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Nanoporous Polymer Crystals with Cavities and Channels

Vittorio Petraccone,*,† Odda Ruiz de Ballesteros,† Oreste Tarallo,† Paola Rizzo,‡ and Gaetano Guerra*,‡

Dipartimento di Chimica "Paolo Corradini", Università di Napoli "Federico II", Complesso di Monte S. Angelo, via Cintia, 80126 Napoli, Italy, and Dipartimento di Chimica and INSTM Research Unit, Università degli Studi di Salerno, via Ponte Don Melillo, 84084 Fisciano (SA), Italy

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A cheap, commercial, and easy-to-process hydrocarbon polymer (syndiotactic polystyrene, s-PS) can be crystallized in two different nanoporous phases (δ and ε) that show large uptake of several guest molecules and hence are suitable for applications in chemical separations and air/water purification as well as in sensorics. The recently discovered ε phase of s-PS is characterized by channel-shaped cavities crossing the unit cells along the c axis rather than by isolated cavities as observed for the already known δ phase. Guest sorption from the δ and ε nanoporous phases eventually leads to two different classes of polymer cocrystals, where planar guest molecules present their planes roughly perpendicular and parallel to the polymer chain axes. The ε phase channels allow cocrystal formation with guest molecules much longer than the chain axis periodicity and, due to possible reactions between guest molecules, open the possibility to achieve new hybrid materials.

Introduction

The improvement of molecular recognition, separation, and storage techniques represents a strategic industrial and environmental objective. Selective techniques are often based on inclusion of guest molecules into cavities of crystalline materials leading to host−guest cocrystalline phases. The available nanoporous crystalline frameworks can be inorganic (e.g., zeolites),[1–3] metal−organic,[3–6] as well as organic.[7–10]

As for polymers, up to now, only a nanoporous crystalline framework has been reported, i.e., the δ phase of syndiotactic polystyrene (s-PS), a robust and commercial thermoplastic polymer presenting a complex polymorphic behavior.[11,12] This nanoporous δ phase presents two identical cavities per unit cell[13,14] where low-molecular-mass guest molecules are rapidly absorbed, also from very dilute solutions, eventually producing the corresponding cocrystals.[15] Hence, this polymeric framework is suitable for applications in chemical separations and air/water purification[16,17] as well as in sensorics.[18,19] Moreover, the corresponding polymer cocrystals reducing guest diffusivity[20] and imposing guest orientational order[21] have been proposed as advanced materials mainly for optical applications (e.g., photoreactive,[22] chromophore,[23] fluorescent,[24] and non-linear optical[25] materials).

The easy processing (both by solution and melt methods) adds to this polymer crystalline framework the advantage, with respect to the other crystalline frameworks, of easy production of suitable morphologies, such as films,[20,21]

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* To whom correspondence should be addressed. Phone: +39-081-674309 (V.P.); +39-089-969558 (G.G.). Fax: +39-081-674090 (V.P.); +39-089-969603 (G.G.). E-mail: vittorio.petraccone@unina.it (V.P.); gguerra@unisa.it (G.G.).

† Università di Napoli "Federico II".

‡ Università degli Studi di Salerno.

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membranes, and aerogels.[17] However, the presence of isolated cavities has limited the size of the possible guest molecules as well as the possibility of reactions between different guest molecules.

Recently a fifth crystalline phase (named ε) of s-PS has been discovered.[26] The ε phase of s-PS is able to form cocrystals with several polar guest molecules, whose molecular dipoles assume orientation nearly parallel to the polymer chain axes,[26] rather than perpendicular as occurs when the same polar molecules are guests of the nanoporous δ phase.[27] In this paper, guest sorption experiments from dilute aqueous solutions and diffraction studies have allowed to establish that also the ε phase of s-PS is nanoporous and that its porosity is distributed as channels, thus opening the possibility of cocrystal formation with much longer guest molecules and of reactions between guest molecules.

