

PCSP: a computer program to predict and analyze the packing in crystalline polymers

S. León, J.J. Navas, C. Alemán*

Departament d'Enginyeria Química, E.T.S. d'Enginyers Industrials de Barcelona, Universitat Politècnica de Catalunya, Diagonal 647, Barcelona E-08028, Spain

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Abstract

A computational strategy based on force-field calculations was developed to predict and analyze the packing in crystalline polymers. The strategy, which was incorporated in a computer program called Prediction of the Crystal Structure of Polymers (PCSP), takes advantage of the information provided by X-ray and/or electron diffraction. The program evaluates all the modes of packing for a given lattice dimensions, being able to predict the lowest energy one. The ability of the method to provide reliable results was proved by analyzing the crystal structure of four different polymers. Further, an insight on the applicability of the PCSP program to estimate the mechanical properties of polymers was provided by computing the elastic constants of the orthorhombic polyethylene. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: PCSP; Crystalline polymers; Orthorhombic polyethylene

1. Introduction

Diffraction studies play a crucial role in determining the three-dimensional (3D) structure of crystalline polymers. However, polymers are unable to render monocrystalline samples of the size required for the application of standard X-ray diffraction techniques. Thus, fibrous specimens are usually employed to ascertain the structure of crystalline polymers. Unfortunately, the amount of data obtained by diffraction is usually limited due to the partially ordered nature of polymer fibers and thus, the molecular structure cannot be accurately determined. Computational methods based on energy calculations, combined with such diffraction data are of great help in ascertaining the 3D structure of the polymer.

A method to predict the crystal structure of polymers would be useful not only in determining the molecular structure of a crystalline polymer, but also in understanding and rationalizing the fundamental properties of polymeric materials, in which the crystal packing has a major influence. Further, reliable predictions of whether an existing molecular solid could crystallize in another structure would have major implications for processing design. Any computational procedure to predict polymer crystal structures should

include three schemes of simulation: (i) a method to generate all the confident conformations of the polymer chain as starting points; (ii) a method to generate all the modes of packing compatible with a starting conformation; and (iii) a method to compute the forces which bind the molecules together to form the crystal. Various methods of screening the multi-dimensional potential energy surface of possible crystal structures of small organic molecules have been proposed recently [1–5]. However, the approximation usually employed to predict the crystal structure of polymers consists of a combination of very different theoretical methodologies [6–11], therefore a complete and consistent computational method is not available at the moment.

We have recently reported a simple and efficient strategy for the generation of polymer molecular conformations compatible with X-ray diffraction data [12], which has been implemented in a computer program named GEMOX (GEneration of polymer MOlecular models compatible with X-ray diffraction data). The method creates all the conformations compatible with both the experimentally determined axial repeat length of the chain and the helix symmetry. The sterically hindered conformations are then discarded using an energy criteria. The reliability of this computational strategy to generate suitable molecular models has been recently proved in some derivatives of nylons 3 and 4 [12–14].

In the present work, we extended our simulation strategy by developing a computational method to predict the crystal

*Corresponding author. Tel.: + 34-93401-6680/6681; fax: + 34-93401-6600/7150.

E-mail address: aleman@eq.upc.es (C. Alemán)

