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Polymorphism of Syndiotactic Poly(*m*-methylstyrene)

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ABSTRACT: The synthesis and a preliminary structural characterization of syndiotactic poly(*m*-methylstyrene) are reported. A complex polymorphic behavior has been revealed. Three different polymorphic forms and two clathrate structures, characterized by the inclusion of guest molecules in the crystalline lattice, have been found. The conditions for the obtaining of the various polymorphic forms, in unoriented and oriented fiber samples, are described. Form I, obtained by crystallization from the melt or from the amorphous phase, is characterized by chains in the s(2/1)2 helical conformation. The same helical conformation has been found in the clathrate structures containing molecules of *o*-dichlorobenzene or benzene. Form II can be obtained by crystallization from solutions of solvents which do not form clathrate structure or by removing the guest molecules from the clathrate forms. Form III, obtained in oriented fibers by stretching amorphous films, is a mesomorphic modification characterized by chains in the trans-planar conformation with a high degree of disorder in the lateral packing of the chains. Annealing treatments or solvent-induced crystallization of the oriented mesomorphic form allow the obtaining of oriented fibers in some of the polymorphic forms. The differences and analogies with the polymorphic behavior of syndiotactic poystyrene and poy(*p*-methylstyrene) are outlined.

Introduction

It is well-known that homogeneous catalytic systems, based on titanium or zirconium compounds and methylaluminoxane, are able to produce highly syndiotactic polystyrene (s-PS)[1,2] and substituted polystyrenes.[3−8]

The complex polymorphic behavior of s-PS has been described,[9−12] and the crystal structures of the various different modifications have been reported.[13−23]

Among substituted polystyrenes, syndiotactic poly(*p*-methylstyrene) (s-PPMS) has been extensively studied.[24−33] A complex polymorphic behavior has been revealed also for s-PPMS,[24−29] and the crystal structures of some polymorphic forms have been described.[30−33]

The crystalline forms of s-PS and s-PPMS are characterized by the same conformations of the chains, that is, trans-planar and s(2/1)2 helical conformations. Moreover, clathrate crystalline forms, which include guest molecules in the cavities of the crystalline lattice, have been found for both s-PS[9,10,12,17−20] and s-PPMS.[24,25,28,29,31,32] In the case of s-PS, 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.[10] The crystalline forms with chains in the 2-fold helical conformation crystallize in the presence of solvents, by casting or precipitation from polymer solutions or solvent diffusion in amorphous samples.[9,10] In this case clathrate structures are generally obtained.[9,10,12,17−20] Pure helical forms of s-PS (γ-form[10,12] and δ_e form[12,19]) are obtained by removing the guest molecules, by annealing or extraction procedures.[12]

Also, for s-PPMS the polymorphic forms with chains in the helical conformation (forms I, II and clathrate structures) are obtained in the presence of solvent.[24] Moreover, two crystalline forms with chains in the trans-planar conformation (forms III and V) are obtained by annealing at high temperature of amorphous samples.[24,25]

Finally, mesomorphic modifications with chains in the trans-planar conformation have been found for either s-PS[23] or s-PPMS.[33]

In this paper a preliminary structural characterization of syndiotactic poly(*m*-methylstyrene) (s-PMMS) is presented. Also, this polymer presents a complex polymorphic behavior; possible routes for obtaining the different pure polymorphic forms, even in oriented fiber samples, are presented. The obtaining of fibers and the corresponding X-ray diffraction patterns allow us to suggest models for the conformations of the chains in some of the polymorphic forms. The differences and analogies with the polymorphic behaviors of s-PS and s-PPMS are outlined.

Experimental Section

The s-PMMS sample was prepared in our laboratories using the homogeneous catalytic system composed of pentamethylcyclopentadienyltitanium trichloride (Cp*TiCl$_3$) and methylalumoxane (MAO) in toluene.

m-Methylstyrene (Aldrich) was purified by distillation under reduced pressure over CaH$_2$. MAO was prepared by reaction of Al(CH$_3$)$_3$ with FeSO$_4$·7H$_2$O in toluene.[34] Cp*TiCl$_3$ was prepared according to published procedure.[35] Toluene was refluxed 48 h over metallic sodium and distilled under a nitrogen atmosphere.

