit cell. The method for calculating the required z-offset is an adapted version of Mario Blanco's "Molecular Silverware" (Blanco). The advantage of this method is that it is very fast as it is not a trial-and-error method (by shifting along the c-axis with a small interval), but as it calculates the required z-shift directly. Only solutions for which the z-offset falls in the range  $-c/2$  to  $c/2$  are accepted (otherwise always two solutions will be found with the new helical repeat unit just outside the "gap"). Then it is checked whether the chain at  $0.5,0.5,z$  overlaps with one of its translational equivalents in neighbour cells (e.g. at  $-0.5,0.5,z$ ). If not, the solution is accepted, and all the necessary coordinates are written to an archive file. If no suitable solution is found another random angle  $\phi_2$  is chosen and the process is repeated. For a given setting angle  $\phi_1$  random angles  $\phi_2$  are chosen until the maximum number of trials is exceeded (100-1000 has been found to be an appropriate number) or until a maximum allowed number of solutions for that setting angle  $\phi_1$  (e.g.10) has been obtained. Then  $\phi_1$  is increased by  $\delta\phi_1$  until full rotation ( $360^\circ$ ) has been achieved.

If no solutions have been obtained at all, the area of the ab-plane of the unit cell can be altered (altering the density), or the Van der Waals radii can be changed somewhat. This can also be performed when the number of solutions obtained is too small.

All solutions are then energy-minimised using a molecular mechanics program (with periodic boundary conditions) and with all coordinates of atoms and cell parameters free to change. In our case all solutions were energy-minimised using the Discover 94 molecular mechanics software from Biosym Techn. Inc. (7) and the cff91 forcefield (8). In most cases the number of structures

then reduces to a lower number, as several solutions minimise to the same crystal structure:

Fig.1: Graphical representation of the Polymer Crystal Silverware algorithm.



### Computer program

A Fortran computer program has been written using the above described method for the calculation of possible starting crystal structures. It reads the cartesian coordinates of the helical repeat unit from a Biosym cartesian coordinate file, together with the cell parameters. The latter can then be altered. The number of chains per unit cell is asked for, and the number of trials which has to be performed before quitting the "Molecular Silverware" algorithm, and starting with a new setting angle  $\phi_1$ . Also the maximum number of solutions per setting angle  $\phi_1$  is asked for. Then the step size for increasing  $\phi_1$  must be given. The computer program then calculates all possible solutions. If the number of solutions is zero or too low, another run can be performed with another density or b/a ratio or with altered Van der Waals radii. When executed on a Silicon Graphics Power Indigo2 workstation these calculations take a few minutes to less than half an hour for the case of two chains per unit cell, depending on the maximum number of trials allowed and the step size for  $\phi_1$ . As an indication, the calculation of all possible crystal structures of Nylon-6,6 took 15 minutes (giving 38 solutions), using 100 trials per setting angle  $\phi_1$ , a maximum of 10 solutions per setting angle  $\phi_1$ , and a step size of  $10^\circ$  for  $\phi_1$ . As the energy-minimisation of each of the resulting starting structures takes less than two minutes, all these possible stable Nylon-6,6 structures were obtained within half a working day, and this almost completely automatically.

### Strategies

Polymer chains with a cylindrical shape, like poly(ethylene), poly(ethylene ketone) and the aliphatic nylons and purely-aliphatic polyesters are expected to pack in a pseudo-hexagonal lattice. Small deviations from the perfect cylindrical shape mostly make them crystallise in near-rectangular unit cells (orthorhombic; monoclinic, triclinic) with cell angles not deviating too much from  $90^\circ$ . As we will be demonstrated in the next sections, this means that for most cylindrically-shaped polymer molecules, using our algorithm, it is sufficient to start with a rectangular unit cell, with  $a=b$ , in order to obtain configurations, which after energy-minimisation, lead to the experimental unit cell as the lowest-energy solution.

For more oblate-shaped polymer chains, or polymer chains with an irregular shape, such as aromatic-aliphatic polyesters, the packing problem will be more difficult to solve. In many cases it will be necessary to generate packings starting from rectangular cells with different a/b ratios, and from skew unit cells (e.g. with  $\alpha$  being  $120^\circ$  or  $135^\circ$ ) with different a/b' ratios (where  $b'=b.\sin(\alpha)$ ).

### Applications

We have used this new method for the calculation of possible crystal structures of poly(ethylene ketone), Nylon 6,6, and poly(ethylene terephthalate). Rather than trying to give an overview of possible crystal structures for a large number of polymers, we have chosen in first instance to work on a small number of examples with increasing complexity. Whereas poly(ethylene ketone) can be expected to pack more or less like poly(ethylene), but with a few more degrees of freedom, Nylon-6,6 is expected to give more possible crystal structures, as there are a number of different ways hydrogen-bonded sheets can pack. The case of poly(ethylene terephthalate) is a more difficult one, as also aromatic rings are involved, giving the polymer chain a more irregular shape.

Results from calculations on other polymers: isotactic poly(propylene), poly(p-phenylene terephthalamide), aliphatic polyester, poly(ethylene naphthalate), and poly(ethylene 4,4'-biphenyldi-carboxylate), will be reported later (6).

