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ARTICLE

Chiro-optical Materials Based on a Racemic Polymer

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ABSTRACT: Intense circular dichroism (CD) phenomena, both in the ultraviolet and infrared spectral regions, are produced in syndiotactic polystyrene (s-PS) amorphous samples, when their crystallization is induced by volatile nonracemic molecules, leading to the formation of cocrystalline phases between the racemic polymer host and the nonracemic guest. These CD phenomena remain essentially unaltered also after complete removal of the nonracemic guest as well as after thermal treatments up to 240 °C, i.e., below the s-PS melting temperature. Hence, the described crystallization procedures, as induced by temporary sorption of nonracemic guests, provide an easy way to produce stable chiro-optical materials of any thickness and shape.

Introduction

It is well-known that stereoregular racemic polymers can lead not only to detection but also to amplification of chirality, since cooperative interactions with low-molecular-mass nonracemic compounds can generate prevalence of one polymer helical hand.[1,2]

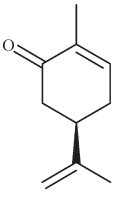
These chirality transfer and amplification phenomena have been observed not only for polymers in solution[1] but also for solid polymer films,[2] which could have in principle applications in chiro-optical devices and data storage systems. These chiral sensing films are based on syndiotactic polystyrene (s-PS), a cheap commercial stereoregular polymer, being easy to process and presenting good mechanical and optical properties as well as thermal and chemical stability.[3]

In particular, suitable s-PS films, as a consequence of exposure to nonracemic volatile guest molecules, develop intense induced circular dichroism (ICD), with a major Cotton band at 200 nm and a minor Cotton band of opposite sign at 223 nm.[2] This chiral sensitivity occurs for s-PS films spin-coated at high spin rates, from selected solvents. In particular, high ICD intensities (in the presence of all the considered nonracemic molecules) have been observed for s-PS thin films (≈0.1 μm) spin-coated from chloroform solutions, for spin rates larger than 1600 rpm,[2b] while negligible ICD phenomena are observed for films spin-coated with most solvents and always for spin rates lower than 100 rpm.[2b]

The task of elucidating the origin of this chiral sensitivity has been made difficult by the very complex polymorphic behavior of s-PS,[4] involving two crystalline phases (α[5] and β[6]) with trans-planar chains and three crystalline phases (γ,[7] δ,[8] and ε[9]) as well as many different cocrystalline phases[10,11] with s(2/1)2 helices. An additional difficulty is given by the low thickness of the known chiral sensing films, being unsuitable for standard Fourier transform infrared (FTIR) or wide-angle X-ray diffraction techniques.

In the first part of this paper, the origin of this chiral sensitivity of thin spin-coated s-PS films (≈0.1 μm) has been elucidated by closely associated infrared reflection absorption spectroscopy (IRRAS) and UV−vis circular dichroism (CD) measurements. In the second part of the paper, the possible chiral sensitivity of much thicker s-PS films (20−50 μm), as obtained by melt extrusion, has been studied by vibrational circular dichroism (VCD), FTIR, and X-ray diffraction measurements.

Scheme 1. Carvone Enantiomer Inducing Positive CD band at $\lambda \approx 200$ nm in s-PS Films Spin-Coated from Chloroform Solutions



(R)-(−)-Carvone

The present study is mainly based on vibrational techniques (FTIR, IRRAS, and VCD), which allow to determine the polymer conformation, the nature of the s-PS crystalline phases,[12] the presence of guest molecules in cocrystalline phases,[13] and the chirality of both guest and host molecules. The use of vibrational techniques has also been facilitated by the recent complete vibrational analysis of infinite s-PS chains both in the trans-planar[14a] and in the helical s(2/1)2[14b,c] conformation.

Experimental Section

Materials. 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 $M_w/M_n = 3.9$.

Chloroform, (*R*)-carvone (98%, e.e. 98%), and (*S*)-carvone (96%) were supplied by Aldrich and were used without further purification. The carvone enantiomer inducing positive CD band at $\lambda \approx 200$ nm in s-PS films is shown in Scheme 1.