The polymerization run was carried out in a 250 mL glass flask provided with a magnetic stirrer and thermostated at 40 °C in an oil bath. The reactor was charged under nitrogen sequentially with toluene (96 mL), MAO (5×10^{-3} mol), and *m*-methylstyrene (4 mL). The polymerization was stopped after 12 h by injecting acidified methanol. The polymer was recovered by filtration, washed with fresh methanol, and dried in vacuo at 60 °C. The yield was 1.5 g.

The polymer fraction insoluble in 2-butanone was 95%. The syndiotacticity of the polymer was evaluated by ^{13}C NMR; the fraction of the fully syndiotactic pentads [*rrrr*] was higher than 95%. The intrinsic viscosity of the fraction insoluble in acetone, measured in tetrahydronaphthalene at 136 °C, was 1.36 dL/g.

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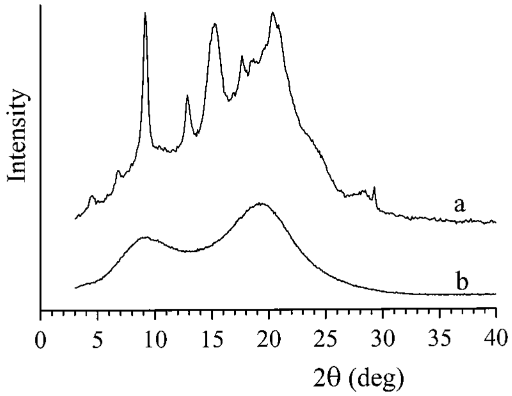

Figure 1. X-ray diffraction patterns of form I of s-PMMS, obtained by slow cooling of the melt (a), and of amorphous s-PMMS, obtained by quenching the melt to room temperature (b).

The ^{13}C NMR spectrum was recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz in the Fourier transform mode and at a temperature of 413 K. The sample was prepared by dissolving 30 mg of polymer in 0.5 mL of tetrachloro-1,2-dideuterioethane. Hexamethyldisiloxane (HMDS) was used as the internal chemical shift reference.

Crystallizations from solution were conducted by casting procedures at room temperature from 1 wt % solutions in various solvents. Melt-crystallized samples were prepared in a hot press by heating as-prepared samples at 240 °C and successive slow cooling to room temperature. Fast cooling from the melt, for instance by quenching in ice−water, gives amorphous s-PMMS samples.

Oriented fiber samples of s-PMMS were obtained by drawing amorphous films. Crystalline oriented fibers of s-PMMS in some polymorphic forms were obtained by performing the stretching at different temperatures, by annealing the stretched fibers at different temperatures, and by solvent diffusion-induced crystallization. The latter is generally performed by exposing stretched films, which are in a mesomorphic form, to the vapor of different solvents. Depending on the conditions used in these different routes, different polymorphic forms were obtained.

The drawing was conducted in a Minimat apparatus with a draw rate of 10 mm/min at temperatures in the range 80−120 °C.

Wide-angle X-ray diffraction patterns were obtained with nickel-filtered Cu Kα radiation. The diffraction patters of oriented samples were registered on a BAS-MS imaging plate (Fujifilm) using a cylindrical camera and processed with a digital imaging reader (FUJIBAS 1800). The patterns of unoriented samples were obtained with an automatic Philips powder diffractometer.

The melting and glass transition temperatures of s-PMMS samples were obtained with a differential scanning calorimeter (Perkin-Elmer DSC-7), performing scans in a flowing nitrogen atmosphere at a heating rate of 10 °C/min.

The thermogravimetric analyses were carried out with a Mettler TG50 thermobalance in a flowing nitrogen atmosphere at a heating rate of 10 °C/min.

Results and Discussion

Unoriented Samples. (a) Melt and Cold Crystallization. s-PMMS crystallizes from the melt when as-prepared samples are heated at temperatures higher than 240 °C and slowly cooled to room temperature. The X-ray powder diffraction pattern of s-PMMS crystallized by cooling the melt at 10 °C/min is reported in Figure 1 (curve a). This polymorphic form is defined form I. Faster cooling to room temperature prevents the crystallization in form I, and amorphous samples of s-PMMS are obtained. The X-ray powder diffraction pattern of the amorphous s-PMMS is also reported in Figure 1 (curve b). Crystallization of form I also occurs by annealing the amorphous sample of s-PMMS at temperatures higher than 120 °C (cold crystallization). The X-ray diffraction pattern of the sample crystallized by annealing the amorphous sample at 180 °C is similar to the pattern of Figure 1a.