Experimental Section

The s-PS used in this study was manufactured by Dow Chemical Company under the trademark Questra 101. The ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic 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 dispersity index of $M_w/M_n = 3.9$.

s-PS amorphous films, 150−200 μm thick, were obtained by extrusion of the melt with an extrusion head of 200 mm × 0.5 mm. These have been uniaxially stretched at a draw ratio λ = (final length/initial length) ≈ 3, at a strain rate of 0.1 s^{-1}, in the temperature range of 105−110 °C with a dynamometer INSTRON 4301. Films in the crystalline δ form have been obtained by room temperature CS_2 vapor treatments for 48 h of the uniaxially stretched films, followed by thermal treatments at 40 °C under vacuum for 48 h. Films in the crystalline ε form have been obtained by room temperature treatments with liquid chloroform (for 4 h) of γ form films, in turn obtained by annealing at 140 °C of s-PS cocrystalline films. The $CHCl_3$ removal was effected by immersion in acetonitrile for 30 min or by carbon dioxide in supercritical conditions.[28,29] The uniaxially oriented s-PS films, used for infrared dichroism and X-ray diffraction measurements, exhibit a high degree of orientation of the crystalline phases (i.e., a high degree of parallelism of the crystalline chain axes with respect to the stretching direction), corresponding to Herman's orientation factor f_c close to 0.9.

Single s-PS/$CHCl_3$ cocrystals have been obtained by exposing at room temperature thin films (1−10 μm) of amorphous s-PS to chloroform vapors. Amorphous films of s-PS have been prepared by smearing few drops of a dilute solution of the polymer in toluene (0.4 wt %) on a glass slide; after evaporation of the solvent the thin film was heated at 300 °C and rapidly quenched in ice. The thin s-PS/$CHCl_3$ films were sputtered with C−Pt, the cocrystals were then removed from the glass slide using poly(acrylic acid) solution and picked up with copper grids prior to transmission electron microscopy (TEM) observations.

Infrared spectra were obtained at a resolution of 2.0 cm^{-1} with a Vector 22 Bruker spectrometer equipped with deuterated triglycine sulfate (DTGS) detector and a Ge/KBr beam splitter. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He−Ne laser. 32 scans were signal averaged to reduce the noise. Polarized infrared spectra were obtained using a KRS-5 polarizer from Specac. The degrees of crystallinity were evaluated by the FTIR procedure described in ref 30. The content of the guest molecules in the films was determined by the intensity of Fourier transform infrared (FTIR) guest peaks, as calibrated by thermogravimetric (TGA) measurements.

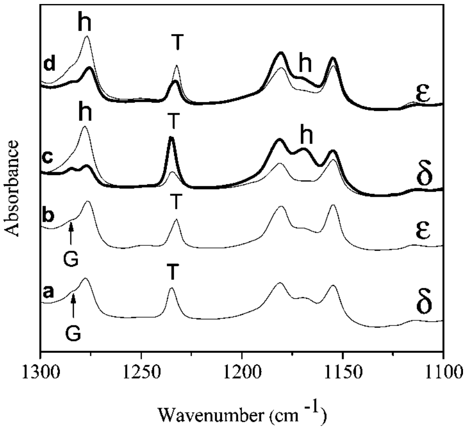

Figure 1. FTIR spectra of δ and ε form uniaxially stretched s-PS films, after DCE sorption from 50 ppm aqueous solutions. Spectra c and d have been taken with *polarized* light parallel (thin lines) and perpendicular (thick lines) to the film stretching direction. Some host peaks are labeled by "h", while two guest (DCE) peaks, corresponding to vibrations of the trans and gauche conformers, are labeled as T and G, respectively.

