A New Clathrate Class of Syndiotactic Poly(*p*-methylstyrene) with a Different Chain Conformation

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ABSTRACT: A new crystalline clathrate class of syndiotactic poly(*p*-methylstyrene) has been found through thermal and WAXS analyses. In these clathrate forms, the polymer chains assume a $T_6G_2T_2G_2$ conformation with a repetition period of 11.7 ± 0.1 Å and *t*2 symmetry. The new conformation, supported by molecular mechanics calculations, presents a cavity, favorable to the formation of clathrate structure, only on one side of the polymer chain. This cavity is bigger than those presented by this polymer with a helical **s**(2/1)2 chain conformation found for all the other clathrates. After annealing, the clathrates of this new class are transformed in form II. For this new class of clathrates the term γ is proposed.

Introduction

Homogeneous catalytic systems, based on titanium or zirconium compounds and methylalumoxane, have allowed producing highly syndiotactic polystyrene and substituted polystyrenes.[1−6] Some of these polymers, i.e., syndiotactic polystyrene (s-PS), syndiotactic poly(*p*-methylstyrene) (s-PPMS), and syndiotactic poly(*m*-methylstyrene) (s-PMMS), are able to cocrystallize with low molecular weight substances to form polymeric clathrates.[7−23] For this class of molecular compounds some promising applications have been suggested in the field of chemical separations, in particular for water or air purification from volatile organic compounds or as the sensing film of resonant sensors.[24]

All the described clathrate forms of these polymers are characterized by a **s**(2/1)2 chain conformation (corresponding to a ...$TTG^+G^+TTG^+G^+$... or ...$TTG^-G^-TTG^-G^-$... sequence of torsion angles for the two isoenergetic enantiomorphous conformations) with a repetition period of 7.7−7.8 Å.[10−14,17−23] The same conformation was found also in the case of some pure forms (γ for s-PS,[7,9] forms I and II for s-PPMS,[25] and form 1 for s-PMMS[21]). Moreover, in the case of s-PPMS, this conformation was assumed also for clathrate forms prepared in unoriented samples only whose structure has not been solved yet.[16]

These three polymers present also pure (crystalline or mesomorphic) forms in which the chain assumes a trans-planar conformation with a repetition period of nearly 5.1 Å (i.e., α and β forms of s-PS;[9] forms III, IV, and V of s-PPMS[25] and a mesomorphic form of s-PMMS[21]).

All the known clathrate structures of s-PS, s-PPMS, and s-PMMS are grouped in two classes, α and β, according to the kind of cavity created between the chains.[20] A clathrate belongs to the α class when its cavities are centrosymmetric and are delimited by eight benzene rings belonging to two enantiomorphous adjacent helical chains. It belongs to the β class when its cavities are arranged around 2-fold screw axes of the lattice and delimited by four benzene rings belonging to one polymer chain and two benzene rings belonging to the adjacent isomorphous one.

The s-PS solved clathrates belong to α class, and they crystallize according to $P2_1/a$ symmetry;[10−14] on the contrary, the s-PMMS solved clathrates belong to β class and crystallize according to *Pcca* symmetry.[22,23] The s-PPMS clathrates have a more complex behavior[26] since their belonging class depends on the shape of the guest: ortho-substituted cyclic molecules as *o*-dichlorobenzene (*o*-DCB) promote α class crystallization according to $P2_1/a$ symmetry,[18] while cyclic molecules like benzene or tetrahydrofuran (THF) promote β class crystallization.[17,19] Moreover, for the s-PPMS clathrates, it has been found that the clathrates of β class can crystallize in two kinds of crystalline lattice: the THF clathrate crystallizes according to $P2_1/a$ symmetry[17] while the benzene clathrate form crystallizes according to $C222_1$ symmetry.[19]

In this paper, for the first time, a new class of s-PPMS clathrates with a different chain conformation is presented.

Experimental Section

s-PPMS was synthesized as described in ref 2. The syndiotacticity of the insoluble fraction in 2-butanone was evaluated by ^{13}C NMR analysis; the amount of the [*rrrr*] pentads was higher than 95%.

Unoriented clathrate samples were prepared by casting procedures in the temperature range 25−45 °C.

Oriented samples were obtained by exposing oriented fibers of mesomorphic form IV to solvent vapors in the temperature range 25−45 °C, keeping fixed the ends of the specimens. Fibers of mesomorphic form IV have been prepared by drawing amorphous specimens at a temperature in the range of 115−120 °C while amorphous samples have been obtained from melted samples quenched in ice−water.

Wide-angle X-ray diffraction patterns of unoriented samples were recorded by using an automatic Philips powder diffractometer (Ni-filtered Cu Kα radiation) equipped with a high-temperature chamber. The X-ray fiber diffraction patterns of oriented samples were obtained on a BAS-MS imaging plate (FUJIFILM) with a cylindrical camera (radius 57.3 mm, Ni-filtered Cu Kα radiation monochromatized with a graphite crystal) and processed with a digital scanner (FUJY-BAS 1800).