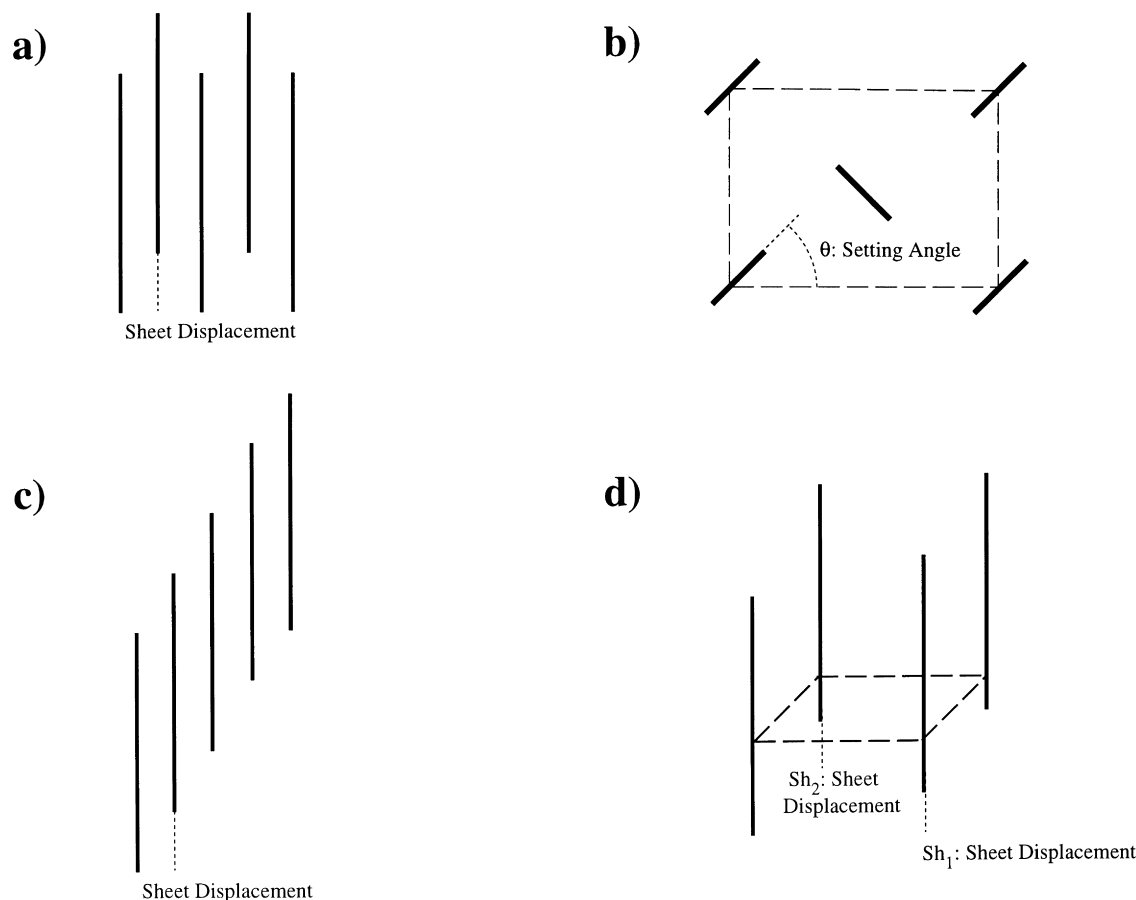


Fig. 1. Scheme of the geometric variables used in PCSP calculations. The energy map of orthorhombic PE was computed by varying the sheet displacement along the c -axis (a) and the setting angle (b). The energy map of 2-6 PES was computed by varying the setting angle (b) and the sheet displacement (c). The energy map of PET was computed by varying the sheet displacements Sh_1 and Sh_2 (d).

structure of polymers. The methodology was incorporated into a manageable computer program named Prediction of the Crystal Structure of Polymers (PCSP). The use of the GEMOX/PCSP computer package permits us to predict not only the molecular conformation, but also the mode of packing of crystalline polymers by combining the information provided by X-ray and/or electron diffraction with energy calculations.

2. Computational procedure

2.1. Structure of the GEMOX/PCSP computer package

In the first stage, the GEMOX program is used to generate a complete set of molecular conformations energetically favored for the polymer which are compatible with the observed helix pitch and helix symmetry. Thus, for a given polymer it is usually expected that multiple conformations are capable of fitting into the same helical backbone. The total energy for a given conformation is estimated by not only considering the internal energy of the chemical repeating unit (CRU) i , but also the interaction energy with

all CRUs between $i - N$ and $i + N$, where N is specified by the user. The molecular conformations were obtained using a corrected grid search algorithm which was reported in our earlier work [12]. Bond lengths and bond angles were considered fixed at the equilibrium values.