The X-ray fiber diffraction patterns of oriented samples were obtained on a BAS-MS imaging plate (FUJIFILM) with a cylindrical camera (radius 57.3 mm, Ni-filtered Cu Kα radiation monochromatized with a graphite crystal) and processed with a digital scanner (FUJI-BAS 1800). Calculated intensities were obtained as $I_c = F_c^2 BLp$ where F_c is the calculated structure factor, B is a thermal factor (B = 8 Å^2), and Lp is the Lorentz-polarization factor for X-ray fiber diffraction

$$Lp = \left(\frac{\left(\frac{0.5(\cos^2 2\theta + \cos^2 2\theta_M)}{1 + \cos^2 2\theta_M} + \frac{0.5(1 + \cos 2\theta_M + \cos^2 2\theta)}{1 + \cos 2\theta_M} \right)}{\sqrt{(\sin^2 2\theta - \zeta^2)}} \right)$$

with $2\theta_M = 26.6°$ the inclination angle of the monochromator and $\zeta = \lambda(l/c)$, l and c being the order of the layer line and the chain axis periodicity, respectively, and λ the wavelength of the used radiation (1.5418 Å). Calculated structure factors were obtained as $F_c = (\Sigma|F_i|^2 M_i)^{1/2}$, where M_i is the multiplicity and the summation is taken over all reflections included in the 2θ range of the corresponding spot observed in the X-ray fiber diffraction pattern. Atomic scattering factors from ref 31 were used. The observed intensities I_o were evaluated integrating the crystalline peaks of the ε form obtained by the subtraction of the background, amorphous, and γ form contributions from the X-ray diffraction profile, read along the equatorial layer line reported in Figure 2a′. No correction has been performed for the layer-line X-ray diffraction profiles, due to the high similarity between layer-line reflections of the ε and γ forms.

Electron diffraction patterns of the s-PS/$CHCl_3$ single cocrystals have been obtained with a Philips CM12 at an acceleration voltage of 120 kV.

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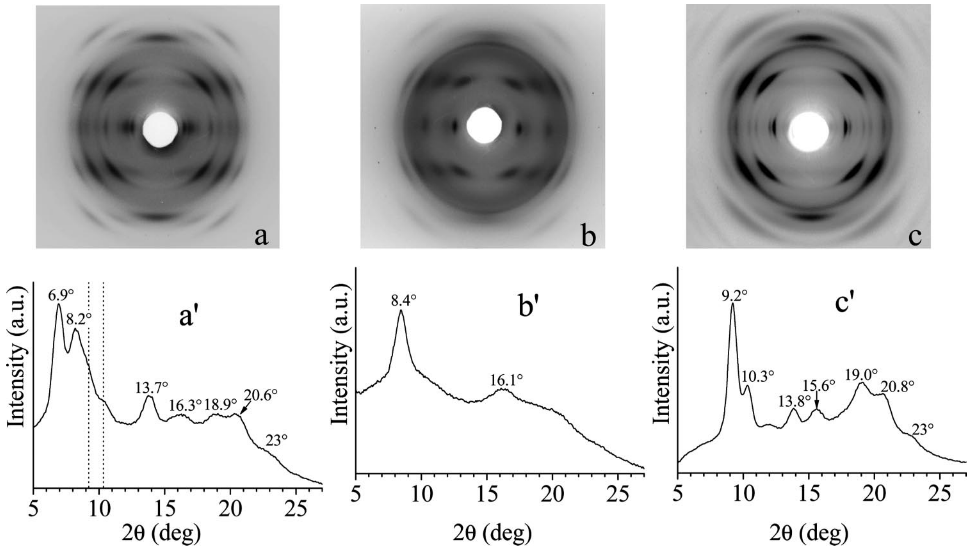

Figure 2. X-ray fiber diffraction patterns of uniaxially oriented samples of s-PS: photographic patterns (a, b, c) and corresponding equatorial profiles (a′, b′, c′) for the ε (a, a′), δ (b, b′), and γ (c, c′) form samples. The dotted lines in a′ at $2\theta = 9.2$ and 10.3° indicate the position of the two strongest reflections of the γ form, present as a shoulder for the ε form sample. The 2θ positions of the peaks are also indicated.

