Geometrical Analysis and Conformational and Packing Energy Calculations on the Isotactic Alternating Copolymer between Carbon Monoxide and Styrene

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ABSTRACT: A geometrical and energy analysis on the isolated chain of the isotactic optically active alternating styrene−carbon monoxide copolymer is presented. Relations between the bond and torsion angles of the main chain, which give helical s(2/1) repetition and highly extended chains, have been found. The results of the conformational energy calculations indicate that the best conformation in the crystalline field corresponds to a slight deviation of the torsion angles from 180°, according to the experimental structure. Packing energy calculations for the space group $P2_1$ and the experimental unit cell with axes $a = 5.47$ Å, $b = 8.367$ Å, $c = 7.57$ Å, and $\gamma = 110°$ are presented. The present analysis indicates that the packing interaction influences the chain conformation. Precisely, the need to optimize intermolecular contacts between the atoms of the phenyl rings of adjacent chains produces a relevant deviation (nearly 30°) of the torsion angle which characterizes the orientation of the lateral phenyl group from the value (≈60°) that keeps the phenyl ring plane bisecting the valence bond at the tertiary carbon. These results are in agreement with those obtained in the refinement of the crystal structure by X-ray diffraction.

Introduction

The synthesis of linear alternating copolymers of styrene and carbon monoxide, using a soluble organometallic Pd catalyst, has been described by Drent.[1] The polymer obtained performing the copolymerization in the presence of catalysts composed of cationic palladium(II) 1,10-phenanthroline and 2,2′-bipyridine complexes has been identified as having a syndiotactic configuration.[2]

We have recently resolved the complete crystal structure of the syndiotactic alternating copolymer of carbon monoxide with styrene (s-STCO)[3] and those of a series of syndiotactic copolymers with styrene derivatives.[4]

With the above achiral ligands, a chain end control of polymerization is considered to be operative.[2] It has been recently found that the coordination of a chiral ligand to the metal switches the chain end control to yield an isotactic optically active alternating styrene−carbon monoxide copolymer.[5−7]

The crystal structure of the isotactic alternating styrene−carbon monoxide copolymer (i-STCO) has been recently determined by us.[8] Extended chains with s(2/1) helical symmetry are packed in a monoclinic unit cell with axes $a = 8.367$ Å, $b = 7.57$ Å (chain axis), $c = 5.47$ Å, and $\beta = 110°$, according to the space group $P2_1$. If we choose the space group $P2_1$ with unique axis c, the unit cell parameters become $a = 5.47$ Å, $b = 8.367$ Å, $c = 7.57$ Å (chain axis), and $\gamma = 110°$. The observed chain conformation[8] has a repeating period (7.57 Å) that is almost identical to that observed in syndiotactic copolymers[3,4] in spite of the different symmetry connecting the monomeric units, s(2/1) in the isotactic polymer, t*c* in the syndiotactic one. A relevant difference concerns the orientation of lateral phenyl rings which, in the isotactic polymer, deviates significantly from the position that keeps the ring plane bisecting the valence bond at the tertiary carbon. This effect seems to arise from the need to optimize intermolecular contacts.

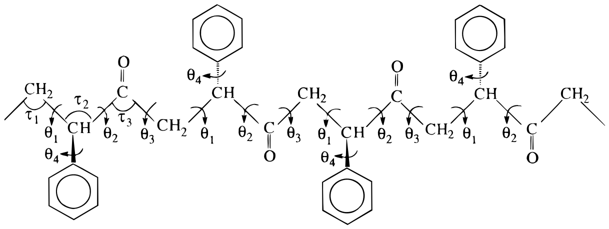

Figure 1. Portion of the chain of i-STCO used in the geometrical and conformational energy calculations. The definition of the torsion angles θ_1, θ_2, θ_3, and θ_4 and of the bond angles τ_1, τ_2, and τ_3 is also shown.

In this paper, we report a conformational analysis on the isolated chain of i-STCO with the aim of finding the relations between the torsion angles of the chain which give the observed chain axis, in comparison with analogous relations found for the syndiotactic polymer reported in the literature.[2,9] The best conformation of the chain of i-STCO in the crystalline field will be predicted by conformational and packing energy calculations and compared with that found by X-ray diffraction.[8]

Geometrical Analysis

In order to find the relations between the internal parameters of the chain of i-STCO which give a highly extended conformation (chain axis 7.5−7.6 Å), a geometrical analysis has been performed by taking into account the symmetry elements of the chain and, therefore, the possible line-repetition group.[10]

The constitution of i-STCO makes the two directions of the chain intrinsically nonequivalent so that the presence of inversion centers, binary axes, and mirror planes perpendicular to the chain axis can be excluded. A glide plane symmetry parallel to the chain axis can be excluded because it is incompatible with isotactic polymers. Hence, only the screw repetition symmetry can be present; therefore, the line-repetition group is s(*M*/*N*).

