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# Guest Conformation and Diffusion into Amorphous and Emptied Clathrate Phases of Syndiotactic Polystyrene

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ABSTRACT: The sorption kinetics of 1,2-dichloroethane (DCE) (pure or dissolved in water at different concentrations) in amorphous and semicrystalline syndiotactic polystyrene films are studied by Fourier transform infrared spectroscopy. Experiments at low DCE concentrations show that the DCE sorption in empty clathrate samples is much faster and leads to much higher sorption equilibrium values than that in the amorphous or other semicrystalline samples. The results of the sorption experiments into emptied clathrate polymer samples can be interpreted by assuming that DCE, for low concentrations in aqueous solutions, is mainly absorbed by the clathrate phase and that, as guest molecule in the polymeric clathrate, it is substantially only in the *trans* conformation. In the assumption that the guest DCE molecules in the clathrate are present only in the *trans* conformation, the kinetics of clathration in the emptied clathrate phase and of sorption in the amorphous phase are separated.

## Introduction

The synthesis of fully syndiotactic polystyrene (s-PS) has been reported only in the last decade.[1] Several structural studies, essentially by X-ray diffraction (XRD),[2] electron diffraction,[3] Fourier-transform infrared spectroscopy (FTIR),[4] and solid-state nuclear magnetic resonance,[5] have shown a very complex polymorphic behavior for this polymer. Using the nomenclature proposed in ref 2c, this can be described in terms of two crystalline forms, α and $\beta$, containing planar zig-zag chains and two forms, the $\gamma$ and $\delta$, containing s(2/1)2 helical chains. The maximum degree of crystallinity for all the crystalline forms is in the range 40−60% and is mainly dependent on the stereoregularity of the sample.

In particular, the term "$\delta$-form" has been used to indicate different clathrate structures, for which the intensities and the precise locations of the crystalline reflections in the XRD patterns change with the kind and amount of the included guest molecules.[6]

The clathrate $\delta$-form can be obtained by sorption of suitable compounds (e.g. methylene chloride, 1,2-dichloroethane, toluene, etc.) in amorphous s-PS samples as well as in semicrystalline s-PS samples being in the α- or $\gamma$-form.[6] The $\beta$-form, instead, is stable in the presence of these solvents, which can be absorbed only in the amorphous phase.[7]

By removal of the guest molecules from the $\delta$-form, by suitable solvent treatments,[8,9] an emptied clathrate form can be obtained, whose crystal structure has been recently described.[10] This emptied clathrate form of s-PS is able to absorb some organic substances also when present at very low activities.[8,11] Sorption studies from liquids and vapors into the empty clathrate form have suggested that this thermoplastic material is promising for applications in chemical separations as well as in water purification.[8,11]

The characterizations of polymeric clathrates are generally more complex than those of clathrates with low-molecular-mass hosts, since the polymeric samples will contain often (as occurs for s-PS) large fractions which are amorphous. Hence, in general, the guest molecules can be not only included in the clathrate phase but also absorbed in the amorphous phase.

In the sorption kinetic studies presented in the literature for s-PS,[7,11,12] the sorption from the amorphous phase and the clathration process generally have not been separated. The only attempt to separate the two contributions has involved comparative sorption and desorption (of methylene chloride) studies into semicrystalline s-PS samples being in the α- and in the $\beta$-form, presenting similar degrees of crystallinity. Since $\beta$-form samples absorb the solvent only in the amorphous phase, while the α crystalline phase is fully transformed into the clathrate phase, the difference between the solvent concentration in the two kinds of samples, after desiccation at different temperatures, has given some crude evaluations of the guest content in the clathrate phase (in the range 6−2 wt % as the desiccation temperature increases in the range 35−90 °C).[7b] This method, however, did not allow us to separate the two contributions in sorption kinetics studies. In fact, in the conditions suitable for the clathrate formation from the α- (or $\gamma$-) phase (e.g., immersion in pure guest liquid) the sorption is further complicated by the gel formation phenomenon.[4d,13]