Methods. s-PS films for the IRRAS and CD measurements, having thickness in the range 0.1−0.2 μm, have been prepared by spin-coating of diluted s-PS solutions onto gold and quartz surfaces, respectively. Because of the low film thickness, a complete guest (chloroform or toluene) desorption occurs spontaneously at room temperature after few hours.[2]

Amorphous s-PS films with thickness in the range 20−50 μm were obtained by melt extrusion; the complete lack of crystallinity was verified by FTIR and X-ray measurements while the complete absence of axial orientation has been established by

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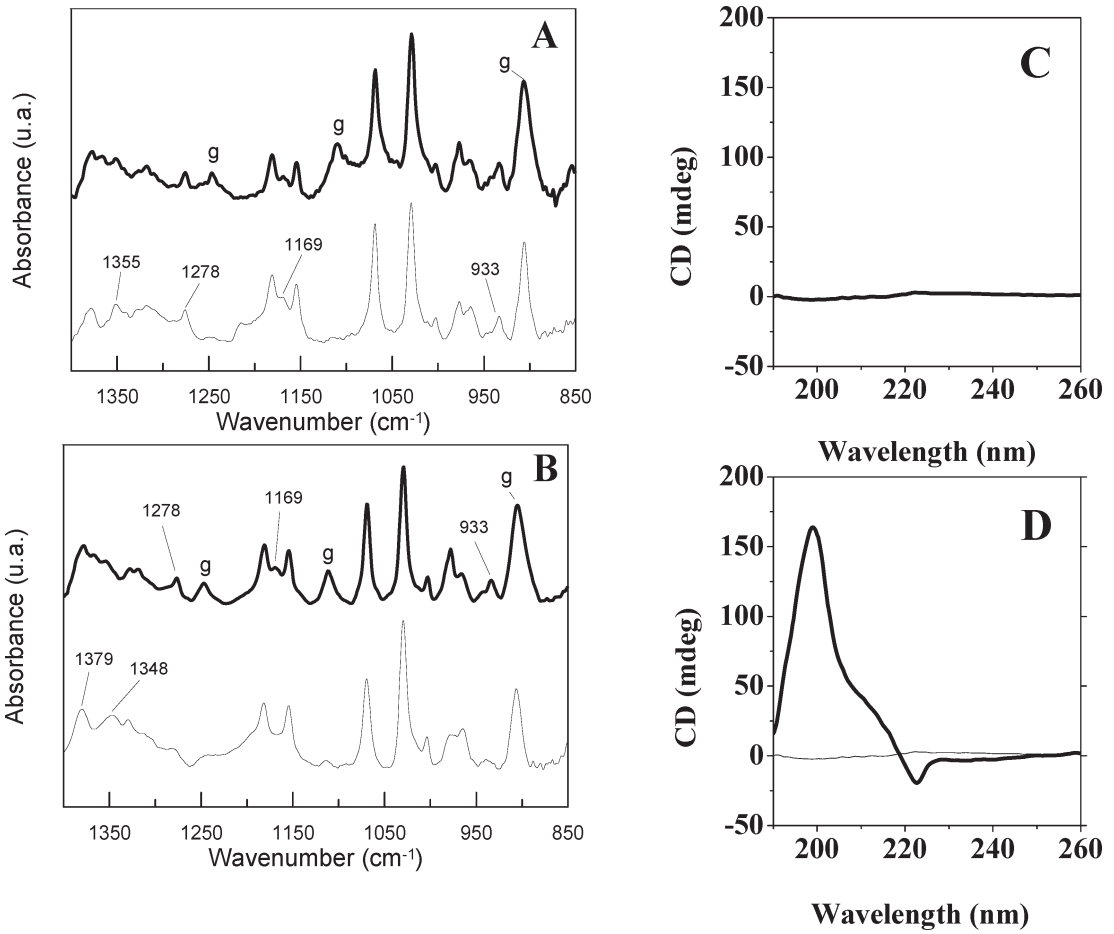

Figure 1. IRRAS (A, B) and CD (C, D) spectra of s-PS films, obtained by spin-coating from chloroform solutions: (A, C) as prepared at spin-rate of 100 rpm (crystalline δ, thin line) and after exposure to vapor of (*R*)-carvone (cocrystalline, thick line); (B, D) as prepared at spin-rate of 1600 rpm (amorphous, thin line) and after exposure to vapor of (*R*)-carvone (cocrystalline, thick line).

polarized infrared spectra, indicating the absence of infrared linear dichroism. However, to eliminate any possible linear dichroism influence, the CD and VCD measurements have been conducted by averaging the spectra as collected for several different in-plane rotation angles.

