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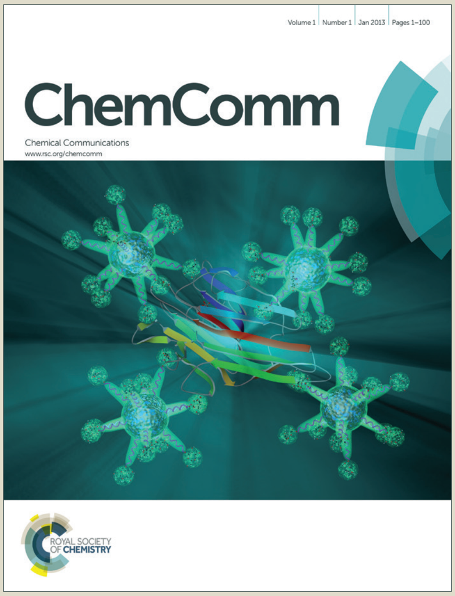

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Enantiomeric Guests with Same Signs of Chiral Optical Responses

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The circular dichroism of non-racemic molecules, being guest of co-crystalline phases of s-PS films, have been studied. Unexpectedly, the chiral response of non-racemic guest molecules does not depend on their R or S molecular chirality but essentially only on the polymer host supramolecular chirality.

Intense chiral optical responses for racemic macromolecules interacting with non-racemic guests are well known for polymers in solution[1] and have been recently observed also in the solid state.[2,3] The induction of circular dichroism (CD) in racemic solid polymers is generally associated with formation of polymer co-crystalline phases,[4] constituted by helical polymer host and non-racemic low-molecular-mass guest molecules.

The induction and amplification of chirality in racemic polymers by co-crystallization with non-racemic guests can occur by a molecular mechanisms, as observed for syndiotactic poly(*p*-methylstyrene)[2a,b] and poly(2,6-dimethyl-1,4-phenylene)oxide (PPO),[2c] where a non-racemic guest induces the formation of co-crystals with a non-racemic unit cell, where polymer chains exhibit only one-sense of helicity.

An alternative supramolecular mechanism, involving the formation of non-racemic helical crystallites that not require the presence of polymer molecular helices, has been presently observed only for syndiotactic polystyrene (s-PS).[3] In fact, the chiral optical response of s-PS remains essentially unaltered up to the polymer melting (≈ 270°C), not only after the non-racemic guest removal but also after thermal crystal-to-crystal transitions,[5] which involve the change of the molecular conformation from chiral helical to achiral trans-planar.

The supramolecular nature of the chiral response of s-PS is also confirmed by the intense chiral optical response of achiral chromophores, when they replace the non-racemic guest in the crystalline cavities of s-PS co-crystalline phases.[3e,g] Hence, chiral optical effects of s-PS films are generally extrinsic to the site of photon absorption,[6,3g] as for instance observed for achiral chromophore molecules ordered in twisted nematic mesophases.[6a,b]

Non-racemic molecules, of course, also exhibit an intrinsic chiral optical response, which is expected to be maintained when guest of polymer co-crystalline phases. In this communication, the intrinsic (molecular) and extrinsic (supramolecular) contributions to the circular dichroism of non-racemic molecules, being guest of s-PS films, have been evaluated. In particular, to better discriminate between the chiral optical response of the low-molecular-mass guests and of the polymer host, vibrational circular dichroism (VCD) studies, with quantitative evaluations of the degree of circular polarization (dissymmetry ratio, *g*) for relevant host and guest peaks, are reported.

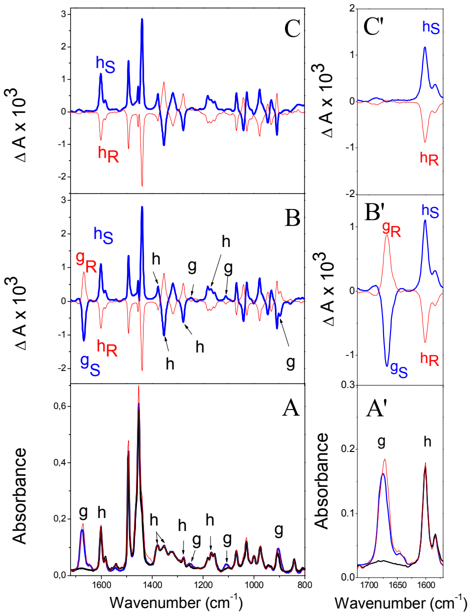

Fig. 1 FTIR (A) and VCD spectra (B) of amorphous s-PS films, having a thickness of nearly 6 μm, after crystallization induced by sorption of (S)-(+)carvone (thick blue line) or (R)-(-)carvone (thin red line), with a carvone content close to 8wt%. FTIR (A, black line) and VCD spectra(C) of the films, after carvone removal. In (A), the main FTIR peaks of the carvone guest are labeled by **g** while the most intense FTIR peaks due to the polymer host are indicated by **h**. In (B) and (C), for the sake of comparison with spectra of Figure 2, isolated VCD peaks of the guest (at 1667 cm^{-1}) and of the host (at 1601 cm^{-1}), corresponding to crystallization induced by (S)-(+)carvone and (R)-(-)carvone are labeled as g_S/h_S and g_R/h_R, respectively. (A'-C') Enlargment of the spectra A-C in the range 1720-1570 cm^{-1}.