In this paper the sorption kinetics of DCE (pure or dissolved in water at different concentrations) in amorphous and semicrystalline s-PS films are studied by Fourier transform infrared spectroscopy (FTIR). The analysis shows that these guest molecules are present in the clathrate prevailingly (perhaps only) in the *trans* conformation, while the *trans* and *gauche* conformations are nearly equally populated for the solvent molecules absorbed in the amorphous phase. This allows us to find particular conditions for which the sorption occurs only in the amorphous phase or prevailingly in the crystalline (empty clathrate) phase. Moreover, when

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sorption occurs in both phases, the kinetics of clathration in the emptied clathrate phase and of sorption in the amorphous phase can be separated, in the assumption that the guest molecules in the clathrate are present only in the *trans* conformation.

## Experimental Section

The s-PS was synthesized in our laboratories using a homogeneous catalyst consisting of $CpTiCl_3$ and methylalumoxane (MAO) in toluene, according to the method described in ref 1b. The polymer fraction insoluble in acetone was 92%. The intrinsic viscosity of the acetone-insoluble fraction, determined in tetrahydronaphthalene at 135 °C with an Ubbelhode viscosimeter, is 0.60 dL $g^{-1}$.

The powder and film samples in the emptied $\delta$-form were obtained by treatments with boiling acetone for 5 h (followed by desiccation at 60 °C for 2 h) on as-polymerized powder and on cast films (from 5% wt/wt solutions in chloroform at room temperature), respectively. The sample in the $\beta$-form was obtained by solution casting from a 5% wt/wt solution in *o*-dichlorobenzene and subsequent drying at 140 °C for 10 h. The amorphous s-PS was obtained by quenching in liquid nitrogen samples melted at 300 °C.

Wide-angle X-ray diffraction patterns were obtained on powder samples with nickel-filtered Cu K$\alpha$ radiation with an automatic Philips diffractometer.

The thermogravimetric analysis was carried out with a Mettler TG50 Thermobalance in a flowing nitrogen atmosphere at a heating rate of 10 K/min.

Infrared spectra were obtained at a resolution of 2.0 $cm^{-1}$ with a Perkin-Elmer System 2000 FTIR spectrometer equipped with a deuterated triglycine sulfate detector and a Ge/KBr beam splitter. The frequency scale was internally calibrated using a He–Ne laser, and 30–300 scans were signal-averaged to reduce the noise. The scanned wavenumber range was 4000–450 $cm^{-1}$. Film thickness was of nearly 30 $\mu$m, chosen so as to maintain the peaks of interest in the range of absorbance linearity (less than 1.2 absorbance units).

In this contribution the conformational equilibrium of the DCE molecule absorbed in the amorphous phase and in the clathrate $\delta$-form is quantitatively evaluated by FTIR spectroscopy. Because of the fast time scale of the FTIR experiment (i.e. picoseconds) separate peaks are observed for the molecules in the *trans* and in the *gauche* conformations. Thus it is possible to select a pair of these peaks belonging to the different conformations and to evaluate the relative population of the *trans* and of the *gauche* forms from their relative intensity. In fact, for the Beer–Lambert law,

$$A_g = \epsilon_g l C_g \tag{1}$$

$$A_t = \epsilon_t l C_t \tag{2}$$

where the symbols have the usual meaning and the subscripts *g* and *t* refer to the *gauche* and *trans* conformations respectively.

From eqs 1 and 2:

$$\frac{A_t}{A_g} = \frac{\epsilon_t}{\epsilon_g} \cdot \frac{N_t}{N_g} \tag{3}$$

and hence

$$\frac{N_g}{N_t} = \frac{\epsilon_t}{\epsilon_g} \cdot \frac{A_g}{A_t} \tag{4}$$

where *N* indicates the number of moles.

