Spectroscopic Investigation of Host−Guest Interactions into Clathrate Phases of Syndiotactic Polystyrene Containing Chlorinated Compounds

Pellegrino Musto* and Mariagrazia Manzari

Institute of Research and Technology of Plastic Materials, National Research Council of Italy, via Toiano 6, 80072 Arco Felice (NA), Italy

Gaetano Guerra

Dipartimento di Chimica, Università di Salerno, 84081 Baronissi (SA), Italy

Received March 30, 1999

ABSTRACT: A Fourier transform infrared spectroscopy investigation relative to clathrate forms of syndiotactic polystyrene (s-PS) with chlorinated organic compounds is presented. In particular, for 1,2-dichloroethane (DCE), 1,2-dichloropropane (DCP), and 1-chloropropane (CP), the absorption peaks which are modified as a result of clathrate formation have been identified and analyzed. The study has shown that in the polymeric clathrate phase, a nearly complete conformational selectivity occurs for DCE and DCP, while the conformational equilibrium of CP remains substantially unaltered. Both for DCE and DCP, the conformational selectivity is in favor of conformations leading to trans chlorine atoms and is associated with specific attractive interactions involving the chlorine atoms. The observation of shifts of C−Cl stretching bands indicates that attractive interactions are possibly established between chlorine atoms and aromatic rings, both in amorphous and in clathrate phase of s-PS.

Introduction

Syndiotactic polystyrene (s-PS) presents a very complex polymorphic behavior, which, making some simplification, can be described in terms of two crystalline forms, α and β, containing planar zigzag chains and two forms, the γ and δ, containing s(2/1)2 helical chains.[1]

In particular, the term "δ-form" has been used to indicate different clathrate structures, for which the intensities and the precise locations of the crystalline reflections in the X-ray diffraction patterns change with the kind and amount of the included guest molecules.[2]

The clathrate δ-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 γ-form.[2] The β-form, instead, is stable in the presence of these solvents, which can be absorbed only in the amorphous phase.[3]

By removal of the guest molecules from the δ-form, by suitable solvent treatments,[4] an empty clathrate form can be obtained, whose crystal structure has been recently described.[5] This empty clathrate form of s-PS is able to absorb some organic substances also when present at very low activities.[4,6] 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.[4,6]

Several studies have been published relative to Fourier transform infrared (FTIR) spectroscopy of the different polymorphic forms of s-PS,[7] and some of them have been devoted to the clathrate δ-forms[7d−f,l] and to the empty δ-form.[4b]

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 paper, the sorption kinetics of 1,2-dichloroethane (DCE) (pure or dissolved in water at different concentrations) in amorphous and semicrystalline s-PS samples has been studied mainly by FTIR, by some of us.[8] The analysis has shown that for these guest molecules in the clathrate phase the trans conformation is largely prevailing, while the trans and gauche conformations are nearly equally populated for the solvent molecules absorbed in the amorphous phase. Moreover, a crystal structure study of the clathrate form including DCE has confirmed this result and has shown that the positioning of the trans conformer in the cavities is such that both chlorine atoms establish a large number of nonbonded attractive interactions.[9]

In the present paper, a FTIR investigation relative to clathrate forms with chlorinated organic compounds presenting analogous conformational equilibria are presented. The aim is to establish the origin of the selectivity in favor of the trans conformation, which has been observed for DCE in the s-PS clathrate.
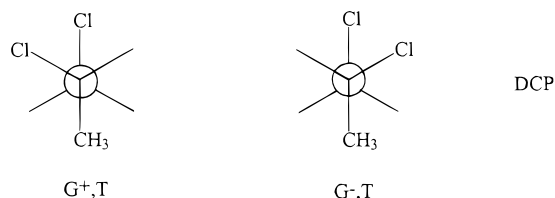
In the hypothesis that the conformational selectivity observed for DCE would be due to nonbonded repulsive interactions, since the chlorine atom and the methyl group present similar van der Waals radii (close to 1.8 Å), 1,2-dichloropropane (DCP) would be expected to assume in the clathrate phase, not only the conformation which is trans (T) relative to the two chlorine atoms and gauche (G+ or G−, depending on the chirality of the C atom in position 2) relative to the terminal chlorine and methyl groups ($P_{Cl}S_{ClH}$ according to the

* Corresponding author. e-mail: musto@mail.irtemp.na.cnr.it.

nomenclature of Mizushima et al.[11]):

Cl
CH₃ | Cl
|CH₃

T,G⁺ | T,G⁻ | DCP
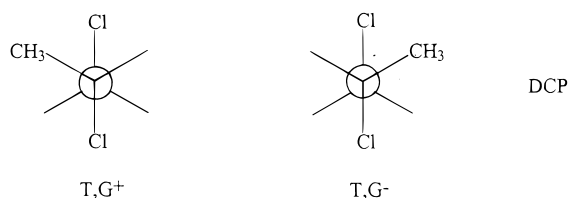
but also the nearly isosteric conformation which is gauche (G⁺ or G⁻, depending on the chirality of the C atom in position 2) relative to the two chlorine atoms and trans relative to the terminal chlorine and methyl groups (P_CS_{HH} conformation[11]):

G⁺,T | G⁻,T | DCP

In the same hypothesis, 1-chloropropane (CP) should assume only the trans conformation:

