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Nanoporous Triclinic δ Modification of Syndiotactic Polystyrene.

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Abstract: For the δ form of syndiotactic polystyrene, a nanoporous triclinic modification, different from the well-established and widely used nanoporous monoclinic modification, is presented. Detailed routes to triclinic or monoclinic modifications, which involve different guest removal procedures from different δ-clathrates, are described and rationalized. Surprisingly, both triclinic and monoclinic δ modifications can be obtained by both triclinic and monoclinic δ-clathrates. The triclinic modification, with respect to the monoclinic one, presents the advantage of higher uptake of pollutants having molecular volume in the range 0.13-0.22 nm^3, mainly when present only as traces in water or in air. In particular, the different molecular selectivity of triclinic and monoclinic δ modifications, favoring *n*-decane and *n*-hexane sorption, respectively, is described. This behavior is attributed to the crystalline cavities of the triclinic δ modification, which are halved in number and increased in volume with respect to those of monoclinic δ modification.

1. Introduction

Nanoporous-crystalline forms[1-9] can be achieved for a large variety of chemical compounds (inorganic, metal-organic as well as organic), generally by removal of low-molecular-mass guest molecules from co-crystalline forms. Materials exhibiting nanoporous-crystalline phases are relevant for several technologies, like e.g. molecular storage, recognition and separation techniques.[1-9]

As for polymers, the removal of the low-molecular-mass guest molecules from co-crystalline forms generally generates host chain rearrangements, leading to dense crystalline forms. However, for two polymers (syndiotactic polystyrene,[10-18] s-PS and poly(2,6-dimethyl-1,4-phenylene ether,[19-25] PPO), nanoporous-crystalline forms, exhibiting densities definitely lower than those of the corresponding amorphous phases, have been obtained.[26,27]

The first polymeric nanoporous-crystalline form, the δ modification of s-PS, was discovered in 1994 and its crystal structure has been thoroughly characterized.[10] Chains in the helical s(2/1)2 conformation are packed in a monoclinic unit cell with axes a = 1.74 nm, b = 1.185 nm, c = 0.77 nm, and γ = 117°, according to the space group P21/a.[10] The calculated density is of 0.98 g cm^{-3}, i.e. definitely smaller than that one of the amorphous phase (1.05 g cm^{-3}). This monoclinic δ modification of s-PS presents isolated cavities having a volume close to 0.12 nm^3 whose number is equal to ¼ of the styrenic units.[10,11,17] In more recent years, a second nanoporous crystalline form of s-PS has been discovered (ε form)[14], which presents an orthorhombic unit cell with axes a = 1.61 nm, b = 2.18 nm and c = 0.79 nm.[15] Its crystal structure is characterized by channel-shaped cavities crossing the unit cells along the c axis,[15] where guest molecules presenting a molecular axis much longer than the s-PS chain axis periodicity can be hosted.[28-34] The packing of the polymer helices of the monoclinic δ and orthorhombic ε nanoporous-crystalline forms are similar to those found for the corresponding monoclinic δ-clathrates[35-40] (e.g., with toluene,[35] iodine,[36] 1,2-dichloroethane[37] or carvacrol[40]) and orthorhombic ε-clathrates[28-34] (e.g. with p-nitro-aniline,[29] TEMPO[30] or azobenzene[32]).

Recently the occurrence of triclinic δ-clathrates of s-PS has been established.[41,42] Triclinic δ-clathrates with guests having molecular volume higher than 0.13 nm^3, like e.g. 1,4-dinitrobenzene (DNB, V_{mol} ≈ 0.134 nm^3) or dibenzofuran (V_{mol} ≈ 0.159 nm^3), are particularly different from the monoclinic δ-clathrates.[41,42] In fact, these triclinic δ-clathrates maintain only one half of the guest locations typical of the monoclinic δ-clathrates, but with an increased volume, and correspondingly the maximum molar ratio between guest molecules and styrenic units decreases from 1/4 down to 1/8.[42] This is shown, for instance, by a comparison between the structures of the triclinic δ-clathrate with DNB[42] (Figure 1A,A') and of the monoclinic δ-clathrate with DCE[37] (Figure 1B,B').

In this paper, we describe a nanoporous triclinic δ modification of s-PS, whose X-ray diffraction pattern is more similar to those of triclinic δ-clathrates[41,42] rather than to that one of the well-known nanoporous monoclinic δ modification.[10-18] We also show that this triclinic modification can be obtained, by suitable guest removal procedures, both from monoclinic[35-40] and triclinic[41,42] δ-clathrates. Guest sorption ability of films exhibiting this new nanoporous triclinic δ modification and the well-established nanoporous monoclinic δ modification has also been compared.