Table 1. Diffraction Angles ($2\theta_0$), Bragg Distances (d_0), and Intensities (I_0) in Arbitrary Units of the Reflections Observed on the Layer Lines (l) in the X-ray Fiber Diffraction Pattern of the Nanoporous ε form of s-PS (Figure 2a)[a]

$2\theta_0$ (deg)	d_0 (Å)	l	I_0[b]
6.90	12.8	0	163
8.20	10.8	0	114
13.7	6.42	0	31
16.3	5.45	0	11
20.6	4.31	0	13
23.0	3.87	0	6
13.1	6.77	1	w
16.1	5.50	1	vs
20.2	4.40	1	s
23.5	3.79	1	mw
24.9	3.57	2	mw
28.2	3.17	2	m

[a] For the equatorial reflections ($l = 0$) the contribution of the γ form has been subtracted. [b] w = weak, m = medium, s = strong, v = very.

Energy calculations were carried out by using commercially available software (*Cerius*^{2} version 4.2 by Accelrys Inc.) using the Compass[32] force field. The energy was minimized using the Open Force Field module by the smart minimizer method with standard convergence. The starting conformation of the s-PS polymer chains was that found by molecular mechanics calculations reported in the literature.[33]

Results and Discussion

The sorption studies have been conducted with 1,2-dichloroethane (DCE), i.e., a contaminant that is present in aquifers and is resistant to remediation techniques based on reactive barriers containing Fe^0.[34] The choice of DCE was also motivated by the additional information, which comes from its conformational equilibrium. In fact, as described in detail in previous papers,[20,35,36] since essentially only its trans conformer is included into the cocrystalline phase while both trans and gauche conformers are included in the amorphous phase, quantitative evaluations of vibrational peaks associated with these conformers allow to evaluate the amounts of DCE confined as guest in the crystalline phase or simply absorbed in the amorphous phase.

FTIR spectra in the range 1300−1100 cm^{-1} of δ and ε uniaxially stretched s-PS films, having a thickness of 0.07 mm after equilibrium DCE sorption from a DCE 50 ppm aqueous solution are shown in parts a and b of Figure 1, respectively. The 1234-cm^{-1} peak, corresponding to the CH_2 wagging vibration of the trans DCE conformer (indicated by T in Figure 1) exhibits a high intensity, while the 1285-cm^{-1} peak, corresponding to the CH_2 wagging vibration of the gauche DCE conformer (G in Figure 1), is barely detectable. It is worth citing that when DCE molecules are absorbed in the amorphous s-PS phase these two peaks present comparable intensities (see, e.g., Figure 1 of ref 37). Hence, the spectra of parts a and b of Figure 1 show that both δ and ε form films absorb from dilute aqueous solution large amounts of the halogenated contaminant (5.0 and 3.5 wt %, for degree of crystallinity of 40 and 35 wt %, respectively) and essentially only as guests of their crystalline phases.

Information relative to the guest orientation with respect to the chain axis (crystallographic c axis) of the host crystalline phases can be easily obtained by FTIR spectra taken with polarized light parallel (thin lines) and perpendicular (thick lines) to the film stretching direction,[25,27] like those shown in parts c and d of Figure 1 for the δ and ε form s-PS films, respectively. The similar dichroism of the host peaks (h in Figure 1) and the opposite dichroism of the guest peak (T in Figure 1) indicate that, as already observed for highly polar guest molecules,[26] the molecular plane of the trans DCE guest tends to assume orientations roughly perpendicular and parallel with respect to the chain axes of

