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Guest-Induced Syndiotactic Polystyrene Cocrystal Formation from γ and α Phases

Alexandra R. Albunia,* Loredana Annunziata, and Gaetano Guerra

Università degli Studi di Salerno, Dipartimento di Chimica and INSTM Research Unit,
Via Ponte don Melillo, 84084, Fisciano, Italy

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ABSTRACT: Guest-induced transitions from α and γ phases of syndiotactic polystyrene (s-PS) toward cocrystalline and nanoporous phases, and related guest-induced orientation phenomena, have been investigated by X-ray diffraction. Guests, being able to induce cocrystal formation in amorphous s-PS samples, are able to induce room-temperature cocrystal formation from γ and α form films, only if their vapor pressure is higher than 20 and 60 Torr, respectively. Guest-induced recrystallizations of unoriented γ form films generally lead to unoriented cocrystalline and δ form films, while chloroform-induced recrystallization leads to cocrystalline and ε form films with perpendicular orientation of chain axes. On the other hand, guest-induced recrystallizations of unoriented α form films generally lead to oriented cocrystalline and derived δ form films. In particular, recrystallizations of unoriented α form films by room-temperature sorption of trichloroethylene and $CHCl_3$ lead to films with (002) uniplanar and $(\bar{2}10)$ uniplanar orientations, i.e., with chain axes perpendicular and parallel to the film plane, respectively. The new procedures to prepare nanoporous films with different uniplanar orientations present substantial advantages with respect to the procedures already described in the literature.

Introduction

The polymorphic behavior of syndiotactic polystyrene (s-PS) has been deeply studied in the last years and can be described (by making some simplification) in terms of two crystal forms, α and β, characterized by chains in trans-planar conformation, and three crystal forms, γ and δ as well as ε where the chains are in the **s**(2/1)2 helical conformation.[1] Moreover, it is well-known that s-PS can form cocrystalline phases (clathrate[2] and intercalate[3]) with several low-molecular-mass molecules (a collection of data is reported in Table 7 of ref 3d), where the polymer always assumes its **s**(2/1)2 helical conformation.

Melt-crystallization procedures lead only to the trans-planar α[4] and β[5] phases. On the other hand, solution crystallization[5a] and solvent-induced crystallization[6] generally lead to the formation of helical cocrystalline[1−3] and γ[1d,6b] phases, although the thermodynamically favored trans-planar β phase is also obtained by solution casting at high temperatures[5a] as well as by annealing above 150 °C of cocrystalline and γ samples in the presence of solvents.[1a,d,7] The nanoporous δ[8] and ε[9] forms are obtained by guest removal from cocrystalline phases by volatile guests, like CO_2, acetone, or acetonitrile.[8b]

Materials (mainly films and aerogels) presenting the nanoporous δ crystalline phase have been deeply studied for their promising applications in chemical separations (mainly air/water purification)[10] as well as in sensorics.[11] Films presenting s-PS/active-guest cocrystals have been proposed as advanced materials, mainly for optical applications (e.g., as fluorescent, photoreactive, and chromophore materials).[12]

As for s-PS cocrystal films,[1−3] *guest-induced oriented crystallizations*, leading to the unprecedented occurrence of three different kinds of uniplanar orientations, have been observed. In particular, depending on the selected technique (solution crystallization procedures[13] or solvent-induced crystallization in amorphous samples[14]) and on the molecular guest, (010),[13,14a] $(\bar{2}10)$,[14d] or (002)[13b,14b,c] crystalline planes are preferentially oriented parallel to the film plane (Figure 1). These three uniplanar orientations (without substantial loss of their degree of orientation) are maintained during guest-removal and thermal treatments leading to δ and γ films, respectively. In this respect, it is worth adding that suitable thermal treatments can also lead to α and β films with planar orientations.[13a,14c] In particular, films with (00*l*) and (*hk*0) orientations lead to crystalline phases with their chain axes preferentially perpendicular and parallel to the film surface.[14c]

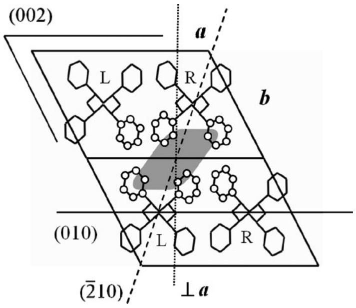

Figure 1. Along the chain projection of two adjacent unit cells of the δ form of s-PS, showing traces of the (010) and $(\bar{2}10)$ crystalline planes (thick and dashed line, respectively), as well as the trace of the plane perpendicular to the *a* axis (dotted line). The (002) crystalline plane is parallel to the plane of the figure. The crystalline cavity is indicated as a gray region. For clarity of presentation, the 10 phenyl rings, which define the cavity, are represented as stick and balls. The symbols R and L indicate the handedness of the polymer helices.