CP

T
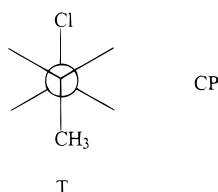
On the other hand, in the hypothesis that the conformational selectivity observed for DCE would be due to the specific attractive interactions involving the chlorine atoms, DCP would be expected to assume in the clathrate phase, only TG⁺ or TG⁻ conformations, while CP could assume, besides the trans conformation, also the gauche (G+ and G⁻) conformations:

G⁺ | G⁻ | CP
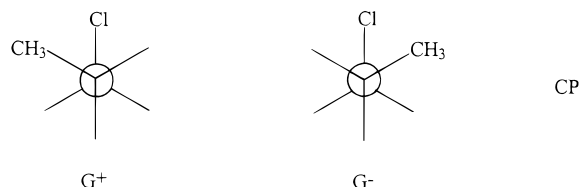
As often occurs for clathrate structures,[12] further information is gained by identification and analysis of those absorption bands of the guest molecules that are shifted along the frequency axis as a result of clathrate formation.

2. Experimental Section

s-PS was synthesized in our laboratories using a homogeneous catalyst consisting of CpTiCl₃ and methylalumoxane (MAO) in toluene, according to the method described in ref 13. 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 viscometer, was 0.60 dL g⁻¹.

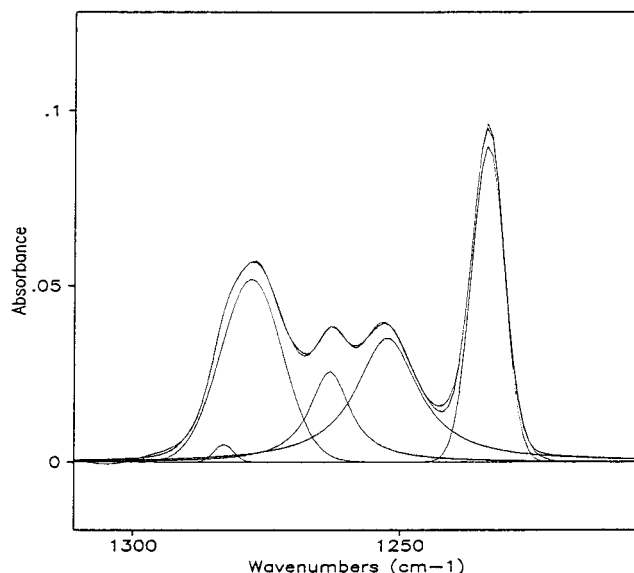The powder and film samples in the empty δ-form were obtained by treatments with boiling acetone for 5

Figure 1. Curve-fitting analysis in the wavenumber range 1300−1200 cm⁻¹ relative to the spectrum of DCP into the β-form of s-PS.

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 samples in the β-form were obtained by solution casting from a 5 wt %/wt solution in *o*-dichlorobenzene at 140 °C.

Wide-angle X-ray diffraction patterns were obtained on film samples with nickel filtered Cu Kα 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 wavenumber scale was internally calibrated using a He−Ne laser to an accuracy of 0.01 cm⁻¹ 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 μm, 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 DCP molecules 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 different 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 conformers from their relative intensity, following the procedure described in detail in ref 8.

In the case of DCP the conformationally sensitive peaks used to evaluate the molar fraction of each conformer were highly overlapped (see Figures 1 and 4) and, therefore, a curve resolving procedure was necessary to separate the individual components. The algorithm employed is based on the Levenberg−Marquardt method;[14] to reduce the number of adjustable parameters and to ensure the uniqueness of the result, the baseline, the band shape, and the number of components (as evaluated by second derivative analysis)
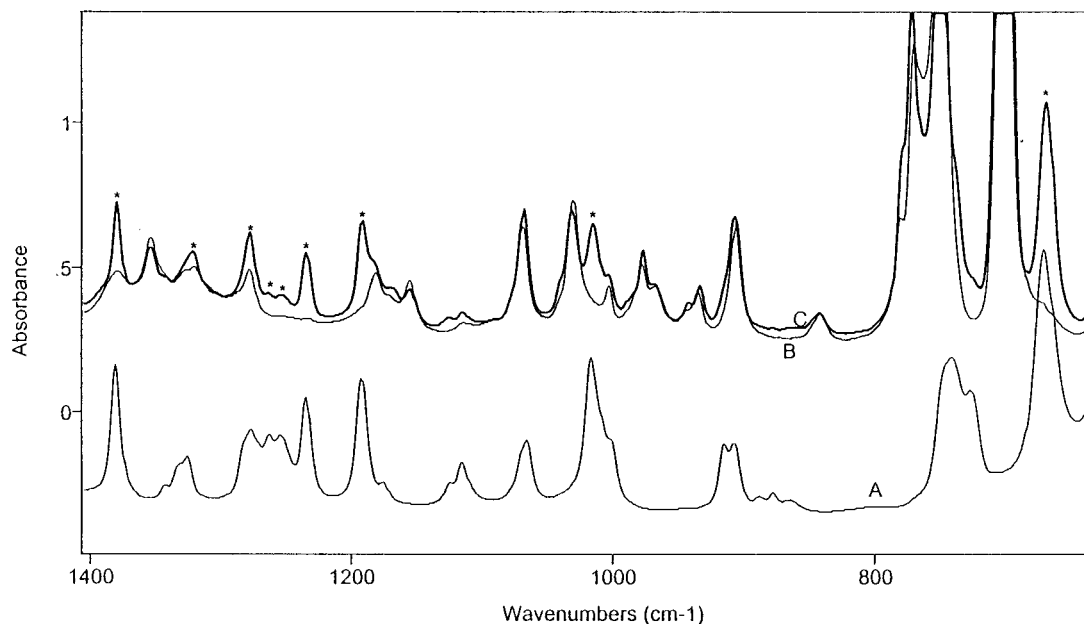
Figure 2. FTIR spectra in the wavenumber range 1400−600 cm^{-1} of (A) liquid 1,2-dichloropropane (DCP), (B) empty δ-form film of syndiotactic polystyrene (s-PS), and (C) empty δ-form film of s-PS, after 2 h of immersion in liquid DCP. (The peaks of the chlorinated compound are marked with an asterisk.)
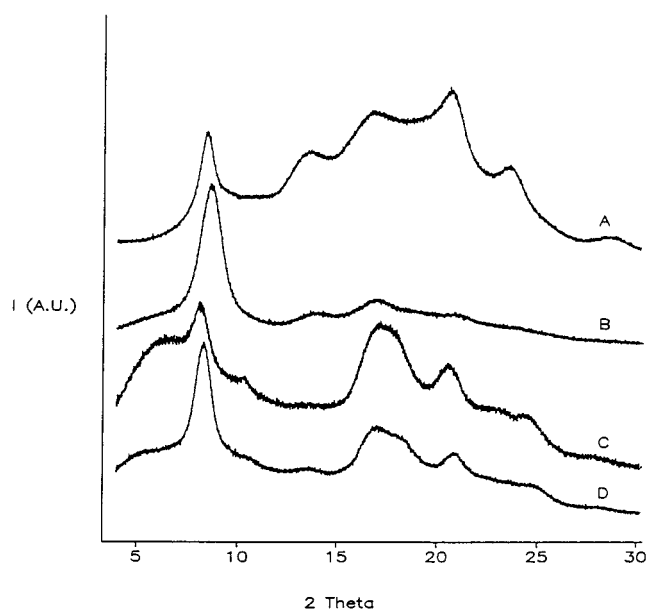

