Conformational Analysis by Molecular Mechanics on Single Chains of Polyketones

Roberto Napolitano and Beniamino Pirozzi*

Dipartimento di Chimica, Università di Napoli "Federico II", via Mezzocannone 4, 80134 Napoli, Italy

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ABSTRACT: A geometrical and energy analysis has been performed on the isolated chain of syndiotactic polymers having the formula $(-CHR-CH_2-CO-)_n$ where R = C_6H_5, (*o*-, *m*-, *p*-) $C_6H_4CH_3$, in comparison with $(-CH_2-CH_2-CO-)_n$ with the aim of predicting the best conformations in the crystalline field. By geometrical analysis the relations between the bond and torsion angles in the main chain have been found in the framework of the **tc** line repetition group. The results of the conformational energy calculations show that the presence of the side groups gives rise to significant deviations from the all trans conformation. On the contrary, secondary effects on the chain conformation are found in relation to the kind of side group. All the results obtained by energy calculations are in good agreement with experimental data.

Introduction

Copolymers of carbon monoxide with olefins, also called polyketones, have been synthesized and characterized for many years. The polymer chains of these copolymers can have a regular constitution. The simplest polyketones, obtained by copolymerization of carbon monoxide and ethylene, were characterized by X-ray diffraction studies in past years.[1,2] A perfectly alternating copolymer of carbon monoxide with styrene has been obtained by homogeneous palladium catalyst systems only in recent times.[3] This copolymer has been identified as syndiotactic poly(1-oxo-2-phenyltrimethylene),[4] and its complete crystal structure has been obtained by X-ray diffraction.[5] Successively, regular alternating copolymers of carbon monoxide and styrene derivatives have been synthesized and characterized as syndiotactic polymers.[6] The complete crystal structures have been resolved by X-ray diffraction on powder samples.[7]

In this paper we report results of the conformational analysis on the isolated chain of syndiotactic polyketones having the formula $(-CHRCH_2CO-)_n$, with R = C_6H_5 [STCO], (*o*-, *m*-, *p*-) $C_6H_4CH_3$ [*o*-MeSTCO, *m*-MeSTCO, *p*-MeSTCO, respectively], in comparison with $(-CH_2CH_2CO-)_n$ [ETCO] with the aim of predicting the best conformation in the crystalline field. The analysis has been carried out both by calculations based on the geometrical conditions, dictated by the constitution and configuration of the polymer chains, and by the evaluation of the energy of the possible conformations, obtained by the method of molecular mechanics.

Geometrical Analysis

Geometrical analysis has been effected with the aim of finding the relations between the internal parameters of the chains of the studied syndiotactic polyketones in the crystalline field. The analysis has been carried out by taking into account the symmetry elements of the chains and, therefore, the possible line repetition groups.[8] The two directions of the chain of these polyketones are intrinsically nonequivalent due to the chemical constitution. Therefore, we can exclude the presence of centers of symmetry and of 2-fold axes of symmetry and mirror planes perpendicular to the chain axis. Also planes of symmetry parallel to the chain axis have to be excluded, caused by the presence of the asymmetric carbon atoms. Finally, the screw repetition as a single symmetry element can be excluded because it is incompatible with syndiotactic polymers. Hence, the only possible symmetry element is the glide plane parallel to the chain axis and the only line repetition group is **tc**. This symmetry implies that adjacent pairs of configurational units,[8] [CU]s, have the same succession of values of the bond angles and opposite values in the sequence of the torsion angles. The following geometrical analysis is therefore exhaustive if we find the relations between the bond and torsion angles of the CU in the framework of the **tc** line repetition group.

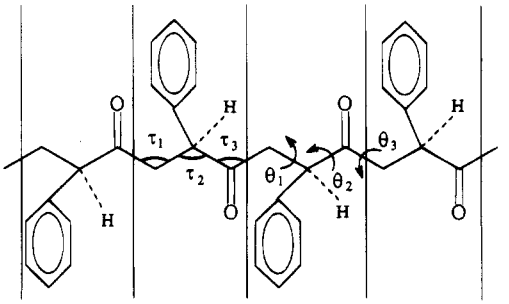

Figure 1. Portion of a chain of STCO considered in the geometrical and energy analysis with the indication of the bond and torsion angles in the main chain. Each CU is between two vertical bars.