The availability of s-PS films with three different kinds of uniplanar orientations can be, of course, relevant also for practical purposes. For instance, it allows guest orientation control[15] for cocrystalline phases and guest diffusivity (and hence permeability) control[16] for the nanoporous δ and ε phases.

The formation of cocrystalline phases can also be obtained by guest exchange in already formed cocrystals,[17] or by absorbing suitable guest molecules from the nanoporous δ and ε phases.[10] Both procedures generally leave unaltered the orientation which has been achieved by primary s-PS solution crystallization.[14c]

The cocrystal formation by absorption of suitable guest molecules in the helical γ phase as well as in the trans-planar α phase was already described in early papers on s-PS.[1a,18] It

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* To whom correspondence should be addressed. Phone. +39 (0) 89 969392. Fax: +39 (0) 89 969603. E-mail: aalbunia@unisa.it.

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Table 1. List of Liquid Solvents Which Are Able to Induce Cocrystal Formation in Amorphous s-PS Films[a]

guest		molecular weight	Bp (°C)	Vp (mm Hg @ 20 °C)	guest-induced nanoporous crystalline phase[b]		
					starting material[c]		
					amorphous	γ	α
dichloromethane (DCM)	CH_2Cl_2	85.92	40	349	$\delta(002)$	δ	δ
carbon disulfide	CS_2	76.14	46	297	$\delta(002)$	δ	δ
chloroform	$CHCl_3$	119.38	61	160	$\delta(002)$	ε (002)	δ $(\bar{2}10)$
tetrahydrofuran (THF)	C_4H_8O	72.11	66	129	$\delta(002)$	δ	δ
benzene (Bz)	C_6H_6	78.11	80	75	$\delta(002)$	δ	δ
1,2-dichloroethane	$ClCH_2CH_2Cl$	98.96	83	64	$\delta(002)$	δ	δ
trichloroethylene (TCE)	$Cl_2C{=}CHCl$	131.39	87	61	$\delta(002)$	δ	δ (002)
1,2-dichloropropane	$CH_3CHClCH_2Cl$	112.99	95−96	40	$\delta(002)$	δ	
toluene	$C_6H_5CH_3$	92.14	110−111	21	$\delta(002)$	δ	
o-xylene	*o*-$C_6H_4(CH_3)_2$	106.17	144	7	$\delta(\bar{2}10)$		
decahydronaphthalene	$C_{10}H_{18}$	138.25	190	42 @ 92 °C	$\delta(\bar{2}10)$		
1,4-dimethylnaphthalene (DMNP)	$C_{10}H_6(CH_3)_2$	156.22	262 (751 mm Hg)	0.004	$\delta(\bar{2}10)$		
1,3-diphenylbutane	$C_{16}H_{18}$	210.31	≈293		$\delta(\bar{2}10)$		

[a] Bp is the boiling point at atmospheric pressure, and Vp is the vapor pressure at 20 °C. The last three columns contain the crystalline phases and the possible crystalline phase orientation, as induced by the guest sorption in amorphous, gamma, and alpha. [b] The nanoporous crystalline phase is obtained by the guest sorption/desorption procedure. The induced crystalline phase orientation is reported only when a single kind of uniplanar orientation occurs. [c] Films obtained as described in the Experimental Section.

has been also found that the denser trans-planar β phase presents a higher stability and it is not transformed into any cocrystalline phase by guest absorption.[18] Solvent-induced recrystallizations in γ and α phases have only been occasionally studied and, in particular, no information on orientation phenomena possibly induced by these recrystallization procedures was reported. Only recently, it has been shown that guest treatments of unoriented γ form s-PS films can produce fully unoriented s-PS cocrystalline (and hence also δ form) films.[19]

In this paper, we investigate guest-induced transitions from α and γ phases toward cocrystalline phases, and related guest-induced orientation phenomena.

Experimental Section

Syndiotactic polystyrene was supplied by Dow Chemical under the trademark Questra 101. ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic polystyrene triads was over 98%. The weight-average molar mass obtained by gel permeation chromatography (GPC) in trichlorobenzene at 135 °C was found to be $M_w = 3.2 \times 10^5$ with the polydispersity index $M_w/M_n = 3.9$.

Pure solvents were purchased from Aldrich and used without further purification.

In Table 1, a list of the used solvent is reported together with their molecular weight, their boiling temperature, and their vapor pressure at 20 °C.[20] All of the considered solvents are able to induce cocrystal formation by sorption in s-PS amorphous films.

