Syndiotactic Polystyrene Clathrates with Polar Guest Molecules

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Stable syndiotactic polystyrene (s-PS) co-crystals with highly polar guests have been prepared by sorption in δ or in co-crystalline phases of molecules dissolved in suitable solvent carriers. These co-crystals are clathrates, that is, isolated molecules are imprisoned as a guest into cavities formed between layers of polymer helices, and the maximum guest molecular volume is close to 0.25 nm^3. Infrared linear dichroism measurements show that molecules included in s-PS molecular complexes are oriented nearly perpendicular to the chain axes of the polymeric crystalline phase. These new materials present in their crystalline phases an ordered three-dimensional arrangement of highly polar molecules with large first-order hyperpolarizability.

Introduction

Syndiotactic polystyrene (s-PS) is a stereoregular polymer presenting a very complex polymorphic behavior (including four crystalline phases) and is capable of forming co-crystals (molecular-complex crystalline phases) with several low-molecular-mass guest molecules.[1]

For most s-PS co-crystals, isolated molecules are imprisoned as a guest into cavities formed between layers of alternated enantiomorphous s(2/1)2 polymer helices.[2] These s-PS co-crystals have been defined as *clathrate* and are generally characterized by a guest/monomer-unit molar ratio 1/4. As a result of the limited volume of the cavities, all known guests of s-PS clathrate phases present a molecular volume lower than 0.26 nm^3.

More recently, the occurrence of a different class of s-PS co-crystals, defined as *intercalate* rather than *clathrate*, has been established.[3] In fact, for some s-PS co-crystals the guest molecules are not isolated into host cavities but contiguous inside layers intercalated with monolayers of enantiomorphous polymer helices. Of course, these intercalate structures present a higher guest content with respect to the clathrate structures and the guest/monomer-unit molar ratio generally is 1/2 rather than 1/4. Presently known s-PS intercalate phases present guest molecular volume in the range 0.15−0.36 nm^3.[3b,c]

Guest molecules of s-PS co-crystals, although with some mobility with respect their minimum energy positions,[4] present well-defined three-dimensional order with respect to the crystalline axes,[2,3] even when volatile gases.[5] Moreover, because s-PS co-crystals depending on their preparation procedure can assume three different kinds of uniplanar orientation,[6] it is possible to control the orientation of the guest molecules not only in the microscopic crystalline phase but also in macroscopic films. On these bases, films presenting s-PS/active-guest co-crystals have been proposed as advanced materials,[7] mainly for optical applications (e.g., as fluorescent, photoreactive, and chromophore materials).[7a−d] This constitutes an innovative approach in the area of functional polymeric materials which are instead characterized by a disordered distribution of active groups into amorphous phases, because they are generally prepared by simple dispersion of active molecules in amorphous phases, by chemical bonding of active groups to the polymer backbone (functionalization), or by copolymerization of standard monomers with co-monomers containing suitable active groups.

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(1) (a) Guerra, G.; Vitagliano, M. V.; De Rosa, C.; Petraccone, V.; Corradini, P. *Macromolecules* **1990**, *23*, 1539−1544. (b) Chatani, Y.; Shimane, Y.; Inoue, Y.; Inagaki, T.; Ishioka, T.; Iijtsu, T.; Yukinari, T. *Polymer* **1992**, *33*, 488−492. (c) Rizzo, P.; Albunia, A. R.; Guerra, G. *Polymer* **2005**, *46*, 9549−9554.

(2) (a) Immirzi, A.; de Candia, F.; Iannelli, P.; Zambelli, A.; Vittoria, V. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 761−764. (b) Chatani, Y.; Shimane, Y.; Inagaki, T.; Iijtsu, T.; Yukinari, T.; Shikuma, H. *Polymer* **1993**, *34*, 1620−1624. (c) Chatani, Y.; Inagaki, T.; Shimane, Y.; Shikuma, H. *Polymer* **1993**, *34*, 4841−4845. (d) De Rosa, C.; Rizzo, P.; Ruiz, de Ballesteros, O.; Petraccone, V.; Guerra, G. *Polymer* **1999**, *40*, 2103−2110. (e) Tarallo, O.; Petraccone, V. *Macromol. Chem. Phys.* **2004**, *205*, 1351−1360. (f) Tarallo, O.; Petraccone, V. *Macromol. Chem. Phys.* **2005**, *206*, 672−679.

(3) (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. (c) Galdi, N.; Albunia, A. R.; Oliva, L.; Guerra, G. *Macromolecules* **2006**, *39*, 9171−9176. (d) Malik, S.; Rochas, C.; Guenet, J. M. *Macromolecules* **2006**, *39*, 1000−1007.

(4) (a) Trezza, E.; Grassi, A. *Macromol. Rapid Commun.* **2002**, *23*, 260−263. (b) Albunia, A. R.; Graf, R.; Guerra, G.; Spiess, H. W. *Macromol. Chem. Phys.* **2005**, *206*, 715−724.

(5) (a) Annunziata, L.; Albunia, A. R.; Venditto, V.; Mensitieri, G.; Guerra, G. *Macromolecules* **2006**, *39*, 9166−9170. (b) Albunia, A. R.; Minucci, T.; Guerra G. Manuscript in preparation.

(6) (a) Rizzo, P.; Lamberti, M.; Albunia, A. R.; Ruiz de Ballesteros, O.; Guerra, G. *Macromolecules* **2002**, *35*, 5854−5860. (b) Rizzo, P.; Costabile, A.; Guerra, G. *Macromolecules* **2004**, *37*, 3071−3076. (c) Rizzo, P.; Spatola, A.; De Girolamo Del Mauro, A.; Guerra, G. *Macromolecules* **2005**, *38*, 10089−10094.