Figure 1 shows a portion of the chain of syndiotactic STCO and the internal parameters in the main chain, bond angles τ_1, τ_2, and τ_3, and torsion angles θ_1, θ_2, and θ_3, which define the conformation of each CU. The same symbols are used for the other studied polyketones.

As for the bond angles, we have selected only values which are reasonable for the considered chemical systems. In particular, we have chosen $\tau_3 = 117°$ in accordance with experimental data[5,9,10] and we have considered values of τ_1 and τ_2 in the range 110−114° as found in polymers having not particularly overcrowded side groups.[11,12] As for the torsion angles, we have examined the relation between θ_2 and θ_3 in the most significant range of values of θ_1.

Figure 2 shows the values of θ_2 and θ_3 in the **tc** line repetition group for $\theta_1 = 150°$, 160°, 170°, and 180° and

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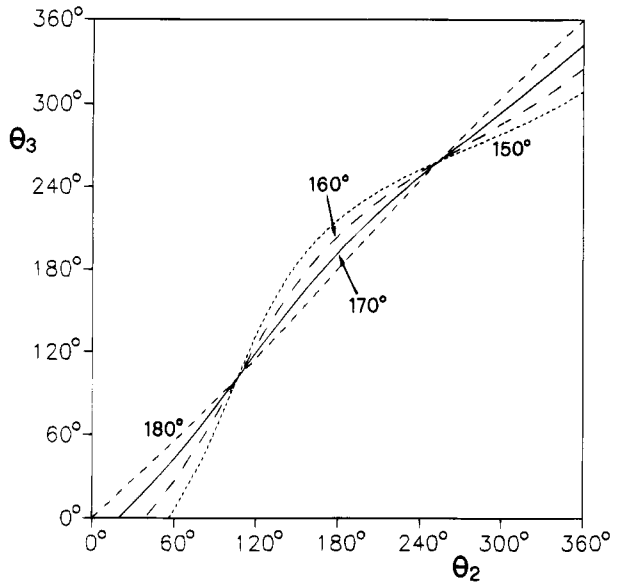


Figure 2. Trends of θ_3 as a function of θ_2 in the **tc** line repetition group for the indicated values of θ_1. The curves have been calculated for $\tau_1 = 113°$, $\tau_2 = 110°$, and $\tau_3 = 117°$.

for $\tau_1 = 113°$ and $\tau_2 = 110°$. The curves obtained for $\theta_1 = 190°$, 200°, and 210° are symmetric with respect to the diagonal line of the curves obtained for $\theta_1 = 170°$, 160°, and 150°, respectively. Slightly different trends are obtained, for each value of θ_1, for different values of τ_1 and τ_2 in the considered range. In the particular case of $\theta_1 = 180°$, θ_3 is always equal to θ_2 when $\tau_1 = \tau_2$.

Energy Calculations

Method of Calculation. The conformational energy E has been calculated as follows:

$$E = E_b + E_t + E_{nb} + E_{el}$$

where $E_b = (K_b/2)(\tau - \tau_0)^2$ represents the energy contribution due to deformations of the bond angles τ with respect to the equilibrium angle τ_0 and K_b is the corresponding energy constant; $E_t = (K_t/2)(1 + \cos n\theta)$ represents the contribution of the intrinsic torsional potential due to the rotation around single bonds, where θ is the torsion angle and the barrier height K_t and the integer number n depend on the kind of bond; $E_{nb} = Ar^{-12} - Br^{-6}$ is the energy contribution due to the interactions between atoms at a distance r separated by more than two bonds, with A and B the repulsive and attractive constants, respectively; and $E_{el} = (K/\epsilon)qq'/r$ represents the contribution due to the electrostatic charges q and q' on the atoms at a distance r, with ϵ the dielectric constant and K a conversion constant. We have considered electrostatic charges only on the atoms of the carbonyl groups.

The nonbonded and electrostatic terms have been calculated by taking into account the interactions between the atoms inside a CU and the interactions between the atoms of a CU and all the other atoms of the macromolecule. The interactions between atomic species at distances greater than twice their van der Waals distance have been neglected because they do not affect the energy differences between the various conformations.