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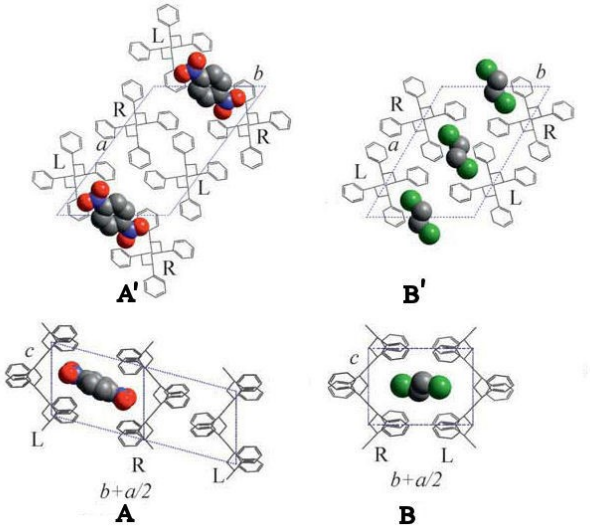

Fig.1. Top and lateral views of the crystalline structures of the triclinic δ-clathrate with DNB[42](A,A') and of the monoclinic δ-clathrate with DCE[37] (B,B'). The number of guest locations of the triclinic δ-clathrate is one half of that one of the monoclinic δ-clathrate. *a*, *b* and *c* are the unit cell parameters of the crystalline structures.

2.Experimental part

The s-PS used in this study was manufactured by Dow Chemical Company under the trademark Questra 101. The ^{13}C NMR 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 Mw = $3.2x10^5$ with the dispersity index Mw/Mn= 3.9.

All the solvents used were purchased from Aldrich and used without any further purification.

Powders exhibiting the triclinic δ-clathrate phase with DNB were obtained by precipitation in acetonitrile of a dichloromethane (DCM) solution with 2wt% of DNB and 2wt% of s-PS. Powders exhibiting the monoclinic δ-clathrate phase with DCM were obtained by precipitation in water of a 3 wt% s-PS solution in DCM.

s-PS films exhibiting the uniplanar a//c// orientation[43-47] were obtained by casting from chloroform solutions.[43] s-PS/DNB δ-clathrate films with uniplanar orientation were obtained by immersion of these cast films in a DNB saturated acetone solution for 18 h and subsequent room-temperature acetone desorption in air, until complete acetone removal (as proved by FTIR measurements).

Axially oriented trans-planar mesomorphic[48-50] films were obtained by uniaxial stretching of amorphous films up to a strain of 300%, with strain rate of 0.1 s^{-1}, in the temperature range 105-110 °C with a dynamometer Instron 4301. Axially oriented δ-clathrate films with DCM and DNB were obtained by immersion of oriented mesomorphic films for 30 minutes in liquid DCM and for 12 hours in a DNB saturated acetone solution.

For guest removal from clathrates, two alternative procedures have been used: i) extraction by supercritical carbon dioxide ($scCO_2$) with a SFX 200 supercritical extractor (ISCO Inc.), generally using the following conditions: T= 40°C, P = 250 bar, extraction time t = 120 min. ii) by immersion in liquid acetonitrile (AN), generally for 4 hours for powders and for 16 hours for films, followed by AN desorption at room temperature.

Fourier Transform Infrared (FTIR) spectra were obtained at a resolution of 2.0 cm^{-1} with a Vertex 70 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. A total of 32 scans were signal averaged to reduce the noise. Polarized infrared spectra were recorded by use of a SPECAC 12000 wire grid polarizer.

The degree of crystallinity was evaluated by FTIR spectra,[51-54] expressed as weight fraction χ_c, according to k = l/l'(1- χ_c), where k is the subtraction coefficient , l and l' are the thickness of the sample and of an amorphous reference film. The l/l' ratio is estimated from the absorbance ratio of a conformationally insensitive peak (at 1601 cm^{-1}).

As far as infrared spectroscopy is concerned, the axial orientation function[55-58] is given by

$$f_{c,IR} = \frac{R-1}{R+2}\,\frac{2\cot^2\alpha+2}{2\cot^2\alpha-1}$$

where $R = A_{//}/A_{\perp}$ is the dichroic ratio, $A_{//}$ and $A_{\perp}$ being the measured absorbance for electric vectors parallel and perpendicular to the draw direction, respectively, and α is the angle between the chain axis and the transition moment vector of the vibrational mode. As usual, an order parameter S can be defined as the ratio:

$$S = (R-1)/(R+2)$$

Wide-angle X-ray diffraction patterns of unoriented samples were obtained with nickel-filtered CuKα radiation with an automatic Bruker D8 Advance powder diffractometer operating in the θ/2θ Bragg–Brentano geometry using specimen holders 2 mm thick. The photographic X-ray diffraction patterns of oriented samples were obtained under vacuum on a BAS-MS imaging plate (FUJIFILM) with a cylindrical camera (radius 57.3 mm, Ni-filtered CuKα radiation monochromatized with a graphite crystal) and the data were processed with a digital scanner (FUJI-BAS 1800). The photographic patterns of

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axially oriented films were collected by rotating the film around its uniaxial stretching direction. The degree of uniplanar orientation of the (010) crystallographic plane with respect to the film plane, has been determined as described in detail in ref.44.