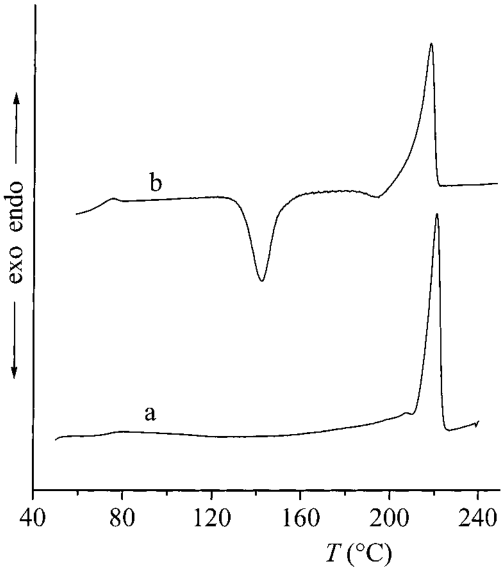

Figure 2. DSC curves (10 °C/min) of melt-crystallized form I (curve a) and amorphous samples (curve b) of s-PMMS. The samples of curves a and b correspond to the samples of parts a and b of Figure 1, respectively.

DSC scans, performed at 10 °C/min, of melt-crystallized and amorphous samples of s-PMMS are reported in Figure 2 (curves a and b, respectively). The cold crystallization exotherm (curve b) at 138 °C and the melting endotherms of form I (curves a and b) are apparent. The melting temperature of form I, evaluated from the peak temperature in curve a of Figure 2, is 220 °C. The melting temperature in curve b is slightly lower than 220 °C, indicating that less perfect crystals of form I are obtained by cold crystallization. The glass transition of s-PMMS, evaluated from curve b of Figure 2, is nearly 80 °C.

(b) Crystallization from Solution. The X-ray diffraction patterns of s-PMMS samples obtained by casting from *o*-dichlorobenzene (*o*-DCB) and benzene solutions at room temperature and dried under vacuum at room temperature are reported in parts a and b of Figure 3, respectively. The patterns of Figure 3 are different from that of form I of Figure 1 and therefore correspond to different crystalline forms of s-PMMS. The thermogravimetric analyses of the samples of Figure 3a,b show weight losses of 25% and 15%, respectively, corresponding to the loss of the solvent molecules included in the crystalline phases. This indicate that, as in the case of s-PS[9,10,12,17−20] and s-PPMS,[24,25,28,29,31,32] also s-PMMS forms clathrate structures characterized by a crystalline lattice containing spaces in which molecules of a second chemical species are located.

It is well-known that in the case of s-PS and s-PPMS the precise location and the intensities of the reflections in the X-ray diffraction patterns of clathrate structures depend on the kind and the amount of guest molecules included in the crystalline cavities.[12,19,25,28] Therefore, the differences observed in the X-ray diffraction pattern of the two clathrates of s-PMMS of Figure 3 could be

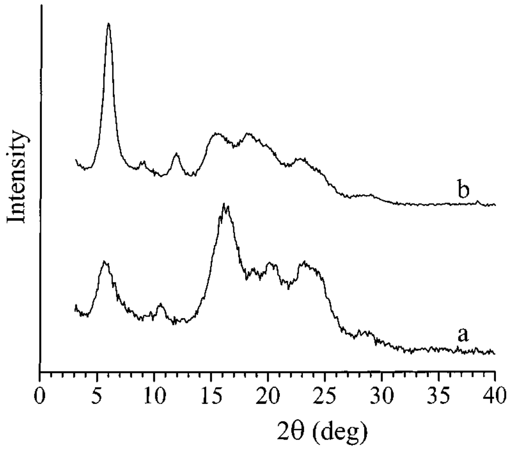

Figure 3. X-ray diffraction patterns of clathrate forms of s-PMMS containing *o*-dichlorobenzene (a) and benzene (b), obtained by casting at room temperature from *o*-dichlorobenzene and benzene solutions, respectively.