The potential energy constants are derived by the data reported by Flory et al.;[13,14] the intrinsic torsional barrier around the bond adjacent to the phenyl ring is taken from Hopfinger.[15] The used energy constants are given in Table 1.

Table 1. Parameters of the Potential Functions Used in the Energy Calculations[a]

Bending Energy

bond angle	K_b	τ_0/deg
C–C–C	0.184	109.47
C–C–H	0.121	109.47
H–C–H	0.100	109.47

Torsional Energy

torsion angle	K_t	n
C_{sp^2}–C_{sp^3}–C_{sp^3}–C_{sp^2}	11.7	3
C_{sp^3}–C_{sp^3}–C_{sp^2}–C_{sp^3}	4.2	3
C–C_{sp^3}–C_{ar}–C_{ar}	2.4	6

Nonbonded Energy

interacting pair	$10^{-3}A$	B	d_W/Å[b]
C_{sp^3}, C_{sp^3}	1653	1519	3.60
C_{sp^3}, C_{ar}	2596	1867	3.75
C_{sp^3}, C_{sp^2}	2034	1869	3.60
C_{sp^3}, O	1175	1522	3.40
C_{sp^3}, H	235.6	530.9	3.10
C_{sp^3}, CH_3	4018	2669	3.80
C_{ar}, C_{ar}	4066	2311	3.90
C_{ar}, C_{sp^2}	3212	2310	3.75
C_{ar}, O	1859	1858	3.55
C_{ar}, H	393.6	666.0	3.25
C_{ar}, CH_3	6271	3302	3.95
C_{sp^2}, C_{sp^2}	2515	2310	3.60
C_{sp^2}, O	1435	1858	3.40
C_{sp^2}, H	294.5	663.6	3.10
C_{sp^2}, CH_3	4971	3302	3.80
O, O	828.3	1543	3.20
O, H	154.4	519.2	2.90
O, CH_3	2886	2652	3.60
H, H	30.2	195.5	2.60
H, CH_3	613.2	949.6	3.30
CH_3, CH_3	9664	4719	4.00

Electrostatic Term[c]

atomic species	q, q'
C_{sp^2}	0.39
O	−0.39

[a] The symbols are referred to the formulas reported in the text. The values of K_b, K_t, A, and B are expressed in such a way that the energy is in kJ·mol^{-1}. [b] d_W is the van der Waals distance between the considered atomic species. [c] The dielectric constant used is $\epsilon = 3.5$; q and q' are in units of elementary charge; $K = 1388$.

The conformational energy has been calculated in two successive steps: (i) maps and (ii) minimizations.

Maps. The maps give an overall indication of the low-energy conformations obtained by varying a few (commonly two) parameters. The main chain parameters of the polymers reported in this paper are θ_1, θ_2, and θ_3, indicated in Figure 1.

We have calculated the maps of the conformational energy of polyketones by imposing in the main chains the sequences ..., τ_1, τ_2, τ_3, τ_1, τ_2, τ_3, ... and ..., θ_1, θ_2, θ_3, $-\theta_1$, $-\theta_2$, $-\theta_3$, ... for the bond and torsion angles, respectively. In this way, a necessary but not sufficient condition in order for the chains to have the **tc** symmetry is obtained. The sets of possible values of the internal parameters which satisfy the **tc** symmetry are included in the maps and can be deduced by the results of the previous geometrical analysis.

Due 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 in the neighborhood of its energy minima (+60°, +180°, −60°). Therefore, the maps of the conformational energy have been calculated as a function of θ_2 and θ_3 for a fixed value of θ_1. Among

Table 2. Bond Lengths and Bond Angles Used in the Maps of the Conformational Energy

Bond Lengths/Å			
$C_{sp^3}-C_{sp^3}$	1.54	$C_{sp^2}-O$	1.21
$C_{sp^3}-C_{ar}$	1.51	$C_{sp^3}-H$	1.10
$C_{sp^3}-C_{sp^2}$	1.51	$C_{ar}-H$	1.08
$C_{ar}-C_{ar}$	1.39		
Bond Angles/deg			
$C-C_{sp^2}-C$	117	$C-C_{ar}-C_{ar}$	120
$C-C-O$	121.5	$C_{ar}-C_{ar}-C_{ar}$	120
$H-C-H$	108	$C_{ar}-C_{ar}-H$	120