Sorption experiments from dilute aqueous solutions have been conducted at 25 °C on s-PS δ monoclinic and triclinic films after immersion in a 1 L solution being maintained under stirring. The aqueous solutions have been changed every three days. The weight gain of samples was obtained by gravimetric measurements.

3. Results and discussion

3.1 Guest removal from δ-clathrates

Guest removal from monoclinic δ-clathrates has been deeply studied.[59-66] It is well known that guest removal by thermal treatments in the range 80-100°C leads to a progressive transformation toward the dense γ form.[59,60] It is also well established that guest removal by treatments with $scCO_2$, leads to the well known nanoporous monoclinic δ form.[61,62] It is also known, since an early patent and confirmed by many reports, that other volatile guests, like acetone, carbon disulfide or AN, used both as liquid and vapor, can lead to the monoclinic δ form.[63-66] No information is presently available in the literature on guest removal from triclinic δ-clathrates. The present section shows that the structure of the empty δ form of s-PS can depend on the packing (monoclinic or triclinic) of the starting δ-clathrate, on the method used for guest removal (based on AN or $scCO_2$) as well as on the morphology (powder or film) of the clathrate samples.

3.1.1 Clathrate powders.

The X-ray diffraction patterns of powders, exhibiting the monoclinic s-PS/DCM and the triclinic s-PS/DNB δ clathrate phases, are reported in Figures 2a and 2a', respectively. The main difference between the two patterns is the position of the two lower angle peaks being at 2θ≈ 8.25°, 10.3° and 8.6°, 9.8° for the monoclinic and triclinic δ-clathrates, respectively.[42]

The X-ray diffraction patterns of these clathrate powders, after complete guest removal by AN and $scCO_2$, are shown in Figures 2b,b' and Figures 2c,c', respectively. It is apparent that, independently of the used procedure, the guest removal from the monoclinic δ clathrate powder, moves the 010 peak from 2θ ≈ 8.25° up to ≈ 8.4°, leading to the typical pattern of the monoclinic δ form.[10-13] Moreover, again independently of the used procedure, guest removal from the triclinic δ-clathrate powder, moves the 010 peak in the opposite direction (from 2θ ≈ 8.6° up to ≈ 8.8°), thus leading to patterns definitely different from that one of the monoclinic δ modification.

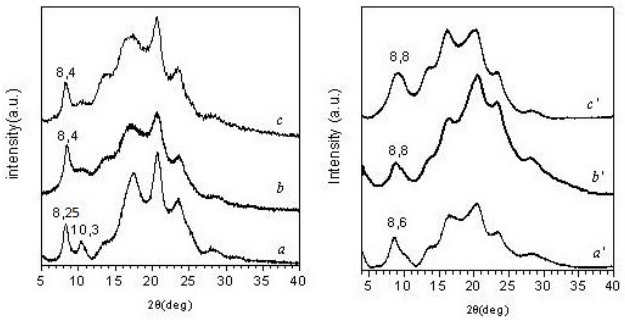

Fig. 2. X-ray diffraction patterns of s-PS powders: (a-c) monoclinic s-PS/DCM δ clathrate; (a'-c') triclinic s-PS/DNB, δ clathrate. (a,a') As prepared; (b,b') after complete guest removal by acetonitrile; (c,c') after complete guest removal by $scCO_2$.

Hence, by guest removal from s-PS powders, monoclinic δ-clathrates lead to the monoclinic δ modification while triclinic δ-clathrates lead to a somewhat different crystalline phase, exhibiting below 2θ < 12° only a broad peak centered at 2θ ≈ 8.8°.

3.1.2 Clathrate films.

As described in previous papers,[43-47] a precise evaluation of the diffraction angle (and hence of the Bragg distance) of the 010 reflection can be easily obtained for films exhibiting the a//c// uniplanar orientation,[43-47] for which the ac layers are preferentially parallel to the film plane. In fact, for this kind of orientation, the 010 reflection is predominant in X-ray diffraction patterns taken by an automatic powder diffractometer. This is shown, for instance, by the X-ray diffraction patterns, as collected by an automatic powder diffractometer, of s-PS films exhibiting the uniplanar a//c// orientation (with a degree of orientation close to 0.75) as obtained by solution casting from $CHCl_3$ (Figure 3). In particular, patterns of films exhibiting the monoclinic s-PS/$CHCl_3$ and the triclinic s-PS/DNB δ-clathrates are shown in Figures 3a and 3a', respectively. The X-ray diffraction patterns of these films, after complete guest removal by AN and $scCO_2$, are shown in Figure 3b,b' and Figure 3c,c', respectively. It is apparent that, contrary to the case of powders, the X-ray diffraction patterns of the empty films are mainly dependent on the guest removal procedure. In fact, for both monoclinic s-PS/$CHCl_3$ and triclinic s-PS/DNB δ-clathrate films, as a consequence of guest removal by AN and $scCO_2$ the 010 peak is located at 8.8° and 8.4°, respectively.

