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Chiral Optical Films Based on Achiral Chromophore Guests

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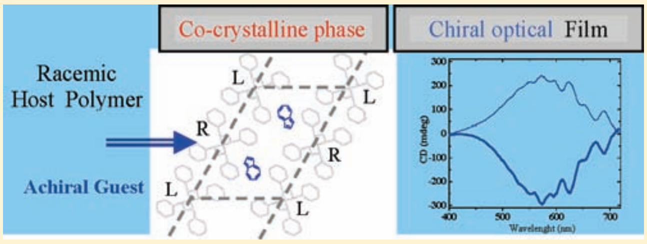
Supporting Information



ABSTRACT: Films constituted by an achiral host polymer and an achiral guest chromophore, which exhibit intense chiral optical responses for both host and guest peaks in the infrared as well as in the UV−visible regions, have been obtained. Such films can have any thickness from the nanoscale up to the macroscopic scale. This unexpected chiral optical behavior is easily achieved by crystallization of a robust commercial stereoregular host polymer (syndiotactic polystyrene, s-PS) from the amorphous phase as induced by a nonracemic guest, followed by exchange of the nonracemic guest with the achiral guest, leading to the formation of polymer-host/chromophore-guest cocrystalline phases. This finding opens the possibility to achieve s-PS-based films with chiral optical response at selected wavelengths. It has been also found that the chiral optical cocrystalline phase of s-PS with azulene exhibits a monoclinic δ-clathrate form with equal proportions of left- and right-handed helices. This confirms that the observed chiral optical behavior arises by the nonracemic native morphology of the crystalline regions, which has been induced by the temporary nonracemic guest.

INTRODUCTION

Chiral optical materials have received attention from the scientific community owing to their possible applications for chiral molecular recognition, chiral sensors, and data storage.[1,2] Chiral optical materials are often based on nonracemic macromolecules, not only due to typical advantages of polymeric materials (e.g., processability, robustness, and durability), but also due to the amplification of chirality associated with the formation of polymer helices with prevalence of one handedness.[3−6]

Intense chiral optical responses have been also obtained for macromolecular racemic receptors interacting with target nonracemic guests,[6−9] and chirality transfer and amplification phenomena have been observed not only for polymers in solution[6,7] but also for solid polymer films.[8,9]

In particular, robust chiral optical polymer films have been recently obtained by crystallization of a stereoregular polymer (syndiotactic polystyrene, s-PS),[10,11] as induced by sorption of suitable volatile organic nonracemic molecules, which led to crystallites exhibiting a cocrystalline phase[12−14] between the racemic polymer host and the nonracemic guest.[8,9] The obtained chiral optical response of the polymer films occurs for both infrared and ultraviolet−visible spectral regions and remains essentially unaltered[8] as a consequence of the nonracemic guest removal leading to the nanoporous crystalline δ phase[15,16] as well as after thermal treatments (up to 240 °C), leading to the dense helical γ phase[17] or even to the trans-planar α phase.[18] These results have suggested that the observed chiral optical behavior arises by the nonracemic native morphology of the crystalline regions, which has been induced by the temporary nonracemic guest.[9]

In this paper, we present chiral optical films based on s-PS exhibiting stable circular dichroism (CD) phenomena also in the visible region. These films can be easily obtained by inducing cocrystallization of amorphous s-PS by sorption of suitable nonracemic guests and then exchanging the nonracemic guest with an achiral (or racemic) guest chromophore.

This opens the possibility to achieve s-PS based films with chiral optical response at desired wavelengths.

RESULTS AND DISCUSSION

Fourier transform infrared (FTIR) and vibrational circular dichroism (VCD) spectra of amorphous s-PS films, having a thickness of nearly 20 μm, after sorption of nonracemic carvone are shown in Figure 1 panels A and B, respectively. In particular, the VCD spectra as obtained after sorption of (−)-(*R*)-carvone and (+)-(*S*)-carvone are shown as thick and thin lines, respectively. For both films, according to thermogravimetric analyses, the carvone content is close to 20 wt %.

