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Oriented Nanoporous Host δ Phases of Syndiotactic Polystyrene as a Tool for Spectroscopic Investigation of Guest Molecules

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Summary: An efficient method to align low-molecular-mass molecules by enclosing them as isolated guests of the nanoporous host δ phase of syndiotactic polystyrene oriented films, is presented. This new method is compared with the classic method consisting in the absorption of low- molecular-mass molecules as a solute of amorphous phases of highly oriented semicrystalline polymeric films. It is shown that this new molecular alignment method provides a powerful tool to study in detail several features (spectroscopic properties, molecular motions) of relevant molecules, by separating with unprecedented selectivity their anisotropic spectral responses. The reported results refer to infrared and solid-state-^{2}H-NMR spectra.

Keywords: anisotropic spectral response; guest orientation; host-guest systems; infrared spectroscopy; nuclear magnetic resonance

Introduction

The use of stretched polymers has been defined as the simplest and least expensive method to impart partial orientation to solute molecules. According to that method the solute molecule is absorbed in the amorphous phase of (generally uniaxially) stretched semicrystalline films, mainly polyethylene or polyvinylalchool.[1] However, the orientation control of the solute molecules is generally poor, since their absorption occurs in poorly oriented polymer amorphous phases (orientation factors generally lower than 0.5). Moreover the mobility of the molecules in the amorphous phase is quite high and hence low temperatures experiments are often needed.[1–3] Herein we present a more efficient method to orient low-molecular-mass molecules, consisting in enclosing them as guest in a highly oriented nanoporous polymeric host crystalline phase.

Several polymers are able to form crystalline molecular complexes with low molecular mass compounds.[4,5] However, the guest removal from the molecular complex crystalline phases generally produces the formation of dense polymer crystalline phases or loss of crystallinity. To our knowledge, only for syndiotactic polystyrene (s-PS) the guest removal can lead to formation of a nanoporous empty structure, where the guest molecules are replaced by crystalline cavities whose size and shape have been thoroughly established[6,7] (Figure 1A). This nanoporous crystalline phase, which has been named δ phase, is able to form molecular complex (clathrate[7] and intercalate[8]) phases with hundreds of molecules and shows the capability to adapt itself to the guest molecule requirements. In particular, the formation of the s-PS clathrates is associated with an increase of the spacing of the *ac* layers of s(2/1)2 helices, being roughly proportional to the guest dimension ($d_{010} = b\sin\gamma$ is 10.5 Å for the empty δ form

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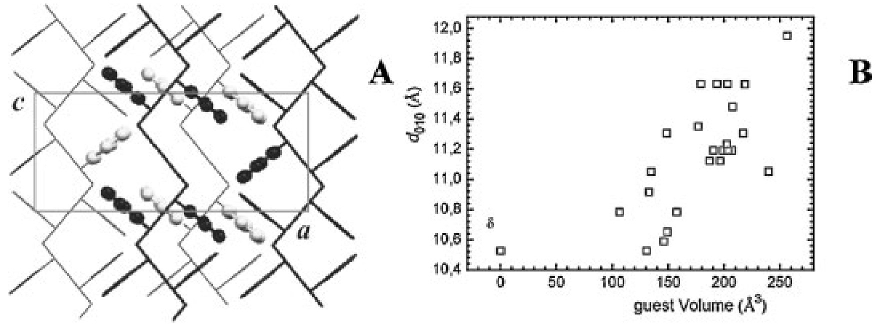

Figure 1.

(A) Projection in the *ac* plane of the crystal structure of the nanoporous δ-phase. The carbon atoms of the ten phenyl rings confining the crystalline cavity have been indicated by balls. The two darker and the two lighter helices are located on *ac* planes at a distance of 10.5 Å. (B) This interplanar distance (d_{010}) plotted versus the molecular volume of the guests, for several s-PS clathrate phases.

and increases at least up to 12 Å, Figure 1B).[7,8]

This host δ-phase of s-PS can be easily attained with high degrees of crystalline phase orientation (e.g, uniaxial orientation factors $f_c > 0.9$, for draw ratios, λ = final length/initial length, larger than 3), as usually occurs for crystalline phases of semicrystalline polymeric films.

In the present paper we show that nanoporous host δ phases of s-PS, presenting different kinds of crystalline phase orientation, can be a helpful tool for spectroscopic investigation of guest molecules. In particular, we will present some results achieved by Fourier Transform Infrared (FTIR) and solid state Deuterium Nuclear Magnetic Resonance (^{2}H-NMR) techniques.