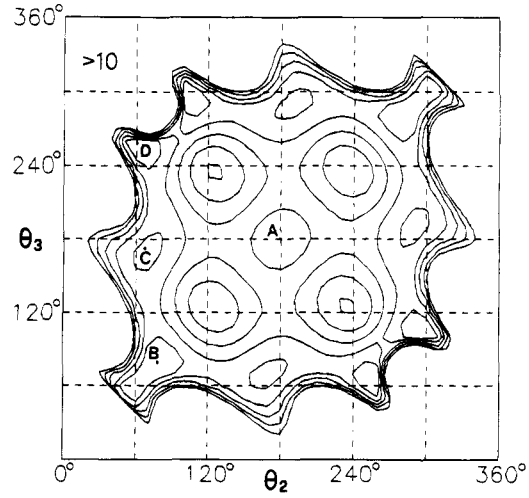


Figure 3. Map of the conformational energy of ETCO as a function of θ_2 and θ_3 calculated in correspondence with $\theta_1 = 180°$, $\tau_1 = 112°$, and $\tau_2 = 112°$. The level curves are reported at intervals of 2 kJ·(mol of CU)$^{-1}$ with respect to the absolute minimum B assumed as zero.

the torsional energy minima of θ_1 we have chosen 180°. In fact, only for $\theta_1 = T(\sim)^8$ can the chain assume a highly extended conformation in such a way as to have a more efficient mode of packing.

All the bond lengths and the bond angles have been taken as fixed. Local C_{2v} and C_{3v} symmetries have been assumed on the CH_2 and CH groups, respectively. The phenyl rings have been positioned on the planes bisecting the angles τ_2 in such a way as to minimize the interactions with the neighboring CH_2 and CO groups. The values of the fixed parameters for all the calculated maps are given in Table 2. The values of τ_1 and τ_2 have been chosen depending on the considered polyketone. In the case of ETCO τ_1 and τ_2 are equivalent and we have chosen for both angles the value of 112°. We think that in all the other cases the bond angle τ_2, having as a vertex the substituted carbon atom, has a lower value with respect to τ_1. In these cases we have chosen $\tau_1 = 113°$ and $\tau_2 = 110°$.

We have first calculated the map of the simplest polyketone, that is ETCO, and then the maps of STCO and of MeSTCOs in order to evaluate the effects on the conformation caused by the presence of a bulky side group, phenyl group or a methyl-substituted phenyl group, instead of a hydrogen atom.

Figure 3 shows the map of the conformational energy of ETCO. This map has four independent minima indicated by A, B, C, and D. The absolute minimum B corresponds to a sequence G^+ (~), G^+ (~) which gives rise to a not extended chain having a low packing efficiency. The presence of a trans instead of a gauche value for θ_2 or for θ_3 (minimum C and equivalent minima) increases the energy by about 1.5 kJ·(mol of CU)$^{-1}$. As a consequence, the energy of the all trans-planar chain (minimum A) is only 2.9 kJ·(mol of CU)$^{-1}$ higher with respect to the absolute minimum. This little energy amount is easily compensated by a more efficient mode of packing that can be realized by the extended chains. In support of these considerations we note that the all trans-planar conformation was experimentally found in the crystal structure of ETCO.[1]

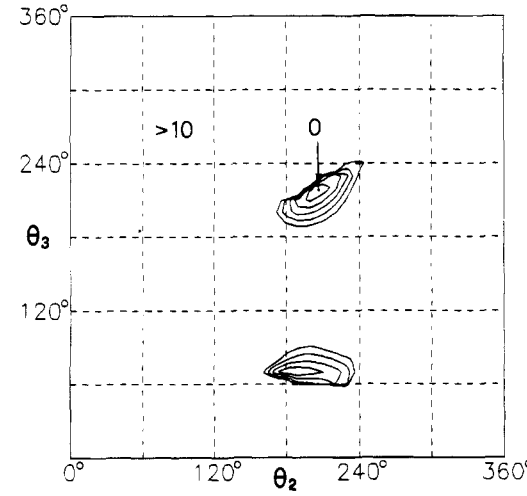


Figure 4. Map of the conformational energy of STCO as a function of θ_2 and θ_3 calculated in correspondence with $\theta_1 = 180°$, $\tau_1 = 113°$, and $\tau_2 = 110°$. The level curves are reported at intervals of 2 kJ·(mol of CU)$^{-1}$ with respect to the absolute minimum assumed as zero.