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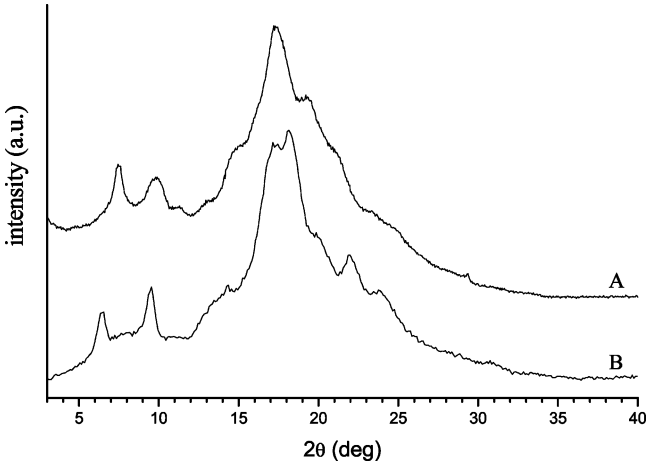

Figure 1. X-ray diffraction patterns of unoriented samples of the two different forms A and B obtained by casting procedures with cyclohexanone.

The annealing procedures for 30 min were carried out directly in the powder diffractometer, with a temperature control of ±0.5 °C, while those for 24 h were done in an oven with a temperature control of ±1.0 °C.

The differential scanning calorimetry (DSC) measurements were carried out with a Mettler DSC822 apparatus at a heating rate of 10 °C/min, and the thermogravimetric analyses (TGA) were carried out with a Mettler TG50 apparatus at a heating rate of 10 °C/min.

The X-ray diffraction pattern shown in Figure 5 was calculated as a weighted summation of the profiles read along the different layer lines of the X-ray diffraction pattern reported in Figure 3, after the subtraction of the amorphous contribution (obtained on the basis of intermediate profiles drawn between the layers). For each profile, the observed intensities, sampled every 0.25° of 2θ, were divided by the Lorentz and polarization factors for a rotating crystal. Then, the contributions of the different layer lines for the same 2θ were summed. In this sum, the contributions of the first, second, and third layer lines were multiplied by a factor of 2. Finally, the results of the summation obtained in this way were multiplied for the Lorentz and polarization factors for an unoriented sample. To allow a better visual comparison between the calculated and experimental unoriented X-ray diffraction pattern, a 60% contribution of amorphous phase was added to the calculated pattern. The shape of the amorphous halo is that already reported, for the same polymer, in ref 17.

Results and Discussion

Experimental Evidences of a New Conformation. During the preparation of s-PPMS clathrates containing cyclohexanone by casting procedures, samples showing different X-ray diffraction patterns have been obtained (A and B of Figure 1). A diffraction pattern of an unoriented samples corresponding to type A of Figure 1 has been already obtained in the past,[15] and successively, it was supposed to belong to β class clathrates.[16] The diffraction pattern B, instead, was new and not referable to any known pure form.[15] For this reason this fact was indicative of a new polymorphism phenomenon for this polymer.

To better understand this polymorphic behavior, attempts were carried out to obtain oriented samples of the crystalline forms A and B.

After several trials, exposing oriented specimens of the mesomorphic form IV to cyclohexanone vapors at different temperatures, only one type of fiber has been obtained. Its diffraction pattern is showed in Figure 2.

Figure 2. X-ray fiber diffraction pattern of the crystalline form of s-PPMS obtained by exposing an oriented sample of mesomorphic form IV to cyclohexanone vapors. The arrow indicates the presence of some residual mesomorphic form. Fiber axis direction is vertical.

Table 1. Relative Intensities and Diffraction Angles (2θ) Observed in the X-ray Diffraction Patterns of the Fiber of the Crystalline Form Obtained by Exposing Oriented Sample of Form IV to Cyclohexanone Vapors (See Figure 2) and of the Unoriented Crystalline Form A Obtained by Casting Procedure (See Figure 1)

X-ray fiber reflections						X-ray powder reflections	
equatorial layer line		first layer line		second layer line			
int	2θ (deg)	int	2θ (deg)	int	2θ (deg)	int	2θ (deg)
s	7.5					ms	7.5
		vw	8.0				
		w	9.4			ms	9.8
ms	10.1						
		mw	11.3			w	11.3
		w	13.2			w	13.1
m	14.5						
		m	15.1			ms	15.0
mw	16.3						
ms	17.4	ms	17.4				
				s	18.0	vs	17.3
		m	19.5			m	19.2

The position and the intensities of the reflections for this diffraction pattern are in good agreement with those observed in the powder diffraction pattern of Figure 1A. A comparison, for 2θ < 20°, of the observed reflections in the X-ray fiber diffraction pattern of Figure 2 and in the powder diffraction pattern of Figure 1A is reported in Table 1. Therefore, it can be stated that those two samples present the same crystalline form.