CD spectra were measured using a Jasco J-715 spectropolarimeter. All measurements were performed using the following parameters: single scan, continuous scanning mode (350−190 nm range), 200 nm/min scanning speed, 2 nm SBW (constant bandpass mode), 0.2 nm data interval, vertical scale in autoranging mode, no baseline correction. The CD data have been expressed as the ellipticity (1 mdeg equals 0.001 deg).

The IRRAS spectra (600 scans and 2 cm^{-1} resolution) were collected using a Bruker Tensor 27 FTIR spectrometer coupled to a PMA50 external module equipped with a linear KRS5 linear polarizer, a ZnSe 50 kHz photoelastic modulator (PEM, by HINDS), an optical filter (transmitting below 4000 cm^{-1}), a variable angle reflection accessory, and a narrow band MCT (mercury cadmium telluride) detector. An incidence angle of 85° from the normal to the surface was used for samples obtained by spin-coating at 1600 rpm while for samples obtained at 100 rpm an incidence angle of 77° was used.

IR and VCD measurements were recorded using a commercial Bruker Tensor 27 FT-IR spectrometer coupled to a PMA50 external module (needed to double modulate the infrared radiation) using a linear KRS5 polarizer, a ZnSe 50 kHz photoelastic modulator (PEM, by HINDS) with a proper antireflecting coating, an optical filter (transmitting below 2000 cm^{-1}), and a narrow band MCT (mercury cadmium telluride) detector.

All VCD spectra were recorded for 5 min of data collection time at 4 cm^{-1} resolution.

According to experimental procedures described in the literature,[15] films were tested for satisfactory VCD characteristics by comparison of the VCD obtained with the film rotated by ±45° around the light beam axis. In separate measurements with 1 h data collection time, we have also tested ±90° rotation of the film; VCD bands were found to be unaffected by changing collection time as well as by changing the rotation of the film.

Results and Discussion

Thin Films. *IRRAS and CD of Spin-Coated Films before and after Sorption of a Nonracemic Guest*. The IRRAS spectra of s-PS films, having a thickness of nearly 0.1 μm, obtained by spin-coating at 100 rpm and at 1600 rpm of 1 wt % solutions in chloroform onto gold surfaces are compared in parts A and B of Figure 1 (thin lines), respectively. Both spectra do not show the absorbance peaks of chloroform, indicating that the solvent was completely evaporated after the spin-coating procedures. The film prepared at low spin rate exhibits a high degree of helical crystallinity (nearly 40%) as pointed out, for instance, by the peaks at 1355, 1278, 1169, and 933 cm^{-1} (Figure 1A), being associated with the helices of the crystalline phase.[14c] The film prepared at high spin rate is, instead, fully amorphous, as for instance pointed out by the broad and intense amorphous peak at 1379 cm^{-1} (Figure 1B).[12b,j]

The IRRAS spectra of s-PS films obtained by spin-coating at 100 rpm and at 1600 rpm of chloroform solutions after exposure to (*R*)-carvone are compared in parts A and B of Figure 1 (thick lines), respectively. Both spectra show the