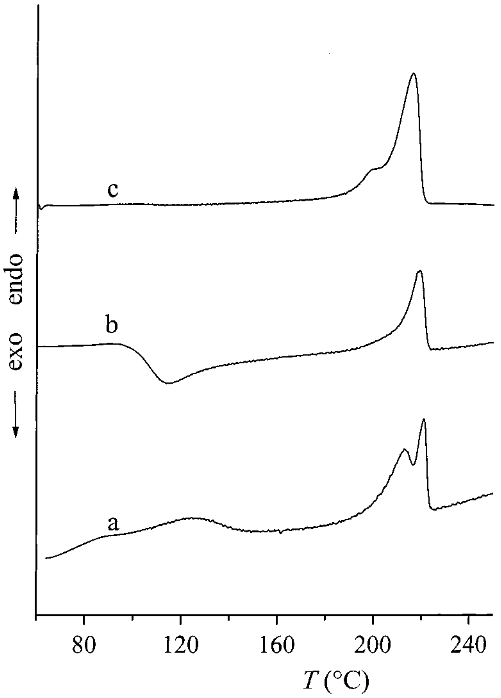

Figure 4. DSC curves (10 °C/min) of clathrate samples of s-PMMS containing *o*-dichlorobenzene (curve a) and benzene (curve b) and of form II of s-PMMS, obtained by annealing at 160 °C for 20 min the clathrate sample containing *o*-dichlorobenzene (curve c). The samples of curves a, b, and c correspond to the samples of Figures 3a, 3b, and 5, respectively.

due to the different kind and amount of guest molecules included, even though a different mode of packing of the polymeric chains could be also involved.

The DSC scans of the clathrate forms containing *o*-dichlorobenzene and benzene are reported in Figure 4 (curves a and b, respectively). It is apparent the presence in the DSC curve (a) of a broad endotherm in the range 80−140 °C corresponding to the loss of the guest molecules from the samples, in agreement with the thermogravimetric analysis. In the DSC scan of Figure 4b, the endotherm corresponding to the loss of the benzene molecules overlaps with a large exotherm at 113 °C, which suggests a transition into a different crystalline phase. Both the DSC scans of Figure 4a,b indeed show melting endotherms at nearly 218−219 °C,

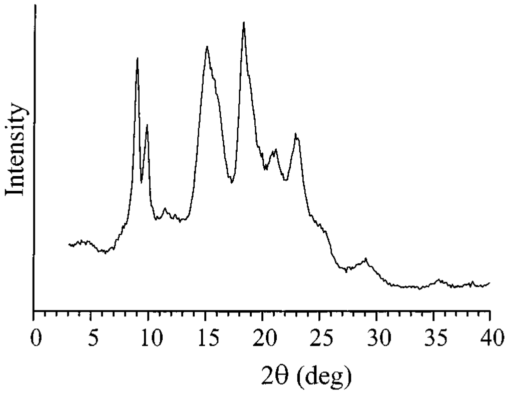

Figure 5. X-ray diffraction pattern of form II of s-PMMS, obtained by annealing at 160 °C for 20 min the clathrate sample of s-PMMS containing *o*-dichorobenzene of Figure 3a.

indicating that a crystalline phase is present after the removal of the guest molecules. The double melting peak observed in Figure 4a is probably due to the occurrence of recrystallization phenomena.

To understand the nature of this crystalline phase, both the clathrate forms have been annealed in the range 140−160 °C.

The X-ray diffraction pattern of the clathrate form containing *o*-dichlorobenzene annealed at 160 °C for 20 min is reported in Figure 5. The same pattern is obtained by annealing the clathrate form containing benzene. The X-ray pattern of Figure 5 is different from either that of the clathrate forms of Figure 3 or that of form I of Figure 1. It therefore corresponds to a different crystalline form of s-PMMS, which we define form II. The DSC scan of the sample of form II of Figure 5, reported in the Figure 4c, shows a melting endotherm at nearly 216 °C. Since the annealing of the clathrate forms induces the formation of form II, the endotherms observed at 216−220 °C in the DSC scans of Figure 4a,b also correspond to the melting of form II.

The data of Figures 4 and 5 indicate that the clathrate forms of s-PMMS transform into the crystalline form II upon the removal of the guest molecules. This behavior is similar to that of s-PS, where the clathrate δ forms transform into the γ form by removing the guest molecules (by annealing treatments at 130 °C).[10] In the case of s-PPMS, instead, the removal of the guest molecules produces amorphous samples or crystalline modifications, depending on the annealing temperature.[24,25,28]

Casting procedures from different solvents, like toluene or chloroform, do not induce the formation of clathrate structures, but a direct crystallization of form II of s-PMMS is observed. The X-ray diffraction patterns of samples obtained by casting from these solvents are, indeed, very similar to that of form II of Figure 5. However, clathrate structures, containing toluene, tetrahydrofuran, etc., can be obtained by exposing amorphous samples to the vapors of these compounds.