Semicrystalline unoriented film samples, 100–150 μm thickness, in the α and in the γ form were obtained, from amorphous s-PS films, by annealing at 200 °C for 1 h and by immersion in pure acetone for 1 day at room temperature, respectively. The amorphous films were obtained by melt extrusion with an extrusion head of 200 mm × 0.5 mm.

Cocrystalline films were obtained by immersion of the α and γ unoriented films in pure liquids, generally for 1 day at room temperature.

Wide-angle X-ray diffraction patterns with nickel filtered Cu Kα radiation were obtained, in reflection, with an automatic Bruker diffractometer. The degree of crystallinity of the unoriented films was determined, resolving the diffraction patterns into two areas, A_c and A_a, that can be taken as being proportional to the crystalline and the amorphous fraction of the polymer, respectively, and calculated through the expression $X_c = 100 \times A_c/(A_c + A_a)$.

Wide-angle X-ray diffraction patterns were also obtained, in transmission, by using a cylindrical camera (radius = 57.3 mm). In the latter case, the patterns were recorded on a BAS-MS imaging plate (FUJIFILM) and processed with a digital imaging reader (FUJIBAS 1800). In particular, to recognize the kind of crystalline phase orientation, photographic X-ray diffraction patterns were taken by having the X-ray beam parallel to the film surface and by placing the film sample parallel to the axis of the cylindrical camera.

Results and Discussion

Cocrystal Formation from the Amorphous Phase. Recent studies have shown that guest-induced crystallizations in amorphous s-PS films[3f,14,19] lead to host−guest cocrystalline phases always exhibiting uniplanar orientation. In particular, depending on the used guest, (002)[14c] or $(\bar{2}10)$[14d] uniplanar orientations can be induced, thus leading to crystalline chain axes preferentially perpendicular or parallel to the film plane, respectively. All of these cocrystalline phases, after guest removal, lead to the nanoporous δ phase always maintaining the initial uniplanar orientation.

Information on the kind of uniplanar orientation in δ form films, as prepared by guest sorption/desorption procedures in amorphous s-PS films, mainly taken from refs 14b and 14c, is collected in the sixth column of Table 1. It is immediately apparent that more volatile guests (Bp < 120 °C or Vp > 20 Torr) induce (002) uniplanar orientation while less volatile guests (Bp > 140 °C or Vp < 7 Torr, last four lines of Table 1) induce $(\bar{2}10)$ uniplanar orientation.

Hence, for guests presenting faster and slower diffusion kinetics in the polymer film, the cocrystalline phase formation occurs with polymer chains perpendicular and parallel to the advancing guest front, respectively. This clearly suggests that, when the rate of advancement of the guest front is slow, a sort of two-dimensional confinement of the cocrystallization process favors the orientation of the host polymer chains parallel to the film surface. This hypothesis is also supported by recent studies by Gupper et al.,[6c] proving that solvent diffusion is the rate-determining factor in the overall cocrystallization processes of amorphous s-PS films.

Cocrystal Formation from the γ Phase. X-ray diffraction patterns of unoriented γ form films, exhibiting crystallinity close to 30%, before and after immersion for 1 day in dichloromethane (DCM), benzene (Bz), and trichloroethylene (TCE) are shown in Figure 2a−d. These patterns show that, as a consequence of the guest treatment, typical γ form peaks (like, e.g., those at $2\theta_{CuK\alpha} = 9.25$ and 16.0°)[1a,6a,13a] disappear, being replaced by peaks typical of clathrate cocrystals (like, e.g., those at $2\theta_{CuK\alpha} \approx 8$ and 10°).[1a,2,8] The relative intensities of the diffraction peaks of the obtained cocrystal films, qualitatively similar to those

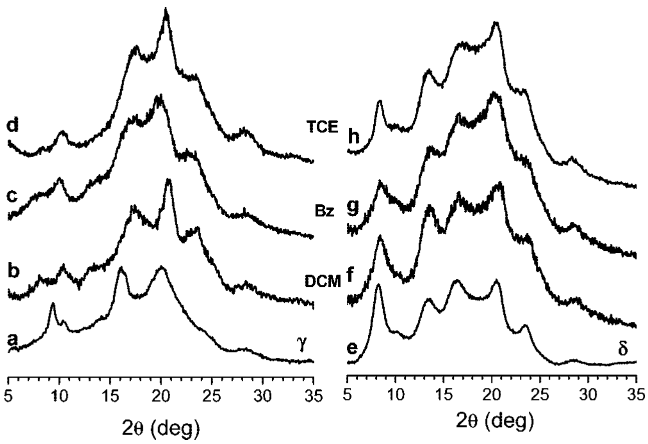

Figure 2. X-ray diffraction patterns (Cu Kα) of s-PS semicrystalline samples: (a) γ form film; (b−d) cocrystalline clathrate films, obtained by immersion of the γ form film in DCM (b), Bz (c), and TCE (d); (e) δ form powder; (f−h) δ form films obtained by guest removal from the clathrate films, whose spectra are shown in parts b−d.