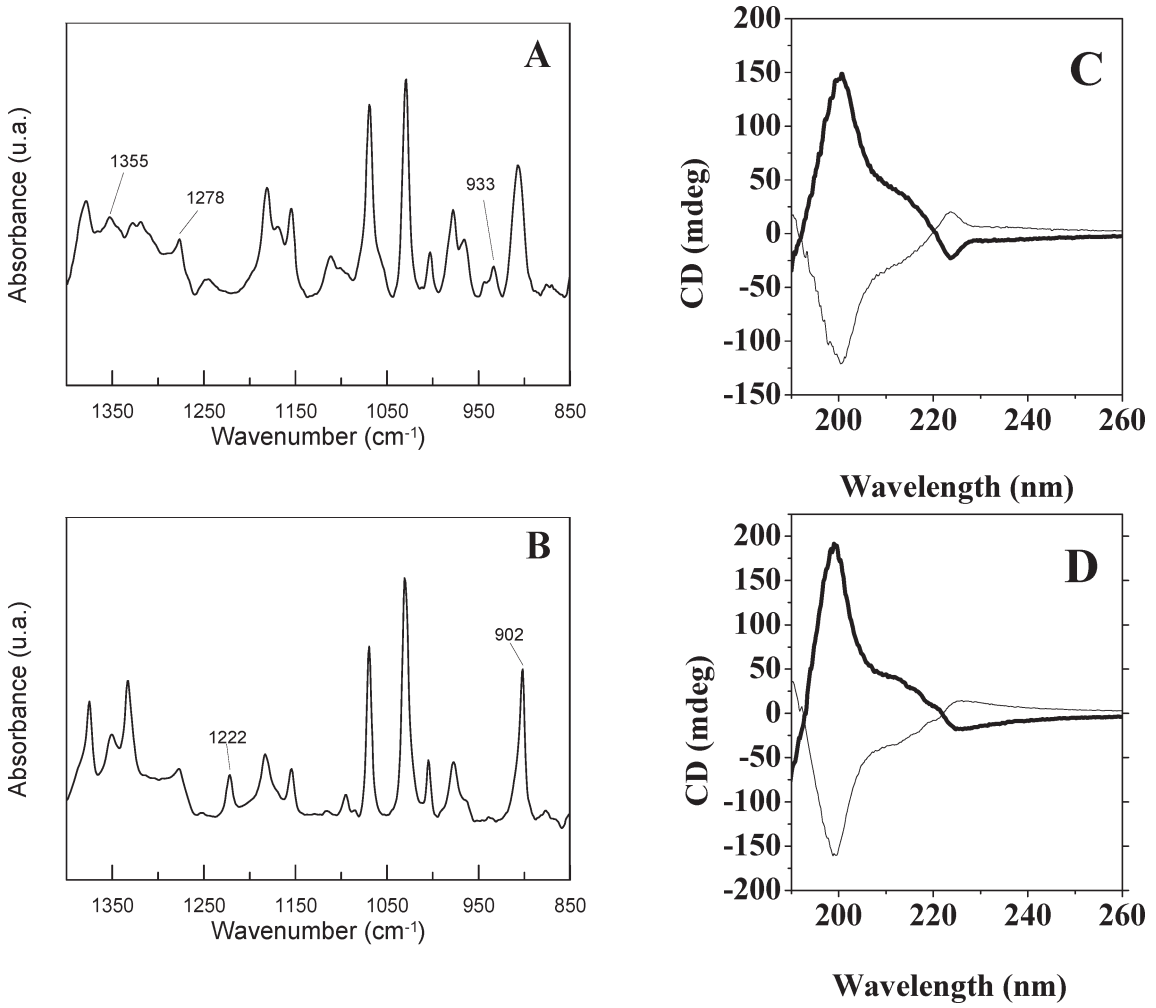

Figure 2. IRRAS (A, B) and CD (C,D) spectra of s-PS films, obtained by spin-coating at 1600 rpm from chloroform solutions and exposed to vapor of (*R*)-carvone (thick line) or (*S*)-carvone (thin line): (A, C) after carvone desorption (helical crystalline); (B, D) after annealing at 240 °C (trans-planar crystalline).

intense carvone absorbance peaks at 1247, 1111, and 903 cm^{-1} (labeled as g in Figure 1). The spectra of Figure 1B also show that the carvone sorption induces crystallization of the amorphous s-PS film (see, e.g., the appearance of the helical crystalline peaks at 1278, 1169, and 933 cm^{-1}) and the formation of a sPS/carvone cocrystalline phase.

The CD spectra of the s-PS films obtained by spin-coating at 100 and 1600 rpm of chloroform solutions after exposure to (*R*)-carvone are compared in parts C and D of Figure 1, respectively. It is clearly apparent that the CD spectra of the films, containing essentially the same amount of the nonracemic guest (roughly 7%) and being crystalline or amorphous before carvone sorption, are negligible (Figure 1C) or intense (with Cotton bands at 200 and 223 nm, Figure 1D, thick line), respectively.

The IRRAS spectra of s-PS films obtained by spin-coating with most solvents, like e.g. benzene, toluene, and 1,3,5-trimethylbenzene, which do not produce chiral-sensing films,[2b] are strictly similar to that one of Figure 1A and indicate the presence of the δ crystalline phase with a degree of crystallinity, which is typically in the range 30−45%.