Oriented Samples. Oriented fiber samples of s-PMMS have been obtained by stretching amorphous films of s-PMMS, which have been prepared by quenching compression molded films in ice−water. The X-ray fiber diffraction pattern of an amorphous film of s-PMMS stretched at 90 °C is reported in Figure 6. The reflections present in the pattern of Figure 6 do not correspond to those present in the powder patterns of forms I and II of Figures 1a and 5, respectively. A new crystalline polymorphic form, which we define form III,

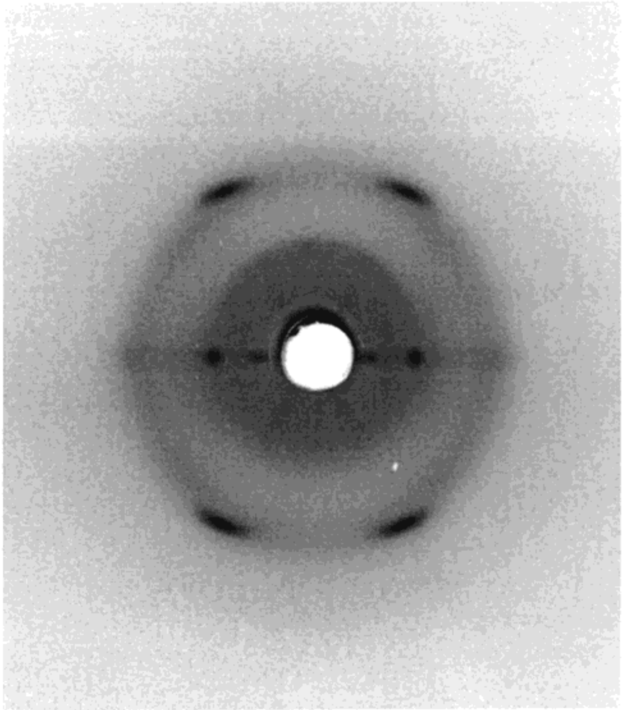

Figure 6. X-ray fiber diffraction pattern of the mesomorphic form III of s-PMMS, obtained by stretching at 90 °C of amorphous films.

has been obtained by stretching the amorphous s-PMMS. The X-ray diffraction pattern of form III of Figure 6 presents diffuse haloes on the equator, centered at $2\theta = 6.0°$ and $2\theta = 11.2°$ ($d = 14.7$ and 7.90 Å, respectively), and only one strong reflection on the first layer line at $2\theta = 20.2°$ ($d = 4.40$ Å). From the reflection on the first layer line a chain axis periodicity of 5.1 Å has been evaluated. This value of the chain axis indicates that form III is characterized by chains in a trans-planar conformation. The absence of sharp reflections on the equator indicates that a high degree of disorder in the lateral packing of the trans-planar chains is present in form III, whereas a long-range order is maintained only along the chain axis. These data clearly sugget that form III may be considered as a mesomorphic modification, characterized by a degree of order intermediate between the order typical of a crystal and the disorder of the amorphous phase. It is worth noting that mesomorphic forms with chains in trans-planar conformation have been found also for s-PS[23] and s-PPMS.[24,33]

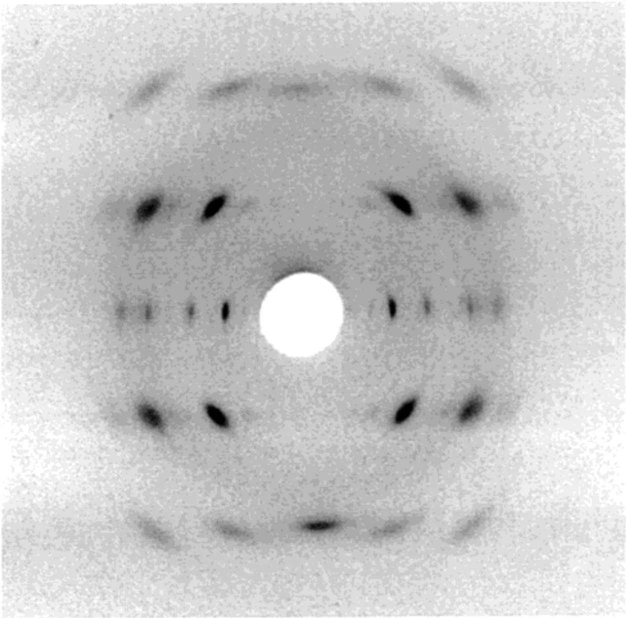

Figure 7. X-ray fiber diffraction pattern of form I of s-PMMS, obtained by annealing the fiber in form III at 180 °C.