As already observed in a previous report,[8] the carvone sorption induces crystallization, as shown by the appearance of the helical crystalline peaks (e.g., those at 1278 and 1169 cm^{-1}, labeled h in Figure 1A).[20] The VCD spectra of Figure 1B show many intense peaks, being of opposite signs for films crystallized by (−)-(*R*)-carvone and (+)-(*S*)-carvone. In fact, large circular dichroism values are observed not only for the peaks of the nonracemic

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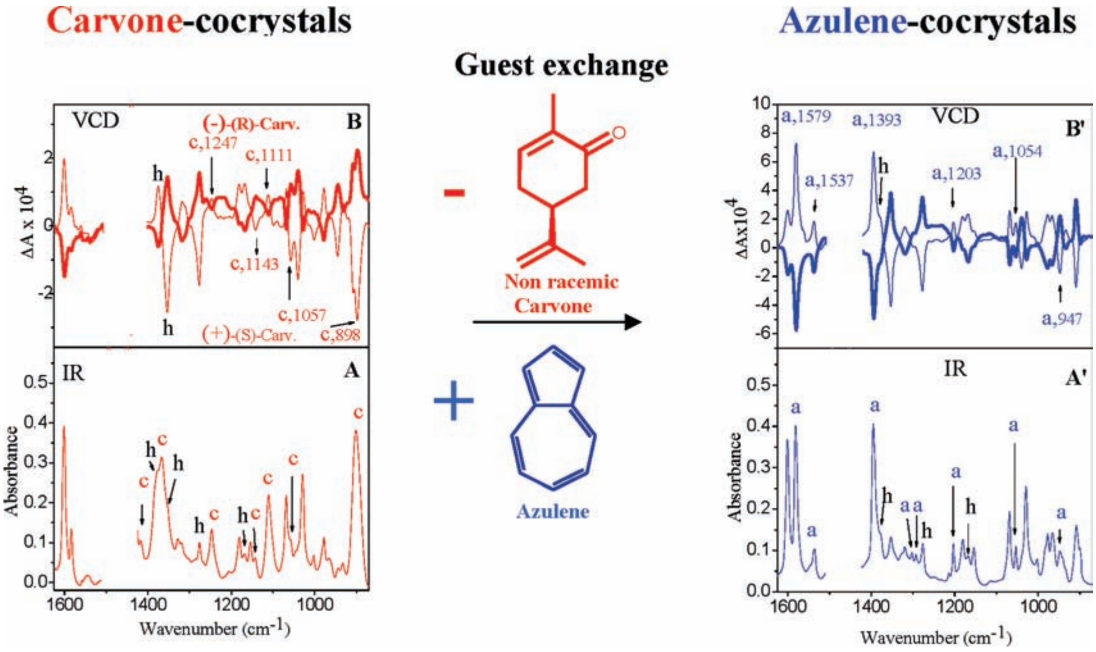

Figure 1. (A, A′) FTIR and (B, B′) VCD spectra of amorphous s-PS films, having a thickness of nearly 20 μm, after crystallization induced by sorption of (−)-(*R*)-carvone (thick lines) or (+)-(*S*)-carvone (thin lisne). (A′, B′) Spectra of the film crystallized by (−)-(*R*)-carvone or (+)-(*S*)-carvone sorption after exchange of the nonracemic carvone guest with the achiral azulene guest. The carvone content is close to 20 wt % while the azulene content is close to 14 wt %. The main peaks of the carvone and azulene guest molecules are labeled by c and a, respectively, while some typical peaks of the *s*(2/1)2 helices of s-PS crystalline phases are indicated by h.

guest (e.g., those at 1247, 1143, 1111, 1057, and 898 cm^{-1}, labeled c in Figure 1B)[19] but also for many polymer host peaks.[20] In this respect, it is worth noting that the VCD peak, corresponding to the intense IR peak of the nonracemic guest at 1368 cm^{-1}, is negligible with respect to the polymer host VCD peaks of opposite sign, being located at 1376 and 1352 cm^{-1}.