(7) (a) Venditto, V.; Milano, G.; De Girolamo Del Mauro, A.; Guerra, G.; Mochizuki, J.; Itagaki, H. *Macromolecules* **2005**, *38*, 3696−3702. (b) Stegmaier, P.; De Girolamo Del Mauro, A.; Venditto, V.; Guerra, G. *Adv. Mater.* **2005**, *17*, 1166−1168. (c) Uda, Y.; Kaneko, F.; Tanigaki, N.; Kawaguchi, T. *Adv. Mater.* **2005**, *17*, 1846−1850. (d) D'Aniello, C.; Musto, P.; Venditto, V.; Guerra, G. *J. Mater. Chem.* **2007**, *17*, 531−535. (e) Kaneko, F.; Kajiwara, A.; Uda, Y.; Tanigaki, N. *Macromol. Rapid Commun.* **2006**, *27*, 1643−1647.

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Most s-PS co-crystals can be prepared by solution crystallization procedures (e.g., casting, spin-coating, gel desiccation[8]) or by solvent-induced crystallization in amorphous s-PS films.[9] All s-PS co-crystals can be obtained by guest sorption into s-PS samples presenting the nanoporous δ-phase[10] or by guest exchange in co-crystals.[11] In fact, for some guests (mainly volatile, like carbon dioxide,[5a] butadiene,[5a] or ethylene[5b] but also bulkier guests like acetone, limonene,, or carvone), the two latter are the only available procedures to obtain the corresponding s-PS co-crystals.

Although several dozen of the s-PS co-crystals have been described, all the presented guests are apolar or poorly polar. In particular, the guest of highest polarity which has been presently reported in the literature is *o*-dichlorobenzene[1a,2e] ($\mu = 2.5$ D). In this respect, it is worth recalling that the nanoporous δ-phase[10] of s-PS is extremely efficient in separating molecules of different polarity (like, e.g., removing traces of organic pollutants from aqueous solutions)[12] as a result of its ability to include apolar molecules as a guest of its crystalline cavities and to exclude polar water molecules ($\mu = 1.8$ D).

In this paper it will be shown that by sorption in δ or in co-crystalline s-PS samples of guests dissolved in suitable solvent carriers, clathrate phases can be easily obtained with molecules of very high polarity, also for molecular volume close to the upper limit typical of guests of s-PS clathrate phases ($V_m = 0.26$ nm). These co-crystalline materials presenting a stable and three-dimensionally ordered disposition of polar guests, characterized by also large first-order hyperpolarizability, can be in principle used for nonlinear optical or electrical applications.

Experimental Section

The s-PS used in this study was manufactured by Dow Chemicals under the trademark Questra 101. ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic triads was over 98%. Mass average molar mass obtained by gel permeation chromotography (GPC) in trichlorobenzene at 135 °C was found to be $M_w = 3.2 \times 10^5$ g mol^{-1} with a polydispersity index $M_w/M_n = 3.9$. Solvents were purchased from Aldrich and used without further purification.

Oriented films were obtained by monoaxial stretching of amorphous films obtained by extrusion of the melt, at different draw ratios at a constant deformation rate of 0.1 s^{-1}, in the temperature range 105−110 °C with an Instron stretching machine. These films have been crystallized by CS_2 sorption, and uniaxially oriented nanoporous δ-form films have been obtained from s-PS/CS_2 clathrate films by vacuum treatment. Uniaxially oriented s-PS/tetrahydrofuran (THF) clathrate films have been obtained by THF sorption in uniaxially stretched films. Uniaxially oriented γ-form films have been obtained from δ-form films by annealing at 160 °C for 12 h.

Infrared Spectroscopy. Infrared spectra were obtained at a resolution of 2.0 cm^{-1} with a Vector 22 Bruker spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and a Ge/KBr beam splitter. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He−Ne laser. Thirty-two scans were signal averaged to reduce the noise. Polarized infrared spectra were obtained using a KRS-5 polarizer from Specac.

As far as infrared spectroscopy is concerned, the axial orientation function is given by[13]

$$f_{c,IR} = \frac{(R-1)}{(R+2)} \frac{(2\cot^2\alpha + 2)}{(2\cot^2\alpha - 1)} \quad (1)$$

where $R = A_{\parallel}/A_{\perp}$ is the dichroic ratio, $A_{\parallel}$ and $A_{\perp}$ being the measured absorbance for electric vectors parallel and perpendicular to the draw direction, respectively, and α being the angle between the chain axis and the transition moment vector of the vibrational mode. For the evaluation of the α angle relative to transition moment vectors of guest vibrational modes, the orientation factor relative to the helical chains of the host polymer phase ($f_{c,IR}$) has been evaluated by the dichroic ratio of the 571 cm^{-1} infrared band.[14] As usual, an order parameter S can be defined as the ratio

$$S = (R-1)/(R+2) \quad (2)$$

Most films used in the present study have been stretched up to a draw ratio (λ = final length/initial length) close to 3 and present