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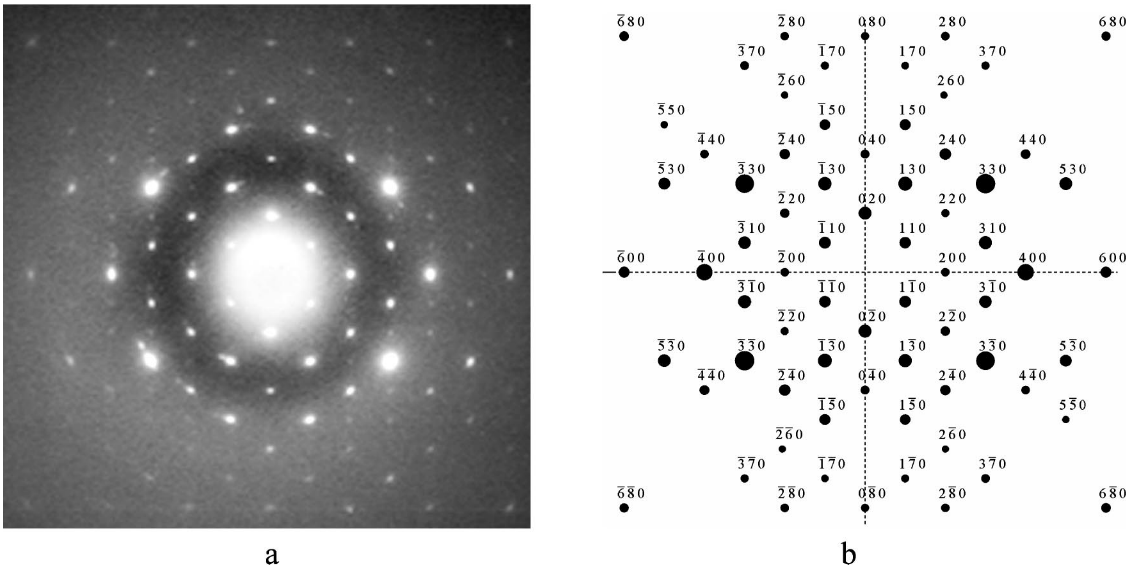
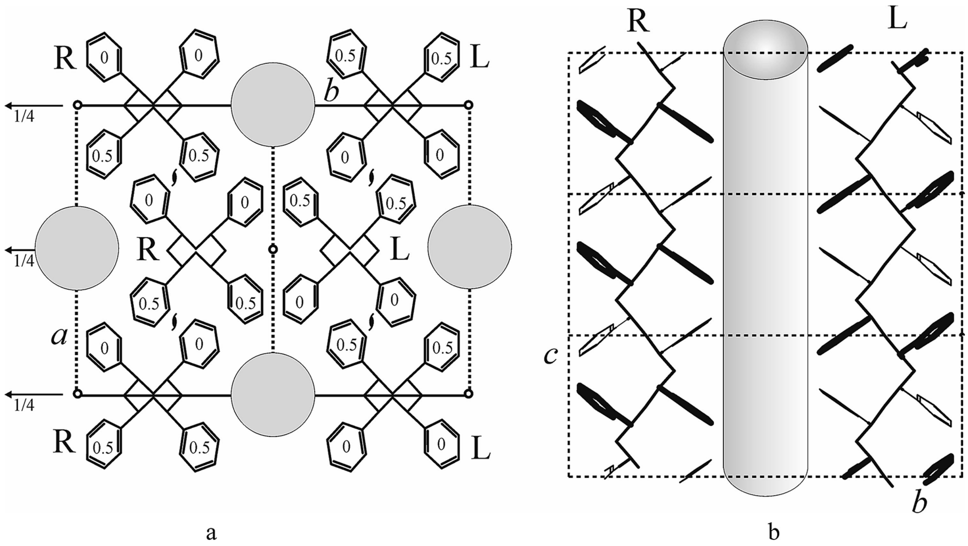


a b

Figure 3. Equatorial electron diffraction patterns of a s-PS/$CHCl_3$ cocrystal: observed (a) and calculated for the model of Figure 4, by assuming 1.1 $CHCl_3$ molecules included in each channel per unit cell (b).



