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FTIR spectra of pure helical crystalline phases of syndiotactic polystyrene

Alexandra R. Albunia [a,*], Pellegrino Musto [b], Gaetano Guerra [a]

[a] Dipartimento di Chimica, Università degli Studi di Salerno, via S. Allende, 84081 Baronissi (SA), Italy
[b] Institute of Chemistry and Technology of Polymers, National Research Council of Italy, via Campi Flegrei 34, 80078 Pozzuoli (Na), Italy

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Abstract

By quantitative evaluation of the spectral changes associated with guest removal from clathrate films as well as by infrared dichroism measurements on uniaxially oriented films, three infrared absorbance peaks (at 1379, 1154 and 841 cm^{-1}) prevailingly associated with the amorphous phase have been located for syndiotactic polystyrene (s-PS) samples with helical crystalline phases. A detailed study relative to the infrared peaks in the wavenumber range 870–820 cm^{-1}, corresponding to phenyl C–H out-of-plane bending, has shown that the 841 cm^{-1} peak is fully associated with conformationally disordered sequences only for samples including trans-planar crystalline phases (α and β) but not for samples including helical crystalline phases (γ, δ and clathrates). This result has been rationalized on the basis of different intermolecular interactions between phenyl rings, occurring for trans-planar and helical s-PS crystalline phases. Moreover, a preparation procedure leading to fully unoriented films has been described for helical semicrystalline films, which generally present different kinds of uniplanar orientation. FTIR spectra of these fully unoriented semicrystalline films, by subtracting out the amorphous phase contribution with a procedure based on the 1379 cm^{-1} peak, have allowed a straightforward isolation of the spectra of the helical s-PS crystalline phases and the quantitative determination of the amorphous content.

Keywords: Syndiotactic polystyrene; Unoriented helical crystalline phases; Degree of crystallinity

1. Introduction

Syndiotactic polystyrene (s-PS) is characterized by a complex polymorphic behavior, which, making some simplifications, can be described in terms of two crystalline forms, α and β, containing planar zigzag chains and two forms, γ and δ, containing s(2/1)2 helical chains generated by TTGG conformational serquences [1].

Moreover, by solution crystallization or by sorption of suitable compounds (e.g. methylene chloride, toluene, chloroform, etc.) in amorphous s-PS samples as well as in samples in the α, γ or δ form, clathrate crystalline phases, always containing s(2/1)2 helical chains, can be obtained [1–7]. As a consequence of suitable treatments [8–10], guest molecules can be removed and all clathrate phases can be transformed into the nanoporous δ phase [11].

The δ form presents in place of the guest molecules two identical cavities per unit cell [11], whose shape and volume have been thoroughly characterized [12], and presents a very low density (0.98 g/cm^3), also lower than the density of the amorphous phase (1.05 g/cm^3) [11]. Sorption studies have shown that the nanoporous δ form rapidly and selectively absorbs, both from solutions [13–16] and gas phase [9,17–20], molecules of suitable volatile organic compounds even at very low activities, thus transforming into the corresponding clathrate forms. Hence, it has been suggested that this thermoplastic material is promising for applications in chemical separations and air/water purification [13–19], as well as in sensorics [20].

Several Fourier transform infrared (FTIR) studies of the different crystalline [21–33] and clathrate [13,17,25,34–42] phases of s-PS have been reported in the literature. These studies have clearly established characteristic absorption peaks of the trans-planar conformation which occurs for α and β as well as of the s(2/1)2 helical conformation, which occurs for γ and δ crystalline phases and in all s-PS molecular complex phases [1].

As for the crystalline forms including trans-planar chains, a number of structural order effects has been identified and spectral subtraction analyses on FTIR spectra have allowed to isolate the spectra of the pure hexagonal α and orthorhombic β crystalline phases. As a consequence FTIR spectral subtraction

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* Corresponding author. Tel.: +39 89 965362; fax: +39 89 965296.
E-mail address: aalbunia@unisa.it (A.R. Albunia).

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analyses [32,43–46] allow an easy evaluation of the degree of crystallinity and of the amount of α and β phases (often simultaneously present in melt-crystallized samples). As discussed in detail in Ref. [32], spectral subtraction procedures are made straightforward by the presence of the low absorption peak centered at 841 cm^{-1}, which upon crystallization is shifted to higher frequencies. In fact, its exact position was found to depend on the crystalline phase α or β as well as on the degree of perfection of crystallites (that is on the occurrence of α' or α'' modifications [1]) and the shifts are large enough (from 11 up to 17 cm^{-1}) to afford spectroscopic resolution of the amorphous and the crystalline components.

Recently, by following the approach developed earlier for the α and β forms, an attempt to isolate the spectrum of the pure crystalline monoclinic δ phase has been reported [17]. However, in that case, application of difference spectroscopy was not straightforward, not only owing to the difficulty of identifying well-resolved purely amorphous peaks [17] but also due to the not fully recognized presence of uniplanar orientation of the crystalline phase. In fact, recent studies have pointed out the nearly general occurrence of uniplanar orientation (of three different kinds) [47–51] for clathrate phases as obtained by solution casting [47,48] and by solvent induced crystallization procedures [49–51] (as well as for the derived δ and γ crystalline phases) [48–51], which produce large variations of relative intensities of infrared absorbance peaks [49,50]. It is also worth noting that these kinds of uniplanar orientation are present in most s-PS films presenting helical crystalline phases, whose spectra have been reported in the literature [17,21–42].

In this paper, an analysis aimed at identifying possible amorphous peaks, for helical semicrystalline samples of s-PS, has been afforded by quantitative evaluations of the spectral changes associated with guest removal from clathrate phases in different conditions (Section 3.1), and by linear infrared dichroism measurements on uniaxially oriented s-PS films (Section 3.2). In the central part of the paper the achievement of films including fully unoriented γ, δ and clathrate s-PS phases is described (Section 3.3). These unoriented semicrystalline films can be used for easier FTIR spectral subtraction procedures. In fact, in the final section of the paper, we have isolated the spectra of the pure crystalline γ and δ phases from those of semicrystalline unoriented films, by subtracting out the contribution of the amorphous phase (Section 3.4), as established on the basis of the results of Sections 3.1 and 3.2.