(8) (a) Kobayashi, M.; Nakaoki, T.; Ishihara, N. *Macromolecules* **1990**, *23*, 78−83. (b) Deberdt, F.; Berghmans, H. *Polymer* **1994**, *35*, 1694−1704. (c) Daniel, C.; Dammer, C.; Guenet, J.-M. *Polymer* **1994**, *35*, 4243−4246. (d) Kobayashi, M.; Yoshioka, T.; Kozasa, T.; Tashiro, K.; Suzuki, J.-I.; Funahashi, S.; Izumi, Y. *Macromolecules* **1994**, *27*, 1349−1354. (e) Roels, T.; Deberdt, F.; Berghmans, H. *Prog. Colloid Polym. Sci.* **1996**, *102*, 82−85. (f) Daniel, C.; Deluca, M. D.; Guenet, J.-M.; Brulet, A.; Menelle, A. *Polymer* **1996**, *7*, 1273−1280. (g) Daniel, C.; Menelle, A.; Brulet, A; Guenet, J.-M. *Polymer* **1997**, *38*, 4193−4199. (h) Rastogi, S.; Goossens, J. G. P.; Lemstra, P. J. *Macromolecules* **1998**, *31*, 2983−2998. (i) Van Hooy-Corstjens, C. S. J.; Magusin, P. C. M. M.; Rastogi, S.; Lemstra, P. J. *Macromolecules* **2002**, *35*, 6630−6637. (j) Daniel, C.; Musto, P.; Guerra, G. *Macromolecules* **2002**, *35*, 2243−2251. (k) Daniel, C.; Alfano, D.; Guerra, G.; Musto, P. *Macromolecules* **2003**, *36*, 5742−5750. (l) Malik, S.; Roizard, D.; Guenet, J.-M. *Macromolecules* **2006**, *39*, 5957−5959. (m) Daniel, C.; Avallone, A.; Guerra, G. *Macromolecules* **2006**, *39*, 7578−7582.

(9) (a) Vittoria, V.; Russo, R.; de Candia, F. *J. Macromol. Sci. Phys.* **1989**, *B28*, 419−431. (b) Vittoria, V.; Russo, R.; de Candia, F. *Polymer* **1991**, *32*, 3371−3375. (c) Rapacciuolo, M.; De Rosa, C.; Guerra, G.; Mensitieri, G.; Apicella, A; Del Nobile, M A. *J. Mater. Sci. Lett.* **1991**, *10*, 1084−1087. (d) Manfredi, C.; Del, Nobile, M. A.; Mensitieri, G.; Guerra, G.; Rapacciuolo, M. *J. Polym. Sci., Polym. Phys. Ed.* **1997**, *35*, 133−140. (e) Gupper, A.; Chan, K. L. A.; Kazarian, S. G. *Macromolecules* **2004**, *37*, 6498−6503.

(10) (a) De Rosa, C.; Guerra, G.; Petraccone, V.; Pirozzi, B. *Macromolecules* **1997**, *30*, 4147−4152. (b) Reverchon, E.; Guerra, G.; Venditto, V. *J. Appl. Polym. Sci.* **1999**, *74*, 2077−2082. (c) Milano, G.; Venditto, V.; Guerra, G.; Cavallo, L.; Ciambelli, P.; Sannino, D. *Chem. Mater.* **2001**, *13*, 1506−1511. (d) Gowd, E. B.; Shibayama, N.; Tashiro, K. *Macromolecules* **2006**, *39*, 8412−8418.

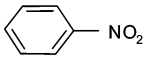
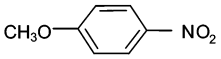
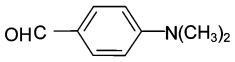
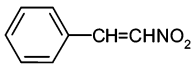
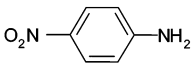
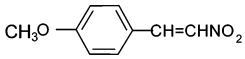
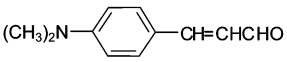
(11) (a) Yoshioka, A.; Tashiro, K. *Macromolecules* **2003**, *36*, 3593−3600. (b) Uda, Y.; Kaneko, F.; Kawaguchi, T. *Macromol. Rapid Commun.* **2004**, *25*, 1900−1904. (c) Rizzo, P.; Della Guardia, S.; Guerra, G. *Macromolecules* **2004**, *37*, 8043−8049. (d) Uda, Y.; Kaneko, F.; Kawaguchi, T. *Macromolecules* **2005**, *38*, 3320−3326.

(12) (a) Guerra, G.; Manfredi, C.; Musto, P.; Tavone, S. *Macromolecules* **1998**, *31*, 1329−1334. (b) Musto, P.; Manzari, M.; Guerra, G. *Macromolecules* **1999**, *32*, 2770−2776. (c) Guerra, G.; Milano, G.; Venditto, V.; Musto, P.; De Rosa, C.; Cavallo, L. *Chem. Mater.* **2000**, *12*, 363−368. (d) Giordano, M.; Russo, M.; Cusano, A.; Mensitieri, G.; Guerra, G. *Sens. Actuators, B* **2005**, *109*, 177−184. (e) Cusano, A.; Pilla, P.; Contessa, L.; Iadicicco, A.; Campopiano, S.; Cutolo, A.; Giordano, M.; Guerra, G. *Appl. Phys. Lett.* **2005**, *87*, 234105/1−234105/3. (f) Venditto, V.; De Girolamo Del Mauro, A.; Mensitieri, G.; Milano, G.; Musto, P.; Rizzo, P.; Guerra, G. *Chem. Mater.* **2006**, *18*, 2205−2210.

(13) (a) Read B. E. In *Structure and Properties of Oriented Polymers*; Ward, I. M., Ed.; Appl. Sci. Publishers: London, 1975; Chapter 4, pp 150−184. (b) Jasse, B.; Koenig, J. L. *J. Macromol. Sci., Rev. Macromol. Chem.* **1979**, *C17*, 61−135.

