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Chain conformations of syndiotactic poly(*m*-methylstyrene) in the crystalline state

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Abstract

A conformational energy analysis of the isolated chain of syndiotactic poly(*m*-methylstyrene) under the constraint of a crystalline field is reported. Two different minimum energy conformations having similar energy have been found; the *trans*-planar conformation with **t***cm* symmetry and the two-fold helical conformation with **s**(2/1)2 symmetry, according with the observed polymorphic behavior of this polymer. The calculated chain axes are in agreement with the experimental axes of 5.1 and 7.9 Å found for the different polymorphic forms of syndiotactic poly(*m*-methylstyrene). However, only a metastable disordered modification (form III) having chains in *trans*-planar conformation has been described. This indicates that, even though the *trans*-planar conformation is, in the isolated chain as stable as the helical conformation, the packing of the chains in helical conformation is probably more efficient than that of the *trans*-planar chains.

Keywords: Syndiotactic poly(*m*-methylstyrene); Chain conformations; Energy calculations

1. Introduction

Syndiotactic polymers of styrene and substituted styrene have been prepared with homogeneous catalytic systems, based on titanium or zirconium compounds and methylaluminoxane [1–8], and interesting high-melting thermoplastic materials have been produced.

The complex polymorphic behavior and the physical properties of syndiotactic polystyrene (sPS) have been extensively studied [9–22]. Among substituted polystyrenes, syndiotactic poly(*p*-methylstyrene) (sPPMS) has been studied as well [23–27], and a complex polymorphic behavior has also been revealed.

The crystalline forms of sPS and sPPMS are characterized by the same conformations of the chains, that is, the extended *trans*-planar conformation and the two-fold helical conformation with **s**(2/1)2 line repetition symmetry. In the case of sPS, the crystalline forms with chains in the *trans*-planar conformation (α and β forms) are the most stable forms and are obtained by crystallization from the melt [9–16,22]. The crystalline forms with chains in the two-fold helical conformation crystallize in the presence of solvents, by casting or precipitation from polymer solutions or solvent diffusion in amorphous samples [9,17–22].

Also for sPPMS the polymorphic forms with chains in the helical conformation (forms I, II and clathrate structures) are obtained in the presence of solvent [23,26, 27]. Moreover, two crystalline forms with chains in the *trans*-planar conformation (forms III and V) are obtained by annealing amorphous samples at high temperatures [23–25]. For both sPS and sPPMS disordered mesomorphic modifications with chains in *trans*-planar conformation have been described [24,29,30].

A preliminary structural characterization of syndiotactic poly(*m*-methylstyrene) (sPMMS) has been recently reported [28]. Three different polymorphic forms and various clathrate structures have been found so far. The values of the chain axes of 5.1 and 7.7–7.9 Å found by the analysis of the X-ray fiber diffraction patterns of the various crystalline forms of sPMMS, have suggested that, in the different crystalline forms, the polymer chains assume *trans*-planar or two-fold helical conformations [28].

Therefore, the polymorphic behavior of sPMMS shows some analogies with the behaviors of sPS and sPPMS. The various polymorphic forms are, indeed, characterized by chains in *trans*-planar and two-fold helical conformations. Moreover, as in the case of sPS and sPPMS, sPMMS forms clathrate structures characterized by polymer chains in two-fold helical conformation, which are packed in a crystalline lattice containing cavities occupied by guest molecules. In

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addition, disordered mesomorphic modifications with chains in *trans*-planar conformation have been found for sPMMS [28] as well as for sPS [29,30] and sPPMS [24].

However, noticeable differences between sPMMS, sPS and sPPMS have been revealed [28]. By crystallization from the melt or from the amorphous glassy state, polymorphic forms with chains in *trans*-planar conformation are obtained for sPS (α and β forms) [9,12–14,22], whereas a crystalline form with chains in helical conformation is obtained for sPMMS (form I) [28]. Moreover, while in the case of sPS and sPPMS the mesomorphic *trans*-planar forms transform by annealing into stable crystalline forms with chains in *trans* planar conformation [24,29,30], in the case of sPMMS the *trans*-planar mesomorphic form III transforms into the stable helical form I [28]. A stable crystalline form of sPMMS with chains in *trans*-planar conformation has not been found so far, and only a disordered mesomorphic form having chains in *trans*-planar conformation has been obtained by stretching amorphous samples [28]. These data indicate that crystalline modifications of sPMMS having chains in *trans*-planar conformation are less stable than the polymorphic forms having chains in helical conformation.

