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Communication

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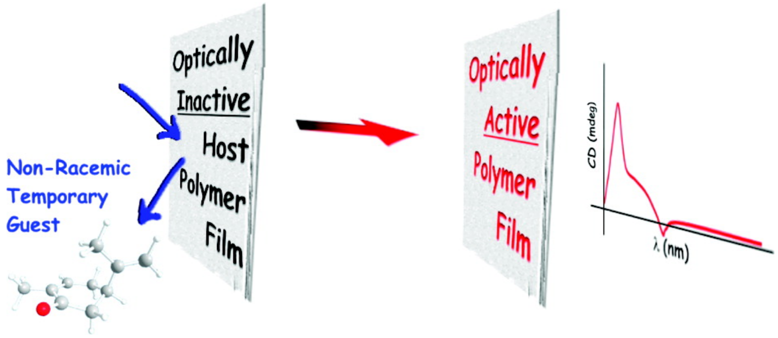

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Detection and Memory of Nonracemic Molecules by a Racemic Host Polymer Film

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Methods for sensing chirality are generally based on nonracemic host receptors interacting with target nonracemic guests. Optically active cyclic compounds, such as modified cyclodextrins, cyclophanes, and crown ethers[1,2] and optically active polymers[3] are among the most extensively studied host molecules. However, these receptors are generally unsuitable for chiral sensing by circular dichroism (CD) measurements, owing to their high specificity and their possible intrinsic CD.

Methods for sensing chirality based on racemic host receptors interacting with target nonracemic guests have been also proposed.[4,5] For chromophoric racemic receptor molecules, their noncovalent bonding to a nonracemic guest can provide an induced circular dichroism (ICD) in the absorption region of the receptor.[4,5]

Particularly suitable are macromolecular receptors, being able to form regular helices and hence in most cases being stereoregular.[6−13] In fact, 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.

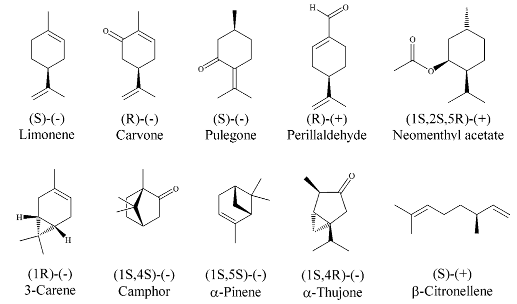
These chirality transfer and amplification phenomena have been generally observed in solution.[6−13] However, the possible occurrence of transfer and amplification of chiral information could be particularly relevant for solid polymer films, since they could in principle have applications in chirooptical switches and data storage systems. In our knowledge, as for films, there is only a report of transfer of chirality to an optically inactive polysilane film from an optically active rigid rodlike polysilane.[14]

In recent years, the polymorphic behavior[15] of a stereoregular polymer (syndiotactic polystyrene, s-PS) obtained by homogeneous Ziegler−Natta catalysis has been extensively studied. Several studies have been devoted to the so-called δ crystalline phase (including s(2/1)2 polymer helices) which is nanoporous since it presents two identical cavities and eight styrene monomeric units per unit cell.[16,17] In fact, it rapidly and selectively absorbs suitable guest molecules (both from gas phase and aqueous solutions, even at very low concentrations),[18−20] eventually leading to polymer/guest clathrate[17,21] or intercalate[22] cocrystals. Hence, these new materials are promising for applications in chemical separations and air/water purification,[18−20] as well as in sensorics.[23,24] In particular, δ form s-PS films have been used as sensing elements of molecular sensors based on a quartz crystal microbalance[23] and on a fiber optic refractometer.[24]

In this Communication we show that suitable nanoporous crystalline s-PS δ-phases, although racemic since they contain an equal number of enantiomorphous helices, can be an extremely efficient tool in the detection of nonracemic molecules. In fact, these nanoporous films not only can concentrate volatile nonracemic molecules, as generally observed for organic compounds,[18−20] but they can also become optically active, because of the also temporary formation of cocrystalline phases with nonracemic guests.

CD spectra of suitable δ-form s-PS films, after exposure to several nonracemic molecules (like those shown in Scheme 1), can present intense ICD phenomena in the polymer absorption region. In particular, independently of the chemical nature of the chiral molecules, a major Cotton band at about 200 nm and a minor Cotton band of opposite sign at about 224 nm are observed. Hence, the contribution of the intrinsic CD of the guest molecules, to the CD spectra of the polymer films, is negligible.

Scheme 1. Enantiomers Inducing Positive CD Bands at $\lambda \approx 200$ nm in δ-Form s-PS Films



This is shown, for instance, by the CD spectra of δ-form s-PS films, having a thickness of 0.1 μm and spin-coated onto quartz surfaces, after a few minutes of exposure to the vapor of (*R*)- and (*S*)-limonene and of (*R*)- and (*S*)-carvone (Figure 1A and B, respectively). The intensity of the ICD phenomena is strongly dependent on the chemical nature of the chiral molecules (e.g., for carvone roughly ten times more intense than for limonene, see Figure 1) and remains essentially unaltered after complete guest removal (for instance, by extraction by supercritical carbon dioxide) as well as after successive absorption of other racemic or nonracemic guests.