(14) (a) Albunia, A. R.; Di Masi, S.; Rizzo, P.; Milano, G.; Musto, P.; Guerra, G. *Macromolecules* **2003**, *36*, 8695−8703. (b) Albunia, A. R.; Milano, G.; Venditto, V.; Guerra, G. *J. Am. Chem. Soc.* **2005**, *127*, 13114−13115.

Table 1. Molecular Structure, Melting Temperature, Molecular Volume (V_m), Dipole Moment (μ)[15], and Hyperpolarizability (β)[15] Values of Guest Molecules Considered in This Paper

Compound	Molecular structure	T_m(°C)	V_m[a] (nm^3)	μ (D)	β (x10^{-30} esu)
nitrobenzene[15a]		6	0.170	4.0	1.9
4-nitro-anisole[15a]		52-55	0.208	4.6	5.1
4-(dimethyl-amino) benzaldehyde[15a]		70-75	0.231	5.1	6.3
trans-β-nitrostyrene[15a]		55-61	0.222	3.8	8.0
4-nitroaniline[15a]		143-150	0.161	6.2	9.2
trans-4-methoxy-β-nitrostyrene[15b]		81-87	0.250	4.6	17
4-(dimethyl-amino)-cinnamaldehyde[15b]		148-150	0.275	5.6	30

[a] The molecular volume of the molecules has been calculated from their molecular mass (M) and density (ρ) $V_m = M/\rho N_A$ where N_A is the Avogadro's number (6.02×10^{23} molecules/mol).

a degree of axial orientation, as evaluated according to the Fourier transform infrared (FTIR) method,[14a] close to 0.93.

The guest molecules considered in this paper are those listed in Table 1. Their melting temperature (T_m), molecular volume (V_m), and polarity (μ) expressed in debye[15] as well as hyperpolarizability (β) expressed in esu[15] are also indicated in Table 1.

Results and Discussion

s-PS/Polar-Guest Clathrates by Guest Sorption in δ or Co-Crystalline Phases. FTIR spectra in the wavenumber range 1650−450 cm^{-1} of a uniaxially oriented δ-form s-PS film ($\lambda \cong 3$) immerged for 30 min in nitrobenzene (NB), taken with polarization plane parallel and perpendicular to the draw direction, are reported in Figure 1 by thin and thick lines, respectively.

We can clearly observe from the spectra that the absorption peaks characteristic of the s(2/1)2 helical polymer chain conformation (i.e., polymer chains included in the crystalline phase) located at 502, 548, 571, 769, and 1278 cm^{-1} are highly dichroic while the absorption peak prevailingly associated with the amorphous phase[16] located at 1154 cm^{-1} does not show any significant dichroism. As already discussed in previous reports,[14] this indicates that the crystalline phase presents a high degree of axial orientation ($f_{c,IR} \approx 0.93$) while the amorphous phase presents a poor orientation.

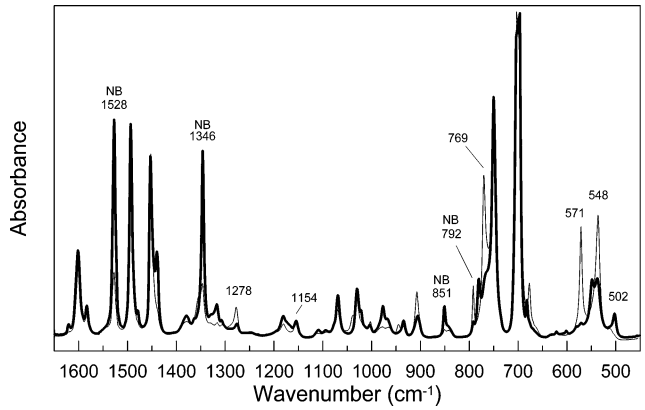


Figure 1. FTIR spectra in the wavenumber range 1650−450 cm^{-1} taken with the polarization plane parallel (thin line) and perpendicular (thick line) to the draw direction for an uniaxially stretched δ-form s-PS film immerged in NB.

From Figure 1, we can also observe that absorption peaks of NB located at 1528, 1346, 851, and 792 cm^{-1} are highly dichroic. This feature indicates that NB molecules are forming a co-crystalline phase with s-PS.

As shown in previous reports,[14] information relative to the orientation of the guest with respect to the chain axis of the polymeric crystalline host can be obtained from infrared dichroism measurements on films uniaxially stretched at different draw ratios. By using a procedure analogous to that one described in ref 14a, the infrared order parameter $S =$

(15) (a) Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631−10643. (b) Cheng, L.-T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643−10652.

(16) Albunia, A. R.; Musto, P.; Guerra, G. *Polymer* **2006**, *47*, 234−242.

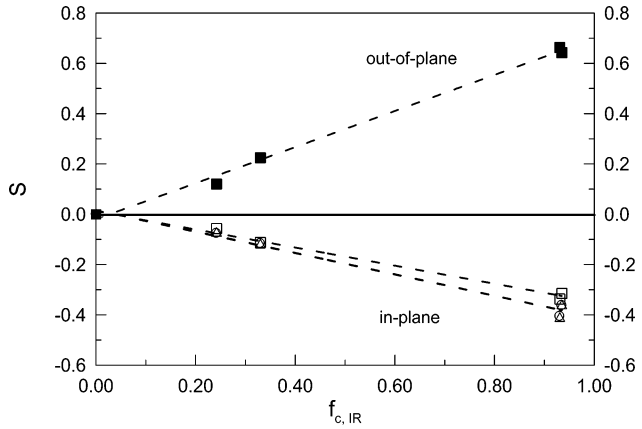


Figure 2. Order parameter *S* of infrared peaks of NB guest molecules vs the axial orientation factor of the host polymer phase ($f_{c,IR}$): (■) 792 cm^{-1} (out of plane, along *z* of Figure 3A); (○) 851 cm^{-1} and (Δ) 1346 cm^{-1} (in plane, along *x* of Figure 3A); and (□) 1528 cm^{-1} (in plane, along *y* of Figure 3A).