Finally the mole fraction in the *trans* form, $x_t$, is evaluated from the relationship

$$x_t = \frac{1}{N_g/N_t + 1} \tag{5}$$

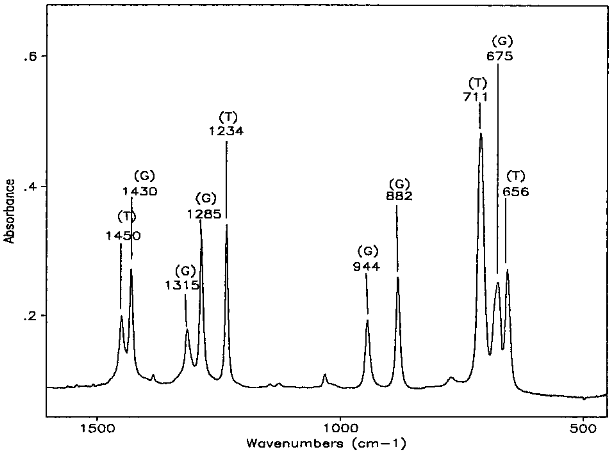

**Figure 1.** FTIR spectrum of liquid 1,2-dichloroethane in the frequency range 1500–500 $cm^{-1}$.

## Results and Discussion

**FTIR Spectra.** To study the diffusion processes in the emptied clathrate structure of s-PS, the DCE has been chosen for several reasons. First it has a simple conformational equilibrium with a *trans* and a *gauche* form and in the liquid phase the high-energy conformation is reasonably populated and readily detectable by spectroscopic means. Furthermore, the FTIR spectrum of the liquid DCE, reported in Figure 1 in the frequency range 1550–450 $cm^{-1}$, presents a number of well-resolved peaks. Due to the relative simplicity of the molecule, it was possible to perform a complete normal vibrational analysis and to assign the various absorptions to the normal modes of the *trans* and the *gauche* forms.[14] In Figure 1 the various absorptions are marked G or T depending on whether they originate from the *gauche* or the *trans* form, respectively. Among the various characteristic peaks, the one at 1285 $cm^{-1}$ ($CH_2$ wagging in the *gauche* form) and that at 1234 $cm^{-1}$ ($CH_2$ rocking in the *trans* form) were chosen for quantitative purposes. The choice was dictated by the fact that they are completely resolved and have a sufficiently high intensity and, more importantly, because the spectrum of the polymeric substrate is relatively free from interfering absorptions in the frequency range 1300–1225 $cm^{-1}$.

It is noted that, in order to characterize quantitatively the conformational equilibrium of DCE by using eqs 4 and 5, it is necessary to know the ratio $\epsilon_t/\epsilon_g$. This ratio has been evaluated from the value of $x_t$ in the liquid phase reported in the literature (0.35) and from the absorbance ratio of the two analytical peaks in the FTIR spectrum of liquid DCE. Its value was estimated to be 1.5, in close agreement with that evaluated on the basis of absolute intensity calculations performed by using the electro-optical parameters approach.[14]

**DCE Sorption Kinetics into s-PS Samples.** The sorption kinetics of DCE from a 0.5 wt % aqueous solution, into amorphous and semicrystalline (emptied clathrate form) s-PS films have been monitored. The measurements were performed by immersing the samples in the solutions at ambient temperature; the films were then periodically removed and blotted, and their FTIR spectrum was collected. The spectra reported in Figure 2A refer to the sorption kinetics in the amorphous sample. Both the DCE peaks are clearly detectable, which confirms the contemporary presence of the two conformers in the amorphous s-PS phase.