The fiber diffraction pattern of Figure 2 clearly indicates that a new conformation for this polymer has been found. In fact, the repetition period that can be derived from that diffraction pattern is 11.8 Å, clearly different from that one evaluated for the trans-planar (c = 5.1 Å) and helical **s**(2/1)2 (c = 7.8 Å) conformations found in the pure and clathrate forms of this polymer studied so far.[25]

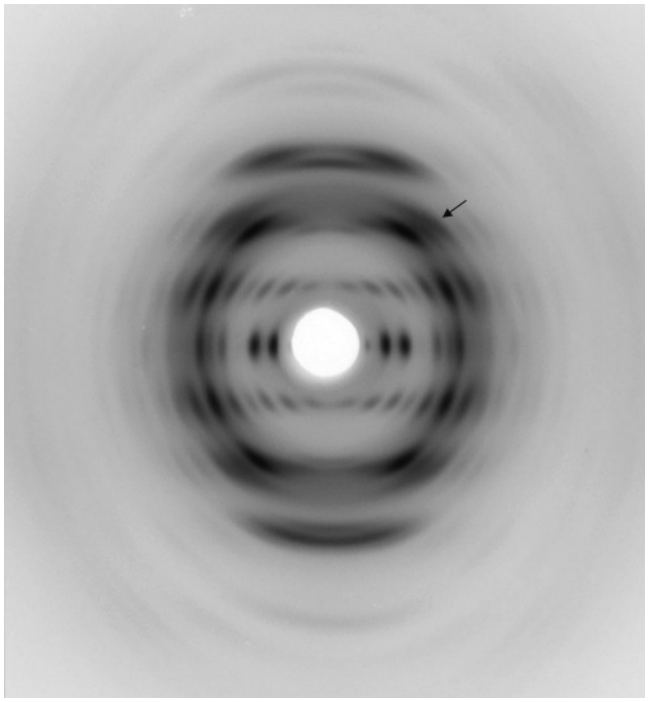

Figure 3. X-ray fiber diffraction pattern of the crystalline form of s-PPMS obtained by exposing an oriented sample of the mesomorphic form IV to cyclohexane vapors. The arrow indicates the presence of some residual mesomorphic form. Fiber axis direction is vertical.

A detailed discussion on this new conformation is reported in a subsequent paragraph.

Reasonably, the form B could be the cyclohexanone clathrate form belonging to the β class.

It is worth noting that, at the moment, the exact experimental conditions in which one or the other form can be obtained are still not clear.

To find out whether this new conformation could be obtained also with other solvents, several attempts were carried out by exposing specimens of the mesomorphic form to vapors of different solvents. Up to now, an X-ray diffraction pattern showing the same repeating period of the fiber previously described has been obtained with cyclohexane. The X-ray fiber diffraction pattern of this new sample is shown in Figure 3. A repetition period of 11.6 Å has been found.

Also in this case, unoriented samples have been prepared by casting procedures, at different temperatures, with cyclohexane. Only one type of diffraction pattern has been obtained. The X-ray diffraction pattern of an unoriented sample obtained in such a way is shown in Figure 4.

The position and the intensities of the reflections observed in the diffraction pattern of Figure 3 are in good agreement with those observed in the powder diffraction pattern of Figure 4. A comparison, for $2\theta < 20°$, of the observed reflections in the two diffraction patterns is reported in Table 2. Therefore, it can be stated that those two samples present the same crystalline form.

To confirm further on the hypothesis that unoriented and oriented samples correspond to the same crystalline structure, an appropriate summation (see experimental part) of the profiles taken on the different layer lines of the fiber diffraction pattern of the sample exposed to cyclohexane vapors has been performed. The resulting calculated unoriented diffraction pattern (shown in Figure 5) is to be compared with the experimental one (shown in Figure 4). The agreement between the experimental and calculated unoriented patterns is very good. The only discrepancy is on the intensity of the equatorial reflection at $2\theta \cong 7.5°$, which, in the calcu-

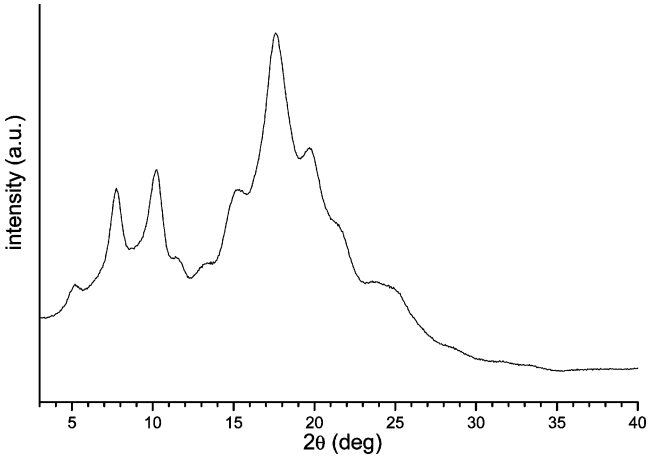

Figure 4. X-ray diffraction pattern of an unoriented sample obtained by casting procedure with cyclohexane.