According to the equivalence principle,[11] a helical repetition s(*M*/*N*) could occur in the case of isotactic

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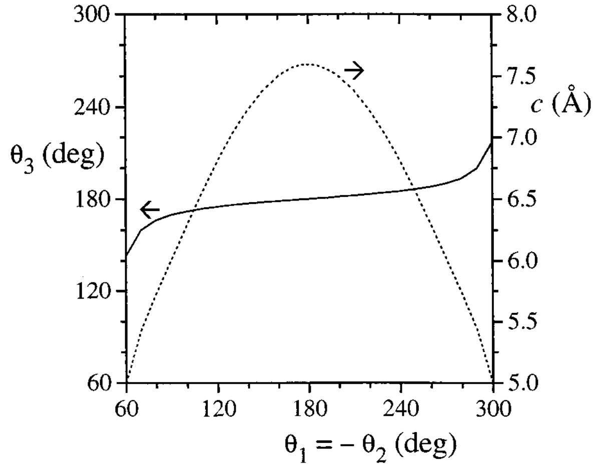

Figure 2. Torsion angles θ_3 (continuous line) which give the helical s(2/1) repetition for a chain of i-STCO and corresponding identity periods c (dashed line), as a function of $\theta_1 = -\theta_2$. The curves are calculated for $\tau_1 = \tau_2 = 111°$ and $\tau_3 = 117°$.

configuration with the same succession of values of the bond angles and with a succession of the torsion angles of the kind ...$\theta_1\theta_2\theta_3\theta_1\theta_2\theta_3$... (Figure 1).

Highly extended chains with a chain axis of 7.5–7.6 Å are obtained with a nearly trans planar conformation and a helix repeating after two monomeric units. Therefore, in this geometrical analysis, we find the relations between the bond and torsion angles of a monomeric unit in the framework of the s(2/1) line-repetition group.

As far as the bond angles are concerned, we have chosen $\tau_3 = 117°$ and $\tau_1 = \tau_2 = 111°$ (Figure 1) in order to compare the results with the geometrical analysis reported in the literature for s-STCO.[3] On the other hand, these values are very close to those found in the crystal structures of i-STCO[8] and s-STCO.[3,4] Backbone bond lengths C_{sp^3}-C_{sp^3} = 1.54 Å and C_{sp^3}-C_{sp^2} = 1.51 Å were used.

Calculations were performed varying θ_1 and θ_2 and determining the outcoming value of θ_3, which give the required helical s(2/1) repetition.

We have first performed calculations under the simplifying assumption that $\theta_2 = -\theta_1$. This assumption arises from qualitative energy considerations that indicate that bonds of opposite chirality[11] adjoining a tertiary carbon atom may have opposite slight deviations from the staggered conformation.[11,12] The value of θ_3, which gives the helical s(2/1) repetition, and the corresponding identity period c are reported in Figure 2 as a function of $\theta_1 = -\theta_2$. It is apparent that for every value of θ_1, near 180°, the helical s(2/1) symmetry is obtained when $\theta_3 \approx 180°$.

Highly extended chain conformations with $c = 7.5$–7.6 Å are obtained, for a helical s(2/1) symmetry, when θ_1 and θ_2 are in the range 180° ± δ, with $\delta = 25$–$30°$.

The condition that $\theta_3 \approx 180°$ in order to have s(2/1) symmetry under the assumption $\theta_2 = -\theta_1$ can be interpreted considering that a nearly *trans* planar chain with helical s(2/1) symmetry is obtained when the torsion angles θ_1, θ_2, and θ_3 have slight deviations from 180°, but their average value must remain approximately 180°. The assumption $\theta_2 = -\theta_1$ satisfies this condition because for a positive deviation of θ_1 from 180° ($\theta_1 = 180° + \delta$), there is a negative deviation of θ_2 ($\theta_2 = 180° - \delta$). Since the succession of torsion angles is ...$\theta_1\theta_2\theta_3\theta_1\theta_2\theta_3$..., the assumption $\theta_2 = -\theta_1$ imposes that $\theta_3 = 180°$ because any deviation of θ_3 from 180° is propagated along the chain and the average value of the torsion angles becomes very different from 180°.

