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# Analysis of modes of packing of the most stable form of syndiotactic polypropylene

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Conformational energy calculations have been performed on the chain of syndiotactic polypropylene having **s(2/1)2** symmetry with the aim to find the best conformation in the crystalline field. A detailed packing analysis by molecular mechanics has been effected in order to clarify some features of the crystal structure of the most stable form. The close packing is obtained along the direction of the *b* axis with chains having opposite chirality. A statistical arrangement of right- and left-handed chains is found in each site along the direction of the *a* axis. The results are in agreement with experimental data reported in the literature, and provide a satisfactory explanation of the discrepancies present in previously proposed structures. © 1997 Elsevier Science Ltd.

**(Keywords: syndiotactic polypropylene; packing analysis; molecular mechanics)**

## INTRODUCTION

Syndiotactic polypropylene (sPP) exhibits a complex and widely studied polymorphism due both to the presence of different chain conformations and to different modes of packing of chains having the same conformation.

At least three different conformations are known. One of them is characterized by a helical symmetry[1] corresponding to the **s(2/1)2** line repetition group[2]. A second conformation[1] is characterized by a glide plane containing the chain axis according to the *tc* line repetition group, and the corresponding crystalline form was studied by different authors[3–5]. Recently, a third conformation corresponding to $(T_6G_2T_2G_2)_n$ helices has been obtained and structurally characterized[6].

The most important crystalline forms contain polymer chains in the **s(2/1)2** symmetry having different modes of packing. One of them, obtained in fibre samples, corresponds to a C-centred structure having a unit cell with axes $a = 14.50$ Å, $b = 5.60$ Å, $c = 7.40$ Å[7]. The most stable form, obtained by crystallization from the melt and solution, corresponds to a B-centred structure having a unit cell with axes $a = 14.50$ Å, $b = 11.20$ Å, $c = 7.40$ Å[8]. The proposed space group in the ideal limit-ordered structure is *Ibca*, in which right-handed (R) and left-handed (L) chains succeed each other in both the *a* and *b* directions, as shown in *Figure 1*. This structure is in general good agreement with the diffraction data. However, some experimental features, such as the presence of a weak reflection having (011) indices[9] extinct in the *Ibca* space group and the splitting of $CH_3$ bands in the n.m.r. spectra[10], need to be explained.

Recently, several reports[9–21] have provided the experimental conditions to obtain the B-centred or the C-centred structure contributing to the understanding of structural features. In this framework different kinds of disorder and the presence of conformational or configurational defects have been postulated. However, only a partial analysis of the modes of packing performed by molecular mechanics has been until now reported[13,21].

In this paper we report the results of new conformational energy calculations and of a detailed packing energy analysis by semiempirical potential functions, with the purpose of clarifying the features of the crystal structure of the most stable form of sPP.

## NEW CONFORMATIONAL ENERGY CALCULATIONS

A partial conformational analysis aimed at the study of the crystalline forms of sPP has been reported[1,22]. More recently, we performed more complete conformational energy calculations[5] on the different polymorph forms of sPP and compared the results with experimental data on new crystal structures[4,8]. In the previous paper[5] we calculated the best conformations of the chains of sPP satisfying the equivalence principle and the chain axis repeats both for the *tc* and for the **s(2/1)2** line repetition groups. We considered all the atoms, including the hydrogen atoms of the methyl groups, as distinct atomic species and we assumed for the **s(2/1)2** line repetition group that all the $C–CH_2–C$ bond angles had the same value in the optimized conformation, even if this assumption was not strictly dictated by the equivalence principle.

We have now performed new conformational energy calculations on the polymorph form of sPP in the **s(2/1)2** symmetry with the purpose of finding the best conformation to be used in the packing energy calculations. We have independently varied the $C–CH_2–C$ bond angles of adjacent methylene groups and we have

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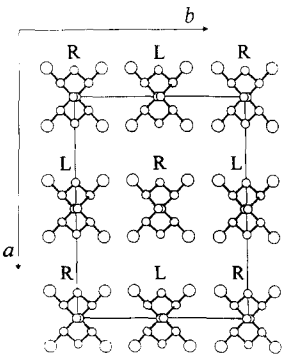