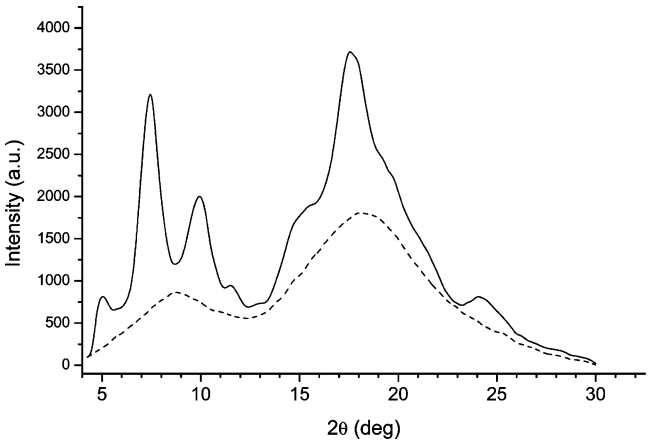

Figure 5. Calculated X-ray unoriented diffraction pattern obtained by the layer line profiles of the fiber exposed to cyclohexane vapors, shown in Figure 3, after the summation of an amorphous contribution indicated by the dashed line (see experimental part for details).

Table 2. Relative Intensities and Diffraction Angles (2θ) Observed in the X-ray Diffraction Patterns of the Fiber of the Crystalline Form Obtained by Exposing Oriented Sample of Form IV to Cyclohexane Vapors (See Figure 3) and of the Unoriented Crystalline Form Obtained by Casting Procedure (See Figure 4)

X-ray fiber reflections						X-ray powder reflections	
equatorial layer line		first layer line		second layer line			
int	2θ (deg)	int	2θ (deg)	int	2θ (deg)	int	2θ (deg)
w	5.3					w	5.2
s	7.6					s	7.7
		w	8.2				
		mw	9.6			s	10.2
ms	10.1						
		mw	11.4			w	11.5
		w	13.3			w	13.3
m	14.6						
		m	15.2			ms	15.3
w	15.9						
ms	17.2	ms	17.3				
				s	17.7	vs	17.6
		m	19.6			ms	19.7

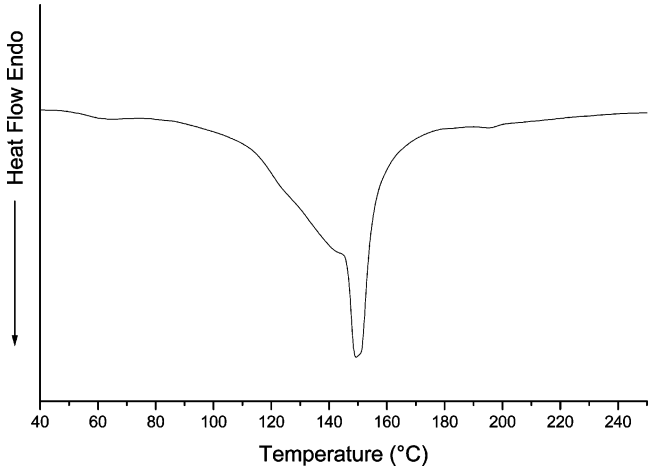

Figure 6. DSC heating scan of the sample obtained by casting procedure with cyclohexane whose X-ray diffraction pattern is shown in Figure 4.

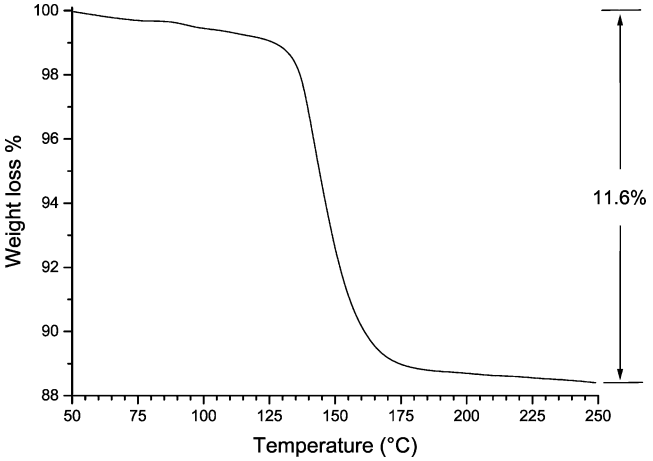

Figure 7. TGA scan of the sample obtained by casting procedures with cyclohexane whose X-ray diffraction pattern is shown in Figure 4. The weight loss is indicated.

