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Analysis of the Modes of Packing of the α and β Forms of Syndiotactic Polystyrene

Roberto Napolitano and Beniamino Pirozzi*

Dipartimento di Chimica, Università di Napoli, via Mezzocannone 4, I-80134 Napoli, Italy

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ABSTRACT: Packing energy calculations have been performed on the α and β forms of syndiotactic polystyrene by using three different sets of potential functions. In the case of the α form the modes of packing of the chains in the $R3$, $P3$, $R\bar{3}$, and $P\bar{3}$ space groups have been considered. In the case of the β form the $P2_12_12_1$ and $Cmcm$ space groups have been considered. The results indicate that the energy of the β form is lower than that of the α form for all the space groups considered, while the energies corresponding to the space groups of the α form are very similar. A statistical positioning of the chains can be realized at a low energy cost for both crystalline forms.

Introduction

Different crystalline polymorphic forms of syndiotactic polystyrene (s-PS) have been evidenced in recent times.[1] The various forms differ both for the conformation of the polymer chain and for the mode of packing of chains having the same conformation. In particular, two crystalline forms, indicated as α and β,[2] have a chain axis repeat of 5.045–5.1 Å and a nearly trans planar conformation,[1,3–7] while the other two forms, indicated as γ and δ,[2] have a chain axis repeat of 7.5–7.8 Å and a helical conformation.[4,8–10] Different crystalline modifications corresponding to different degrees of order have been evidenced both for the α and the β form.[1,5–7]

In a previous paper[8] we have attributed by a geometric and energetic analysis a *tcm* symmetry to the chains having a nearly trans planar conformation and a s(2/1)2 symmetry to the chains having a helical conformation.

The crystal structure of the α form of s-PS has been proposed by Greis et al.[5] by transmission electron microscopy analysis and by De Rosa et al.[1] by X-ray diffraction analysis. These structural data indicate that the chains are arranged in triplets around 3-fold axes parallel to the chain axes. The triplets have the backbone of the chains at van der Waals contact in the core around the axes and phenyl rings at the periphery. The minimum distance between the 3-fold axes is $a' = 15.16$ Å. Greis et al. proposed a hexagonal arrangement of the triplets in a unit cell with $a = 26.25$ Å (a is related to a' as follows: $a = a'(2 \cos 30°)$) and $c = 5.045$ Å. De Rosa et al. proposed a rhombohedral arrangement of the triplets for both limit ordered (α'') and disordered (α') modifications, with the same value of the a ($=b$) axis of the unit cell proposed by Greis et al. A refinement of the structure of the α form was recently performed by energy calculations considering both the rhombohedral and the hexagonal mode of packing of the triplets.[11]

The crystal structure of the β form of s-PS has been reported by De Rosa et al.[6] and by Chatani et al.[7] The orthorhombic space groups $P2_12_12_1$ and $Cmcm$ have been proposed for the ordered (β'') and disordered (β') modifications, respectively, with $a = 8.81$ Å, $b = 28.82$ Å, and $c = 5.06$ Å. Hence, the β form consists of chains having a conformation similar to that in the α form and differs from the latter in the mode of packing of the chains.

As for the γ and δ forms, less complete structural characterizations have been till now performed.[4,10]

In this paper we report results of a packing analysis performed by energy calculations on the α and β forms of s-PS with the aim to evaluate the relative stability both of the two forms and of the ordered and disordered modifications of each form.

Method of Calculation

The energy calculations have been performed by considering a conformational and a packing term.

The conformational term has been obtained by the optimization of the energy of the isolated chain, under the constraint of maintaining the *tcm* line repetition group, as a function of all the bond and torsion angles. The portion of the chain used is reported in Figure 1, together with the succession of the bond angles τ and of the torsion angles θ in the backbone which characterize the *tcm* line repetition group. The mode of calculation of the conformational energy is reported in ref 8.

The packing energy has been calculated by taking into account the nonbonded interactions between the atoms of one monomeric unit (mu) and all the atoms of the surrounding macromolecules within spheres having radii twice the sum of the van der Waals distances for each pair of considered atoms. The variables are the a and b axes of the unit cells and the parameters that define the relative positions of the chains in the space groups considered. In the optimizations of the packing energy we have used a rigid chain conformation (and therefore a fixed value of the c axis) as obtained by the conformational energy minimizations.

In order to have results independent of the choice of a particular force field, we have used sets of potential functions proposed by different authors.[12–14] The potential functions by Flory have been extensively used with good results in previous papers concerning the predictions of crystal structures of hydrocarbon polymers.[15–18] As the nonbonded terms of the C_{sp^2} carbon atom of these functions can be rather hard, we have used also the softer set by Scheraga which, as does Flory's, uses a Lennard–Jones function in the calculations of the nonbonded term. Finally, we have chosen the set by Allinger which is self-consistent and contains a Buckingham function in the nonbonded term.

