Isothermal Guest Desorption from Crystalline and Amorphous Phases of Syndiotactic Polystyrene

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ABSTRACT: Isothermal desorption kinetics at different temperatures of 1,2-dichloroethane (DCE) from syndiotactic polystyrene films have been studied by Fourier transform infrared spectroscopy. For β-form films, where DCE is present only into the amorphous phase, nearly equal populations of trans and gauche conformers, during the whole desorption processes, are observed. On the other hand, for clathrate films, where DCE is present in both amorphous and crystalline phases, its trans conformer becomes largely predominant, as the desorption processes proceed. In agreement with previous FTIR and X-ray diffraction studies, these results can be rationalized by assuming that essentially only the DCE trans conformer is present in the clathrate phase. In this assumption, experimental desorption kinetics from clathrate samples can be separated into faster processes from the amorphous phase and slower processes from the crystalline phase. The validity of this separation procedure is confirmed by the close similarity between the desorption kinetics observed for the amorphous phase of β-form films and calculated for the amorphous phase of clathrate films.

1. Introduction

Syndiotactic polystyrene (s-PS), whose synthesis has been reported about a decade ago,[1] is characterized by an elevated melting point (260 °C) and a high crystallization rate. Structural studies carried out by X-ray diffraction,[2] electron diffraction,[3] Fourier transform infrared spectroscopy (FTIR),[4] and solid-state NMR spectroscopy[5] have revealed a complex polymorphic behavior.

The different crystalline modifications differ with respect to the chain conformation as well as for the chain packing within the unit cell. Referring to the nomenclature proposed in the literature,[2c] four main crystalline forms may be distinguished, denoted α, β, γ, and δ. The first two, α and β, have the chains in the trans-planar, zigzag conformation (identity period 5.1 Å) while the γ and δ show a helical s(2/1)2 conformation of the chain with identity period of 7.7 Å.

Treatments by several volatile organic compounds (mainly halogenated or aromatic hydrocarbons) not only can induce crystallization of amorphous samples but also can transform α and γ crystalline forms into the clathrate δ form; only for the β form are these low molecular mass compounds selectively absorbed in the amorphous phase, while leaving the crystalline phase unaltered.[6] This is possibly related to the higher density of this crystalline form (1.078 g/cm^3) with respect to the others.

Recently it has been found that suitable extraction procedures[7] can remove the guest molecules from the clathrate δ forms, and an empty δ form has been obtained, whose crystalline structure has been recently described.[8]

This form has revealed the ability to rapidly absorb a considerable amount of guest molecules to yield the clathrate form, even from very diluted solutions,[7a,9,10] and it is potentially relevant for purification of water and air contaminated by volatile organic compounds as well as for chemical separations.[7a]

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 not only be included in the clathrate phase but also absorbed in the amorphous phase.

In a recent investigation[10] the sorption kinetics of 1,2-dichloroethane (DCE) in amorphous and semicrystalline syndiotactic polystyrene films have been studied by FTIR spectroscopy. Experiments at low DCE concentrations have shown 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 in the clathrate phase and, as guest molecule in the polymeric clathrate, is substantially only in the trans conformation. This hypothesis has been confirmed by an X-ray diffraction study relative to the s-PS clathrate form including DCE.[11] In the assumption that the guest DCE molecules in the clathrate are present only in the trans conformation, the amount of DCE included in each (amorphous and crystalline) phase of s-PS has been estimated, on the basis of conformer population evaluations combined with thermogravimetric analyses.[10]

In the present contribution, a detailed investigation by use of in situ FTIR spectroscopy of isothermal desorption kinetics of DCE from the amorphous phase of β-form films and from both phases of clathrate δ-form

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samples is reported. A precise knowledge of the phenomenon of guest desorption from both phases of these semicrystalline materials is of course relevant for possible control of their use in chemical separation processes as well as for their regeneration.

2. Experimental Section

2.1. Materials. sPS was synthesized in the laboratories of the Department of Chemistry of University of Salerno, using a homogeneous catalyst consisting of C_pTiCl_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 Ubbelhöde viscometer was 0.60 dL g^{-1}.

The film samples in the emptied δ form were obtained by treatment with boiling acetone (5 h) of s-PS films cast at room temperature from 5% w/w solutions in chloroform. The treatment with boiling acetone was followed by desiccation at 60 °C for 2 h.

The samples in the β form were prepared by solution casting from a 5% w/w solution in *o*-dichlorobenzene and subsequent drying at 140 °C for 10 h.

2.2. Techniques. FTIR transmission spectra were obtained at a resolution of 2 cm^{-1} with a Perkin-Elmer System 2000 spectrometer, equipped with a deuterated triglycine sulfate detector and a Ge/KBr beam splitter. The frequency scale was internally calibrated to an accuracy of better than 0.01 cm^{-1} by use of a He−Ne laser source. A total of 10−300 scans were signal averaged to improve the signal-to-noise ratio, which is generally better than 5000:1. The scanned wavenumber range was 4000−400 cm^{-1}. Film thickness was chosen so as to keep the peaks of interest in the range of absorbance linearity (less than 1.2 absorbance units), which corresponds to thickness comprised between 20 and 40 μm.