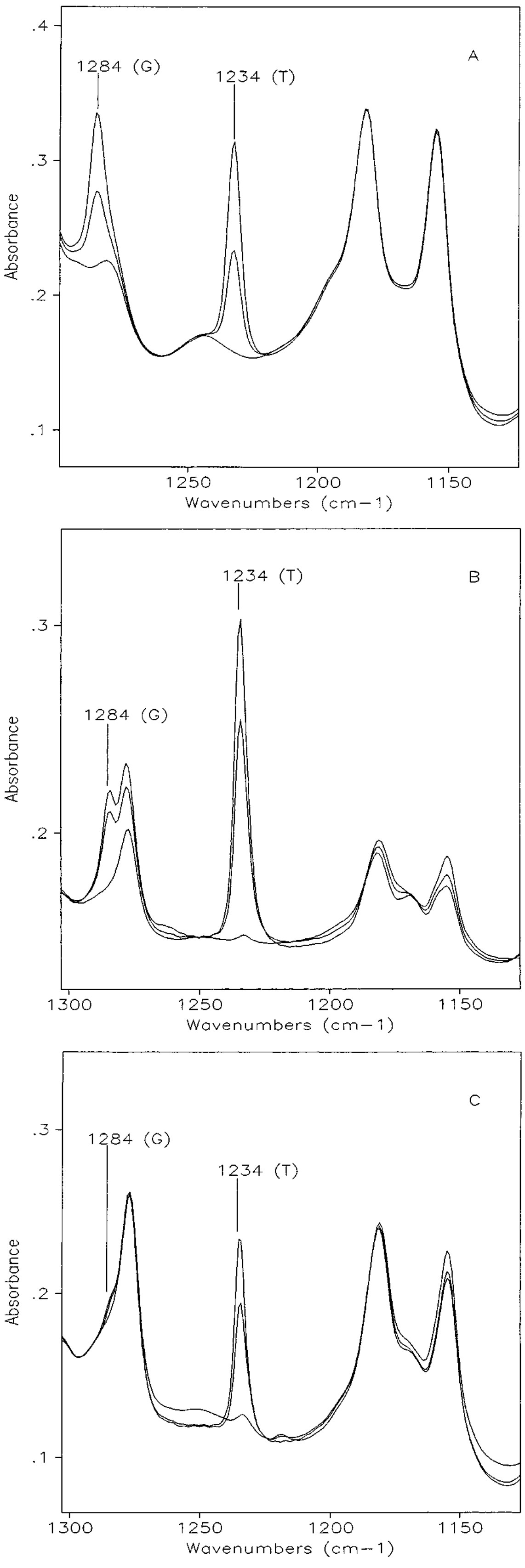

**Figure 2.** FTIR spectra in the 1350−1150 cm$^{-1}$ region, for s-PS samples: (A) amorphous, after DCE sorption from a 0.5 wt % aqueous solution; (B) emptied $\delta$-form, after DCE sorption from a 0.5 wt % aqueous solution; (C) emptied $\delta$-form, after DCE sorption from a 10 ppm solution. In all the figures the three lines refer to the initial spectrum, to a spectrum collected at an intermediate sorption time, and to the final spectrum.

Figure 2B displays spectra collected at various times for the sorption experiments performed on the emptied $\delta$-form. The 1234 cm$^{-1}$ peak relative to the *trans* conformer is largely predominant over the *gauche* peak at 1284 cm$^{-1}$.

Different sorption experiments were conducted by using a much more diluted DCE aqueous solution (10 ppm). Spectra collected at various times for these sorption experiments are reported in Figure 2C. It is apparent that the *gauche* absorption becomes barely detectable as a weak shoulder of an intense s-PS absorption, thus indicating that, when the sorption process is carried out in these conditions, the absorbed DCE is almost completely in the *trans* conformation. In the same conditions, the sorption of DCE into amorphous s-PS films is negligible, not allowing an evaluation of the relative populations of the *trans* and *gauche* conformers.

From the spectral data of Figure 2, it is possible to evaluate not only the total amount of DCE absorbed in the polymeric substrate as a function of time but also the concentration of the *trans* and of the *gauche* conformers.

