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Perpendicular Orientation of Host Polymer Chains in Clathrate Thick Films

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Introduction

Orientation is a phenomenon of great technical and theoretical importance for nearly all materials. In fact, many examples could be quoted to illustrate how orientation affects the properties of solids.[1] For polymeric materials, the effects of orientation on properties, although formally similar to those on other materials, are more relevant. For instance, for polymers, the extent to which it is possible to increase stiffness, and more particularly strength, and the ease with which this can be done find no parallel with other materials.

Orientation is particularly relevant for functional polymeric materials, like, for instance, polymers presenting ferroelectric or conductive[2] or nonlinear optical[3] properties. Of course, when the functionality is due to the crystalline phase, the control of the orientation of the crystalline phase is particularly relevant.

Different kinds of crystalline phase orientations, which present the chain axes (generally corresponding to the crystallographic *c* axis) parallel to the film plane,[4] can easily be achieved for semicrystalline polymeric films of industrially relevant thickness (1−100 μm), for instance by deformation in the solid state of initially unoriented systems.

The crystalline phase orientation for which the chain axes are perpendicular to the film plane, although generally achieved for solution grown polymeric single crystals lamellae (with a typical thickness of tenths of nanometers) as well as for single-crystal mats,[5] is on the contrary not available for films of industrially relevant thicknesses.

In this paper, the achievement of polymeric films of high thickness (at least up to 100 μm), which present a crystalline phase with a high degree of perpendicular *c* axis orientation with respect to the surface, is described. This perpendicular orientation, to our knowledge unprecedented for high thickness films, has been achieved for syndiotactic polystyrene (s-PS), by suitable solution casting procedures leading to formation of clathrate phases.

The achievement of perpendicular orientation and more importantly, in general, of the control of the crystalline phase orientation can be particularly relevant for s-PS, due to the functional properties of its nanoporous crystalline δ phase[6] as well as of its clathrate phases.[7−11]

Experimental Section

The s-PS used in this study was manufactured by Dow Chemical Co. 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 polydispersity index, $M_w/M_n = 3.9$.

Films presenting a s-PS/trichloroethylene (TCE) clathrate phase with perpendicular *c* axis orientation with respect to the surface were obtained by casting at room temperature from 0.5% s-PS solutions in TCE. Films presenting a s-PS/$CHCl_3$ clathrate phase with uniplanar *ac* orientation[4b] were obtained by casting at room temperature from 0.5% s-PS solutions in $CHCl_3$. Nanoporous δ semicrystalline films, presenting perpendicular and uniplanar orientations, were obtained by exposition to vapors of CS_2 (and by subsequent drying at 50 °C under vacuum) of the above-described s-PS/TCE and s-PS/$CHCl_3$ clathrate films, respectively. Films presenting a s-PS/TCE clathrate phase with uniplanar *ac* orientation were obtained by exposition of a δ uniplanar film to TCE vapors for 60 min followed by desorption at room temperature for at least 2 days. Films presenting s-PS/1-chloropropane (CP) clathrate phases were obtained by exposition of a δ form films, with perpendicular or uniplanar orientations, to CP vapors for 1 day followed by desorption at room temperature for 1 day. Powders including the TCE clathrate phase were obtained by precipitation in acetone of 0.5% s-PS solutions in TCE.

Wide-angle X-ray diffraction patterns with nickel-filtered Cu Kα radiation were obtained, in reflection, with an automatic Philips diffractometer as well as, in transmission, by using a cylindrical camera (radius = 57.3 mm). In the latter case the patterns were recorded on a BAS-MS imaging plate (FUJIFILM) and processed with a digital imaging reader (FUJIBAS 1800).

In particular, to recognize the kind of crystalline orientation present in the samples, photographic X-ray diffraction patterns were taken by having the X-ray beam parallel to the film surface and by placing the film sample parallel to the axis of the cylindrical camera.