An accurate determination of the sample thickness, essential for a quantitative comparison of the transport properties among different samples, was achieved spectroscopically. To this end a calibration curve was constructed plotting the integrated absorbance of the conformationally insensitive s-PS peak at 1601 cm^{-1} as a function of the thickness for a series of PS standards of different taticity, having a carefully controlled and homogeneous thickness. All spectra are reported in absorbance units and have been normalized, when necessary, by use of the 1601 cm^{-1} peak as internal standard.

The desorption measurements were carried out in an environmental chamber (SPECAC Mod 20100) directly mounted in the spectrometer for the *real-time* monitoring of the process. The chamber allows careful control of the temperature, pressure, and atmosphere. The isothermal measurements were carried out at 40, 60, and 80 °C under a nitrogen atmosphere at a pressure of 760 mmHg. The sampling rate of the measurements was 2 spectra/min in the early stages of the desorption process and slower (1 spectrum every 10 min) at later stages and was fast enough to follow the desorption kinetics at all investigated temperatures.

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

Differential scanning calorimetry (DSC) thermograms were measured by a Mettler TA3000 instrument under nitrogen atmosphere and with a heating rate of 20 °C/min.

For the thermogravimetric analysis (TGA) a Mettler TG50 thermobalance was employed with the same measurement conditions as for the DSC.

2.3. Methods for the Analysis of the Spectroscopic Data. In the present contribution the total concentration of DCE into the clathrate structure and the concentration of the trans and gauche conformers of DCE are evaluated in situ by FTIR spectroscopy. Since the time scale of the FTIR experiment (of the order of 10^{-12}−10^{-14} s) is faster than the lifetime of the conformers, the peaks arising from the trans and gauche conformations can be separately observed. Thus, it is possible to identify a pair of these peaks and to evaluate the population of the relative conformers as follows:

From the Beer−Lambert relationship

$$\frac{A_t}{A_g} = \frac{\epsilon_t}{\epsilon_g}\frac{N_t}{N_g} \tag{1}$$

$$\frac{N_g}{N_t} = \frac{\epsilon_t}{\epsilon_g}\frac{A_g}{A_t} \tag{2}$$

where A is the absorbance area, ϵ is the molar absorptivity, N represents the number of moles, and the subscripts g and t refer to the gauche and trans conformers, respectively.

Finally, the molar fraction of the trans form, $X_t = N_t/(N_g + N_t)$, is obtained from eq 2 recalling that

$$X_t = \frac{1}{N_g/N_t + 1} \tag{3}$$

It is worth noting that, to employ eq 2, it is necessary to known the value of ϵ_t/ϵ_g. The DCE peaks employed in the present contribution are located at 1285 and 1234 cm^{-1} and correspond respectively to the CH_2 *wagging* vibration in the cis conformer and to the same vibrational mode in the trans conformer. The molar absorptivity ratio of this pair of peaks has been evaluated from the X_t value in the liquid phase reported in the literature[12] (0.35) and from the absorbance ratio of the two analytical peaks in the spectrum of liquid DCE. The $\epsilon_{1234}/\epsilon_{1285}$ ratio was estimated to be 1.5, in close agreement with the value obtained from absolute intensity calculations performed by using the electrooptical parameters approach.[12]

From the spectroscopic data it is possible to evaluate not only the ratio between the conformers' population (N_t/N_g or X_t) but also the absolute concentration of each conformer as well as the total concentration of DCE in the system.

In fact, in terms of reduced absorbance, the Beer−Lambert law may be expressed as

$$\bar{A}_{1285} = \alpha C_g \tag{4}$$

$$\bar{A}_{1234} = \beta C_t \tag{5}$$

Here $\bar{A}$ (reduced or normalized absorbance) is the ratio between the absorbance of the analytical peak and that of the internal standard peak at 1601 cm^{-1}. Thus, the constants α and β represent respectively $\epsilon_{1285}/\epsilon_{1601}$ and $\epsilon_{1234}/\epsilon_{1601}$, and the ratio α/β is equal to $\epsilon_{1285}/\epsilon_{1234} = 1.5$.

Rearranging eq 4 and 5, we may write

$$\frac{\bar{A}_{1285}}{\alpha} + \frac{\bar{A}_{1234}}{\beta} = C_g + C_t = C_{tot} \tag{6}$$

from which

$$\bar{A}_{1285} + \frac{\alpha}{\beta}\bar{A}_{1234} = \alpha C_{tot} \tag{7}$$

The value of α has been determined from eq 7, by evaluating, for a series of samples, $\bar{A}_{1285}$, $\bar{A}_{1234}$, and C_{tot}. In turn, C_{tot} has been obtained by TGA measurements. The mean values of α and β are 0.069 and 0.104, respectively; these allow to obtain C_g, C_t, and C_{tot} from the values of $\bar{A}_{1285}$ and $\bar{A}_{1234}$ by use of eqs 4, 5, and 7, respectively.