2. Experimental section

2.1. Materials

Syndiotactic polystyrene was supplied by Dow Chemical under the trademark Questra 101. ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic polystyrene triads was over 98%. The weight-average molar mass obtained by gel permeation chromatography (GPC) in trichlorobenzene at 135 °C was found to be $M_\mathrm{w}=3.2\times10^5$ with the polydispersity index, $M_\mathrm{w}/M_\mathrm{n}=3.9$.

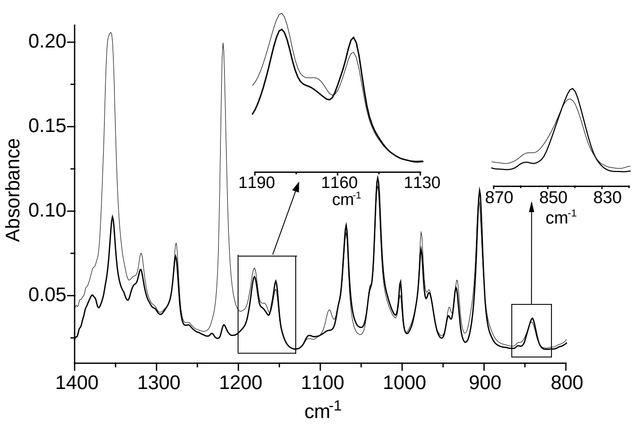

Fig. 1. FTIR spectra for the spectral range 1400–800 $\mathrm{cm}^{-1}$of: (thin line) a s-PS/acetone clathrate film with an acetone content close to 15 wt%; (thick line) a nanoporous δ form film, obtained after 1 day of acetone desorption at room temperature.

The s-PS/acetone films whose FTIR and WAXS spectra are reported in Figs. 1 and 2 were obtained by casting at room temperature from 5 wt % solutions in chloroform. The cast films were subsequently immersed in acetone for 3 h and then allowed to desorb in air for few minutes, before measurements.

The s-PS/1,2-dichloroethane (DCE) clathrate films of Figs. 4 were prepared by DCE absorption into a nanoporous δ form film from a 0.5 wt% DCE aqueous solution. The DCE amount sorbed at equilibrium was 8.0 wt%. In turn, the δ form film was prepared from a chloroform cast films, after treatment with boiling acetone for 5 h followed by desiccation at 60 °C for 2 h.

Both s-PS/acetone and s-PS/DCE clathrate films, as well as the corresponding δ form films, present a degree of uniplanar orientation (*ac* plane tendentially parallel to the film surfaces [47,48]) close to 0.7.

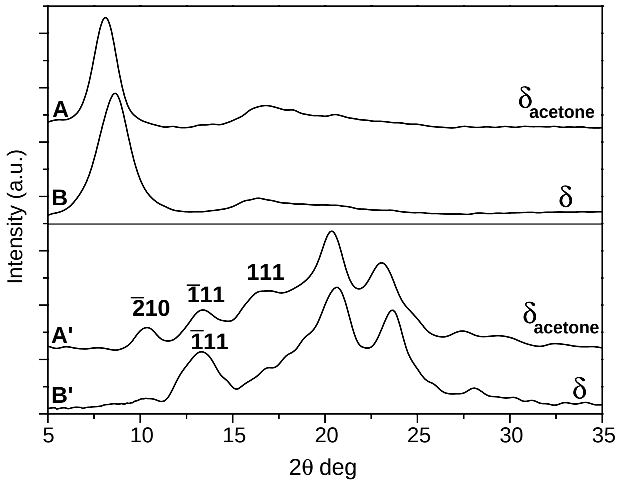

Fig. 2. X-ray diffraction patterns (Cu Kα) of the films of Fig. 1, before (A) and after (B) acetone desorption: (A,B) obtained by an automatic powder diffractometer; (A′,B′) obtained with beams perpendicular to the film plane by using a photographic cylindrical camera. These data indicate that the acetone desorption involves a transition from the s-PS/acetone clathrate toward the nanoporous δ phase.

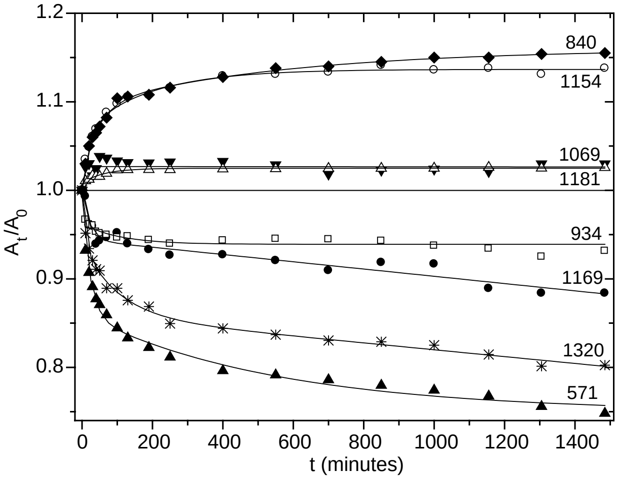

Fig. 3. Quantitative comparison of the variations of the s-PS peak intensities, obtained from FTIR spectra like those of Fig. 1, upon acetone removal at room temperature.