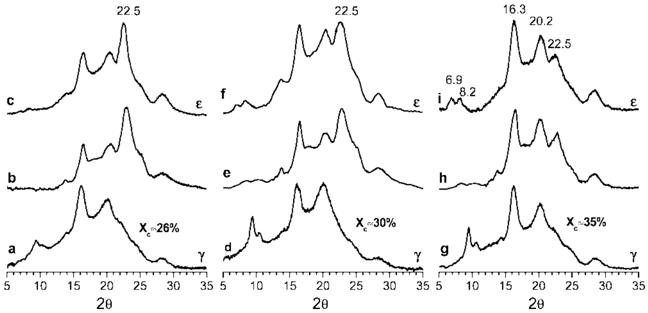

Figure 3. X-ray diffraction patterns (Cu Kα) of γ semicrystalline films presenting different degrees of crystallinity of (a) 26%, (d) 30%, and (g) 35%; the cocrystalline s-PS/$CHCl_3$ films obtained immersion in liquid $CHCl_3$ of these γ form films (parts b, e, and h, respectively); the ε semicrystalline films obtained by subsequent guest extraction with acetonitrile (parts c, f, and i, respectively).

observed for powder samples, indicate that all of these films are substantially unoriented.

To establish the possible occurrence of even low degrees of crystalline orientation, particularly suitable is a comparison between X-ray diffraction patterns of δ form films (Figure 2f−h) obtained by guest removal from the cocrystalline films of Figure 2b−d and the X-ray diffraction pattern of a δ form powder (Figure 2e). The comparison shows for the films a reduced intensity of the (010) peak (at $2\theta_{CuK\alpha} \approx 8.4°$), which suggests a reduced probability for crystalline chain axes with an orientation parallel to the film plane. However, the comparison confirms that the obtained δ form films are essentially unoriented.

Recrystallization phenomena analogous to those shown in Figure 2 have been observed for γ form film samples treated with other guest molecules like CS_2, 1,2-dichloroethane, 1,2-dichloropropane, tetrahydrofuran, and toluene.

The cocrystal phase formation induced by chloroform absorption in γ form films is definitely different from those observed with the other guest molecules (Figure 2). The X-ray diffraction patterns of cocrystalline phases obtained by immersion in chloroform of unoriented γ form films exhibiting degrees of crystallinity of 26, 30, and 35% (Figure 3a, d, and g) are shown in parts b, e, and h of Figure 3, respectively. The X-ray diffraction patterns of the cocrystalline films of Figure 3b, e, and h, after guest extraction with acetonitrile (Figure 3c, f, and i, respectively), present peaks at $2\theta_{CuK\alpha} = 6.9$, 8.2, 16.3, and 20.2°, clearly indicating the formation of the ε form.[9]

All patterns, both those of cocrystalline films (Figure 3b, e, and h) and of ε form films (Figure 3c, f, and i), show a strong reflection at $2\theta_{CuK\alpha} = 22.5°$, whose intensity increases as the crystallinity of the starting γ form film is decreased. In fact, the peak at $2\theta_{CuK\alpha} = 22.5°$ is the most intense for the cocrystalline and ε form films, as obtained from the less crystalline γ form film (Figure 3b and c, respectively). This peak, whose Bragg spacing is $d = 0.395$ nm, corresponds to the (002) reflection of the ε phase[9] and hence to the along the chain periodicity of 0.79 nm. These observations suggest that both the s-PS/$CHCl_3$ cocrystalline phase and the ε phase, as formed from the γ phase, exhibit a preferential perpendicular orientation of the crystalline chain axes with respect to the film plane.

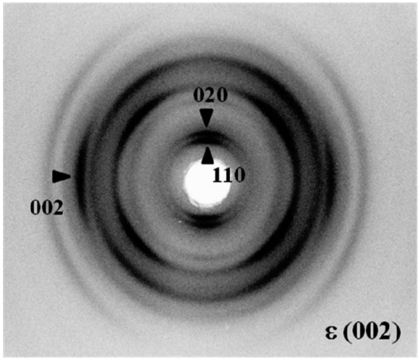

Figure 4. X-ray diffraction pattern taken with the beam parallel to the film plane, collected on a photographic cylindrical camera of the ε form film of Figure 3c (obtained from an unoriented γ form film).