### A. Poly(ethylene ketone)

Two different crystal structures of poly(ethylene ketone), the copolymer of ethylene and carbon monoxide have been described in literature. The  $\alpha$ -structure occurs for the perfectly alternating copolymer at room temperature (9). The  $\beta$ -structure has been described by Chatani et al. (10,11) and is found in the case of non-perfectly alternating copolymer (11) or obtained by heating the  $\alpha$ -structure (12). It also occurs (partially) when some of the ethylene is replaced by propylene (12). We used our method to see whether it can predict both the crystal forms and to see whether also other stable crystal structures can exist. We started from a unit cell with  $a=b=6.2$  Å and two molecules in the unit cell (density  $1.28 \text{ g.cm}^{-3}$ ). The conformation used was the all-trans conformation. Van der Waals radii of 1.5, 1.3 and 1.1 Å for C, O and H respectively were used. Using a step size of  $10^\circ$  for  $\phi_1$ , a maximum of 100 trials per setting angle  $\phi_1$ , and a maximum number of 10 solutions per setting angle, 11 structures were obtained. Decreasing the Van der Waals radii by  $0.05\text{Å}$  gave 34 additional structures. All these structures were then energy-minimised using the Discover 94 molecular mechanics program with all the atom coordinates and the six cell parameters free to change. This leads to 3 different crystal structures. Their obtained cell parameters and packing energies are given in table 1. The lowest-energy structure obtained is found to be corresponding to the  $\alpha$ -structure described by Lommerts et al. (9). Also the  $\beta$ -structure as described by Chatani et al. (10,11) was obtained. To our surprise also a third crystal structure was predicted. It is somewhat more stable and has a higher density than the  $\beta$ -structure. The structure is monoclinic, although we started from a rectangular unit cell. This structure has not been found experimentally yet. The fact however that as well the  $\alpha$ - as the  $\beta$ -structure were correctly predicted, indicates that it may be possible that also this third structure ( $\gamma$ -structure) of poly(ethylene ketone) exists under certain conditions. Further details of this  $\gamma$ -structure will be given in a subsequent publication (6).

Table 1: Packing energies and cell parameters for the 3 crystal structures of poly(ethylene ketone) as obtained using Polymer Crystal Silverware

Packing En. (J/g)	a(Å)	b(Å)	c(Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	$\rho$ ( $\text{g.cm}^{-3}$ )	Remarks
-696.6	6.58	5.39	7.69	90	90	90	1.37	$\alpha$ -structure
-655.7	7.74	4.94	7.79	90	98.5	90	1.28	$\beta$ -structure
-663.9	7.15	5.17	7.71	90	90	79.9	1.33	new structure ( $\gamma$ )

### B. Nylon-6,6

We took Nylon-6,6 as a typical representative of the Nylons for which many crystal structures are in principle possible. Most of the Nylon crystal structures consist of hydrogen-bonded sheets. These sheets can be packed in several ways each leading to a different crystal structure. For Nylon-6,6 two crystal structures have been described in more detail. The  $\alpha_1$ -structure (13) has one chain per unit cell. A second structure (the  $\alpha_2$ -structure, high temperature form) has been described by Vergelati et al. (14) based on the cell parameters of Starkweather and Jones (15) and also has one chain per unit cell. We performed our calculations with two chains in the unit

cell ( $Z=2$ ) starting from a rectangular unit cell with  $a=b=6.35 \text{ \AA}$  (density  $1.05 \text{ g.cm}^{-3}$ ), and an all-trans conformation for the polymer chain. We must emphasise here that no a priori assumption was made about the way the chains are packed: no hydrogen bonding between chains is imposed by the algorithm at all. 38 solutions were obtained (using the same parameters as for poly(ethylene ketone) and an additional Van der Waals radius of  $1.4 \text{ \AA}$  for N) which were then energy-minimised resulting in 6 different stable crystal structures. Cell parameters and packing energies are listed in table 2. Surprisingly all energy-minimised structures show hydrogen-bonded sheets, three of them with the hydrogen bonds along the a- or b-axis and the other three showing the hydrogen bonds between the corner and the centre chains. All these crystal structures have a triclinic unit cell. The lowest-energy structure obtained is the  $Z=2$  equivalent of the  $\alpha_1$ -structure: it can easily be reduced to the  $\alpha_1$ -structure by an appropriate unit cell transformation. The other crystal structures all have packing energies at least  $84 \text{ J/g}$  above that of the  $\alpha_1$ -structure. The only difference between these structures and the  $\alpha_1$ -structure is the way the hydrogen-bonded sheets are packed. We realise that besides these 6 structures more packings are possible, as e.g. the  $\alpha_2$ -structure was not obtained. As however we already obtained the stable  $\alpha_1$ -structure from a first calculation, without any a priori knowledge about the packing and the unit cell size, we decided not to continue the search for still more possible structures, but to move our attention to a more difficult problem, i.e. the crystal structure of poly(ethylene terephthalate).