a b

Figure 4. Packing model of the nanoporous ε form of s-PS in the projections along *c* (a) and along *a* (b). All the distances between carbon atoms belonging to neighboring chains are higher than 3.65 Å. In part a the approximated *z* fractional coordinates of the barycentres of the phenyl rings and some crystallographic symmetry elements of the space group (*Pbcn*) are indicated. Grey circles (a) and cylinders (b) indicate the channels where guest molecules can be hosted. In part b the phenyl rings of s-PS helical chains towards the reader are drawn with bold lines, and only a couple of polymer chains delimiting the channel are represented. R = right-handed, *L* = left-handed helical chains.

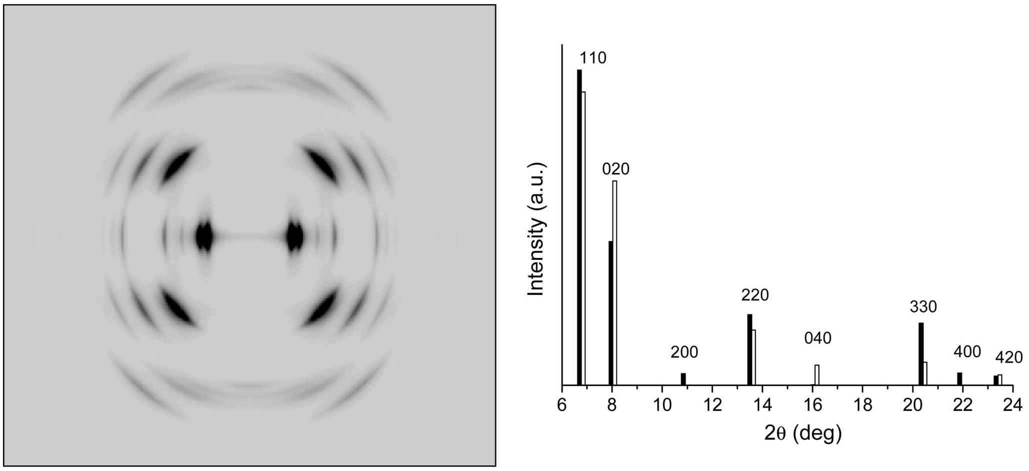
the host δ and ε phases, respectively. This suggests that, while the crystalline cavity of the δ phase presents its shorter extension parallel to the polymer chain axis,[14] the crystalline cavity of the ε phase should exhibit its longer extension parallel to the polymer chain axis.

The X-ray fiber diffraction pattern and the corresponding profile read along the equatorial line of an ϵ form uniaxially oriented s-PS film are reported in parts a and a′ of Figure 2, respectively. For the sake of comparison, the X-ray fiber diffraction patterns of δ and γ form uniaxially oriented films are reported in the same figure.

The intensity and position of the reflections of the ε form, after subtraction of the background and of the amorphous contributions as well as of the contribution of a minor content of γ form (mainly the two shoulders at $2\theta \approx 9$ and 10°, corresponding to the two strongest reflections of γ form of Figure 2c′), are reported in Table 1.

The reflections reported in Table 1 can be interpreted by an orthorhombic unit cell with axes $a = 16.1$ Å, $b = 21.8$ Å, and $c = 7.9$ Å, which matches the equatorial unit cell ($a = 16.2$ Å, $b = 22.0$ Å, $\gamma = 90°$) deduced by the electron diffraction pattern of a single cocrystal of s-PS with chloroform reported in Figure 3a.