Experimental Part

Benzene and 1,1,2-trichloroethylene (from Aldrich) and benzene-d_6 (from Armac) were used without further purification.

Syndiotactic polystyrene was supplied by Dow Chemical under the trademark Questra 101. ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic polystyrene 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, $M_w/M_n = 3.9$.

s-PS amorphous films, 100–120 μm thick, were obtained by melt extrusion with an extrusion head of 200 mm × 0.5 mm.

Uniaxially oriented films, 20–50 μm thickness, were obtained by monoaxial stretching of extruded ones, in the temperature range 105–110 °C with an Instron stretching machine. The stretched films, still essentially amorphous, were crystallized into the nanoporous δ form by exposure for one day to CS_2 vapor, followed by treatment under vacuum at 40 °C for three days. The clathrate samples were obtained by exposure of the nanoporous δ form to vapor of the corresponding pure compounds. Uniaxially oriented α form films were obtained by annealing the δ form films at 210 °C for 30 min.

Infrared spectra were obtained at a resolution of 2.0 cm^{-1} with a Vector 22 Brucker spectrometer equipped with deuterated triglycine sulphate (DTGS) detector and a Ge/KBr beam splitter. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He-Ne laser. 32 scans were signal averaged to reduce the noise. Polarized infrared spectra were recorded by the use of a SPECAC 12500 wire grid polarizer.

The degree of axial orientation relative to the host crystalline phase has been formalized on a quantitative numerical basis using the Hermans' orientation function. In particular, as far as infrared spectroscopy is considered, the axial orientation function is given by:

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

where $R = A_{//}/A_{\perp}$ is the dichroic ratio, $A_{//}$ and $A_{\perp}$ being the measured absorbance for electric vectors parallel and perpendicular to the draw direction respectively, and α is the angle between the chain axis and the transition moment vector of the vibrational mode. As described in ref. 10, the order parameter S of the 571 cm^{-1} bands has been directly used as a measure of the axial orientation function (f_{c},IR) for helical crystalline phases, since its transition moment vector is parallel to the chain axis.

Solid state ^{2}H-NMR spectra were recorded with a Bruker DSX, operating at 46.07 MHz ^{2}H Larmor-frequency, using the solid echo pulse sequence, with an echo delay $\tau = 30$ μs. The 90° pulse length was in the range of 2.0–4.0 μs, and the recycle time was 0.5 s. The oriented clathrate films were cut into slices parallel to the draw direction. The slices were packed together and introduced into the NMR sample tube so that the draw axis was perpendicular to the tube long axis.

Results and Discussion

FTIR studies

FTIR spectroscopy has proven to be a technique capable to provide information at molecular level and to probe the local environment of both guest molecules and polymeric host of s-PS polymer-complex phases.[9–11] In fact, host-guest interactions not only often produce shifts of vibrational peaks but also can change the conformational equilibria of the guest molecules. Both phenomena can be studied by FTIR spectroscopy with fast sampling rate, high sensitivity and accurate quantitation, thus giving the opportunity, for instance, to evaluate the guest amount in both amorphous and crystalline polymeric phases.[9,10]

In this contribution we will focus on additional structural and spectroscopic information on guest molecules which can be achieved by FTIR spectra on *oriented* s-PS films. In particular, three sub-sections will be devoted to *polarized* spectra of uniaxially stretched films while the last sub-section will deal with *unpolarized* spectra of s-PS films presenting trhee different kinds of planar orientation of the nanoporous crystalline phase.

Linear Dichroism of FTIR Peaks of Guest Molecules Included in The Uniaxially Oriented δ Phase

High linear dichroism of FTIR peaks of low-molecular-mass molecules can be achieved by enclosing them as guest of the crystalline nanoporpous δ phase of uniaxially stretched s-PS films.

Just as an example, the FTIR spectra in the wavenumber range 1510–475 cm^{-1}, taken with polarization plane parallel and perpendicular to the draw direction (thin and thick lines, respectively) of uniaxially oriented s-PS films ($\lambda \approx 3$) including benzene and benzene-d_6 molecules are reported in Figure 2.

