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New Host Polymeric Framework and Related Polar Guest Cocrystals

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Nanoporous crystalline structures can be achieved for a large variety of chemical compounds: inorganic (e.g., zeolites),[1] metal−organic,[2] as well as organic.[3] These materials, often referred as inorganic, metal−organic, and organic "frameworks", are relevant for molecular storage, recognition, and separation techniques.

Recently, a "polymeric framework", i.e., a semicrystalline polymeric material presenting a nanoporous crystalline phase, has also been discovered.[4−6] In fact, the δ-phase of syndiotactic polystyrene (s-PS) presents two identical cavities and eight styrene monomeric units per unit cell[4] and is promising for applications in chemical separations and air/water purification[5] as well as sensorics.[6]

The δ-phase rapidly and selectively absorbs low-molecular-mass guest molecules even at very low activities, producing clathrate[7] and intercalate[8] cocrystals (also referred to as molecular-complex crystalline phases). The self-assembling of this polymeric framework and several active guest molecules into cocrystals can be relevant for several applications. In fact, polymer-based host−guest cocrystals not only reduce guest diffusivity and prevent guest self-aggregation (without recurring to chemical reactions), but also allow control of the location and orientation of active guest molecules, by controlling the orientation (axial[9] or planar[10]) of the host crystalline phase. On this basis, films presenting s-PS/active-guest cocrystals have been proposed as advanced materials, mainly for optical applications (e.g., fluorescent, photoreactive, and chromophore materials).[11]

Very recently, it has been shown that the δ-phase, although apolar, is also able to absorb, from solutions in suitable carrier-solvents, high-polarity guests, eventually leading to highly stable apolar-host/polar-guest clathrate phases.[12] According to that study, the formation of these cocrystals from δ-form s-PS occurs only for polar-guest molecules having a volume lower than the limiting maximum value (0.25−0.26 nm^3) observed for s-PS clathrate phases.[8b] In particular, the bulkiest observed guest was trans-4-methoxy-β-nitro-styrene, which presents a hyperpolarizability $\beta = 17 \times 10^{30}$ esu. Moreover, several X-ray diffraction[7,8a] and infrared linear dichroism studies[9,11a,12] have shown that, for cocrystals obtained by guest absorption in the δ-phase, guest molecular

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(1) (a) Kuznicki, S. M.; Bell, V. A.; Nair, S.; Hillhouse, H. W.; Jacubinas, R. M.; Braunbarth, C. M.; Toby, B. H.; Tsapatsis, M. *Nature* **2001**, *412*, 720. (b) Zecchina, A.; Bordiga, S.; Vitillo, J. G.; Ricchiardi, G.; Lamberti, C.; Spoto, C.; Bjorgen, M.; Lillerud, K. P. *J. Am. Chem. Soc.* **2005**, *127*, 6361.

(2) (a) Eddaoudi, M.; Li, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 1391. (b) Pan, L.; Adams, K. M.; Hernandez, H. E.; Wang, X.; Zheng, C.; Hattori, Y.; Kaneko, K. *J. Am. Chem. Soc.* **2003**, *125*, 3062. (c) Kitaura, R.; Seki, K.; Akiyama, G.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 428. (d) Millward, A. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 17998.

(3) (a) Soldatov, D. V.; Moudrakovski, I. L.; Ripmeester, J. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 6308. (b) Blau, W. J.; Fleming, A. J. *Science* **2004**, *304*, 1457. (c) Atwood, J. L.; Barbour, L. J.; Jerga, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 2948. (d) Sozzani, P.; Bracco, S.; Comotti, A.; Ferretti, L.; Simonutti, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1816.