For a quantitative evaluation of the intensities of the peaks at 1285 cm^{-1} (gauche form) and at 1234 cm^{-1} (trans form), the interference of the s-PS peaks at 1278 and at 1225 cm^{-1} needs to be eliminated. This is accomplished by use of subtraction spectroscopy, whereby the spectrum of the β form (the reference) is subtracted from that of the sample according to

$$A_d = A_s - KA_r \tag{8}$$

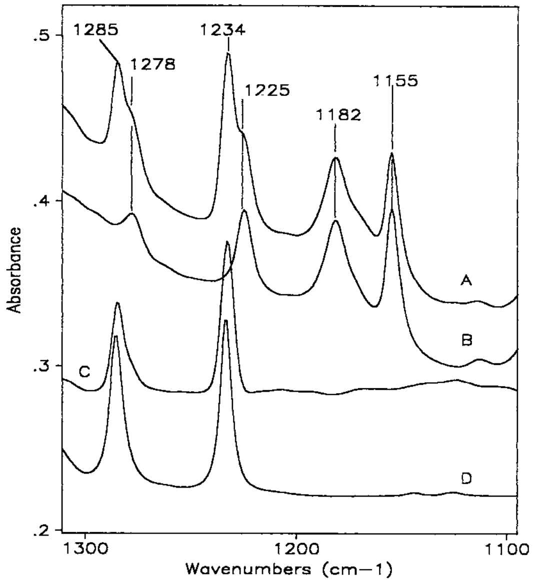

Figure 1. FTIR transmission spectra in the 1300−1100 cm^{-1} wavenumber range of (A) β form after absorption of DCE, (B) as-prepared β form, (C) subtraction spectrum A − B, and (D) pure DCE (liquid).

where the subscripts d, s, and r denote respectively the difference, the sample, and the reference spectra.

The adjustable parameter K is used to compensate for thickness differences between the sample and the reference spectra and is chosen so as to reduce to the baseline the internal standard peak at 1601 cm^{-1}. All the above calculations have been performed using absorbance areas.

3. Results and Discussion

3.1. Isothermal Desorption from β-Form Films.

As a first step toward the characterization of the transport processes of DCE in s-PS, we have investigated film samples in the β form, whose crystalline phase is unaffected by sorption phenomena.[6] This crystalline modification behaves as most polymeric materials in that it absorbs the solvent only into the amorphous phase, while the crystalline structure remains unaffected.

A s-PS film in the β form having thickness between 20 and 40 μm, when immersed in DCE at room temperature, absorbs after 10 h between 4.5 and 5.0 wt % of DCE.

The spectrum of such a sample is reported in Figure 1, trace A, in the frequency range 1300−1100 cm^{-1}. In the same figure, the spectrum of the same sample before the DCE absorption is reported for comparison (trace B). In the 1300−1100 cm^{-1} region as well as in the whole frequency range, the spectrum of the polymeric substrate remains unaltered after DCE absorption, thus confirming that the guest molecules diffuse selectively into the amorphous phase and do not induce any structural modification into the crystalline phase. It is worth noting that such a behavior is peculiar of the β form, while all the other crystalline modifications of s-PS are strongly affected by the presence of pure chlorinated solvents.

In Figure 1A the peaks characteristic of the two DCE conformers are clearly identified at 1285 cm^{-1} (gauche form) and at 1234 cm^{-1} (trans form), thus confirming the presence of both conformers in the amorphous phase of s-PS. For a quantitative evaluation of their concentration, the spectral subtraction procedure described in the Experimental Section is used.

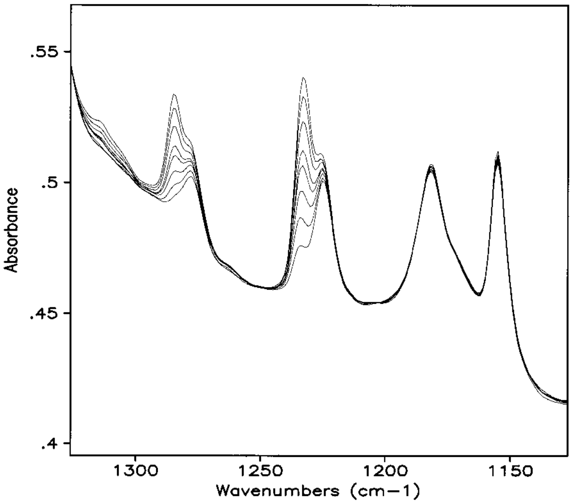

Figure 2. FTIR transmission spectra in the wavenumber range 1350−1100 cm^{-1} collected at various times between 0 and 25 h during the desorption measurement carried out on the β form at 40 °C.