It is worth noting that in the case of sPS and sPPMS an opposite behavior has been observed, i.e. the *trans*-planar crystalline forms are more stable than the helical forms [9,22–24]. Therefore crystalline modifications having chains in *trans*-planar conformation are more stable in sPS and sPPMS than in sPMMS. This different behavior may be due either to the intrinsically less stable *trans*-planar conformation of the sPMMS chain, with respect to the two-fold helical confirmation, or simply to the difficulties of packing of *trans*-planar chains of sPMMS in a crystalline lattice. In the first hypothesis, the trans-planar conformation of the sPMMS chain should be less stable that the trans planar conformation of the sPS chain.

Conformational energy analysis of the isolated sPS chain, reported in the literature [31], has shown that the two possible conformations assumed by the sPS chain in the crystalline state, *trans*-planar and two-fold $(\mathrm{TTGG})_n$ helical, have a similar energy. In this paper conformational energy calculations on the isolated chain of sPMMS under the constraint of a crystalline field have been performed in order to analyze the relative stability of the *trans*-planar and helical conformations of sPMMS and give new insight into the reasons of the metastability of the polymorphic forms of sPMMS with chains in *trans*-planar conformation.

2. Method of calculation

The conformational energy has been calculated with the method described in Ref. [31]. The energy has been calculated as the sum of the terms:

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

where E_{t} are the energy contributions associated with torsions angles (θ) around single bonds, assumed to be the kind:

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

with the barrier height K_{t} and the integer 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:

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

with K_{b} 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. In order to avoid negative contribution [31], E_{nb} are calculated as:

$$E_{\mathrm{nb}} = (Ar^{-12} - Br^{-6}) - (Ar_0^{-12} - Br_0^{-6})$$

with $E_{\mathrm{nb}} = 0$ for $r \geq r_0$, where r_0 is the interatomic distance corresponding to the minimum of E_{nb} and A and B are the repulsive and attractive constants, respectively.

The calculations of the conformational energy have been performed on the portion of the isolated chain of sPMMS shown in Fig. 1, under the constraint of a crystalline field, that is assuming a regular succession of the backbone torsion angles, as imposed by the equivalence principle [32]. The nonbonded energy has been evaluated calculating the interactions between the atoms of the first two monomeric units of the chain of Fig. 1 (two monomeric units related by the twofold axis perpendicular to the chain axis in the $\mathbf{s}(M/N)2$ symmetry, correspond to the conformational repeating unit) and the interactions between these atoms and the remaining atoms, up to distances corresponding to twice the van der Waals distance for each pair of atoms. All the reported energies are referred to one monomeric unit and correspond to half of the energy calculated with this procedure. The potential energy constants are those reported by Flory et al. [33]. The intrinsic torsional potential of single bonds adjacent to benzene rings reported by Hopfinger [34], has been used. The energy parameters are reported in Table 1.

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

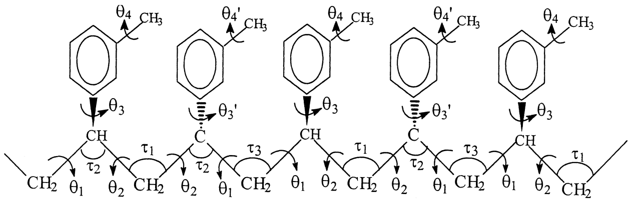

Fig. 1. Portion of the chain of sPMMS used in the energy calculations. The sequences of torsion angles and bond angles in the $\mathbf{s}(M/N)2$ line repetition group are indicated. The structural unit used as reference unit in the energy calculation corresponds to two monomeric units.

Table 1
Parameters of the potential functions used in the energy calculations

Torsion angle	K_t (kJ/mol)	n
$C-C_{sp3}-C_{sp3}-C$	11.7	3
$C_{sp3}-C_{sp3}-C_{sp2}-C_{sp2}$	2.43	6
Bond angle	K_b (kJ mol^{-1} deg^{-2})	τ_0 (°)
$C_{sp3}-C_{sp3}-C$	0.184	109.47
$C-C_{sp3}-H$	0.121	109.47
$H-C-H$	0.100	109.47
Non-bonded interacting pair	$A \times 10^{-3}$ (kJ mol^{-1} Å^{12})	B (kJ mol^{-1} Å^{6})
$C_{sp3}-C_{sp3}$	1666.4	1532
$C_{sp3}-C_{sp2}$	2595.9	1867
$C_{sp3}-H$	238.7	536
$C_{sp3}-CH_3$	4016.8	2691
$C_{sp2}-C_{sp2}$	4065.6	2311
$C_{sp2}-H$	393.6	666
$C_{sp2}-CH_3$	6274.1	3305
$H-H$	30.6	197
$H-CH_3$	544.3	965
CH_3-CH_3	9682.2	4727