In fact the Beer−Lambert law may be expressed as

$$\bar{A}_{1285} = \alpha C_g \qquad (6)$$

$$\bar{A}_{1234} = \beta C_t \qquad (7)$$

Here $\bar{A}$ represents the reduced absorbance obtained by the ratio between the absorbance of the peak of interest and that of an internal thickness band which, in the present case, is located at 1601 cm$^{-1}$. This is in order to eliminate the unknown sample thickness from eqs 6 and 7. Thus the constants $\alpha$ and $\beta$ represent the absorptivity ratios $\epsilon_{1285}/\epsilon_{1601}$ and $\epsilon_{1234}/\epsilon_{1601}$, respectively, and the ratio $\alpha/\beta$ is equal to $\epsilon_{1285}/\epsilon_{1234}$.

Rearranging eqs 6 and 7, we may write

$$\frac{\bar{A}_{1285}}{\alpha} + \frac{\bar{A}_{1234}}{\beta} = C_g + C_t = C_{\mathrm{tot}} \qquad (8)$$

and hence

$$\bar{A}_{1285} + \frac{\alpha}{\beta}\bar{A}_{1234} = \alpha C_{\mathrm{tot}} \qquad (9)$$

The value of $\alpha$ has been evaluated from eq 9 by determining, on a series of samples, $\bar{A}_{1285}$, $\bar{A}_{1234}$, and $C_{\mathrm{tot}}$. This latter value has been obtained by thermogravimetric analysis.

$C_g$, $C_t$, and $C_{\mathrm{tot}}$ values are hence obtained from the values of $\bar{A}_{1285}$ and $\bar{A}_{1234}$ by eqs 6, 7, and 9, respectively. A proper correction was introduced to express the concentrations as the percent weight gain with respect to the weight of the dry sample ($W_g$, $W_t$, and $W_{tot}$, respectively), as generally reported in sorption diagrams.

The sorption kinetics of DCE, from a 0.5 wt % aqueous solution, into amorphous and semicrystalline (emptied clathrate form) s-PS films are reported in parts A and B of Figure 3, respectively.

As happens for several organic compounds, the DCE sorption into the emptied clathrate sample is faster, and higher equilibrium contents are reached.[8,11]

The X-ray diffraction pattern of the sample in the emptied clathrate form (curve a in Figure 4) is modified upon DCE sorption from 0.5 wt % (curve b in Figure 4)

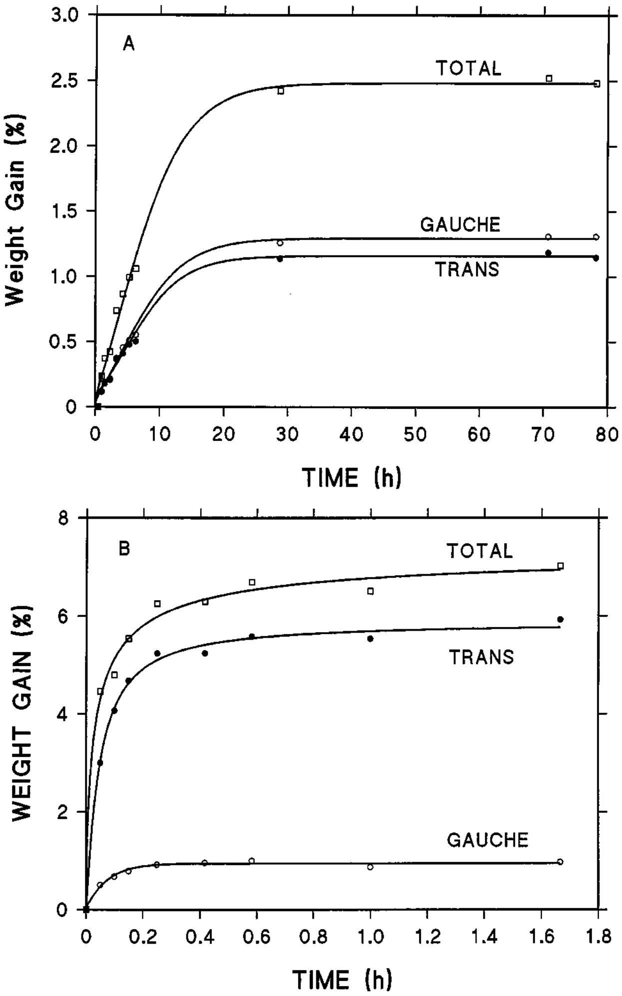

**Figure 3.** Weight gain as a function of the sorption time for s-PS samples immersed in a 0.5 wt % aqueous DCE solution: (A) amorphous; (B) emptied $\delta$-form; (□) total weight gain; (○) weight gain relative to the *gauche* form; (●) weight gain relative to the *trans* form.

