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Anisotropic Guest Diffusion in the δ Crystalline Host Phase of Syndiotactic Polystyrene: Transport Kinetics in Films with Three Different Uniplanar Orientations of the Host Phase

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The sorption and desorption of a guest (1,2-dichloroethane) in syndiotactic polystyrene (s-PS) films, presenting three different kinds of uniplanar orientation ((010), (210), or (002)) of the nanoporous host δ phase, have been investigated, mainly by Fourier transform infrared measurements. For guest uptake from dilute aqueous solutions (e.g., 50 ppm), the sorption in the amorphous phase is negligible with respect to sorption in the nanoporous crystalline phase. Correspondingly the guest sorption and desorption kinetics are influenced by the orientation of the anisotropic host crystalline phase. In particular, as for the guest diffusivity (D) measured by both sorption and desorption experiments, $D(010) \leq D(002) < D(\text{unoriented}) < D(210)$. These results can be rationalized on the basis of previous molecular dynamics simulations, predicting an anisotropic guest diffusion in the δ crystalline phase.

1. Introduction

Recent studies relative to the polymorphic behavior of syndiotactic polystyrene (s-PS) have shown that one of its four crystalline forms (the δ form) is nanoporous and has a density (0.98 g/cm³) definitely lower than amorphous s-PS (1.05 g/cm³), which is close to that one of atactic polystyrene.^{1,2}

The monoclinic structure of the δ form of s-PS (space group $P2_1/a$; $a = 1.74$ nm; $b = 1.18$ nm; $c = 0.77$ nm; $\gamma = 117^\circ$) has per unit cell two identical cavities centered on the center of symmetry, bound by 10 phenyl rings (Figure 1).^{2,3}

Sorption studies from liquid and gas phases have shown that δ form s-PS samples are able to absorb suitable guest molecules, even when present at very low concentrations.^{4–6} These guest sorption procedures can eventually lead to

formation of molecular complex phases, being clathrate⁷ or intercalate⁸ phases. In particular, it has been clearly demonstrated that for sorption at low activities most penetrants are located essentially only as a guest into the crystalline phase, while their concentration in the amorphous phase can be negligible.^{5a,e}

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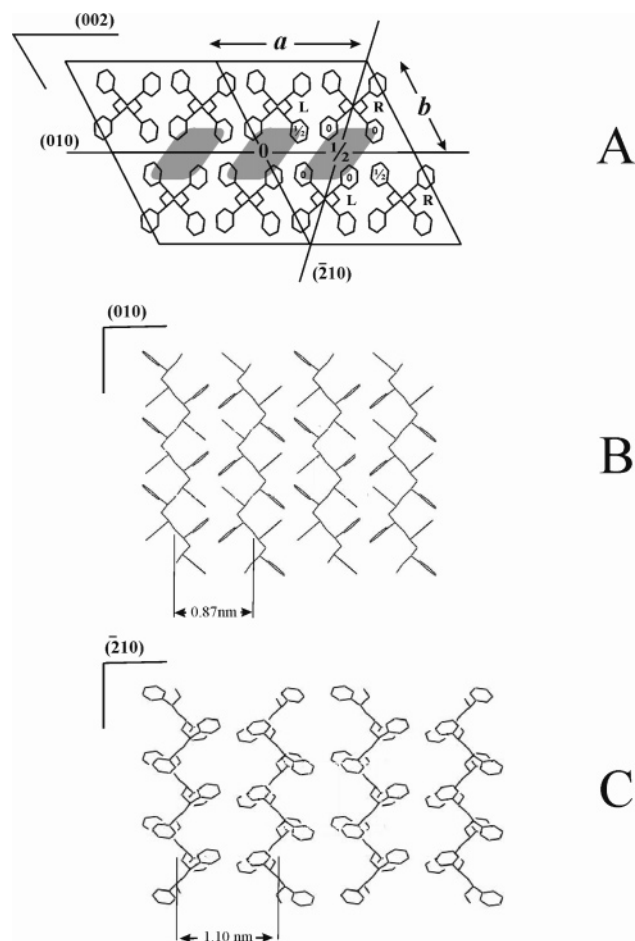