Figure 3. X-ray diffraction patterns of s-PS samples: (A) powder in the empty clathrate form, (B) cast film in the empty clathrate form, (C) film sample B treated by liquid DCP, and (D) film sample B treated by liquid CP.

were fixed. The program was allowed to evaluate, by nonlinear curve fitting of the experimental data, the height, the full width at half-height (fwhh), and the position of the individual components.

The peak function was a mixed Gauss−Lorentz line shape of the form:

$$f(x) = (1 - L)H \exp{-\left[\left(\frac{x - x_0}{w}\right)^2 (4 \ln 2)\right]} + L\frac{H}{4\left(\frac{x - x_0}{w}\right)^2 + 1}$$

where x_0 = peak position; H = peak height; w = fwhh; L = fraction of Lorentz character.

A typical result of the curve fitting analysis in the 1300−1200 cm^{-1} range, relative to the spectrum of DCP in the δ-form of sPS, is reported in Figure 1.

For a quantitative evaluation of the intensities of the analytical peaks, it has been necessary to eliminate the interference of the medium in which the chlorinated compounds were dissolved (a solvent or a s-PS crystalline form). This was accomplished by use of subtraction spectroscopy, whereby the spectrum of the substrate (the reference) was subtracted from that of the sample according to

$$A_\mathrm{d} = A_\mathrm{s} - KA_\mathrm{r}$$

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

The adjustable parameter K was used to compensate for thickness differences between the sample and the reference spectra and was chosen so as to reduce to the baseline an internal standard peak characteristic of the substrate.

3. Results and Discussion

3.1. Conformational Equilibria of Chlorinated Compounds in s-PS Samples.
For the conformational study in clathrate samples of s-PS, DCE, DCP, and CP have been chosen as guest molecules, since they present simple conformational equilibria and in the liquid phase a high-energy conformation is reasonably populated and readily detectable by spectroscopic means. In fact, the FTIR spectra of these liquid chlorinated compounds in the wavenumber range 1500−450 cm^{-1}, present a number of well-resolved peaks. Moreover, due to the relative simplicity of these molecules a complete normal vibrational analysis is feasible, which has allowed unambiguous assignment of the various absorptions to the normal modes of the different conformers.[15−17]