Uniaxially oriented films of Figs. 6 and 7 were obtained by monoaxial stretching of extruded s-PS films, at different draw ratios up to $\lambda \approx 3$ and at constant deformation rate of 0.1 s^{-1}, in the temperature range 105–110 °C with a Brukner stretching machine. The stretched films, still essentially amorphous, were crystallized into the nanoporous δ form by exposure for three days to CS_2 vapor, followed by treatment under vacuum at 40 °C for other 3 days. The clathrate films were obtained from δ form films by exposure to DCE vapors for 2 h. Films in γ and α semicrystalline forms, were obtained from films in δ form by increasing the temperature (≈2 °C/min) from room temperature up to 160 and 220 °C, respectively, and then maintaining the samples at those temperature for 30 min.

Unoriented amorphous s-PS films with thickness 40–60 μm were obtained by compression molding process at 300 °C, followed by quenching in ice-water.

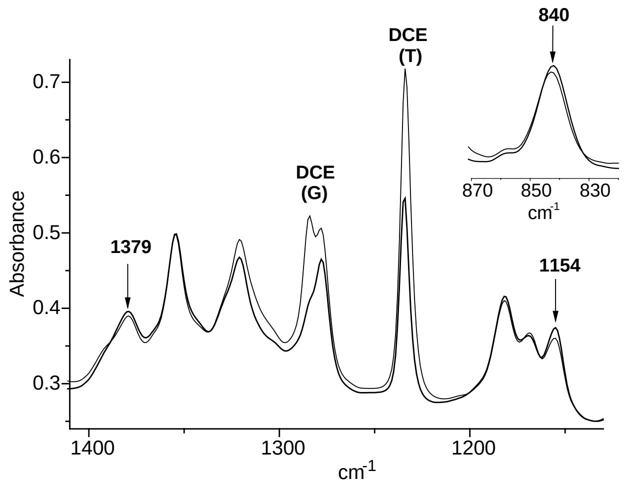

Fig. 4. FTIR spectra for the spectral range 1400–1130 and 870–820 cm^{-1} (inset) of: (thin line) a s-PS/DCE clathrate film with a DCE content close to 8 wt%; (thick line) the same clathrate film with a DCE content close to 4 wt%, obtained after 60 h of DCE desorption at 40 °C.

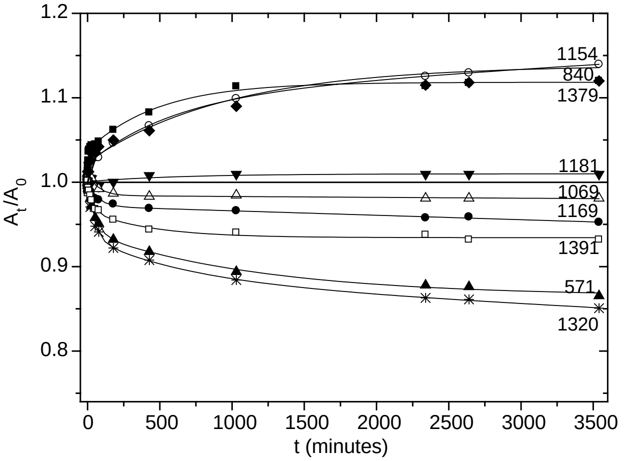

Fig. 5. Quantitative comparison of the variations of the s-PS peak intensities, obtained from FTIR spectra like those of Fig. 4, upon DCE removal at 40 °C.

The preparation of the unoriented semicrystalline γ and δ form films of Figs. 9 and 10 is described in detail in Section 3.3.

2.2. Techniques

Infrared spectra were obtained at a resolution of 2.0 cm^{-1} with a Vector 22 Brucker spectrometer and/or with a Perkin Elmer System 2000 spectrometer. Both instruments were

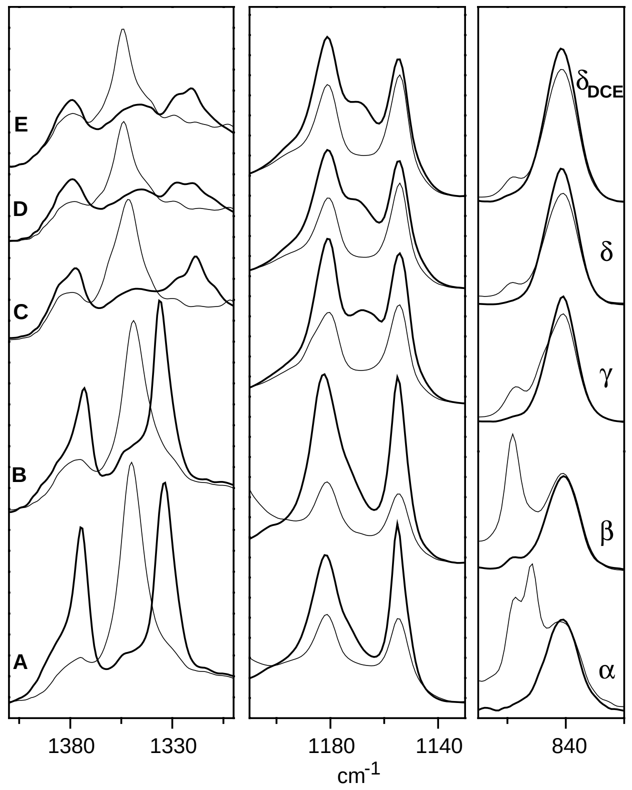

Fig. 6. FTIR spectra for three different wavenumber ranges of uniaxialy oriented s-PS films ($\lambda \approx 3$ and Herman's orientation factor $f \approx 0.95$), taken with polarization plane parallel (thin lines) and perpendicular (thick lines) to the draw direction. The spectra of semicrystalline samples presenting the α, β, γ, δ and DCE-clathrate phases are presented by curves (A)–(E), respectively.