Figure 1. Three different views of the host crystalline delta form of s-PS: (A) Along the c axis view of four adjacent unit cells, showing traces of the (002) crystallographic plane as well as the traces of the (010) and (210) planes, being perpendicular to the plane of the figure. Each crystalline cavity (gray region) is confined by 10 host phenyl rings (whose approximate center of mass z fractional coordinates are indicated), and the shown adjacent cavities are along the $\langle 101 \rangle$ direction.³ (B and C) Rows of alternated enantiomorphous helices parallel to the (010) and $(\bar{2}10)$ crystallographic planes, respectively. s-PS crystalline films presenting (002) or (010) or (210) planes parallel to their surface have been used for the guest transport experiments of the present paper.

s-PS films with three different kinds of orientation of the host δ crystalline phase, for which three different crystal planes (010),⁹ $(\bar{2}10)$,¹⁰ or (002)¹¹ tend to be parallel to the film plane, have been recently achieved by casting^{9,11a} or by solvent induced crystallization^{10,11b} procedures. These three kinds of orientation, which according to the terminology by Heffelfinger and Burton¹² can be defined as “uniplanar”, are schematically shown in Figure 1A, for the along-the-chain-axis (along c) view of four adjacent δ unit cells. Of course, ideal (010) and $(\bar{2}10)$ orientations present the chain axes of the crystalline phase parallel to the film plane (Figure 1B and 1C, respectively) while the ideal (002) orientation

presents these chain axes perpendicular to the film plane (Figure 1A).

The anisotropic diffusional behavior of small guest molecules in the host δ form of s-PS has been studied by means of molecular simulation.¹³ Minimum diffusivity between crystalline cavities has been calculated for the direction perpendicular to the crystallographic (010) planes.^{13a} In fact, these planes correspond to rows of parallel helices with minimum interchain distances (interchain distance = $a/2 = 0.87$ nm, see Figure 1) and present the highest planar density.^{2,3,7} On the other hand, preferred diffusion pathways would be parallel to the (010) planes and in particular along $\langle 101 \rangle$ directions.^{13a}

The present availability of semicrystalline films with three different kinds of uniplanar orientation of the δ crystalline phase gives the opportunity to study the possible influence of the orientation of the host crystalline phase on guest diffusion kinetics. In principle, this could be more easily observed for diffusion experiments conducted at low activities, which ensure guest sorption essentially only by the nanoporous crystalline phase.⁵

Transport kinetic studies are conducted by using 1,2-dichloroethane (DCE) as the low molecular mass guest. This guest choice was motivated by the additional information that comes from its conformational equilibrium. In fact, as described in detail in previous papers,^{5a-d} because essentially only its trans conformer is included into the clathrate phase while both trans and gauche conformers are included in the amorphous phase, quantitative evaluations of vibrational peaks associated with these conformers allow the amounts of DCE confined as the guest in the clathrate phase or simply absorbed in the amorphous phase to be evaluated.

2. Experimental Section

s-PS was supplied by Dow Chemical under the trademark Questra 101. ¹³C nuclear magnetic resonance characterization showed that the content of syndiotactic triads was over 98%. The weight-average molar mass obtained by gel permeation chromatography in trichlorobenzene at 135 °C was found to be $M_w = 3.2 \times 10^5$ with the polydispersity index of $M_w/M_n = 3.9$.

All films considered in this paper present the nanoporous crystalline δ phase and a thickness in the range 30–40 μm . The films with uniplanar (010) and (002) orientations have been obtained by casting from 0.5 wt % solutions, at room temperature from chloroform⁹ and at 50 °C from trichloroethylene,¹¹ respectively. The film with uniplanar $(\bar{2}10)$ orientation has been obtained by *o*-xylene diffusion at 50 °C into an unoriented amorphous film.¹⁰ The unoriented semicrystalline film has been obtained by tetrahydrofuran diffusion at 50 °C in γ form films, in turn obtained by acetone treatment at 50 °C of an amorphous film.^{14a} The amorphous films were obtained by extrusion of the melt with an extrusion head of 200 mm \times 0.5 mm.