3.1.1. DCP Conformations in s-PS Samples. The FTIR spectrum of liquid DCP and of an empty δ-form film of s-PS, in the frequency range 1400−600 cm^{-1}, are presented in Figure 2, parts A and B, respectively. The
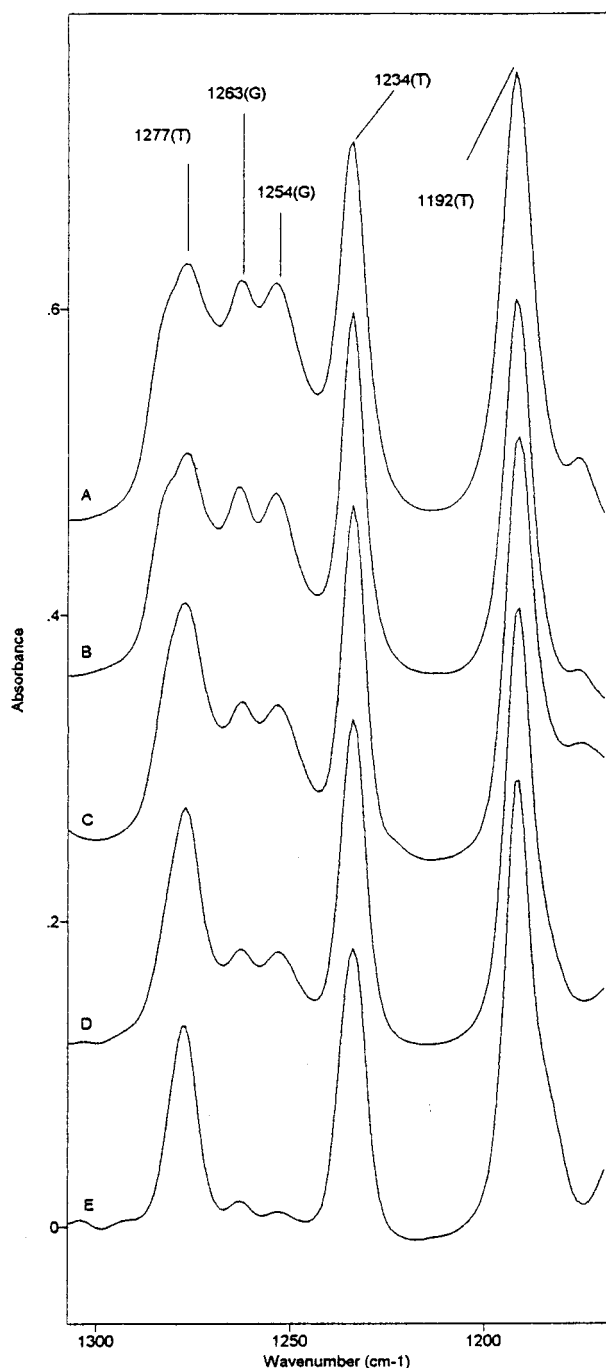
Figure 4. FTIR spectra in the wavenumber range 1300–1150 cm^{-1} of DCP: (A) liquid, (B) in a 5% benzene solution, (C) absorbed in the amorphous phase of a β-form s-PS sample, (D) absorbed in the empty clathrate s-PS sample, and (E) sample D, after 12 months of desorption at ambient conditions. Curves B, C, D, and E have been obtained by spectral subtraction procedures.

empty δ-form film of s-PS, after 2 h of immersion in liquid DCP, absorbs nearly 15 wt % of chlorinated compound and presents the FTIR spectrum shown in Figure 2C (where bands typical of the chlorinated compound have been indicated by asterisks).

For the sake of comparison, also a β-form films of s-PS, which can absorb the chlorinated compound only into the amorphous phase, has been immersed in liquid DCP. After 12 h of immersion, β-form samples absorb nearly 6 wt % of chlorinated compound.

The X-ray diffraction pattern of an empty δ-form s-PS film, obtained by our casting and extraction procedure,

is compared with that of a fine powder in the empty δ-form (curves B and A in Figure 3, respectively). The diffraction peak positions for the film and powder samples are identical, however large variations of the peak relative intensities are observed for the film samples, due to the presence of preferential orientation of the crystallites. The occurrence of preferential orientation for the film sample is confirmed by substantial differences between X-ray diffraction patterns obtained with beam perpendicular or parallel to the film surface.

The X-ray diffraction pattern of the nanoporous s-PS film sample, after DCP sorption, is shown by curve C in Figure 3 and presents, with respect to the pattern of the empty δ-form film (Figure 3B), typical variations related to the guest clathration.[4,5] In fact, a shift to lower angle of the 010 reflection (from $2\theta \approx 8.4°$ to $2\theta \approx 8.2°$, for Cu Kα radiation), a reduction of the intensities of the 010 as well as of the superimposed 101 and $\bar{1}11$ reflections (at $2\theta \approx 13°$, for Cu Kα radiation) and an increase of the intenity of the $\bar{2}10$ reflection (at $2\theta \approx 10.5°$, for Cu Kα radiation) are observed. In contrast, the X-ray diffraction pattern of the β-form s-PS samples remain substantially unchanged, upon DCP sorption.

This indicates that, as expected, DCP is sorbed only in the amorphous phase of semicrystalline samples being in the β-form. In contrast, in the same sorption conditions, in samples being in the empty δ-form, DCP is not only absorbed in the amorphous phase but also included in the cavities of the crystalline phase (forming a clathrate structure).

For the evaluation of the conformational equilibrium of DCP in different environments from FTIR spectra, the wavenumber range between 1300 and 1150 cm^{-1} has been chosen. In fact, this range is relatively free from s-PS bands (Figure 2C) while includes peaks relative to the different DCP conformations. In the spectrum of liquid DCP shown in Figure 4A, the bands are labeled as T or G depending on the conformation relative to the two chlorine atoms.[16] Hence T corresponds to the TG$^+$ (or the enantiomeric TG$^-$) conformation, while G corresponds to the G$^+$T and G$^+$G$^-$ or the enantiomeric G$^-$T, G$^-$G$^+$) conformations. In particular, the peaks at 1283 cm^{-1} and at 1263 cm^{-1} have been assigned to the CH$_2$ wagging vibrations of the G conformers, while the 1277 cm^{-1} band is due to the same deformation in the T conformer. The 1254 cm^{-1} and the 1234 cm^{-1} peaks correspond to the CH deformation of the G and T conformers, respectively.[16] Finally, the strong peak at 1192 cm^{-1} corresponds to a CH$_2$ *twist* mode of the trans conformer.[16]

The spectra of DCP in a 5% benzene solution (curve B), of DCP absorbed in the amorphous phase of the β-form (curve C) and absorbed in the empty clathrate s-PS sample (curve D), all obtained by spectral subtraction procedures, are also shown in Figure 4. The spectral subtractions produce complex profiles with equal band components, as far as positions and shapes are concerned, but the intensity ratios between the individual components change remarkably with the chemical environment of the DCP molecules. In particular, it is immediately apparent, on inspection of Figure 4, that the G bands decrease with respect to the T bands, for all the investigated environments and mainly for the case of absorption in the clathrate s-PS sample.