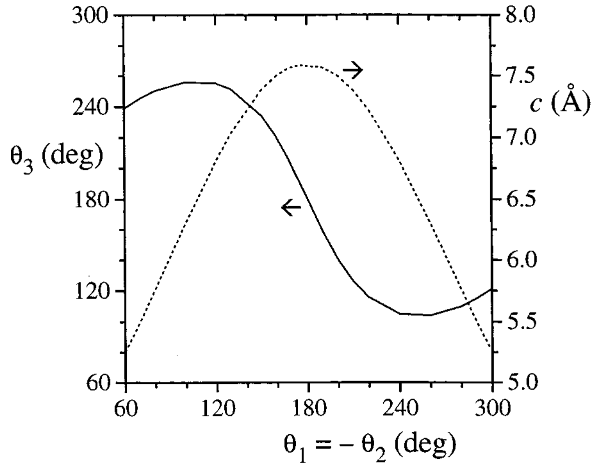

Figure 3. Torsion angles θ_3 (continuous line) which give the *tc* glide plane repetition for a chain of s-STCO and corresponding identity periods c (dashed line), as a function of $\theta_1 = -\theta_2$ (taken from ref 3). The curves are calculated for $\tau_1 = \tau_2 = 111°$ and $\tau_3 = 117°$.

In Figure 3, we show, for comparison, analogous geometrical relations found for the syndiotactic styrene–CO copolymer, taken from ref 3. In this case, the torsion angle θ_3 which give the *tc* glide plane repetition may have also a great deviation from 180°. Indeed, a glide plane repetition *tc* occurs in the case of a syndiotactic configuration with a succession of torsion angles ...$\theta_1\theta_2\theta_3{-}\theta_1{-}\theta_2{-}\theta_3$...; also in this case, highly extended chains and a *tc* repetition are obtained when the average value of the torsion angles along the chain is nearly 180°. Hence, if $\theta_2 = -\theta_1$, θ_3 can also be different from 180°, because for any deviation of θ_3 from 180° there is an opposite deviation of $-\theta_3$ in the successive monomeric unit.

More general relations between θ_1, θ_2, and θ_3 can be obtained for i-STCO if the simplifying assumption $\theta_2 = -\theta_1$ is removed. Calculations were performed with $\theta_2 \neq \theta_1$, by varying θ_2 and determining the outcoming value of θ_3, which gave helical s(2/1) symmetry for various values of θ_1 in the most significant range $\theta_1 = 180° \pm 40°$. The values of θ_2 and θ_3 which give, for chains of i-STCO, the helical s(2/1) symmetry are reported in Figure 4 for different values of θ_1, still for $\tau_1 = \tau_2 = 111°$. The values of the corresponding identity period c are reported in Figure 5A and B as a function of θ_2.

It is apparent that highly extended chains are obtained if θ_1, θ_2, and θ_3 are near 180°, that is, $\theta_i = 180 + \delta_i$ with δ_i small, and in order to have a helical s(2/1) conformation of a highly extended chain, it must be $\delta_1 + \delta_2 + \delta_3 \approx 0$. Indeed, under this condition, for a succession of the torsion angles ...$\theta_1\theta_2\theta_3\theta_1\theta_2\theta_3$..., the average value of the torsion angles along the chain remains ≈180°. For instance, for a chain with $\tau_1 = \tau_2 = 111°$ and $\tau_3 = 117°$, if $\theta_1 = 162°$ and $\theta_2 = -153°$, then $\theta_3 = 169.3°$ (Figure 4) (with $\delta_1 = -18°$, $\delta_2 = 27°$, and $\delta_3 = -10.7°$; i.e., $\delta_1 + \delta_2 + \delta_3 \approx 0$) and the chain axis is 7.45 Å (Figure 5A). In the particular case of $\theta_1 = 180°$ and $\tau_1 = \tau_2$, $\theta_3 = -\theta_2$ (Figure 4). Experimental identity periods ($c = 7.5$–7.6 Å) are obtained, for a s(2/1) helical symmetry, for $\theta_i = 180° \pm \delta_i$ with $\delta_i = 20$–$25°$ (Figure 5). Slightly different trends are obtained, for each value of θ_1, for different values of τ_1 and τ_2 in the range 110–114°.

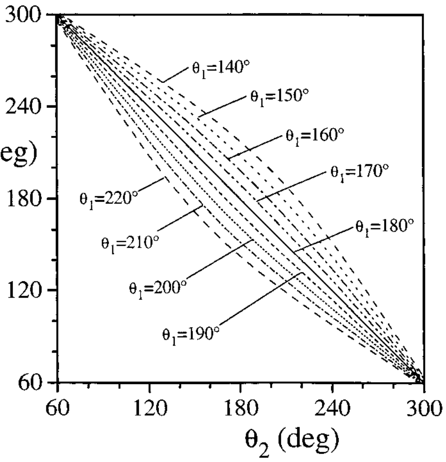

Figure 4. Torsion angles θ_3 as a function of θ_2, for the indicated values of θ_1, which give the helical s(2/1) repetition for a chain of i-STCO. The curves are calculated for $\tau_1 = \tau_2 = 111°$ and $\tau_3 = 117°$.