In particular, in Figure 2A the polarized spectra of an uniaxially oriented δ form film including 9 wt % of benzene are reported. Due to the high similarity between the guest and host molecular structure, most of the hydrogenated guest vibrations lie under the host absorption peaks and only two guest vibrational peaks (indicated by *g* in Figure 2A) are visible. FTIR spectra have been collected also for an uniaxially oriented δ form film including 10 wt % benzene-d_6 (Figure 2B-B′). The four infrared active fundamentals as well as other combination peaks of the guest, indicated by *g* in Figure 2B-B′, are clearly visible.

The occurrence of a high degree of orientation of the host crystalline phase (f_{c},IR = 0.9) is clearly apparent from the high dichroic ratio observed for the peaks at 1276, 1320, 1354, 769 and 571 cm^{-1}, typical

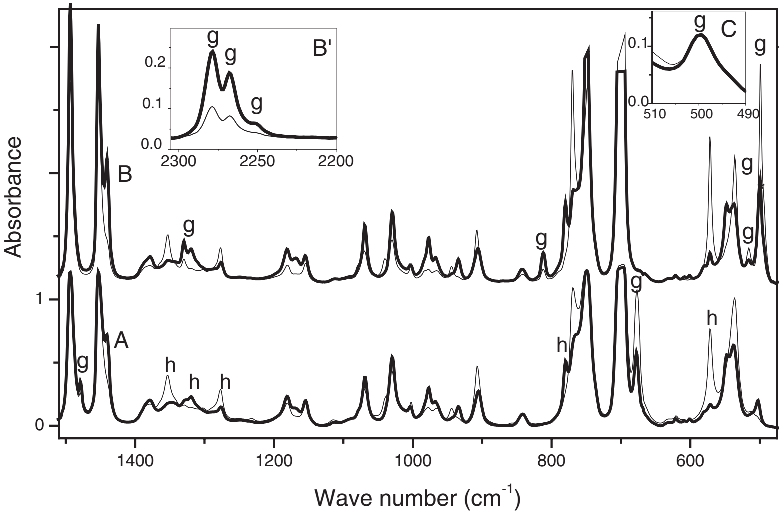

Figure 2.

FTIR polarized spectra taken with light polarization parallel (thin line) or perpendicular (thick line) to the stretching direction of s-PS uniaxially oriented films: (A) δ form film including 9 wt % of benzene in the crystalline phase, (B, B′) δ form film including 10 wt % of benzene-d$_6$ in the crystalline phase (C) α form film including nearly 1 wt % of benzene-d$_6$ in the amorphous phase. *h* and *g* label peaks of the host crystalline phase and of the guest, respectively.

of the helical crystalline phase, indicated by *h* in the Figure 2A. It is worth noting that also most guest peaks show large dichroic ratios (Figure 2A, B-B′).

On the other hand, the absorption of benzene molecules in amorphous phases of s-PS is generally much lower. For instance, in the same experimental conditions, the amount of guest molecules absorbed in the amorphous phase of uniaxially oriented α form film ($f_c = 0.94$) is only 1 wt % and the observed peaks clearly are not dichroic. This is shown, for instance, for the peak at 500 cm^{-1} of benzene-d$_6$ in the inset C of Figure 2.

It is worth adding that, since the guest molecules are highly oriented in the crystalline phase and essentially unoriented in the amorphous phase, the measured dichroic ratios strongly depend on the partition of the guest molecules between the two phases. As discussed in detail in previous papers,[8,12,13] after sorption into semicrystalline nanoporous samples, guest molecules can be partitioned almost evenly in amorphous and crystalline phases, but the amorphous phase generally loses the guest molecules at a much faster rate than does the crystalline one and after substantial desorption, most of the residual low-molecular-mass molecules are located in the crystalline phase. As a consequence, the order parameter ($S = (R-1)/(R+2)$) of the guest peaks tend to increase (in absolute value) with guest desorption, gradually reaching a plateau value. On the basis of these plateau values, linear dichroism measurements can also allow to evaluate the partition of the guest molecules between the crystalline and the amorphous phase.[8,12]

A Clear-Cut FTIR Method to Discriminate Between in-Plane and Out-of-Plane Molecular Transition Moments

Polarized FTIR spectra of uniaxially stretched films including s-PS clathrate phases, like those of Figure 2, also allow a clear-cut discrimination between in-plane and out-of-plane guest transition moments.[14]

Table 1.
FTIR peaks (ν) and their relative dichroism (LD^r) for benzene and benzene-d_6 molecules being guest of the crystalline host δ phase of s-PS ($f_c = 0.9$). The FTIR peaks of the liquid compounds and their symmetry and vibrational assigment[17] are also reported (op stands for out-of-plane and ip for in-plane vibrations). The angles (degrees) between the vibrational transition moment vectors and the chain axis are reported in the last column.