The observed chiroptical behavior is similar to that one observed and calculated for co-isotactic copolymers of a nonracemic α-olefin ((*R*)-3,7-dimethyl-1-octene) with styrene, which has been attributed to phenyl substituents of helical chains.[25] On the basis of these literature helicity assignments, it is possible to suggest that negative and positive Cotton bands at $\lambda \approx 200$ nm can be attributed to right-handed and left-handed syndiotactic polystyrene helices, respectively.

s-PS films, being amorphous or presenting dense crystalline phases (α, β, or γ), do not show any ICD phenomenon after exposure to the considered optically active molecules. Hence, the presence of a nanoporous crystalline phase is a necessary condition to observe the described ICD phenomena.

Wide-angle X-ray diffraction (WAXD) and Fourier-transform infrared (FTIR) linear dichroism measurements show that the chiral molecules of Scheme 1 are absorbed as guest of the host δ nanoporous phase, eventually leading to cocrystalline phases. Just as an example, WAXD patterns of δ-form s-PS films, before (A) and after room temperature absorption of limonene or carvone (nearly 15 wt %) are shown in Figure 2. The pattern of the δ form (Figure 2A) shows the presence of 010 and 020 reflections clearly indicating the occurrence of the (010) uniplanar orientation typical of films cast (or spin-coated) from tetrahydrofuran or chloroform.[26]

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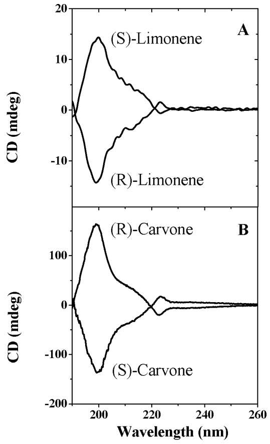

Figure 1. CD spectra of δ-form s-PS films spin-coated onto quartz surface after exposure to vapors of (A) (*R*)- or (*S*)-limonene; (B) (*R*)- or (*S*)-carvone.

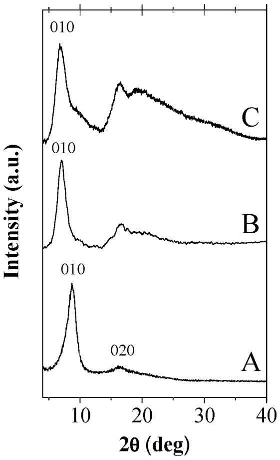

Figure 2. X-ray diffraction patterns (Cu Kα) of spin-coated δ-form s-PS films (presenting (010) uniplanar orientation), before (A) and after room temperature sorption of limonene (B) or of carvone (C). The shift of the (010) peak indicates the formation of cocrystalline phases between the polymer-host and the chiral-guest.

The absorption of limonene and carvone produces significant shifts of the 010 diffraction peak ($d_{010} \approx 10.5$ Å for the δ phase increases up to 12.5 and 13.0 Å for limonene and carvone absorption, respectively), clearly indicating the formation of host−guest cocrystals.[22b]

Hence, the observed ICD phenomena of Figure 1 are related to the recrystallization of the racemic nanoporous δ phase into nonracemic cocrystalline phases, being induced by absorption of nonracemic guests. The permanence of these ICD phenomena after guest removal indicates that cocrystals of s-PS with nonracemic guests present a prevalence of helices with a given handedness. The most simple hypothesis is that recrystallization could lead to crystallites presenting only isomorphic helices, as observed, for instance, for a strictly similar polymer (syndiotactic poly-*p*-methylstyrene) in its cocrystals with different guest molecules.[27] Studies on crystalline structures and morphologies, as induced by sorption of nonracemic guests in δ-form s-PS films, are in progress.

In summary, this paper presents nonracemic polymer films with a nanoporous host crystalline phase, which are able to detect, amplify, and memorize the chirality of several volatile organic molecules. In particular, nonracemic organic molecules induce recrystallization phenomena in nanoporous s-PS crystalline phases, possibly leading to nonracemic crystalline phases. These ICD phenomena remain unaltered after complete guest removal. Hence, racemic host polymer crystals become nonracemic as a consequence of temporary interactions with nonracemic low-molecular-mass guests.

This behavior can be considered a sort of antonym of the results described by Farina et al., where low-molecular-mass racemic monomers (e.g, *trans*-1,3-pentadiene) give rise to nonracemic polymers (e.g., isotactic *trans*-1,4-polypentadiene), when enclosed as guest and polymerized into nonracemic host low-molecular-mass crystals (e.g, perhyrotriphenylene).[29] In synthesis, in our case a nonracemic guest induces the formation of nonracemic host polymer crystals, while in the Farina's experiments a nonracemic host crystal induces the formation of nonracemic guest polymers.

It is worth adding that the obtained chiral-sensing films are based on a cheap commercial polymer, being easy to process and presenting good mechanical and optical properties as well as thermal and chemical stability.