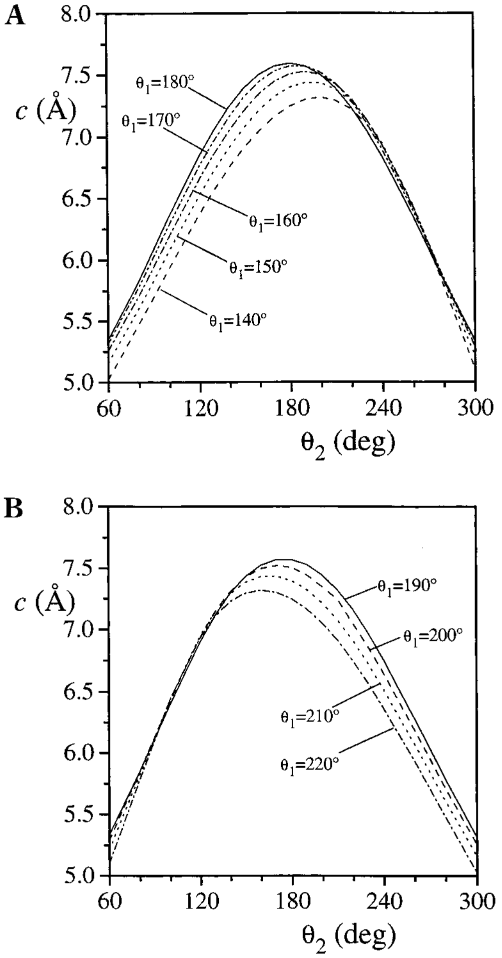

Figure 5. Chain axes *c* of the conformations with s(2/1) helical symmetry of Figure 4 as a function of θ_2 for various values of θ_1. The corresponding values of θ_3 are shown in Figure 4. (A) $\theta_1 = 140°, 150°, 160°, 170°, 180°$; (B) $\theta_1 = 190°, 200°, 210°, 220°$.

Similar geometrical relations between θ_1, θ_2, and θ_3 are reported, for the syndiotactic styrene−CO copolymer, in ref 9.

As shown in the following section, slight deviations of the torsion angles of the main chain from the staggered conformation are feasible because of the low value of the barrier energy in the torsional potential energy around the bond C−CO[9] and are suitable in order to relax nonbonded interactions between atoms appended to the chain.

Conformational Energy Calculations

Method of Calculations. The conformational energy has been calculated as the sum of the terms

$$E_{\text{conf}} = \sum E_{\text{t}} + \sum E_{\text{b}} + \sum E_{\text{nb}} + \sum E_{\text{el}}$$

where E_t are the energy contributions associated with torsion angles (θ) around single bonds, assumed to be of the kind

$$E_{\text{t}} = (K_{\text{t}}/2)(1 + \cos n\theta)$$

with the barrier height K_t and the integer number n depending on the kind of bond.

E_b are the energy contributions due to bond-angle (τ) deformations with respect to the equilibrium angle τ_0, assumed to be of the kind

$$E_{\text{b}} = (K_{\text{b}}/2)(\tau - \tau_0)^2$$

with K_b being the corresponding energy constant.

E_{nb} are the energy contributions due to nonbonded interactions between atoms at a distance r separated by more than two bonds, assumed to be of the kind

$$E_{\text{nb}} = Ar^{-12} - Br^{-6}$$

where A and B are the repulsive and attractive constants, respectively.

E_{el} are the energy contributions due to electrostatic charges q and q' on atoms at a distance r, assumed to be of the kind

$$E_{\text{el}} = (K/\epsilon)qq'/r$$

with ϵ being the dielectric constant and K a conversion constant.

The calculations of the conformational energy have been performed on the portion of the isolated chain of i-STCO shown in Figure 1. The nonbonded energy has been calculated by taking into account the interactions between the atoms of the first monomeric unit and the interactions between these atoms and the remaining atoms. The potential energy constants are those reported by Flory[13,14] and also given in ref 9. We have considered electrostatic charges only on the atoms of the carbonyl groups; 0.39 and −0.39 (in units of elementary charge) are used for the carbon and oxygen atoms, respectively.[13,9]

We have first calculated a map of the conformational energy as a function of two torsion angles, and then, we have performed minimizations of the energy with respect to all the internal parameters.

Map. The energy map has been calculated by application of the equivalence principle[11] to successive constitutional units by assuming a line-repetition group s(M/N) for the polymer chain and, as a consequence, by imposing the sequences ...$\tau_1\tau_2\tau_3\tau_1\tau_2\tau_3$... and ...$\theta_1\theta_2\theta_3\theta_1\theta_2\theta_3$... (Figure 1) for the bond and torsion angles. The sets of possible values of the torsion angles which satisfy the s(2/1) symmetry are included in the map and can be deduced by the results of the geometrical analysis.