The degree of orientation of the crystallites with respect to the film plane have been formalized on a quantitative numerical basis using Hermans' orientation functions as defined in refs 12−14. In particular, as for the perpendicular orientation

$$f_c = (3\overline{\cos^2\gamma} - 1)/2 \tag{1}$$

where $\overline{\cos^2\gamma}$ is the average cosine squared value of the angle γ between the normal to the film surface and the chain axes where as for the uniplanar orientation f_{010} has been evaluated as described in ref 4b.

In these assumptions, f_c or f_{010} is equal to 1 if the chain axes or the 0*k*0 crystallographic planes (*ac* planes) of all crystallites are perfectly perpendicular or parallel to the film plane, respectively. Since, in our cases, a θ_{hkl} incidence of X-ray beam is used, the quantity $\overline{\cos^2\gamma}$ can be easily experimentally evaluated. In particular

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

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

The diffracted intensities $I(\chi_{hkl})$ of eq 2 was obtained, in transmission, by using an AFC7S Rigaku automatic diffractometer (with a monochromatic Cu Kα radiation) and maintaining an equatorial geometry. Because the collection was performed at constant 2θ values and in the equatorial geom-

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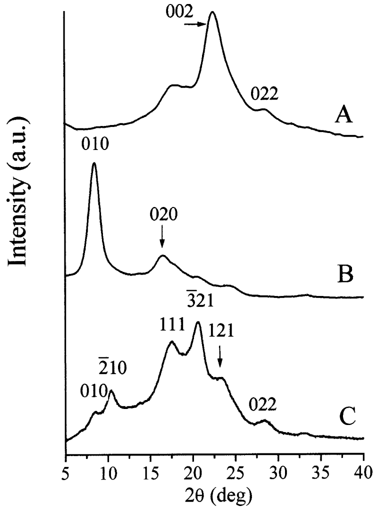

Figure 1. X-ray diffraction patterns (Cu Kα) obtained with an automatic powder diffractometer of samples including the s-PS/TCE clathrate phase: (A) cast film from 0.5% s-PS solutions in TCE; (B) cast film from 0.5% s-PS solutions in $CHCl_3$, subsequently exposed to TCE vapors; (C) powder. The main Miller indexes of the most intense reflections of the clathrate phase are indicated near to the peaks.

etry, the Lorentz and polarization corrections were unnecessary.

Infrared spectra were obtained at a resolution of 1.0 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. A total of 32 scans were signal averaged to reduce the noise.

The refractive indexes, along directions parallel and perpendicular to the film plane, were obtained by using an Abbè refractometer "Atago 3T" with a rotatable film analyzer mounted on the eyepiece according to the procedure decribed in ref 15.

Results and Discussion

Preparation and Structural Characterization of Films with Perpendicular Polymer Chain Orientation. The X-ray diffraction patterns obtained by an automatic powder diffractometer of two trichloroethylene (TCE) chlathrate films both of thickness of ≈ 50 μm are shown in Figure 1, parts A and B. Figure 1A refers to a film obtained by TCE solution casting at room temperature, while Figure 1B refers to a film obtained by TCE vapor treatment of a nanoporous δ form film which was, in turn, obtained by extraction procedures[16] on a film cast from chloroform solution.[4b] For the sake of comparison, the X-ray diffraction pattern of a TCE clathrate powder is shown by curve C of Figure 1. All diffraction peaks of Figure 1 can be indexed by a monoclinic unit cell with $a = 17.11$ Å, $b = 12.17$ Å, $c = 7.7$ Å, and $\gamma = 120°$. This unit cell has been established by a corresponding X-ray diffraction fiber pattern and is substantially identical to that one observed for the clathrate phase with 1,2-dichloroethane.[8a]

Substantial differences between the relative intensities of the reflections, for the profiles of Figure 1, clearly indicate the occurrence of high and completely different orientations for both film samples. In particular, for the TCE cast film (curve A), the most intense reflection (at $2\theta_{\mathrm{Cu\ K}\alpha} \approx 23°$), which is not clearly apparent in the X-ray diffraction powder pattern (curve C), is indexed as (002), thus suggesting a preferential perpendicular orientation of the crystalline chain axes with respect to the film plane. On the other hand, for the TCE clathrate film obtained by guest substitution into a chloroform cast film, the most intense reflections are indexed as (010) and (020), thus indicating (as already discussed in detail in ref 4b) an orientation of the *ac* planes (and, of course, also of the crystalline chain axes) preferentially parallel to the film plane.