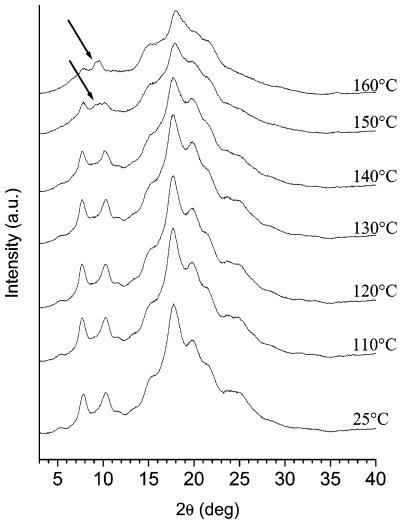

Figure 8. X-ray diffraction patterns of an unoriented sample obtained by casting procedure with cyclohexane annealed for 30 min at the indicated temperatures. The arrows indicate the peak at $2\theta = 9.5°$ indicative of form II.

lated diffraction pattern, is more intense than in the experimental one. This discrepancy may be attributed to a different degree of occupancy of the cavities of the clathrate form in the two samples (oriented and unoriented), which is quite realistic considering the two very different experimental procedures used to obtain them (exposition to solvent vapors of a mesomorphic form and casting, respectively). A similar behavior has been already pointed out in the literature for clathrate structures of syndiotactic polystyrenes in which the fact that some cavities of the clathrate phases are not occupied by guest molecules is highlighted by variation of the relative intensity of some reflections (in particular at low angles).[13,14,22,27]

Experimental Evidences of a New Clathrate Class. The diffraction patterns of the oriented (Figures 2 and 3) and the unoriented (Figures 1A and 4) samples at issue are very similar, apart form the solvent used in their preparation. This fact could be consistent both with a new pure crystalline form and with two clathrate forms containing very similar guest molecules.

To distinguish between these two hypotheses, X-ray, DSC, and TGA measurements have been carried out on freshly prepared and annealed unoriented samples.

In the following, only the data obtained for the samples prepared with cyclohexane are presented and discussed since analogous conclusions have been obtained also for the samples prepared with cyclohexanone.

Figures 6 and 7 show the DSC and TGA scan for a freshly prepared (touch dry) sample obtained by casting with cyclohexane, whose diffraction pattern is shown in Figure 4.

In the DSC scan it is evident a sharp endothermic peak at 150 °C. Correspondingly, at the same temperature, in the TGA scan it is possible to observe a clear weight loss due to the removal of the solvent.

These data are in good agreement with the hypothesis that the new form obtained by casting from cyclohexane solution is a clathrate structure showing a melting temperature of 150 °C.

This hypothesis is confirmed by the analysis of the X-ray diffraction patterns, collected at room temperature, on samples annealed for half an hour (Figure 8) and 24 h (Figure 9) in a temperature range from 25 to 160 °C. The samples used were parts of the same casting preparation whose DSC and TGA scans are shown in Figures 6 and 7, respectively.

With reference to Figure 8, it is worth noting that the new crystalline form is stable until 140 °C, while at 150 °C the partial transformation in form II can be highlighted by the peak at $2\theta = 9.5°$. This transformation is almost complete for the sample annealed at 160 °C that keeps a small amount of the new form yet.

Concerning the samples annealed for 24 h (see Figure 9), the new crystalline structure is completely stable up to 110 °C. At 120 °C it is still present, although with a lower degree of crystallinity. At 130 °C, instead, the form II can be already revealed by the peak at $2\theta = 9.5°$ even if the new crystalline phase is still present. At this temperature, the crystallinity reaches the lowest value. Finally, at 140 °C, the transformation into the form II is complete.

This different behavior regarding different annealing conditions can be easily related to the fact that the examined samples are clathrates. As a matter of fact, the decrease of the degree of crystallinity observed in the X-ray diffraction patterns with increasing annealing temperature and with increasing time for a given annealing temperature (cf. the diffraction patterns in

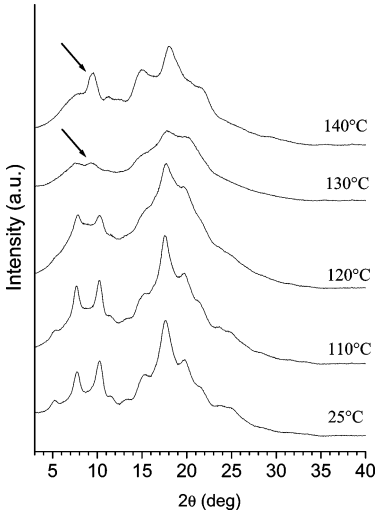

Figure 9. X-ray diffraction patterns of unoriented samples obtained by casting procedure with cyclohexane annealed for 24 h at the indicated temperatures. The arrows indicate the peak at $2\theta = 9.5°$ indicative of form II.

the range 120−130 °C of Figures 8 and 9), while the positions of the reflections remain unchanged (excluding the obvious case in which form II is obtained), can be explained only assuming that this is a clathrate form, in which the solvent removal from the crystal (and its subsequent destruction, as found for the other clathrate forms of s-PPMS)[20] is favored by higher annealing temperatures and longer annealing times.

On the other hand, these data rule out completely the hypothesis of a simple case of swelling of the crystalline phase. In fact, in the case of a swelled structure, annealing it at different temperatures and for an increasing time would leave the degree of crystallinity unchanged (or even improved) and shift the positions of the reflections due to a decrease of the unit cell constants.

To distinguish these new clathrate forms from those previously grouped into α and β classes, the term γ class is suggested.

The possibility of obtaining clathrates belonging to this class also for s-PS and s-PMMS is under examination.