The map has been calculated for fixed values of bond lengths and for $\tau_1 = 111°$, $\tau_2 = 111°$, and $\tau_3 = 117°$. The

Table 1. Bond Lengths and Bond Angles Used in the Map of the Conformational Energy

Bond Lengths, Å	
$C_{sp^3}-C_{sp^3}$	1.54
$C_{sp^3}-C_{ar}$	1.51
$C_{sp^3}-C_{sp^2}$	1.51
$C_{ar}-C_{ar}$	1.39
$C_{sp^2}-O$	1.21
$C_{sp^3}-H$	1.10
$C_{ar}-H$	1.08
Bond Angles,[a] deg	
$\tau_1 = \tau_2$	111.0
τ_3	117.0
C−C−O	121.5
H−C′−C	107.9
H−C″−C	109.45
H−C″−H	108.0
$C_{ar}-C_{ar}-C_{ar}$	120.0
$C-C_{ar}-C_{ar}$	120.0
$H-C_{ar}-C_{ar}$	120.0
$C_{ar}-C-C$	111.0

[a] C′ indicates a methine carbon atom; C″ indicates a methylene carbon atom.

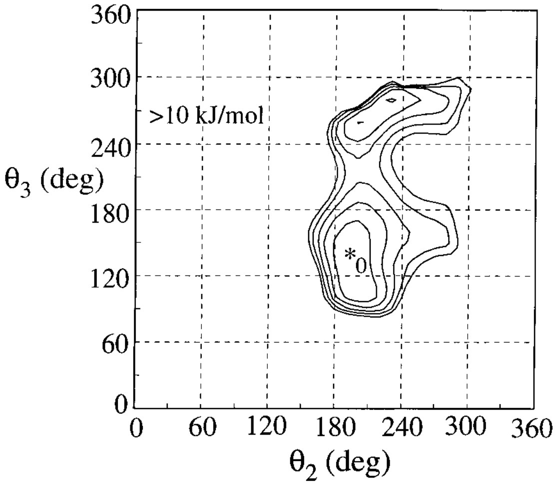

Figure 6. Map of the conformational energy of i-STCO as a function of θ_2 and θ_3 in the s(M/N) line-repetition group for $\tau_1 = \tau_2 = 111°$ and $\tau_3 = 117°$. θ_2 and θ_3 are scanned every 10°, θ_1 and θ_4 are scanned every 5°, and the minimum energy values are reported. The level curves are reported at intervals of 2 kJ/mol of monomeric unit with respect to the absolute minimum (indicated with an asterisk) assumed as zero.

values of the fixed parameters for the calculated map are shown in Table 1. Local C_{2v} and C_{3v} symmetries have been assumed on the CH$_2$ and CH groups, respectively.

Owing to the higher barrier of the intrinsic torsional potential around θ_1 with respect to θ_2 and θ_3, this angle has a lower degree of variability near its energy minima. Therefore, the map of the conformational energy has been calculated as a function of θ_2 and θ_3, by scanning θ_1 in the range 180° ± 40°.

The phenyl ring has been positioned on the plane bisecting the bond angle τ_2 ($\theta_4 = -62°$) in order to minimize the interactions with the neighboring CH$_2$ and CO group; then the map has been calculated by scanning θ_4 in the range 62° ± 40°.

The map of the conformational energy of i-STCO as a function of θ_2 and θ_3 is shown in Figure 6. In this map, for each pair of θ_2 and θ_3, the torsion angles θ_1 and θ_4 were varied in steps of 5° and the energy minimum was reported. The map presents two minima; the absolute minimum ($\theta_1 = 175°$, $\theta_2 = 190°$, $\theta_3 = 140°$, $\theta_4 = -70°$) corresponds to a nearly trans planar conformation. In the region of the minimum, the electrostatic contribution to the conformational energy is very small, since in a nearly trans planar conformation the carbonyl groups are rather far. The carbonyl atom charges influence only slightly the molecular conformation.

Table 2. Values of the Bond and Torsion Angles, Chain Axes *c*, and Conformational Energy E_{conf} Obtained by the Minimization of the Conformational Energy of i-STCO under the Constraint of s(2/1) Symmetry, in Comparison with the Values Obtained by the Energy Map

	map	minimization
τ_1, deg	111	113.2
τ_2, deg	111	111.4
τ_3, deg	117	117
θ_1, deg	175	171.2
θ_2, deg	190	195.6
θ_3, deg	140	172.8
θ_4, deg	−70	−67.1
E_{conf}, kJ/mol of mu	0	−0.32
c, Å		7.59

Minimizations. We have performed minimizations of the conformational energy under the constraint of s(2/1) symmetry, choosing as the starting point the minimum energy conformation obtained by the map. The energy has been minimized by considering as variable parameters all the bond and torsion angles with two minor restrictions: (i) the local C_{2v} symmetry on the CH$_2$ groups has been maintained; (ii) the bond angles having as vertices the carbon atoms of the carbonyl groups have been taken as fixed because their variations should scarcely influence the relative positions of the side groups.[9]

The values of the internal parameters of the chain of i-STCO in the minimum conformational energy, of the corresponding values of the chain axis and of the energy, are reported in Table 2. The energy value is referred to the minimum of the map assumed as zero.