A better understanding of the crystalline orientations of the films of Figure 1, parts A and B, can be achieved by X-ray diffraction patterns taken with beam parallel to the film plane and collected on a photographic cylindrical camera (Figure 2, A and B, respectively). A schematic sketch showing the directions of beam and of cylindrical camera axis with respect to film sample have been also reported on the left of Figure 2.

In particular, the diffraction pattern of the TCE cast film (Figure 2A) presents reflection arcs typical of partially oriented clathrate fibers (cf., e.g, Figure 2 of ref 6c), although, for film placement parallel to the axis of the cylindrical camera, the pattern presents the *hk*0 reflections centered on the meridional line and the 002 reflection centered on the equatorial line. This clearly indicates the occurrence of a preferential orientation of the crystalline chain axes perpendicular to the film plane. On the other hand, the X-ray diffraction pattern of the clathrate film obtained by guest substitution (Figure 2B) is similar to those shown for 1,2-dichloroethane clathrate and emptied δ form in ref 4b, with intense (010) reflection arcs centered on the equatorial line, and indicates an uniplanar orientation of the *ac* planes of the crystallites.

Schematic representations of perpendicular and uniplanar orientations, which have been achieved for the s-PS/TCE clathrate phase of films of Figures 1A and 2A and Figures 1B and 2B are reported in Figure 2, parts A′ and B′, respectively. In these sketches, the plane of the figure is representative of the film plane and the arrows remind the absence of axial orientation, that is the occurrence of a distribution of orientation of crystallites, as determined by their rotation around axes perpendicular to film surface.

For the film presenting a perpendicular chain axis orientation (Figures 1A and 2A), the Herman's orientation factor of the crystallographic *c* axis with respect to the normal to the film plane, as evaluated on the basis of the intensity distribution of the (002) reflection, is $f_c = 0.75$. For the film presenting an uniplanar orientation (Figures 1B and 2B), the Herman orientation factor of the *ac* plane with respect to the film plane, as evaluated on the basis of the intensity distribution of the (010) reflection, is $f_{(010)} = 0.75$.

A preliminary characterization of s-PS cast films obtained by solutions in a dozen of solvents which are suitable guests of sPS clathrates has shown that generally substantial degrees of orientation are present, although depending on the selected solvent this orientation can be perpendicular or uniplanar. An analogous casting procedure, which instead uses THF/acetone (5/95 wt %) solutions promoting the γ-phase formation, leads to essentially unoriented semicrystalline films. It is also worth noting that for high-temperature casting procedures, leading to β-form crystallization,[17] essentially unoriented semicrystalline films are obtained, as shown, for instance by Figure 2 of ref 17. Hence, the unusual perpendicular orientation, for high thickness films by simple casting procedures, seems to be related to the clathrate phase formation.

