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Perpendicular Chain Axis Orientation in s-PS Films: Achievement by Guest-Induced Clathrate Formation and Maintenance after Transitions toward Helical and Trans-Planar Polymorphic Forms

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ABSTRACT: Guest-induced crystallization of amorphous unoriented syndiotactic polystyrene (s-PS) films can generate oriented clathrate phases with the chain axis of **s**(2/1)2 helicies nearly perpendicular to the film plane. This perpendicular crystalline phase orientation can be maintained after lower temperature annealing procedures leading to the γ form, where the same helical conformation is present, as well as after higher temperatures annealing procedures leading to α and β crystalline forms (where trans-planar rather than helical chains are present). A high degree of orientation can be also maintained after extraction procedures leading to helical nanoporous δ crystalline form. Also guest diffusion procedures producing guest replacements into clathrate phases of s-PS films can leave substantially unaltered their possible orientation. To our knowledge, the achievement of crystalline phase orientation by simple solvent diffusion crystallization into amorphous unoriented thick films is unprecedented.

Introduction

s-PS presents a very complex polymorphic behavior.[1,2] Four different crystalline forms have been described. By melt crystallization procedures both high melting α[3−5] and β[6−8] forms, which are characterized by chains in the trans-planar conformation, can be obtained. By solution crystallization procedures, besides the β form, the thermally unstable γ and δ forms as well as clathrate forms, all including chains in the **s**(2/1)2 helical conformation, can be obtained.[1,6]

In the s-PS clathrate phases, **s**(2/1)2 helices (the host) form a crystal lattice containing spaces in which molecules of a second chemical species (the guest) are located. Semicrystalline samples including clathrate phases can be obtained, by different solution crystallization procedures, which use solvents being suitable as guest of s-PS clathrate phases. For instance, suitable procedures for s-PS clathrate phase formation are precipitation from solutions[1] and casting[6] as well as guest molecule sorption in amorphous s-PS samples or in semicrystalline samples in the α, γ, or δ form.[9,10] For the s-PS clathrate structures, the intensities and the precise locations of the reflections in X-ray diffraction patterns only slightly change with the kind and the amount of the included guest molecules.[1,9] The crystal structures of clathrate phases including, as guest molecules, toluene,[11a] iodine,[11b] or 1,2-dichloroethane,[12] which have been determined with good accuracy, are in fact similar to each other.

It is well-known that by suitable annealing procedures on s-PS clathrate phases, γ and α as well as β phases can be obtained.[1] In particular, γ and α phases are obtained by slow annealing in the temperature ranges 100−170 and 180−250 °C, respectively,[1,9] while the β phase is obtained by annealing at temperatures above 150 °C, when the annealing temperature is suddenly reached.[1]

The δ phase can be obtained from all clathrate phases by suitable guest extraction procedures[13−15] and presents a structure similar to those of the s-PS clathrates, but in place of the guest molecules, it includes two identical cavities/unit cell,[16] whose shape and volume have been thoroughly characterized.[17]

s-PS samples in the nanoporous δ form rapidly absorb as guest into the crystalline phase suitable volatile organic compounds, also if present in traces in water or air.[18,19] Sorption studies have suggested that nanoporous δ form samples are promising for applications in chemical separations as well as in water and air purification.[13,17−19] In particular, thin polymeric films have been suggested as sensing elements of molecular sensors.[20]

Recently, by casting procedures for s-PS polymeric thick film (at least up to 100 μm), two different kinds of preferential orientation of the clathrate phases with respect to the film surface have been obtained: (i) perpendicular orientation of the chain axis;[21] (ii) parallel orientation of the *ac* planes (that is the so-called *ac* uniplanar orientation).[22] The kind of orientation (perpendicular or *ac* uniplanar) is mainly determined by the chemical nature of the casting solvent which, at the end of the casting procedures, remains as guest in the clathrate phase.

In this paper new experimental procedures that induce in s-PS films nearly perpendicular orientation of the chain axes of the s-PS clathrate phases with respect to the film plane are described. Moreover, the possible permanence of crystalline phase orientations, after crystalline phase transitions, produced by suitable thermal or solvent treatments, has been investigated.

Experimental Section

The s-PS used in this study was manufactured by Dow Chemical Co. under the trademark Questra 101, already described in ref 21.