(4) (a) De Rosa, C.; Guerra, G.; Petraccone, V.; Pirozzi, B. *Macromolecules* **1997**, *30*, 4147. (b) Milano, G.; Venditto, V.; Guerra, G. G.; Cavallo, L.; Ciambelli, P.; Sannino, D. *Chem. Mater*. **2001**, 13, 1506. (c) Sivakumar, M.; Mahesh, K. P. O.; Yamamoto, Y.; Yoshimizu, H.; Tsujita, Y. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 1873. (d) Gowd, E. B.; Shibayama, N.; Tashiro, K. *Macromolecules* **2006**, *39*, 8412.

(5) (a) Manfredi, C.; Del Nobile, M. A.; Mensitieri, G.; Guerra, G.; Rapacciuolo, M. *J. Polym. Sci., Polym. Phys. Ed.* **1997**, *35*, 133. (b) Guerra, G.; Manfredi, C.; Musto, P.; Tavone, S. *Macromolecules* **1998**, *31*, 1329. (c) Musto, P.; Manzari, M.; Guerra, G. *Macromolecules* **1999**, *32*, 2770. (d) Guerra, G.; Milano, G.; Venditto, V.; Musto, P.; De Rosa, C.; Cavallo, L. *Chem. Mater.* **2000**, *12*, 363. (e) Musto, P.; Mensitieri, G.; Cotugno, S.; Guerra, G.; Venditto, V. *Macromolecules* **2002**, *35*, 2296. (f) Yamamoto, Y.; Kishi, M.; Amutharani, D.; Sivakumar, M.; Tsujita, Y.; Yoshimizu, H. *Polym. J.* **2003**, *35*, 465. (g) Saitoh, A.; Amutharani, D.; Yamamoto, Y.; Tsujita, Y.; Yoshimizu, H.; Okamoto, S. *Polym. J.* **2003**, *35*, 868. (h) Larobina, D.; Sanguigno, L.; Venditto, V.; Guerra, G.; Mensitieri, G. *Polymer* **2004**, *45*, 429. (i) Daniel, C.; Alfano, D.; Venditto, V.; Cardea, S.; Reverchon, E.; Larobina, D.; Mensitieri, G.; Guerra, G. *Adv. Mater*. **2005**, *17*, 1515. (j) Venditto, V.; De Girolamo Del Mauro, A.; Mensitieri, G.; Milano, G.; Musto, P.; Rizzo, P.; Guerra, G. *Chem. Mater*. **2006**, *18*, 2205. (k) Malik, S.; Roizard, D.; Guenet, J.-M. *Macromolecules,* **2006**, *39*, 5957. (l) Annunziata, L.; Albunia, A. R.; Venditto, V.; Mensitieri, G.; Guerra, G. *Macromolecules* **2006**, *39*, 9166.

(6) (a) Mensitieri, G.; Venditto, V.; Guerra, G. *Sens. Actuators, B* **2003**, *92*, 255. (b) Giordano, M.; Russo, M.; Cusano, A.; Mensitieri, G.; Guerra, G. *Sens. Actuators, B* **2005**, *109*, 177. (c) Giordano, M.; Russo, M.; Cusano, A.; Cutolo, A.; Mensitieri, G.; Nicolais, L. *Appl. Phys. Lett.* **2004**, *85*, 5349. (d) Cusano, A.; Pilla, P.; Contessa, L.; Iadicicco, A.; Campopiano, S.; Cutolo, A.; Giordano, M.; Guerra, G. *Appl. Phys. Lett.* **2005**, *87*, 234105.

(7) (a) Chatani, Y.; Inagaki, T.; Shimane, Y.; Ijitsu, T.; Yukimori, T.; Shikuma, H. *Polymer* **1993**, *34*, 1620. (b) Chatani, Y.; Inagaki, T.; Shimane, Y.; Shikuma, H. *Polymer* **1993**, *34*, 4841. (c) De Rosa, C.; Rizzo, P.; Ruiz de Ballesteros, O.; Petraccone, V.; Guerra, G. *Polymer* **1999**, *40*, 2103. (d) Tarallo, O.; Petraccone, V. *Macromol. Chem. Phys.* **2004**, *205*, 1351. (e) Tarallo, O.; Petraccone, V. *Macromol. Chem. Phys.* **2005**, *206*, 672.