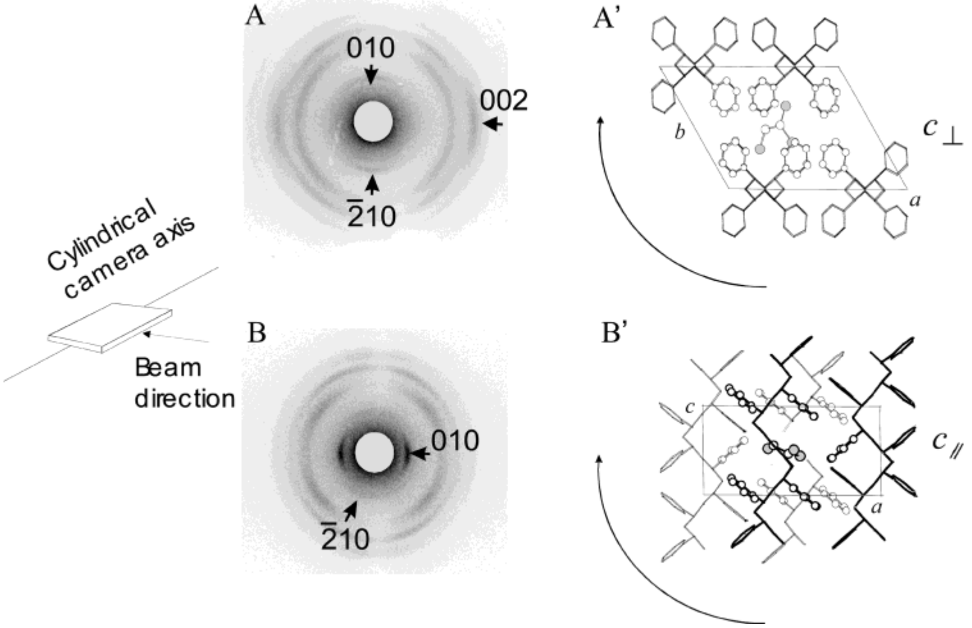

Figure 2. (A and B) X-ray diffraction patterns taken with beam parallel to the film plane and collected on a photographic cylindrical camera, for film placement parallel to the axis of the camera: (A) cast film from 0.5% s-PS solutions in TCE; (B) cast film from 0.5% s-PS solutions in $CHCl_3$, subsequently exposed to TCE vapors. On the left, a schematic sketch showing the directions of beam and of cylindrical camera axis with respect to film sample is reported. (A′ and B′) Schematic representations of the corresponding orientations of the s-PS/TCE clathrate unit cell with respect to the film plane (simulated by the plane of Figure): (A′) perpendicular polymer chain orientation; (B′) parallel polymer chain orientation (more precisely, uniplanar orientation as for the *ac* plane). For clarity of presentation only the guest molecule and the 10 phenyl rings, which define the cavity including the guest molecule, are represented as stick and balls. The arrows in these sketches remind the occurrence of a distribution of orientation of crystallites, as determined by their rotation around axes perpendicular to film surface.

Anisotropic Physical Properties of Films with Perpendicular and Uniplanar *ac* Orientation. The control of the crystalline phase orientation for s-PS could be relevant for its structural properties. In fact, s-PS is a high performance thermoplastic semicrystalline material, which has recently become commercially available and presents good mechanical properties associated with a high melting temperature (close to 270 °C).

The control of the crystalline phase orientation for s-PS can be also more relevant for its functional properties. For instance, the perpendicular and uniplanar orientations of the crystalline phases of these thick s-PS films generate opposite and high anisotropy as for the refractive indexes. In fact, for a film presenting a s-PS/chloroform clathrate phase with perpendicular orientation (similar to that one of the film of Figure 1A and 2A), with a thickness close to 120 μm and with $f_c = 0.50$, trirefringence measurements indicate that the refractive index perpendicular to the film ($n_\perp = 1.586$) is definitely lower than that one parallel to the film ($n_\| = 1.596$). The opposite holds for a s-PS/ chloroform clathrate film presenting uniplanar orientation (similar to that one of the film of Figures 1B and 2B), with a thickness close to 120 μm and with $f_{010} = 0.76$, which presents the refractive index perpendicular to the film ($n_\perp = 1.616$) as much higher than that one parallel to the film ($n_\| = 1.575$). It is worth noting that these results also indicate that the refractive indexes are reduced in the direction of preferential orientation of the chain axes of s-PS helices.

As for semicrystalline films with clathrate crystalline phases, whose crystalline unit cells include s(2/1)2 helices of the polymer (the host) and generally isolated guest molecules,[8] the orientation of s-PS clathrate phases could alter not only the properties of the host but also the properties of the guest molecules.