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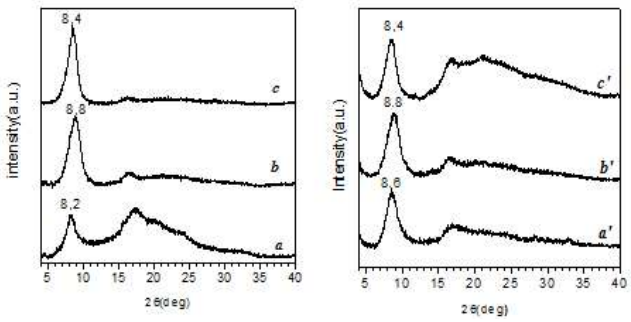

Fig. 3. X-ray diffraction patterns of s-PS films exhibiting a//c// uniplanar orientation: (a-c) s-PS/$CHCl_3$ monoclinic δ clathrate; (a'-c') s-PS/DNB, triclinic δ clathrate. (a,a') As prepared; (b,b') after complete guest removal by acetonitrile; (c,c') after complete guest removal by $scCO_2$

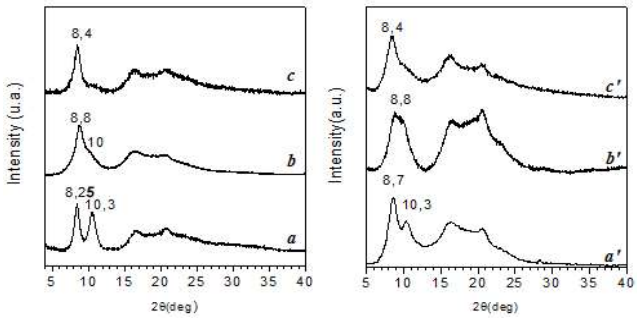

Fig. 4. X-ray diffraction patterns of s-PS films exhibiting *axial* orientation: (a-c) monoclinic s-PS/DCM δ-clathrate; (a'-c') triclinic s-PS/DNB, δ-clathrate. (a,a') As prepared; (b,b') after complete guest removal by AN; (c,c') after complete guest removal by $scCO_2$.

An analogous behavior is observed for films exhibiting different kinds of orientations. For instance, X-ray diffraction patterns of axially stretched s-PS films, as collected by an automatic powder diffractometer, are shown in Figure 4. Both monoclinic s-PS/DCM (Figure 4a) and triclinic s-PS/DNB (Figure 4a') δ clathrate films, after guest removal by $scCO_2$, present typical patterns of axially oriented monoclinic δ modification,[67,68] with a high intensity 010 peak located at $2\theta \approx 8.4°$ and a low intensity $\bar{2}10$ peak roughly located at $2\theta \approx 10.5°$ (Figures 4c and 4c'). Both monoclinic s-PS/DCM and triclinic s-PS/DNB δ-clathrate films, on the contrary, after guest removal by AN, present rather different patterns with 010 peak located at $2\theta \approx 8.8°$ and a shoulder roughly located at $2\theta \approx 10°$ (Figures 4b and 4b'). Hence, the X-ray diffraction patterns of films with uniplanar a//c// orientation (Figure 3) and with axial orientations (Figure 4) confirm the occurrence of a crystalline modification somewhat similar to the known monoclinic δ modification, but with a significant decrease of the Bragg distance (from 1.05 nm down to 1.00 nm) for the peak at lowest diffraction angle, as already shown by X-ray diffraction patterns of powders (Figure 2).

The formation of this anomalous δ modification with $d_{010} \approx 1.00$ nm is determined by the triclinic structure of the starting δ clathrate and by the AN-based guest removal procedure, for powders and films, respectively.

To better understand the effect of temporary AN sorption on the final structure of the δ modification, the X-ray diffraction pattern of δ-clathrate films have been collected immediately after long-term AN treatments. For instance, the X-ray diffraction patterns, as collected by an automatic powder diffractometer, of an axially oriented film with a monoclinic s-PS/DCM δ clathrate phase, before and after 16 hours of room temperature treatment with liquid AN, are shown in Figures 5a and 5b, respectively. The pattern of Figure 5b shows a shift of the 010 peak above $2\theta = 8.5°$, suggesting the formation of a triclinic s-PS/AN clathrate, being only temporary due to the AN guest volatility. In fact, the partial (Figure 5c) and complete (Figure 5d) removal of AN, by simple air exposure at room temperature, leads to a progressive variation of the X-ray diffraction pattern with a shift of the 010 peak up to $2\theta_{010} = 8.8°$.