The occurrence of a preferential (002) orientation is confirmed by the diffraction pattern collected on a photographic cylindrical camera with the beam parallel to the film plane for the film of Figure 3c, as shown in Figure 4, that presents the peaks at $2\theta_{CuK\alpha} = 6.9$ and 8.2° (110 and 020 reflections, respectively)[9b] centered on the meridional line and the 002 reflection centered on the equatorial line. The degree of perpendicular uniplanar orientation is $f_{002} \approx 0.7$, i.e., a degree of uniplanar orientation comparable with those obtained by $CHCl_3$ diffusion in γ form films already exhibiting (002) uniplanar orientation.[9a]

Hence, rather surprisingly, the present results show that films with a high degree of perpendicular orientation of the chain axes of the ε nanoporous phase can be obtained by chloroform treatment not only of γ form films already presenting this perpendicular orientation[9a] but also (and more simply) of unoriented γ form films.

It is worth adding that γ form films remain stable also after long term room-temperature exposure to bulkier guest molecules (last four lines of Table 1) which under similar conditions are able to induce formation of cocrystalline phases in amorphous films.

Cocrystal Formation from the α Phase. X-ray diffraction patterns of unoriented α form film (degree of crystallinity of 38%), before and after immersion for 1 day in CS_2, TCE, chloroform, and tetrahydrofurane (THF), are shown in Figure 5a−e, respectively. These patterns show that, as a consequence of the guest treatment, typical α form peaks (like, e.g., those at $2\theta_{CuK\alpha} = 6.7$, 11.7, and 13.6°)[1a,4] disappear, being replaced by peaks typical of clathrate cocrystals (like, e.g., those at $2\theta_{CuK\alpha} = 8.3$ and 10.5° for CS_2[2d]).[1a,2]

The relative intensities of the diffraction peaks of the cocrystalline film with CS_2 (Figure 5b) and the corresponding δ phase (Figure 5g) obtained by guest removal are qualitatively similar to those observed for powder samples. This indicates that CS_2 induces the recrystallization of the unoriented α phase into a substantially unoriented cocrystalline (and related δ) phase.

As for the cocrystalline films obtained by treatment of the α form film with TCE, its X-ray diffraction pattern (Figure 5c)

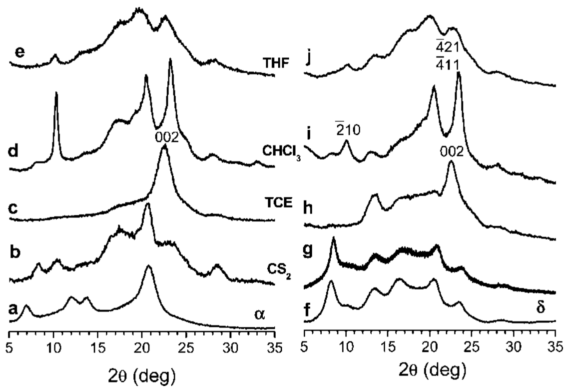

Figure 5. X-ray diffraction patterns (Cu Kα) of s-PS semicrystalline samples: (a) α form film; (b−e) clathrate films, obtained by immersion of the α form film in CS_2 (b), TCE (c), $CHCl_3$ (d), and (e); (f) δ form powder; (g−j) δ form films obtained by guest removal from the clathrate films, whose spectra are shown in parts b−e.

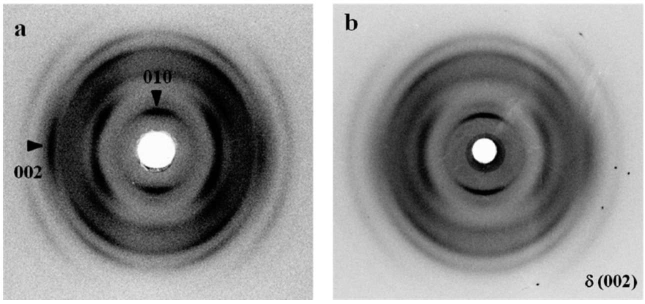

Figure 6. X-ray diffraction pattern taken with the beam parallel to the film plane, collected on a photographic cylindrical camera: (a) of a δ form film sample obtained by immersion of an unoriented α form film in TCE (Figure 5h); (b) of a δ form film sample obtained by TCE solution casting.[14b]

presents essentially only an intense (002) reflection at $2\theta_{\mathrm{CuK}\alpha} = 22.5°$, indicating the presence of a high degree of perpendicular orientation of the crystalline chain axes with respect to the film plane.