(8) (a) Petraccone, V.; Tarallo, O.; Venditto, V.; Guerra, G. *Macromolecules* **2005**, *38*, 6965. (b) Tarallo, O.; Petraccone, V.; Venditto, V.; Guerra, G. *Polymer* **2006**, *47*, 2402. (c) Malik, S.; Rochas, C.; Guenet, J.-M. *Macromolecules* **2006**, 39, 1000. (d) Galdi, N.; Albunia, A. R.; Oliva, L.; Guerra, G. *Macromolecules* **2006**, 39, 9171.

(9) (a) Albunia, A. R.; Di Masi, S.; Rizzo, P.; Milano, G.; Musto, P.; Guerra, G. *Macromolecules*, **2003**, *36*, 8695. (b) Albunia, A. R.; Milano, G.; Venditto, V.; Guerra, G. *J. Am. Chem. Soc.* **2005**, *127*, 13114.

(10) (a) Rizzo, P.; Albunia, A. R.; Milano, G.; Venditto, V.; Guerra, G.; Mensitieri, G.; Di Maio, L. *Macromol. Symp.* **2002**, *185*, 65. (b) Rizzo, P.; Lamberti, M.; Albunia, A.; Ruiz de Ballesteros, O.; Guerra, G. *Macromolecules* **2002**, *35*, 5854. (c) Rizzo, P.; Costabile, A.; Guerra, G. *Macromolecules* **2004**, *37*, 3071. (d) Rizzo, P.; Della Guardia, S.; Guerra, G. *Macromolecules* **2004**, *37*, 8043. (e) Rizzo, P.; Spatola, A.; De Girolamo Del Mauro, A.; Guerra, G. *Macromolecules* **2005**, *38*, 10089.

(11) (a) Venditto, V.; Milano, G.; De Girolamo Del Mauro, A.; Guerra, G.; Mochizuki, J.; Itagaki, H. *Macromolecules* **2005**, *38*, 3696. (b) Stegmaier, P.; De Girolamo Del Mauro, A.; Venditto, V.; Guerra, G. *Adv. Mater.* **2005**, *17*, 1166. (c) Uda, Y.; Kaneko, F.; Tanigaki, N.; Kawaguchi, T. *Adv. Mater.* **2005**, *17*, 1846. (d) Kaneko, F.; Uda, Y.; Kajiwara, A.; Tanigaki, N. *Makrom. Chem. Rapid Commun.* **2006**, *27*, 1643. (e) D'Aniello, C.; Musto, P.; Venditto, V.; Guerra, G. *J. Mater. Chem.* **2007**, *17*, 531.

(12) Daniel, C.; Galdi, N.; Montefusco, T.; Guerra, G. *Chem. Mater.* **2007**, *19*, 3302.

10.1021/cm071099c CCC: $37.00

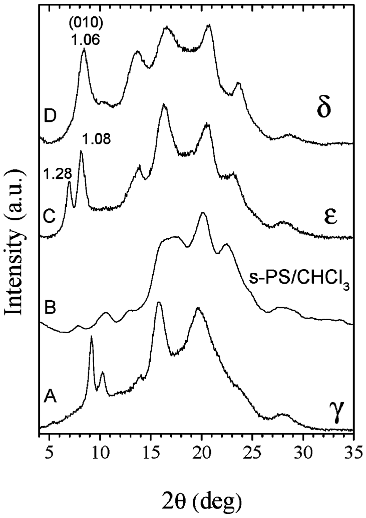

Figure 1. X-ray diffraction patterns (Cu Kα) of s-PS semicrystalline powder samples presenting (A) γ-form; (B) γ-form after $CHCl_3$ sorption (s-PS/$CHCl_3$ cocrystal); (C) s-PS/$CHCl_3$ cocrystal after complete $CHCl_3$ removal (ϵ-form); (D) δ-form. Bragg distances (*d*, nm) and Miller indexes of relevant reflections are indicated close to δ- and ϵ-form patterns.