The parameters corresponding to the nonbonded interactions for the different sets used are reported in Table I. They are referred to the following formula:

$$E = A \exp(-Br)r^{-D} - Cr^{-6}$$

where r is the distance between the interacting atoms and

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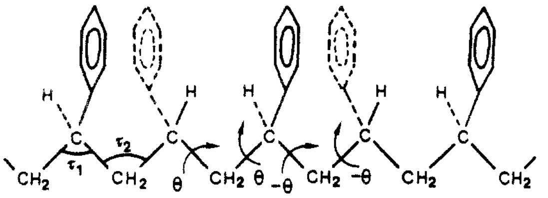

Figure 1. Portion of the chain used in the optimization of the conformational energy. The succession of the bond and torsion angles in the *tcm* line repetition group is also indicated.

Table I. Parameters Used for the Nonbonded Energy Calculations[a]

interacting pair		$10^{-3}A$	B	C	D	d_w
		Set by Flory				
C_{sp^3}	C_{sp^3}	1666	0	1532	12	3.60
C_{sp^3}	C_{sp^2}	2207	0	1867	12	3.65
C_{sp^3}	H	238.7	0	536	12	3.10
C_{sp^2}	C_{sp^2}	2965	0	2311	12	3.70
C_{sp^2}	H	325.3	0	666	12	3.15
H	H	30.6	0	197	12	2.60
		Set by Scheraga[b]				
C_{sp^3}	C_{sp^3}	1196	0	1548	12	3.40
C_{sp^3}	C_{sp^2}	1196	0	1548	12	3.40
C_{sp^3}	H	159	0	536	12	2.90
C_{sp^2}	C_{sp^2}	1196	0	1548	12	3.40
C_{sp^2}	H	159	0	536	12	2.90
H	H	18.7	0	195	12	2.40
		Set by Allinger				
C_{sp^3}	C_{sp^3}	142.0	3.88	709.5	0	3.50
C_{sp^3}	C_{sp^2}	128.2	3.77	758.2	0	3.60
C_{sp^3}	H	173.2	4.18	554.7	0	3.25
C_{sp^2}	C_{sp^2}	114.3	3.67	797.1	0	3.70
C_{sp^2}	H	155.9	4.06	598.8	0	3.35
H	H	211.3	0.53	418.6	0	3.00

[a] A, B, C, and D refer to the formula reported in the text and are expressed in such a way that the nonbonded energy is in kJ/mol. d_w represents the van der Waals distance, in Å. [b] For C_{sp^2} we have used the same parameters as for the C_{sp^3} atomic species.

A, B, C, and D are parameters depending on the kind of potential functions and on the considered pair of atomic species.

Packing of the α Form

For the evaluation of the packing energy of the α form we have at first considered the mode of packing inside a triplet of chains related by a 3-fold rotation axis and then the arrangements of these triplets in the unit cell.

The best conformation of the chains inside the triplet is slightly different from that found by the minimizations of the conformational energy of the isolated chain, as described in ref 11. The values of the parameters in the backbone of the chains inside the triplet, obtained by using the set of potential functions by Flory, are τ_1 = 111.1°, τ_2 = 112.4°, and θ = 193.0° (we follow the convention that attributes the value of 180° to the *trans* conformation), while the corresponding parameters obtained for the minimum energy conformation of the isolated chain are τ_1 = 112.0°, τ_2 = 112.4°, and θ = 186.7°. Values which differ less than 1° are obtained for each parameter of both conformations by the other two sets of potential functions. In the present paper we have adopted the two chain conformations in the calculations of the packing energy of the α and β forms, respectively.

Packing inside the Triplet. The packing energy of the triplet has been minimized as a function of the distance d between the carbon atoms of the CH_2 groups of different chains. Table II shows the values of the d parameter, of the conformational energy (E_{conf}) and of the packing energy of the chains inside the triplet (E_{tripl}) for the different sets of potential functions.

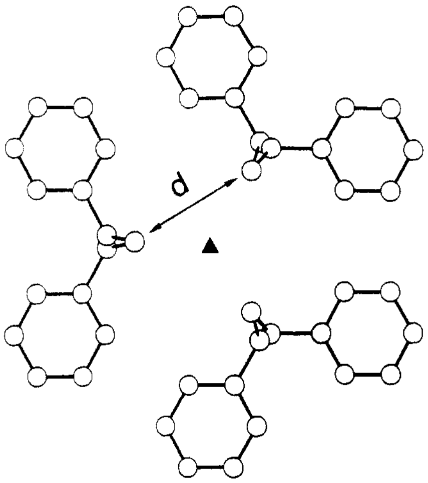

Figure 2. Projection along the 3-fold axis of the triplet of chains in the α form. The values of d are reported in Table II for the three sets of potential functions.