	ν_{obs}, cm^{-1}	LD^r	ν_{rif}, cm^{-1}	Symmetry specie	assignment	α
C_6H_6	677	+1.5	671	op (A_{2u})	γ (HCC_2)	31
	1479	−0.92	1485	ip (E_{1u})	t, α (CC, CCC)	71
C_6D_6	500	+1.98	500	op (A_{2u})	γ (HCC_2)	25
	812	−0.92	813	ip (E_{1u})	β (HCC)	71
	1329	−0.89	1333	ip (E_{1u})	t, α (CC, CCC)	69
	2279	−0.95	2293	ip (E_{1u})	S (CH)	74

In fact, in the case of planar guest molecules of s-PS clathrate phases it has been generally observed that they are oriented with their smallest cross section nearly parallel to the s-PS stretching direction.[14–16] As a consequence, in-plane and out-of-plane vibrational modes maximize their absorption intensities for light polarization nearly perpendicular ($A\perp$) and parallel ($A\|$) to the stretching direction, respectively.[14,15]

Just as an example, the reduced dichroism ($LD^r = LD/A^{isotropic} = 3(A\| - A\perp)/(A\| + 2A\perp)$) for the vibrational peaks of benzene and benzene-d_6 guest molecules, as evaluated from the polarized spectra of Figure 2, are reported in the third column of Table 1. A clear-cut discrimination between in-plane and out-of-plane vibrations is clearly apparent, since the reduced dichroism assumes large negative and positive values, respectively. The experimental results perfectly agree with symmetry species (A_{2u} and E_{1u} correspond in-plane and out-of-plane vibrations, respectively) and normal mode assignments of benzene vibrations (5th column of Table 1).[17]

Directions of Guest Transition Moment Vectors with Respect to The Polymer Host Chain Axis

Polarized FTIR spectra of uniaxially stretched films including s-PS clathrate phases, like those of Figure 2, also allow an evaluation of the angle between the polymer chain axis and the transition moment vector (the angle α of Eq. 1), for each guest vibrational peak.

Just as an example, the order parameter $S = (R-1)/(R+2)$ relative to the benzene-d_6 peaks versus the crystalline orientation factors ($f_{c,IR}$) is plotted in Figure 3. The slope of these lines, by applying Eq. 1, leads to the α angles between the crystallographic c axis and the guest transition-moment-vectors, listed in the last column of Table 1. By using data of film samples for a very broad range of crystalline phase orientation ($0.3 < f_{c,IR} < 0.95$), α angles can be evaluated with a good accuracy (Figure 3).

These α angle evaluations, when associated with independent evaluation of the transition moment vector directions with respect to the molecular structure, allow to get information relative to the location of the guest molecule into the cavity of the s-PS δ phase.

In particular, for benzene guest molecules, a deviation of roughly 20° of the ring plane with respect to the plane perpendicular to the chain axis can be suggested. This result agrees with the data obtained by X-ray diffraction analysis of the crystalline structures of s-PS/toluene[16] and s-PS/*o*-dichloro-benzene[18] clathrate phases. Similar quantitative analyses have been already reported for other halogenated[12] and aromatic[15] molecules.

Directions of Guest Transition Moment Vectors in the Molecular Framework

Due to the cylindrical symmetry of uniaxially oriented crystalline phases, the evaluation of the α angle of a transition

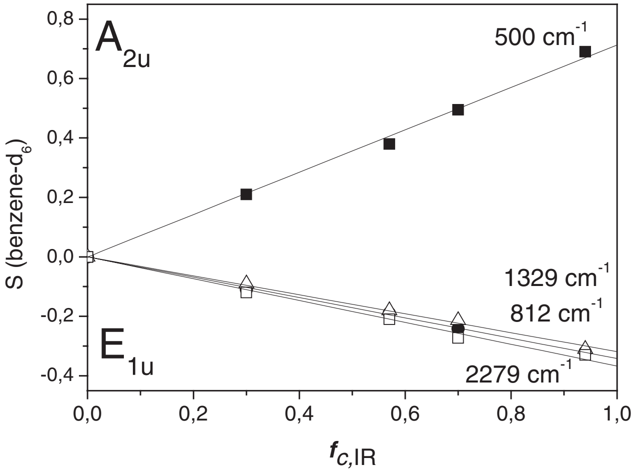

Figure 3.
Plot of the guest order parameter $S = (R - 1)/(R + 2)$ versus the crystalline host orientation factor ($f_{c,IR}$). By the line slopes the angles between the transition moment vector of the benzene peaks and the host chain axis is calculated (last column of Table 1).