The TCE-induced cocrystal formation with perpendicular orientation from unoriented α form films is also clearly apparent by comparing diffraction patterns of δ form films (Figure 5h), obtained by guest removal from the cocrystalline film (Figure 5c). In fact, the pattern of Figure 5h clearly presents the $(\bar{1}11)$ reflection (at $d = 0.66$ nm, i.e., at $2\theta_{\mathrm{CuK}\alpha} \approx 13.3°$) and a very intense (002) reflection, as typical of δ form films with perpendicular orientation (see Figure 6C of ref 14c).

The degree of perpendicular orientation, already on inspection of Figure 5h, seems to be particularly high. This is confirmed by the diffraction pattern of this film, taken with the beam parallel to the film plane, for film placement parallel to the axis of the cylindrical camera (Figure 6a). In fact, the pattern of Figure 6a presents the 010 reflection centered on the meridional line and the 002 reflection centered on the equatorial line.

For the sake of comparison, the diffraction pattern of a δ form film sample obtained by TCE solution casting,[14b] also taken with the beam parallel to the film plane, is shown in Figure 6b. The comparison shows that the degree of perpendicular orientation presently achieved by TCE sorption in unoriented α form films is even slightly higher than the maximum value till now obtained ($f_{002} = 0.75$) by TCE solution casting procedures.[14b] It is worth adding that the δ form films with a high degree of perpendicular orientation, as obtained by the recrystallization procedure, are much less brittle than those obtained by the previously known solution casting procedure.[14b]

In this respect, it is also worth noting that perpendicular orientations, when obtained as a consequence of guest treatments of s-PS amorphous films, generally present definitely lower degrees of orientation, $0.45 < f_{002} < 0.6$.[14c]

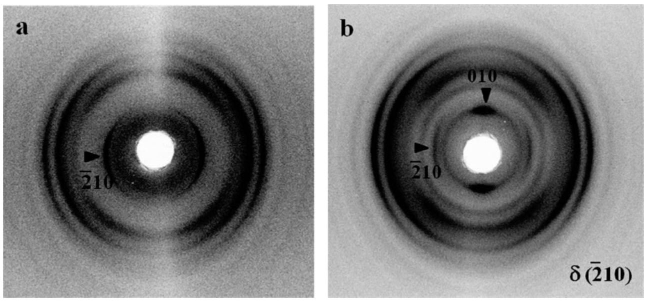

Figure 7. X-ray diffraction patterns taken with the beam parallel to the film plane, collected on a photographic cylindrical camera of (a) a cocrystalline s-PS/$CHCl_3$ film obtained by immersion of an unoriented α form film in $CHCl_3$ (the same film of Figure 5d); (b) the δ form film obtained by guest removal from this cocrystalline film (the same δ form film of Figure 5i).

As for the cocrystalline film obtained by immersion of the α form film in $CHCl_3$, its X-ray diffraction pattern (Figure 5d) shows very intense reflections at $2\theta_{\mathrm{CuK}\alpha} = 10.2$, 20.6, and 23.5°. Also, the pattern of the δ form film (Figure 5i), obtained by $CHCl_3$ removal from the cocrystalline film, shows intense peaks nearly at the same 2θ values, which have been indexed as $(\bar{2}10)$, $(\bar{3}21)$ and $(\bar{4}21)-(\bar{4}11)$, respectively.[8a] Their increased intensities have been associated to an orientation of the $\bar{2}10$ plane preferentially parallel with respect to the film plane.[14d] Of course, for this uniplanar orientation, the polymer chain axes are preferentially parallel to the film plane, rather than perpendicular as for the δ and ε phases with (002) uniplanar orientation.

The occurrence of this kind of orientation is confirmed by the diffraction patterns of the samples of Figure 5d and i, when collected on a photographic cylindrical camera with the beam parallel to the film plane (Figure 7a and b, respectively). It is clearly apparent that both patterns present the peak at $2\theta_{\mathrm{CuK}\alpha} = 10.2°$ ($\bar{2}10$ reflection) on the equatorial line and, for the δ form, the 010 reflection at $2\theta_{\mathrm{CuK}\alpha} = 8.4°$ is centered on the meridional line. For both films, the degree of uniplanar orientation, evaluated as described in ref 14d, is nearly equal to 0.6.