The results of Table 2 indicate that the values of the torsion angles of the main chain deviate from the *trans* value, $\theta_i = 180° + \delta_i$, and the condition $\delta_1 + \delta_2 + \delta_3 \approx 0$, for the s(2/1) repetition, is satisfied.

The deviations of the torsion angles of the main chain from the staggered conformation are suitable in order to relax nonbonded repulsive interactions between the oxygen atoms and the atoms of the side groups and are feasible because of the low value of the barrier energy in the torsional potential energy around the bond C−CO.[9]

The values of the backbone torsion angles of the minimized s(2/1) conformation of Table 2 are close to those found in the resolution and refinement of the crystal structure of i-STCO.[8] A relevant difference concerns the values of $\theta_4 = -67.1°$ with respect to the value of −96° found in the crystal structure.[8] The conformational energy minimum is obtained when the phenyl rings remain on planes nearly bisecting the bond angle τ_2.

It is worth noting, however, that the flexibility of the chain of i-STCO, due to the low barrier energy for the torsion angles θ_2 and θ_3 and the relative ease of rotation of the phenyl rings, as well as to the presence of three single bonds between two consecutive bulky groups that, therefore, scarcely interact,[9] could allow slight changes in the chain conformation owing to the packing interaction. For these reasons, we have performed minimizations of the conformational energy with fixed values of the torsion angles θ_4 in the range −30 to −100°, that is, with θ_4 deviated significantly from the value that

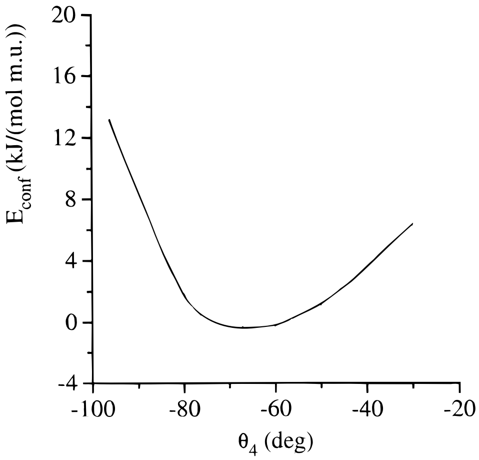

Figure 7. Conformational energy, E_{conf}, obtained by minimizations of the energy performed on the isolated chain of i-STCO, under the constraint of the s(2/1) symmetry, with different fixed values of the torsion angle θ_4, as a function of θ_4.

keeps the phenyl ring plane bisecting the bond angle τ_2. The results of these minimizations are reported in Figure 7, where the conformational energy is reported as a function of θ_4. It is apparent that deviations of θ_4 from the value of −67°, corresponding to the minimum, produce a slight increase of the conformational energy.

Packing Energy Calculations

The packing energy is evaluated as half of the sum of the interaction energies between the atoms of one monomeric unit and all surrounding atoms of the neighboring macromolecules. The calculations were performed with the same parameters used for the conformational energy calculations. The interactions were calculated within spheres of radii equal to twice the sum of the van der Waals radii for each pair of atoms. The conformation of the chain, and hence the chain axis, was kept constant.

Although the results of the minimization of the conformational energy indicate that the energy minimum is obtained when the phenyl rings remain on planes bisecting the bond angles τ_2 ($\theta_4 = -67.1°$), the packing energy has been calculated with a chain of i-STCO having the minimum energy conformation (Table 2, $\theta_4 = -67.1°$) as well as with chains having conformations obtained with the minimizations of the conformational energy performed with θ_4 fixed at different values in the range −30° to −100° (Figure 7).

We have calculated the packing energy for the model of the crystal structure of i-STCO corresponding to chains packed in the monoclinic unit cell with axes a = 5.47 Å, b = 8.367 Å, c = 7.57 Å (chain axis), and γ = 110°, according to the space group $P2_1$ with unique axis c[8] (we recall that in ref 8 we chose the space group $P2_1$ with unique axis b and the unit cell with axes a = 8.367 Å, b = 7.57 Å, c = 5.47 Å, and β = 110°). The position of the chain axis inside the unit cell has been fixed at the fractional coordinates $x/a = y/b = 0$ (corresponding to the position of the crystallographic 2_1 axis of symmetry in the cited space group). Since the packing energy in the space group $P2_1$ does not depend on the height z of the chain, the packing energy has been calculated by maintaining the axes of the unit cell constant, varying only the orientation of the chain around its axis (represented by the angle ω defined in Figure 8).