moment vector, corresponding to a given guest peak, generally do not allow a complete definition of the transition moment vector direction with respect to the molecular framework, also when accurate information of the guest location into the host unit cell is available (e.g. by X-ray diffraction structure characterization).[16,18]

In this sub-section we suggest that a complete definition of the transition moment vector direction with respect to the molecular framework could be achieved by comparing the relative intensities of different guest absorbance peaks, for unpolarized FTIR spectra of s-PS polymer complex films presenting three different kinds of planar orientation.

In fact, recent studies have shown the possibility to obtain, for all clathrate crystalline phases through suitable processing procedures, three different planar orientations, namely the (010),[19] (002)[20] and ($\bar{2}10$)[21] uniplanar orientations, that is orientations of these crystalline planes preferentially parallel to the film surface. The FTIR spectra of the considered δ form s-PS films presenting the three different kinds of uniplanar orientation (the orientation factor being in the range $0.6 < f_{hkl} < 0.75$), after sorption of about 8 wt % of 1,1,1-trichloroethylene (TCE), are shown, for different spectral ranges, in Figure 4A–D.

Due to occurrence of a preferential orientation of the TCE molecules with respect to the host unit cell, the absorbance of the guest peaks is largely dependent on the different s-PS orientations. As expected, the peaks corresponding to out-of-plane vibrational modes[22] whose transition moment vectors are nearly parallel to the chain axis (e.g, at 455 cm^{-1})[14] are of high intensity for the films with (010) and ($\bar{2}10$) uniplanar orientations (thin and dot lines in Figure 4D) and of low intensity for the films with (002) orientation (thick line in Figure 4D). More informative are the peaks corresponding to in-plane vibrational modes[22] whose transition moment vectors are nearly perpendicular to the chain axis and hence of high intensity for films with (002) orientation. In fact, some of them (834 and 929 cm^{-1}, Figure 4B) are of higher intensity for films with (010) orientation and hence their transition moment vectors are roughly along the ⟨010⟩ direction. On the other hand, others ‘‘perpendicular’’ peaks (632 and 1247 cm^{-1}, Figure 4A,C) are of higher intensity for films with ($\bar{2}10$) uniplanar orientation and hence their

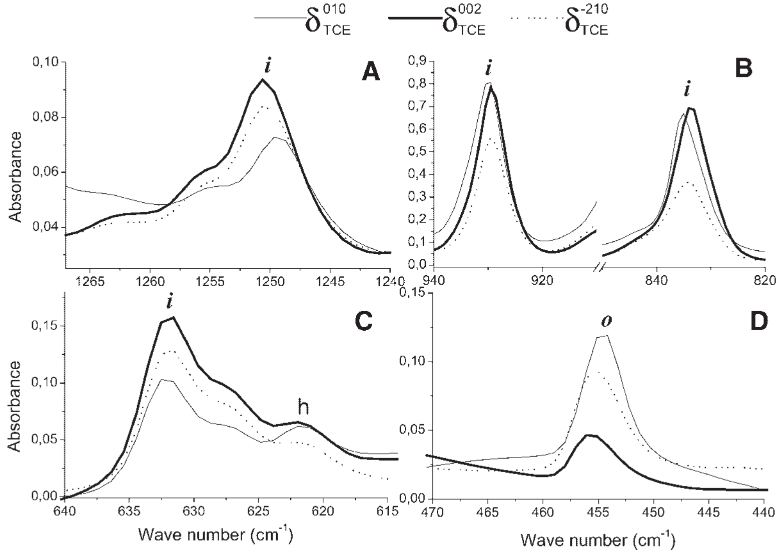

Figure 4.
FTIR peaks of TCE molecules being guest of δ form s-PS films presenting (010) (thin line), (002) (thick line) and $(\bar{2}10)$ (dot line) uniplanar orientations.

transition moment vectors are roughly along the $\langle \bar{2}10 \rangle$ direction. These preliminary results suggest that, by a quantitative analysis of the peak relative absorbances, it is in principle possible to completely define the directions of the guest transition moments with respect to the host unit cell and hence with respect to the guest molecular framework.