$[(A_{\parallel}/A_{\perp}) - 1]/[(A_{\parallel}/A_{\perp}) + 2]$ of NB guest peaks located at 1528, 1346, 851, and 792 cm^{-1} is reported vs the orientation factor relative to the helical chains of the crystalline phase ($f_{c,IR}$ as evaluated on the basis of the dichroic ratio of the 571 cm^{-1} peak)[14a] in Figure 2.

The transition moment vector of in-plane vibrational modes at 1346 cm^{-1} (NO_2 symmetric stretching) and 851 cm^{-1} (NO_2 symmetric bending) are parallel to the C−N direction (*x*-axis in Figure 3A) while the transition moment vector of the vibrational mode at 1528 cm^{-1} (NO_2 antisymmetric stretching) is perpendicular to the C−N direction and in the ring plane (*y*-axis in Figure 3A).[17] The vibration mode at 792 cm^{-1} (CH bending out of plane) has the transition moment vector perpendicular to the NB ring (*z*-axis in Figure 3A).[17]

In the plots of Figure 2, positive and negative slopes correspond respectively to out-of-plane and in-plane vibrational modes, as generally observed for s-PS planar guest molecules (like, e.g., benzene, 1,3,5-trimethyl-benzene, naphthalene, and indole).[14b]

Moreover, by applying eq 1 to the plots of Figure 2, the α angle between the transition moment vectors and the *c*-axis of the host crystalline phase have been calculated: $\alpha_{1346} = \alpha_{851} = \alpha_x = 77°$; $\alpha_{1528} = \alpha_y = 72°$; and $\alpha_{792} = \alpha_z = 25°$ (see Figure 3A).

The X-ray diffraction patterns of a δ-form s-PS powder before and after NB treatment (NB uptake close to 10 wt %) are shown in Figure 4A,B, respectively. The observed changes in the X-ray diffraction patterns (intensity decrease of the 010 and $\bar{1}11$ diffraction peaks, at lattice spacing $d \approx 1.06$ and 0.66 nm, respectively, and increase of the $\bar{2}10$ diffraction peak, at lattice spacing $d \approx 0.84$ nm) are diagnostic of co-crystal formation. Moreover, the location of the (010) peak of the s-PS/NB co-crystal at $d = 1.14$ nm ($2\theta_{CuK\alpha} = 7.75°$), that is, well below the typical upper limit of s-PS clathrate phases (≈1.2 nm) and far from the lower limit of s-PS intercalate phases (≈1.3 nm),[3b] clearly indicates the occurrence of a clathrate rather than an intercalate phase.

It is worth adding that s-PS co-crystals with NB can be also obtained by their diffusion in other s-PS co-crystalline phases as well as by their diffusion in amorphous s-PS samples or by solution crystallization procedures.

The possible formation of co-crystals has been also investigated with the bulkier polar molecules of Table 1, presenting a larger first order nonlinear optical polarizability (β). In particular the polarized FTIR spectra of uniaxially oriented δ-form s-PS films exposed at room temperature to vapor of 4-nitroanisole (for 4 days), trans-β-nitrostyrene, and trans-4-methoxy-β-nitrostyrene (for 50 days) are reported in Figure 5.

The dichroism of absorption peaks of nitroanisole located at 1512, 1341, 1265, 1238, and 1113 cm^{-1} (b) clearly indicates the formation of a s-PS co-crystal with this molecule. We can also note that, as for NB, the in-plane vibrational modes of 4-nitroanisole (in particular $\nu_{as}(NO_2)$ at 1512 cm^{-1} and $\nu_s(NO_2)$ at 1341 cm^{-1})[18] maximize their absorption intensity for polarization perpendicular to the stretching direction. This dichroic behavior indicates that, as for NB, 4-nitroanisole guest molecules are oriented nearly perpendicular to the chain axes of the polymeric crystalline phase.

For molecules less volatile than 4-nitroanisole (see Table 1), polarized IR spectra show that co-crystals with s-PS are not formed by simple exposure of δ-form or co-crystalline samples to these molecules. In particular, with trans-β-nitrostyrene the absence of dichroism of the absorption bands located at 1523 and 1343 cm^{-1} (c in Figure 5) indicates that this molecule is absorbed only in the amorphous phase of s-PS while for trans-4-methoxy-β-nitrostyrene, the absence of any characteristic absorption peak (d in Figure 5) indicates that guest sorption kinetics is negligible.

s-PS/Polar-Guest Clathrates by Sorption in δ or Co-Crystalline Phases of Guests in Carrier Solvents. s-PS molecular complexes with large volume polar guests can be obtained by treatments of δ or co-crystalline s-PS samples with concentrated solutions of these guests in suitable carrier solvents.

Solvents suitable as carriers of bulky, and also polar, guest molecules of s-PS are in general volatile guests of s-PS co-crystals, like, for example, acetone or acetonitrile.

In Figure 6A are reported the polarized FTIR spectra of s-PS/THF clathrate films treated with an acetone solution saturated with 4-nitroaniline, as collected during the progressive desorption of acetone (curves a−c). The polarized spectra of a uniaxially stretched γ-form film treated with a saturated solution of acetone/4-nitroaniline is also reported (curve d).