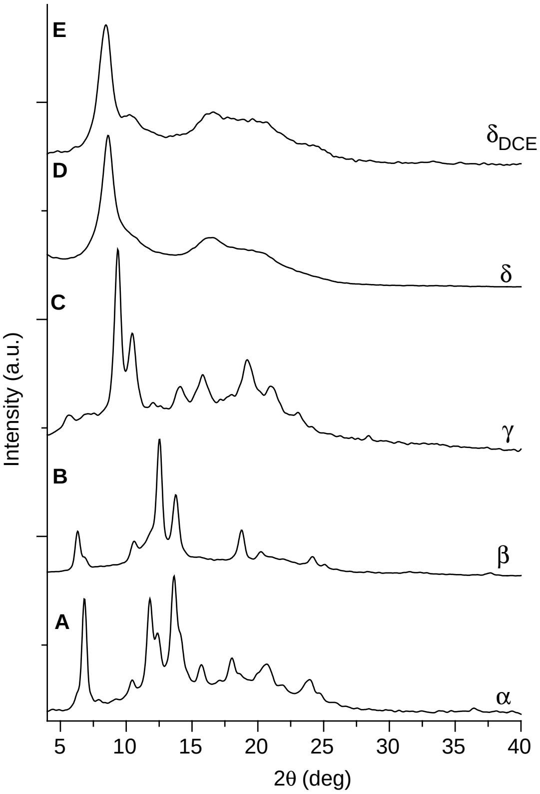

Fig. 7. X-ray diffraction patterns (Cu Kα) of the uniaxially stretched films, whose FTIR spectra are shown in Fig. 6(A)–(E), respectively.

equipped with a deuterated triglycine sulphate (DTGS) detector and a Ge/KBr beam splitter. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He–Ne reference laser. Thirty-two scans were signal averaged to reduce the noise. The thickness of films used for infrared measurements was always comprised between 20 and 40 μm, in order to keep the peaks of interest in the range of absorbance–concentration linearity.

The infrared based degree of crystallinity, expressed as weight fraction X_c, can be evaluated according to $K = l/l'(1-X_c)$ [13,17], where K is the subtraction coefficient, l and l' are the thickness of the sample and of an amorphous reference film. The ratio l/l' is estimated from the absorbance ratio of a conformationally insensitive peak (i.e. at 1601 cm^{-1}).

The desorption measurements were carried out in an environmental chamber (SPECAC Mod 20100) directly mounted in the spectrometer for the real time process monitoring. The isothermal measurements were carried out at room temperature and 40 °C under a nitrogen atmosphere at a pressure of 760 mmHg.

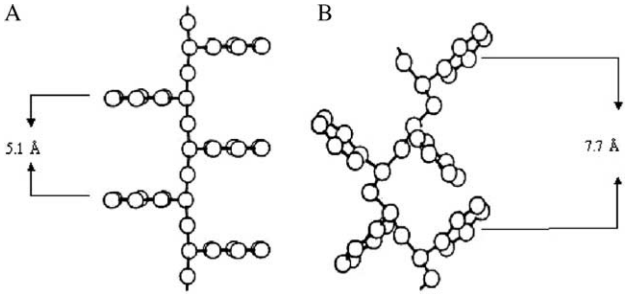

Fig. 8. Side view of models of syndiotactic polystyrene in the: (A) trans-planar conformation; (B) s(2/1)2 helical conformation.

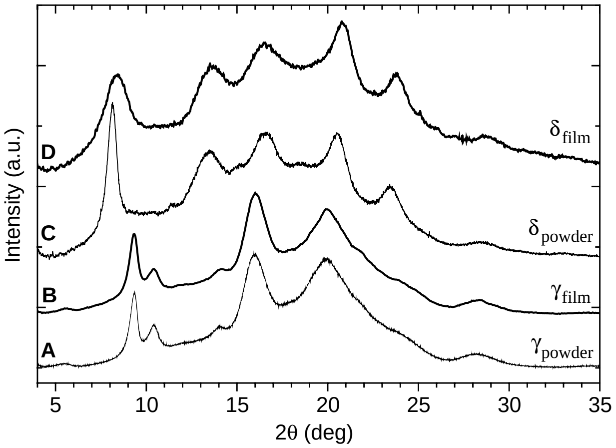

Fig. 9. X-ray diffraction patterns of unoriented s-PS samples: (A) γ form powder; (B) γ form film; (C) δ form powder; (D) δ form film.

Polarized infrared spectra were recorded by the use of a SPECAC 12500 wire grid polarizer. The degree of axial orientation relative to the crystalline phase has been formalized on a quantitative numerical basis using the Hermans' orientation function. In particular, as described in Ref. [38], the order parameter of the 1222 and 571 cm^{-1} bands has been directly used as a measure of the axial orientation function ($f_{c,IR}$, which is equal to unity for perfect alignment and null for random orientation) for trans-planar and helical crystalline phases, respectively.

Wide-angle X-ray diffraction patterns with nickel filtered Cu Kα radiation were obtained, in reflection, with an automatic Bruker diffractometer. The X-ray based degree of crystallinity has been determined by resolving the diffraction pattern in a selected range (5–38°) into two areas A_c and A_a that are taken as being proportional to the crystalline and amorphous weight fractions, respectively, and calculated through the expression $100A_c/(A_c+A_a)$.

The X-ray diffraction patterns of Fig. 2(A′) and (B′) were obtained with X-ray beam perpendicular to the film plane, and the diffracted radiation was collected with a cylindrical camera (radius = 57.3 mm), recorded on a BAS-MS Imaging Plate (FUJIFILM) and processed with a digital imaging reader (FUJIBAS 1800).

3. Results and discussion

3.1. FTIR spectral changes of s-PS clathrate films upon guest removal

This section describes changes of FTIR spectra associated with guest removal from s-PS clathrate phases, wich generally occurs with some loss of cristallinity [52].