In the present structural analysis the orthorhombic cell $a = 16.2$ Å, $b = 22.0$ Å, $c = 7.9$ Å has been assumed for the unit cell of the crystalline ε form. The calculated density is 0.98 g cm^{-3}, with four chains of s-PS in the s(2/1)2 helical conformation included in the unit cell, i.e., very close to the density established for the δ phase[13] and definitely smaller than that one of the amorphous phase (1.05 g cm^{-3}). The space group proposed is *Pbcn*, in accordance with the absence of *hk*0 reflections with $h + k = 2n+1$, supported by the electron diffraction pattern of Figure 3a. The only symmetry element of the isolated s(2/1)2 helical chain



a

b

Figure 5. (a) Calculated X-ray fiber diffraction patterns for the nanoporous ε form of s-PS according to the structural model of Figure 4. (b) Comparison between the experimental equatorial reflections (white rectangles) observed in the X-ray fiber diffraction patterns of the ε form (Table 1) and those calculated (black rectangles) for the model of Figure in the space group *Pbcn*. The *hkl* indices of the reflections according to the orthorhombic unit cell $a = 16.2$ Å, $b = 22.0$ Å, and $c = 7.9$ Å are also indicated. Only the calculated reflections greater than half the lowest experimental one (420) are reported.

preserved in the space group *Pbcn* is a binary axis perpendicular to the chain axis and the structural unit is reduced to two monomeric units. In this space group, two different orientations of the structural unit of s-PS, which differ one each other for a rotation by 90° of the chain around its axis and a translation along z of $^1/_4c$, are feasible. For each of these two orientations packing energy calculations were performed, minimizing the energy with respect to the translation of the structural unit along the b axis. A model of packing in the space group *Pbcn* corresponding to the minimum of the packing energy is shown in Figure 4.

The model of Figure 4 is characterized by channel-shaped cavities crossing the unit cells along the c axis and limited, along the b axis, by two enantiomorphic helical chains. The X-ray fiber diffraction pattern calculated for this structural model is reported in Figure 5a and exhibits a satisfactory agreement with the experimental pattern of Figure 2a. A satisfactory agreement also comes out by the quantitative comparison between the intensities of the experimental and calculated equatorial reflections (Figure 5b).

A further confirmation of the model of Figure 4 has been obtained by placing $CHCl_3$ guest molecules in its channels and by comparing the calculated diffraction patterns with the electron diffraction image of the single s-PS/$CHCl_3$ cocrystal of Figure 3a. The placement and orientation of the chloroform molecules in the channels has been found through molecular mechanics calculations. A good agreement between the experimental electron diffraction pattern (Figure 3a) and the calculated one (Figure 3b) is obtained by assuming 1.1 $CHCl_3$ molecules included in each channel per unit cell.

Figure 6 shows a three-dimensional representation of the cavities of the δ form and of the channels of the ϵ form of s-PS, being empty (a, a′, b, b′) or filled with DCE (a″, b″).

It is apparent that the cavities of the ε crystal structure (Figure 6b) are completely different from those found in the δ crystal structure[13,14] (Figure 6a). The cavities of the δ phase are isolated and delimited mainly by eight parallel benzene rings belonging to two enantiomorphous adjacent helical chains (barycenters of four benzene rings at z and of four benzene rings at $z + 1$),[13,14] and their maximum extension is perpendicular to the polymer chain axis.[14] In