**Figure 1** View along the *c* axis of the unit cell of sPP in the *Ibca* space group

**Table 1** Parameters of the potential functions used in the energy calculations. The symbols are explained in the text. The values of $K_b$, $K_t$, $A$ and $B$ are expressed in such a way that the energy is in kilojoules per mole. $d_w$ is the van der Waals distance

| (a) | Bending terms | | |
|---|---|---|---|
| Bond angle | $K_b$ | | $\tau_0$ |
| C–C–C | 0.184 | | 109.47° |
| C–C–H | 0.121 | | 109.47° |
| H–C–H | 0.100 | | 109.47° |
| (b) | Torsional terms | | |
| Torsion angle | | | $K_t$ |
| C–C–C–C | | | 11.7 |
| (c) | Non-bonded terms | | |
| Interacting pair | $A \times 10^{-3}$ | $B$ | $d_w$ (Å) |
| C, C | 1653 | 1519 | 3.60 |
| C, H | 236 | 531 | 3.10 |
| C, $CH_3$ | 4018 | 2669 | 3.80 |
| H, H | 30 | 196 | 2.60 |
| H, $CH_3$ | 613 | 950 | 3.30 |
| $CH_3$, $CH_3$ | 9664 | 4719 | 4.00 |

considered the lateral methyl groups as single units in such a way that the torsion angles around the C–$CH_3$ bonds do not affect the packing energies. The last assumption can be important because in the following packing energy calculations we have fixed the chain conformation. In fact, in the case of regular vinyl polymers, the conformation of the isolated chain under the constraints of the chain symmetry and of the chain axis repeat is generally maintained in the crystal, and only slight changes can be induced by the crystalline field.

The conformational energy has been evaluated as the sum of a term $E_b = \frac{1}{2}K_b(\tau - \tau_0)^2$ due to the deformations of the bond angles, a term $E_t = \frac{1}{2}K_t(1 + \cos 3\theta)$ due to the intrinsic torsional potential and a term $E_{nb} = Ar^{-12} - Br^{-6}$ due to the interactions between atomic species separated by more than two bonds. The lengths for the C–C and C–H bonds have been fixed at the values 1.54 and 1.10 Å, respectively. We have used the set of potential functions given by Flory[23,24] for polypropylene and poly(methyl methacrylate), which we already adopted in previous conformational and packing energy calculations on different polymers where the methyl lateral groups were considered as rigid single units[25–30]. The parameters of the potential functions are listed in *Table 1*.

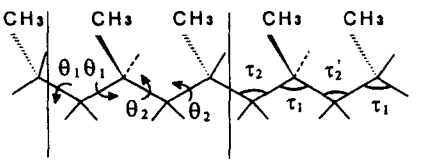


**Figure 2** Portion of the sPP chain with an indication of the main internal parameters varied in the conformational energy calculations. The vertical bars comprise two monomeric units (see text)

**Table 2** Values of the main parameters, *c* axes and energies *E* obtained in the minimizations of the conformation energy

| $\tau_1$ (°) | $\tau_2$ (°) | $\tau_2'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $c$ (Å) | $E$ (kJ (mol mu)$^{-1}$) |
|---|---|---|---|---|---|---|
| 111.5 | 115.0 | 114.7 | 180.3 | 62.0 | 7.52 | 8.0 |
| 110.3 | 115.0 | 115.9 | 181.2 | 60.3 | 7.40[a] | 8.1 |

[a] Imposed value

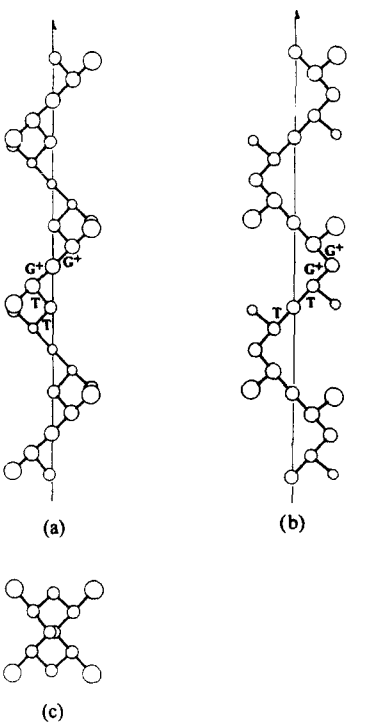


**Figure 3** Projections along three orthogonal axes of the right-handed chain of sPP obtained in the conformational energy calculations. (a, b) Views along the two binary axes; (c) view along the $2_1$ axis. T and $G^+$ indicate the nearly *trans* and *gauche* torsion angles reported in *Table 2*

The conformational energy has been calculated considering a polymer chain, comprising eight monomeric units (mu), under the constraint of maintaining the **s(2/1)2** symmetry. Therefore, we have imposed a $2_1$ screw axis along the chain and binary axes perpendicular to the $2_1$ axis intersecting the carbon atoms of successive $CH_2$ groups. *Figure 2* shows a portion of the polymer chain with an indication of the most significant internal parameters. The conformational energy has been calculated by taking into account the energy terms inside the two indicated monomeric units and considering the non-bonded interactions between the atoms of these monomeric units and all the other atoms. The non-bonded interactions have been neglected for distances greater than twice the van der Waals distances for each kind of interacting pair.