All the molecular models compatible with the experimental data are then introduced in the PCSP program. This program generates the atomic coordinates for the different modes of packing, using the available X-ray data. For this purpose, starting cells are built using the experimentally determined lattice dimensions. Further, parallel and antiparallel arrangements between the polymer chains are also considered and a number of packing arrangements is built for each starting lattice by varying both the setting angle for the polymer chains and sheet displacements. The chain structures built with GEMOX are not relaxed once put in the crystal lattice. The total energy for each packing mode is then determined as a sum over sufficient potential energy interactions to represent the energy of a crystal. Thus, both intra- and inter-molecular interactions are simultaneously considered. This allows us to determine the packing mode of lowest energy for a given polymer.

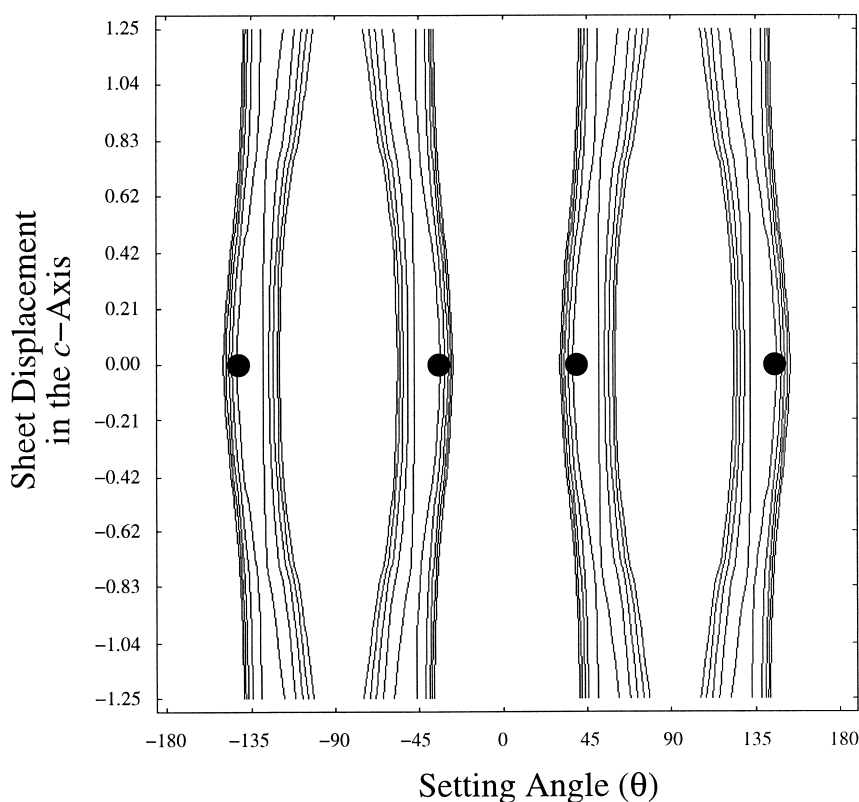


Fig. 2. Energy map computed for orthorhombic PE. The setting angle is expressed in degrees. The sheet displacement is expressed in Å and ranges from $-1/2$ to $+1/2$ length of the repeating unit. The position of the minimum energy arrangements are indicated by black dots.

2.2. Structure of the PCSP computer program

The PCSP program uses the following as input: (i) the molecular information, i.e. molecular connectivity, bond lengths and bond angles of the CRU; (ii) the conformational parameters of the CRU provided by the GEMOX strategy, i.e. the values of the dihedral angles that define the suitable conformation of the CRU; (iii) the torsional and non-bonded parameters required to estimate the energy of the system; and (iv) the experimental data obtained from X-ray and/or electron diffraction, i.e. the lattice dimensions, the number and position, if available, of CRUs by unit cell. In what follows, a molecular chain is generated and oriented with respect to a cartesian coordinate system such that the chain

axis is along the z -axis and the first atom of the repeating unit is on the x -axis at $x = 0$. Then, different crystal lattices are generated using the unit cell parameters and both the number and position of CRUs in the unit cell provided by the user, without relaxing the chain structures. For each crystal lattice, a number of packing arrangements are considered by varying the displacement between different sheets along the a -, b - and/or c -axis, as well as the setting angle between different chains. All the structures are obtained by applying the required translation and/or rotation transformations to the atomic coordinates of the first chain.