Fourier transform Infrared (FTIR) and VCD spectra of melt extruded amorphous s-PS films, having a thickness of nearly 6 μm, after sorption of non–racemic carvone for 1 hour at room temperature, with a carvone content close to 8 wt %, are shown in Figures 1A and 1B, respectively. The FTIR and VCD spectra of the same films of Figure 1B, after complete carvone removal by immersion in acetonitrile for 1 h (and acetonitrile complete desorption in air at room temperature), are shown in Figure 1A (black line) and 1C, respectively. In particular, the VCD spectra as obtained after sorption of (R)-(-)carvone and (S)-(+)carvone are shown, in Figures 1B and 1C, as red thin and blue thick lines, respectively. For the sake of easier comparison with subsequent spectra, isolated VCD peaks of the guest (at 1667 cm^{-1}) and of the host (at 1601 cm^{-1}), produced by s-PS co-crystallization with S and R carvone, are labeled in Figures 1B-C as g_S/h_S and g_R/h_R, respectively.

In agreement with previous reports,[3d,g] the VCD spectra of Figure 1B show that the non-racemic guest and the racemic polymer host present similar VCD peak intensities. Quantitative evaluations of the degree of circular polarization show that the polymer peaks, when associated with vibrational modes of the s(2/1)2 helices of the s-PS crystalline phases,[7] present *g* values even higher than those observed for the non-racemic guest ($g_h(1352) \approx g_h(1278) \approx 1x10^{-2}$ while $g_g(1667) \approx 7x10^{-3}$). The VCD spectra of Figure 1C, show that the chiral response of the polymer host remains unaltered after complete non-racemic carvone removal, clearly indicating the induction of stable chirality in the racemic polymer.

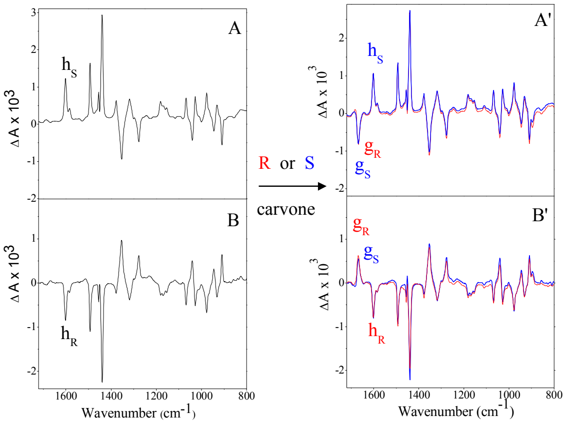

Fig. 2 VCD spectra of chiral optical s-PS films as obtained by crystallization by (S)-(+)carvone (A, A') or (R)-(-)carvone (B, B'): (A,B) after complete carvone removal; (A',B') after renewed sorption of (S)-(+)carvone (thick blue line) or (R)-(-)carvone (thin red line), for 1h at 50°C.

The VCD spectra of s-PS films made chiral by sorption/desorption of S (Figure 2A) and R (Figure 2B) carvone, after renewed sorption of non-racemic carvone (by immersion in pure liquid at 50°C for 1h) are shown in Figures 2A' and 2B', respectively. The chiral response of the host remains unchanged (see, e.g., the intensities of the peaks labeled as h_R or h_S). The chiral response of the guest is of kind g_R or g_S, depending on the chirality induced in the crystalline phase of the polymer host by the first crystallization (Figure 1B), while is independent of the chirality (S or R) of the newly absorbed carvone. These results indicate that for non-racemic molecules being guest of s-PS films, *although the considered peaks correspond to molecular vibrations*, the intrinsic (molecular) contribution to their circular dichroism is negligible with respect the extrinsic (supramolecular) contribution.