The FTIR spectrum of a s-PS/acetone clathrate film, obtained by acetone treatment of a s-PS/$CHCl_3$ clathrate cast film, is shown by a thin line in Fig. 1, for the spectral range 1400–800 cm^{-1}. This spectrum, beside s-PS peaks, presents acetone peaks (e.g. at 1360, 1219 and 1089 cm^{-1}) indicating a concentration close to 15 wt%. The FTIR spectrum of the same film, after 1 day of acetone desorption at room temperature, is shown by a thick line in Fig. 1 and indicates that the acetone content becomes lower than 1%.

X-ray diffraction patterns of the same film of Fig. 1, before and after acetone desorption, obtained by an automatic powder diffractometer (Fig. 2(A) and (B)), are typical of semicrystalline films with a nanoporous δ or clathrate phases, presenting a (010) uniplanar orientation [48]. The corresponding X-ray diffraction patterns obtained with beams perpendicular to the film plane by using a photographic cylindrical camera (Fig. 2(A′) and (B′), show that, upon acetone desorption, the ($\bar{2}10$) reflection decreases markedly while the $\bar{1}11$ reflection increases, thus clearly indicating that the starting material presents a clathrate phase [11,47–51], which includes acetone guest molecules. Hence, the X-ray diffraction data of Fig. 2 indicate that the acetone desorption shown by the FTIR spectra of Fig. 1 also involves a transition from the s-PS/acetone clathrate toward the nanoporous δ phase.

On inspection of Fig. 1, it is apparent that upon guest removal the FTIR helical peaks (e.g. those at 1320, 1277, 1169, 943, 935 cm^{-1}) reduce their absorbances, while the only peaks which clearly increase their absorbances are those at 1154 and 841 cm^{-1} (insets of Fig. 1). A quantitative comparison of the variations of the peak intensities upon guest removal has been obtained by curve fitting analysis of the relative frequency ranges (i.e. 1410–1255, 1215–1135, and 865–825 cm^{-1}). The results, in terms of peak heights, are shown in Fig. 3 and clearly indicate that the intensities of all helical peaks are substantially reduced (depending on the peak from 10 up to 25%) while the other s-PS peaks remain essentially constant, with the exception of the 1154 and 841 cm^{-1} peaks, presenting an intensity increase close to 15%.

It is worth noting that the 1379 cm^{-1} peak, which has been already identified as an amorphous peak [17], is not shown in Figs. 1 and 3, due to its superposition with the intense 1360 cm^{-1} acetone peak.

FTIR spectral changes associated with guest removal have been analogously studied for s-PS/1,2-dichloroethane (DCE) clathrate films. This guest choice was motivated by the additional information, which comes from its conformational equilibrium. In fact, as described in detail in previous papers [13–16,53], since essentially only its trans conformer is included into the clathrate 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 amount of DCE confined as guest in the clathrate phase or simply absorbed in the amorphous phase.

The FTIR spectrum of a clathrate film containing about 8 wt% of DCE (thin line) is compared with the spectrum of the same film after 60 h of desorption at 40 °C (containing 4 wt% of DCE, thick line) for the spectral range 1400–1130 and 870–820 cm^{-1} (inset), in Fig. 4. The isothermal desorption at 40 °C leads to a nearly complete disappearance of the DCE gauche peak at 1285 cm^{-1}, to a much lower reduction of the DCE trans peak at 1234 cm^{-1}, while only minor changes occur for the s-PS peaks. As shown in Fig. 12 of Ref. [14], the difference in the desorption rate between the two phases is dramatic. After about 60 h the DCE content in the amorphous phase has decreased by about 85% of its initial value while in the crystalline phase the reduction is lower than 10%. As a consequence, contrary to the case of acetone desorption of Figs. 1 and 2, the crystalline clathrate phase remains nearly unaltered upon DCE desorption at 40 °C, since its guest content decreases only from about 4 to 3.5 wt%.

Nevertheless, the quantitative comparison of the intensity variations of relevant s-PS peaks upon the isothermal DCE desorption at 40 °C (Fig. 5) is similar to that one observed upon acetone desorption (Fig. 3). In fact, the intensities of all helical peaks are substantially reduced (depending on the peak from 5 up to 15%) while the other s-PS peaks remain essentially constant, with the exception of the 1379, 1154 and 841 cm^{-1} peaks, which present an intensity increase close to 15%. The data of Figs. 3 and 5 can be rationalized by assuming that both kinds of desorption lead to a reduction of crystallinity and that 1379, 1154 and 841 cm^{-1} peaks are prevailingly amorphous peaks, for δ and clathrate s-PS samples.

As for the vibrational origin of the 1379 cm^{-1} band, it is worth noting that a strong absorption has been found in all-trans crystalline forms at 1376 cm^{-1}. According to one normal coordinate analysis [28] this band was assigned to a complex mode to which both backbone vibrations (C–C–H bending, CC stretching) and ring vibrations (C–H bending and C–C stretching) contribute. Conversely, Gupta et al. [31] associated this peak to a phenyl ring mode with contribution from H–C–C ring bending (potential energy distribution, PED, 54%) and ring C–C stretching (PED 39%). According to both studies [28,31], also the peaks at 1154 and 840 cm^{-1} are almost pure ring modes. In particular, the former is ascribed to a ring H–C–C bending (PED 83%), and the latter to a ring C–H out-of-plane bending (PED 83%) and a ring C–C torsion (PED 16%).

The three above absorptions share the common feature that their dispersion curves are essentially flat and are therefore expected to be conformationally insensitive [31]. The observation that their intensity increases considerably with the amorphous content could be tentatively interpreted taking into account the effect of the intermolecular interactions between adjacent chains within the crystal lattice. Thus, a sufficient perturbation of the force constants involved may arise upon the formation of the crystalline phase, so as to induce a more or less significant shift and/or an in-phase and out-of-phase splitting of the original band (correlation or Davidov splitting). This effect is well documented for isolated vibrations such as carbonyl stretching in polyesters [54,55] or aromatic ring modes in syndiotactic polystyrene [13].