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Supporting Information Available: Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Zhang, X. X.; Bradshaw, J. S.; Izatt, R. M. *Chem. Rev.* **1997**, *97*, 3313−3361.
(2) Prins, L. J.; Reinhoudt, D. N.; Timmerman, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2382−2426.
(3) Okamoto, Y.; Yashima, E.; Yamamoto, C. In *Materials Chirality: Topics in Stereochemistry*; Green, M. M., Nolte, R. J. M., Meijer, E. W., Eds.; Wiley: New York, 2003; Vol. 24, Chapter 3, pp 157−208.
(4) Tsukube, H.; Shinoda, S. *Chem. Rev.* **2002**, *102*, 2389−2403.
(5) Allenmark, S. *Chirality* **2003**, *15*, 409−422.
(6) Green, M. M.; Khatri, C.; Peterson, N. C. *J. Am. Chem. Soc.* **1993**, *115*, 4941−4942.
(7) Rowan, A. E.; Nolte, R. J. M. *Angew. Chem.* **1998**, *110*, 65−71.
(8) Yashima, E.; Maeda, K.; Okamoto, Y. *Nature* **1999**, *399*, 449−451.
(9) Green, M. M.; Park, J. W.; Sato, T.; Teramoto, A.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3138−3154.
(10) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013−4038.
(11) Borovkov, V. V.; Lintuluoto, J. M.; Inoue, Y. *J. Am. Chem. Soc.* **2001**, *123*, 2979−2989.
(12) Nakashima, H.; Koe, J. R.; Torimitsu, K.; Fujiki, M. *J. Am. Chem. Soc.* **2001**, *123*, 4847−4848.
(13) Yashima, E.; Maeda, K.; Nishimura, T. *Chem.*−*Eur. J.* **2004**, *10*, 42−51.
(14) Saxena, A.; Guo, G.; Fujiki, M.; Yang, Y.; Ohira, A.; Okoshi, K.; Naito, M. *Macromolecules* **2004**, *37*, 3081−3083.
(15) Guerra, G.; Vitagliano, V. M.; De Rosa, C.; Petraccone, V.; Corradini, P. *Macromolecules* **1990**, *23*, 1539−1544.
(16) De Rosa, C.; Guerra, G.; Petraccone, V.; Pirozzi, B. *Macromolecules* **1997**, *30*, 4147−4152.
(17) Milano, G.; Venditto, V.; Guerra, G.; Cavallo, L.; Ciambelli, P.; Sannino, D. *Chem. Mater.* **2001**, *13*, 1506−1511.
(18) Manfredi, C.; Del Nobile, M. A.; Mensitieri, G.; Guerra, G.; Rapacciuolo, M. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 133−140.
(19) Guerra, G.; Milano, G.; Venditto, V.; Musto, P.; De Rosa, C.; Cavallo, L. *Chem. Mater.* **2000**, *12*, 363−368.
(20) Daniel, C.; Alfano, D.; Venditto, V.; Cardea, S.; Reverchon, E.; Larobina, D.; Mensitieri, G.; Guerra, G. *Adv. Mater.* **2005**, *17*, 1515−1518.
(21) Chatani, Y.; Shimane, Y.; Inagaki, T.; Ijitsu, T.; Yukinari, T.; Shikuma, H. *Polymer* **1993**, *34*, 1620−1624.
(22) (a) Petraccone, V.; Tarallo, O.; Venditto, V.; Guerra, G. *Macromolecules* **2005**, *38*, 6965−6971. (b) Tarallo, O.; Petraccone, V.; Venditto, V.; Guerra, G. *Polymer* **2006**, *47*, 2402−2410.
(23) Mensitieri, G.; Venditto, V.; Guerra, G. *Sens. Actuators, B* **2003**, *92*, 255−261.
(24) Giordano, M.; Russo, M.; Cusano, A.; Mensitieri, G.; Guerra, G. *Sens. Actuators, B* **2005**, *109*, 177−184.
(25) Hug, W.; Ciardelli, F.; Tinoco, I. *J. Am. Chem. Soc.* **1974**, *96*, 3407−3410.
(26) Rizzo, P.; Lamberti, M.; Albunia, A. R.; Ruiz de Ballesteros, O.; Guerra, G. *Macromolecules* **2002**, *35*, 5854−5860.
(27) (a) La Camera, D.; Petraccone, V.; Artimagnella, S.; Ruiz de Ballesteros, O. *Macromolecules* **2001**, *34*, 7762−7766. (b) Esposito, G.; Tarallo, O.; Petraccone, V. *Eur. Polym. J.* **2007**, *43*, 1278−1287.
(28) Spector, M. S.; Selinger, J. V.; Schnur J. M. In *Materials Chirality: Topics in Stereochemistry*; Green, M. M., Nolte, R. J. M., Meijer, E. W., Eds.; Wiley: New York, 2003; Vol. 24, Chapter 5, pp 281−372.
(29) Farina, M.; Audisio, G.; Natta, G. *J. Am. Chem. Soc.* **1967**, *89*, 5071.

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