**Table 2:** Packing energies and cell parameters for the crystal structures of Nylon-6,6 as obtained using Polymer Crystal Silverware

Packing En. (J/g)	a(Å)	b(Å)	c(Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	$\rho$ (g.cm <sup>-3</sup> )	Remarks
-956.2	5.01	9.45	17.7	55.5	98.9	83.0	1.14	$\alpha_1$ -structure
-872.1	4.92	7.93	17.8	67.9	102.6	88.2	1.21	
-864.7	7.57	6.94	17.8	132.4	110.5	84.7	1.19	
-840.6	7.81	5.03	17.8	75.2	90.1	75.4	1.15	
-725.7	7.93	4.98	17.8	104.0	79.3	74.7	1.19	
-650.0	4.65	7.49	17.4	92.0	93.1	82.2	1.25	

### C. Poly(ethylene terephthalate)

The crystal structure of poly(ethylene terephthalate) has been elucidated by de Daubeny, Bunn and Brown as early as 1963 (16). It is triclinic with one monomer unit in the unit cell. As the shape of the polymer chain in its all-trans-configuration is far from cylindrical, it may be expected that starting with a rectangular unit cell with  $a=b$  will not lead to all possible crystal structures for this polymer. Therefore we performed calculations with two monomer units in a rectangular unit cell ( $Z=2$ ) and different  $a/b$  ratios in first instance and later starting from a skew cell (we rather arbitrarily chose  $\alpha=120^\circ$ ) and different  $a/b'$  ratios, where  $b'=b.\sin(\alpha)$ . Starting from a rectangular unit cell with  $a=b$  followed by energy-minimisation of all obtained structures gave eleven different crystal structures, with three of them having a lower energy than

the (energy-minimised) Daubeny structure.

The experimental cell is not found among these results. It is easily understood why when looking at the cell angles of the obtained crystal structures. In no case a deviation from rectangularity of more than  $35^\circ$  is found, and in most cases the deviation is less than  $15^\circ$ . This means that starting from a rectangular cell, it will never be possible to obtain very skew cells, which can be expected in the case of polymer chains with an irregular shape as poly(ethylene terephthalate). Therefore we decided to perform additional calculations starting with the above mentioned skew unit cells, with the same polymer density. 54 different structures were obtained after energy-minimisation, with four structures having a lower energy than that resulting from the energy-minimisation of the experimental cell. The latter is also obtained as the fifth structure. Also surprising is that all the low-energy structures of the first calculation (starting from a rectangular unit cell) are found once again. Cell parameters and packing energies of the 10 lowest-energy structures are given in table 3. The observation that structures are obtained with a lower energy than the structure obtained from an energy-minimisation of the experimental cell needs some consideration. Firstly the energy difference between the lowest-energy structure and the energy-minimised experimental structure is rather low (15 J/g). This may indicate that the forcefield is not accurate enough, although the cif91-forcefield used is one of the best forcefields currently available. It may however, also be possible that the experimental structure is a metastable one. Further studies are necessary to clear this point.

**Table 3:** Packing energies and cell parameters for the 10 lowest-energy crystal structures of poly(ethylene terephthalate) as obtained using Polymer Crystal Silverware

Packing En. (J/g)	a(Å)	b(Å)	c(Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	$\rho$ (g.cm <sup>-3</sup> )	Remarks
-603.9	5.85	7.46	11.1	115.5	78.8	91.2	1.49	
-602.4	4.57	11.72	11.1	67.0	54.4	74.9	1.44	
-595.6	4.62	10.98	11.1	79.7	55.3	72.3	1.44	
-589.6	7.00	5.80	11.1	101.2	91.6	90.1	1.45	
-589.2	11.71	4.59	11.1	125.8	67.9	111.6	1.45	exp.struct.
-588.9	5.75	9.17	11.1	125.3	100.1	97.6	1.42	
-587.1	5.78	9.16	11.1	125.3	100.3	97.6	1.42	
-586.8	11.48	3.81	11.1	116.3	90	90	1.47	
-585.4	10.24	4.68	11.1	118.2	92.3	71.2	1.45	
-585.0	6.93	11.90	11.1	144.4	61.6	126.9	1.50	

### Conclusions

A method has been presented for the prediction of polymer crystal structures. The packing problem is solved by using an adapted version of Mario Blanco's "Molecular Silverware" algorithm. Then the obtained starting structures are energy-minimised using molecular mechanics methods. The only information needed is the conformation of the polymer chain (obtainable from other molecular modelling methods), and a reasonable value for the density. The method was successfully applied to obtain the lowest-energy and other possible structures of poly(ethylene ketone), Nylon-6,6 and poly(ethylene terephthalate).

We expect this method will in future become important as it enables the prediction of the crystal structure, which is needed for the calculation of the ultimate mechanical properties, of polymers that even have not been synthesised yet, and/or shaped e.g. into highly crystalline, well-oriented fibres. This means that using this method it will be possible, in an extremely cost-effective way, to screen if a not-yet-existing polymer can in principle be suitable for a certain application.

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A floppy disc with the coordinates of the above described crystal structures (in Biosym .car format) can be obtained from the author.