Minimizations of the conformational energy have been performed both without constraint on the length of the chain axis repeat and by imposing the experimental value $c = 7.40$ Å. The values of the main variables and of the corresponding $c$ axes and energies obtained in the minimum-energy points are shown in *Table 2*. These parameters refer to a chain having the configuration sketched in *Figure 2* and characterize a right-handed helix. Opposite values of torsion angles characterize a left-handed helix which is enantiomorphous and, therefore, isoenergetic with the right-handed helix. The results of *Table 2* clearly indicate that the two minimizations give conformations having very similar internal parameters. No significant difference is observed with respect to the parameters obtained in the previous minimization[5] performed under the constraint of the experimental value of the $c$ axis and considering the atoms of the methyl groups as distinct atomic species. Three projections of the sPP chain obtained by minimization of the conformational energy are shown in *Figure 3*.

## ANALYSIS OF THE MODES OF PACKING: METHOD OF CALCULATION

The analysis of the modes of packing has been performed in this paper in the framework of the B-centred orthorhombic unit cells as proposed by Lotz *et al.*[8]. Moreover, we have examined the possibility that the chains have the following degrees of freedom: (i) rotation around the $c$ axes; (ii) shifts along the $c$ axes; (iii) variation of the distances between the $c$ axes.

Chains having the rigid conformation with $c = 7.40$ Å reported in the previous paragraph have been packed. The packing energy has been calculated by taking into account the interactions between the atoms of two monomeric units and the atoms of adjacent chains contained in spheres having radii twice the van der Waals distances for each considered atomic species. We have used the same non-bonded terms of the conformational energy calculations both with the parameters given by Flory and with parameters obtained by increasing the van der Waals radii. In fact, it is well known that the potential energy functions tend to reproduce parameters of the unit cells that can be experimentally found at temperatures near 0 K because they do not consider thermal vibrations and defects. A valid method to obtain values of the axes of the unit cell at higher temperatures is to increase the van der Waals radii. This causes an increase of the repulsive term of the non-bonded functions according to the formula $A = (B/2)d_w^6$. This procedure was successfully adopted in previous papers for different polymers[27,31–34].

Considering the size of the unit cell and the shape of the molecule, we deduce that the most important contributions to the packing energy are along the $b$ and $a$ directions, while the diagonal contacts seem less relevant. Therefore, we have calculated the packing energy by taking into account separately the interactions in a row along $b$ and in a row along $a$, also with the aim of finding the direction of close packing. Both chains of the same and of the opposite chirality in adjacent sites have been considered along each row. In the first case, we have related the chains by a translation along the considered axis followed by a shift along the chain axis. In the latter case, the chains of opposite chirality have been related by an inversion centre. The variable parameters in these calculations are the rotation angle $\omega$ of the chains around their axes, the difference in height $\Delta z$ of adjacent chains and the distance $d$ between the axes of adjacent chains along the two directions. $\omega$ and $\Delta z$ are defined in *Figure 4*.

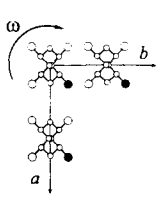


**Figure 4** Definition of $\omega$ and $\Delta z$. $\omega = 0°$ corresponds to the orientation of the chain at the origin of the axes. $\Delta z$ represents the fractional difference in height between the heavy methyl groups of the chains along the $b$ or the $a$ direction

## MAPS OF THE PACKING ENERGY

As a first step we have calculated the maps of the packing energy as a function of $\omega$ and $\Delta z$ for fixed values of the distances between the chain axes equal to the experimental values of 5.60 Å for the $b$ direction and of 7.25 Å for the $a$ direction, using the energy terms reported by Flory[23,24].