The FTIR and VCD spectra of the films of Figure 1A and B, after treatment with an azulene solution followed by desorption of the volatile solvent (as described in the Experimental Section), are reported in Figure 1 panels A′ and B′, respectively. A comparison between the FTIR spectra of Figure 1A and A′ shows that carvone has been completely removed while azulene is absorbed in an amount close to 14 wt %. It is worth adding that, after the complete guest exchange, the intensity of the s-PS helical peaks (e.g., those at 1278 and 1169 cm^{-1})[20] remains high or even slightly increases, clearly indicating the maintenance of a high degree of crystallinity. In particular, quantitative evaluation based on the FTIR method described in the Experimental Section indicates an increase of polymer crystallinity from 35% to 41%. This is consistent with a guest exchange process[21,22] leading to an s-PS/azulene cocrystalline phase.[23]

The VCD spectra of Figure 1B′ clearly indicate that not only is the circular dichroism of the host polymer maintained but also the peaks of the achiral guest are largely dichroic. In fact, VCD peaks are observed not only for the more intense (at 1579 and 1393 cm^{-1}) but also for minor azulene absorbances (at 1537, 1203, 1054, 947 cm^{-1}). It is worth noting that most VCD peaks (at 1579, 1537, 1393, 1203, and 1054 cm^{-1}, all exhibiting transition moment vectors along the azulene symmetry axis)[23−25] present the same sign, while the peak at 947 cm^{-1} (whose transition moment vector is perpendicular to the azulene plane)[23−25] presents the opposite sign. In particular, for the films crystallized by (−)-(*R*)-carvone and (+)-(*S*)-carvone, most azulene VCD peaks are negative and positive, respectively.

The observed VCD behavior is rather surprising since the azulene/s-PS cocrystalline film of Figure 1 is constituted by an achiral polymer host (generally forming racemic helices) and by an achiral guest.

This surprising chiral optical behavior of the azulene/s-PS cocrystalline films of Figure 1 is also observed for the visible light absorbance that characterizes the blue azulene guest, as shown by the spectra of Figure 2A,B. In particular, the CD spectra of Figure 2B show that the whole azulene band in the spectral range 450−710 nm[26] is negative or positive depending on the (+) or (−) chirality of the nonracemic carvone initially used to induce crystallization in amorphous s-PS, which was fully replaced by azulene.

The chiral optical behavior of the azulene/s-PS cocrystalline films can be also observed for the more intense ultraviolet (UV) absorbances, which characterize both the s-PS host and the azulene guest, by using much thinner films. In particular, UV and CD spectra of spin-coated s-PS films having a thickness of 0.1 μm after crystallization induced by (−)-(*R*)-carvone or (+)-(*S*)-carvone sorption, followed by exchange of the nonracemic carvone guest with the achiral azulene guest, are shown for the spectral range 220−400 nm in Figure 2 panels C and D, respectively. The CD spectra of Figure 2D show that the s-PS film, as initially crystallized by (−)-(*R*)-carvone, which presents a negative Cotton band of the polymer at 223 nm,[8] also presents dichroic bands of the achiral guest: an intense positive with maxima at 280, 285, and 289 nm as well as weaker positive and negative bands at 343 and 351 nm, respectively.

In this respect it is worth noting that the visible band (in the range 450−710 nm) and the most intense UV band (in the range 270−295 nm), which are associated with electronic states belonging