Two sets of films presenting s-PS clathrate phases including different guest molecules (benzene, toluene,

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tetrahydrofuran, 1,2,4-trichlorobenzene, chloroform, 1,2-dichloroethane, trichloroethylene, tetrachloroethylene) have been prepared: (i) nearly 40 μm thick, obtained by casting procedure from 0.5 wt %/wt solution at room temperature; (ii) nearly 100 μm thick, obtained by exposition of extruded amorphous s-PS films to the pure organic compounds for 2 days at room temperature (either by immersion for liquids or by exposition to vapors for solids).

δ semicrystalline films were obtained by extraction procedures from clathrate films by CO_2 at 40 °C and 200 bar for 5 h.[15]

γ and α semicrystalline films were obtained from clathrate films by increasing the temperature ($\approx$2 °C/min) from room temperature up to 170 and 220 °C, respectively, and then maintaining the samples at that temperature for 30 min. β semicrystalline films were obtained by abrupt heating of the clathrate films[1] at 230 °C (by inserting them in an oven hold at that temperature) and then maintaining the films at that temperature for 30 min.

Unoriented samples in Figures 1A–6A were obtained by following procedures of precipitation from solutions, analogous to those described in detail in ref 14.

Wide-angle X-ray diffraction patterns with nickel-filtered Cu Kα radiation were obtained as described in detail in refs 21–22.

The degrees of orientation of the crystalline phases have been formalized on a quantitative numerical basis using Hermans' orientation functions as defined in refs 21–24. In particular, as for the orientation of the chain axes nearly perpendicular to the film plane,

$$f_{c,\mathrm{perp}} = (3\overline{\cos^2 \epsilon} - 1)/2 \qquad (1)$$

and as for the uniplanar orientation,[22,25] corresponding to a preferential orientation of the *ac* crystallographic planes parallel to the film plane,[22]

$$f_{010} = (3\overline{\cos^2 \beta} - 1)/2 \qquad (2)$$

where $\overline{\cos^2 \epsilon}$ and $\overline{\cos^2 \beta}$ are the average cosine-squared values of the angles ϵ and β of the normal to the film surface with the *c* axes and with the normal to the *ac* planes, respectively.

In these assumptions, $f_{c,\mathrm{perp}}$ or f_{010} are equal to 1 if the chain axes or the $0k0$ crystallographic planes (*ac* planes) of all crystallites are perfectly perpendicular or parallel to the film plane, respectively. For the case of random orientation both factors are equal to zero.

Since, in our cases, a θ_{hkl} incidence of X-ray beam is used, the quantity $\overline{\cos^2 \epsilon}$ as well as $\overline{\cos^2 \beta}$ can be easily experimentally evaluated. In particular,

$$\overline{\cos^2 \epsilon} = \overline{\cos^2 \chi_{002}} = \frac{\int_0^{\pi/2} I(\chi_{002}) \cos^2 \chi_{002} \sin \chi_{002}\, d\chi_{002}}{\int_0^{\pi/2} I(\chi_{002}) \sin \chi_{002}\, d\chi_{002}} \qquad (3)$$

$$\overline{\cos^2 \beta} = \overline{\cos^2 \chi_{010}} = \frac{\int_0^{\pi/2} I(\chi_{010}) \cos^2 \chi_{010} \sin \chi_{010}\, d\chi_{010}}{\int_0^{\pi/2} I(\chi_{010}) \sin \chi_{010}\, d\chi_{010}} \qquad (4)$$

where $I(\chi_{002})$ and $I(\chi_{010})$ are the intensity distributions of the (002) and (010) diffractions on the Debye rings as collected by sending the X-ray beam parallel to the film surface and χ_{002} and χ_{010} are the azimuthal angles measured from the equator.

The diffracted intensities $I(\chi_{hkl})$ of eqs 3 and 4 were obtained, in transmission, by using an AFC7S Rigaku automatic diffractometer (with monochromatic Cu Kα radiation) and maintaining an equatorial geometry. Because the collection was performed at constant 2θ values and in the equatorial geometry, the Lorentz and polarization corrections were unnecessary.