The so-obtained s-PS semicrystalline films were in a clathrate form. The guest molecules were removed by carbon dioxide at 200

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bar and 40 °C;^{1a,b} thus, the clathrate form was transformed into the nanoporous δ form. The residual solvent content in the samples, after these extraction procedures, as evaluated by thermogravimetric measurements, was lower than 0.1%. Their degree of crystallinity, obtained by Fourier transform infrared (FTIR) spectral subtraction procedures,¹⁴ is in the range 35–40%.

Thermogravimetric analyses were carried out by a Mettler TG50 thermobalance in a flowing nitrogen atmosphere at a heating rate of 10 °C/min.

Wide-angle X-ray diffraction patterns with nickel filtered Cu K α radiation were obtained, in reflection, with an automatic Bruker diffractometer.

The degree of the three different kinds of uniplanar orientation for the δ form s-PS films, that is, the degree of parallelism of the three crystallographic planes with respect to the film plane, have been formalized on a quantitative numerical basis using Hermans' orientation functions,¹⁵ f_{010} , $f_{\bar{2}10}$, and f_{002} , where

$$f_{hkl} = \frac{\overline{\cos^2 \chi_{hkl}} - 1/2}{\overline{\cos^2 \chi_{hkl}} - 1/2} \quad (1)$$

by assuming $\overline{\cos^2 \chi_{hkl}}$ as the squared average cosine value of the angle, χ_{hkl} , between the normal to the film surface and the normal to the (hkl) crystallographic plane.

Because, in our cases, a θ_{hkl} incidence of the X-ray beam is used, the quantity $\overline{\cos^2 \chi_{hkl}}$ can be easily experimentally evaluated:

$$\overline{\cos^2 \chi_{hkl}} = \overline{\cos^2 \chi_{hkl}} = \frac{\int_0^{\pi/2} I(\chi_{hkl}) \cos^2 \chi_{hkl} \sin \chi_{hkl} d\chi_{hkl}}{\int_0^{\pi/2} I(\chi_{hkl}) \sin \chi_{hkl} d\chi_{hkl}} \quad (2)$$

where $I(\chi_{hkl})$ is the intensity distribution of a (hkl) diffraction on the Debye ring and χ_{hkl} is the azimuthal angle measured from the equator.

The diffracted intensities $I(\chi_{hkl})$ of eq 2 were obtained by using an AFC7S Rigaku automatic diffractometer (with monochromatic Cu K α radiation) and were collected sending the X-ray beam parallel to the film surface and maintaining an equatorial geometry. Because the collection was performed at constant 2θ values and in the equatorial geometry, the Lorenz and polarization corrections were unnecessary.

In these assumptions, $f_{hkl} = 1$ and -0.5 if (hkl) planes of all crystallites are perfectly parallel and perpendicular to the plane of the film, respectively.

Infrared spectra were obtained at a resolution of 2.0 cm⁻¹ with a Vector 22 Bruker spectrometer equipped with a deuterated triglycine sulfate detector and a KBr beam splitter. The frequency scale was internally calibrated to 0.01 cm⁻¹ using a He–Ne laser. A total of 32 scans were signal-averaged to reduce the noise. As a result of the orientation dependence of the absorbances of the host peaks, to account for different film thicknesses, the usual normalization procedure based on internal reference peaks (e.g., the 1181 cm⁻¹ or the 1601 cm⁻¹ peak) was avoided. Only films with thickness in the range 30–40 μ m were analyzed, and the guest absorbances were normalized by taking into account the small differences in film thickness, as measured by a micrometer.