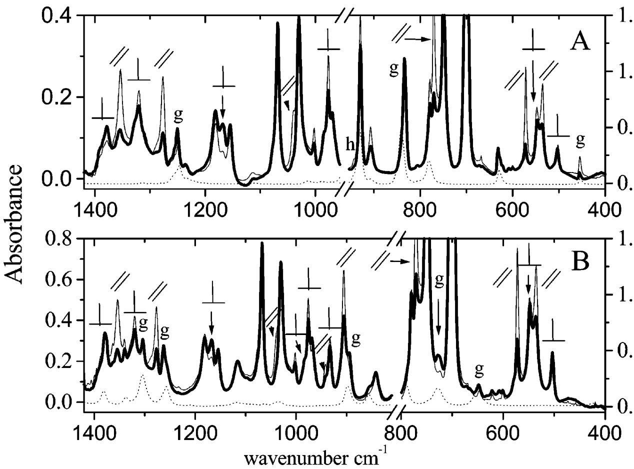

Figure 3. FTIR spectra obtained with nonpolarized radiation in the wavenumber range 1400−400 cm^{-1}, of s-PS clathrate films including TCE (A) and CP (B) guests and presenting polymer chain orientation perpendicular (continuous thick lines, **—**) or parallel (more precisely *ac* uniplanar orientation, continuous thin lines, —) to the film plane. Peaks corresponding to the host helical crystalline phase of s-PS are labeled by ⊥ and // depending on the direction of their transition moment vectors, nearly perpendicular or parallel to the chain axis, whereas peaks due to the guest molecule are labeled by g. The spectra of liquid TCE and CP are shown as dotted lines (···), in parts A and B, respectively.

Just as a preliminary example, variations of relative intensity of infrared absorbance peaks, obtained with nonplarized radiation, of s-PS clathrate films, as a consequence of different crystalline phase orientations, i.e., perpendicular (thick lines) or *ac* uniplanar (thin lines), are shown in Figure 3, parts A and B, for the case of trichloroethylene (TCE) and 1-chloropropane (CP) guests, respectively. The spectral range 1090−920

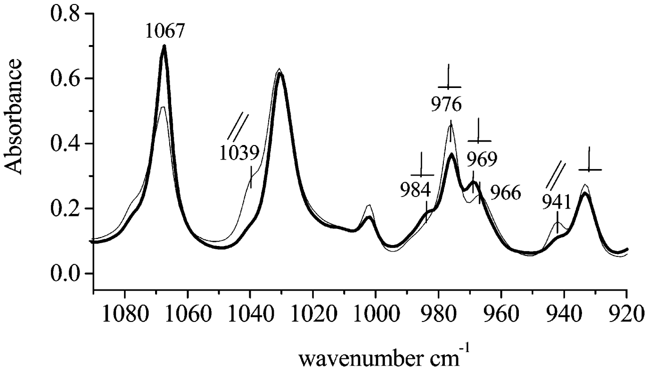

Figure 4. Same spectrum as shown in Figure 3B, but for the narrower spectral range 1090−920 cm^{-1}.

cm^{-1} of the plot of Figure 3B, for which the contribution of the CP guest is nearly negligible, is shown in more detail in Figure 4. It is apparent that the crystalline phase orientation heavily affects the intensity of peaks which are typical of the helical crystalline host phase,[18,19] labeled by ⊥ or || in Figures 3 and 4, depending on the direction of their transition moment vectors, nearly perpendicular or parallel to the chain axis, as established by infrared linear dichroism analysis on uniaxially stretched s-PS clathrate films.[20]