It is also worth noting that, upon guest desorption, the reduction of intensity of the helical peak at 1169 cm^{-1} is smaller than those associated with other helical peaks (Figs. 3 and 5). This contradicts the previous suggestion that the peak at 1169 cm^{-1} would be not only characteristic of the s(2/1)2 helical conformation but would also increase as a consequence of host–guest interactions occurring in the clathrate phase [53,56].

3.2. Linear dichroism of infrared peaks of crystalline and clathrate phases of s-PS

This section describes some information relative to the nature of the s-PS FTIR peaks which can be achieved by linear dichroism measurements on uniaxially stretched films.

FTIR spectra for three different wavenumber ranges of uniaxially oriented s-PS films ($\lambda \approx 3$ and Herman's orientation factor $f_{\mathrm{c,IR}} \approx 0.95$), taken with polarization plane parallel and perpendicular to the draw direction, are shown in Fig. 6 by thin and thick lines, respectively. In particular, the spectra of semicrystalline samples presenting the α, β, γ, δ and DCE-clathrate phases are presented by curves (A)–(E), respectively. The occurrence of these crystalline phases has been clearly established by the X-ray diffraction patterns of uniaxially stretched films, as collected by an automatic diffractometer, shown in Fig. 7(A)–(E), respectively. For instance, the patterns of Fig. 7(A)–(D) present the typical (110), (020),(200) and (010) reflections, at $2\vartheta_{\mathrm{Cu\ K}\alpha} \approx 6.7$, 6.15, 9.25, and 8.4°, typical of α, β, γ and δ phase, respectively. The pattern of Fig. 7(E) presents beside the (010) reflection also the $(\bar{2}10)$ reflection at $2\vartheta_{\mathrm{Cu\ K}\alpha} \approx 10.7°$, as typical of s-PS clathrate phases [3–5,11,12].

The occurrence for samples presenting the helical crystalline phases of a reduced dichroism for the 1379, 1154 and 841 cm^{-1} peaks (Fig. 6(C)–(E)) with respect to other s-PS peaks is in good agreement with their prevailingly amorphous nature, as pointed out by the results of Section 3.1.

However, an accurate examination of the whole FTIR spectra of the uniaxially oriented s-PS films shows that only the 841 cm^{-1} peak, corresponding to ring C–H out-of-plane bending (opb) [28], presents a complete absence of dichroism, but only for α form samples (Fig. 6(A)), or for β form samples (Fig. 6(B)), while the same peak, for all semicrystalline films presenting helical conformations (γ, δ and clathrate, Fig. 6(C)–(E)) presents a noticeable dichroism (for a comparison of FTIR spectra of different α and β form samples, see also Fig. 6 of Ref. [32]).

It is also worth noting that the peaks in the wavenumber range 860–850 cm^{-1} (at 857 and 852 cm^{-1} for the α phase, at 858 cm^{-1} for the β phase and for γ, δ and clathrate phases) are fully dichroic and their transition moment vectors are parallel to the chain axes (and hence perpendicular to the phenyl rings for the trans-planar crystalline phases). These results clearly suggest that the peaks in the wavenumber range 860–850 cm^{-1} correspond to the same C–H opb mode of the 841 cm^{-1} peak, for the conformationally ordered chains of all crystalline phases. However, although the degree of crystallinity for all the samples of Fig. 6 is similar, the absorbance of the crystalline 858 cm^{-1} peaks, for all helical crystalline phases, is markedly smaller (roughly 1/5) with respect to the corresponding crystalline peaks of trans-planar phases.

These results can be rationalized by assuming that for the trans planar crystalline phases the out-of-plane bending of all five phenyl C–H bonds is restricted by the crystalline environment while for the helical crystalline phases a similar restriction would occur only for one phenyl C–H bond. This is in good qualitative agreement with the available information relative to the packing of s-PS crystalline phases, which for trans-planar α [1,57–60] and β [61–63] phases is dominated by the parallel stacking of the phenyl rings (see a side view of the trans-planar chain in Fig. 8(A) and, e.g. for the packing of the α form, Fig. 3 in Ref. [57]) while for the helical δ [11] and clathrate [3–7] phases is dominated by the formation of *ac* parallel layers of s(2/1)2 helices (see a side view of these helices in Fig. 8(B) and, e.g. for the packing of the δ form, Fig. 4 in Ref. [11]), leading to short intermolecular contacts between only few phenyl CH groups [11].

In summary, the present results indicate that, for all semicrystalline s-PS samples, the crystalline peaks in the wavenumber range 860–850 cm^{-1} should be attributed to the same vibrational mode of the 841 cm^{-1} (ring C–H opb [28]). However, only for the trans-planar (α and β) phases, the intermolecular packing produces a substantial shift of the peak position for all the ring C–H opb of the crystalline phase while for the helical (γ, δ and clathrate) phases, the intermolecular packing would produce a substantial shift of the peak position only for a fraction of the ring C–H opb of the crystalline phase. As a consequence, for samples including trans-planar crystalline phases, the 841 cm^{-1} peak can be considered as fully associated with conformationally disordered sequences, and hence used as basis of quantitative evaluations of crystallinity, as already suggested in a previous report [32]. On the other hand, for semicrystalline s-PS samples with helical crystalline phases, the 841 cm^{-1} peak is not only associated with conformationally disordered sequences but also with a large fraction of the ring C–H of the crystalline phase, and hence it is not suitable as basis of quantitative evaluations of crystallinity.

More in general, for semicrystalline films with helical crystalline phases (γ, δ and clathrate), FTIR spectra like those of Fig. 6 shows that some noticeable dichroism occurs for all infrared peaks, thus indicating that no isolated infrared peak can be fully associated with the amorphous phase.

3.3. Fully unoriented films presenting the helical s-PS crystalline phases

To get infrared spectra of pure crystalline phases by spectral subtraction procedures, good quality spectra, like those obtained for films samples, are generally needed. Moreover, both semicrystalline and amorphous films have to be characterized by the absence of molecular orientation, since this can substantially alter the relative intensities of the measured absorbances.