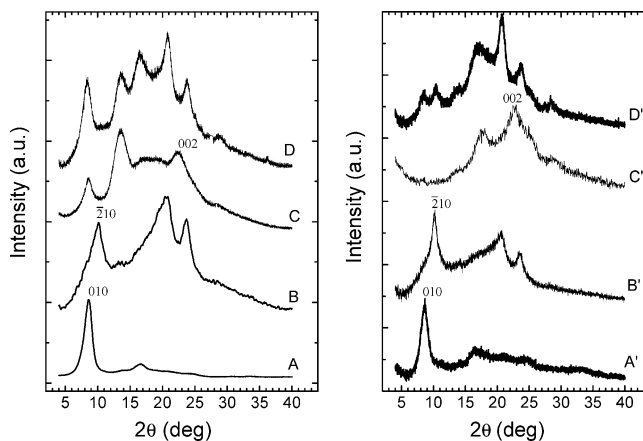


Figure 2. X-ray diffraction patterns collected by an automatic diffractometer (Cu K α radiation) of s-PS films presenting the nanoporous crystalline δ phase with different kinds of uniplanar orientation: (010) (A, A'); ($\bar{2}10$) (B, B'); (002) (C, C'); and unoriented (D, D'). Primed symbols refer to the films after equilibrium sorption uptake of DCE from 50 ppm aqueous solutions.

The apparent diffusivities (D_{abs} , D_{des}) were obtained by the slope of the lines fitting the linear part of the absorption and desorption kinetic curves.

3. Results and Discussion

X-ray Diffraction Characterization of Host δ Form s-PS Films with Three Kinds of Uniplanar Orientation.

X-ray diffraction patterns (nickel filtered Cu K α radiation) obtained by an automatic diffractometer, for s-PS films with the host δ phase, presenting three different kinds of uniplanar orientation and unoriented, which have been used for our guest transport studies, are shown in Figure 2A–D. The high intensities of the (010), ($\bar{2}10$), and (002) reflections for the patterns of Figure 2A–C, respectively, clearly indicate the occurrence of the corresponding kinds of uniplanar orientation.^{9–11} The orientation factors for the three films of Figure 2A–C, by following the procedure described by eqs 1 and 2 of the experimental section, have been evaluated as $f_{010} \approx 0.8$, $f_{\bar{2}10} \approx 0.63$, and $f_{002} \approx 0.6$, respectively.

For all the films of Figure 2, which present the nanoporous δ phase with similar degrees of crystallinity, the equilibrium guest uptake from 50 ppm aqueous solutions of DCE is similar (in the range 4–5 wt % of total polymer weight, as determined by thermogravimetric analysis).

The X-ray diffraction patterns of the s-PS films of Figure 2A–D after equilibrium sorption of DCE are shown in Figure 2A'–D', respectively. As a consequence of the DCE sorption, a substantial decrease of the intensities of the (010) (at $2\theta \approx 8.4^\circ$, Figure 2A,C,D) and ($\bar{1}11$) (at $2\theta \approx 13.3^\circ$, Figures 2C,D) reflections as well as an increase of the ($\bar{2}10$) reflection (at $2\theta \approx 10.5^\circ$, Figure 2 B,D) is clearly apparent. These intensity changes are diagnostic of inclusion of guest molecules into the cavities of the host nanoporous δ phase.²

The comparison between the patterns of Figure 2A–C with those of Figures 2 A'–C' also shows that, as described in previous studies,^{10,11} the (010), ($\bar{2}10$), and (002) uniplanar orientations are maintained after the guest sorption procedure.

FTIR Characterization of Host δ Form s-PS Films with Three Kinds of Uniplanar Orientation. The FTIR spectra, for the spectral range 1300–1100 cm⁻¹, of the δ form s-PS