In particular, the spectra of films with perpendicular orientation (thick lines in Figures 3 and 4) present, as expected for this kind of orientation, high intensities for the peaks corresponding to vibrational modes whose transition moment vectors are nearly perpendicular to the chain axis, located at 1378, 1320, 1169, 984, 976, 934, 548, and 505 cm^{-1}.[20] As also expected, the spectra of films with uniplanar *ac* orientation (thin lines in Figures 3 and 4) present high intensities for the peaks corresponding to vibrational modes whose transition moment vectors are nearly parallel to the chain axis, being located at 1354, 1278, 1039, 941, 769, 571, and 538 cm^{-1}. Moreover the latter spectra present high intensities for the perpendicular peaks at 1320, 976, and 934 cm^{-1}, thus suggesting an orientation of the corresponding transition moment vectors nearly parallel to the *ac* plane and, hence, nearly parallel to the *a* crystallographic axis. It is also worth noting that the band, which for unoriented clathrate samples (e.g., sPS/CP clathrate powders) is located at 967 cm^{-1}, for oriented films with perpendicular and uniplanar orientation presents its maximum at 969 and 966 cm^{-1}, respectively (Figure 4). This apparent peak shift, associated with the two different crystalline phase orientations, is possibly due to opposite variations of intensity for two peak components of the band.

It is also worth adding that the substantial changes of the relative intensity of the peaks which contribute to the absorption band in the range 990−960 cm^{-1}, which was observed for different clathrate s-PS phases and tentatively attributed to possible interactions of the chains with the guest molecules or to different kinds of chain packings, (Figure 3 of ref 18) can be now easily rationalized by the occurrence of different kinds and degrees of orientation produced by different preparation procedures (see Figure 4).

An also more relevant feature of the spectra of Figure 3 is that the kind of crystalline phase orientation also affects the intensity of absorption peaks of the guest molecules (labeled by g). In particular, some absorption peaks of TCE and CP guest molecules, after spectral subtraction of the polymer absorbance, are shown for narrower spectral ranges in Figure 5, parts A−C and A′−C′, respectively. The plots of Figure 5 also show, for comparison, the absorption peaks of TCE and CP molecules in their liquid state (dotted lines) or absorbed into the amorphous phase of β form s-PS films (dashed lines).

As for TCE (Figure 3A and Figure 5A−C), well-defined peak shifts associated with guest clathration are clearly apparent: most relevant are the shifts of the C−Cl IR bands [21] at 840 cm^{-1} , due to the ν_5(A′) vibrational mode,[21] down to 834 cm^{-1} (Figure 5B) and of the peak at 1247 cm^{-1} up to 1250 cm^{-1} (Figure 5A). Analogous shifts, possibly due to specific interaction between guest molecules and s-PS helical nanoporous structure, have been already observed for C−Cl stretching bands of 1-chloropropane, 1,2-dichloroethane, and 1,2-dichloropropane [6f] as well as for the $\delta_{\mathrm{Cl-C-H}}$ peak of chloroform,[6h] when these chlorinated molecules are included in the corresponding s-PS clathrate phases. As for the intensities of the TCE guest molecules, the film with perpendicular chain axis orientation (thick line) presents high absorption intensity for the whole band 1265−1225 cm^{-1} (Figure 5A) due to the in plane ν_3(A′) vibrational mode, [21] and low absorption intensity for the peak at 455 cm^{-1} (Figure 5C), due to the out of plane ν_{11}(A″) vibrational mode.[21] This is a clear indication of a location of the TCE molecular plane roughly parallel to the film surface, and hence, nearly perpendicular to the host polymer chains.