Table 2
Bond lengths and bond angles used in the calculation of the conformational energy maps

Bond lengths (Å)	
$C_{sp3}-C_{sp3}$	1.53
$C_{sp3}-C_{sp2}$	1.51
$C_{sp2}-C_{sp2}$	1.39
$C_{sp3}-H$	1.10
$C_{sp2}-H$	1.08
Bond angles (°)[a]	
$C''-C'-C''$	111.0
$C'-C''-C'$	113.0
$C'-C''-H$	108.9
$C''-C'-H$	107.9
$C''-C'-C_{sp2}$	111.0
$C_{sp2}-C'-H$	107.9
$H-C''-H$	108.0
$C'-C_{sp2}-C_{sp2}$	120.0

[a] C'' indicates a methylene carbon atom, C' indicates a methine carbon atom.

3. Results and discussion

3.1. Conformational energy maps

The energy map has been calculated by application of the equivalence principle [32] to successive constitutional units by assuming a line repetition group **s**(M/N)2 for the polymer chain. As a consequence, the sequence of torsion angles in the main chain …$\theta_1\theta_1|\theta_2\theta_2$… (the vertical bar indicates the tertiary carbon atom) has been assumed (Fig. 1). The maps have been calculated for fixed values of bond lengths and for bond angles $\tau_1 = \tau_3 = 113°$, and $\tau_2 = 111°$. The values of the fixed parameters used in the calculated map are shown in Table 2. Local C_{2v} and C_{3v} symmetries have been assumed on the CH_2 and CH groups, respectively. The torsion angles θ_3 and θ_3', which define the position of the benzene rings, have been fixed to values which put the planes of the phenyl rings in the planes bisecting the angles τ_2

Energy calculations have been performed for each of the four possible relative *meta*-positions of the methyl groups bounded to the two benzene rings of two successive monomeric units (Fig. 2). As shown in Fig. 2, the four possible isomers have been identified with the symbols 5–5′, 3–5′, 3–3′ and 5–3′.

The map of the conformational energy of sPMMS as a function of θ_1 and θ_2 is shown in Fig. 3, in the case of the 5–5′ isomer. The map present there minima; the absolute minimum corresponds to the extended *trans*-planar conformation, whereas the other two equivalent minima at $\theta_1 = T$ and $\theta_2 = G^+$ and $\theta_1 = G^-$ and $\theta_2 = T$, correspond to the enantiomorphous two-fold helical conformations $(TTGG)_n$ and $(G^-G^-TT)_n$. The maps of the other three isomer chains 3–3′, 3–5′ and 5–3′ are very similar and only slight differences in the energy differences between the minima is observed. The values of the energy of the absolute minimum, corresponding to the *trans*-planar conformation, are the same in the four maps and have been assumed as zero. The general shape of these maps is very similar to that found for the energy maps of sPS [31], and of other syndiotactic polyolefins [35].

3.2. Minimizations

The conformational energy has been minimized considering variable parameters all the bond and torsion angles. The experimental values of the chain axes found for the various polymorphic forms of sPMMS are 7.9 and 5.1 Å [28]. These values can be geometrically obtained for **s**(2/1)2

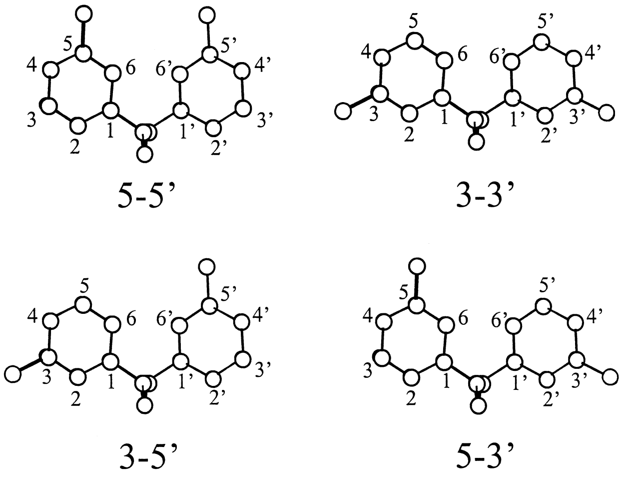

Fig. 2. Projections along the chain axis of sPMMS chains in *trans*-planar conformation, and definition of four isomeric chains. The four isomeric chains 5–5′, 3–5′, 3–3′ and 5–3′ correspond to the four different relative positions of the two methyl groups in the two *meta*-positions of the benzene rings of two successive monomeric units.