Table 1. Bragg Angles (2θ), Bragg Distances (d), Reciprocal Cylindrical Coordinates ξ and ζ, and Intensities (I) of the Reflections Observed on the Layer Lines l of the X-ray Fiber Diffraction Pattern of Form I of s-PMMS of Figure 7[a]

oriented sample						unoriented sample		
2θ (deg)	d (Å)	ξ (Å^{-1})	ζ (Å^{-1})	l	I	2θ (deg)	d (Å)	I
4.4	20.1	0.050	0	0	vw	4.5	19.6	vw
6.8	13.0	0.077	0	0	vw	6.8	13.0	vw
9.1	9.72	0.103	0	0	s	9.2	9.6	vs
12.9	6.86	0.146	0	0	m	12.9	6.9	m
17.6	5.04	0.198	0	0	m	17.6	5.0	m
20.7	4.29	0.233	0	0	m			
11.2	7.90	0.012	0.126	1	w			
15.1	5.87	0.115	0.126	1	vs	15.2	5.8	vs
18.7	4.74	0.169	0.126	1	vw	18.7	4.7	w
20.8	4.27	0.197	0.126	1	s	20.3	4.4	vs
24.2	3.68	0.240	0.126	1	w			
22.9	3.88	0.	0.252	2	n.e.[b]			
24.2	3.65	0.107	0.252	2	m			
28.3	3.15	0.193	0.252	2	m	28.3	3.2	w

[a] The Bragg angles, the Bragg distances, and the intensities of the reflections observed in the X-ray powder diffraction pattern of form I of Figure 1a are also reported for comparison. [b] n.e. = not evaluated.

By annealing oriented fiber samples in the mesomorphic form III of s-PMMS at temperatures higher than 90 °C, crystallization occurs, and oriented fibers in a crystalline polymorphic form of s-PMMS are obtained. The X-ray fiber diffraction pattern of the fiber of Figure 6 (form III) annealed at 180 °C for 30 min, keeping the fiber under tension, is reported in Figure 7. Sharp reflections are present on the equator and on the layer lines corresponding to a chain axis periodicity of 7.9 Å. This indicates that a crystalline form with chains in the 2-fold helical conformation, with s(2/1)2 symmetry, has been obtained. All the reflections presents in the fiber pattern of Figure 7 are listed in the Table 1 and compared to the Bragg distances and the intensities of the reflections present in the X-ray powder diffraction pattern of form I of Figure 1. It is apparent that the reflections in the fiber pattern of Figure 7 well correspond to those of form I. Therefore, annealing of the oriented trans-planar form III induces the crystallization into form I of s-PMMS, characterized by chains in 2-fold helical conformation. If amorphous films of s-PMMS are stretched at temperatures higher than 90 °C, fibers with a mixture of crystals of the mesomorphic form III and form I are obtained.

X-ray fiber diffraction patterns of form I, similar to that of Figure 7, have been also obtained by solvent diffusion in fibers of the mesomorphic form III. For example, by exposing the fiber sample of form III, keeping the fiber under tension, to the vapors of toluene, tetrahydrofuran, cyclohexane, cyclohexanone, or *o*-dichlorobenzene at room temperature, form I always crystallizes and X-ray fiber patterns similar to that of Figure 7 are obtained. It is worth noting that, whereas in the case of powder samples casting procedures from solutions of these solvents induce the crystallization of form

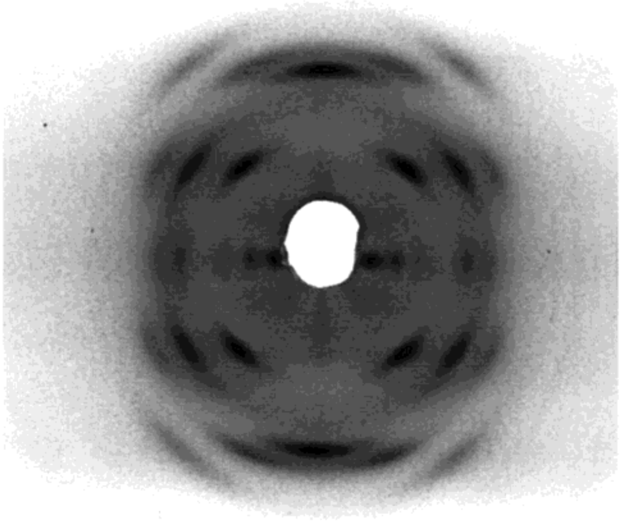

Figure 8. X-ray fiber diffraction pattern of the clathrate form of s-PMMS containing benzene, obtained by exposing the fiber in form III to the vapors of benzene.