As for CP (Figure 3B and Figure 5A′−C′), the spectral comparison of Figure 5A′ confirms that the intensity of the 1263 cm^{-1} (which is only a shoulder for the CP absorbed into the amorphous s-PS phase) is strongly increased by inclusion of the CP guest molecule into the s-PS host crystalline phase, as already described for uniaxially stretched s-PS/CP clathrate films.[20] Moreover, the broad absorption band of the CP molecules (at 728 cm^{-1} for the liquid and at 725 cm^{-1} for the molecules absorbed into the amorphous phase) is splitted in at least two peak components at 728 and 723 cm^{-1}, the first one being maximized for perpendicular crystalline phase orientation while the second one being similar for both kinds of orientation (Figure 5C′). A general analysis of the spectra of Figure 3B and Figure 5A−C′ shows that the gauche (G) peaks at 1304, 1257, and 649 cm^{-1} (Figure 3) present similar intensity for perpendicular and *ac* uniplanar clathrate phase orientations while the trans (T) peaks at 1263, 894, and 727 cm^{-1} are definitely more intense for the films with perpendicular orientation (Figure 5A−C′, respectively). This increased intensity, of peaks of the trans conformer, for the films presenting a perpendicular chain axis orientation, can be rationalized on the basis of the preferential placement of the planar conformer nearly perpendicular to the polymer host chain axis [6f,g] and hence nearly parallel to the film surface. This implies that for perpendicular chain axis orientation the transition moment vectors of the guest in-plane vibrational modes (like, e.g., the ν_{14} at 1263 cm^{-1} and ν_{23} at 727 cm^{-1})[20] are nearly parallel to the film surface and hence their interaction with the electric field of the normally incident infrared beam tends to be maximized.

It is worth noting that the control of the clathrate phase orientation could be particularly relevant for the case of active guests (e.g., fluorescent, photochromic, nonlinear optical, photoreactive, etc.). Experimental studies on clathrate films including active guest mol-