The formation of a temporary s-PS/AN clathrate is confirmed by the corresponding polarized infrared spectra. In particular, the polarized FTIR spectrum of the axially oriented films of Figure 5a, reported in Figure 5a', shows a high dichroism of the DCM peaks (e.g., the 1266 cm^{-1} peak) and indicates that most DCM molecules are included in the polymer film as guest of the highly oriented crystalline phase. The FTIR spectrum of the AN treated film of Figure 5b, reported in Figure 5b', shows that all the DCM molecules have been removed and the presence of some dichroism of the AN peaks (e.g. the 2252 cm^{-1}, associated to the C-N vibration mode ν_{C-N}),[69] which indicate that a fraction of the AN molecules is guest of the crystalline phase. Also informative is the polarized FTIR spectrum of the film after partial AN desorption, reported in Figure 5c'. It is apparent that, as a consequence of desorption of 30 wt% of the AN molecules from the polymer film, the order parameter of the 2252 peak increases from $S = -0.09$ up to $S = -0.24$. This indicates that, as already observed for many other s-PS guests,[55-57] the AN molecules being guest of the clathrate phase are more strongly retained than those dissolved in the polymer amorphous phase. The whole set of data of Figure 5 indicates that the determinant influence of the AN based guest removal procedure, on the achievement of the empty δ modification with $d_{010} \approx 1.00$ nm, is due to the temporary formation of a s-PS/AN triclinic δ-clathrate. The lack of this effect for s-PS powder is possibly due to the much faster AN sorption and desorption processes. The overall information from the X-ray diffraction patterns of Figures 2-5 clearly indicates that, by suitable guest removal procedures, a new s-PS δ modification, different from the monoclinic one, can be obtained.

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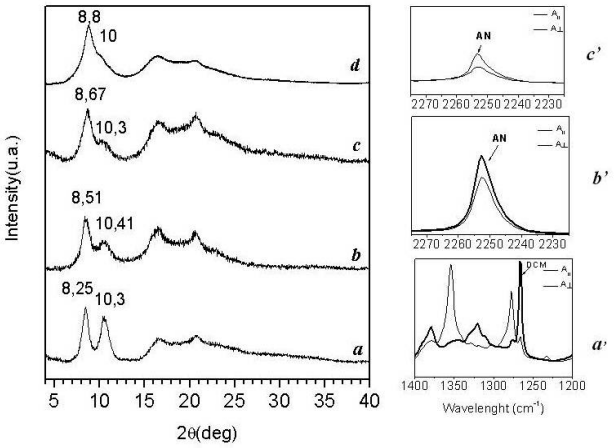

Fig.5 Axially stretched s-PS films exhibiting the monoclinic s-PS/DCM δ-clathrate phase: (a,a') as prepared; (b,b') immediately after equilibrium uptake of AN (triclinic s-PS/AN δ- clathrate); (c,c') after partial AN removal; (d) after complete AN removal (new δ modification). (a-d) X-ray diffraction patterns, as taken by an automatic powder diffractometer; (a'-c') Polarized FTIR spectra, as taken with polarization plane parallel (thin lines) and perpendicular (thick lines) to the draw direction

Detailed information relative to the diffraction of this new s-PS modification has been achieved by fiber patterns. In particular, the X-ray diffraction photographic fiber pattern of the film of Figure 4b, as obtained by guest removal with AN from a monoclinic δ-clathrate, is shown in Figure 6 and the information relative to the observed peaks has been collected in columns 8-10 of Table 1. A strictly similar fiber pattern (not shown) is observed for the film of Figure 4b', as obtained by guest removal by AN from the triclinic δ-clathrate with DNB and the data have been collected in columns 5-7 of Table 1.

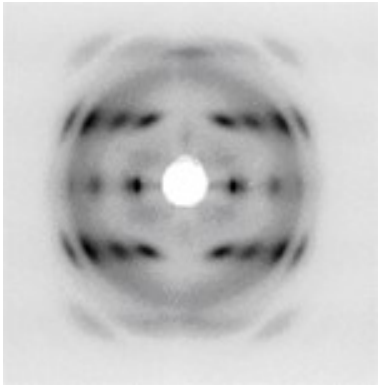

Fig.6 Photographic X-ray diffraction pattern of the s-PS axially oriented film of Figure 4b, as obtained from s-PS/DCM δ clathrate after complete guest removal by AN (exhibiting the new triclinic δ modification). Fiber axis is vertical.

For the sake of comparison, analogous data as taken from the fiber pattern of the triclinic δ-clathrate including DNB have been collected in columns 2-4 of Table 1. Moreover, the diffraction data as taken from fiber patterns of the monoclinic nanoporous δ modification of Figure 4c (as obtained from the axially oriented monoclinic s-PS/DCM δ-clathrate of Figure 4a, after complete guest removal by $scCO_2$) and of ref.10, are also collected in Table 1, columns 11-13 and 14-16, respectively. The last column of Table 1 presents the Miller indexes of the reflections of the monoclinic δ modification, as taken from ref.10.

The data of Table 1 clearly show that the new δ modification of s-PS (columns 5-10) exhibits X-ray diffraction patterns more similar to those of the triclinic δ-clathrate (columns 2-4) rather than to those of the nanoporous monoclinic δ modification (columns 11-16). This is particularly apparent by comparing the *d* spacings of the two equatorial reflections at lowest diffraction angles (010 and $\bar{2}10$, 3rd and 4th rows of Table 1).