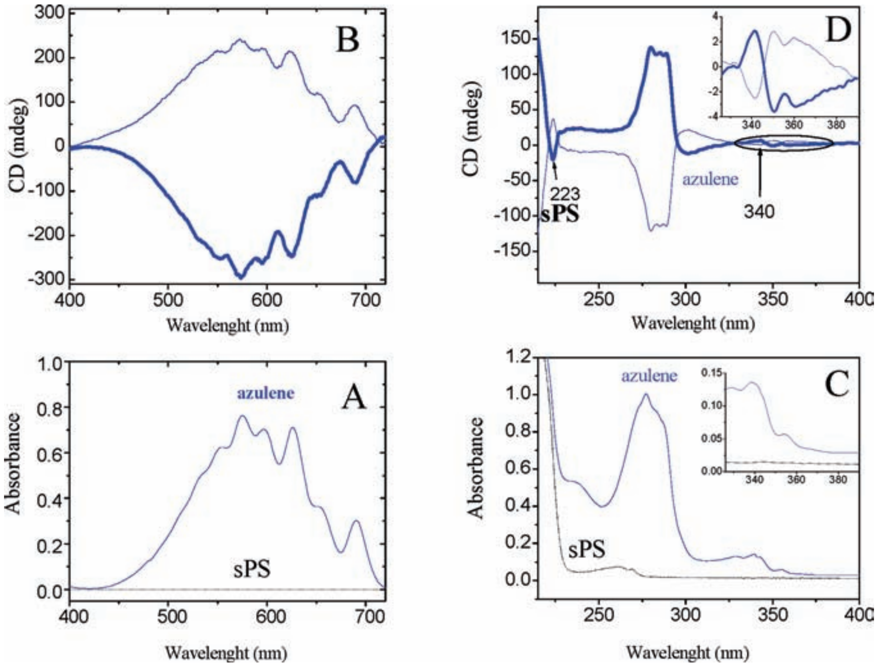

Figure 2. UV–visible and CD spectra of azulene/s-PS cocrystalline films, as obtained by (−)-(*R*)-carvone (thick line) or (+)-(*S*)-carvone (thin line) induced crystallization, followed by complete exchange of the nonracemic carvone with the achiral azulene guest: (A, B) thick films of Figure 1 (20 μm); (C, D) spin-coated s-PS films, having a thickness of nearly 0.1 μm. The Visible and UV spectra of the s-PS films after azulene removal are shown for comparison as a dotted lines in A and C, respectively. The insets in C and D enlarge the UV and CD spectra for the wavelength range 330−390 nm.

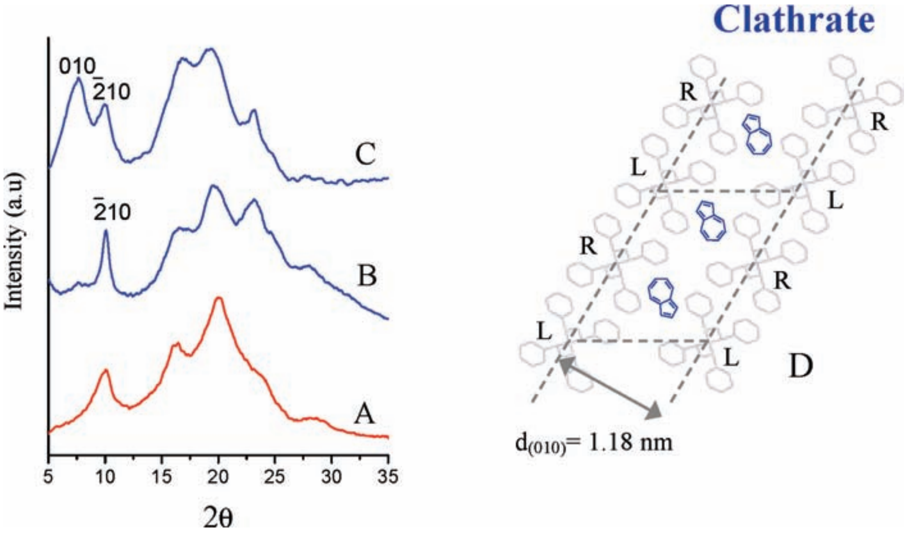

Figure 3. X-ray diffraction patterns (Cu Kα) of chiral optical s-PS films, having a thickness of nearly 20 μm: (A) obtained by crystallization of an amorphous film as induced by sorption of nonracemic carvone (carvone content close to 20 wt %); (B) after exchange of the nonracemic carvone guest with the achiral azulene guest (azulene content close to 14 wt %). (C) Diffraction profile of the photographic pattern taken with X-ray beam perpendicular to the film surface, for the same film of spectrum B. (D) Schematic along the polymer chain projection of the δ-clathrate structure of the s-PS/azulene cocrystalline phase. The orientation of the azulene guest molecules has not been defined and a random distribution of the two sketched orientations possibly occurs.

to the irreducible representations A_1 and B_1 of the symmetry group C_{2v}, respectively,[27] present opposite CD signs (Figure 2).

VCD and CD behaviors, strictly similar to those shown in Figures 1 and 2, have been observed for the films first subjected to removal of the nonracemic guest, thus leading to an empty δ phase,[15] and then subjected to azulene sorption from dichloromethane solution. Hence a direct nonracemic/achiral guest-exchange procedure is not needed for the maintenance of the chiral optical response.