After removal of the clathrate film from the solution (curve a, $t_{desorption} = 0$), we can observe that the absorption peak of acetone at 1220 cm^{-1} is highly dichroic while the absorption peaks of 4-nitroanile (in particular 1119 cm^{-1} and 836 cm^{-1}) display a lower dichroism. This indicates that acetone has substituted THF in the clathrate crystalline phase while NA is mainly included in the amorphous phase. The dichroism

(17) Stephenson, C. Y.; Coburn, W. C., Jr.; Cox, W. S. *Spectrochim. Acta* **1961**, *17*, 933−946.

(18) Vijaya Kumar, D.; Ashok Babu, V.; Ramana Rao, G.; Pandey, G. C. *Vib. Spectrosc.* **1992**, *4*, 39−57.

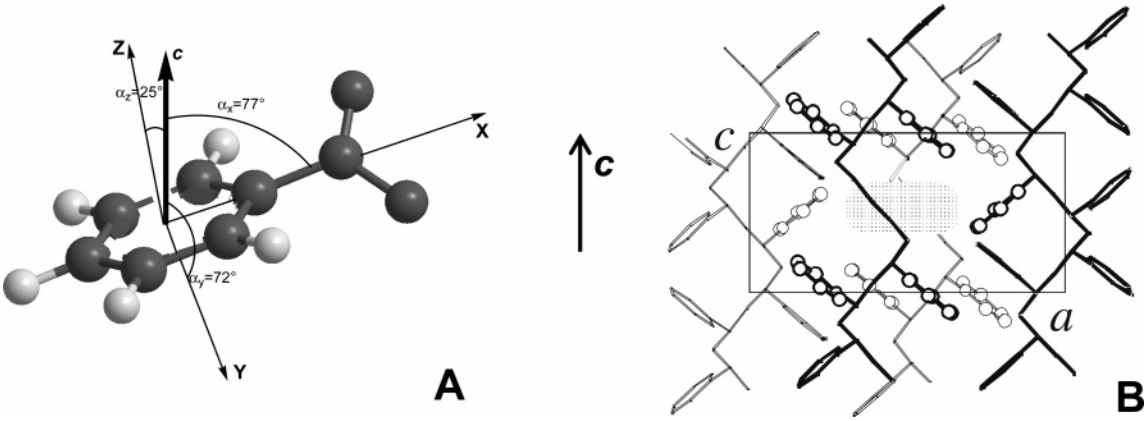


Figure 3. (A) NB orientation with respect to the *c*-axis of the host polymeric crystalline phase; (B) projection in the *ac* plane of the unit cell of the nanoporous δ-form of s-PS showing its molecular cavity. The more significant structural variation induced by NB inclusion in this unit cell is the increase of the distance between the layers of helices being parallel to the *ac* planes (d_{010}) from 1.06 nm up to 1.14 nm. Linear dichroism measurements allow establishing NB orientation with respect to the *c*-axis but not with respect to the *a*-axis.

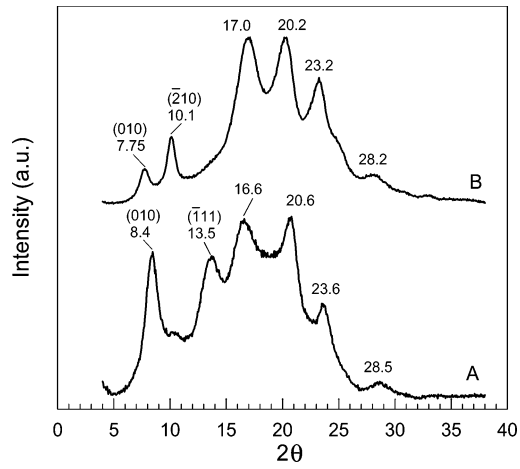


Figure 4. X-ray diffraction patterns with Cu Kα radiation, of powder samples presenting the s-PS δ-phase (A) and s-PS/NB co-crystal phase (B).

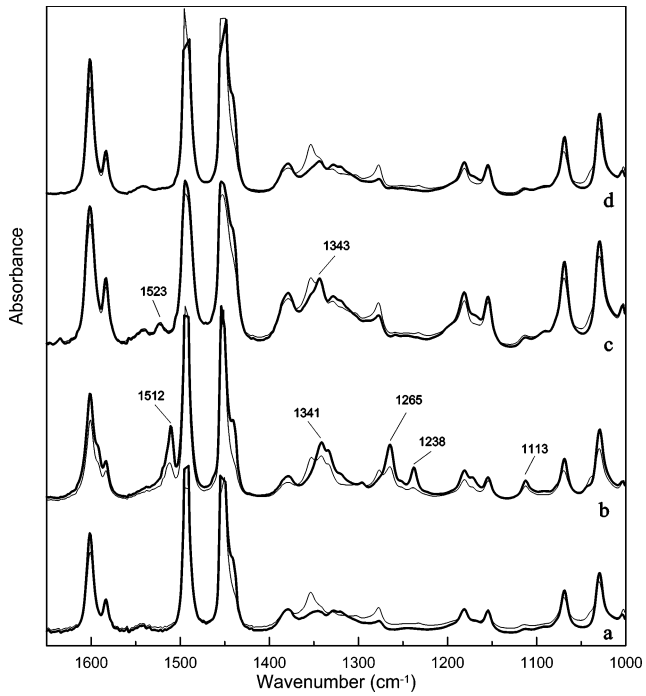


Figure 5. FTIR spectra in the wavenumber range 1650−1000 cm^{-1} taken with the polarization plane parallel (thin line) and perpendicular (thick line) to the draw direction, for uniaxially stretched δ-form films: untreated (a) and exposed to 4-nitroanisole (b), trans-β-nitrostyrene (c), and trans-4-methoxy-β-nitrostyrene (d).

of NA peaks increases as a consequence of acetone desorption (see, e.g., the increase of dichroism of the 836 cm^{-1} peak going from spectrum a to spectra b and c in Figure 6A). This phenomenon is more clearly shown by the plot of Figure 6B, where the acetone content (as evaluated by the absorbance of the peak at 1220 cm^{-1}) and the order parameter *S* of two NA peaks (out-of-plane peak at 836 cm^{-1} and in-plane peak at 1119 cm^{-1}) are reported versus the desorption time.