The energy of each packing arrangement is evaluated using an empirical force-field. The total energy is computed by adding both the electrostatic and van der Waals non-bonding contributions to the energy involved in the torsion of the bonds of the chains contained in the unit cell. The electrostatic and van der Waals contributions were computed by applying the Coulombic and 12-6 expressions, respectively. As a result of the lattice periodicity, the non-bonding interactions were computed not only within the chains of the unit cell, but also between a reference unit cell and external units. For this purpose, the atomic coordinates of the existing external unit cells within a cutoff distance defined by the user are also generated. The torsional energy was computed using the classical 3-Fourier expression.

The results provided by the PCSP program permits us to

Table 1

Comparison between the setting angle (θ) and the sheet displacement (Sh) predicted by the PCSP program for the orthorhombic PE and the results reported in the literature

Reference	Source	θ ($^\circ$)	Sh (Å)
[15]	X-ray diffraction	48.8	0
[16]	Neutron diffraction	41.1 ± 1	0
[17]	X-ray diffraction	~ 45	0
[18]	Neutron diffraction	45	0
[19]	Force-field calculations	46.9	0
[20]	Force-field calculations	41.9	0
This work	PCSP program	42	0

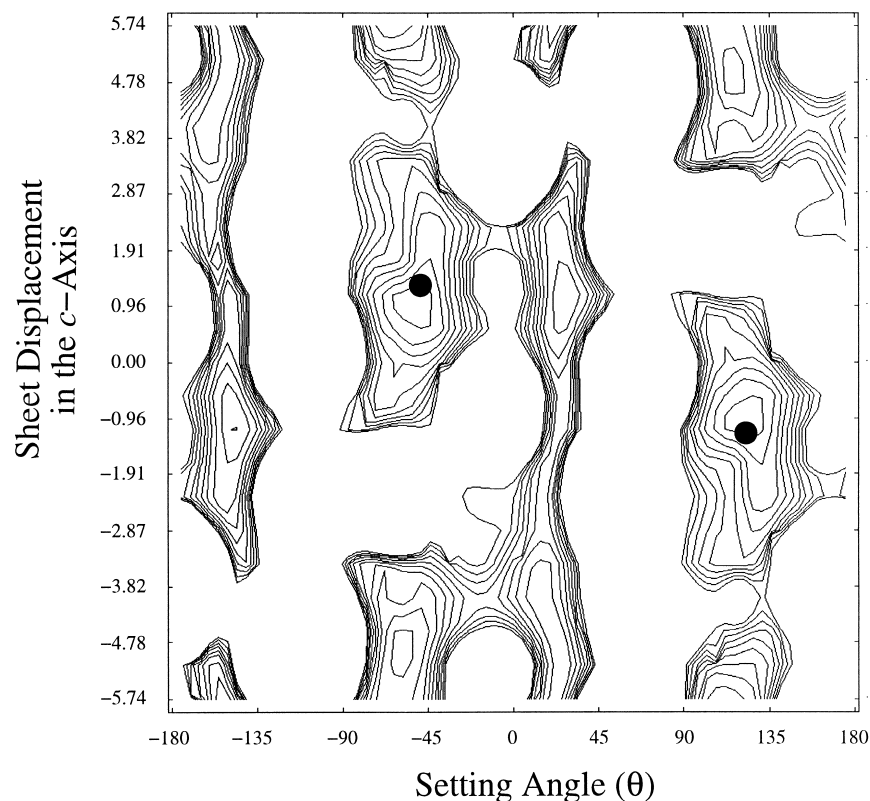


Fig. 3. Energy map computed for monoclinic 2-6 PES. The setting angle is expressed in degrees. The sheet displacement is expressed in Å and ranges from $-1/2$ to $+1/2$ length of the repeating unit. The position of the minimum energy arrangements are indicated by black dots.

identify the packing arrangement of lowest energy which is a very useful tool in solving the 3D structure of polymer fibers. Further, the suitable use of the PCSP program for a given crystal lattice allows us to predict the mechanical properties of the crystal that are related to the packing energy.