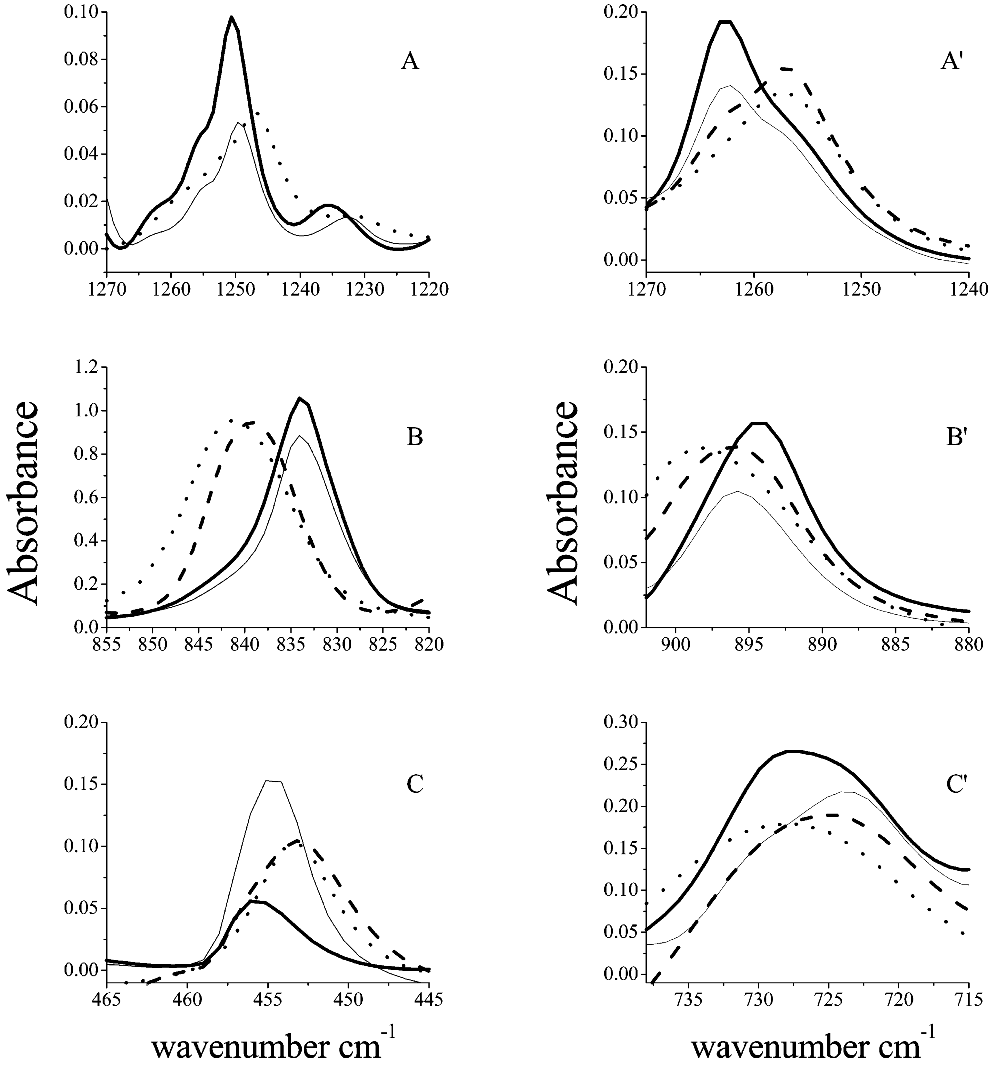

Figure 5. FTIR absorption spectra of TCE (A–C) and CP (A′-C′) molecules: guests of the s-PS clathrate phase with perpendicular polymer chain orientation (continuous thick lines, —) or *ac* uniplanar orientation (continuous thin lines, —) or simply absorbed into the amorphous phase of a β form s-PS film (dashed lines, - -) or in the liquid state (dotted lines, ···). FTIR absorption spectra in the wavenumber ranges 1270–1220 cm^{-1} (A), 855–820 cm^{-1} (B), 465–445 cm^{-1} (C) and 1270–1240 cm^{-1}(A′), 905–880 cm^{-1} (B′), and 740–715 cm^{-1} (C′) are shown for TCE and CP guest molecules, respectively.

ecules and presenting both kinds of crystalline phase orientations described in the present paper are in progress.

More in general, the achievement of different kinds of clathrate phase orientations gives the opportunity to make spectroscopical characterizations of "isolated" guest molecules, presenting two different and well-defined orientations with respect to the incident radiation beam.

Conclusions

Syndiotactic polystyrene films which include clathrate crystalline phases with high degrees of parallel (uniplanar as for the *ac* planes) or perpendicular orientation of their chain axes with respect to the film surface have been achieved, also for high thickness films (at least up to 100 μm). To our knowledge, the perpendicular orientation is unprecedented for high thickness polymeric films.

Both kinds of orientation can be achieved by solution casting procedures, leading to clathrate phases, and the kind of orientation is determined by the choise of the solvent, which eventually becomes guest of the clathrate phase.

A precise control of the orientation of the crystalline phases should allow a fine-tuning of structural and functional properties of semicrystalline s-PS films. For instance, perpendicular and *ac* uniplanar orientations of the crystalline phases of these thick s-PS films generate opposite and high anisotropy, as for the refractive indexes.

Moreover, the achievement of different kinds of clathrate phase orientations gives the opportunity to make spectroscopical characterizations of "isolated" guest molecules, presenting two different and well-defined orientations with respect to the incident radiation beam. In particular, large variations of intensity of infrared absorption peaks of the host helical chains as well as of trichloroethylene and 1-chloropropane guest molecules, as a consequence of perpendicular or *ac* uniplanar orientation of the crystalline phase with respect to the film surface, have been described.

These infrared absorption intensity variations give some information relative to directions of transition moment vectors associated with vibrational modes of host helical chains and of guest molecules. In particular, it has been established that the vibrational modes associated with the host bands at 1320, 976, and 934 cm^{-1}, are nearly parallel to the *a* crystallographic axis. Moreover, based on the available knowledge of the vibrational modes of TCE and CP molecules, an orientation of the planes of TCE and of the CP trans conformer roughly perpendicular to the host polymer chains, for the s-PS clathrate phases, has been established. The latter result is in agreement with those of previous X-ray diffraction[8a] and molecular modeling analyses,[6g] for trans conformers of chlorinated guests (of CP but also of 1,2-dichloroethane and of 1,2-dichloropropane).

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