The maps calculated in the cases of adjacent chains of the same and of opposite chirality along $b$ are shown in *Figures 5* and *6*, respectively. Flat minima centred at $\omega = 0°$ and $\Delta z = 0$ are present in both maps, and the energy difference between the minima is only 0.1 kJ (mol mu)$^{-1}$. The energy is high at $\omega$ near $\pm 90°$ whatever the

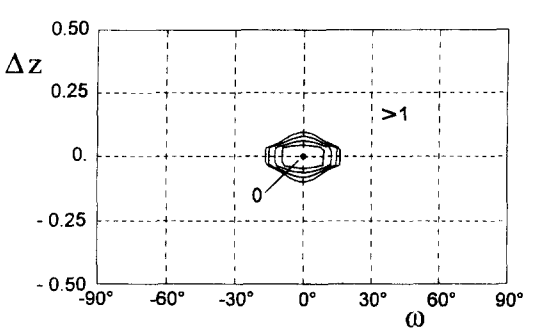


**Figure 5** Map of the packing energy as a function of $\omega$ and $\Delta z$ of chains having the same chirality along the $b$ direction. The curves are reported at intervals of 0.25 kJ (mol mu)$^{-1}$ with respect to the absolute minimum, assumed as zero

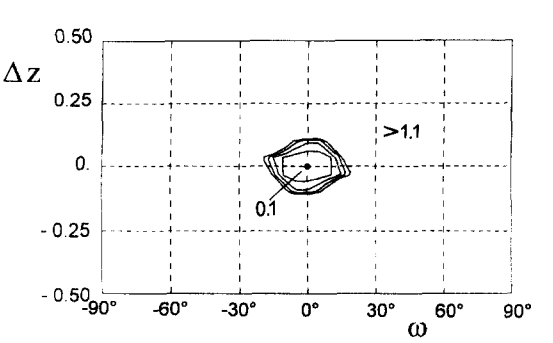


**Figure 6** Map of the packing energy as a function of $\omega$ and $\Delta z$ of adjacent chains having opposite chirality along the $b$ direction. The curves are reported at intervals of 0.25 kJ (mol mu)$^{-1}$ with respect to the absolute minimum of the map of *Figure 5*

values of $\Delta z$. This indicates that, even if the projections of the methyl groups on the *ab* plane roughly lie at the vertices of a square, the modes of packing with $\omega = 0°$ (or 180°) and $\omega = 90°$ (or $-90°$) are completely different. In order to have good van der Waals distances at $\omega = \pm 90°$, the values of *d* along the *b* direction should be significantly higher. The projections in the *bc* plane of pairs of chains having the same and the opposite chirality in the minimum energy points are shown in *Figures 7a* and *7b*, respectively. The two modes of packing require the interdigitation of $CH_2$ and $CH_3$ groups, and present the methyl groups in the same position independently of the chirality of the chain. This is an indication that chains of opposite chirality could have a statistical positioning.

The maps calculated in the cases of chains of the same and of opposite chirality along the *a* direction are shown in *Figures 8* and *9*, respectively. The absolute energy minima of these maps are very much higher with respect to the minima of the maps of *Figures 5* and *6*. This suggests that the close packing is realized along the *b* direction. A second feature of both the maps of *Figures 8* and *9* is the presence of very large regions of low energy around the minima. In particular, all the values of $\Delta z$ in correspondence to $\omega \cong 0°$ are possible at an energy cost $\leq 0.8$ kJ (mol mu)$^{-1}$.

The absolute minimum in the map of *Figure 8* is only 0.1 kJ (mol mu)$^{-1}$ lower than the two equivalent absolute minima of the map of *Figure 9*. This implies that the packing of isochiral chains along the *a* direction, up to now only outlined[13], must be taken into account. Moreover, the absolute minimum is obtained for values of $\Delta z = 0.5$ (or $-0.5$), that is, the only value compatible with an *a* axis equal to $2d$, unless independent chains in the unit cell along this axis are considered.

*Figures 10a* and *10b* show two projections on the *ac* plane of pairs of chains of the same chirality corresponding to the points of the map of *Figure 8* having coordinates ($\omega = 0°$, $\Delta z = 0$) and ($\omega = 0°$, $\Delta z = 0.5$), respectively. In the first case the closest contacts between methyl groups occur at 3.56 Å, a distance which is considered too short. In the latter case ($\Delta z = 0.5$) the closest contacts correspond to a distance of 3.86 Å between carbon atoms of methylene groups. This means that it is possible to obtain a packing of isochiral chains along the *a* direction, for which no repulsive contact arises. Therefore, a good packing of isochiral chains along the *a* direction which does not require the interdigitation of $CH_2$ and $CH_3$ groups can be realized.