3. Test cases

The crystal structures of the orthorhombic polyethylene (PE) [15–20], monoclinic 2-6 polyester [21,22], tetragonal poly(α -isobutyl- β -L-aspartate) [23–25] and triclinic poly(ethylene terephthalate) [26,27] were used to test the PCSP program as these polymers have been previously investigated by other authors. However, in order to extend the applicability of the PCSP program, the elastic constants of the orthorhombic PE along the a - and b - directions were predicted. The results were compared with the experimental data reported in the literature [28,29], and also with values obtained using other theoretical methods [2,30–32]. All the energy calculations were performed considering the all-atom force-field parameters included in the AMBER libraries [33]. Electrostatic charges for monomeric units of all the polymers were explicitly derived at the AM1 level [34]. Calculations were performed on a Silicon Graphics O₂-5000 at our laboratory. An energy cutoff of 15 Å was

applied in all cases. This distance corresponds to more than one and a half the size of the crystal lattices built. Pilot calculations considering larger values for the cutoff provided insignificant changes in the computed energies.

3.1. Crystal structure of the orthorhombic polyethylene

The lattice dimensions chosen for the PCSP calculations of the orthorhombic PE were those described by Bunn [15]: $a = 7.42$ Å, $b = 4.95$ Å and $c = 2.49$ Å. The sheet displacement (Sh) and the setting angle (θ) were varied as shown in Fig. 1(a) and (b), respectively. Grid steps of 1° and 0.25 Å were used for θ and Sh, respectively.

The energy map obtained by varying θ and Sh is shown in Fig. 2, the contour lines being drawn at 1 kcal/mol interval. However, the values of θ and Sh corresponding to the lowest energy structure found by the PCSP program are shown in Table 1, where experimental and theoretical results reported by other authors are also listed [15–20]. Fig. 2 presents four symmetric regions which are degenerated in energy, as was expected by both the symmetry of the 2₁-helix and the position of the two chains in the unit cell. The positions of the four symmetric minima are indicated by black dots in the figure. It should be mentioned that each point of the map takes less than one second of computer time to point the computer efficiency of the PCSP program. It is worth noting that both θ and Sh values predicted by our