Fourier transform infrared (FTIR) spectra were obtained with a Brucker Vector 22 spectrophotometer. The

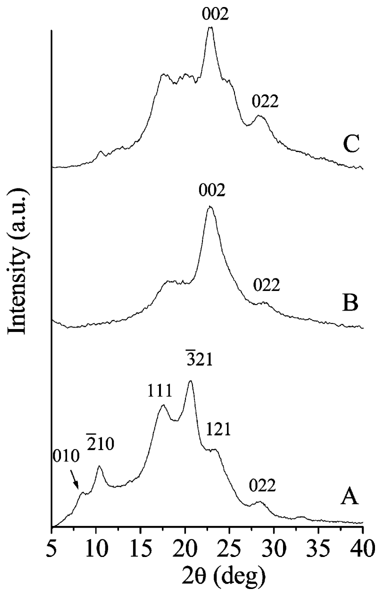

Figure 1. X-ray diffraction patterns obtained with nickel-filtered Cu Kα radiation by an automatic powder diffractometer of s-PS/TCE clathrate powder (A) and s-PS/ TCE clathrate films, obtained by solution casting (B) or by immersion of an amorphous s-PS film in liquid TCE (C). The diffraction peaks have been indexed by a monoclinic unit cell with $a = 17.11$ Å, $b = 12.17$ Å, $c = 7.7$ Å, and $\gamma = 120°$.

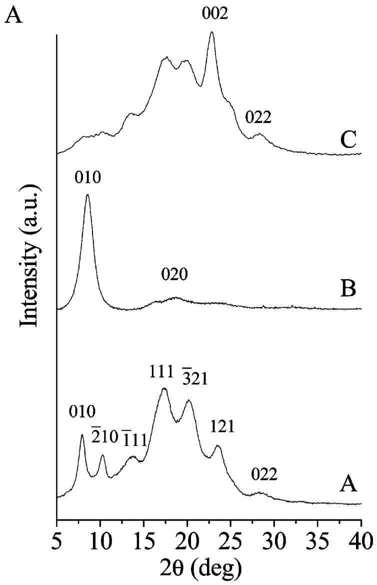

Figure 2. X-ray diffraction patterns of s-PS/benzene clathrate powder (A) and s-PS/ benzene clathrate films, obtained by solution casting (B) or by immersion of an amorphous s-PS film in liquid benzene (C). The diffraction peaks have been indexed by the monoclinic unit cell reported in the literature for the clathrate phase with toluene.[11a]

wavenumber range scanned was 400−4000 cm^{-1} at resolution of 2 cm^{-1}. Typically 32 spectra were signal-averaged in the conventional manner to reduce spectral noise.

Results and Discussion

Film Orientation by Guest-Induced Clathrate Formation. X-ray diffraction patterns obtained by an automatic powder diffractometer of a s-PS/trichloroethylene(TCE) clathrate powder (curve A) and of s-PS/TCE clathrate films, obtained by casting (curve B) or by immersion of an amorphous s-PS film in liquid TCE (curve C) are reported in Figure 1. The diffraction peaks of Figure 1 have been indexed by a monoclinic unit cell with a = 17.11 Å, b = 12.17 Å, c = 7.7 Å (chain axis), and γ = 120°, established by X-ray diffraction fiber patterns and substantially identical with that one observed for the clathrate phase with 1,2-dichloroethane.[12]

As already discussed in ref 21 for cast s-PS/TCE clathrate films, the strong increase of the (002) reflection, associated with a strong decrease of the intensities of all (hk0) reflections (Figure 1B), indicates the occurrence of a crystalline phase orientation with c axes nearly perpendicular to the film plane. Already on inspection of the patterns, it is apparent that the cast film (Figure 1B) has a higher degree of perpendicular orientation with respect to film crystallized by guest diffusion (Figure 1C). In fact, quantitative evaluations of the Hermans' orientation factors give for the two samples $f_{c,\mathrm{perp}} = 0.75$ and $f_{c,\mathrm{perp}} = 0.6$, respectively.

X-ray diffraction patterns obtained by an automatic powder diffractometer of s-PS/benzene clathrate powder (curve A) and of s-PS/benzene clathrate films, obtained by casting (curve B) or by immersion of an amorphous s-PS film in liquid benzene (curve C), are reported in Figure 2. The diffraction peaks of Figure 2 has been indexed by a monoclinic unit cell analogous to that one reported in the literature for the clathrate phase with toluene.[11a]

It is apparent the occurrence of different and strong molecular orientations in s-PS clathrate films obtained by different experimental procedures, as clearly pointed out by the strong variations of the relative intensities of the reflections with respect to the unoriented sample of Figure 2A. In particular, the X-ray diffraction pattern of the cast benzene clathrate film (Figure 2B) shows essentially only (010) and (020) reflections, indicating an orientation of ac planes prevailingly parallel to the film plane, as observed for s-PS films cast from chloroform.[22] The X-ray diffraction pattern of the s-PS/benzene clathrate film obtained by guest-induced crystallization (Figure 2C), which is similar to that one of the s-PS/TCE clathrate film obtained by TCE induced crystallization (Figure 1C), instead indicates the occurrence of a crystalline phase orientation with c axes nearly perpendicular to the film plane ($f_{c,\mathrm{perp}} = 0.6$).