Chain Conformation Analysis. The values of the chain repeat observed in the fiber diffraction pattern of the samples reported in Figures 2 and 3 (i.e., 11.7 ± 0.1 Å) suggest that the conformation of the backbone is analogous to that one found for the other two syndiotactic polymers (whose structure has been determined so far), showing a similar chain axis. In detail, the $T_6G_2T_2G_2$ chain conformation proposed for the form IV of syndiotactic poly(propylene) (c = 11.6 Å)[28,29] and for the form I of syndiotactic 1,2-poly(4-methyl-1,3-pentadiene) (c = 11.25 Å),[30,31] both characterized by a $t2$ symmetry, has been hypothesized for our polymer, too.

To describe into more detail this conformation, energy calculations were carried out by using commercially available software (Cerius^2 version 4.2 by Accelrys Inc.). The force field used was the Compass Force Field.[32] $t2$ symmetry was imposed, considering a structural unit made of three monomeric units (see Figure 10).

For comparison, the same type of calculation has been performed also imposing the helical **s**(2/1)2 and transplanar (*tcm*) symmetries, found for the crystalline forms described in the literature.[25]

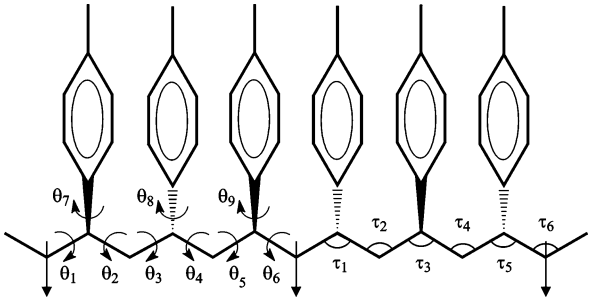

Figure 10. Schematic representation of two structural units of the chain of s-PPMS considered in the conformational energy calculations (assuming a $t2$ symmetry). The definition of the most significant independent internal parameters of the structural unit (with reference to Table 4) is shown. The position of the binary axes is also indicated.

Table 3. Energy and Calculated (c_{calc}) and Experimental (c_{exp}) Repetition Period Found for All the Known Conformations of s-PPMS

conformation	energy (kcal/m.u.)[a]	c_{calc} (Å)	c_{exp} (Å)	ref
tcm	0.09	5.17	5.1	25
s(2/1)2	0.09	7.79	7.8	25
*t*2	0.00	12.01	11.7	
*t*2[b]	0.01[b]	11.70[b]	11.7	

[a] m.u. = monomeric unit. [b] These data have been obtained by imposing in the calculation the repetition period equal to the experimental one.

At first, energy minimization was performed without imposing any constraint on the repetition period. The results are presented in Table 3, in which the experimental values found for all the conformations of s-PPMS have been reported, too. The calculated repetition period is in very good agreement with the experimental one in the case of the **s**(2/1)2 and *tcm* symmetries while it is slightly longer for the $t2$ symmetry. For this last case, the calculation has been repeated, imposing the repetition period equal to the experimental one. The calculated energy for the resulting conformation is only 0.01 kcal/(monomeric unit) higher than the previous one. A schematic representation of the chain conformation for this last case is reported in Figure 11 while its most significant internal parameters are reported in Table 4.

It is worth noting that the backbone parameters found for $t2$ conformation of s-PPMS do not differ significantly from those reported by Chatani et al.[28] for the structure of form IV of syndiotactic poly(propylene).

The conformation proposed is characterized by an orientation of the benzene rings generating, on one side (see Figure 11), cavities in which properly shaped molecules can be nested, a fact that is itself particularly favorable to the formation of clathrate structures. Otherwise, the **s**(2/1)2 conformation, found for all the clathrate forms of this polymer whose structure has been determined so far, presents cavities on both sides.[17−20,23] As far as the shape of the cavities is concerned, a comparison between the two conformations is presented in Figure 12, in which are shown two side views relative to the $t2$ (a) and **s**(2/1)2 (b) conformations relative to the portion of the chain pointing out the shape of the cavities. As apparent, the dimension of the cavity, along the chain axis, that in the **s**(2/1)2 conformation is almost 7.8 Å, in the new one becomes almost 11.7 Å. At the same time, the dimension of the cavity in the direction perpendicular to the chain axis tends to decrease in respect to the helical conformation due