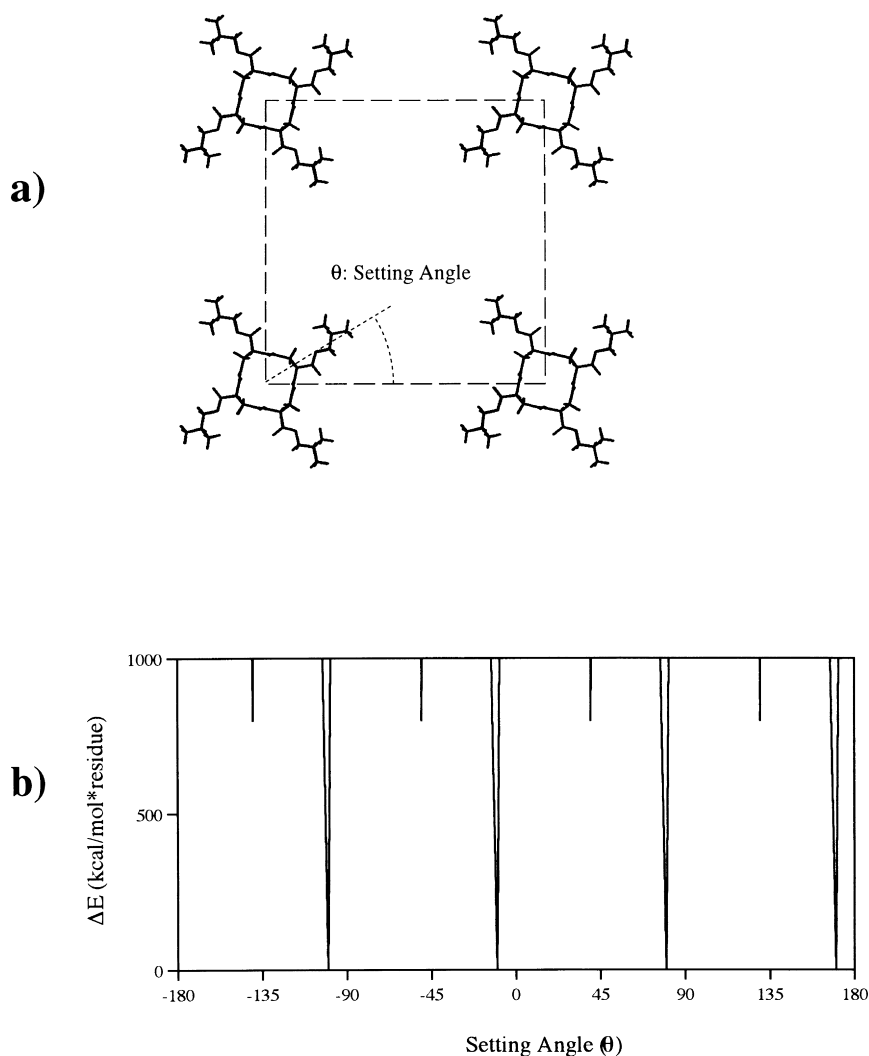


Fig. 4. The setting angle (a) of the tetragonal lattice of PAIBLA was varied to compute the energy profile (b) with the PCSP computer program. The setting angle is expressed in degrees. The position of the minimum energy arrangements are indicated by black dots.

program are within the range of experimentally found data. Thus, X-ray [15,17] and neutron [16,18] diffraction experiments provided θ values ranging from 41 to 49°, whereas a value of $Sh = 0 \text{ \AA}$ was found in all the cases. The results predicted by the PCSP program were $\theta = 42^\circ$ and $Sh = 0 \text{ \AA}$. Further, the PCSP values are also in good agreement with the results provided by other authors using more complex and computationally demanding methods [19,20]. Thus, Boyd and co-workers [19] predicted $\theta = 46.9^\circ$ and $Sh = 0 \text{ \AA}$ using a sophisticated force-field developed by us, whereas the results reported by Goddard III and co-workers [20] using the MCXX force-field were $\theta = 41.9$ and $Sh = 0 \text{ \AA}$.

3.2. Crystal structure of the monoclinic 2-6 polyester

The unit cell of 2-6 polyester (PES) consists of a monoclinic lattice with parameters $a = 5.47 \text{ \AA}$, $b = 7.23 \text{ \AA}$, $c = 11.72 \text{ \AA}$, $\beta = 113.5^\circ$ and two chains per cell [21]. The chain

was built by considering a complex kink conformation, similar to that found by Liao and Boyd [22]. Thus, the three consecutive dihedral angles of the diol unit adopt a *gauche*⁺, *trans* and *gauche*⁻ conformation. The θ and Sh values were varied according to Fig. 1(b) and (c), respectively. The energy map obtained from such variations is shown in Fig. 3, the positions of minimum energy being indicated by black dots. The contour lines are drawn every 1 kcal/mol.

The energetically allowed space is quite restricted, θ values ranging from 45° to 90° and from -90° to -135° being unfavored due to steric clashes between neighbouring chains. Further, it should be noted that for the energetically favored θ values, the energy surface is rather flat in the Sh coordinate direction. The lowest energy structure predicted by the PCSP program corresponds to $\theta = 125^\circ$ and $Sh = -1.15 \text{ \AA}$, which consist of a unit cell with parameters $a = 5.52 \text{ \AA}$, $b = 7.23 \text{ \AA}$, $\beta = 112.6^\circ$. These results are consistent with the experimental parameters proposed by Turner-Jones