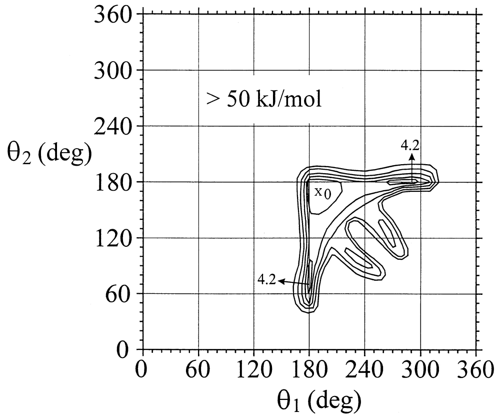

Fig. 3. Map of the conformational energy of the sPMMS chain (5–5′ isomer) as a function of θ_1 and θ_2 in the **s**(M/N)2 line repetition group for $\tau_1 = \tau_3 = 113°$ and $\tau_2 = 111°$. The isoenergetic curves are reported at intervals of 5 kJ/(mol of monomeric unit) with respect to the absolute minimum of the map assumed as zero. The maps of the other three isomeric chains 3–5′, 3–3′ and 5–3′ are very similar to that shown here for the 5–5′ isomer.

and **t**c or **t**cm line repetition symmetries, respectively. Therefore, we have performed minimizations of the conformational energy under the constraint of the **s**(M/N)2 symmetry, choosing as starting points the minimum energy conformations obtained in the map of Fig. 3. Minimizations of the energy have been performed for all the four isomeric chains 3–3′, 3–5′, 5–3′, and 5–5′ of sPMMS.

The values of the internal parameters of the chain of sPMMS in the minimum conformational energy, of the corresponding values of the chain axis and of the energy, are reported in Table 3. The energy values are referred to the absolute minimum of the maps assumed as zero. The minimization performed under the constraint of the **s**(M/N)2 symmetry, starting from the absolute minimum of the map of Fig. 3, corresponding to the *trans*-planar conformation, gives the same result as a minimization (not reported in the Table 3) performed under the constraint of the **t**c line repetition symmetry, which corresponds to assumption of a sequence of backbone torsion angles $\ldots\theta_1\theta_2| - \theta_1 - \theta_2\ldots$ (the vertical bar indicates the tertiary carbon atom). It is apparent that in all cases the obtained minimum corresponding to the *trans*-planar conformation is characterized by values of the backbone torsion angles $\theta_2 = -\theta_1$, and by a sequence of torsion angles $\ldots\theta_1\theta_1| - \theta_1 - \theta_1\ldots$, corresponding to the **t**cm line repetition symmetry. During the minimizations, the **s**(M/N)2 (with $M/N = 1$) and the **t**c symmetries degenerate in the **t**cm line repetition symmetry. It is also apparent from the values of θ_3 that in all conformations the benzene rings lie in planes bisecting the bond angle τ_2.

The results of Table 3 clearly indicate that the *trans*-planar and the **s**(2/1)2 helical (TTGG)$_n$ conformation assumed by sPMMS chains in the crystalline lattice have similar energies, whichever the relative positions of the methyl groups. The *trans*-planar conformation is slightly more stable than the helical one. The values of chain axes calculated from the minimized conformations are in good agreement with the experimental values of 5.1 and 7.9 Å. For both *trans*-planar and helical conformations, different positioning of the methyl groups gives similar values of the energy, indicating that, at least in the isolated chain, the methyl group does not assume a preferential position between the two possible *meta*-positions. Projections of the *trans*-planar conformation with **t**cm symmetry and the helical conformation with **s**(2/1)2 symmetry are shown in Fig. 4.

Experimental data on the polymorphic behavior of sPMMS have indicated that the more stable crystalline forms is the form I, characterized by chains in **s**(2/1)2 helical conformation [28]. Only a metastable disordered modification (form III) with chains in *trans*-planar conformation has been found [28]. This indicates that, even though the *trans*-planar conformation is, in the isolated chain of sPMMS, slightly more stable than the helical conformation, the packing of the helical chains is probably more efficient than that of the *trans*-planar chains.