The formation in the chiral optical films of an s-PS/azulene cocrystalline phase is clearly confirmed by X-ray diffraction measurements, as obtained by an automatic wide-angle diffractometer. In particular, the X-ray diffraction patterns of the chiral optical s-PS 20 μm films containing carvone and azulene, whose

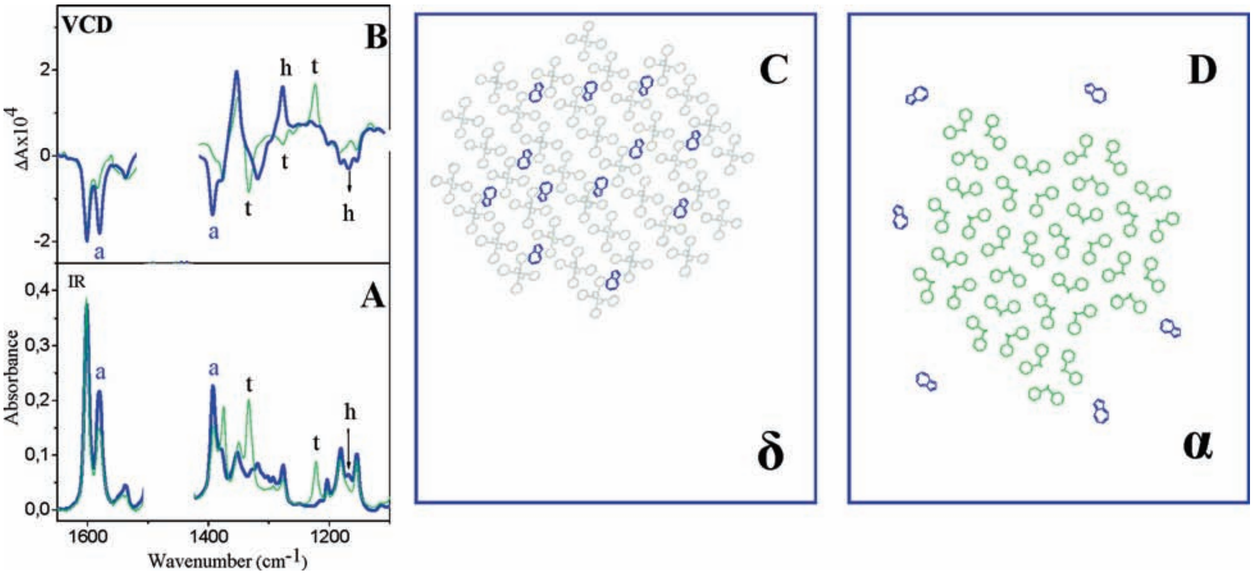

Figure 4. (A) FTIR and (B) VCD spectra of amorphous s-PS films, having a thickness of nearly 20 μm, after crystallization induced by sorption of (−)-(R)-carvone: (thick lines) after exchange of the nonracemic carvone guest with the achiral azulene guest, with an azulene content close to 4 wt % mainly as guest of the δ-clathrate phase (schematically shown in panel C); (thin lines) after thermal annealing leading to the formation of the trans-planar α crystalline phase followed by azulene sorption, close to 2 wt %, only in the amorphous phase (as schematically shown in panel D). The main peaks of the azulene guest molecules are labeled a. The main peaks of the helical and trans-planar chains of s-PS are labeled h and t, respectively.

IR/VCD spectra are those of Figures 1A/B and 1A′/B′, are shown in Figure 3 as spectra A and B, respectively.

Substantial variations of the X-ray diffraction patterns associated with the guest exchange (cf. Figure 3A,B) are apparent, clearly suggesting the formation of an s-PS/azulene cocrystalline phase. The pattern of Figure 3B is fully consistent with the one (Figure 2b in ref 23) reported for the δ-clathrate structure suggested by Kaneko and co-workers.[23] In particular, the higher intensity of the peak at d = 0.875 nm ($2\theta_{\mathrm{CuK}\alpha} \approx$ 10,1°), corresponding to Miller indexes ($\bar{2}10$), suggests the occurrence of some degree of $a_{\perp}c_{\parallel}$ uniplanar orientation.[28] This has been confirmed by photographic X-ray diffraction patterns, as taken by having the X-ray beam parallel (*edge*) and perpendicular (*through*) to the film surface.[28] In particular, the diffraction profile of the photographic pattern taken with X-ray beam perpendicular (*through*) to the film surface, reported in Figure 3C, allows us to precisely locate the (010) reflection at d = 1.18 nm ($2\theta_{\mathrm{CuK}\alpha} \approx$ 7.5°). On the basis of this d_{010} value and of the guest molecular volume (V_{mol} = 0.185 nm^3) (as discussed in detail in ref 29), we can also anticipate the formation of a monoclinic[30,31] (rather than a triclinic)[32] δ-clathrate.