Guest-induced cocrystalline formation from unoriented α form films has also been obtained by immersion in all of the liquid solvents of Table 1, having a boiling point lower than 90 °C and a vapor pressure higher than 60 Torr. With the exception of the above-described s-PS/CS_2 cocrystalline phase, for all of the other solvents, guest-induced orientation phenomena are observed. However, while for the cocrystals with TCE and $CHCl_3$ high degrees of a well defined uniplanar orientation are obtained, for the other guests, lower degrees of orientation are observed. This is shown, for instance, for an unoriented α form film treated by THF (Figure 5e) and for the corresponding δ form (Figure 5j). In particular, for the δ form, the (010) peak, which is generally the most intense for unoriented samples (Figure 5f and g), is barely detectable, while the $(\bar{2}10)$ and (002) peaks (at $2\theta_{\mathrm{CuK}\alpha} = 10.2$ and 22.5°, respectively), which are weak for unoriented samples, are well apparent (Figure 5j). These results suggest that some orientation occurs, although possibly some crystallites present the uniplanar (002) orientation (as observed for TCE sorption) while other crystallites present the uniplanar $(\bar{2}10)$ orientation (as observed for $CHCl_3$ sorption).

It is worth adding that the kind of uniplanar orientation obtained by guest-induced recrystallization in unoriented α form films is not simply related to the kind of uniplanar orientation induced by the same guest in the crystallization of amorphous films[14] or in solution casting procedures.[13] In fact, all eight guests being able to recrystallize the α form films (first eight lines of Table 1) induce uniplanar (002) orientation for cocrystal

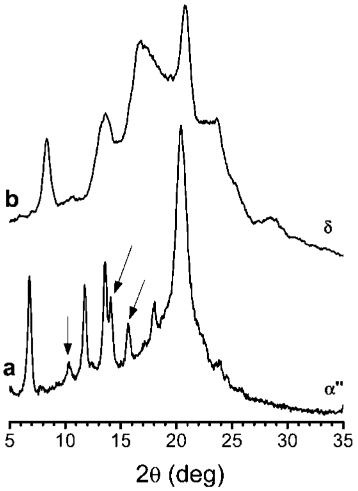

Figure 8. X-ray diffraction patterns (Cu Kα) of s-PS semicrystalline films, taken with an automatic diffractometer: (a) an α″ form s-PS film ($X_c = 50\%$); (b) the same film after immersion for 1 day in TCE and complete guest removal.

formation by diffusion in amorphous s-PS films. On the other hand, by solution casting, dichloromethane, chloroform, THF, and benzene induce (010) uniplanar orientation while 1,2-dichloroethane and TCE induce (002) uniplanar orientation.

It is also worth adding that, as already observed for guest-induced cocrystal formation from the γ phase (Figure 3), also for cocrystal formation from the α phase the guest-induced orientation phenomena are reduced as the degree of crystallinity of the starting film is increased.

For instance, sorption experiments with different guest molecules have been affected on the highly crystalline α form film, whose X-ray diffraction pattern is reported in Figure 8a. This pattern shows the presence of the more ordered α″ modification,[1a,4] as clearly pointed out by reflections with $-h + k + l \neq 3n$, e.g., the (210), (310), and (400) reflections at $2\theta_{\mathrm{CuK\alpha}}$ of 10.3, 14.0, and 15.7° (indicated by arrows in the pattern of Figure 8a), which are absent for the less ordered α′ modification (see, e.g., the pattern of Figure 5a). Moreover, the degree of crystallinity of this film is close to 50% and hence definitely higher than that of the α′ film sample of Figure 5a (38%). The pattern of the δ form film, obtained by guest removal by the cocrystalline phase induced by TCE sorption in the α″ film of Figure 8a is presented in Figure 8b. The relative peak intensities of this pattern clearly indicate the formation of an essentially unoriented crystalline phase. Poorly oriented cocrystalline and δ form films are also obtained by absorption in the film of Figure 8a of the other guest molecules of Table 1.

Comments on the δ Form Films with the Uniplanar $\bar{2}10$ Orientation. The X-ray diffraction patterns of Figure 5i and of Figure 7b, according to the results presented in the previous section, would correspond to a δ form film with a $\bar{2}10$ orientation of its crystalline phase. It is, however, worth noting that these patterns are somewhat different from those of s-PS films obtained from an unoriented amorphous film by immersion in DMNP (followed by guest removal by supercritical carbon dioxide) which also have been described as δ form films with a uniplanar $\bar{2}10$ orientation (Figure 9a; see also Figure 5B of ref 14d). In fact, the X-ray diffraction patterns of the films obtained by DMNP-induced crystallization present a much more intense $\bar{2}10$ reflection (cfr. Figures 9a and 5i).

A careful Fourier transform infrared (FTIR) analysis of these films shows that the usual procedure (by supercritical carbon dioxide, at 40 °C and 200 atm, also after repeated treatments for 90 min) is not sufficient for a complete removal of the poorly volatile DMNP guest. In fact, the presence of a small peak at 824 cm^{-1} clearly indicates the presence of a residual amount of DMNP in the film, which is close to 1 wt %. This residual guest content strongly affects the intensity of the $\bar{2}10$ (see, e.g., Figure 5A and B of ref 14d). In fact, complete DMNP removal by a different procedure (e.g., successive room-temperature treatments with chloroform and acetonitrile) leads to the X-ray diffraction pattern of Figure 9b, which is extremely similar to the pattern of Figure 5i.