Table II. Values of the Distance between the Carbon Atoms of CH_2 Groups of Different Chains (d), of the Conformational Energy (E_{conf}), and of the Packing Energy inside the Triplet (E_{tripl}) of the α Form for the Considered Sets of Potential Functions (Energies Reported in kJ/(mol of mu))

potential functions	d/Å	E_{conf}	E_{tripl}
set by Flory	4.11	-11.5	-14.6
set by Scheraga	4.00	-24.8	-14.8
set by Allinger	4.49	17.6	-9.3

The values of the d parameter comprise the range 4.00–4.49 Å. These distances, rather large with respect to the van der Waals distances for carbon atoms, arise as a consequence of interactions between the hydrogen atoms of the CH_2 groups. In fact, the interacting pairs of hydrogen atoms are approximately at the same height in the case of the ideal 3-fold symmetry of the triplet and of the *tcm* symmetry of the chains.

The mode of packing of the chains inside the triplet is reported in Figure 2 as a projection along the 3-fold axis.

Packing among the Triplets. The different arrangements of the triplets have been examined in accordance with the $R3$, $P3$, $R\bar{3}$, and $P\bar{3}$ space groups. These space groups are obtained from those experimentally proposed[1,5] when the glide planes of the chains are not taken as crystallographic symmetry elements. In this way a better mode of packing can be obtained, as already reported.[11]

In the $R3$ and $P3$ space groups the adjacent triplets are related by a 3-fold screw and by a 3-fold rotation axis, respectively. $R\bar{3}$ and $P\bar{3}$ are obtained from the $R3$ and $P3$ space groups, respectively, if we introduce a symmetry center on the 3-fold axis inside the triplet. In these cases each triplet is statistically disposed in one of two alternative modes. These modes are related by a rotation of 60° around the 3-fold axis inside the triplet followed by a shift of $^1/_2c$, in such a way that the phenyl rings remain at the same height. The projection along the c axis of the two statistically related triplets is reported in Figure 3.

The energies of the different arrangements of triplets in the space groups considered have been minimized with respect to the a' distance and to the rotation angle ω of the triplet around its axis, as defined in Figure 4.

Table III shows the optimized values of a', ω, and the packing energy among the triplets (E'_{pack}) for the space groups considered and for the different sets of potential functions. The values of the corresponding total packing

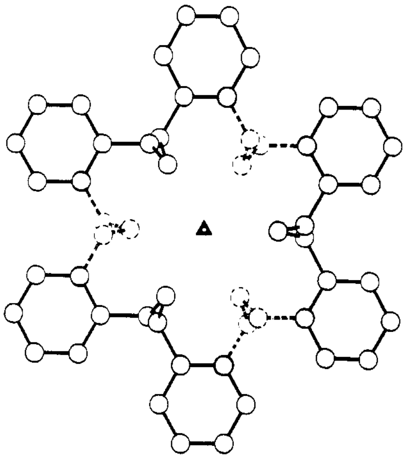

Figure 3. Projection along the 3-fold axis of the two alternative modes (full and dashed chains) in which the triplets are statistically disposed both in the $R\bar{3}$ and in the $P\bar{3}$ space groups.

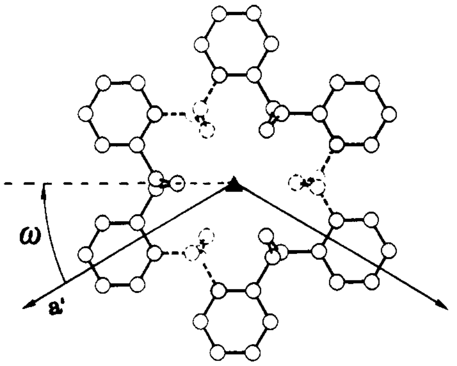

Figure 4. Definition of the rotation angle ω of a triplet around its 3-fold axis.