3.2 Crystal structure of the new δ modification

FTIR spectra like those of Figure 5 indicate that the conformation of the polymer chains of the new δ modification is s(2/1)2, as already well known for the monoclinic δ form.[70-76]

The X-ray diffraction data reported in section 3.1 show that the new δ modification presents X-ray diffraction patterns characterized by only few and broad reflections suggesting the presence of some disorder. For this reason a complete structural characterization is far from trivial.

From the data reported in Table 1 it is apparent that the new empty modification presents the first two equatorial reflections at lower 2θ angles (indexed in the δ monoclinic form as 010 and $\bar{2}10$)[10] at significantly different positions with respect to the monoclinic δ modification. A slightly lower diffraction angle is observed also for the reflection on the first layer line (indexed as 111 in the δ monoclinic form)[10] whose position, as shown for several δ clathrates of s-PS, is strictly related to the value of the α angle of the unit cell.[41,42]

Similarly to the case of the recently described triclinic δ clathrates of this polymer,[41,42] these differences suggest that also this new empty δ modification could present a triclinic unit cell. In particular, we hypothesize two different limit structures: i) the triclinic model of the s-PS/NA δ clathrate,[41] when deprived of the guest, i.e. containing two guest locations per cell; ii) the triclinic model of the s-PS/DNB δ clathrate,[42] when deprived of the guest, i.e. with only one guest location per cell.

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Table 1. Diffraction angles (2θ), Bragg distances (d) and relative intensities (I) of the reflections on the layer lines (l) of X-ray fiber patterns of axially oriented s-PS films, exhibiting the triclinic δ clathrate with DNB, the triclinic δ nanoporous modification (as obtained by two different routes) and the monoclinic δ modification (as obtained by two different routes). Miller indexes of reflections of the monoclinic δ modification are taken from ref. 10.

l	Triclinic δ clathrate with DNB			Triclinic δ modification By AN extraction of triclinic clathrate with DNB			Triclinic δ modification By AN extraction of monoclinic clathrate with DCM			Monoclinic δ modification By $scCO_2$ extraction of monoclinic clathrate with DCM			Monoclinic δ modification [2a]			hkl δ[2a]
	2θ (deg)	d(nm)	I	2θ (deg)	d(nm)	I	2θ (deg)	d(nm)	I	2θ (deg)	d(nm)	I	2θ (deg)	d(nm)	I	
0	8.7	1.02	s	8.65	1.02	vs	8.7	1.02	vs	8.4	1.06	vs	8.4	1.06	vs	010
0	9.7	0.91	s	9.85	0.90	w	9.95	0.89	w	10.4	0.85	vw	10.6	0.83	vw	$\bar{2}10$
0	-			-			-			11.5	0.77	vw	11.5	0.77	vw	200
0	15.8	0.56	mw	16.05	0.55	w	16	0.55	w	15.4	0.58	mw	15.0	0.59	w	$\bar{2}20$
0	18.8	0.47	mw							16.7	0.53	mw	17.0	0.52	w	020 210
0	20.1	0.44	mw	20.5	0.43	w	20.5	0.43	w	20.6	0.43	mw	20.8	0.43	w	$\bar{4}10$ $\bar{4}20$
1	13.4	0.66	s	13.5	0.66	vs	13.3	0.67	vs	13.6	0.65	vs	13.4	0.66	vs	101 $\bar{1}11$
1	16.2	0.55	vs	16.35	0.54	s	16.3	0.54	s	16.7	0.53	ms	16.8	0.53	ms	111
1	19.6	0.45	s	20.6	0.43	vs	20.65	0.43	vs	20.8	0.43	s	20.7	0.43	s	211 301 $\bar{3}21$
1	23.0	0.39	m	23.3	0.38	m	23.35	0.38	m	23.7	0.38	s	23.5	0.38	s	$\bar{4}11$ $\bar{4}21$
2	24.5	0.36	w	24.3	0.37	w	24.3	0.37	w	24.8	0.36	mw	24.8	0.36	mw	$\bar{1}02$ $\bar{1}12$ 012 $\bar{2}12$ 202 112
2	28.5	0.31	w	28.6	0.31	w	28.3	0.32	w	28.7	0.31	vw	28.7	0.31	vw	212 302 $\bar{3}22$

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Due to the limited number of reflections, the determination of a unit cell accounting for the experimental data was far to be unique. However, for both triclinic structural hypotheses, we have chosen two unit cells accounting for all the reflections of Table 2: for the model containing two guest locations per cell, a = 1.84 nm, b = 1.17 nm, c = 0.77 nm, α = 93°, β = 90° and γ = 120.6°, while for the model with only one guest location per cell, a = 1.77 nm, b = 1.30 nm, c = 0.77 nm, α = 99°, β = 90° and γ = 128°.

Schematic presentations of two plausible crystalline structures for the new δ modification of s-PS, exhibiting triclinic unit cells with one or two guest locations, are shown in Figures 7B and 7C, respectively.