It is worth adding that AFM images of films spin-coated from toluene at any rate or from chloroform at low rate show similar fine morphologies (Figure 6 of ref 2b) also suggest high crystallinity while AFM images of films spin-coated from chloroform at high rates show only isolated morphologies (Figure 7 of ref 2b) and suggest difficult and sporadic nucleation.

On the basis of the above-reported results, it is possible to conclude that the intense ICD phenomena observed for s-PS films[2] are associated with the crystallization of the amorphous s-PS phase, as induced by sorption of nonracemic guest molecules.

IRRAS and CD of Spin-Coated Films after Desorption of the Nonracemic Guest and Subsequent Thermal Treatments. The IRRAS spectrum of the s-PS film whose crystallization has been induced by carvone sorption (Figure 1B, thick line), after complete carvone desorption (10 days at room temperature), is changed as shown in Figure 2A. This spectrum indicates, beside the carvone loss, the maintenance of a helical crystalline phase, with a degree of crystallinity close to 35%.

The CD spectra of s-PS films, whose crystallization has been induced by (*R*)- or (*S*)-carvone treatments, are shown in Figure 2C (thick and thin line, respectively) and are essentially unaltered with respect to those of the starting cocrystalline films, still including the nonracemic guest (compare, e.g., Figure 1D and Figure 2C, thick lines).

The IRRAS spectrum of helical semicrystalline film of Figure 2A, after annealing at 240 °C, is shown in Figure 2B. The spectrum indicates the presence of a trans-planar crystalline

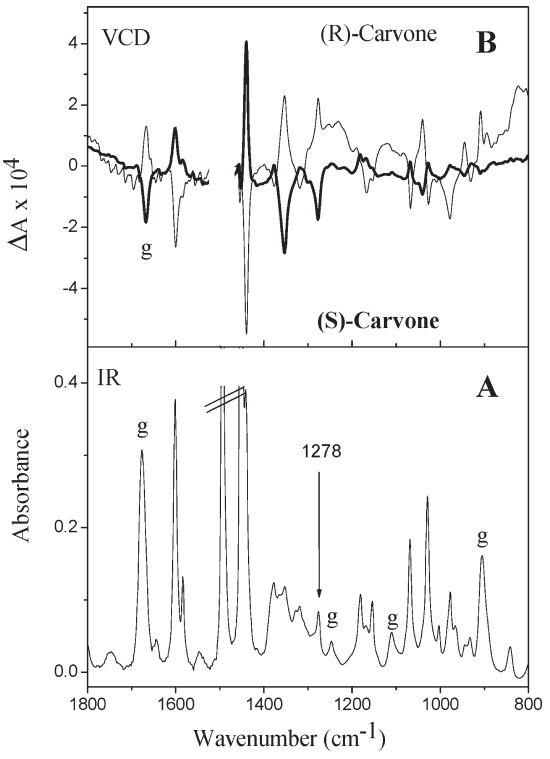

Figure 3. FTIR (A) and VCD spectra (B) of amorphous s-PS films, having a thickness of nearly 20 μm, after sorption of (*S*)-carvone (thick line) or (*R*)-carvone (thin line). The main peaks of the carvone guest molecules are labeled by "g".

phase (see, e.g., the intense peak at 1222 cm^{-1}) with a degree of crystallinity close to 35%. Moreover, the peak located at 902 cm^{-1} clearly indicates the presence of the α phase,[14a] as expected for the used crystallization procedure.[4a]

The CD spectra of these α-form films, obtained from helical crystalline phases as induced by (*R*)- or (*S*)-carvone treatments (Figure 2D, thick and thin line, respectively), exhibit intense Cotton bands at 199 and 225 nm, i.e., only slightly shifted with respect to those of the starting cocrystalline films (Figure 2C).[2b]

In summary, the intense ICD phenomena are maintained, independently of any possible crystal-to-crystal tranformation, provided that the initial crystallization had been induced by sorption of nonracemic guest molecules.

Thick Films. On the basis of the results of the previous section, it is reasonable to make the hypothesis that any amorphous s-PS sample could develop intense ICD phenomena, if nonracemic guest molecules induce its crystallization. This hypothesis has been verified for unoriented melt-extruded films having a thickness of 20−50 μm. It is worth noting that, for such a thickness for the study of the chiral sensitivity, the available UV−vis CD technique is not applicable, and a vibrational CD technique has been used instead.