Table 2. Bragg Angles (2*θ*), Bragg Distances (*d*), Reciprocal Cylindrical Coordinates *ξ* and *ζ*, and Intensities (*I*) of the Reflections Observed on the Layer Lines *l* of the X-ray Fiber Diffraction Pattern of the Clathrate Form of s-PMMS Containing Benzene of Figure 8[a]

oriented sample						unoriented sample		
2θ (deg)	d (Å)	ξ (Å^{-1})	ζ (Å^{-1})	l	I	2θ (deg)	d (Å)	I
6.0	14.6	0.068	0	0	vs	5.8	15.3	vvs
9.2	9.61	0.104	0	0	m	8.9	9.9	w
12.3	7.17	0.139	0	0	vvw	11.9	7.4	m
18.1	4.90	0.204	0	0	w	18.0	4.9	m
15.3	5.77	0.116	0.129	1	vs	15.1	5.9	m
20.3	5.25	0.140	0.129	1	vs	20.1	4.4	m
23.5	3.78	0.231	0.129	1	w			
23.1	3.85	0.	0.255	2	n.e.[b]	22.5	3.9	m
24.4	3.65	0.100	0.255	2	w	24.6	3.6	m
28.4	3.14	0.191	0.255	2	w	29.0	3.1	vw

[a] The Bragg angles, the Bragg distances, and the intensities of the reflections observed in the X-ray powder diffraction pattern of clathrate form containing benzene of Figure 3b are also reported for comparison. [b] n.e. = not evaluated.

II, the exposition of oriented fibers of form III to the vapors of the same solvents induces the crystallization of the oriented form I.

Therefore, the helical form I can be obtained in unoriented samples, by crystallization from the melt or cold crystallization (annealing of the amorphous sample) and, in oriented fibers, by crystallization of the mesomorphic form III by annealing at temperatures higher than 90 °C or by diffusion of the most common solvents. In the latter procedures a transformation of chains in trans-planar conformation (form III) into helical conformation (form I) is involved. It is worth noting that a different behavior has been observed for s-PS and s-PPMS, where annealing of the trans-planar mesomorphic forms induces the crystallization of crystalline forms with chains still in the trans-planar conformation.[23,25]

The X-ray fiber diffraction pattern of the fiber in the mesomorphic form III exposed to the vapor of benzene at room temperature for 12 h, keeping the fiber under tension, is reported in Figure 8. Also in this case the solvent induces crystallization, and reflection peaks are present on the equator and layer lines. The pattern of Figure 8 is different from that of form I of Figure 7, but also in this case the reflections on the layer lines correspond to a chain axis periodicity of 7.8 Å, typical of a 2-fold helical conformation of the chains. All the reflections in the pattern of Figure 8 are listed in Table 2. The Bragg distances and the intensities are compared in Table 2 with those of the reflections present in the X-ray powder diffraction patterns of the clathrate form containing benzene of Figure 3b. It is apparent that this comparison indicates that the reflections in the fiber pattern of Figure 8 well correspond to those of the clathrate form. Therefore, oriented fibers of the clathrate forms of s-PPMS containing benzene have been obtained by exposing fibers in the mesomorphic form III to the vapors of this compound. The fiber pattern clearly indicate that the clathrate form of s-PMMS is characterized by chains in helical conformation with s(2/1)2 symmetry. As in the case of the clathrate structures of sPS[17−20] and s-PMMS,[31,32] also for the clathrate structures of s-PMMS, the crystalline lattice containing cavities occupied by the guest molecules is formed by the packing of polymer chains in 2-fold helical conformation.

Annealing of the oriented fibers of the clathrate structure of sPMMS containing benzene in the temperature range 120−160 °C produces removal of the guest molecules, and fibers in form I have been obtained. It is worth noting that, whereas powder samples of the clathrate structure of sPMMS containing benzene transforms into form II by annealing, the same clathrate form transforms into the pure helical form I in oriented fiber specimens.