It is worth noting that in the case of sPS and sPPMS a different behavior has been observed. In fact, as for sPMMS, the *trans*-planar conformation is slightly more stable than

Table 3
Values of the internal coordinates, chain axes and energies obtained in the minimization of the conformational energy of the sPMMS chain for the four isomers 5–5′, 5–3′, 3–5′ and 3–3′ (Fig. 2)

	Chain 5–5′		Chain 5–3′		Chain 3–5′		Chain 3–3′	
	tcm TTTT	s(2/1)2 T_2G_2	tcm TTTT	s(2/1)2 T_2G_2	tcm TTTT	s(2/1)2 T_2G_2	tcm TTTT	s(2/1)2 T_2G_2
θ_1 (deg)	−176.0	180.0	−176.0	178.7	−176.0	179.0	−176.0	177.8
θ_2 (deg)	176.0	73.0	176.0	64.0	176.0	65.8	176.0	60.2
θ_3 (deg)	62.9	64.3	62.9	63.3	−117.1	−114.8	−117.1	−115.9
θ_4 (deg)	90.0	89.9	90.0	89.7	90.0	89.5	90.0	90.3
τ_1 (deg)	114.1	115.2	114.1	115.7	114.1	115.6	114.1	115.9
τ_2 (deg)	109.4	111.2	109.4	111.6	109.4	111.6	109.4	111.7
τ_3 (deg)	114.1	115.3	114.1	116.3	114.1	116.3	114.1	116.3
c (Å)	5.0	8.2	5.0	7.7	5.0	7.8	5.0	7.4
E (kJ/mol)	−1.6	1.5	−1.6	2.0	−1.6	1.9	−1.6	2.2

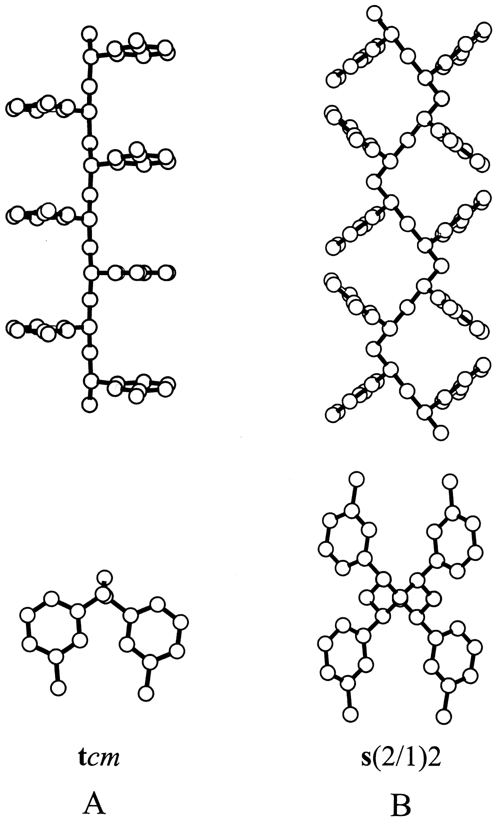

Fig. 4. Side views and projections along the chain axes of the *trans*-planar conformation with **t***cm* symmetry (A) and the two-fold helical conformation with **s**(2/1)2 symmetry (B) assumed by the chain of sPMMS in the crystalline lattice. Only the methyl groups in the 5–5′ relative position are shown.

the helical one, but the corresponding polymorphic crystalline modifications with chains in *trans*-planar conformation are the most stable forms. Although the presence of methyl groups in *meta*-position of the phenyl rings does not alter the relative stability of the conformations of the isolated chains of sPMMS, it probably produces difficulties in the packing of the *trans*-planar chains in a regular lattice, preventing the regular crystallization of a *trans*-planar crystalline form of sPMMS.

4. Conclusions

Conformational energy calculations have indicated that sPMMS chains assume in the crystalline phase two nearly isoenergetic conformations. The first one corresponds to the fully extended *trans*-planar conformation with **t***cm* symmetry, the second to the two-fold helical conformation, characterized by a sequence of torsion angles $(TTGG)_n$ and a **s**(2/1)2 symmetry. This is in agreement with the polymorphism observed for sPMMS [28]. The *trans*-planar conformation seems slightly more stable than the helical conformation. The values of the internal parameters and the energy of the two conformations are not influenced by the relative positioning of the methyl groups between the two possible *meta*-positions. The same conformations have been found for sPS and sPPMS. The values of the internal parameters found for the conformations of minimum energy are very similar to those found for sPS [31] and sPPMS [25,26,27].

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