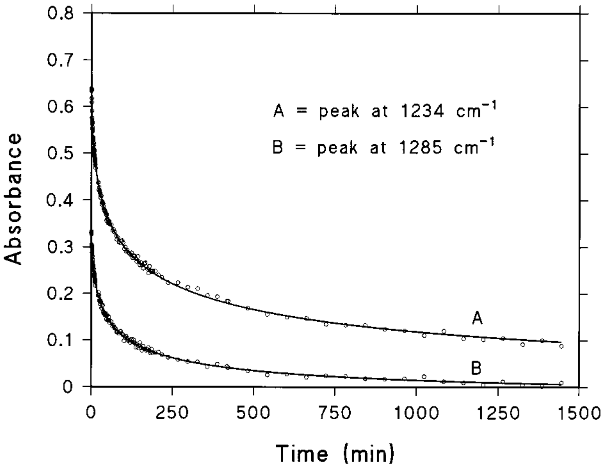

Figure 3. Absolute absorbance area of the 1234 cm^{-1} peak (curve A) and of the 1285 cm^{-1} peak (curve B) as a function of time for the desorption measurement carried out on the β form at 40 °C.

The difference spectrum is reported in Figure 1, trace C, while trace D of the same figure represents the spectrum of liquid DCE.

A comparison between traces C and D of Figure 1 clearly indicates that, in the amorphous phase of s-PS, the relative amount of gauche conformer decreases with respect to the pure liquid phase. By applying the method described in the Experimental Section, the molar fraction of the trans conformer, X_t, in the β form is evaluated as 0.51, in good agreement with recently published results[10] for amorphous s-PS samples absorbing DCE from diluted aqueous solutions. In the pure liquid phase, instead, X_t is equal to 0.35.[12]

The above sample has been subjected to isothermal desorption using the apparatus described in the Experimental Section. In Figure 2 are reported the spectra in the 1350−1100 cm^{-1} range collected at various times between 0 and 25 h, for the measurement carried out at 40 °C.

The absorbance of the two DCE peaks is reported, as a function of time, in Figure 3, while in Figure 4 are

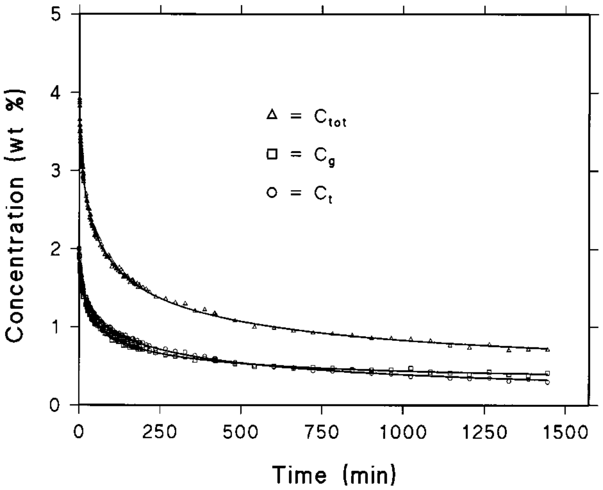

Figure 4. Total concentration of DCE (△), concentration of the trans conformer (□), and concentration of the gauche conformer (○) as a function of time for the isothermal desorption test carried out on the *β* form at 40 °C.

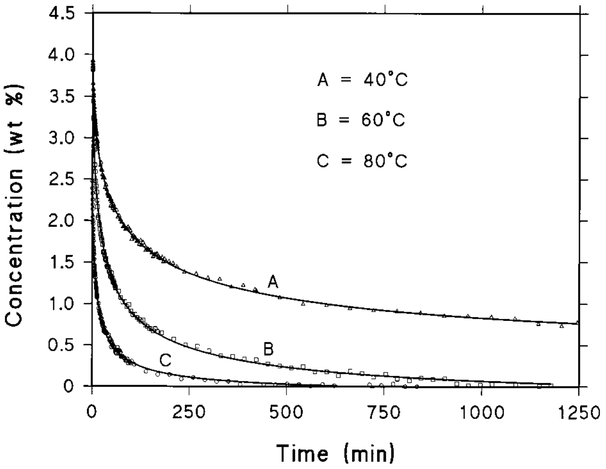

Figure 5. Total concentration of DCE as a function of desorption time for the three investigated temperatures.

shown the total concentration of DCE and the concentrations of the two conformers as a function of time.

The desorption proceeds at a considerable rate in the early stages of the process, approaching a plateau value after about 250 min. After 24 h, the DCE content remains substantially constant (0.7 wt %). Over the whole time range examined, the populations of trans and gauche conformers are very close to each other.

The curves of the total DCE concentration as a function of time relative to the desorption measurements carried out at 40, 60, and 80 °C are reported in Figure 5.