aqueous solutions. In fact, the typical, gradual reduction of the intensity ratio of the two diffraction peaks at $2\theta \approx 8.4°$ and $10.5°$, related to the guest clathration,[8-10] is observed. On the contrary, the X-ray diffraction halos of the amorphous s-PS samples remain substantially unchanged, upon DCE sorption from aqueous solutions, and no crystalline diffraction peak appears.

This indicates that, in the considered conditions, the DCE sorption in the samples being in the emptied clathrate form produces DCE clathration, while DCE sorption in the amorphous samples does not induce crystallization (and clathration).

It is worth noting that pure DCE is, instead, rapidly absorbed in amorphous s-PS samples, inducing partial crystallization into the clathrate $\delta$-form, giving rise to X-ray diffraction patterns similar to pattern b of Figure 4.

**DCE Conformations in s-PS Samples.** The molar fractions of DCE being in the *trans* conformation ($x_t$), as evaluated for all the samples of Figure 3, are reported versus the sorption time in curves A and B of Figure 5. The $x_t$ values evaluated for the sorption experiments conducted on a 10 ppm DCE aqueous solution (Figure 2C) have also been reported in curve C of Figure 5. It is apparent that, for all the considered sorption studies, $x_t$ is constant with the sorption time.

The $x_t$ value (0.46), obtained for the case of sorption from a 0.5% solution into an amorphous sample (line A in Figure 5), as discussed before, can be considered typical of DCE in a pure amorphous phase. This is confirmed by the fact that nearly the same $x_t$ value (0.47) is obtained for the case of sorption of pure DCE into a semicrystalline sample in the $\beta$-form (the only crystalline form which cannot be transformed into clathrate by solvents[7]).

It is worth noting that, for DCE, the fraction of the *trans* conformer in the amorphous s-PS phase is intermediate between those observed for the pure liquid (0.35) and for the vapor (0.75).[14]

The $x_t$ values measured for DCE absorbed into the emptied clathrate form films, that is when the clathration occurs, are much higher than those for the DCE absorbed in the amorphous phase. Moreover, $x_t$ approaches unity for samples obtained by sorption from diluted DCE solutions (cf. curves B and C in Figure 5).

These data can be interpreted by assuming that DCE, for low concentrations in aqueous solutions, is mainly absorbed by the clathrate phase and that, as guest molecule in the polymeric clathrate, it is substantially only in the *trans* conformation.

The constancy of $x_t$ with the sorption time, for all the considered samples, suggests that also the relative populations of the two conformers in both phases, as well as the distribution of the guest molecules in the amorphous phase and in the clathrate phase, are independent of the sorption time.

**Evaluation of the Amounts of DCE Sorbed in the Amorphous Phase and the Crystalline Phase of s-PS.** In the previous section, it has been shown that a simple diffusion in an amorphous polymer sample occurs for the DCE sorption from a 0.5% aqueous solution into an amorphous s-PS sample (Figure 3A). On the contrary a diffusion process which involves mainly the crystalline (emptied clathrate) phase occurs for the DCE sorption from diluted aqueous solutions into an emptied clathrate s-PS sample (Figure 3B).