*Figure 10c* shows a projection on the *ac* plane of a pair of chains having opposite chirality corresponding to the point of the map of *Figure 9*, whose coordinates are $\omega = 0°$ and $\Delta z = 0.5$. This point is a relative maximum of the map and corresponds to the mode of packing along the *a* direction in the *Ibca* space group. This

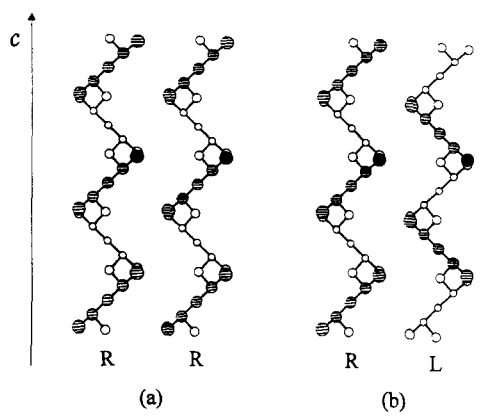


**Figure 7** Projections in the *bc* plane of pairs of chains having (a) the same and (b) opposite chirality in the minimum energy points of the maps of *Figures 5* and *6*, respectively. The heavy atoms represent the pairs of methyl groups to which $\Delta z$ is referred

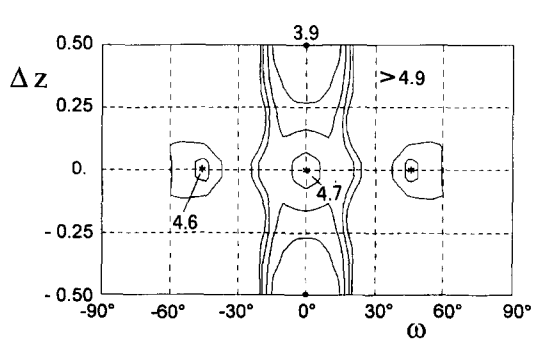


**Figure 8** Map of the packing energy as a function of $\omega$ and $\Delta z$ of chains having the same chirality along the *a* direction. The curves are reported at intervals of 0.25 kJ (mol mu)$^{-1}$ with respect to the absolute minimum of the map of *Figure 5*. The minima and the relative maxima are indicated by points and asterisks, respectively

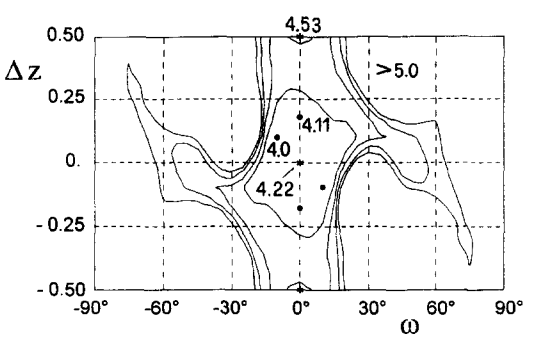


**Figure 9** Map of the packing energy as a function of $\omega$ and $\Delta z$ of adjacent chains having opposite chirality along the *a* direction. The curves are reported at intervals of 0.25 kJ (mol mu)$^{-1}$ with respect to the absolute minimum of the map of *Figure 5*. The minima and the relative maxima are indicated by points and asterisks, respectively

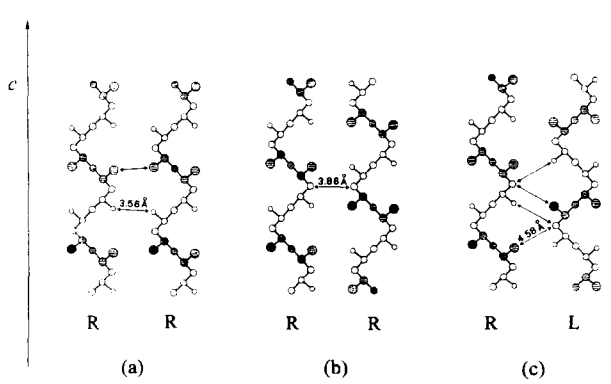


**Figure 10** Projections in the *ac* plane of pairs of chains. (a) Chains having the same chirality with $\omega = 0°$ and $\Delta z = 0$; (b) chains having the same chirality with $\omega = 0°$ and $\Delta z = 0.5$; (c) chains having opposite chirality with $\omega = 0°$ and $\Delta z = 0.5$. The closest distances are also indicated. The heavy atoms represent the pairs of methyl groups to which $\Delta z$ is referred

relative maximum arises as a consequence of too large distances between the closest interacting atoms and not as a consequence of repulsive interactions. Lacks[21] suggested that a shift along the $c$ direction is necessary to optimize the interactions. We observe that interactions are optimized not only by a shift along the line at $\omega = 0°$ but also by a variation of $\omega$. The combined effects produce the absolute minimum of the map of *Figure 9*.