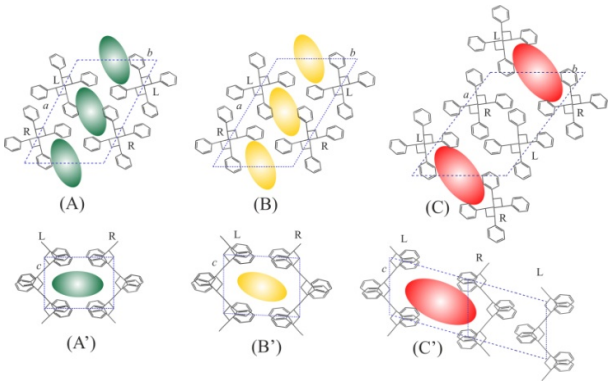

Fig. 7. Schematic projections perpendicular to the chains (A,B,C) and along the chains (A',B',C') of s-PS δ crystalline modifications: (A, A') monoclinic, structure of ref.10; (B,B') triclinic, with two guest locations per cell (cell parameters a = 1.84 nm, b = 1.17 nm, c = 0.77 nm, α = 93°, β = 90° and γ = 120.6°); (C, C') triclinic, with only one guest location per cell (cell parameters a = 1.77 nm, b = 1.30 nm, c = 0.77 nm, α = 99°, β = 90° and γ = 128°). The cavities where guest molecules can be hosted are reported as colored ellipses.

3.3 Guest sorption experiments

A well established criterion to define as *nanoporous* a given polymer crystalline form consists in guest uptakes for semicrystalline samples being higher than for corresponding fully amorphous samples.[10-18,26,27]

As for s-PS, particularly informative are sorption experiments of 1,2-dichloroethane (DCE) from aqueous dilute solutions. In fact, for this guest, additional information comes from its conformational equilibrium, because essentially only its *trans* conformer is included into the δ and ε clathrate phases while both *trans* and *gauche* conformers are included in the amorphous phase.[51,77,78] Hence, quantitative evaluations of vibrational peaks associated with these conformers allow evaluating the amounts of DCE confined as guest in the clathrate phase or simply absorbed in the amorphous phase.[51,77,78]

DCE uptakes from dilute aqueous solutions for the new triclinic δ modification are close to those of the monoclinic δ modification and hence much higher than those of amorphous PS phases. For instance, the room-temperature DCE uptake from 50 ppm aqueous solutions after 8 days, from axially oriented films having a thickness of nearly 50 μm and degree of crystallinity of nearly 25%, is close to 1.5 wt%, both for films exhibiting the new and the monoclinic modifications (like those of Figure 4b and 4c, respectively). In the same conditions, the DCE uptake is negligible for amorphous s-PS (or atactic-PS) films presenting analogous thickness.

Moreover, as already observed for both nanoporous-crystalline (monoclinic δ[34,77,78] and orthorhombic ε forms),[15,34] also for films exhibiting the triclinic δ modification the DCE molecules for low concentrations are absorbed essentially only as *trans* conformer. This clearly indicates that most absorbed DCE molecules are guest of the crystalline phase. Hence, both sorption and conformational analyses of DCE, in films exhibiting the triclinic δ modification, clearly indicate its nanoporous nature.

The occurrence of largely different sorption behaviors of the triclinic δ modification with respect to the monoclinic one can be shown, for instance, by considering different *n*-alkanes.[79-84] In particular, we have compared sorption of *n*-hexane and *n*-decane, i.e. of guest molecules exhibiting molecular volume similar (0.128 nm^3) and definitely larger (0.194 nm^3) than that one of the cavity of the monoclinic δ modification (≈ 0.12 nm^3)[11] and forming with s-PS a monoclinic and a triclinic δ clathrate,[83] respectively.

Sorption experiments of *n*-hexane and *n*-decane from 100 ppm aqueous solutions, in axially oriented s-PS films of similar thickness (≈ 21μm) and similar crystallinity, but exhibiting the monoclinic or the triclinic δ modification, are compared in Figure 8A. For the δ monoclinic modification (blue thin curves), the maximum uptake of *n*-hexane (9.0 wt%) is definitely higher than of *n*-decane (4.5 wt%). This result can be easily rationalized by the crystalline cavity volume smaller than the *n*-decane molecular volume. For the δ triclinic modification (red thick curves), on the contrary, the maximum uptake of *n*-hexane (1.6 wt%) is much lower than of *n*-decane (7.0 wt%), possibly due to a reduction of crystallinity degree after prolonged *n*-hexane sorption time. It is worth adding that similar sorption experiment of *n*-decane and *n*-hexane from 100 ppm aqueous solutions, were performed with amorphous s-PS films of similar thickness and the maximum uptake was 1.3 wt%.and 1.0 wt% respectively (black dashed curves in Figure 8A).

Because, for sorption experiment from dilute solutions, guest molecules of s-PS samples are preferentially hosted

as guest of the nanoporous crystalline phases,[10-18,51-54] beside the guest weight uptake (Figure 8A), also the guest molar uptake per mol of styrenic unit of the crystalline phases is reported (Figure 8B). It is apparent, that the maximum molar uptake of *n*-hexane in the monoclinic modification is nearly double than the *n*-decane molar uptake in the new modification. Moreover, these maximum molar ratios are not far from 1/4 and 1/8, i.e. the guest/host molar ratios of monoclinic δ clathrate with n-hexane [79,81] and of triclinic δ clathrate with n-decane [83] respectively.