FTIR and VCD of Melt-Extruded s-PS Films after Crystallization Induced by a Nonracemic Guest. FTIR and VCD spectra of amorphous s-PS films, having a thickness of nearly 20 μm, after sorption of nonracemic carvone samples are shown in parts A and B of Figure 3, respectively (for (*S*)- and (*R*)-carvone, thick and thin lines, respectively). The carvone content, according to a thermogravimetric analysis, is close to 8%.

As already observed for the thin films of Figure 1B, also for the thick films the carvone sorption induces crystallization, as shown by the presence of the helical crystalline peaks (like, e.g., the 1278 cm^{-1} peak, labeled in Figure 3A). The VCD spectra of Figure 3B show many intense peaks, being of

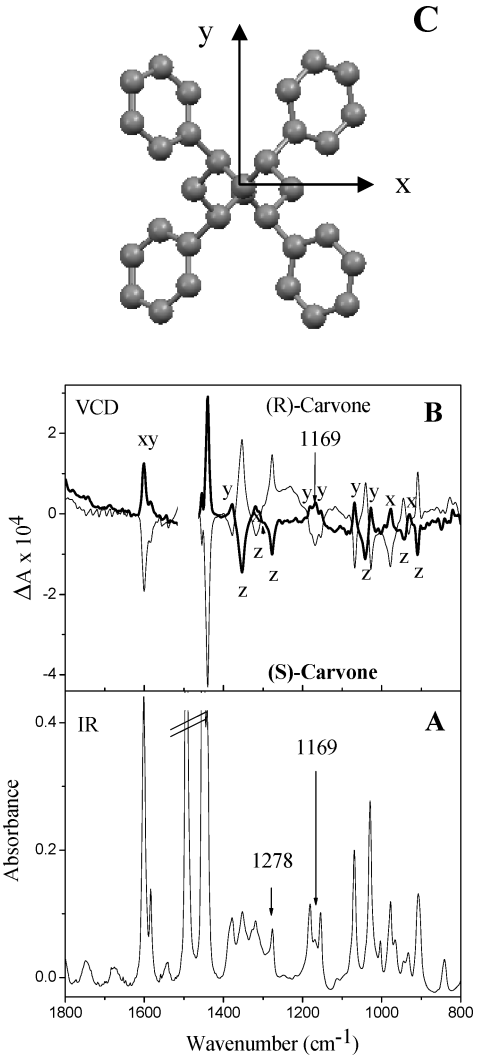

Figure 4. FTIR (A) and VCD spectra (B) of s-PS films, as obtained by sorption and desorption, in amorphous films, of (*S*)-carvone (thick line) or (*R*)-carvone (thin line). (C) Along the chain axis (along *z*) representation of the s(2/1)2 helical chain of s-PS. Symmetry considerations impose that transition moment vectors (TMV) have to be parallel or perpendicular to the chain axis. TMV perpendicular to the chain axis have to be along the binary axes, indicated by *x* and *y*. The labels in (B) indicate the direction of the TMV associated with each VCD (and FTIR) peak.

opposite signs for films treated with (*S*)- and (*R*)-carvone. In fact, large circular dichroism values are observed not only for the peaks of the nonracemic guest (e.g., at 1667, 1247, 1111, and 1057 cm^{-1}) but also for many polymer host peaks.

The FTIR and VCD spectra of the films of Figure 3, after extraction of the nonracemic guest by supercritical carbon dioxide, are reported in parts A and B of Figure 4, respectively. A comparison between the FTIR spectra of Figures 3A and 4A shows that the guest removal is complete, while the amount of the polymer helices remains essentially unaltered (not far from 35%).

After the removal of the nonracemic guest, most vibrational peaks of the host helical crystalline phase remain largely dichroic (Figure 4B). Because of the absence of the nonracemic guest, the sign and intensity of the dichroism associated with the different host vibrational peaks (and hence to different vibrational modes) can be more easily established.