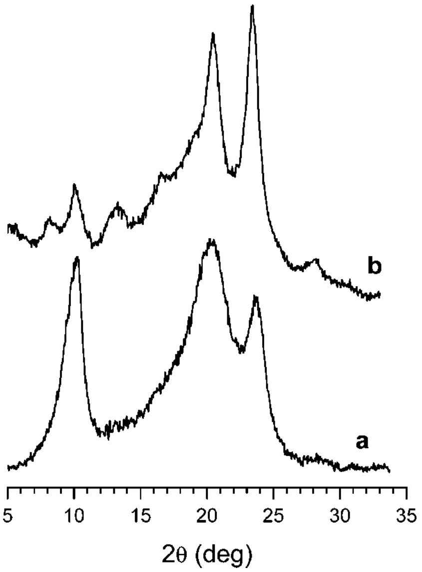

Figure 9. X-ray diffraction patterns (Cu Kα) of s-PS semicrystalline films, taken with an automatic diffractometer: (a) a s-PS film obtained from an unoriented amorphous film by immersion in DMNP followed by guest removal by supercritical carbon dioxide (DMNP content close to 1 wt %); (b) the same film after complete guest removal.

In summary, due to the higher volatility of chloroform, δ form films with the uniplanar $\bar{2}10$ orientation are more easily obtained by chloroform treatment of unoriented α form films rather than by the already known procedure of DMNP treatment of unoriented amorphous films.

The X-ray diffraction pattern of Figure 7b represents the first reported spectrum of a completely emptied δ form film with the so-called $\bar{2}10$ orientation. It is worth adding that this pattern clearly shows the presence of $\bar{2}10$ arcs on the equator being definitely broader than the 010 arcs on the meridian. This suggests that the uniplanar orientation of s-PS, which has been named the $\bar{2}10$ orientation, could rather exhibit as preferentially parallel to the film plane the crystal plane perpendicular to the *a* axis (dotted trace in Figure 1) being rotated only 17° with respect to the $\bar{2}10$ crystal plane (dashed trace in Figure 1). Further more accurate studies are in progress in the attempt to give a precise description of this kind of s-PS uniplanar orientation.

Conclusions

The formation of s-PS cocrystalline phases by absorption of several guest molecules in the helical γ phase as well as in the trans-planar α phase, and related guest-induced orientation phenomena, has been investigated by X-ray diffraction measurements.

The considered guests, being able to induce cocrystal formation in amorphous s-PS samples, are able to induce cocrystal formation from γ and α form films, by room-temperature diffusion, only if their vapor pressure is higher than 20 and 60 Torr, respectively.

Guest-induced recrystallizations of unoriented γ form films generally lead to unoriented cocrystalline films, which in turn by guest removal lead to essentially unoriented δ form films. However, by chloroform treatment of unoriented γ form films, a cocrystalline phase is obtained with orientation of chain axes prevailingly perpendicular to the film plane. Moreover, the nanoporous ε form films obtained by chloroform removal[9] also present a preferential perpendicular orientation of chain axes, which is also quantitatively similar to that one previously obtained by chloroform treatment of γ form films already presenting the perpendicular orientation.[9a]

On the other hand, guest-induced recrystallizations of unoriented α form films generally lead to oriented cocrystalline and derived δ form films. However, the kind and degree of uniplanar orientation strongly depends on the guest molecule. In particular, recrystallizations of unoriented α form films by room-temperature sorption of CS_2, TCE, and $CHCl_3$ lead to films with unoriented, (002) uniplanar, and ($\bar{2}$10) uniplanar orientations. These two orientations present chain axes preferentially perpendicular and parallel to the film plane, respectively. The degrees of (002) and ($\bar{2}$10) uniplanar orientations, achieved by TCE and $CHCl_3$ sorption in unoriented α form films, are similar to the maximum values till now obtained by other techniques, i.e., by TCE solution casting procedures ($f_{002} = 0.75$)[14b] and by DMNP-induced crystallization of amorphous films ($f_{\bar{2}10} = 0.7$), respectively.[14d]

It is worth noting that nanoporous δ form films with (002) orientation, as derived by this TCE-induced recrystallization procedure, are much less brittle than those obtained by the previously known solution casting procedure. Moreover, δ form films with ($\bar{2}$10) uniplanar orientation are more easily obtained by the $CHCl_3$-induced recrystallization of α form films than by the known procedure based on DMNP-induced crystallization in amorphous films.

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