As for s-PS, it is quite easy to get fully unoriented amorphous films (by quenching procedures from the melt state [1]) as well as fully unoriented semicrystalline films presenting the trans-planar crystalline phases (α and/or β, e.g. by melt crystallization techniques [1]). However, as for semicrystalline films presenting the helical crystalline phases (γ, δ and clathrate), which are obtained by solution crystallization procedures, oriented semicrystalline films are generally obtained.

In fact, solution casting [47,48] as well as solvent induced crystallization procedures [49–51] lead to s-PS films which generally present oriented clathrate phases. In particular, the occurrence of three different kinds of uniplanar orientation, which present a preferential orientation parallel to the film plane for the (010), (002) or ($\bar{2}$10) crystal planes, has been recently pointed out [47–51]. High degrees of uniplanar orientations are generally observed also for δ and γ crystalline phases which are obtained by guest removal or thermal treatments, respectively [48–51]. Moreover, it has been clearly pointed out that these uniplanar orientations produce large variations of relative intensities of the infrared absorbance peaks corresponding to the conformationally ordered helical sequences [49,50].

Fully unoriented films presenting the γ phase can be obtained by solvent induced crystallization by guests giving rise to unstable clathrate phases, like acetone [49] or carbon dioxide [64]. This is shown, for instance, by the similarity of the X-ray diffraction patterns of a γ form powder (Fig. 9(A)) and of a γ form film (Fig. 9(B)), obtained by supercritical carbon dioxide treatment (at 40 °C and 200 atm for 90 min) and subsequent annealing at 150 °C for 2 h of a quenched amorphous film.

By treatment of these unoriented γ form films with suitable guest molecules, unoriented films presenting clathrate phases can be obtained. After guest removal from the latter films, unoriented films presenting the nanoporous δ phase can be also achieved. This is shown by the similarity of the X-ray diffraction patterns of a δ form powder (Fig. 9(C)) and of a δ form film (Fig. 9(D)) obtained from a γ form film after 12 h immersion in tetrahydrofuran, followed by supercritical carbon dioxide extraction.

3.4. Spectra of the pure crystalline γ and δ phases

The results reported in Sections 3.1 and 3.2 clearly show that, for δ and clathrate s-PS samples, the 1379 and 1154 and 841 cm^{-1} peaks are prevailingly, although not fully, associated with conformationally disordered chains and they are sufficiently isolated from neighboring absorptions and of sufficiently high intensity to be employed for quantitative purposes. As a consequence, these peaks have been considered for a possible isolation of the spectra of pure γ and δ crystalline phases, by following a spectral subtraction procedure analogous to that one previously described for α and β form samples, based on the 841 cm^{-1} peak [32].

The FTIR spectra of the semicrystalline γ and δ form films of Fig. 9, being fully unoriented and hence suitable for this kind of spectral subtraction procedures, are shown in the upper part of Fig. 10. The FTIR spectrum of a unoriented amorphous film, which has been subtracted to the spectra of the semicrystalline films is shown by a thin line in the middle of Fig. 10. The subtraction spectra, which can be assumed as the spectra of the pure crystalline γ and δ phases, are shown in the lower part of Fig. 10. The spectral subtraction was accomplished by attempting to reduce the three above selected prevailingly amorphous peaks (at 1379 and 1154 and 841 cm^{-1}) to the baseline.

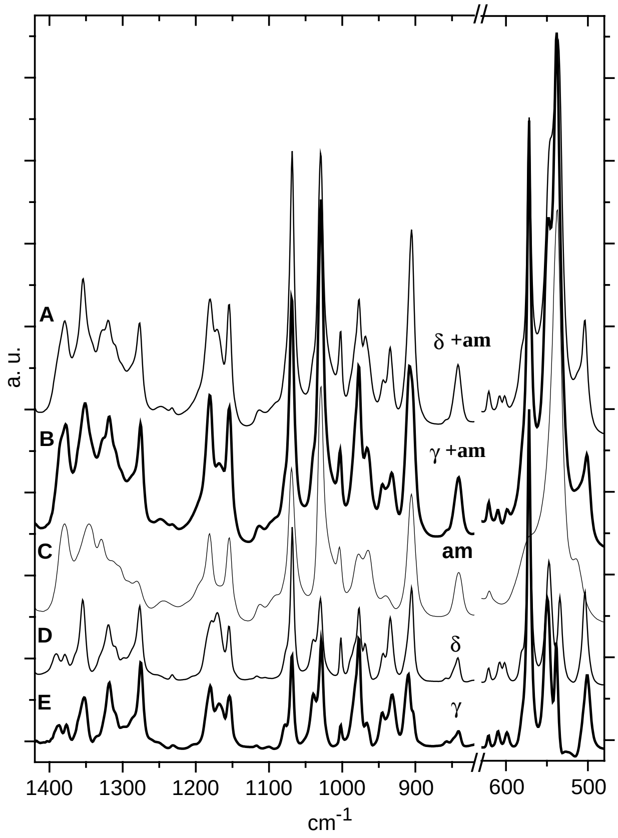

Fig. 10. FTIR spectra in the range 1400-500 cm^{-1} of unoriented s-PS films: (A) semicrystalline δ, of Fig. 9(D); (B) semicrystalline γ, of Fig. 9(B); (C) amorphous; (D) subtraction spectrum (A)–(C), pure crystalline δ phase; (E) subtraction spectrum (B) and (C), pure crystalline γ phase.