X-ray diffraction characterizations, analogous to those reported in Figures 1 and 2, have been affected for s-PS films presenting clathrate phases including a dozen of different guest molecules. Casting procedures produce oriented films, for all the considered guests, although depending on the selected guest, the kind (perpendicular or uniplanar as for the ac planes) and the degree of orientation are highly variable. In particular, chloroform, benzene, toluene, and tetrahydrofuran induce ac uniplanar orientation whereas trichloroethylene, tetrachloroethylene, 1,2-dichloroethane, and 1,2,4-trichlorobenzene induce perpendicular chain axes orientation.

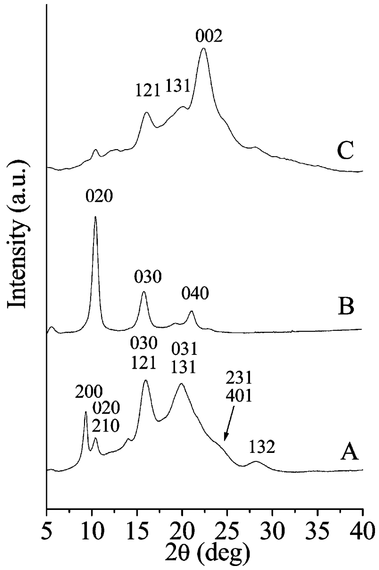

Figure 3. X-ray diffraction patterns of γ semicrystalline samples, obtained by annealing at 170 °C of s-PS/benzene clathrate powder (A) (from sample A of Figure 2), cast s-PS/benzene (B) (from sample B of Figure 2), and cast s-PS/TCE (C) (from sample B of Figure 1) clathrate films. The diffraction peaks have been indexed on the basis of an orthorhombic unit cell with a = 19.15 Å, b = 17.0 Å, and c = 7.7 Å, derived by electron diffraction measurements on single crystals.[22,34]

Completely different behavior is observed for clathrate films obtained by guest induced crystallization on amorphous unoriented films. In fact, for the same dozen of guests, crystalline phase orientations with chain axes nearly perpendicular to the film surface have been observed, independently of the chemical nature of the guest. It is worth noting that annealing procedures (e.g. at 210 °C) on the same amorphous s-PS films induce crystallization in unoriented α crystalline form; this result clearly indicates that the chain axes perpendicular orientation is related to the guest-induced crystallization phenomenon.

It is worth noting that although several detailed studies relative to the guest induced crystallization on amorphous s-PS films have been affected,[26−33] the achievement of this perpendicular chain axis orientation was not previously reported. Moreover, to our knowledge, this would be the first case of crystalline phase orientation simply produced by solvent-induced crystallization on amorphous unoriented polymeric films. A somewhat unexpected result is that this perpendicular guest-induced crystallization of s-PS has been obtained also for unoriented amorphous films of high thickness, at least up to 200 μm.

Crystalline Phase Transitions of Oriented Clathrate Films. (a) Thermal Treatments. X-ray diffraction patterns, of γ semicrystalline samples, obtained by annealing at 170 °C of a s-PS/benzene clathrate powder (Figure 2A) and of s-PS/benzene (Figure 2B) and s-PS/TCE (Figure 1B) clathrate films are reported in Figure 3A−C, respectively. The diffraction peaks of Figure 3 have been indexed on the basis of an orthorhombic unit cell with a = 19.15 Å, b = 17.0 Å, and c = 7.7 Å derived by electron diffraction measurements on single crystals,[34] which is suitable to rationalize diffraction data for γ form samples with ac uniplanar orientation.[22]

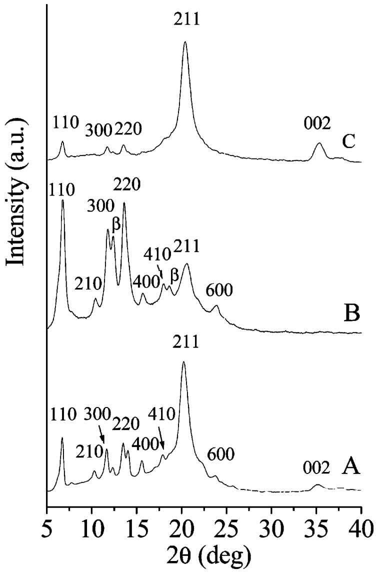

Figure 4. X-ray diffraction patterns, of α form samples, obtained by slow annealing at 220 °C of s-PS/benzene clathrate powder (A), cast s-PS/benzene (B), and cast s-PS/TCE (C) clathrate films. The diffraction peaks have been indexed by the hexagonal unit cell with $a = 26.26$ Å, $b = 5.04$ Å, and $c = 5.1$ Å according to ref 4.