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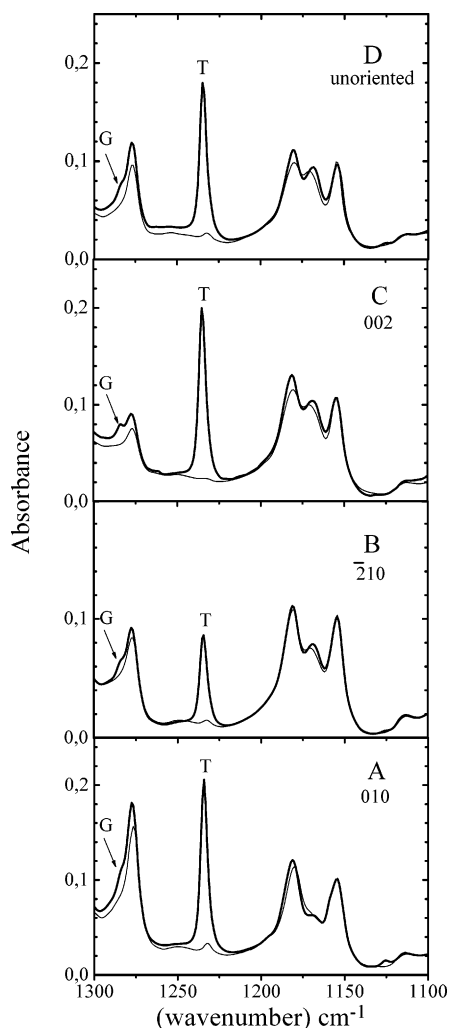


Figure 3. FTIR spectra in the 1300–1100 cm^{-1} region, for δ form s-PS films presenting the different kinds of uniplanar orientation sketched in Figure 1, and whose X-ray diffraction patterns are shown in Figure 2: (010) (A); ($\bar{2}10$) (B); (002) (C); and unoriented (D). In all figures the thin line shows the initial spectrum while the thick line shows the spectrum after room-temperature equilibrium sorption from 50 ppm DCE aqueous solutions, corresponding to a weight gain close to 5%. The two peaks of the trans (T) and gauche (G) DCE conformers, used for our quantitative evaluations of Figures 4 and 5, are explicitly labeled.

films of Figure 2A–D are shown by thin lines in Figure 3A–D, respectively. As described in previous papers,^{10,11a,16} the absorbance of most s-PS FTIR peaks is highly dependent on the orientation of the crystalline phase as shown, for instance, in Figure 3 for the host crystalline peaks at 1277 and 1169 cm^{-1} . On the other hand, the absorbances are essentially independent of the crystalline phase orientation for the prevalently amorphous peaks, like the one located at 1155 cm^{-1} .^{14a}

The FTIR spectra of the considered δ form s-PS films presenting the three different kinds of uniplanar orientation and unoriented, after equilibrium DCE sorption, are shown by thick lines in Figure 3A–D. In agreement with previous results relative to DCE sorption from diluted aqueous solutions,⁷ it is apparent that, for all the considered planar orientations, the 1234 cm^{-1} peak relative to the trans DCE conformer is largely predominant over the gauche peak at

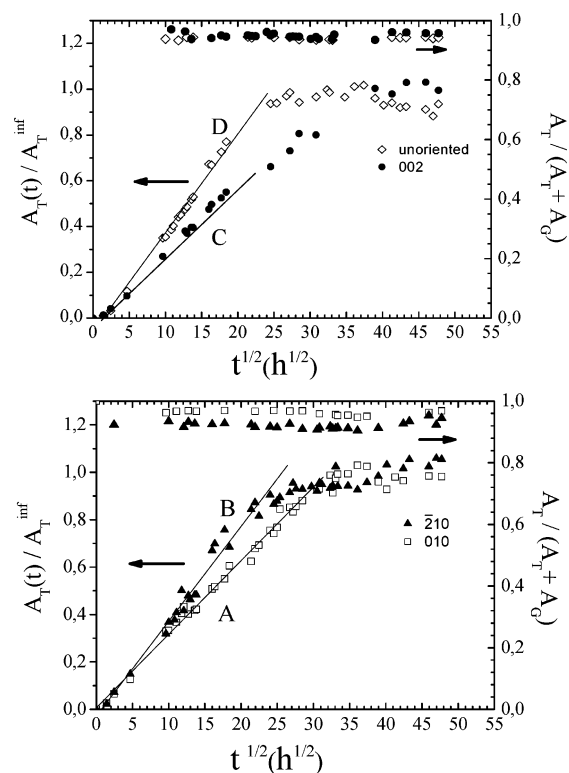


Figure 4. Sorption kinetics at room temperature of DCE from 50 ppm DCE aqueous solutions, based on the absorbance of its T peak, for δ form s-PS films presenting the three different kinds of uniplanar orientation sketched in Figure 1: (010) (A); ($\bar{2}10$) (B); (002) (C); and unoriented (D). On the right scale is the absorbance ratio $A_T/(A_T + A_G)$, based on the T and G DCE peaks labeled in Figure 3.