A detailed analysis of the VCD spectra of Figure 4B clearly shows that for the films treated with (*S*)-carvone positive and

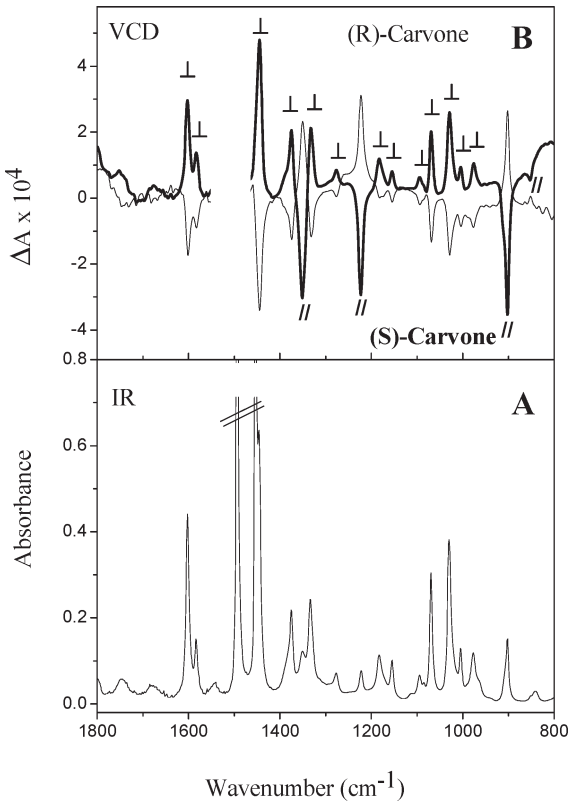

Figure 5. FTIR (A) and VCD spectra (B) of s-PS films exhibiting the trans-planar α-crystalline phase, as obtained as a consequence of annealing of the cocrystalline films at 240 °C. The labels in (B) indicate the direction (parallel or perpendicular to the chain axis) of the TMV associated with each VCD (and FTIR) peak.

negative VCD peaks are associated with vibrational modes whose transition moment vectors (TMV) are perpendicular (along x or y) and parallel (along z) to the s(2/1)2 helical axis (Figure 4C), respectively. Moreover, higher VCD intensities are observed for infrared peaks associated with a single helix vibrational mode, whose TMV is along only one of the three possible directions: x, y, or z.[14c] As an example, it is worth noting that the 1169 cm^{-1} peak, exhibiting a lower FTIR intensity, with respect to the close 1181 and 1155 cm^{-1} peaks (Figure 4A), becomes prominent in the VCD spectra (Figure 4B). This is possibly related to the high anisotropy of the former peak (corresponding to a TMV directed along y) and the poor anisotropy of the other two peaks (last column of Table 3 of ref 14c). On this basis, the main VCD peaks of Figure 4B have been indicated by the x, y, or z labels.

FTIR and VCD of Melt-Extruded s-PS Films after Crystallization Induced by a Nonracemic Guest and Subsequent Thermal Treatments. As already observed for CD spectra of thin spin-coated s-PS films,[2b] the IR and VCD spectra of Figure 4B remain essentially unaltered as a consequence of annealing of the cocrystalline films at 170 °C, leading to the helical γ-form.

Of course, dramatic changes in the IR spectra are, instead, associated with the crystal-to-crystal transition due to annealing of the cocrystalline films at 240 °C, leading to the trans-planar α form (Figure 5A). As already observed for the CD in the ultraviolet region, also for the infrared region intense VCD peaks are maintained (Figure 5B), even when the chain molecules of the crystalline phase have lost their helicity. In particular, for the α-form films obtained by annealing of films whose crystallization has been induced by (*S*)-carvone, positive and negative dichroism is observed for peaks corresponding to vibrational modes perpendicular (⊥) and parallel (||) to the chain axes, respectively.[14a] On this basis the main VCD peaks of Figure 5B have been indicated by ⊥ or || labels. In this respect, it is worth adding that the absence of any axial orientation has been carefully established, according to the methods described in the Experimental Section.

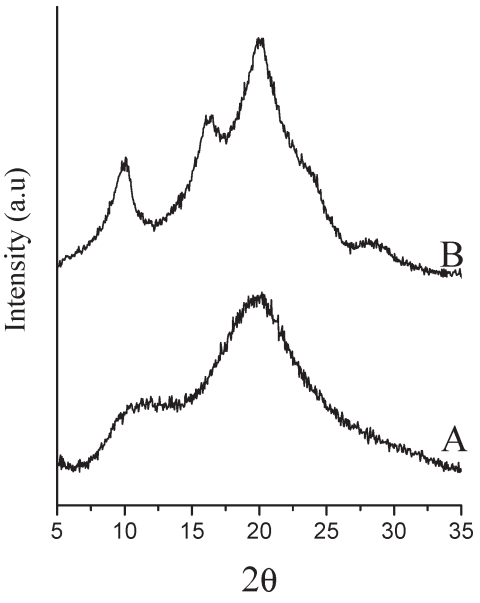

Figure 6. X-ray diffraction patterns of an amorphous s-PS film before (A) and after (B) carvone sorption at room temperature.