This conclusion is also supported by VCD measurements on non-racemic carvone molecules being guest of δ clathrate phases of s-PS films, whose crystallites are racemic, because their initial crystallization has been induced by achiral guest molecules. In particular, amorphous s-PS films as crystallized by immersion in dichloromethane[5a] (for 1 h at room temperature), exhibit a monoclinic δ clathrate form (Figure 3A).[8] The high intensity of the 002 peak (at $2\vartheta_{CuK\alpha}$= 22.8°) indicates the presence of an orientation of the helices of the crystalline phase, which is preferentially perpendicular to the film plane[9] (more precisely named $a_{//}c_{\perp}$).[9c] The film of Figure 3A, as a consequence of guest desorption (by treatment by acetonitrile for 1h at room temperature), exhibits the X-ray diffraction pattern shown in Figure 3B. This pattern shows a weak peak at $2\vartheta_{CuK\alpha}$=8.4° and an intense peak at $2\vartheta_{CuK\alpha}$=13.5°, as typical of 010 and $\bar{1}11$ peaks of the nanoporous δ form[10] with preferential $a_{//}c_{\perp}$ orientation[9] (see, e.g., the similar pattern shown in Figure 6C of ref.9a). The immersion of the δ form film in the liquid carvone for 1h at 50°C leads to a sorption of nearly 12 wt% of carvone, with a substantial change of the X-ray diffraction pattern, as shown in Figure 3C. In fact, a diffraction peak, which can be indexed as $\bar{2}10$ and indicates the formation of a δ clathrate form, appears at $2\vartheta_{CuK\alpha} \approx 10°$.[10] This implies that most carvone molecules are included as guest of the co-crystalline phase (Figure 3D), rather than dissolved in the amorphous phase.

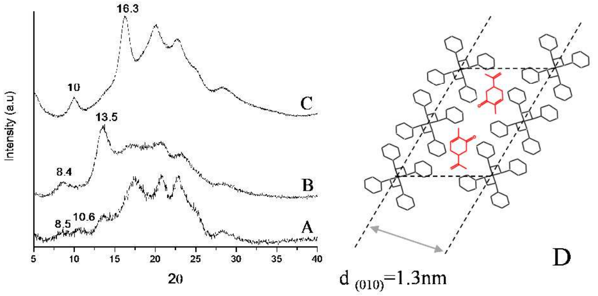

Fig. 3 (A-C) X-ray diffraction patterns (CuKα) of s-PS films having a thickness of 20 μm: (A) as crystallized from the amorphous state by immersion in dichloromethane and exhibiting the corresponding δ clathrate form; (B) then extracted by acrilonitrile and exhibiting the nanoporous δ form; (C) finally immersed in carvone and exhibiting the corresponding δ clathrate form. (D) Schematic along the polymer chain projection of the clathrate structure of the δ clathrate form of s-PS with carvone, with the d_{010} as established in ref.3a.

FTIR and VCD spectra of a racemic clathrate δ form film having a thickness of 6 μm (as prepared with same procedure used for the film of Figure 3C), after sorption of (S)-(+)carvone (thick blue line) or (R)-(-)carvone (thin red line) from the pure liquid at 50°C for 1 hour, with a guest carvone close to 8wt%, are shown in Figure 4.

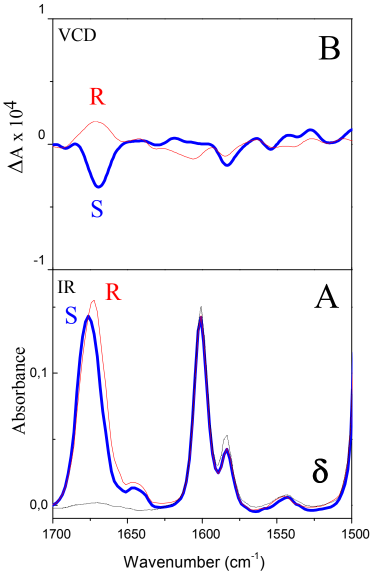

Fig. 4 FTIR (A) and VCD (B) spectra of δ clathrate films with (S)-(+)carvone (thick blue line) or (R)-(-)carvone (thin red line), for a guest content close to 8 wt%. FTIR (A, dotted black line) of δ form film, after carvone removal is also reported.

It is immediately apparent that the chiral response of carvone, when guest of racemic s-PS crystallites, which hence is only molecular, is only slightly higher than the spectral noise (VCD spectrum of Figure 4B). In particular, the *g* values of the 1667 cm^{-1} peak of carvone is close to $1x10^{-4}$, i.e. nearly two orders of magnitude lower than those observed for the same molecule when guest of non racemic s-PS crystallites, as obtained by co-crystallization with non-racemic carvone guest (Figure 1B).

The chiral optical behavior observed for non-racemic carvone molecules being guest of s-PS co-crystalline films, i.e. the negligible molecular contribution with respect the overwhelming supramolecular contribution (see Figures 2 and 4), is also observed for vibrational bands of different non-racemic guest molecules, like e.g. limonene and α-pinene (Scheme 1 and Figures S1 and S2 in the ESI†).

In summary, the chiral optical response (even in the molecular vibration range) of non-racemic guest molecules does not depend on their R or S chirality but on the supramolecular chirality of the host polymer film. This chirality, in turn, is determined by the chirality of the non-racemic guest molecules which formerly have induced co-crystallization of the racemic polymer from the amorphous state. The present study also shows that chiral optical effects for s-PS co-crystalline films are extrinsic to photon absorption sites, not only for the host polymer peaks but also for the guest peaks.

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