1284 cm^{-1} , which is barely detectable as a weak shoulder of the intense 1277 cm^{-1} s-PS absorption. This confirms that the most DCE molecules are included as the guest into the cavities of the host nanoporous crystalline phase.

It is also worth noting that the absorbance of the 1234 cm^{-1} peak (corresponding to the ν_9 CH_2 wagging mode)¹⁶ is largely dependent on the different s-PS orientations. These differences are mainly due to the occurrence of a preferential orientation of the DCE guest molecules with respect to the host unit cell, as already pointed out by the high dichroism of this guest peak observed for uniaxially stretched films (Figure 2 of ref 16).

Guest Sorption Kinetics. Sorption kinetics from 50 ppm aqueous solutions of DCE, based on the absorbance of its 1234 cm^{-1} trans peak (A_T), in the three films presenting different uniplanar orientations and in an unoriented film, are compared in Figure 4.

The ratio between the absorbance of the 1234 cm^{-1} trans peak and the overall absorbance of this peak and of the 1285 cm^{-1} gauche peak ($A_T/(A_T + A_G)$) are also reported versus the sorption times in Figure 4. It is apparent that for all the considered conditions this ratio is essentially constant, indicating that, for all sorption times, most guest molecules are included in the crystalline phase.^{5,17}

As already established in previous papers,^{4,5,18} the kinetic curves for guest absorption from the nanoporous δ phase are formally fitted by means of Fick's model (Figure 4), and the apparent diffusivities (D^{abs}) obtained by the slopes of the lines are listed in Table 1.

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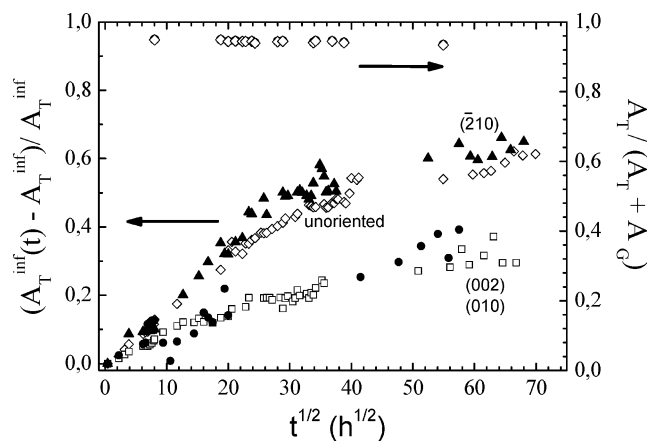


Figure 5. Desorption kinetics of DCE at room temperature, after the equilibrium sorption experiments of Figure 4, for δ form s-PS films presenting the three different kinds of uniplanar orientation sketched in Figure 1: (010) (square symbol); (210) (triangle symbol); (002) (circle symbol); and unoriented (diamond symbol). On the right scale is the absorbance ratio $A_T/(A_T + A_G)$, based on two T and G DCE peaks. For the sake of simplicity only the data relative to the unoriented sample are reported.

Table 1. Apparent Diffusivity Constants at Room Temperature of DCE in s-PS Films (Thickness of 30–40 μm), Presenting Different Kinds of Uniplanar Orientation of the Crystalline Nanoporous δ Phase, for Absorption from a 50 ppm Aqueous Solution and Subsequent Desorption in Air

cryst. phase orientation	degree of orientation	D^{abs} [cm^2/s]	D^{des} [cm^2/s]
010	0.8	$6.8 \pm 0.2 \times 10^{-13}$	$0.3 \pm 0.1 \times 10^{-13}$
002	0.6	$7.7 \pm 0.2 \times 10^{-13}$	$0.4 \pm 0.1 \times 10^{-13}$
unoriented	0	$8.6 \pm 0.2 \times 10^{-13}$	$1.1 \pm 0.1 \times 10^{-13}$
210	0.63	$9.9 \pm 0.2 \times 10^{-13}$	$4.3 \pm 0.1 \times 10^{-13}$