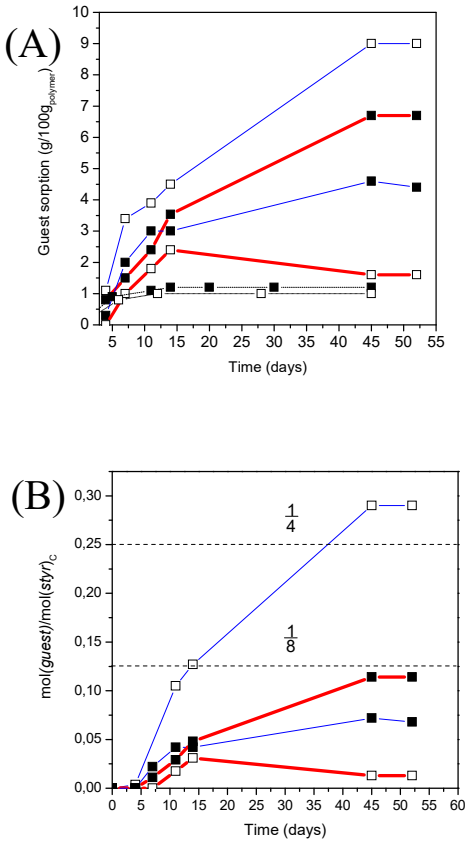

Fig. 8. Sorption kinetics of *n*-hexane (empty squares) and *n*-decane (filled squares) from 100 ppm aqueous solutions in axially oriented s-PS δ-form films, with a thickness of ≈ 21μm and degree of crystallinity of nearly 33%, exhibiting monoclinic (blue thin lines) and triclinic (red thick lines) crystalline modifications: (A) Guest weight uptake, expressed as grams of guest per 100 grams of polymer; (B) Guest molar uptake, expressed as mol of guest per mol of styrenic units of the polymer crystalline phase. In A the *n*-hexane and *n*-decane sorption in amorphous s-PS films of similar thickness is shown for comparison.

The whole set of data of Figure 8 clearly suggests that the selectivity of the triclinic δ modification of s-PS, favoring the sorption of *n*-decane with respect to *n*-hexane, being opposite with respect to that one observed for the monoclinic δ modification, is due to the presence in the triclinic modification of larger cavities, whose number is nearly halved with respect to the cavities of the monoclinic modification.

Hence, on the basis of the *n*-alkane sorption data, the triclinic empty structure of Figure 7C,C', with only one cavity per unit cell, appear to be definitely more realistic than the alternative structure with two cavities per unit cell of Figure 7B,B'.

4. Conclusions

A triclinic δ modification of s-PS, whose X-ray diffraction pattern is more similar to those of triclinic δ clathrates[41,42] rather than to that one of the well-known monoclinic δ modification,[10-18] is presented. Distinctive features of this new δ modification, with respect the monoclinic one, are a reduced number of equatorial reflections and the location of the peak at lowest diffraction angle at $2\theta_{CuK\alpha} \approx 8.8°$ rather than at $2\theta_{CuK\alpha} \approx 8.4°$ (Table 1).

For s-PS powders, the triclinic modification can be obtained starting from triclinic δ-clathrates, independently on the used guest removal procedure. For films, the triclinic modification can be instead obtained starting from both triclinic and monoclinic δ-clathrates. In this case the formation of the triclinic modification is mainly due to the guest removal procedure, which has to be based on a solvent (like acetonitrile), which tends to form a temporary triclinic δ-clathrate with s-PS.

Sorption and conformational studies of absorbed DCE molecules, being present in traces in water, clearly show that the triclinic δ modification (as the known monoclinic δ modification) is nanoporous, i.e. is characterized by permanent crystalline cavities. However, the molecular selectivity of the new triclinic δ modification is largely different with respect to the selectivity of the well-established monoclinic δ modification.[10-18] In fact, the triclinic modification presents lower uptakes of guests that well fit the cavities of the monoclinic modification (≈0.12 nm^3) while higher uptakes of molecules with a molecular volume in the range 0.13-0.20 nm^3. For instance, for sorption experiments of traces in water, the uptake of *n*-hexane is much higher for the monoclinic modification while the uptake of *n*-decane is much higher for the triclinic modification.

These sorption tests with *n*-alkanes of different molecular volumes are clearly in favour of a structural hypothesis, with the triclinic unit cell exhibiting only one cavity (Figures 7C,C'). In fact, the sorption data well agree with a unit cell with crystalline cavities halved in number (going from 1/4 to 1/8 of the styrenic units of the cystalline phase) but increased in volume, with respect to those of the well-known monoclinic cell (Figures 7A,A').

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The largely different molecular selectivity of the new triclinic nanoporous δ modification, with respect to the monoclinic one, will possibly increase applications of s-PS based materials in molecular separations.

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Graphical Abstract