Since oriented fibers of form II have not been obtained, we cannot suggest models for the conformation of the chains in form II. By analogy with the behavior of s-PS[10] and s-PPMS,[24] the obtaining of this form of s-PMMS by crystallization from solutions or by annealing of clathrate structures suggests that form II could probably be characterized by chains in helical conformation. Further studies are in progress in order to clarify this point.

Conclusions

Syndiotactic poly(*m*-methylstyrene) presents a complex polymorphic behavior. Three different polymorphic forms and various clathrate structures have been found so far. In the different crystalline forms, the polymer chains assume trans-planar or 2-fold helical conformations. The possible routes for obtaining the pure polymorphic forms in unoriented and oriented fiber samples are reported in the scheme of Figure 9.

Form I is characterized by chains in s(2/1)2 helical conformation and is obtained by crystallization from the melt or by annealing the amorphous phase. Form II is obtained by crystallization from solutions of various solvents or by removing the guest molecules from the clathrate forms by annealing treatments. Form III, obtained in oriented fibers by stretching of amorphous films, is a mesomorphic form, characterized by chains in a regular trans-planar conformation with a high degree of disorder in the lateral packing of the chains. Oriented fibers of form I are obtained by annealing of the fibers in the mesomorphic form III or by exposing the same fibers of form III to the vapors of various solvents.

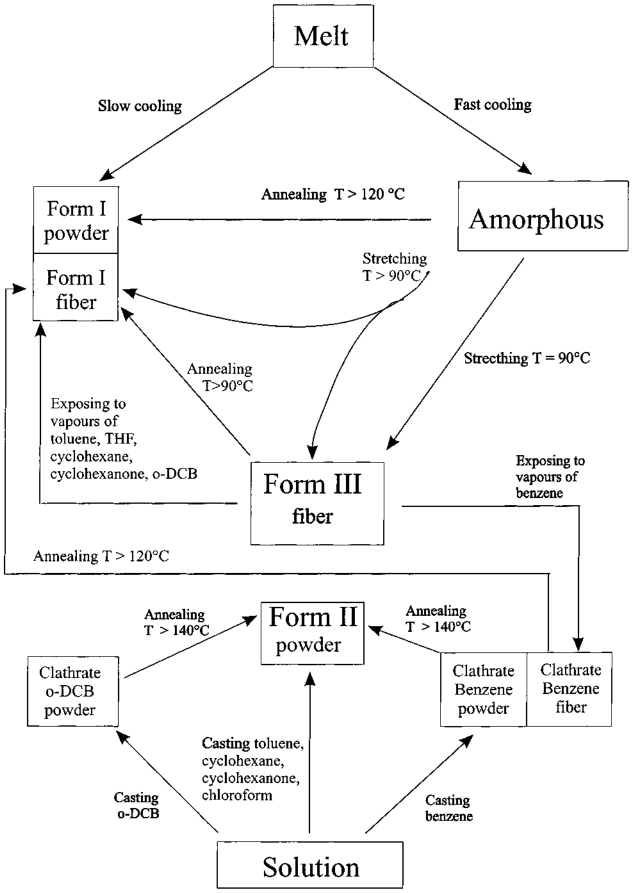

Figure 9. Scheme showing the possible routes for obtaining the different polymorphic forms of s-PMMS.

Two clathrate structures, containing molecules of benzene or *o*-dichlorobenzene in the crystalline lattices, have been found and characterized. In these clathrate forms the polymer chains assume a s(2/1)2 helical conformation.

The polymorphic behavior of s-PMMS shows some analogies with the behaviors of s-PS and s-PPMS. First of all, the various polymorphic forms are characterized by chains in trans-planar and 2-fold helical conformations. Second, as in the case of s-PS and s-PPMS, also s-PMMS forms clathrate structures characterized by polymer chains in 2-fold helical conformation which are packed in a crystalline lattice containing cavities occupied by guest molecules. Moreover, mesomorphic modifications with chains in the trans-planar conformation have been found for s-PMMS as well as for s-PS and s-PPMS.

However, notable differences between s-PMMS, s-PS, and s-PPMS have been revealed. By melt and cold crystallization polymorphic forms with chains in the trans-planar conformation are obtained for s-PS (α and *β* forms), whereas a crystalline form with chains in helical conformation is obtained for s-PMMS (form I). Moreover, while in the case of s-PS and s-PPMS the mesomorphic trans-planar forms transform by annealing into crystalline forms with chains in the trans-planar conformation, in the case of s-PMMS the trans-planar mesomorphic form III transforms into the helical form I.

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