A different mode of packing along the $a$ direction in which each site can be statistically occupied by a right-handed or a left-handed chain can be taken into account. We have examined the energy feasibility of this statistical mode of packing considering the interactions in a row having in each site a pair of chains of opposite chirality related by an inversion centre. Pairs of chains of adjacent sites have been related by a translation $d + \frac{1}{2}c$, in such a way as to have a periodicity corresponding to $a = 2d$. The map of the energy as a function of $\omega$ and $\Delta z$ is shown in *Figure 11*. In this map $\Delta z$ indicates the difference in height of corresponding methyl groups of adjacent chains having opposite chirality, i.e. it has the same meaning as in *Figure 9*. The map presents a wide range of low energy around $\omega = 0°$ for any value of $\Delta z$. The value of the energy minimum is practically equal to the energy values of the absolute minima of the maps of *Figures 8* and *9*. A significant feature of this map is the disappearance of the relative maximum at $\Delta z = 0.5$ present in the map of *Figure 9*.

## MINIMIZATIONS OF THE PACKING ENERGY

In the next step we have considered as variable parameters also the interchain distances $d$, which in the previous maps were fixed at the experimental values. In this framework we have minimized the packing energy as a function of $\omega$, $\Delta z$ and $d$ starting from the minima of all the maps. The optimized values of the variable parameters and the corresponding energies are listed in *Table 3*. As expected, all the values of the optimized $d$ distances are lower with respect to the corresponding experimental values, though the percentage decreases $\Delta d$ assume different values.

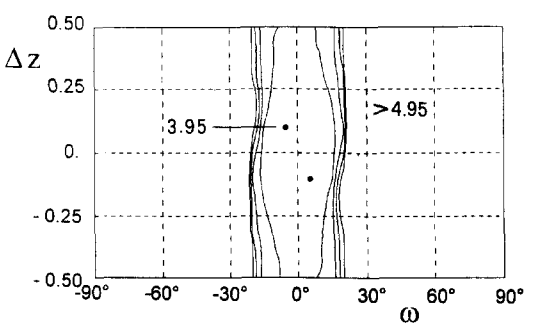


**Figure 11** Map of the packing energy as a function of $\omega$ and $\Delta z$ calculated by considering that each site along the $a$ direction can be statistically occupied by a right-handed or a left-handed chain. The curves are reported at intervals of 0.25 kJ (mol mu)$^{-1}$ with respect to the absolute minimum of the map of *Figure 5*

The results of *Table 3* confirm that the close packing is realized along the $b$ direction. The optimized values of $\omega$ and $\Delta z$ for chains along this direction are the same as in the minimum energy points of the corresponding maps. However, while in the maps the packing of isochiral and antichiral chains are nearly isoenergetic, the minimizations give the indication that the packing of antichiral chains is preferred. This suggests that a statistical positioning along $b$ of chains having opposite chirality in the same site should require an energy increase.

As far as the packing along the $a$ direction is concerned, the minimization confirms that chains having the same chirality, in the minimum energy point, are positioned in such a way that the interdigitation of $CH_2$ and $CH_3$ groups is not realized. For chains having opposite chirality, a shift along $c$ ($\Delta z = 0.40$ instead of $\Delta z = 0.50$) and a rotation of $-8°$ around the chain axis with respect to the perfect interdigitation shown in *Figure 10c* are required, but the resulting value of $d$ is too low. Moreover, we recall that the energy minimum for chains along the direction of close packing is found for $\omega = 0°$. Therefore, we have again minimized the energy for antichiral chains along $a$ as a function of $\Delta z$ and $d$ with $\omega$ fixed at 0°. Also in this case the $d$ result is abnormally low ($\Delta d = 11.3\%$), and it should remain low ($\Delta d \geq 10.1\%$) even when considering a possible lower value of the $a$ axis (14.3–14.45 Å) which could be deduced by some experimental data[8,16].

The energy values corresponding to the modes of packing of isochiral and antichiral chains are similar. A slightly higher energy value is obtained in the case of a statistical arrangement of the chains. However, we consider that the statistical arrangement of chains along the $a$ direction must be taken into account since the value of $\Delta d$ is near the values found in the cases of the chains along the $b$ directions and of isochiral chains along the $a$ direction.