Hence, X-ray diffraction data indicate that the cocrystalline phase, which is present in the film exhibiting chiral optical azulene response, exhibits a δ-clathrate monoclinic structure, as schematically shown in Figure 3D. It is worth noting that these δ-clathrate structures are characterized by the *ac* layers of closely packed enantiomorphous (R and L) polymer helices, typical of the empty δ phase.[31] Moreover, the planar guest molecules, being imprisoned into isolated cavities cooperatively generated by the enantiomorphous helices of two adjacent *ac* layers, assume an orientation nearly perpendicular to the helical axes of the crystalline polymer chains.

This perpendicular orientation of the azulene guest molecules with respect to the polymer chain axes can rationalize the sign of the VCD host and guest peaks of Figure 1B′. Most vibrational modes of the observed azulene guest peaks are parallel to its molecular plane and hence nearly perpendicular to the polymer chain axis in the monoclinic δ-clathrate phase. Hence it is not surprising that most azulene peaks exhibit the same and opposite VCD sign of the host peaks, corresponding to vibrational modes perpendicular and parallel to the chain axis,[20] respectively.

It is relevant adding that the observed chiral optical response of the achiral guest chromophore occurs only when such molecules are included as guest in the nanoporous crystalline phase. This is shown, for instance, by the FTIR and VCD spectra of Figure 4, which compare s-PS polymer films as crystallized by sorption of (−)-(R)-carvone in amorphous films (20 μm) and subsequently subjected to different azulene sorption procedures. The thick lines correspond to a cocrystalline film with azulene, as obtained by exchange of the (−)-(R)-carvone guest (like that of Figure 1A′), but having an azulene content close to 4 wt %, due to equilibrium sorption of azulene from 5 wt % acetone solution. The thin lines correspond to a film exhibiting the s-PS α crystalline phase, as obtained by annealing at 210 °C of a chiral optical s-PS/(−)-(R)-carvone film (like that of Figure 1A), followed by equilibrium sorption of azulene from 5 wt % acetone solution (azulene content in the film close to 2 wt %).

The FTIR spectra of Figure 4A show, beside the azulene peaks (labeled a), the peaks corresponding to vibrational modes of the s(2/1)2 helix (e.g., the 1169 cm^{-1} peak, labeled h)[20] or of the trans planar s-PS chains (like those, for example, at 1334 and 1223 cm^{-1}, labeled t)[33] typical of cocrystalline or α form films, respectively. It is worth adding that, in the latter case, the absence of the helical s-PS peaks clearly indicates the absence of cocrystalline phases and hence that the azulene molecules are simply absorbed in the amorphous phase rather than included as guest in the crystalline phase (see scheme of Figure 4D).

The corresponding VCD spectra, shown in Figure 4B, clearly indicate that, for some azulene peaks (labeled by a close to the thick curve), intense VCD peaks are maintained when the azulene molecules are guest of the polymer cocrystalline phase, also after a large reduction of azulene content (compare with Figures 1B′). On the other hand, for chiral optical α form films presenting the azulene molecules simply absorbed in the amorphous phase, VCD phenomena remain intense for peaks of the trans- planar polymer chains of the crystalline phase while are negligible for the azulene peaks (thin line in Figure 4B).

The presently described procedure of s-PS crystallization by a suitable nonracemic guest, followed by guest exchange, induces chiral optical responses to other achiral guests. Just as an example, s-PS amorphous films crystallized by (*R*)- or (*S*)-carvone sorption and then treated by dichloromethane exhibit a s-PS/CH_2Cl_2 δ-clathrate phase (X-ray diffraction pattern in Figure S1, Supporting Information) and present VCD spectra with an intense 1267 cm^{-1} peak of the achiral guest[34] (Figure S2, Supporting Information).