For a quantitative evaluation of the conformers population, a separation of the complex spectral profiles into single band components, through the curve-fitting

Table 1. Results of the Curve-Fitting Analysis of the Spectrum of DCP in the Wavenumber Range 1300−1200 cm^{-1} [a]

	peak 1 (G)			peak 2 (T)			peak 3 (G)			peak 4 (G)			peak 5 (T)			
	center (cm^{-1})	fwhh (cm^{-1})	H (AU)	center (cm^{-1})	fwhh (cm^{-1})	H (AU)	center (cm^{-1})	fwhh (cm^{-1})	H (AU)	center (cm^{-1})	fwhh (cm^{-1})	H (AU)	center (cm^{-1})	fwhh (cm^{-1})	H (AU)	X_t
neat	1284	6.0	0.036	1277	15.0	0.151	1263	10.0	0.090	1253	15.6	0.131	1234	8.3	0.232	0.62
C$_6$H$_6$	1284	5.4	0.026	1277	13.9	0.101	1263	8.7	0.059	1253	13.2	0.078	1234	7.1	0.174	0.65b
β	1282	6.8	0.010	1276	11.5	0.040	1263	9.5	0.017	1252	14.3	0.022	1234	7.1	0.058	0.68
δ				1277	13.0	0.162	1263	7.8	0.037	1253	13.6	0.058	1234	7.8	0.211	0.78
δ*				1277	11.7	0.117	1263	7.4	0.021	1253	13.5	0.031	1234	8.0	0.161	0.83
δ**				1277	8.62	0.068	1263	6.0	0.0068	1253	15.3	0.0065	1234	8.1	0.094	0.91

[a] Abbreviations: neat, liquid DCP; C$_6$H$_6$, DCP in benzene solution (concentration 5.0 wt %); β, DCP in the β-form of s-PS (concentration 5.6 wt %); δ, DCP in the δ-form of s-PS (concentration 15 wt %); δ*, the above sample after thermal treatment at 40 °C for 3 h (concentration 11 wt %); δ**, the above sample after 12 months in air at 25 °C (concentration 6.5 wt %). [b] Value taken from ref 16.
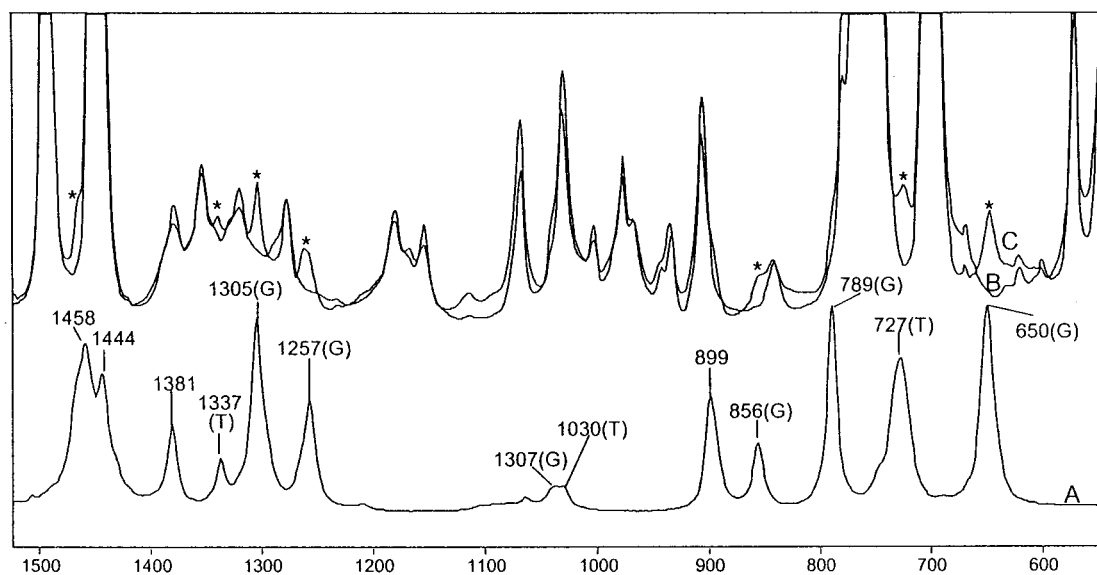

Figure 5. FTIR spectra in the wavenumber range 1000−550 cm^{-1} of (A) liquid CP (the various absorptions are marked G or T depending on whether they originate from the gauche or from the trans conformers, respectively), (B) empty δ-form film of s-PS, and (C) empty δ-form film of s-PS, after 3 h of immersion in liquid CP. (Bands of the chlorinated compound have been indicated by asterisks.)

procedure described in the Experimental Section, was performed. The results of such an analysis are reported in Table 1. It is apparent that the positions of the single components remain substantially coincident in all the samples examined and also the fwhh varies within reasonable limits ($\pm$20%), which confirm the reliability of the method. On the basis of a literature value of molar fraction of the TG conformer of DCP in diluted benzene solutions (0.65),[16] by considering the bands at 1264 cm^{-1} (for the G conformer) and at 1234 cm^{-1} (for the T conformer) and by applying the procedure described in ref 8, it is possible to derive the molar fraction of the TG conformers in the liquid (0.62), in the amorphous phase of the β-form s-PS film (0.68) and in the chlatrate s-PS film (0.78).