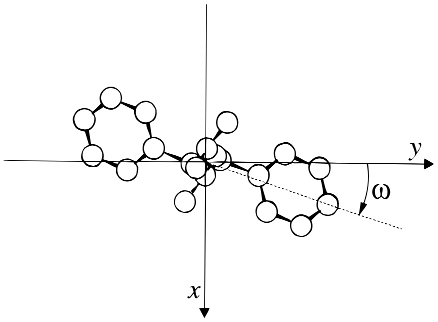

Figure 8. Definition of the variable ω used in the packing energy calculations. ω is the angle of rotation (positive for a clockwise rotation) of the s(2/1) helical chain of i-STCO around the chain axis.

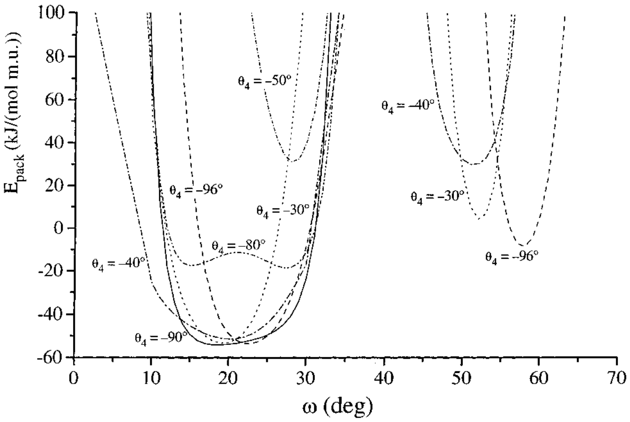

Figure 9. Curves of the packing energy, E_{pack}, of i-STCO as a function of ω (defined in Figure 8), for the space group $P2_1$ and unit cell with axes a = 5.47 Å, b = 8.367 Å, c = 7.57 Å, and γ = 110°, with chains having helical s(2/1) conformation and the indicated values of θ_4.

The curves of the packing energy, as a function of ω, for the space group $P2_1$, with chains of i-STCO having different values of θ_4 in the range −30 − to −100° are reported in Figure 9.

The curves present energy minima for similar values of ω (ω = 20−30°). The lowest values of the packing energy are obtained with conformations of the chain having $\theta_4 = -90°$ or −30°. The values of the minima of the packing energy are reported in Table 3. It is apparent that for the conformation of the lowest conformational energy (Table 2), with $\theta_4 = -67.1°$, a very high value of the packing energy (>100 kJ/mol of monomeric unit) is obtained.

The values of the packing energy of Table 3 are reported in Figure 10 as a function of θ_4. In the same figure, the curves of the conformational energy of Figure 7 and of the total energy ($E_t = E_{conf} + E_{pack}$) are also shown.

It is apparent that in correspondence to the minimum of the conformational energy, $\theta_4 = -67.1°$, the packing energy and the total energy are very high; deviations of ±30° of θ_4 from −67° produce a slight increase of the conformational energy and a significant lowering of the packing energy. Equivalent minima of the total energy are obtained for $\theta_4 = -90°$ and −40°, according to the value of −96° found in the refinement of the crystal structure.[8]

A model of packing of i-STCO in the space group $P2_1$, corresponding to the minimum of the total energy, $\theta_4 = -90°$ and ω = 18°, is shown in Figure 11. It is

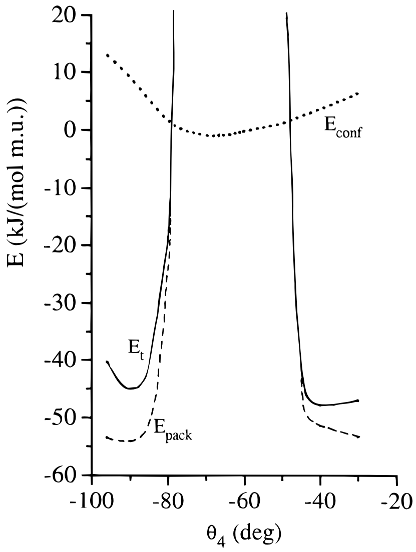

Figure 10. Conformational energy of Figure 7, E_{conf}, obtained by minimizations performed on isolated chain of i-STCO with different fixed values of θ_4 (dotted line), packing energy, E_{pack}, of Table 3 (dashed line), and total energy, $E_{tot} = E_{conf} + E_{pack}$ (solid line), as a function of θ_4.

Table 3. Packing Energy in the Space Group $P2_1$, for Chains of i-STCO having Helical s(2/1) Conformations and Different Values of the Torsion Angle θ_4[a]

θ_4, deg	ω, deg	E_{pack}, kJ/mol of monomer unit
−30	19	−53.3
−40	20	−51.4
−50	28	31.0
−60	29	>100
−67.1	29	>100
−80	27	−18.6
−90	18	−54.1
−96	22	−53.5

[a] The values of the angles of rotation of the chain around the chain axis, ω, and the packing energy, E_{pack}, are given as a function of θ_4.

apparent that this model is very similar to that found by X-ray diffraction.[8] The values of the internal parameters of the chain of i-STCO in the model of Figure 11 are: $\tau_1 = 115.4°$, $\tau_2 = 112.5°$, $\tau_3 = 117°$, $\theta_1 = 170.8°$, $\theta_2 = 206.7°$, $\theta_3 = 162.3°$, and $\theta_4 = -90°$.