CONCLUSIONS

Intense CD and VCD phenomena have been induced to achiral chromophores by sorption in a suitable crystalline host phase of a racemic polymer (s-PS). In particular, these unexpected CD and VCD phenomena are produced provided that (i) the initial crystallization of s-PS has been induced by a nonracemic guest from an amorphous phase and (ii) the chromophore molecules are suitable as guests of an s-PS cocrystalline phase.

This opens the possibility to achieve s-PS based films with chiral optical response at given wavelengths. In this respect, it is worth adding that s-PS is a commercially available engineering thermoplastic exhibiting several relevant properties, such as a high melting point (≈ 270 °C), excellent chemical resistance, outstanding dimensional stability, and negligible moisture sorption as well as good transparency.[10] Moreover, this polymer can be easily melt-processed (also in industrial plants) leading not only to films but also to solid samples of any shape (e.g., by injection molding), which can be made fully amorphous by simple quenching procedures.[35,36] As a consequence, materials and devices exhibiting chiral optical responses in selected wavelengths, based on the procedures described in the present paper, can be easily designed and produced.

X-ray diffraction characterizations have shown, for the case of the azulene guest, the formation of a δ-clathrate monoclinic structure, exhibiting both R and L helical polymer chains. This confirms the previous hypothesis[37] that CD phenomena induced in amorphous s-PS films by the temporary sorption of nonracemic guests are not due to the formation of nonracemic unit cells but to the formation of nonracemic morphologies of cocrystalline phases, which are maintained also after solvent or thermal treatments leading to different crystal-to-crystal transformations.

MATERIALS AND METHODS

Materials. The s-PS used in this study was manufactured by Dow Chemical Co. under the trademark Questra 101. ^{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, dichloromethane, (−)-(*R*)carvone [enantiomeric excess (ee) 98%] (+)-(*S*)-carvone (ee 96%), and azulene (99%) were supplied by Aldrich and were used without further purification.

Film Preparation Procedures. Amorphous s-PS films with thickness in the range 20−40 μm were obtained by melt extrusion. Absence of axial orientation has been established by polarized infrared spectra, indicating the absence of infrared linear dichroism.

Amorphous s-PS films with thickness in the range 0.1−0.2 μm were obtained by spin-coating of diluted s-PS solutions in chloroform onto quartz surfaces at a spin rate of 1600 rpm.[8,37]

s-PS crystallization was induced by (−)-(*R*)carvone or (+)-(*S*)-carvone sorption at room temperature for 1 h. Liquid or vapor carvone has been used for the thick and thin s-PS films, respectively.

Exchange of the carvone guest with the azulene guest has been generally effected by film immersion in 3.5 wt % azulene solutions in CH_2Cl_2 (for 3 h for the thick extruded films or 15 min for the thin spin-coated films) followed by CH_2Cl_2 desorption (at 50 °C and at room temperature for thick and thin films, respectively).

Characterization Methods. IR and VCD measurements were recorded on a commercial Bruker Tensor 27 FT-IR spectrometer coupled to a PMA50 external module (needed to double-modulate the infrared radiation) by use of 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,[38,39] films were tested for satisfactory VCD characteristics by comparison of the VCD obtained with the film rotated by ±45° around the light beam axis. However, to eliminate any possible linear dichroism influence, the VCD measurements have been conducted by averaging the spectra as collected for several different in-plane rotation angles.

The degree of crystallinity of the polymer films has been evaluated by the FT-IR spectral subtraction procedure described in ref 40.

UV−visible spectra were recorded on a Perkin-Elmer Lambda 201 spectrophotometer.

CD spectra were measured on a Jasco J-715 spectropolarimeter. All measurements were performed with the following parameters: single scan, continuous scanning mode (800−190 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 (one mdeg equals 0.001 deg).

Wide-angle X-ray diffraction patterns with nickel-filtered Cu Kα radiation were obtained, in reflection, with an automatic Bruker diffractometer. Wide-angle X-ray diffraction patterns were also obtained, 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 phase orientation, photographic X-ray diffraction patterns were taken by having the X-ray beam parallel (*edge*) and perpendicular (*through*) to the film surface and by placing the film sample parallel to the axis of the cylindrical camera.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Two figures showing X-ray diffraction patterns of chiral optical s-PS films and FTIR and VCD spectra of amorphous s-PS films. This material is available free of charge via the Internet at http://pubs.acs.org.

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