Immediately after solution sorption in the uniaxially stretched s-PS film, when the acetone concentration is high, dichroism of all NA peaks is low. However, when the acetone molecules are spontaneously desorbed from the polymeric film, the dichroism of out-of-plane and in-plane NA peaks[18] becomes markedly positive and negative, respectively (Figure 6B). Hence, as a consequence of acetone desorption, NA molecules tend to assume an orientation of their molecular plane nearly perpendicular to the crystalline polymeric chain axes. Data of Figure 6A,B can be rationalized by assuming that the volatile acetone guest molecules are replaced in the cavities of the host nanoporous crystalline phase by NA molecules, formerly absorbed in the amorphous phase.

When the same treatment is applied to a uniaxially stretched γ-form film, the NA infrared peaks do not display any dichroism after acetone desorption (curve d). The NA molecules remain simply absorbed in the amorphous phase of the film and do not form a co-crystal. It is worth adding that the use of solvent carriers does not lead to s-PS/polar-guest co-crystals also when the solution diffusion occurs in s-PS samples presenting different crystalline phases (α or β).

In Figure 7 are reported the polarized FTIR spectra of uniaxially oriented s-PS/THF clathrate films treated with saturated acetone solutions with trans-β-nitrostyrene, trans-4-methoxy-β-nitrostyrene, and 4-(dimethyl-amino)-cinnamaldehyde, after total acetone desorption.

We can observe that absorption peaks of trans-β-nitrostyrene (at 1637, 1259, 1199, and 845 cm^{-1}) and trans-4-methoxy-β-nitrostyrene (1631, 1339, 1309, 1173, and 824 cm^{-1}) are highly dichroic. This indicates that co-crystals have

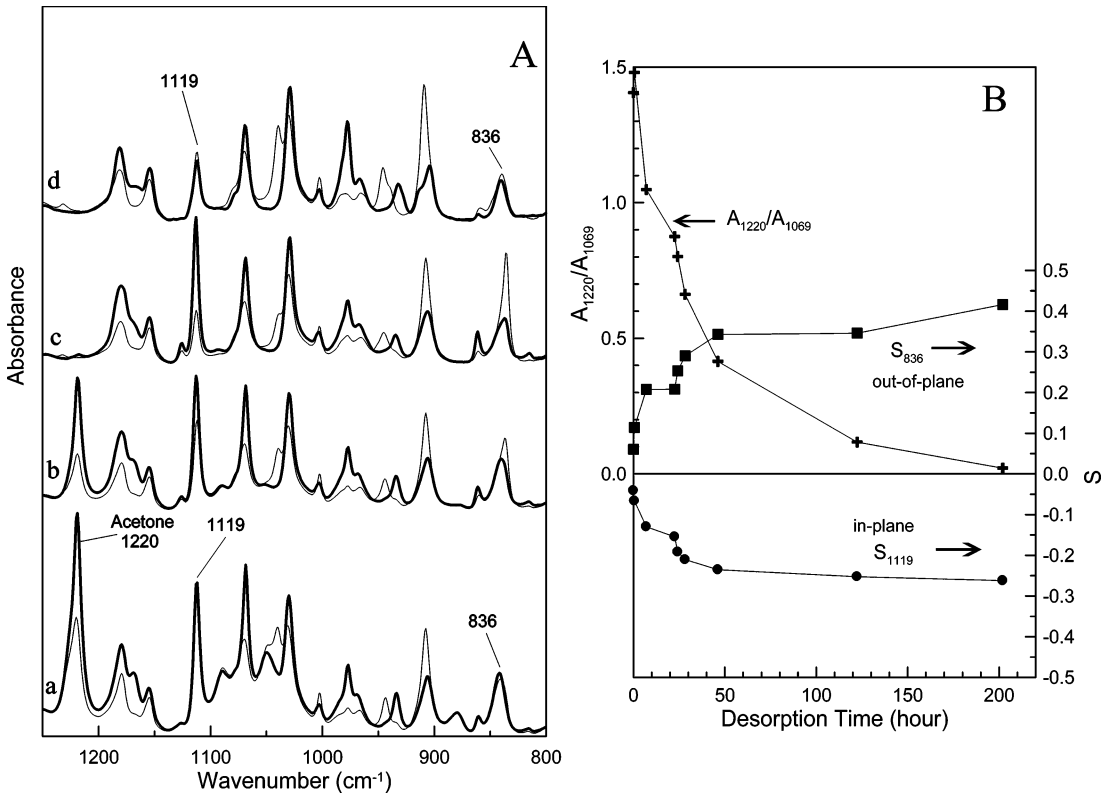


Figure 6. (A) FTIR spectra in the wavenumber range 1250−800 cm^{-1} taken with the polarization plane parallel (thin line) and perpendicular (thick line) to the draw direction for a uniaxially stretched s-PS/THF clathrate film treated with a solution of acetone/4-nitroaniline during the progressive desorption of acetone, t_{des}= 0 (a), t_{des} = 7 h (b), and t_{des} = 225 h (c), and for a uniaxially stretched γ-form film treated with a solution of acetone/4-nitroaniline after acetone desorption (d). (B) Absorbance of the acetone peak at 1220 cm^{-1} (left scale) and the linear dichroism of NA peaks (right scale) at 836 cm^{-1} (out-of-plane) and 1119 cm^{-1} (in plane).