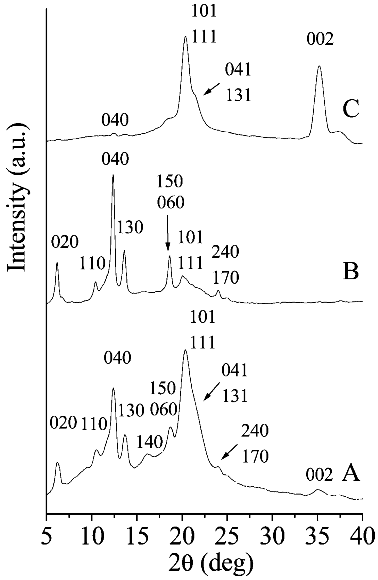

Figure 5. X-ray diffraction patterns, of β form samples, obtained by abrupt annealing at 230 °C of s-PS/benzene clathrate powder (A), cast s-PS/benzene (B), and s-PS/TCE (C) clathrate films. The diffraction peaks have been indexed by the orthorhombic unit cell $a = 8.81$ Å, $b = 28.82$ Å, and $c = 5.1$ Å according to ref 6.

The X-ray diffraction patterns of γ form films obtained by thermal treatments of benzene clathrate cast films (Figure 3B) are very similar to those of annealed s-PS/chloroform cast films (Figure 2C of ref 22) and show the presence of strong (020), (030), and (040) reflections, thus indicating an orientation of the *ac* planes mainly parallel to the film plane.

As for γ films obtained by annealing of s-PS/TCE clathrate cast film (Figure 3C), it is apparent that the strongest reflection (at 2θ =23.0), which is barely detectable as a shoulder for the powder pattern of Figure 3A, can be indexed as (002) (corresponding to the typical *c* value of **s**(2/1)2 vinyl helices, i.e., 7.7 Å). This indicates the maintenance into the γ form film of the orientation with the chain axes nearly perpendicular to the film plane, observed on the starting clathrate film. Quantitative evaluations of the degree of orientation indicate that the γ form film of Figure 3C presents a $f_{c,\mathrm{perp}}$ value not far from the value of the starting clathrate film ($f_{c,\mathrm{perp}}$= 0.75).

X-ray diffraction patterns, of α and β form samples, obtained by slow and abrupt annealing at 220 and 230 °C are reported in Figures 4 and 5, respectively. In particular, samples obtained by annealing of s-PS/benzene clathrate powder and of cast s-PS/benzene and s-PS/TCE clathrate films are shown by curves A−C, respectively. The reflections of the α form samples (Figure 4) have been indexed by the hexagonal unit cell with $a = 26.26$ Å, $b = 5.04$ Å, and $c = 5.1$ Å according to ref 4, while the reflections of the β form samples have been indexed by the orthorhombic unit cell $a = 8.81$ Å, $b = 28.82$ Å, and $c = 5.1$ Å according to ref 6. As for the X-ray diffraction patterns of α and β form films obtained from cast benzene clathrate films (Figures 4B and 5B), it is apparent that the layer line reflections reduce their relative intensities with respect to the equatorial reflections, as already reported for annealed chloroform cast films in Figure 2D−E of ref 22, indicating the tendency of the *c* axes to remain nearly parallel to the film plane (planar orientation according to nomenclature of ref 25).

As for the X-ray diffraction patterns of α and β form films obtained from cast TCE clathrate films (Figures 4C and 5C), it is apparent that all the equatorial reflections reduce their intensities with respect to the layer line reflections, and in particular, the (002) reflection becomes very intense. These data strongly suggest the maintenance of crystalline phase orientation with the chain axes nearly perpendicular to the film plane, also after thermal treatments leading to α and β form films. Particularly strong appears the intensity of the (002) reflections in the β form film (Figure 5C), suggesting that the quick removal of the guest molecules, typical of the abrupt treatment leading to the β phase formation, can maintain more efficiently the orientational order of the starting clathrate film. In fact, quantitative evaluations indicate that, for a starting clathrate film with $f_{c,\mathrm{perp}}$= 0.75, the corresponding α and β form films present $f_{c,\mathrm{perp}} = 0.6$ and $f_{c,\mathrm{perp}} = 0.65$, respectively.