A separation between the amounts of DCE included in the amorphous phase and in the crystalline phase of s-PS is possible by making the assumptions that for this molecule the *trans* conformation is the only one present in the clathrate phase (as suggested by the data of Figure 5) and that in the amorphous phase the equilibrium between the DCE conformers is independent of the DCE concentration. In fact, in these assumptions the weight gain due to the *trans* DCE conformer in the amorphous phase $W_{t,\mathrm{am}}$ is equal to $(0.46/0.54)W_g$ and the DCE weight gains in the amorphous ($W_{\mathrm{am}}$) and crystalline ($W_{\mathrm{c}}$) phases are equal to $(W_g + W_{t,\mathrm{am}})$ and $(W_t - W_{t,\mathrm{am}})$, respectively.

The thus evaluated sorption kinetics relative to the amorphous and the emptied clathrate phases, corresponding to the experimental sorption kinetics of Figure 3B, are, for instance, reported in Figure 6.

It is worth noting that, in all the considered sorption kinetics and independently of the considered weight gains ($W_{\mathrm{tot}}$, $W_t$, $W_g$, $W_{\mathrm{am}}$, $W_{\mathrm{c}}$), the sorption behavior is not linear with time, while it is linear (for short times) with the square root of the time. This indicates that in our experimental conditions solvent diffusion in the amorphous phase and guest diffusion in the emptied clathrate phase both follow the Fickian behavior.

A Fickian behavior has been already observed by some of us[11] for the chloroform vapor sorption into

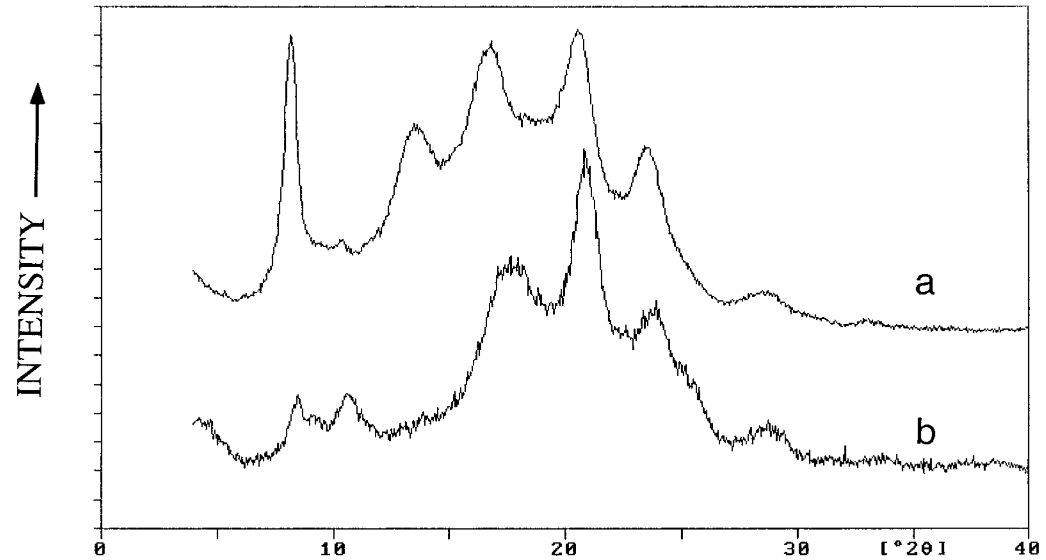

**Figure 4.** X-ray diffraction pattern of emptied clathrate s-PS samples: (a) untreated; (b) after equilibrium sorption from a 0.5 wt % aqueous solution of DCE.