It is apparent that a reduction close to the baseline is possible only for the 1379 cm^{-1} peak, since after spectral subtraction only two minor crystalline peaks (located at 1376 and 1387 cm^{-1} for the γ phase and at 1378 and 1390 cm^{-1} for the δ phase) are left. It is worth adding that this crystalline doublet is possibly responsible for the dichroic behaviour of the peak at 1379 cm^{-1} in the helical semicrystalline samples (Fig. 6(C)–(E)). The 1154 and 841 cm^{-1} peaks, although heavily reduced with respect to the other peaks, are well apparent in the spectra of the pure crystalline γ and δ phases and hence are not helpful to the spectral subtraction procedure. This indicates that, for semicrystalline samples presenting helical crystalline phases, the 1379 cm^{-1} peak is the most suitable for crystallinity evaluation. In particular, the crystallinity degrees, evaluated according to this spectral subtraction, by following the procedure of Refs. [32,17], is 40 and 38% for γ and δ phase, respectively. These values are in agreement with the crystallinity degrees evaluated by X-ray diffraction (39% for γ and 36% for δ).

A close comparison between the spectra of the pure crystalline γ and δ phases shows, in several spectral regions,

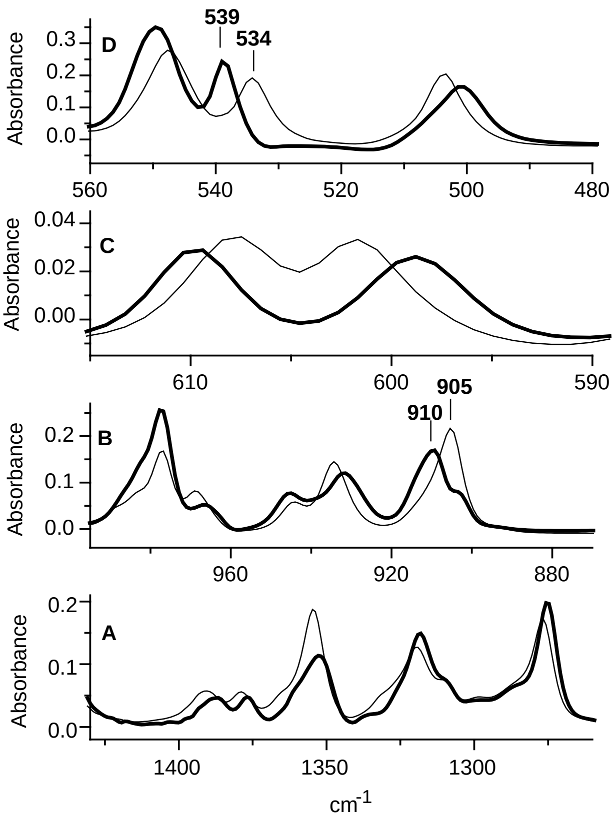

Fig. 11. Comparison between the spectra of the pure crystalline phases of Fig. 10(D) and (E), for four different spectral regions: (thin lines) δ phase (thick lines) γ phase.

some clear differences (Fig. 11), some of which have been already pointed out in the literature, on the basis of unsubtracted spectra of semicrystalline samples. In particular, with reference to the (A)–(D) sections of Fig. 11: (A) A shift to higher frequencies of nearly 2 cm^{-1} for all the bands in the range 1400–1250 cm^{-1} is observed for the δ phase (as already observed by Tashiro and co-workers for the 1354 and 1320 cm^{-1} peaks) [56]. (B) Substantial intensity and position variations for all the peaks in the range 980–920 cm^{-1} (as already pointed out in Fig. 3 of Ref. [25]) and the presence of a shoulder at 938 cm^{-1} only for the γ phase (as already pointed out in Refs. [33,39,56]). It is also worth noting that the γ phase presents an intense well defined peak at 910 cm^{-1}, largely shifted with respect to the 905 cm^{-1} peak typical of amorphous and δ phases. (C) The band positions in the 615–595 cm^{-1} region are significantly different for the two crystalline phases (as already shown in detail by Tashiro and co-workers [36,56]). (D) Large shifts for all the peaks in the range 560–480 cm^{-1} are observed, in particular well defined and intense peaks are centered at 539 and 534 cm^{-1} for the γ and δ phase, respectively.

4. Conclusions

Quantitative evaluations of the variations of FTIR absorbances for s-PS clathrate films, upon guest removal procedures leading to crystallinity reduction, indicate that the 1379, 1154 and 841 cm^{-1} peaks, corresponding to ring vibrational modes, are prevailingly associated with the amorphous phase. This suggestion is confirmed by linear dichroism measurements on uniaxially stretched s-PS films, indicating for these peaks a lower dichroism than for the other s-PS peaks. However, the dichroism measurement indicate that only the phenyl C–H out-of-plane bending peak at 841 cm^{-1}, and only for samples including trans-planar crystalline phases (α and β), can be considered as fully associated with conformationally disordered sequences, and hence safely used as basis of quantitative evaluations of crystallinity. This behavior has been rationalized on the basis of the different intermolecular interactions between phenyl rings occurring for the chain packings of trans-planar and helical s-PS crystalline phases.

As for helical (γ, δ and clathrate) s-PS semicrystalline films, which generally present different kinds of uniplanar orientation, a procedure leading to films with fully unoriented crystalline phases has been described. The availability of these fully unoriented semicrystalline films allows a more accurate isolation of the spectra of the pure crystalline helical phases, with respect to those achieved on the basis of FTIR spectra of powder samples.

A comparison between the spectra of pure γ and δ crystalline phases has allowed to identify a number of structural order effects (corresponding to the same helical conformation) only in part described in the literature.

A satisfactory evaluation of the degree of crystallinity for γ, δ and clathrate s-PS samples, can be obtained by FTIR spectral subtraction procedures based on the use of the 1379 cm^{-1} peak. This procedure of crystallinity evaluation can be particularly relevant for clathrate samples, for which the traditional methods based on measurements of density or based on X-ray diffraction spectra of unoriented samples are practically useless, due to the presence of large and variable (from null up to 30–40 wt%) amounts of guest molecules, which can be present in both amorphous and clathrate crystalline phases.

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