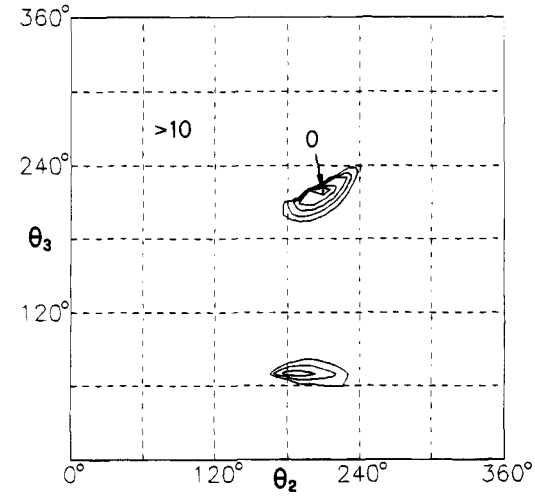


Figure 5. Map of the conformational energy of *p*-MeSTCO as a function of θ_2 and θ_3 calculated in correspondence with $\theta_1 = 180°$, $\tau_1 = 113°$, and $\tau_2 = 110°$. The level curves are reported at intervals of 2 kJ·(mol of CU)$^{-1}$ with respect to the absolute minimum assumed as zero.

The substitution of a hydrogen atom in the chain of ETCO with a phenyl ring produces a dramatic change in the map of the conformational energy. In fact, the map of STCO, shown in Figure 4, has only two minima. The values of the internal parameters of the chain conformation corresponding to the absolute minimum are very close to those of a chain having **tc** symmetry, as can be deduced by comparison with Figure 2.

The map of *p*-MeSTCO, shown in Figure 5, is very similar to that of STCO both in the shapes and in the positions of the minima. This is a not surprising result because the presence of a methyl group in the para position, that is far from the chain backbone, does not affect significantly the intramolecular interactions. Possible differences in the crystal structures of the two

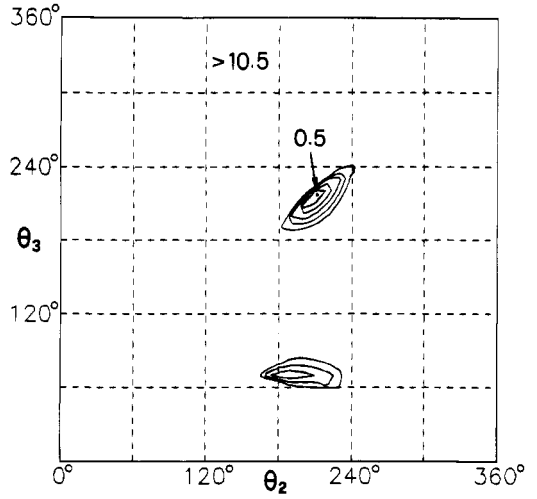


Figure 6. Map of the conformational energy of *i m*-MeSTCO as a function of θ_2 and θ_3 calculated in correspondence with $\theta_1 = 180°$, $\tau_1 = 113°$, and $\tau_2 = 110°$. The level curves are reported at intervals of 2 kJ·(mol of CU)$^{-1}$ with respect to the absolute minimum of the map. The energy of the absolute minimum is referred to the absolute minimum of the map of *p*-MeSTCO.