**Table 3** Values of optimized parameters and energy $E$ as obtained in the minimizations of the packing energy performed with the van der Waals radii reported by Flory[23,24]. The energy values are referred to the absolute minimum of the map of *Figure 5*. The percentage decreases in distance $\Delta d$ with respect to the corresponding experimental values are also reported

| Row | Chain handedness | $\omega$ (°) | $\Delta z$ | $d$ (Å) | $E$ (kJ (mol mu)$^{-1}$) | $\Delta d^a$ |
|---|---|---|---|---|---|---|
| Along $b$ | R, R | 0 | 0.00 | 5.33 | −0.91 | 4.8 |
| Along $b$ | R, L | 0 | 0.00 | 5.24 | −1.25 | 6.4 |
| Along $a$ | R, R | 0 | 0.50 | 6.80 | 2.92 | 6.2 |
| Along $a$ | R, L | −8 | 0.40 | 6.20 | 1.86 | 14.5 |
| Along $a^b$ | R, L | 0 | 0.50 | 6.43 | 2.76 | 11.3 |
| Along $a$ | R or L, R or L | 0 | 0.50 | 6.73 | 3.09 | 7.2 |

L, left; R, right
[a] $\Delta d = (d_{exp} - d)/d_{exp} \times 100$
[b] Minimization under the constraint $\omega = 0°$

## MINIMIZATIONS WITH INCREASED VAN DER WAALS RADII

The results of *Table 3* have confirmed that the potential functions, even if they predict the best mode of packing, give interchain distances which can be found near 0 K, rather than at room temperature. We have already discussed that a method to predict the values of the axes of the unit cells at higher temperatures is to increase the van der Waals radii. In previous cases[27,31–34] concerning various polymers we found that increases of the van der Waals radii of between 0.15 and 0.25 Å, depending on the kind of packing of the considered polymer, can be used. In order to find the best increase of the van der Waals radii in the case of sPP, we have calculated the distances along *b* between chains of opposite chirality, that is, the best mode of packing, at various van der Waals radii. *Figure 12* shows the trend of the distance *d* along the *b* direction as a function of the increase of the van der Waals radii $\Delta r_w$. The values of $\Delta r_w$ that reproduce the experimental value $d = 5.60$ Å are in the range 0.20–0.25 Å. Therefore, we have effected further calculations of the packing energy along the two directions by using potential functions obtained with $\Delta r_w = 0.25$ Å, also considering that the values of the *a* axis resulting from the above reported minimizations are quite low. The results of the new minimizations of the packing energy as a function of $\omega$, $\Delta z$ and *d* are listed in *Table 4*.

It is apparent that the *b* direction remains the close packing direction. The best mode of packing is obtained for chains of opposite chirality, as the energy difference with respect to the packing of isochiral chains is still about 0.3 kJ (mol mu)$^{-1}$. For packing along the *a* direction, the lowest energy is again obtained for chains having opposite chirality. However, we show that the *d* value obtained in this case remains too low. At variance, the *d* values obtained both in the case of isochiral chains and in the case of a statistical positioning of the chains are in satisfactory agreement with the experimental data ($d = 7.25$ Å), and the corresponding energy values are practically the same. On the other hand, the value of the packing energy of chains of opposite chirality calculated by imposing both $\omega = 0°$ and $d = 7.25$ Å increases to 2.48 kJ (mol mu)$^{-1}$, very close to that obtained for chains of the same chirality. Therefore, we conclude that the statistical arrangement along the *a* direction can be realized without energy cost. An example of this arrangement is sketched in *Figure 13*. It can be seen that a regular sequence of chains having opposite chirality is present along the rows in the *b*

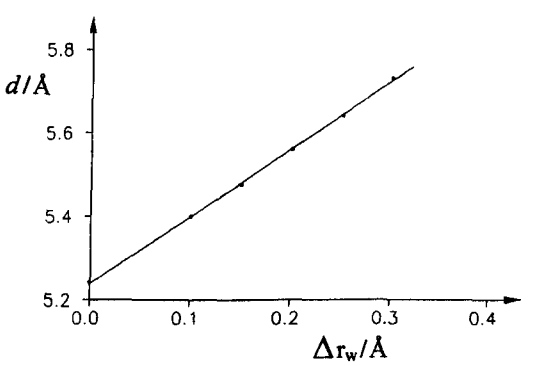


**Figure 12** Trend of the *d* distance between chains having opposite chirality along the *b* direction as a function of the increase of the van der Waals radii $\Delta r_w$