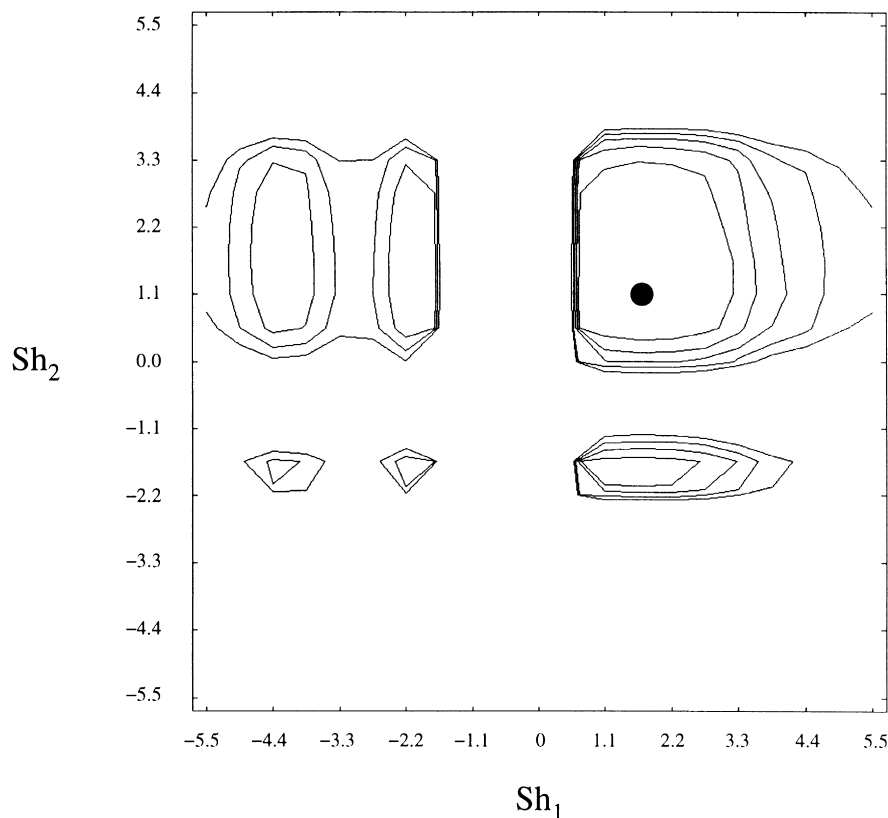


Fig. 5. Energy map computed for triclinic PET. The sheet displacements are expressed in Å and range from $-1/2$ to $+1/2$ length of the repeating unit. The position of the minimum energy arrangements are indicated by black dots.

and Bunn [21]. These results provided by the PCSP program are also in good agreement with those reported by Liau and Boyd [22], who investigated the crystalline packing of this polymer using force-field calculations. The values predicted by these authors were $\theta = 125^\circ$ and $Sh = -1.09$ Å, indicating that our computer strategy is able to provide good results for polymeric systems with complex conformations.

3.3. Crystal structure of the tetragonal poly(α -isobutyl- β -L-aspartate)

The tetragonal form of poly(α -isobutyl- β -L-aspartate) (PAIBLA) was recently investigated using X-ray diffraction [23–25]. The crystallographic parameters of this structure are $a = b = 13.98$ Å and $c = 4.94$ Å. The 3D structure of the tetragonal PAIBLA was determined using both linked-atom least-squares methodology applied to X-ray data [24] and

force-field calculations [25]. A structure constituted by 4_1 -helices arranged in parallel was obtained. The most favored setting angle (see Fig. 4(a)) for the tetragonal form of PAIBLA was investigated using the PCSP program. For this purpose, a 4_1 -helix conformation obtained from a conformational search with the GEMOX computer program was used. Results are shown in Fig. 4(b).

It is worth noting that only four equivalent θ values were energetically favored, which are clearly indicated by the four sharp peaks in Fig. 4(b). They are isoenergetic and correspond to $\theta = 80^\circ, 170^\circ, -100^\circ$ and -10° . Thus, these values are related by a four-fold periodicity indicating that there is a 4_1 -axis in the center of the cell as was found in previous studies [23–25]. All the other positions are largely unfavored from an energetic point of view due to the severe steric clashes between the isobutyl side groups. The value obtained by refining the packing against the X-ray

Table 2

Calculated and experimental lattice parameters (distances and angles in Å and degrees, respectively) for triclinic PET

Reference	Source	a	b	c	α	β	γ
[26]	X-ray diffraction ^a	4.56	5.94	10.75	98.5	118	112
[27]	Force-field calculations ^a	4.48	6.02	10.86	102.5	119.8	107.0
This work	PCSP program	4.35	6.01	10.75	100.4	112.2	112.8

^a Data derived at 300 K.

