

Supporting Information

Enantiomeric Guests with Same Signs of Chiral Optical Responses

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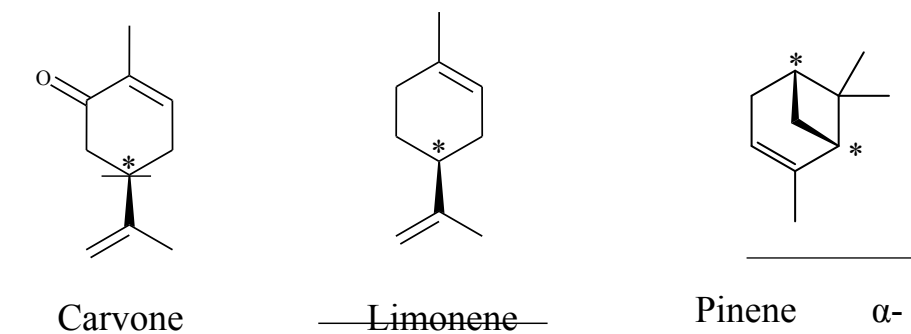
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SI 1. Experimental Section.

Materials.

The s-PS used in this study was manufactured by Dow Chemical Company under the trademark Questra 101. The ¹³C 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, $M_w/M_n=3.9$.

All solvents as well as non-racemic guest molecules (carvone, limonene and α -pinene, see Scheme 1) were supplied by Aldrich and were used without further purification



Scheme 1. Structural formulas of the used non racemic guest molecule. The asterisks * label the asymmetric atoms.

In particular, the used (R)-(-)carvone has a purity of 98% and an enantiomeric excess of 98% while (S)-(+)-carvone has a purity of 96%.

Methods.

Amorphous s-PS films with thickness of nearly 4 μm and 20 μm were obtained by melt extrusion; the complete lack of crystallinity was verified by FTIR and X-ray measurements while the absence of axial orientation has been established by 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.

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 minutes of data collection time, at 4 cm^{-1} resolution. According to experimental procedures described in literature,¹¹ films were tested for satisfactory VCD characteristics by comparison of the VCD obtained with the film rotated by $\pm 45^\circ$ around the light beam axis. In separate measurements with 1h data collection time, we have also tested $\pm 90^\circ$ 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.

The degree of circular polarization (dissymmetry ratio, g) is as usual defined as

$$g = \frac{A_L - A_R}{\frac{1}{2}(A_L + A_R)}$$

where A_L and A_R denote the absorbance for left and right circular polarized light.

SI 2. Chiral optical behavior of non-racemic guest molecules of s-PS co-crystalline films.

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 is also observed for vibrational bands of different non-racemic guest molecules, like e.g. limonene and α -pinene Figures S1 and S2, respectively.

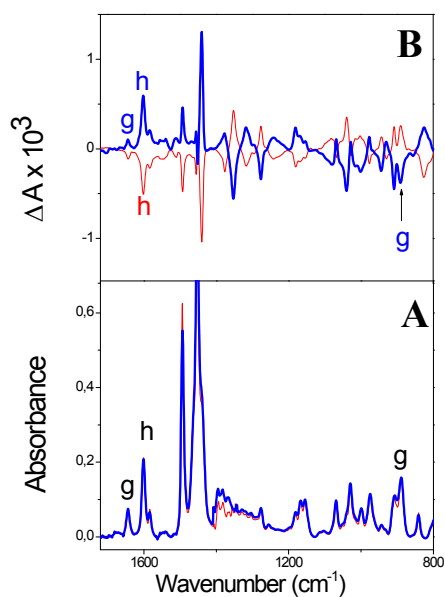


Figure S1 FTIR (A) and VCD spectra (B) of amorphous s-PS films, having a thickness of nearly 6 μm , after crystallization induced by sorption of (R)(+)limonene (thick blue line) or (S)(-)limonene (thin red line). In (A), the main FTIR peaks of the limonene guest are labeled by **g** while the intense FTIR peak due to the polymer host at 1601 cm^{-1} is indicated by **h**.

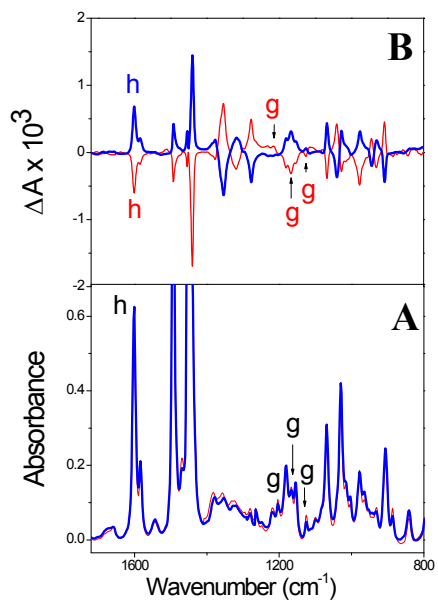


Figure S2 FTIR (A) and VCD spectra (B) of amorphous s-PS films, having a thickness of nearly 25 μm , after crystallization induced by sorption of (+) α -pinene (thick blue line) or (-) α -pinene (thin red line). In (A), the main FTIR peaks of the α -pinene guest are labeled by **g** while the intense FTIR peak due to the polymer host at 1601 cm^{-1} is indicated by **h**.