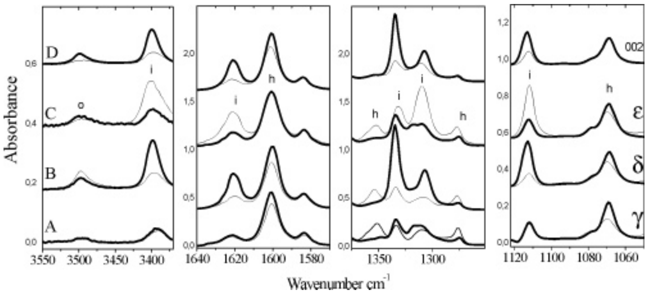

Figure 2. FTIR spectra taken with polarized light parallel (thin lines) and perpendicular (thick lines) to the film stretching direction, for four relevant spectral ranges: (A) γ-form (B) δ-form, and (C) ϵ-form s-PS films treated with NA. (D) Unpolarized FTIR spectra of s-PS/NA cocrystalline films as obtained by NA absorption in δ-form (thick line) and ϵ-form (thin line) films with (002) uniplanar orientation. Host peaks are labeled by *h*, whereas NA guest peaks are labeled by *i* or *o* when corresponding to in-plane or out-of-plane vibrational modes, respectively.

planes are generally oriented (independently of molecular size and polarity) nearly perpendicular to the polymer host chain axes.

In this paper, we present a new host crystalline form of s-PS, thereafter named ϵ,[13] which is able to form cocrystals with high-polarity guests for molecular volumes higher than the above limiting value as well, thus allowing us to obtain s-PS cocrystals with polar guests presenting larger hyperpolarizability (at least up to $\beta = 30 \times 10^{30}$ esu). Moreover, this new host crystalline form of s-PS imposes orientation of guest molecular planes nearly parallel rather than perpendicular to the polymer host chain axes, thus allowing us to obtain orientation of the molecular dipoles perpendicular to the surface of (also macroscopic) films, as generally preferred for electrical poling processes.

A suitable procedure to prepare ϵ-form s-PS samples[13] comprises the preliminary preparation of a γ-form sample,[10b,14] like for instance, the γ-form powder, whose X-ray diffraction pattern is shown in Figure 1A. The γ-form powder after treatment with liquid chloroform for 20 h (and chloroform desorption at room temperature at least for 24 h), presents a chloroform content of nearly 11 wt %, and its X-ray diffraction pattern (Figure 1B, rather similar to that reported in Figure 3b of ref 5a) clearly shows the transformation of the crystalline γ-phase in a cocrystalline s-PS/$CHCl_3$ phase.

By any suitable procedure of guest removal, like for instance, extraction by carbon dioxide in supercritical conditions,[15] or by volatile guests of s-PS, such as acetone or acetonitrile, the chloroform content becomes negligible (<0.1 wt %) and X-ray diffraction patterns like that one of Figure 1C are obtained. This pattern is definitely different from the pattern of the δ-form,[4a] obtained for instance by guest extraction from cocrystals with other guests (like, e.g., carbon disulfide, 1,2-dichloroethane, styrene, toluene, etc.) and shown in Figure 1D. In fact, in the low 2θ range, two well-defined reflections for Bragg distances $d = 1.28$ and 1.08 nm ($2\theta_{CuK\alpha} \approx 6.9$ and 8.2° in Figure 1C) are present, whereas for the δ-form, samples only a peak at $d = 1.06$ nm ($2\theta_{CuK\alpha} \approx 8.4°$ in Figure 1D) is present. Additional substantial differences between the diffraction patterns of δ and ϵ crystalline structures, observed for s-PS samples with uniaxial and uniplanar orientations, will be reported in a forthcoming paper.