Table III. Optimized Values of a′, ω, Packing Energy among the Triplets (E'_{pack}), Packing Energy ($E_{pack} = E_{tripl}{}^{a} + E'_{pack}$), and Total Energy ($E_{tot} = E_{conf}{}^{a} + E_{pack}$) of the α Form, for the Space Groups and Sets of Potential Functions Considered (Energies Reported in kJ/(mol of mu))

space group	a'/Å	ω/deg	E'_{pack}	E_{pack}	E_{tot}
		Set by Flory			
$R3$	14.76	6.8	-14.3	-28.9	-40.4
$P3$	14.73	16.9	-15.8	-30.4	-41.9
$R\bar{3}$	14.76	6.8	-14.3	-28.8	-40.3
$P\bar{3}$	14.73	16.9	-15.8	-30.4	-41.9
		Set by Scheraga			
$R3$	14.39	6.5	-15.5	-30.3	-55.1
$P3$	14.45	17.2	-16.8	-31.6	-56.4
$R\bar{3}$	14.41	6.3	-15.4	-30.2	-55.0
$P\bar{3}$	14.45	17.2	-16.8	-31.6	-56.4
		Set by Allinger			
$R3$	15.58	7.0	-7.4	-16.7	0.9
$P3$	15.49	16.8	-8.4	-17.7	-0.1
$R\bar{3}$	15.59	6.9	-7.3	-16.6	1.0
$P\bar{3}$	15.49	16.8	-8.4	-17.7	-0.1

[a] E_{tripl} and E_{conf} are reported in Table II.

energy ($E_{pack} = E_{tripl} + E'_{pack}$) and total energy ($E_{tot} = E_{conf} + E_{pack}$) are also reported.

The results reported in Table III indicate that the energies corresponding to $R3$ are very similar to those corresponding to the $P3$ space group. The energy differences, calculated by the three sets of potential functions, are in the range 1.0–1.5 kJ/(mol of mu). Moreover, these differences tend to become lower if we perform packing energy calculations under the constraint of maintaining the experimental a' axis.[11] Finally, the energies in the $R\bar{3}$ and $P\bar{3}$ space groups are practically identical to those of the $R3$ and $P3$ space groups, respectively, for each set of potential function. This means that a statistical positioning of the triplets can be realized without any cost in energy.

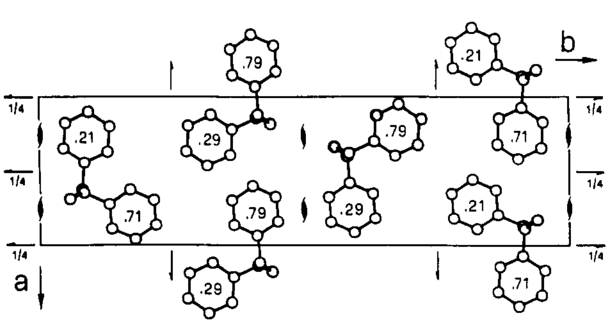

Figure 5. Projection along the c axis of the unit cell of the β form in the space group $P2_12_12_1$ obtained by the minimization of the packing energy performed by the set of potential functions by Flory. The fractional heights of the phenyl rings are also indicated.

Packing of the β Form

In accordance with the experimental evidence,[6,7] we have considered the $P2_12_12_1$ and the $Cmcm$ space groups. As described in ref 6, in the $P2_12_12_1$ space group two kinds of ac bilayers of chains alternate along the b direction. Instead, in the $Cmcm$ space group the two kinds of bilayers are in a statistical succession along the b direction. However, the positions of the phenyl rings are the same in the two space groups.

We have performed minimizations of the packing energy in accordance with the symmetry elements of the considered space groups by assuming the conformation of the chain corresponding to the minimum conformational energy. Therefore, we have taken as variables the a and b axes of the unit cell, the rotation of the chain around its axis, the position of the chain axis with respect to the a and b axes, and the heights of the chains. The crystal structures obtained by the energy minimizations performed by using the different sets of potential functions are in very good agreement with the experimental crystal structure. Figure 5 shows a projection along the c axis of the unit cell obtained for the $P2_12_12_1$ space group by the set of Flory.

The optimized values of the a and b axes and of the conformational (E_{conf}) and the packing (E_{pack}) energies, together with the total energy ($E_{tot} = E_{conf} + E_{pack}$), obtained by the three sets of potential functions are reported in Table IV. The results indicate that the energy of the β form is significantly lower with respect to the α form for each set of potential functions considered. Moreover, the statistical $Cmcm$ space group can be realized at a relatively low energy cost.

Discussion

The results of the packing energy calculations indicate that the β form of s-PS is more stable than the α form. The energy differences obtained by the three sets of potential functions are in the range 5.3–6.5 kJ/(mol of mu). This is in accordance with recent experimental observations which indicate that, by annealing under pressure, a transition from the α to the β form is obtained[19] while no transition from the β to the α form has yet been observed.