Solid state ^{2}H-NMR Spectra

By solid state ^{2}H-NMR measurements information about the reorientational dynamics of molecules in the microsecond time scale has been achieved. The investigation has been focused on the guest molecules by preparing clathrate phase with deuterated molecules. It has been demonstrated that the reorientation dynamics of molecules included in the clathrate phase is much more restricted with respect to the molecules absorbed in the amorphous phase.[23,24] Just as an example, the spectrum of benzene-d_6 molecules included in the nanoporous crystalline s-PS unoriented phase is reported in Figure 5A. The observed Pake pattern, showing a quadrupolar splitting of 67 kHz, clearly indicates that the guest motion is restricted to a rotation about its C_6 symmetry axis.[23,24]

Particularly informative can be ^{2}H NMR spectra of deuterated guest molecules included in uniaxially oriented δ form s-PS films. In fact, highly anisotropic spectra of most volatile organic compounds can be achieved, already at room temperature. Just as an example, the ^{2}H NMR spectra of benzene-d_6 included in the δ crystalline phase of an uniaxially oriented film ($\lambda = 3$, $f_c = 0.9$) for film stretching direction parallel ($B_{\parallel}$, Figure 5B) and perpendicular ($B_{\perp}$, Figure 5C) to the magnetic field, show large spectral differences. To our knowledge, the degree of anisotropy observed in these spectra has never been reported in the literature, for solute molecules in a polymer.

Information about the orientation of the guest molecule, into the host crystalline framework, can be easily obtained from these spectra. For instance, the enhanced intensity of the outer components at 134 kHz in the $\|$ spectrum and of the inner components at 67 kHz in the $\perp$ spectrum (Figure 5), clearly indicate,[25] in agreement

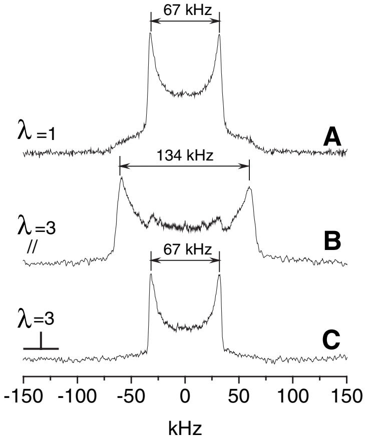

Figure 5.
Solid state ^2H NMR spectra of benzene-d_6 molecules included in nanoporous s-PS samples: unoriented ($\lambda = 1$, A) and oriented ($\lambda = 3$), collected for film stretching directions parallel (||, B) and perpendicular ($\perp$, C) to the magnetic field.

with previous linear dichroism and X-ray diffraction measurements, that the benzene ring plane is roughly perpendicular with respect to the chain axis.

The anisotropy of solid state ^2H NMR spectra of less symmetric volatile deuterated molecules can be helpful also to separate complex powder patterns into their constituents patterns, making easier the investigation of molecular motions. ^2H NMR studies of less symmetric molecules, like 1,2-dichloroethane-d_4, are in progress.

Conclusions

In this paper the use of oriented δ form s-PS films as a host compound to get high degrees of guest molecular alignment is proposed. Due to the guest inclusion in the crystalline phase, their orientation degrees are higher than those obtained by absorption in amorphous oriented polymeric phases. This provides a powerful tool to study in detail several molecular properties (spectroscopic properties, molecular motions) of relevant molecules, already at room temperature.

By polarized FTIR spectra of uniaxially oriented s-PS films, information relative to the partition of the solute molecules between amorphous and crystalline phases and relative to the location of the guest molecule into the cavity of the s-PS δ phase can be achieved. Moreover, it has been shown that, by using δ form s-PS films presenting different uniplanar orientations, it is in principle possible to completely define the directions of the guest transition moment vectors with respect to the host unit cell and hence with respect to the guest molecular framework.

High degree of anisotropy have also been found for ^2H NMR measurements on deuterated guest molecules, by collecting the spectra for film stretching directions parallel ($B_{\parallel}$) and perpendicular ($B_{\perp}$) to the magnetic field. These anisotropic spectral responses can contribute to establish the guest orientation with respect to the host and the nature of the guest motions, which are accessible in the solid state at different temperatures.

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