The concentration versus time data at all temperatures show a Fickian-like behavior, that is, when plotted as M_t/M_∞ versus $t^{1/2}/L$ show a linear behavior in the early stages of the process, afterward approaching a plateau with a downward concavity. As usual, M_t and M_∞ represent the mass of DCE desorbed at time t and at equilibrium, respectively, and L is the sample thickness.

The Fick plot for the desorption measurement carried out at 60 °C is reported, as an example, in Figure 6.

Finally, in Figure 7 are reported the X_t values as a function of time relative to the three investigated desorption kinetics.

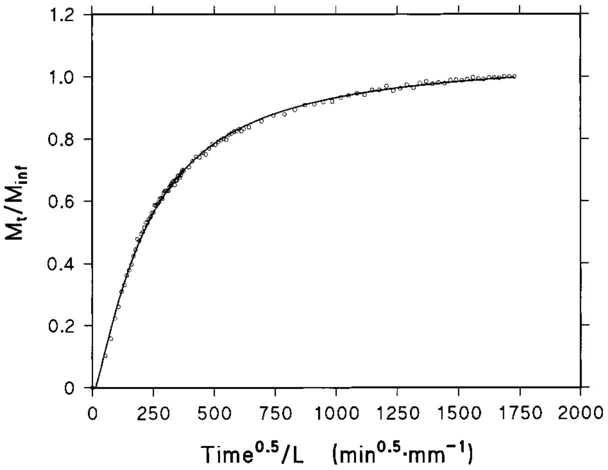

Figure 6. Fick's diagram of the isothermal desorption measurement on the *β* form at 60 °C.

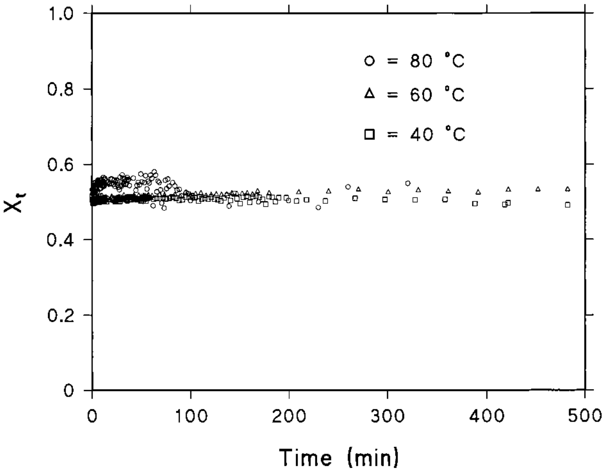

Figure 7. Molar fraction of the trans conformer, X_t, as a function of time for the desorption tests on the *β* form at the various investigated temperatures.

In all cases X_t appears to be constant with time, indicating that DCE reaches a conformational equilibrium in the amorphous phase of s-PS, irrespective of its concentration.

The mean value of X_t are 0.54 ± 0.02 at 80 °C, 0.52 ± 0.01 at 60 °C, and 0.51 ± 0.02 at 40 °C. Thus, the variation of X_t in the considered temperature range is very limited and is of the some order of magnitude as the experimental error.

3.2. Isothermal Desorption from Clathrate *δ*-Form Films. Isothermal desorption measurements in the temperature range 40−80 °C have been carried out also on clathrate *δ*-form samples. The reported results refer to samples prepared by immersing a emptied *δ* film into a 0.5 wt % aqueous solution of DCE. This procedure for the preparation of the clathrate has been preferred over the absorption from pure DCE (for which the equilibrium absorption is higher than 30 wt %) since it allows to reach DCE sorption comparable with that of the *β*-form film from pure DCE. In fact, the sample was found to absorb at equilibrium (after 12 h), from the considered aqueous solution, about 8.0 wt % of DCE.

The spectrum of the clathrate form in the frequency range 1300−1100 cm^{-1} is reported in Figure 8 (trace A). In the same figure, trace B refers to the spectrum of the empty *δ* form prior to DCE absorption, while trace C is the subtraction spectrum of DCE absorbed in the

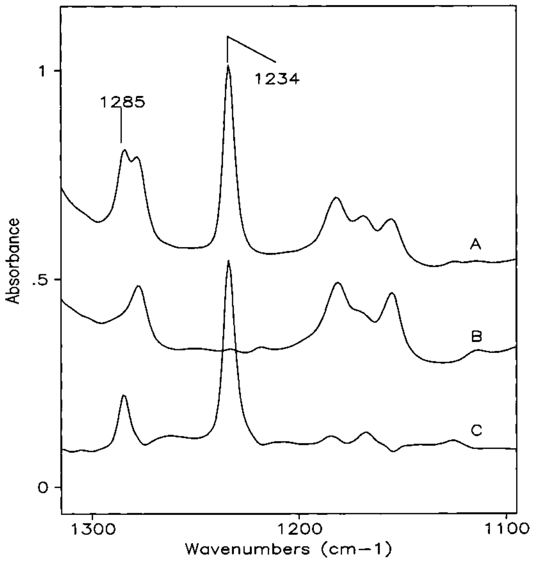

Figure 8. FTIR transmission spectra in the 1300−1100 cm^{-1} wavenumber range of (A) the δ form after absorption of DCE, (B) the δ_e form, and (C) subtraction spectrum A − B.