The apparent diffusivity constants of Table 1 are close to those measured for the transport of chloroform in δ form s-PS films at low vapor pressure (at $T = 56^\circ\text{C}$, $P = 5$ Torr, and $D^{\text{abs}} = 8.6 \times 10^{-13}$).^{5c} Moreover, they are significantly different for films with different uniplanar orientations and, in particular, $D^{\text{abs}}(010) < D^{\text{abs}}(002) < D^{\text{abs}}(\text{unoriented}) < D^{\text{abs}}(\bar{2}10)$.

Guest Desorption Kinetics. Desorption experiments, at room temperature in air, from s-PS films, after the DCE equilibrium sorption experiments of Figure 4, for the three films presenting different uniplanar orientations and for an unoriented film, are compared in Figure 5.

It is apparent that, for all kinds of orientation of the host crystalline phase, guest desorption is significantly slower than guest absorption. In particular, as for the films with $\bar{2}10$ uniplanar orientation, there is a reduction of the apparent diffusivity by a factor not far from 2, and after 3000 h of desorption nearly 40% of DCE is still present in the polymer film. Much stronger is the diffusivity reduction for the films with uniplanar orientation of the (002) and (010) crystalline

planes, and (by a factor not far from 20) after 3000 h of desorption, nearly 65% of DCE is still present in the polymer films.

The ratio $A_T/(A_T + A_G)$, also reported versus the desorption time in Figure 5 (right scale), remains essentially constant during the desorption experiment, thus indicating that the guest molecules remain essentially only included in the crystalline phase.

In summary, the dependence of guest diffusivity on the kind of orientation of the host crystalline phase is qualitatively similar for sorption and desorption experiments (Table 1). In particular, films with (010) and (002) uniplanar orientations present diffusivities lower than those observed for unoriented films while films with $\bar{2}10$ uniplanar orientation present diffusivities higher than those observed for unoriented films.

Comparison between Observed and Calculated Anisotropic Guest Diffusivities. On the basis of previous analyses,^{5,18} the amorphous phase, which represents at least 60–70% of the semicrystalline films investigated, displays for low DCE concentrations a negligible guest solubility⁵ but higher guest diffusivity¹⁸ with respect to the δ crystalline phase. For instance, gas (O_2 and CO_2) diffusivities in the δ phase, in the limit of small concentrations, are about 2 orders of magnitude lower than in the amorphous phase.¹⁸

In a rather simplified view it can be assumed that, because of the much lower diffusivity in the crystalline phase, for the samples at hand, the time needed to saturate by a diffusive process the amorphous regions with DCE is much smaller than that necessary to saturate the crystallites. As a consequence, in a sorption test, the DCE concentration in the amorphous phase can be hypothesized to readily attain a rather homogeneous equilibrium value while crystals are still free of the guest molecule. Subsequently, diffusion proceeds in the crystallites embedded in the amorphous matrix. Crystalline domains can be hence assumed to be initially exposed to the same uniform guest concentration, independently of their position inside the sample. The uniplanar oriented films are likely characterized by a lamellar (or, more in general, platelike) morphology for which the lamellae tend to be parallel to the film surface, with an area of the basal surfaces much larger than the area of the lateral surfaces. Lamellar morphologies have been in fact observed by several authors for solution crystallized clathrate samples.¹⁹ As a result of the lamellar structure of the crystallites, the one-dimensional diffusion process can be assumed to occur in the crystalline domains. On this basis, the observed differences of macroscopic transport kinetics of DCE guest molecules in films presenting different kinds of uniplanar orientation of the δ crystalline phase mirrors the different mass transport features of the crystalline domains and can be rationalized recalling previous results of molecular dynamics (MD) simulations for transport of small penetrants in the pure δ crystalline domains (He and CO_2).^{13a} In fact, the highest DCE diffusivity has been measured for the films