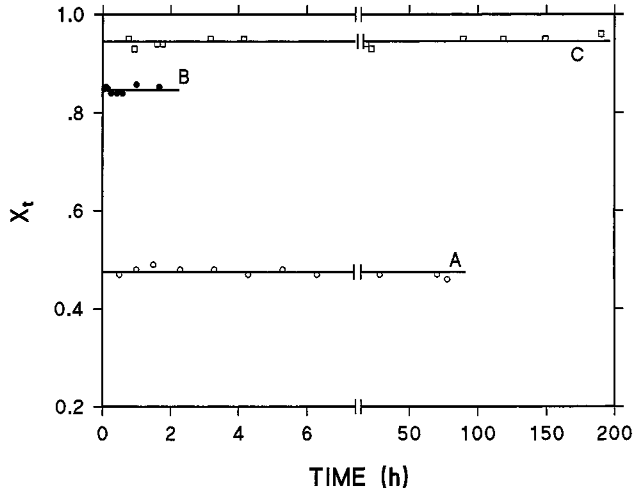

**Figure 5.** Molar fraction of the *trans* conformer, $x_t$, as a function of sorption time: (A) amorphous s-PS sample immersed in a 0.5 wt % aqueous solution of DCE; (B) emptied $\delta$-form immersed in a 0.5 wt % aqueous solution of DCE; (C) emptied $\delta$-form immersed in a 10 ppm aqueous solution of DCE.

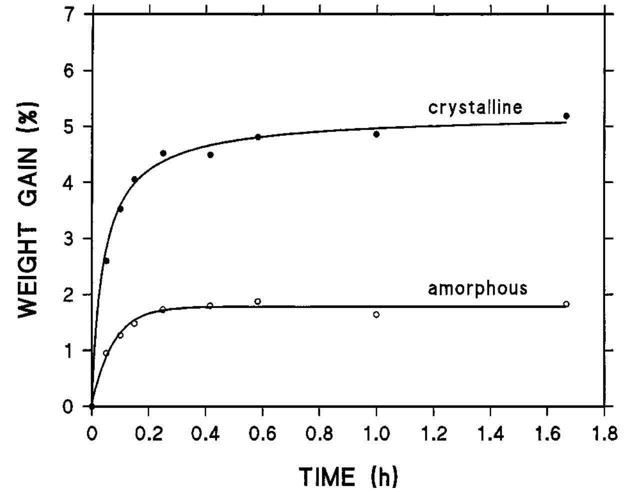

**Figure 6.** Weight gain relative to the amorphous and the crystalline phases as a function of the sorption time for the emptied $\delta$-form immersed in a 0.5 wt % aqueous solution of DCE.

emptied clathrate samples (involving both sorption in the amorphous phase and clathration in the crystalline phase).

## Conclusions

The Fourier transform infrared spectroscopy on 1,2-dichloroethane absorbed in amorphous and semicrystalline s-PS samples shows that the *trans* and *gauche* conformations are nearly equally populated ($x_t \approx 0.46$) for the solvent molecules absorbed in the amorphous phase. The fraction of the *trans* conformer in the amorphous s-PS phase is hence intermediate between those observed for the pure liquid (0.35) and for the vapor (0.75).

Experiments at low DCE concentrations show that the DCE sorption in empty clathrate samples is much faster and leads to much higher sorption equilibrium values than that in the amorphous or other semicrystalline samples. Moreover, for low DCE concentrations, the molecules absorbed in the emptied clathrate samples are prevailingly in the *trans* conformation ($x_t > 0.9$). These data can be interpreted by assuming that DCE for low concentrations is mainly absorbed by the clathrate phase and that, as a guest molecule in the polymeric clathrate, it is substantially only in the *trans* conformation.

In the assumption that the guest DCE molecules in the clathrate are present only in the *trans* conformation, the amounts of DCE included into each s-PS phase (amorphous and crystalline) can be evaluated. This can be helpful for accurate sorption, desorption, and structural characterizations of these materials, which are promising for molecular separations.

In particular, in the present paper, the kinetics of clathration in the emptied clathrate phase and of sorption in the amorphous phase have been separated, for the case of DCE sorption from diluted aqueous solutions. In all the considered sorption kinetics and independently of the considered weight gains ($W_{tot}$, $W_t$, $W_g$, $W_{am}$, $W_c$), the sorption behavior is not linear with time, while it is linear (for short times) with the square root of the time. This indicates that solvent diffusion in the amorphous phase and guest diffusion in the emptied clathrate phase both follow the Fickian behavior.

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