It is worth noting that the position of the conformational equilibrium of DCP is nearly the same in the amorphous phase of s-PS and in the benzene solution. However, as already observed for DCE,[8] the conformational equilibrium is shifted toward the conformer presenting two trans chlorine atoms, when the absorption involves not only the amorphous phase but also the clathrate crystalline phase.

This effect can be amplified after partial desorption, by thermal treatments, of DCP molecules from the s-PS clathrate film, which is expected to occur preferentially from the amorphous phase. In fact, for the case of DCE it has been demonstrated that at 40 °C the removal of the chlorinated compound is substantial from the amor-

phous phase while it is negligible from the clathrate phase.[18]

The spectra of DCP included in the clathrate s-PS film after 3 h of desorption at 40 °C (trace not shown, residual DCP content 11 wt %) and after 12 months of desorption at ambient conditions (Figure 4E, residual DCP content 6.5 wt %) display a further reduction of the intensities of the gauche peaks relative to those of the trans conformer. This effect is more marked for the highest desorption time; in fact for the clathrate sample treated 12 months at ambient conditions the gauche peaks became barely detectable.

By applying the method described previously for the evaluation of the conformers' population, the molar fraction, X_t, of DCP in the two above samples was 0.81 and 0.91, respectively.

These results can be interpreted by assuming that into the clathrate crystalline phase of s-PS, as already observed for DCE,[8] the conformational equilibrium of DCP is shifted toward the conformers presenting trans arrangement of the chlorine atoms.

3.1.2. CP Conformations in s-PS Samples. The FTIR spectrum of liquid CP and of an empty δ-form film of s-PS, in the wavenumber range 1600−550 cm^{-1}, are presented in Figure 5, parts A and B, respectively. In the spectrum of liquid CP the peaks marked G or T are those that can unambiguously assigned to the gauche or trans conformers, respectively.[17] It is noted that the

only peak of reasonable intensity characteristic of the trans conformer, is the one located at 727 cm^{-1} (a ν_{C-Cl} mode).

The empty δ-form film of s-PS, after 3 h of immersion in liquid CP, absorbs nearly 14 wt % of chlorinated compound, as evaluated by TGA analysis, and presents the FTIR spectrum shown in Figure 5C (where the peaks due to the chlorinated compound have been indicated by asterisks).

It is apparent, upon inspection of Figure 5C, that CP in the clathrate sample presents all the peaks characteristic of the gauche conformer (at 1305 cm^{-1}, CH$_2$ wag; 1257 cm^{-1}, CH$_2$ twist; 856 cm^{-1}, CH$_2$ rock; and 650 cm^{-1}, CCl stretch), along with the ν_{C-Cl} absorption of the trans conformer at 727 cm^{-1}.

The clathrate s-PS film whose FTIR spectrum is shown in Figure 5C, after 3 h of desorption at ambient conditions, presents a residual CP content of about 9 wt %, as evaluated spectroscopically, and of 6.5 wt % after additional 24 h of desorption in the same conditions. Contrary to what has been found for DCE and DCP, in the spectra of these two samples (not shown) the peaks of the gauche conformer remain predominant.

A semiquantitative evaluation of X_t for CP in the investigated clathrate samples was attempted by considering the absorbance ratio of the ν_{C-Cl} peaks of the gauche and trans conformers at 650 and 727 cm^{-1}, respectively. The uncertainty associated with this evaluation is considerably larger than in the cases of DCE and DCP, due to the severe overlapping of the 727 cm^{-1} peak to strong absorptions of the polymeric substrate (see Figure 5C). In any case, X_t was found to be constant for the three investigated samples at a value of 0.20 ± 0.05, close to the X_t of CP in the liquid phase[17] (0.27).

The X-ray diffraction pattern of the nanoporous s-PS film sample, after CP sorption, is shown by curve D in Figure 3 and is similar to that obtained upon DCP sorption (Figure 3C), i.e., typical of a filled clathrate form.

β-Form films of s-PS, which could absorb the chlorinated compound only into the amorphous phase, after 48 h of immersion in pure liquid CP, do not present any appreciable absorption of the chlorinated compound. This is possibly a consequence of the very fast desorption of CP from the amorphous phase of the β-form, due to the high volatility of such a compound (T_e = 46−47 °C). Therefore it is reasonable to assume that in the clathrate sample, at least after significant desorption, the CP molecules are substantially present only into the cavities of the clathrate phase.

It is possible to conclude that, at variance with DCE and DCP, the conformational equilibrium of CP is not substantially altered upon inclusion in the cavities of the nanoporous structure of s-PS.

As discussed in the introduction of the paper, this result again supports the hypothesis that the conformational selectivity favoring the trans conformer for DCE and DCP in the cavities of the δ-form of s-PS, is due to specific attractive interactions involving the chlorine atoms, rather than imposed by nonbonded repulsive interactions.