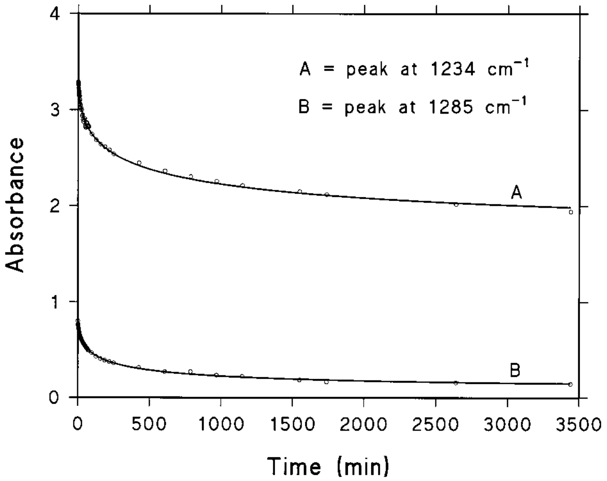

Figure 9. Absolute absorbance area of the 1234 cm^{-1} peak (curve A) and of the 1285 cm^{-1} peak (curve B) as a function of time for the desorption measurement carried out on the δ form at 40 °C.

polymer film. By comparing the DCE spectrum in the β form (Figure 1C) with that in the δ form (Figure 8C), it is immediately apparent that in the latter case the population of the trans conformer becomes predominant ($X_t \approx 0.74$). This finding is in agreement with recent reported results[10] which were interpreted assuming that, while in the amorphous phase of s-PS the conformational equilibrium of DCE is such that the concentration of the two conformers is nearly the same, in the cavities of the crystalline δ form the DCE assumes prevailingly the trans conformation.

The absorbance values of the peaks at 1285 and 1235 cm^{-1} are reported as a function of desorption time, for the experiment carried out at 40 °C, in Figure 9. Again, by applying eqs 4, 5, and 7, it has been possible to evaluate the total and the conformers' concentrations, which are reported, as a function of time, in Figure 10.

It is apparent that the overall desorption is strongly reduced with respect to that occurring in the β form. In fact, at equilibrium (after 60 h) 4.0% of DCE is still present in the sample while the residual DCE content in the β form was 0.7 wt %. Moreover, in the clathrate structure, most of the residual DCE is present in the trans conformation. In Figure 11, curve A, are reported the X_t values as a function of time: also in this case the behavior markedly differs from that of the desorption experiment on the β form (cf. Figure 7, curve A). For the δ form, in fact, X_t is not constant with time but increases rapidly in the early stages of the process, and more gradually at a longer times, approaching a plateau value close to 0.9.

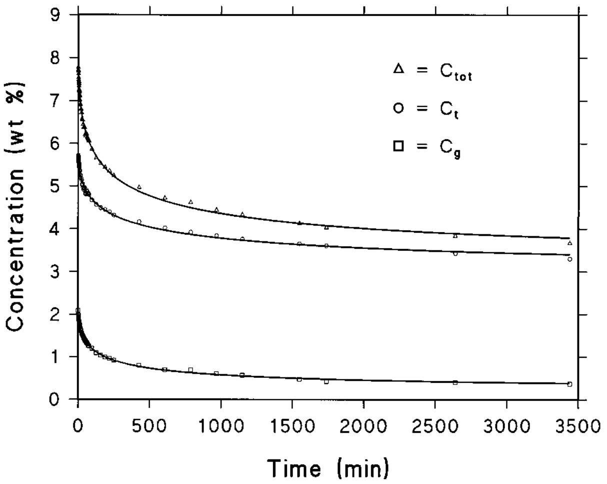

Figure 10. Total concentration of DCE (△), concentration of the trans conformer (○), and concentration of the gauche conformer (□) as a function of time for the desorption measurement carried out on the δ form at 40 °C.

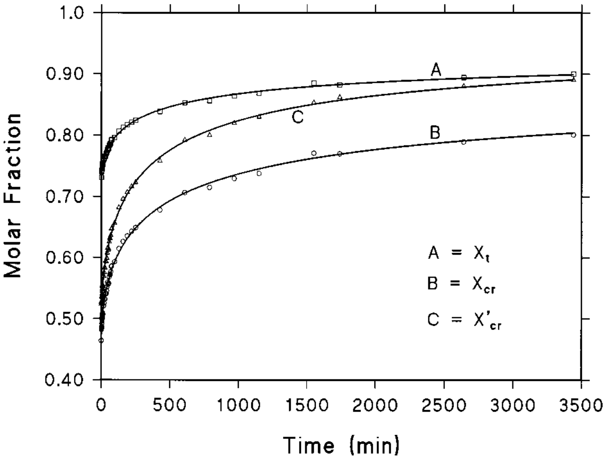

Figure 11. Curve A: molar fraction of the trans conformer, X_t, as a function of time. Curve B: molar fraction of DCE in the crystalline phase, X_{cr}, evaluated by assuming $X_{t,cr} = 1$, as a function of time. Curve C: molar fraction of DCE in the crystalline phase, X'_{cr}, evaluated by assuming $X_{t,cr} = 0.94$, as a function of time. The data refer to the desorption test carried out at 40 °C on the δ form.