**Table 4** Values of optimized parameters and energy *E* as obtained in the minimizations of the packing energy with the van der Waals radii increased by 0.25 Å. The energy values are referred to the absolute minimum, assumed as zero, which corresponds to the packing of chains having opposite chirality along the *b* direction

| Row | Chain handedness | $\omega$ (°) | $\Delta z$ | *d* (Å) | *E* (kJ (mol mu)$^{-1}$) |
|---|---|---|---|---|---|
| Along *b* | R, R | 0 | 0.00 | 5.75 | 0.32 |
| Along *b* | R, L | 0 | 0.00 | 5.64 | 0 |
| Along *a* | R, R | 0 | 0.50 | 7.26 | 2.44 |
| Along *a*[a] | R, L | 0 | 0.50 | 6.90 | 2.17 |
| Along *a* | R or L, R or L | 1 | 0.48 | 7.15 | 2.43 |
| Along *a*[b] | R, L | 0 | 0.50 | 7.25 | 2.48 |

L, left; R, right
[a] Minimization under the constraint of $\omega = 0°$
[b] Minimization under the constraints of $\omega = 0°$ and $d = 7.25$ Å

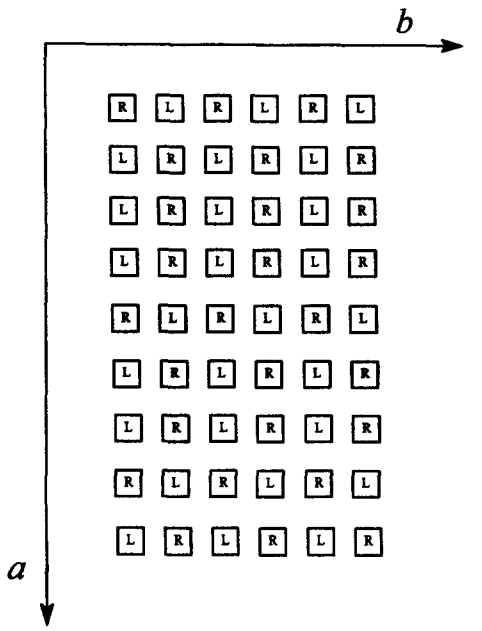


**Figure 13** Schematic representation of the proposed mode of packing for the most stable form of sPP in a view along the chain axis. Chains having opposite chirality succeed each other in a regular manner in rows along the *b* direction. Chains of both chirality alternate in a statistical way in rows along the *a* direction

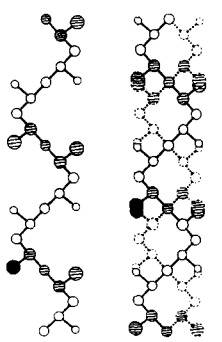

**Figure 14** Projection on the *ac* plane of the mode of packing in the minimum energy point of chains having opposite chirality which occupy statistically the same site. Only the right-handed chain is represented on the left-hand side. The right- and the left-handed chains are indicated by full and dashed lines, respectively, on the right-hand side

direction, while right- or left-handed chains statistically succeed each other along *a*. A shift by $\frac{1}{2}b$ of any row along the *b* direction gives an isoenergetic structure and maintains the regularity along *b* and the disorder along *a*. As a consequence, in this structure each site could be occupied by a right- or a left-handed chain, even if the regular alternance of chains of opposite chirality is maintained along *b*.

*Figure 14* shows a projection in the *ac* plane of the mode of packing in the minimum energy point of a right-handed chain with a right- or a left-handed chain which occupies statistically the same site. The interactions between a right-handed chain with a right- or a left-handed chain in the adjacent site are analogous to those shown in *Figures 10b* and *10c*, respectively. It can be noted that the best mode of packing is realized when the methyl groups of chains having opposite chirality in the same site are nearly isosteric.

## CONCLUSIONS

The results of the analysis of the modes of packing along the *a* and *b* directions of the most stable form of sPP performed by molecular mechanics clearly indicate that close packing is realized along *b* by adjacent chains having opposite chirality. In contrast, the mode of packing along *a* can be obtained by adjacent chains having the same or opposite chirality. These results give a satisfactory explanation of the presence of the reflection having (011) indices, which is extinct in the *Ibca* space group. Moreover, our model is in agreement with the splitting in one direction of the $CH_3$ bands observed in n.m.r. spectra. Finally, our energy calculations show that the best mode of packing is also obtained along the *a* direction with chains having opposite chirality, as in the *Ibca* space group. We think that this space group could correspond to the structure obtainable in crystallization under thermodynamic control. However, in this case the length of the *a* axis should be smaller than the value reported in literature.

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