3.2. Band Shifts of Chlorinated Compounds in s-PS Samples. The presence, in s-PS clathrates with chlorinated compounds, of host−guest attractive interactions involving chlorine atoms is also supported by analysis of possible band shifts after guest sorption experiments.
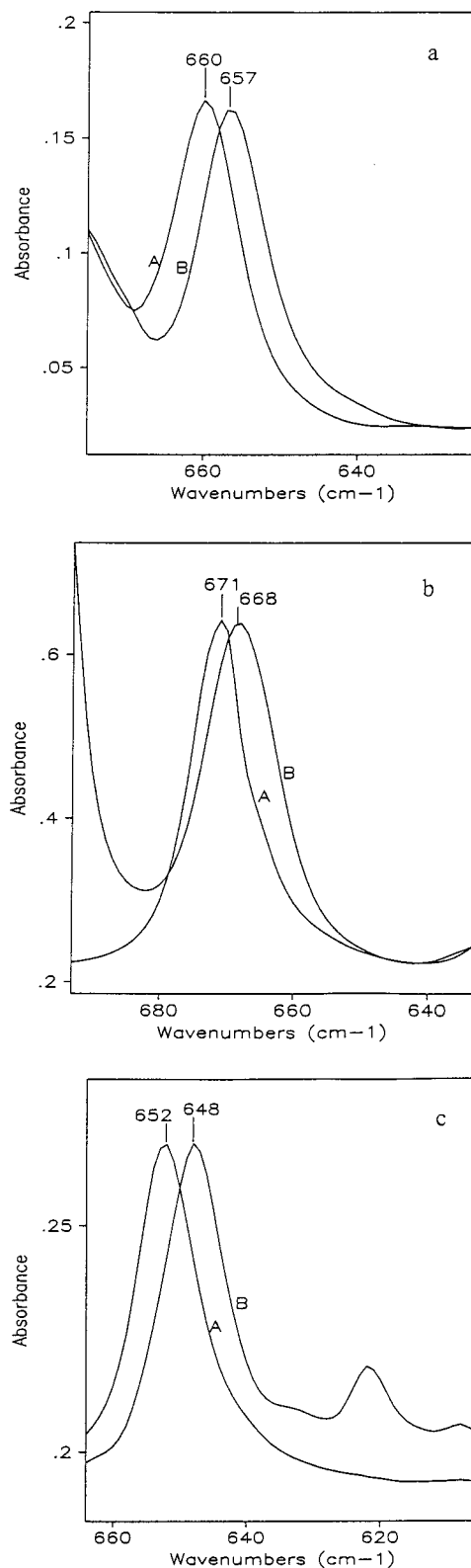

Figure 6. C−Cl stretching bands of (a) DCE (trans conformer), (b) DCP (trans conformer), and (c) CP (gauche conformer). In the three figures, curves labeled A refer to 2.5 wt % solutions in CS$_2$, while curves labeled B refer to the respective chlorinated compounds absorbed into films of the s-PS clathrate form.

In fact, all the considered chlorinated compounds, when absorbed by s-PS samples, display a shift toward lower frequencies of the ν_{C-Cl} peaks, with respect to their position in diluted solutions of noninteracting solvents. This indicates a reduction of the force constant

of the C−Cl bond, caused by an attractive interaction on the chlorine atom. The effect is shown in Figure 6, where the ν_{C-Cl} peaks of DCE (trans conformer), DCP (trans conformer), and CP (gauche conformer) in the s-PS clathrate form are compared with the same peaks in a 2.5 wt % solution in CS_2.

The observed band shifts are in all cases in the range 3−4 cm^{-1}, which, by assuming the harmonic oscillator model, indicate reductions of the force constant of the C−Cl bonds into the s-PS environment, close to 1%.

Analogous band shifts are observed for DCE and DCP also when absorbed into the amorphous phase of s-PS (for instance, by treatments of β-form films). Moreover, for all the considered chlorinated compounds, analogous shifts are also observed for diluted solutions in benzene or toluene, that is, in solvents containing, as polystyrene, aromatic rings.

These results indicate that attractive interactions are possibly established between chlorine atoms and aromatic rings, both in amorphous and in the clathrate phase of s-PS.

4. Conclusions

Combined FTIR and X-ray diffraction investigation on s-PS samples has shown that in the cavities of its nanoporous form, a substantial conformational selectivity occurs for DCE and DCP, while the conformational equilibrium of CP remains substantially unaltered. Both for DCE and DCP, the conformational selectivity is in favor of the conformations leading to trans chlorine atoms.

The absence of conformational selectivity for CP clearly indicates that the observed conformational selectivity for DCE and DCP, in the s-PS clathrates, is not due to nonbonded repulsive interactions but to specific attractive interactions involving the chlorine atoms.

The observation of shifts of C−Cl stretching bands (of nearly 3−4 cm^{-1}), for the considered chlorinated compounds, both into polystyrene samples and into aromatic solvents, with respect to the same bands into solutions in noninteracting solvents, indicate that attractive interactions are possibly established between chlorine atoms and aromatic rings, both in amorphous and in the clathrate phase of s-PS.

It is reasonable to assume that the well-defined locations of the phenyl rings with respect to the cavities of the nanoporous structure would influence the location of the two chlorine atoms of DCE and DCP, thus determining the observed conformational selectivities.

References and Notes

(1) Guerra, G.; Vitagliano, V. M.; De Rosa, C.; Petraccone, V.; Corradini, P. *Macromolecules* **1990**, *23*, 1539.