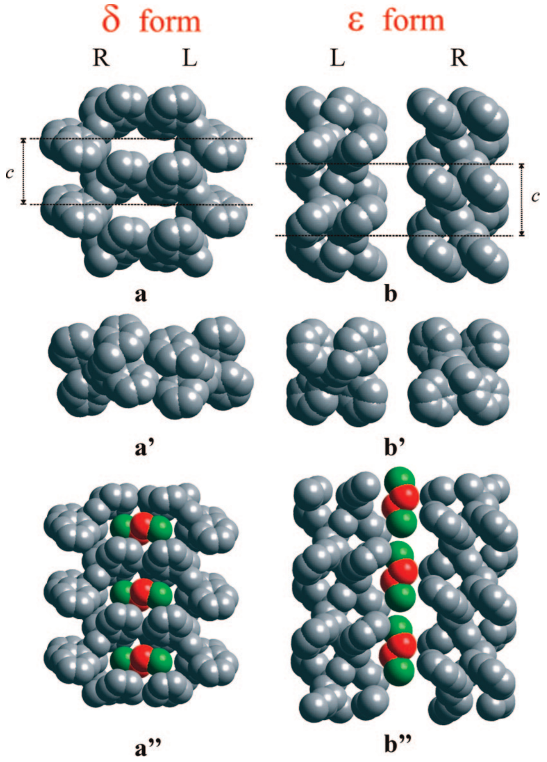


Figure 6. Three-dimensional representation of the cavities of the δ form and of the channels of the ε form of s-PS, being empty (a, a′, b, b′) or filled with DCE (a″, b″). (a, b, a″, b″) Views perpendicular to the chain axis. (a′, b′) View along the chain axis. The spheres represent the van der Waals encumbrance of CH and CH_2 groups and of Cl atoms. In parts a″ and b″ spheres have been slightly reduced for better guest visualization. Both cavities and channels of δ and ϵ forms are delimited by two enantiomorphous chains (R = right-handed, L = left-handed helical chains) but with a different rotation around their chain axis. The molecular plane of the trans conformer of DCE is roughly perpendicular and parallel to the chain axis of the host δ and ε forms, respectively. The guest proximity in the channels of the ε form could be relevant for possible intermolecular reactions.

the δ form unit cell, the number of cavities is equal to the number of chains while the maximum number of guest molecules per cavity is a well defined integer (generally one or two, depending on guest molecular volume).[13,16,21–25] For planar guests, the molecular planes are roughly perpendicular to the polymer chain axis, as shown for instance for the trans conformer of DCE in Figure 6a″.

On the other hand, the ε form presents channels parallel to chain axis that pass through all the crystal. Also these cavities are generated by a couple of s(2/1)2 enantiomorphous helices, but they are rotated at nearly 90° around their chain axis, with respect to the arrangement found for the δ form (cf. parts a′ and b′ of Figure 6). In these channels, planar guest molecules are expected to be hosted with their molecular planes roughly parallel to the polymer chain axis, as shown for instance for the trans conformer of DCE in Figure 6b″. Moreover, the presence of channels easily allows to rationalize the formation of polymer cocrystals with guest molecules presenting a molecular axis much longer than the s-PS chain axis periodicity, e.g., 4-(dimethyl-amino)-cinnamaldehyde), which is not able to form polymer cocrystals with the δ host phase.[26] It is also worth adding that in these channels, in principle, there is no strict requirement of an integer maximum number of guest molecules per unit cell.

Conclusions

Sorption experiments of organic guest molecules from dilute aqueous solutions from semicrystalline s-PS films have shown that the guest solubility, being generally negligible for polymer crystalline phases, is rather high for the ε phase and comparable with that one of the well-known nanoporous δ phase. This clearly indicates that the ε crystalline form is nanoporous. Linear dichroism FTIR measurements on uniaxially stretched s-PS films show that completely different guest orientations are generally imposed by the two different polymeric crystalline frameworks. In particular, for planar guest molecules, molecular planes generally tend to assume orientations roughly perpendicular and parallel to the crystalline chain axis of the δ and ε phases, respectively. X-ray diffraction fiber patterns of ε form samples and electron diffraction patterns of a single cocrystal with chloroform can be interpreted by the model of packing of Figure 4, characterized by channel-shaped cavities crossing the unit cells along the c axis and delimited, along b axis, by two enantiomorphic helical chains.

The ε crystalline phase is the first polymeric framework in which the nanoporosity is organized as channels, rather than as isolated cavities. The easy processing of the polymer should ensure easy production of suitable morphologies and easy recycling, as already established for the δ phase. The presence of crystalline nanochannels allows absorption of guest molecules also having an axis much longer than the polymer chain axis periodicity. Moreover, the guest−guest proximity which can be obtained in the polymer host channels, opens the possibility of reactions between guest molecules and as a consequence opens the possibility to achieve new classes of hybrid materials.

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