The occurrence of preferential orientations with chain axes nearly perpendicular to the film plane, maintained after annealing procedures leading to γ, α, and β crystalline phases, has been confirmed by additional X-ray diffraction patterns collected with beam parallel to the film plane (see the Supporting Information).

It is worth noting that the maintenance, after crystalline phase transitions, of the *c* axis orientation is not obvious, mainly for the transitions leading to the α and β phases, which involve an irreversible change of the chain conformation from helical to trans-planar. In fact, for clathrate crystal mats obtained by crystallization from dilute ethylbenzene solutions, which present a *c* axis orientation perpendicular to the mat surface, upon annealing leading to a transition toward the α phase, a new lamellar morphology is formed with the chain orientation parallel to the mat surface.[35]

(b) Solvent Treatments. It is well-known that treatments of s-PS clathrate samples by a solvent which is volatile guest of s-PS clathrate phases (like, e.g., carbon dioxide, carbon disulfide, acetone, etc.) allow the achievement of the nanoporous δ phase.[13−16]

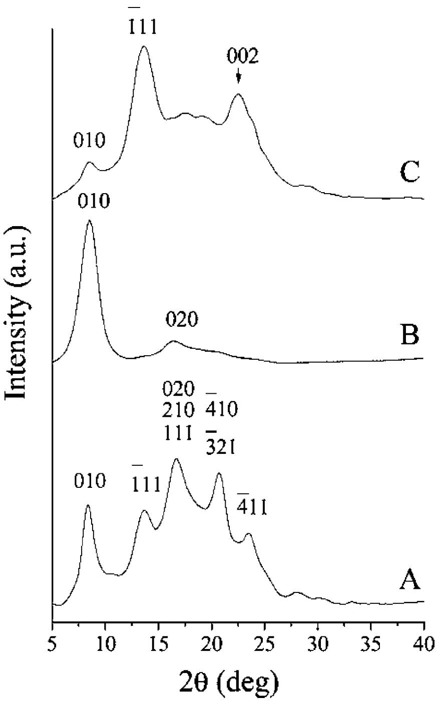

Figure 6. X-ray diffraction patterns, of δ semicrystalline samples, obtained after guest extraction by carbon dioxide treatments of clathrate powder (A), cast film presenting *ac* uniplanar orientation (B) (cast from benzene of Figure 2B), and cast film presenting perpendicular orientation (C) (cast from TCE of Figure 1B). The diffraction peaks have been indexed by the monoclinic unit cell described in ref 16.

X-ray diffraction patterns of δ semicrystalline samples, obtained after guest extraction by carbon dioxide treatments of a clathrate powder, of a cast film presenting *ac* uniplanar orientation (cast from benzene of Figure 2B), and of a cast film presenting perpendicular orientation (cast from TCE of Figure 1B) are reported in Figure 6A−C, respectively.

As described in detail in ref 16, the δ form presents a monoclinic crystal structure ($a = 17.4$ Å, $b = 11.85$ Å, $c = 7.7$ Å, and $\gamma = 117°$) analogous to those of the corresponding clathrate phases. As for the relative intensities of the diffraction peaks, the major differences refer to the increased intensities of the 010 and $(\bar{1}11)$ reflections and the decreased intensity of the $(\bar{2}10)$ reflection (e.g., cf. Figure 6A with Figures 1A and 2A).

The X-ray diffraction pattern of the δ form film obtained by CO_2 treatment of the *ac* uniplanar oriented clathrate film (Figure 6B) is similar to the diffraction pattern of the starting clathrate film cast from benzene (Figure 2B). This confirms that suitable solvent treatments leading to formation of the nanoporous δ phase can maintain the *ac* uniplanar orientation of the starting clathrate phase, as already observed for CS_2 treatments of films cast from chloroform which also present the *ac* uniplanar orientation (Figure 2A,B of ref 22).

The X-ray diffraction pattern of the δ form film obtained from the perpendicularly oriented clathrate film (Figure 6C) is instead markedly different from that one of the s-PS/TCE starting film (Figure 1B). In particular, there is a strong reduction of the (002) reflection and increase of the (010) and mainly of the $(\bar{1}11)$ reflections as expected for the nanoporous δ phase.[16] A quantitative evaluation of the degree of orientation leads to $f_{c,\text{perp}} \cong 0.7$, not far from the orientation factor of the starting cast film ($f_{c,\text{perp}} = 0.75$).