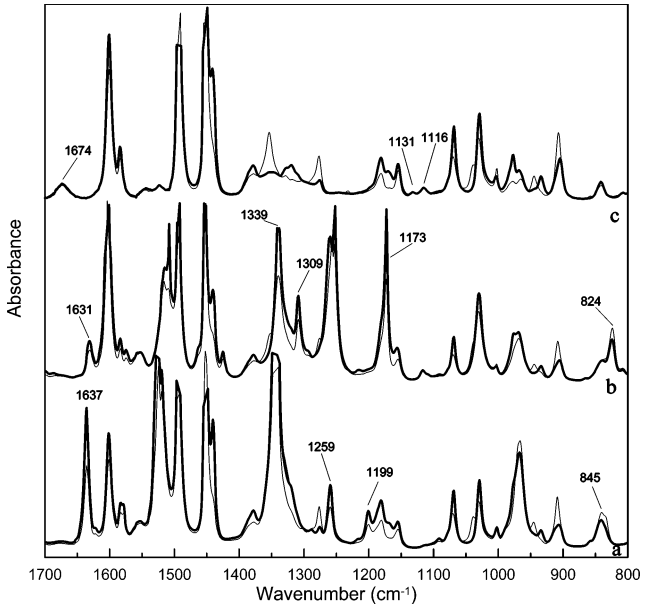


Figure 7. FTIR spectra in the wavenumber range 1700−800 cm^{-1} taken with the polarization plane parallel (thin line) and perpendicular (thick line) to the draw direction for uniaxially stretched s-PS/THF clathrate films treated with acetone solutions of trans-β-nitrostyrene (a), trans-4-methoxy-β-nitrostyrene (b), and 4-(dimethyl-amino)-cinnamaldehyde (c), after complete acetone desorption.

been obtained between these molecules and s-PS. Conversely, the absence of dichroism of the absorption bands of 4-(dimethyl-amino)-cinnamaldehyde at 1674, 1131, and 1116 cm^{-1} indicates that this molecule is only absorbed in the amorphous phase.

The results of Figure 7 can be easily rationalized because only the molecular volume of 4-(dimethyl-amino)-cinnamaldehyde (0.275 nm^3) is larger than the upper limit observed for guests of s-PS clathrate phases (0.26 nm^3).[3b]

The dichroic behavior of trans-β-nitrostyrene and trans-4-methoxy-β-nitrostyrene suggests that, also for these compounds, the guest molecules included in the s-PS co-crystals are oriented with their molecular plane nearly perpendicular to the crystalline polymer chain axis. In particular, for trans-β-nitrostyrene for polarization perpendicular to the stretching direction, in-plane (e.g., ν(arom. C—C) at 1259 cm^{-1}, ν-(vinyl C═C) at 1637 cm^{-1})[19] and out-of-plane vibrations peaks (e.g., C—H deformation at 845 cm^{-1})[19] present increased and decreased intensities, respectively.

Conclusions

A highly stable clathrate co-crystalline phase of s-PS with NB, a guest molecule having molecular polarity of 4.0 D, has been obtained and characterized by X-ray diffraction and infrared linear dichroism measurements. In particular, linear dichroism measurements have allowed the orientation of the molecular axes of NB to be established with respect to the polymer chain axis of the co-crystalline phase (α_x = 77°; α_y = 72°; α_z = 25°, see Figure 3). Suitable preparation procedures for this co-crystal include not only guest sorption in s-PS samples presenting the δ-form or different co-

(19) Clavijo, R. E.; Araya-Maturana, R.; Cassels, B. K.; Weiss-López, B. *Spectrochim. Acta* **1994**, *50A*, 2105−2115.

crystalline forms but also guest sorption in amorphous s-PS samples as well as solution crystallizations.

Sorption in δ s-PS of 4-nitroanisole, a bulkier guest molecule having also a higher polarity (4.6 D), also allows a highly stable co-crystal with s-PS to be obtained.

A different procedure, involving the sorption into δ or co-crystalline s-PS samples of guests dissolved in suitable solvent carriers, not only allows the preparation of s-PS co-crystals with NB and 4-nitroanisole but also allows it with guests of very high-polarity such as 4-nitroaniline (μ= 6.2 D), as well as for polar and bulkier molecules like 4-(dimethyl-amino)benzaldehyde, trans-β-nitrostyrene, or trans-4-methoxy-β-nitrostyrene. Suitable solvent carriers are in general volatile guests of s-PS co-crystals, like, for example, acetone or acetonitrile.

All the achieved s-PS co-crystals with polar molecules present clathrate structures, and the guest molecules are oriented with their molecular plane nearly perpendicular to the crystalline polymer chain axis.

s-PS co-crystals have not been obtained with 4-(dimethyl-amino)-cinnamaldehyde, that is, the bulkiest molecule of Table 1. This result can be easily rationalized because the guest molecular volume (0.275 nm^3) is larger than the upper limit observed for guests of s-PS clathrate phases (0.26 nm^3).[3b]

It is worth noting that these polar guests are characterized by non-zero first-order hyperpolarizability (see Table 1), being relatively high for trans-4-methoxy-β-nitrostyrene ($\beta = 17 \times 10^{-30}$ esu), and hence films with these co-crystalline phases could be possibly considered for nonlinear optical applications.

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