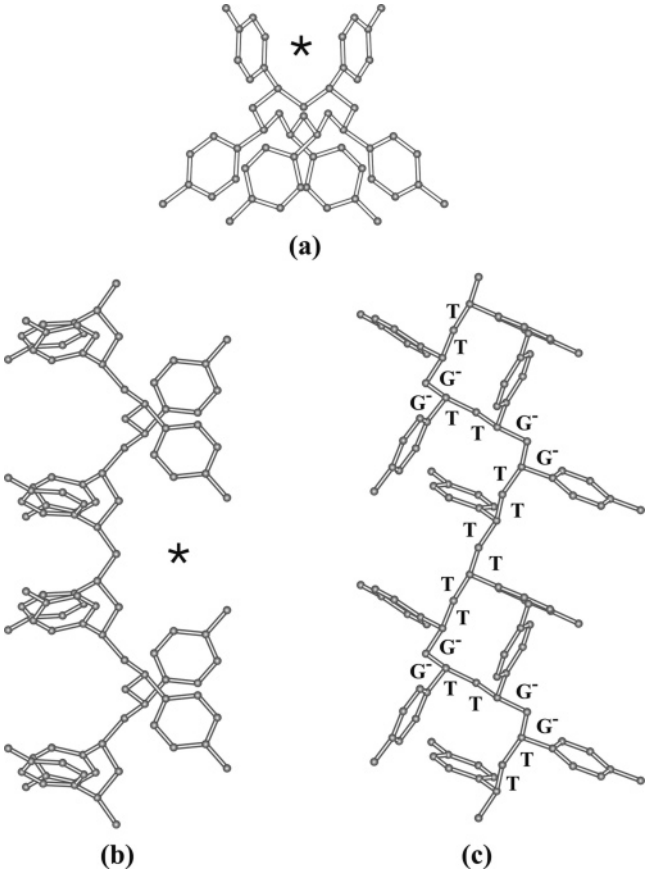

Figure 11. Projection along the chain axis (a) and two side views (b, c) of the model suggested for the chain conformation expected in the crystalline clathrate form of s-PPMS containing cyclohexanone or cyclohexane. In the (c) projection the conformations of the bonds of the backbone putting beside each bond the terms *trans* (T), *gauche plus* (G^+), or *gauche minus* (G^-) have been reported. To obtain the isoenergetycal enantiomorphous chains, G^- must be changed to G^+. The asterisks indicate the side of the chain favorable to the formation of the cavities of the clathrate structures.

Table 4. Torsion and Bond Angles (in deg) Found for the Minimum-Energy Conformation with *t*2 Symmetry of s-PPMS Imposing $c = 11.7$ Å[a]

torsions		bond angles	
θ_1	179.7	τ_1	110.9
θ_2	−58.3	τ_2	115.4
θ_3	−58.8	τ_3	113.6
θ_4	−179.5		
θ_5	177.1	τ_4	114.6
θ_6	176.9	τ_5	113.3
θ_7	117.9	τ_6	115.5
θ_8	−109.5		
θ_9	112.6		

[a] The nomenclature is referred to Figure 10.

to a slightly different orientation of the phenyl rings delimiting the cavity.

Evaluation of the Guest Content in the Crystalline Phase. To make an evaluation of the guest content in the crystalline phase, the TGA result obtained for the freshly prepared (touch dry) sample of Figure 7, whose diffraction pattern is reported in Figure 4, has been considered. In the hypothesis of a homogeneous distribution of the guest molecules between the amorphous and the crystalline phase of the specimen, the calculated molar ratio between guest molecule and repeating unit is about 1. This value is the same found

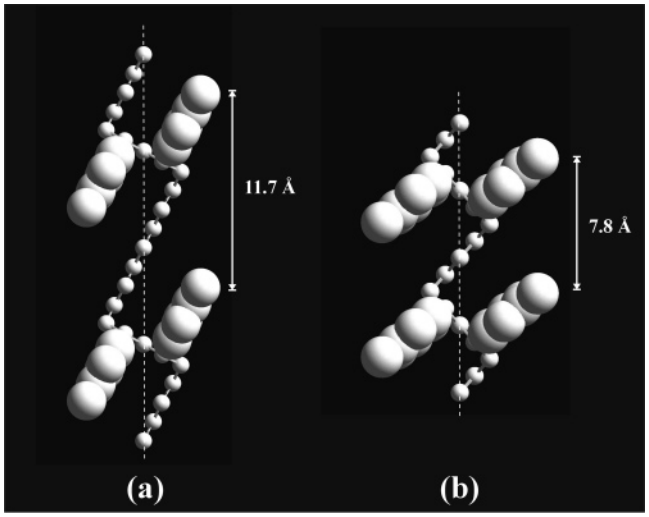

Figure 12. Side view of the model for the chain of s-PPMS in the *t*2 conformation (a) and in the **s**(2/1)2 one[25] (b). The phenyl rings delimiting the cavities in which guest molecules could be hosted are highlighted. For each conformation, the chain repetition is indicated. The dashed lines indicate the chain axis direction.

in the case of the α class of clathrate forms of this polymer,[18] differently from the case of the β class for which the ratio between guest molecules and repeating unit is 2.[17,19,20] However, since in this case the repeating unit is made of six monomeric units (while in the clathrates belonging to α and β class is made of four monomeric units), the content of guest molecules per monomeric unit is lower than in the case of α class.

The determination of the crystalline structure of these new clathrate forms is in progress.

Conclusions

A new clathrate class of s-PPMS containing cyclohexanone or cyclohexane characterized by chains having a repetition period of 11.7 ± 0.1 Å has been found. This repetition period is very similar to that found for the form IV of syndiotactic poly(propylene) and for the form I of syndiotactic 1,2-poly(4-methyl-1,3-pentadiene). Similarly to those polymers, a $T_6G_2T_2G_2$ chain conformation has been proposed and supported by molecular mechanics calculations.