By room-temperature treatment with concentrated solutions of 4-nitro-aniline (thereafter NA) in a solvent that is a volatile guest of s-PS (e.g., acetone or acetonitrile), δ- and ϵ-films absorb up to 6 wt % NA, whereas γ-films absorb less than 2 wt % NA.

For uniaxially stretched s-PS films treated by NA, FTIR spectra with polarized light parallel (thin lines) and perpendicular (thick lines) to the film stretching direction have been reported in Figure 2. It is apparent that most host peaks (indicated by h in Figure 2) are dichroic, although independent of the nature of the polymer crystalline phase, the NA peaks (indicated by i and o in Figure 2, depending on the in-plane or out-of-plane direction of their transition moment vectors[16]) are not dichroic when these molecules are simply absorbed in the amorphous phase of the γ-form sample (Figure 2A), whereas they are highly dichroic when absorbed by δ-form (Figure 2B) and ϵ-form (Figure 2C) films. Moreover, surprisingly, the sign of the dichroism of all NA peaks is opposite for molecules absorbed in δ- and ϵ-form films. In particular, NA absorption peaks corresponding to in-plane vibrational modes maximize their absorption intensity for light polarization perpendicular ($A_\perp$) and parallel ($A_\|$) to the stretching direction, when absorbed into δ- and ϵ-form films, respectively.

As discussed in detail for other s-PS guest molecules,[9,8a] this dichroic behavior indicates that NA molecules are

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(13) Rizzo, P.; Daniel, C.; De Girolamo Del Mauro, A.; Guerra, G. It. Pat. Appl. SA2006A22.

(14) (a) Immirzi, A.; De Candia, F.; Iannelli, P.; Vittoria, V.; Zambelli, A. *Makrom. Chem. Rapid Commun.* **1988**, *9*, 761. (b) Guerra, G.; Vitagliano, V. M.; De Rosa, C.; Petraccone, V.; Corradini, P. *Macromolecules* **1990**, *23*, 1539. (c) Rizzo, P.; Albunia, A. R.; Guerra, G. *Polymer* **2005**, *46*, 9549.

(15) (a) Reverchon, E.; Guerra, G.; Venditto, V. *J. Appl. Polym. Sci.* **1999**, *74*, 2077. (b) Ma, W.; Yu, J.; He, J. *Macromolecules* **2005**, *38*, 4755.

(16) (a) Kumar, D. V.; Babu, V. A.; Rao, G. R.; Pandey, G. C. *Vib. Spectrosc.* **1992**, *4*, 39. (b) Pachler, G. R. *Merck-FT-IR Atlas*; VCH: Weinheim, Germany, 1988; 997. (c) Binder, G.; Scandella, L.; Kritzenberger, J.; Gobrechy, J.; Koegler, J. H.; Prins, R. *J. Phys. Chem. B* **1997**, *101*, 483.

enclosed essentially only as spatially ordered guests in δ- and ϵ-crystalline phases. Moreover, the negative and positive linear dichroism values (LD $= A_{\parallel} - A_{\perp}$) for the in-plane vibrational modes of NA absorbed into δ- and ϵ-form films clearly indicate that the guest molecular plane is oriented nearly perpendicular and parallel, respectively, with respect to the chain axes of the polymeric crystalline phase.

Moreover, the large LD values observed (Figure 2C) for the stretching peaks of NH_2 (symmetric, nearly at 3400 cm^{-1}) and of CN (nearly at 1110 cm^{-1}),[16a] indicate that NA guest molecules present both molecular plane and dipole nearly parallel to the chain axes of the ϵ phase.

The same behavior, i.e., opposite dichroism of infrared peaks of molecules being guest of δ and ϵ uniaxially stretched films, is observed for other polar molecules, e.g., trans-β-nitro-styrene or trans-4-methoxy-β-nitro-styrene.