It is worth noting that CD spectra of thin films and VCD spectra of thick films give similar information. In fact, both CD and VCD peaks of the polymer host are unaffected by the nonracemic guest desorption. Moreover, for both CD and VCD spectra, circular dichroism phenomena remain intense also after the crystal phase transition that transforms the polymer helices into trans-planar chains.

These results support the previous suggestion[2b] that the intense ICD phenomena observed for the s-PS films are not due to some molecular chirality but to a supramolecular chirality, associated with the native cocrystal morphology. In particular, these results well agree with previous atomic force microscopy (AFM) studies showing that spin-coated s-PS films, when treated with suitable guest molecules, form complex morphologies (also presenting some helical features) that remain substantially unchanged after guest removal as well as after thermal treatments above the helix → trans-planar transition.[2b]

X-ray Diffraction of Melt-Extruded s-PS Films before and after Sorption of a Nonracemic Guest. The crystallization of amorphous films as a consequence of carvone sorption (at room temperature) has been also studied by X-ray diffraction. The X-ray diffraction patterns of an amorphous s-PS film (having a thickness of nearly 50 μm) before and after (*R*)-carvone sorption are shown in parts A and B of Figure 6, respectively. The carvone-induced crystallization is clearly shown by the appearance of intense diffraction peaks at d = 0.88, 0.55, and 0.45 nm, compatible with the intercalate s-PS/carvone cocrystalline phase as obtained by carvone sorption in δ-form films.[2a]

X-ray diffraction patterns strictly similar to that one of Figure 6B are obtained after crystallization of amorphous samples, as induced by sorption of carvone racemic mixtures. These results could suggest, for the s-PS cocrystalline

phase with the nonracemic guest, the presence of enantiomorphic polymer helices (as presently observed for all known cocrystalline phases of s-PS),[9b,10,11] rather than of only isomorphic helices (as observed for cocrystals of syndiotactic poly(*p*-methylstyrenes) with different guest molecules).[16]

Conclusions

The ICD phenomena developed by s-PS films, in the presence of nonracemic volatile molecules, have been investigated by infrared reflection absorption spectroscopy (IRRAS) and UV−vis circular dichroism (CD), for thin spin-coated films (≈0.1 μm), and by vibrational circular dichroism (VCD) and standard FTIR and X-ray diffraction measurements, for thick melt-extruded films (20−50 μm). The vibrational characterizations have also been supported by the recent complete vibrational analysis of infinite s-PS chains both in the trans-planar[14a] and in the helical s(2/1)2[14b,c] conformation.

The reported results indicate that the ICD and chiral memory phenomena, which have been recently described for spin-coated s-PS thin films, are associated with the crystallization of amorphous phases, as induced by nonracemic guests. This guest-induced crystallization leads to crystallites exhibiting a cocrystalline phase between the racemic polymer host and the nonracemic guest.

Moreover, the intense CD and VCD phenomena remain essentially unaltered as a consequence of the nonracemic guest removal as well as after thermal treatments leading to the dense helical γ-phase or to the trans-planar α-phase. In particular in the latter case, the VCD spectra clearly indicate that the ICD phenomena remain intense also for the trans-planar chains of the crystalline phase, i.e., for an achiral molecular structure. Hence, the present results support the previous hypothesis[2b] that ICD phenomena are possibly due to guest-induced formation of nonracemic crystalline morphologies, which are maintained also after solvent or thermal treatments leading to different crystal-to-crystal transformations.

The most relevant result of the present study is that not only thin films, as spin-coated by special procedures,[2] but any amorphous s-PS sample, independently of its thickness and of its preparation procedure, is able to detect amplify and memorize the chirality of nonracemic volatile molecules. This provides an easy way to prepare chiro-optical components of any shape.

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