Table 3
Comparison of theoretical and experimental elastic constants (in GPa) for orthorhombic PE

Reference	Source	C_{11}	C_{22}
[28]	Ultrasonic measurements	8.4 ^a	
[29]	Neutron diffraction	11.5 ^b	
[30]	Molecular mechanics	13.3	11.2
[31]	Molecular mechanics	12.6	12.4
[32]	Molecular mechanics	14.3	12.2
[33]	Molecular mechanics	7.99	9.92
This work	PCSP program	8.1	9.9

^a Elastic constant at 213 K.

^b Elastic constant at 77 K.

diffraction data was 82° [24], which is in excellent agreement with the value predicted by the PCSP program.

3.4. Crystal structure of the triclinic poly(ethylene terephthalate)

The lattice parameters of poly(ethylene terephthalate) (PET) used in PCSP calculations are those originally proposed by Daubeny et al. [26]: $a = 4.56 \text{ \AA}$, $b = 5.94 \text{ \AA}$, $c = 19.75 \text{ \AA}$, $\alpha = 98.5^\circ$, $\beta = 118^\circ$ and $\gamma = 112^\circ$. There is one repeat unit per unit cell. An energy map for triclinic PET was obtained by displacing two consecutive sheets along the c -axis. Such displacements are indicated by Sh_1 and Sh_2 in Fig. 1(d). Results are displayed in Fig. 5, the lowest energy structure being indicated by a black dot.

It is worth noting that only the Sh_2 values ranging from 0.0 to 3.7 Å are favorable from an energetic point of view due to the steric clashes between the aromatic rings out of this range, whereas the number of energetically allowed values for Sh_1 is widest, ranging from 1 to 9 Å. The unit cell parameters of the lowest energy structure predicted by the PCSP program are compared in Table 2 with those found by both X-ray diffraction [26] and other computational methodologies [27]. The predicted lattice is remarkably close to that found by X-ray diffraction. The discrepancy between PCSP and experimental parameters is < 5% for all lengths and angles. Further, it must be noted that the PCSP computer program uses static structure calculations, i.e. 0 K without explicit treatment of zero point vibrations. By contrast, the discrepancy between the experimental lattice and that predicted by Rutledge [27] at 300 K using a self-consistent form of lattice dynamics is < 4.5% for all lengths and angles. Thus, the improvement provided by this sophisticated methodology with respect to the PCSP strategy is almost negligible.

3.5. Mechanical properties of the orthorhombic polyethylene

The elastic constants along the a and b directions for PE were estimated by computing the response given by the minimum energy structure obtained by the PCSP program in the previous section to a uniform static external force,

which was applied in these directions. The work done by the external force was assumed to be transformed exclusively into internal energy, neglecting any change in entropy. This is a reasonable assumption as only small conformational variations are expected if the external forces are applied along the a and b directions. In a crude approach, the elastic constants C_{11} and C_{22} were computed by fitting a quadratic expression to the internal energy variation provided by the PCSP program as a function of the distances a and b .

The a and b distances were systematically changed from –2% to 7% in steps of 1% from the parameters observed by X-ray diffraction [15]. The elastic constants C_{11} and C_{22} predicted by PCSP strategy together with those reported by other authors using experimental [28,29] and theoretical [2,30–32] methodologies are reported in Table 3. The values predicted by the PCSP strategy are in good agreement with the experimental data, being also within the range of values estimated by other theoretical approaches.

4. Summary

We have developed a computational method, called PCSP, to predict the energetically most favorable modes of packing for crystalline polymers. This method combined with the GEMOX computer program, which allows to find the molecular conformation, constitutes a powerful tool in determining the 3D structure of polymers using the X-ray and/or electron diffraction data. Systematic studies of polymer structures by this method, followed by a comparison with both the experimental data and the theoretical results obtained using sophisticated methodologies reveal the performance of the PCSP computer program, even though it makes broad assumptions and is thus a lot quicker. In all the cases, the packing modes predicted by the PCSP program were in excellent agreement with the experimental data. Further, a preliminary analysis of the utility of the method to predict the mechanical properties of the polymers was performed. Application of the PCSP program may assist in providing a comprehensive picture of the crystalline polymer structures based on energy criteria, but using the data provided by diffraction experiments.

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