These new clathrate forms annealed at temperature near their melting temperature give rise to form II. For this new class of clathrate forms the term γ class is proposed.

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References and Notes

(1) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2464−2465.
(2) Zambelli, A.; Longo, P.; Pellecchia, C.; Grassi, A. *Macromolecules* **1987**, *20*, 2035−2037.
(3) Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356−3360.
(4) Resconi, L.; Albizzati, E.; Giannini, U.; Giunchi, G.; Mazzocchi, R.; Italian Patent Application 22827 A, 1986.
(5) Grassi, A.; Longo, P.; Proto, A.; Zambelli, A. *Macromolecules* **1989**, *22*, 104−108.
(6) Pellecchia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 277−279.
(7) Immirzi, A.; de Candia, F.; Ianelli, P.; Zambelli, A.; Vittoria, V. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 761−764.

(8) Vittoria, V.; de Candia, F.; Iannelli, P.; Immirzi, A. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 765−769.
(9) Guerra, G.; Vitagliano, M. V.; De Rosa, C.; Petraccone, V.; Corradini, P. *Macromolecules* **1990**, *23*, 1539−1544.
(10) Chatani, Y.; Shimane, Y.; Inagaki, T.; Iijtsu, T.; Yukimori, T.; Shikuma, H. *Polymer* **1993**, *34*, 1620−1624.
(11) Chatani, Y.; Inagaki, T.; Shimane, Y.; Shikuma, H. *Polymer* **1993**, *34*, 4841−4845.
(12) De Rosa, C.; Rizzo, P.; Ruiz de Ballesteros, O.; Petraccone, V.; Guerra, G. *Polymer* **1999**, *40*, 2103-2110.
(13) Tarallo, O.; Petraccone, V. *Macromol. Chem. Phys.* **2004**, *205*, 1351−1360.
(14) Tarallo, O.; Petraccone, V. *Macromol. Chem. Phys.* **2005**, *206*, 672−679.
(15) Iuliano, M.; Guerra, G.; Petraccone, V.; Corradini, P.; Pellecchia, C. *New Polym. Mater.* **1992**, *3*, 133−144.
(16) Dell'Isola, A.; Floridi, G.; Rizzo, P.; Ruiz de Ballesteros, O.; Petraccone, V. *Macromol. Symp.* **1997**, *114*, 243−249.
(17) Petraccone, V.; La Camera, D.; Pirozzi, B.; Rizzo, P.; De Rosa, C. *Macromolecules* **1998**, *31*, 5830−5836.
(18) Petraccone, V.; La Camera, D.; Caporaso, L.; De Rosa, C. *Macromolecules* **2000**, *33*, 2610−2615.
(19) La Camera, D.; Petraccone, V.; Artimagnella, S.; Ruiz de Ballesteros, O. *Macromolecules* **2001**, *34*, 7762−7766.
(20) Petraccone, V.; Tarallo, O. *Macromol. Symp.* **2004**, *213*, 385−394.
(21) De Rosa, C.; Buono, A.; Caporaso, L.; Petraccone, V. *Macromolecules* **2001**, *34*, 7349−7354.
(22) Petraccone, V.; Tarallo, O.; Califano, V. *Macromolecules* **2003**, *36*, 685−691.
(23) Tarallo, O.; Buono, A.; Califano, V.; Petraccone, V. *Macromol. Symp.* **2003**, *203*, 123−130.
(24) (a) Guerra, G.; Milano, G.; Venditto, V.; Musto, P.; De Rosa, C.; Cavallo, L. *Chem. Mater.* **2000**, *12*, 363−368. (b) Mensitieri, G.; Venditto, V.; Guerra, G. *Sens. Actuators B* **2003**, *92*, 255.
(25) De Rosa, C.; Petraccone, V.; Guerra, G.; Manfredi, C. *Polymer* **1996**, *37*, 5247−5253.
(26) La Camera, D.; Petraccone, V.; Artimagnella, S.; Ruiz de Ballesteros, O. *Macromol. Symp.* **2001**, *166*, 157−164.
(27) De Rosa, C.; Guerra, G.; Petraccone, V.; Pirozzi, B. *Macromolecules* **1997**, *30*, 4147−4152.
(28) Chatani, Y.; Maruyama, H.; Asanuma, T.; Shiomura, T. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 1649−1652.
(29) Auriemma, F.; De Rosa, C.; Ruiz De Ballesteros, O.; Vinti, V.; Corradini, P. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 395−402.
(30) Meille, S. V.; Capelli, S.; Ricci, G. *Macromol. Rapid Commun.* **1995**, *16*, 891−897.
(31) Immirzi, A.; Tedesco, C.; Meille, S. V.; Famulari, A.; van Smaalen, S. *Macromolecules* **2003**, *36*, 3666−3672.
(32) Sun, H. *J. Phys. Chem. B* **1998**, *102*, 7338−7364.

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