It is also well-known that, by treatments of clathrate s-PS samples with excess of a solvent which is a nonvolatile guest of a s-PS clathrate phase, it is possible to achieve a direct transformation from a clathrate phase with a given guest to a new clathrate phase with a different guest.[36]

In the following, the possible maintenance of the perpendicular and *ac* uniplanar clathrate orientations after solvent treatments leading to guest replacement into s-PS clathrate phase has been studied.

As a first example, X-ray diffraction patterns and FTIR spectra of a perpendicularly oriented s-PS/TCE clathrate film (similar to that one of Figure 1B) and of the same film after treatment with chloroform vapor for 2 days and desiccation at room temperature for 2 weeks are compared in Figure 7. The FTIR spectra clearly indicate a complete replacement of the TCE guest (peaks labeled by g in Figure 7B) with the chloroform guest (peaks labeled by g′ in Figure 7B′). Moreover, as discussed in ref 21, the relative intensity of the absorbance peaks of the polymer helical chains of the clathrate phases[37−40] (e.g., see the higher intensity of the peak at 1320 cm^{-1} with respect to the peak at 1354 and 1278 cm^{-1}) clearly indicates the presence of perpendicular *c* axis orientation for both films. This is also shown by the similarity of the X-ray diffraction patterns of Figure 7A,A′, and in fact, quantitative evaluations of the crystalline phase orientation factor indicate that, by this guest replacement procedure, $f_{c,\text{perp}}$ is reduced from 0.75 to 0.7. This gives the opportunity to obtain s-PS/chloroform clathrate phases with a degree of perpendicular orientation definitely higher than those achieved by the guest diffusion crystallization procedures (typically, $f_{c,\text{perp}} \approx 0.5$).

As a second example, X-ray diffraction patterns and FTIR spectra of an *ac* uniplanar oriented s-PS/chloroform clathrate film and of the same film after treatment with TCE vapors for 10 h and desiccation at 50 °C for 2 weeks are compared in Figure 8. The FTIR spectra clearly indicate a complete replacement of the guest chloroform with the guest TCE and the presence of preferential *ac* uniplanar orientation in both films (e.g., see the higher intensities of the peaks at 1354 and 1278 cm^{-1} with respect to the peak at 1320 cm^{-1}). This is confirmed by the similarity of the X-ray diffraction patterns of Figure 8A,A′, and in fact, quantitative evaluations of the crystalline phase orientation factor indicate that by this guest replacement procedure f_{010} is only slightly reduced with respect to the starting value (0.75). This gives the opportunity to achieve with TCE, which is a solvent producing perpendicular orientation with both casting and guest diffusion procedures, s-PS clathrate phases with a high degree of *ac* uniplanar orientation.

More in general, the results of Figures 7 and 8 show that it is possible to maintain the preferential crystalline phase orientation of the starting sample (both for the cases of *ac* uniplanar and perpendicular orientations) also after guest replacement procedures leading to direct transformations between two different s-PS clathrate phases. Of course, more drastic solvent treatments can strongly reduce the degree of orientation. For instance, for immersion in chloroform at 50 °C for 6 h of the TCE cast film of Figure 1B, the degree of orientation is reduced from 0.75 to 0.5.

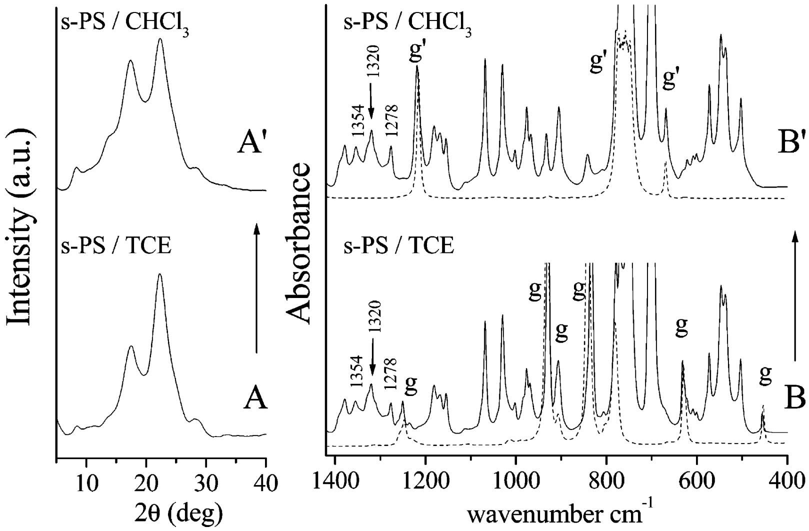

Figure 7. X-ray diffraction patterns and FTIR spectra of a perpendicularly oriented s-PS/TCE clathrate film (A, B) and of the same film after treatment with chloroform vapors (including the s-PS chloroform clathrate phase) (A′, B′). The FTIR peaks of TCE and chloroform guests are labeled as g and g′, respectively. FTIR absorption spectra of liquid TCE and chloroform are shown by dashed lines in B and B′, respectively.