- (17) It is worth noting that because the $A_T/(A_T + A_G)$ ratio is significantly different for the different uniplanar orientations, a correct evaluation of the fraction of the trans conformer of DCE included as the guest in the host s-PS δ phase can be only obtained by the absorbances measured for unoriented s-PS/DCE clathrate films, like the one of Figure 3D ($x_T = 0.94$, by following the procedure described by eqs 1–5 in ref 5a,b). It is, however, worth noting this x_T value is not significantly different from the one previously evaluated on the basis of DCE sorption in films presenting the (010) uniplanar orientation.^{5a,b}
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with uniplanar orientation of the $\bar{2}10$ crystalline phase, whose normal forms an angle of only 17.5° with the a axis which, according to the MD calculations, would be the δ form crystalline axis of maximum diffusivity (see Table 1 of ref 13a, for $T = 25^\circ\text{C}$). On the other hand, the lowest diffusivity has been measured for the films with uniplanar orientation of the (010) crystalline planes, whose normal has been calculated as the crystallographic direction of minimum diffusivity ($\perp ac$ in Table 1 of ref 13a). It is worth noting that comparison with MD simulations is only possible in qualitative terms because no information is at the moment available on the thickness of the crystalline platelike domains.

The differences observed in sorption experiments among the samples with different orientations were also detected for desorption experiments, although the latter are significantly slower. The differences observed between sorption and desorption rates are consistent with a "Fickian" diffusivity (D) in the crystalline domain which is an increasing function of the concentration of guest molecules inside the crystal.^{20a} In fact, in analogy with diffusion of small molecular weight penetrants in microporous zeolites,^{20b} the "intracrystalline" Fickian mass flux (J) of guest molecules can be expressed as

$$J = -D \frac{dc}{dx}, \quad D = D_0 \frac{d \ln a}{d \ln c}$$

where c is the intracrystalline guest concentration, a is the activity of the guest in the phase in contact with the crystal, and $d \ln a / (d \ln c)$ represents the gradient of the equilibrium sorption isotherm of guest molecules in the pure crystalline phase, in logarithmic form. D is then given by the product of a mobility coefficient (D_0 , referred as "corrected diffusivity") and of a thermodynamic coefficient ($d \ln a / (d \ln c)$). In the case of the δ crystalline phase, where the adsorption of guest molecules occurs according to a Langmuir-type sorption isotherm,^{5e,18} the effect of the thermodynamic coefficient is expected to be the prevailing one and promotes a strong increase of D with DCE concentration.

Conclusions

The DCE sorption from dilute aqueous solutions (50 ppm) and its room-temperature desorption after equilibrium sorp-

tion uptake, for s-PS films presenting three different kinds of uniplanar orientation of the nanoporous δ phase (the crystallographic planes (010),⁹ ($\bar{2}10$),¹⁰ or (002)¹¹ preferentially parallel to the film surface), have been investigated, mainly by FTIR measurements.

The reported sorption and desorption data indicate that, at low guest activities, the sorption occurs nearly only by the anisotropic δ crystalline phase and the guest transport behavior is dependent on the kind of uniplanar orientation of the host crystalline phase.

In particular, the lowest diffusivity has been measured for films with uniplanar orientation of the (010) crystalline plane, whose normal was calculated as the crystallographic direction of minimum guest diffusivity^{13a} while the highest diffusivity has been measured for films with uniplanar orientation of the ($\bar{2}10$) crystalline plane, whose normal forms an angle of only 17.5° with the a axis, which was calculated as the δ form crystalline axis of maximum diffusivity.^{13a}

The possibility to change the guest diffusivity by controlling the crystalline phase orientation could be useful for several possible applications of δ form films. For instance, for application as sensing elements of molecular sensors,²¹ high diffusivity films presenting the ($\bar{2}10$) uniplanar orientation would be in principle most suitable, because they should maximize the sensor response rates. On the other hand, for applications requiring a long-term stability of the host-guest complexes, like for instance for films including active guests (e.g., fluorescent, photoreactive, etc.),²² low diffusivity films presenting the (010) uniplanar orientation should be most suitable.

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