This behavior of X_t may be interpreted by assuming that DCE is desorbed much faster from the amorphous phase than from the crystalline phase.

In fact, if the gauche conformer is present essentially in the amorphous regions, the rapid emptying of this phase would determine an increase of the trans conformers with respect to the total DCE population, that is, an increase of X_t.

From the spectral data, the amount of DCE present in the clathrate and in the amorphous phases can be evaluated, by assuming X_t values for the two phases. For the amorphous phase X_t can be reasonably assumed to be equal to 0.51 (the value obtained for the β form as well as for amorphous s-PS samples) while, for the clathrate phase, X_t is expected to be comprised between 0.94 and 1, i.e., larger than the highest value experimentally observed for DCE molecules absorbed in s-PS samples[10] in the δ form.

For $X_t = 1$ in the crystalline phase and $X_t = 0.51$ in the amorphous phase, the amount of DCE in the two phases is evaluated as follows:

$$X_{am} = \frac{N_g + N_{t,am}}{N_{tot}} \tag{9}$$

$$X_{cr} = \frac{N_{t,cr}}{N_{tot}} \tag{10}$$

where $N_{t,am}$ and $N_{t,cr}$ represent the number of moles of trans conformer present in the amorphous and in the crystalline phases, respectively. Furthermore, $N_{tot} = N_g + N_{t,am} + N_{t,cr}$.

From the data obtained on the β form at 40 °C it was found that

$$\frac{N_g}{N_{t,am}} = 0.92 \tag{11}$$

from which

$$X_{am} = \frac{N_g + N_g/0.92}{N_{tot}} = \frac{N_g}{N_{tot}}\left(1 + \frac{1}{0.92}\right) \tag{12}$$

or

$$X_{am} = 2.08X_g \tag{13}$$

In the same way it is possible to evaluate X_{cr} and X_{am} when we assume that $X_t = 0.94$ in the crystalline phase and 0.51 in the amorphous phase. In this case a further equation is needed, which is the mass balance ($X_t + X_g = 1$).

The behavior of X_{cr} as a function of time is reported in Figure 11, where curve B is evaluated assuming $X_{t,cr} = 1$ and curve C with $X_{t,cr} = 0.94$. Initially X_{cr} lies between 0.46 and 0.50; i.e., the DCE is partitioned almost evenly in the amorphous and the crystalline phases. It increases very rapidly at the beginning of the process and reaches a value between 0.80 and 0.90 by the end of the time interval investigated.

Finally, the calculated X_{cr} values allow to obtain the DCE concentration in the amorphous and crystalline phases of the δ form, which are plotted in Figure 12 as a function of time. Again, the open symbols refer to the concentrations evaluated assuming $X_{t,cr} = 1$, while the solid symbols are relative to the values obtained with $X_{t,cr} = 0.94$. The two curves are to be considered as the limiting boundaries within which the true concentration curve is located. It is found that the difference in the desorption rate between the two phases is dramatic. After about 60 h the DCE content in the amorphous phase has decreased by about 85% of its initial value, while in the crystalline phase, the reduction is lower than 10%. The data of Figure 12 indicate that, although a large fraction of the sorbed molecules is lost at 40 °C, the clathrate δ form remains substantially unaltered. This is confirmed by X-ray diffraction patterns of unannealed and annealed samples, indicating substantially unaltered intensities of the diffraction peaks which depend on the degree of occupancy of the cavities.[7,8]

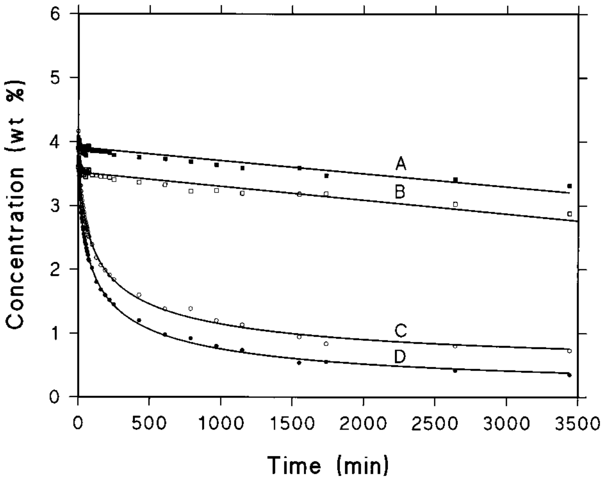

Figure 12. Concentration of DCE in the amorphous phase and in the crystalline phase as a function of time for the desorption test carried out at 40 °C on the δ form. The open symbols (curves B and C) refer to concentrations evaluated assuming $X_{t,cr} = 1$; the solid symbols (curves A and D) are relative to the concentrations calculated assuming $X_{t,cr} = 0.94$.