On the other hand, as reported by different authors,[2,9] the crystallization of the α or of the β form is strongly dependent on the experimental conditions and, therefore, on the formation of nuclei. In this framework we have

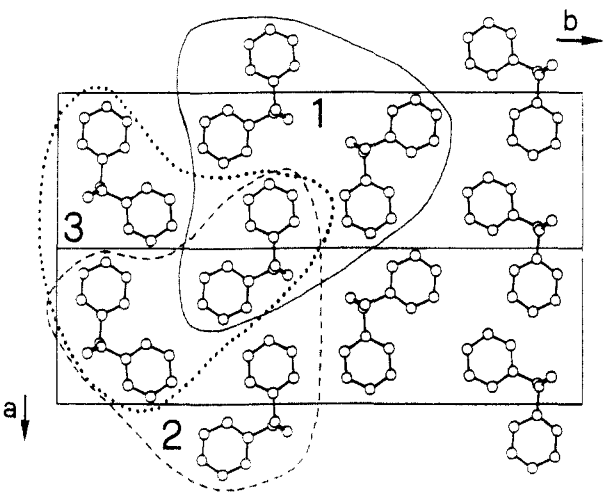

Figure 6. Nonequivalent clusters of three chains of s-PS in the crystal structure of the β form.

Table IV. Optimized Values of the *a* and *b* Axes of the Unit Cell and of the Conformational (E_{conf}), Packing (E_{pack}), and Total ($E_{tot} = E_{conf} + E_{pack}$) Energies of the β Form for the Space Groups and Sets of Potential Functions Considered (Energies Reported in kJ/(mol of mu))

space group	a/Å	b/Å	E_{conf}	E_{pack}	E_{tot}
		Set by Flory			
$P2_12_12_1$	8.20	28.82	−14.0	−33.2	−47.2
Cmcm	8.42	28.84	−14.0	−32.0	−46.0
		Set by Scheraga			
$P2_12_12_1$	8.53	27.07	−28.5	−34.4	−62.9
Cmcm	8.61	27.44	−28.5	−33.1	−61.6
		Set by Allinger			
$P2_12_12_1$	8.84	29.54	14.0	−19.4	−5.4
Cmcm	8.81	29.59	14.0	−19.3	−5.3

Table V. Optimized Energies of the Clusters of Three Chains of the β Form Indicated in Figure 6 in Comparison with the Energy inside the Triplet of the α Form, Obtained by the Set of Potential Functions by Flory[a]

	E_{conf}	E_{clust}	E
cluster 1 of the β form	−14.0	−13.7	−27.7
cluster 2 of the β form	−14.0	−10.8	−24.8
cluster 3 of the β form	−14.0	−7.8	−21.8
triplet of the α form	−11.5	−14.6	−26.1

[a] The energy E represents the sum of the conformational energy (E_{conf}) of the chain used and of the packing energy (E_{clust}) inside the considered cluster. The energies are reported in kJ/(mol of mu).

considered also the stability of possible nuclei of the α and β forms. To this end, we have evaluated the packing energies of the three nonequivalent clusters of three chains inside the minimum energy crystalline lattice of the β form indicated in Figure 6. The energies obtained by using the set of potential functions by Flory are reported in Table V in comparison with the energy of the triplet of the α form. The lowest energy cluster is the cluster 1 inside the lattice of the β form, while a slightly higher energy is obtained for the triplet of the α form. This is in accordance with the experimental observation[2] that, in absence of any sort of memory, the crystallization of the β form is obtained because it could be favored also for kinetic reasons.

As for the possibility of statistical arrangements of the chains, the energies of the ordered and disordered modifications (α'' and α', β'' and β') are comparable in both crystalline forms. These results can be explained because the interactions determining the mode of packing occur by the atoms of the phenyl rings which remain nearly in the same positions both in the $R3$ (or $P3$) and $R\bar{3}$ (or $P\bar{3}$) and in the $P2_12_12_1$ and *Cmcm* space groups. On the contrary, in both space groups of each form the positions of the atoms of the backbones, less important in determining the mode of packing, are different.

A concluding remark concerns the results obtained by the various sets of potential functions used. The crystal structures obtained by the three different sets are very similar for both the α and the β forms. However, as for the axes of the unit cells, the values calculated by the sets of potential functions by Flory are slightly lower with respect to the experimental values. The same trend was previously found for other polymers,[15-17] and it is expected because the energy calculations do not take into account the thermal vibrations and the defects present in the real crystals of polymers. The axes calculated by the potential functions by Scheraga are even lower due to the softness of this set. On the contrary, the values of the axes obtained by the set by Allinger are higher with respect to the experimental values as a consequence of the particularly high value of the van der Waals radius of the hydrogen atom.

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