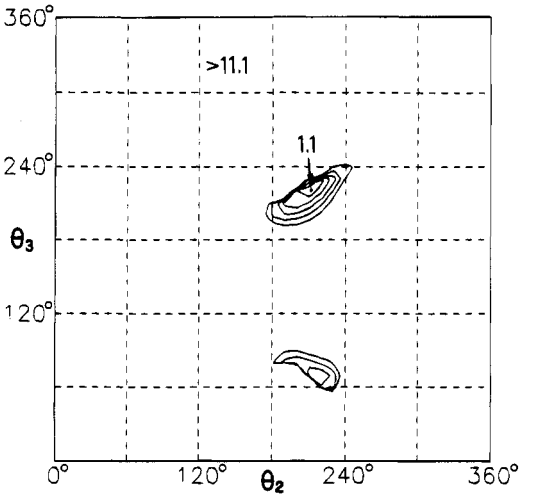
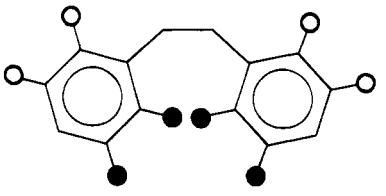


Figure 7. Map of the conformational energy of *e m*-MeSTCO as a function of θ_2 and θ_3 calculated in correspondence with $\theta_1 = 180°$, $\tau_1 = 113°$, and $\tau_2 = 110°$. The level curves are reported at intervals of 2 kJ·(mol of CU)$^{-1}$ with respect to the absolute minimum of the map. The energy of the absolute minimum is referred to the absolute minimum of the map of *p*-MeSTCO.

Chart 1



polymers should be therefore ascribed mainly to the intermolecular interactions.

As for *m*-MeSTCO and *o*-MeSTCO, two different chain conformations, obtainable one from the other by the rotation by 180° of the phenyl ring around the C−C_{ar} bond, are possible. These conformations can be distinguished by the positions of the methyl groups, as indicated in Chart 1 representing a projection on a plane perpendicular to the chain axis of the chain in all trans conformation with the phenyl rings bisecting the angles τ_2. For both polymers, the conformation having the methyl groups in the positions indicated by full circles is henceforth named *i*, while the conformation corresponding to the positions indicated by empty circles is named *e*. We have calculated the maps of these polymers both for *i* and for *e* conformations.

Figure 6 and Figure 7 show the maps of *i* and *e m*-MeSTCO, respectively. These maps are very similar to that of *p*-STCO. The absolute minimum energy, obtained in the case of *i m*-MeSTCO, is slightly lower with respect to the absolute minimum of *e m*-MeSTCO and slightly higher with respect to the absolute minimum of *p*-MeSTCO.

Figure 8 shows the map of *e o*-MeSTCO. The absolute minimum has a much higher energy with respect to the minima of the preceding maps. The map of *i o*-MeSTCO is not reported because its results are high in energy for all the values of θ_2 and θ_3.

Minimizations. The minimizations give the most accurate values of the internal parameters of the chain conformations and the corresponding energy values. We have effected minimizations of the conformational energy for all the mentioned polyketones under the constraint of the **tc** symmetry, choosing as starting points the most significant minimum energy conformations obtained by the maps. We have considered 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.

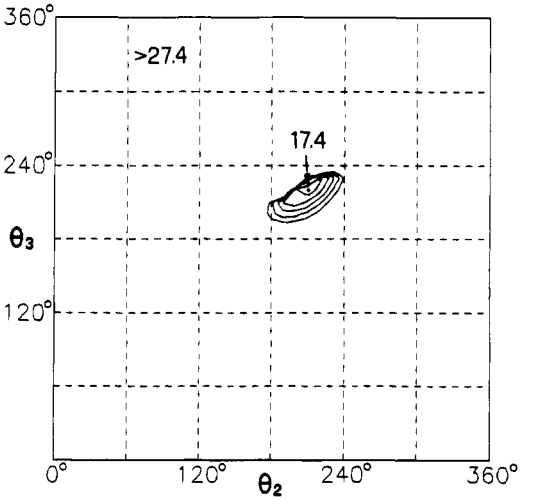


Figure 8. Map of the conformational energy of *e o*-MeSTCO as a function of θ_2 and θ_3 calculated in correspondence with $\theta_1 = 180°$, $\tau_1 = 113°$, and $\tau_2 = 110°$. The level curves are reported at intervals of 2 kJ·(mol of CU)$^{-1}$ with respect to the absolute minimum of the map. The energy of the absolute minimum is referred to the absolute minimum of the map of *p*-MeSTCO.

The values of the main internal parameters in the minimum energy point are given in Table 3 together with the corresponding values of the chain repeating distance and of the energy, for each polymer. In the case of both ETCO and STCO the energy value is referred to the minimum of the corresponding map, while in the case of all MeSTCOs the reference value is the absolute minimum of the map of *p*-MeSTCO.