The deviation of θ_4 from −67° to −90° arises from the need to optimize intermolecular contacts between the atoms of the phenyl rings belonging to the two adjacent chains along the *a* axis of the unit cell (Figure 11). Indeed, in the model of packing with chains having $\theta_4 = -67°$, contact distances lower than 3 Å between these atoms are present, whereas for chains with $\theta_4 = -90°$ the shortest distances between these atoms are at 3.8 Å, compatible with the van der Waals distance. This deviation indicates also the relative ease of rotation of the phenyl groups.

These results have been confirmed by performing calculations of the packing energy varying, besides the angle ω, the parameters *a*, *b*, and γ of the unit cell. The packing energy has been minimized varying ω, *a*, *b*, and γ, starting from the experimental values of the unit cell parameters, with chains of i-STCO having different values of θ_4. For the model of packing with chains having $\theta_4 = -67°$, low values of the packing energy are obtained only with an expansion of the *a* axis of the unit cell (values of $a = 6.5$ Å, $b = 8.5$ Å, and $\gamma = 119°$ are obtained). This indicates for this model a need to relax the short distances between the atoms of adjacent chains along *a*. Unit cell dimensions close to the experimental values are obtained from these minimizations only for models of packing with chains having $\theta_4 = -90$ to $-96°$ or $\theta_4 = -30$ to $-40°$.

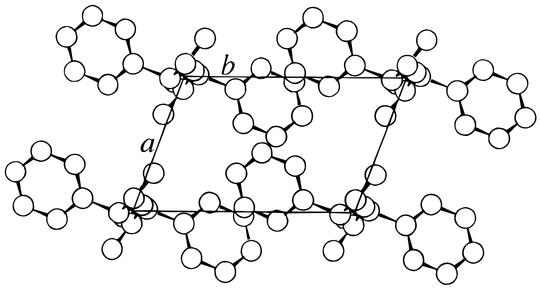

Figure 11. Model of packing of i-STCO in the space group $P2_1$, corresponding to the minimum of the total energy of Figure 10 with $\theta_4 = -90°$.

Conclusions

Highly extended chains (chain axis 7.5−7.6 Å) of i-STCO are obtained if the torsion angles of the main chain θ_1, θ_2, and θ_3 are near 180°, that is, $\theta_i = 180 + \delta_i$, with δ_i small. Assuming $\theta_2 = -\theta_1$, a helical s(2/1) repetition occurs if $\theta_3 \approx 180°$.

In any case, a 2-fold s(2/1) helix conformation of a highly extended chain occurs when θ_1, θ_2, and θ_3 have slight different deviations from 180°, $\theta_i = 180 + \delta_i$, but it must be $\delta_1 + \delta_2 + \delta_3 \approx 0$.

Conformational energy calculations support the previous geometrical analysis. The values of the identity period and of the internal parameters obtained by the minimization of the conformational energy, performed under the constraint of the helical s(2/1) symmetry, are in good agreement with the experimental values, found in the resolution of the crystal structure by X-ray diffraction.[8] θ_1 and θ_2 have opposite deviations from 180°, and θ_3 is near 180°.

The torsion angles of the backbone are very similar to those found for the syndiotactic styrene-CO copolymer;[3,4] the configurational change at the tertiary carbons has no relevant effect on the conformation and, hence, on the chain repeating period. In both polymers, isotactic and syndiotactic, the presence of a substituent phenyl group on the backbone produces slight deviations of the torsion angles from 180°.

Packing energy calculations confirm the model of packing proposed by us[8] and can allow us to interpret the only relevant difference between the conformations of the chains found for i-STCO[8] and s-STCO[3,4] in the crystalline field. This difference concerns the value of the torsion angle θ_4, which defines the orientation of the lateral phenyl groups. In i-STCO, θ_4 deviates significantly from 60°, the value which keeps the phenyl ring plane bisecting the bond angle at the tertiary carbon. Since the best conformation obtained by minimization of the conformational energy of the isolated chain has θ_4 near 60°, this effect arises from the need to optimize intermolecular contacts between the carbon atoms of the phenyl rings of adjacent chains.

Although the best conformation obtained by the energy minimizations of the isolated chain of polymers is generally found unvaried in the crystalline lattice, in the structure of i-STCO, the packing interaction produces changes in the chain conformation. It is worth noting that also for aromatic polyamides, it was found that the conformation of the isolated chain is distorted by the intermolecular packing.[15,16]

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