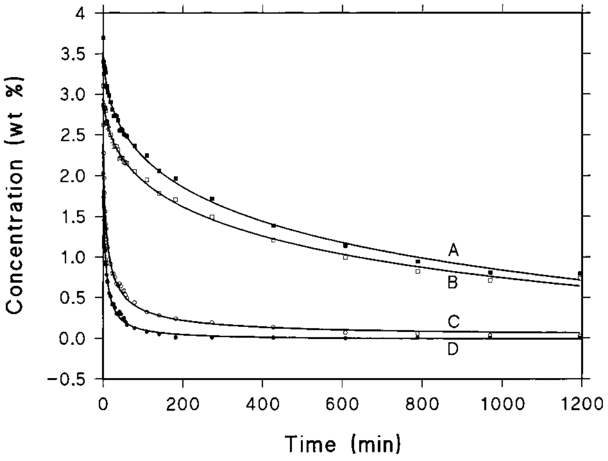

Figure 13. Concentration of DCE in the amorphous phase and in the crystalline phase as a function of time for the desorption test carried out at 60 °C on the δ form. The open symbols (curves B and C) refer to concentrations evaluated assuming $X_{t,cr} = 1$; the solid symbols (curves A and D) are relative to the concentrations calculated assuming $X_{t,cr} = 0.94$.

A further relevant observation is that the desorption curve relative to the amorphous phase closely resembles that of the β form, both with respect to the overall shape and for the initial and final DCE concentration (compare Figure 4 with Figure 12C,D). Also in this case a Fickian-like behavior is found. This result indicates that the transport behavior of the amorphous phase of sPS is scarcely influenced by the crystalline modification present in the sample.

The desorption kinetics of the δ form have been investigated also at 60 and 80 °C. The relative concentration curves are reported in Figures 13 and 14, respectively. The overall behavior is similar to that observed at 40 °C, with the amorphous phase losing DCE at a much faster rate than the crystalline phase. In particular, the DCE content in the amorphous phase becomes negligible after 100−200 min of desorption while the guest concentration in the clathrate phase

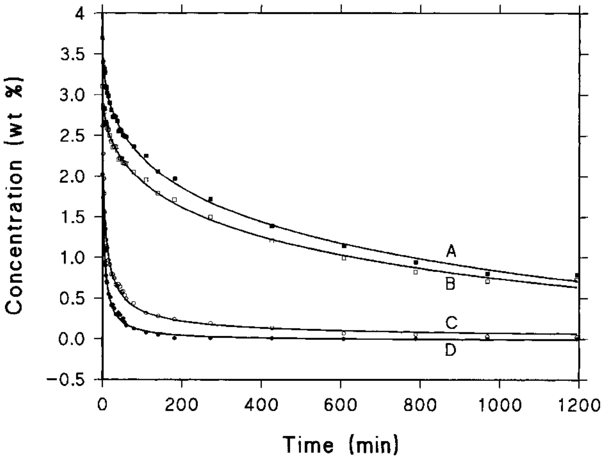

Figure 14. Concentration of DCE in the amorphous phase and in the crystalline phase as a function of time for the desorption test carried out at 80 °C on the δ form. The open symbols (curves B and C) refer to concentrations evaluated assuming $X_{t,cr} = 1$; the solid symbols (curves A and D) are relative to the concentrations calculated assuming $X_{t,cr} = 0.94$.

remains close to 1 wt % also after months of desorption at these temperatures.

4. Conclusions

In the present contribution the transport properties and, in particular, the isothermal desorption of DCE from syndiotactic polystyrene films, being in β and δ crystalline forms, have been investigated in detail by means of FTIR spectroscopy. This approach allows not only to determine in situ the concentration of DCE into the polymeric substrate but also to investigate the conformational equilibrium of the guest molecule.

It has been confirmed that, while in the β form, i.e., in the amorphous phase of s-PS, the trans and gauche conformers of DCE are nearly equally populated ($X_{t,am} = 0.51$), in the clathrate δ form DCE assumes essentially the trans conformation ($0.94 \leq X_{t,cr}$). This experimental observation has allowed to separate out the DCE desorption kinetics from amorphous and crystalline clathrate phases of s-PS films, at different temperatures.

It has been found that, although initially in clathrate samples guest molecules can be partitioned almost evenly in amorphous and clathrate phases, the amorphous phase loses DCE at a much faster rate than does the clathrate one. At the end of desorption processes in the temperature range 40−80 °C, most of the residual DCE is located in the crystalline phase.

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