The results of Table 3 give a clear indication of the values assumed by the internal parameters of the substituted polyketones in comparison with ETCO. The

Table 3. Values of the Internal Parameters, Chain Repeating Distances (c), and Energies (E) Obtained by the Minimization of the Conformational Energy of the Studied Polyketones

polymer	τ_1/deg	τ_2/deg	θ_1/deg	θ_2/deg	θ_3/deg	c/Å	E/kJ·(mol of CU)$^{-1}$
ETCO	112.3	112.3	180	180	180	7.64	2.9
STCO	112.2	110.6	173	210	218	7.51	−0.1
p-MeSTCO	112.7	110.7	175	211	218	7.52	0.6
i m-MeSTCO	112.6	110.6	175	212	218	7.52	−0.9
e m-MeSTCO	112.6	110.0	171	216	226	7.47	0.9
e o-MeSTCO	113.0	109.7	167	212	227	7.48	11.8

bond angles τ_2, having as vertices the substituted carbon atoms, are closer to the tetrahedral value than the bond angles τ_1. This trend, in accordance with results experimentally found for many polymers, can be ascribed both to the higher bending energy constants of the bond angles of the CHR group with respect to the CH_2 group and to the nonbonded interactions between the phenyl rings and the oxygen atoms. The values of the torsion angles deviate from the trans value, corresponding to the minimum of intrinsic torsional potential, as a consequence of the presence of the side groups. The widest deviations are observed for θ_2 and θ_3. In fact, these deviations, necessary in order to reduce repulsive interactions between the oxygen atoms and the side groups, are possible because of the quite low intrinsic potential barrier for rotations around bonds adjacent to carbonyl groups. On the contrary, slight deviations are found for θ_1. As for the torsion angles around the side groups, they are not given in Table 3 because in all the minimizations the phenyl rings remain approximately on the planes bisecting the τ_2 angles.

We have performed further minimizations in order to study the influence on the conformational energy of slight deviations of the internal parameters from the values corresponding to the absolute minima given in Table 3. As result, we have found that the values of θ_1 can be varied within a range of ~5° and the values of θ_2 and θ_3 within a range of ~10° at a low energy cost (few tenths of kJ·(mol of CU)$^{-1}$) without a significant change of the values of the repeating distances c. This is a clear indication of the flexibility of the chains of the studied polyketones. This flexibility can be explained by the presence of three single bonds between two consecutive bulky groups that, therefore, scarcely interact. On the contrary, more rigid chains were found, for example, in the case of syndiotactic polypropylene[16] which has only two single bonds between the side groups. Therefore, we think that, while the best conformation obtained by the energy minimizations of the isolated chain is generally found unvaried in the crystalline field, the packing interaction can produce slight changes in the chain conformation for the studied polyketones.

Conclusions

The results of the conformational energy calculations show that the values of the chain repeating distances c obtained by the minimizations performed under the only constraint of the **t***c* symmetry are in very satisfactory accordance with the experimental data.[1,5,7]

As far as a comparison between the studied polymers, the main consequence of the presence of a substituent group on the backbone, in our case a phenyl or methyl-substituted phenyl group, is that the all trans conformation, which is predicted and observed in the case of ETCO, is not realized. A further consequence is that the values assumed in all the substituted polymers by the bond angles τ_1 and τ_2 are different while they are equal in ETCO. On the contrary, secondary differences in the conformational parameters are obtained in relation to the kind of the substituent group.

A comparison of the values of the minimum energy can be done for MeSTCOs. The lowest energy is obtained for *i m*-MeSTCO. A slightly higher energy is obtained for *p*-MeSTCO while a much higher energy corresponds to *o*-MeSTCO. The higher energy obtained for the conformation of *e m*-MeSTCO in comparison with *i m*-MeSTCO indicates that the latter is favored. This result is in accordance with the experimental evidence.[7] No comparison with experimental data is possible for *o*-MeSTCO, because the synthesis of this polymer has not been reported until now. On the other hand, the high value found for the conformational energy of *o*-MeSTCO indicates that, if the activated complex in the synthesis reaction is similar to the product, it is not easy to obtain this polymer.

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