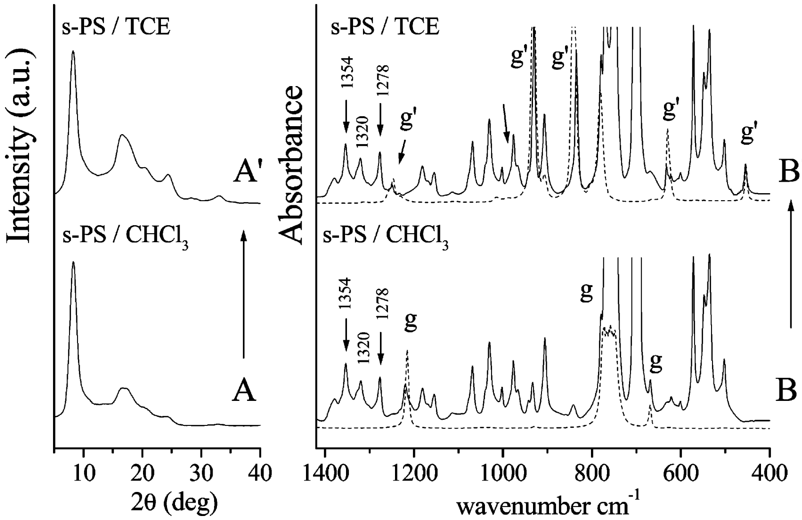

Figure 8. X-ray diffraction patterns and FTIR spectra of an *ac* uniplanar oriented s-PS/chloroform clathrate film (A, B) and of the same film after treatment with TCE vapors (including the s-PS TCE clathrate phase) (A′, B′). The FTIR peaks of chloroform and TCE guests are labeled as g and g′, respectively. FTIR absorption spectra of liquid chloroform and TCE are shown by dashed lines in B and B′, respectively.

Conclusions

Orientation of s-PS clathrate phases with their chain axes nearly perpendicular to the film plane can be easily achieved by guest induced crystallization of amorphous unoriented s-PS films. This phenomenon has been observed not only for guests which, by casting, produce perpendicular orientation (1,2-dichloroethane, trichloroethylene, tetrachloroethylene, 1,2,4-trichlorobenzene) but also for guests which by casting produce *ac* uniplanar orientation (chloroform, benzene, toluene, tetrahydrofuran). The orientation factors of the perpendicularly oriented s-PS clathrate films obtained by guest induced crystallization are generally in the range $0.45 < f_{c,\mathrm{perp}} < 0.6$, which is definitely lower than the maximum values which can be achieved by suitable casting procedures (e.g., for films cast from TCE typically $f_{c,\mathrm{perp}} \approx 0.75$). To our knowledge, the achievement of crystalline phase orientation by simple solvent diffusion crystallization into amorphous unoriented thick films is unprecedented.

Suitable thermal and solvent treatments on perpendicularly oriented films (both from casting and guest-induced crystallization procedures) allow the maintenance of this kind of orientation, and substantially also of the degree of orientation, after crystal phase transitions toward the helical γ and δ phases as well as toward the trans-planar α and β phases.

The precise control of the crystalline phase orientation is particularly relevant for films presenting the nanoporous δ form, since a control of the permeability of small molecules could be in principle possible. In fact, molecular dynamics simulations of diffusion of small molecules into the δ nanoporous phase[41−43] have shown a largely anisotropic behavior.

In this paper, it has also been shown the possibility to maintain the kind of orientation and nearly unaltered the degree of orientation, after guest replacement procedures leading to direct transformations between two different s-PS clathrate phases. This result is particularly relevant since allows the achievement of films, with whatever s-PS clathrate phase, presenting high degrees of *ac* uniplanar or perpendicular orientations. Since each cavity of the clathrate phase generally includes one isolated guest molecule,[11a,12,17,44−45] whose mobility is generally low,[44] the control of the orientation of the host crystalline phase also allows the control of the orientation of the isolated guest molecules.[21,47]

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Supporting Information Available: Text describing X-ray diffraction patterns and a figure showing such patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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