(2) (a) Immirzi, A.; de Candia, F.; Iannelli, P.; Vittoria, V.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 761. (b) Vittoria, V.; de Candia, F.; Iannelli, P.; Immirzi, A. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 765. (c) Vittoria, V.; Russo, R.; de Candia, F. *Polymer* **1991**, *32*, 337. (d) Chatani, Y.; Shimane, Y.; Inoue, Y.; Inagaki, T.; Ishioka, T.; Ijitsu, T.; Yukinari, T. *Polymer* **1992**, *33*, 488. (e) Chatani, Y.; Shimane, Y.; Inagaki, T.; Ijitsu, T.; Yukinari, T.; Shikuma, H. *Polymer* **1993**, *34*, 1620. (f) Chatani, Y.; Inagaki, T.; Shimane, Y.; Shikuma, H. *Polymer* **1993**, *34*, 4841.

(3) (a) Guerra, G.; Vitagliano, V. M.; Corradini, P.; Albizzati, E. (Himont, Inc.) It. Pat. 19588, Feb 1989. (b) Rapacciuolo, M.; De Rosa, C.; Guerra, G.; Mensitieri, G.; Apicella, A.; Del Nobile, M. A. *J. Mater. Sci., Lett.* **1991**, *10*, 1084.

(4) (a) Guerra, G.; Manfredi, C.; Rapacciuolo, M.; Corradini, P.; Mensitieri, G.; Del Nobile M. A. (C.N.R.) Ital. Pat. 1994. (b) Manfredi, C.; De Rosa, C.; Guerra, G.; Rapacciuolo, M.; Auriemma, F.; Corradini, P. *Makromol. Chem.* **1995**, *196*, 2795.

(5) De Rosa, C.; Guerra, G.; Petraccone, V.; Pirozzi, B. *Macromolecules* **1997**, *30*, 4147.

(6) Manfredi, C.; Del Nobile M. A.; Mensitieri, G.; Guerra, G.; Rapacciuolo, M. *J. Polym. Sci., Polym. Phys. Ed.* **1997**, *35*, 133.

(7) (a) Conti, G.; Santoro, E.; Resconi, L.; Zerbi, G. *Mikrochim. Acta* **1988**, *1*, 297. (b) Niquist, R. A. *Appl. Spectrosc.* **1989**, *43*, 440. (c) Reynolds, N. M.; Savage, J. D.; Hsu, S. L. *Macromolecules* **1989**, *22*, 2867. (d) Kobayashi, M.; Nakaoki, T.; Ishihara, N. *Macromolecules* **1990**, *23*, 78. (e) Guerra, G.; Musto, P.; Karasz, F. E.; MacKnight, W. J. *Makromol. Chem.* **1990**, *191*, 2111. (f) Vittoria, V. *Polym. Commun.* **1990**, *31*, 263. (g) Filho, A. R.; Vittoria, V. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 199. (h) Reynolds, N. M.; Hsu, S. L. *Macromolecules* **1990**, *23*, 3463. (i) Reynolds, N. M.; Stidham, H. D.; Hsu, S. L. *Macromolecules* **1991**, *24*, 3662. (l) Nakaoki, T.; Kobayashi, M. *J. Mol. Struct.* **1991**, *242*, 315. (m) Rastogi, S.; Gupta, V. D. *J. Macromol. Sci.-Phys.* **1994**, *B33*, 129. (n) Musto, P.; Tavone, S.; Guerra, G.; De Rosa, C. *J. Polym. Sci., Polym. Phys. Ed.* **1997**, *35*, 1055.

(8) Guerra, G.; Manfredi, C.; Musto, P.; Tavone, S. *Macromolecules* **1998**, *31*, 1329.

(9) De Rosa, C.; Rizzo, P.; Ruiz de Ballesteros, O.; Petraccone, V.; Guerra, G. *Polymer* **1999**, *40*, 2103.

(10) See, for example: Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1996**, *118*, 11225.

(11) Mizushima, S.; Shimanouchi, T.; Nakamura, K.; Hayashi, M.; Tsuchima *J. Chem. Phys.* **1957**, *26*, 970.

(12) (a) Akyüz, S.; Dempster, A. B.; Morehouse, R. L.; Zengin, N. *J. Chem. Soc. Chem. Commun.* **1972**, 307. (b) Davies, J. E. D. *J. Chem. Soc., Dalton Trans.* **1972**, 1182. (c) Cleaver, K. D.; Davies, J. E. D. *J. Mol. Struct.* **1977**, *36*, 61.

(13) Zambelli, A.; Longo, P.; Pellecchia, C.; Grassi, A. *Macromolecules* **1987**, *20*, 2035.

(14) Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 441.

(15) Tanabe K. *Spectrochim. Acta* **1972**, *28A*, 407.

(16) Thorbjornsrud, J.; Ellestad, O. H.; Klaboe, P.; Torgrimsen, T. *J. Mol. Struct.* **1973**, *15*, 45.

(17) (a) Tanabe, K.; Saeki, S. *J. Mol. Struct.* **1975**, *27*, 79. (b) Ogawa, Y.; Imazeki, S.; Yamaguchi, H.; Matsuora, H.; Harada, I.; Shimanouchi, T. *Bull. Chem. Soc. Japan* **1978**, *51*, 748.

(18) Musto, P.; Manzari, M. G.; Guerra, G. Guest Desorption from Crystalline and Amorphous Phases of a Syndiotactic Polystyrene Clathrate. *Macromolecules*, submitted for publication.

MA990455C