Bulkier polar molecules, e.g., 4-(dimethyl-amino)-cinnamaldehyde (molecular volume $V_m = 0.275$ nm^3 and hyperpolarizability $\beta = 30 \times 10^{30}$ esu), when absorbed by δ-form samples, are present only in their amorphous phase.[12] This molecule, on the contrary, when absorbed by ϵ-form samples is prevailingly enclosed in the crystalline phase with its molecular planes (and dipoles) nearly parallel to the polymer chain axes, as clearly pointed out by polarized FTIR spectra analogous to those presented in Figure 2C.

The formation of apolar-host/polar-guest cocrystals gives the opportunity to prepare polymeric films with polar guest molecules being spatially ordered also in a macroscopic scale. In this respect, the unique ability of helical crystalline phases of s-PS to be formed as films with three different kinds of uniplanar orientations, which are generally maintained after crystal-to-crystal phase transformations, are particularly relevant.[10]

Just as an example, starting from γ-form films with (002) uniplanar orientation (i.e., with chain axes of the crystalline phase nearly perpendicular to the film surface),[10c,d] it is possible to maintain this kind of orientation after transformation into δ- and ϵ-form films as well as into the corresponding s-PS/NA cocrystals. This is proved by X-ray diffraction patterns (not shown), as collected, for instance, by an automatic powder diffractometer, which present an high intensity of the (002) reflection located at $d \approx 0.38$ nm ($2\theta_{CuK\alpha} \approx 23°$),[10c,d] corresponding to the typical c value of s(2/1)2 helices, i.e., 0.77 nm.

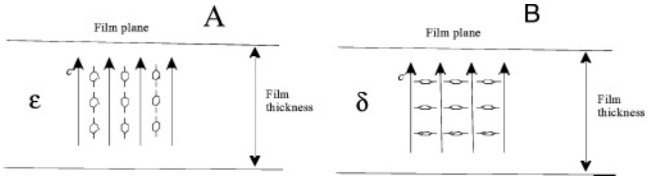

Figure 3. Schematic presentation of the orientation of the cocrystal chain axes (c) and of NA guest molecules, as obtained by NA absorption in (A) ϵ- and (B) δ-form films, presenting an ideal perpendicular (002) orientation.

The unpolarized FTIR spectra of cocrystalline sPS/NA films, as obtained by NA absorption (nearly 4 wt %) in δ- and ϵ-form films with (002) uniplanar orientation, are shown in Figure 2D. As for NA guest molecules of δ- and ϵ-form, the unpolarized FTIR spectra for the (002) oriented films (thick and thin line of Figure 2D) are similar to the polarized spectra for uniaxially stretched films, taken with polarized light perpendicular to the stretching direction (thick lines of panels B and C in Figure 2, respectively). This unambiguously confirms that NA guest molecules of δ- and ϵ-form (002) oriented films present their molecular planes preferentially oriented parallel and perpendicular to the film surface, respectively (see the schemes in panels A and B of Figure 3, respectively). Hence, the control of the orientation of the host δ- and ϵ-crystalline phases allows, at a macroscopic scale, the orientation control of the guest NA dipoles.

Particularly interesting can be the preferential orientation of the molecular dipoles perpendicular to the film surface (achieved starting from ϵ-form films, Figure 3A), which makes these new materials suitable candidates for electrical poling processes, possibly leading not only to nonlinear optical but also to ferroelectric and piezoelectric properties.

In summary, we have discovered a fifth crystalline phase (ϵ) of s-PS, which (as the already known δ phase) is nanoporous and able to form cocrystals with several guest molecules. For polar guests, the molecular dipoles are nearly parallel to the chain axes of the ϵ phase, whereas they are nearly perpendicular to the chain axis of the δ-phase. Films presenting guest dipole orientation nearly perpendicular to their surface, and hence mostly suitable for poling processes, have been prepared starting from ϵ-form films with crystalline chain axes orientation perpendicular to their surface. The ϵ-phase with respect to the δ-phase also presents the advantage to form cocrystals with guest molecules of larger volume and higher hyperpolarizability.

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

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