Thermoplastic Molecular Sieves

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An inexpensive and reusable thermoplastic material that is promising in the field of chemical separations, and in particular of water and air purification from volatile organic compounds, is presented. This semicrystalline material based on syndiotactic polystyrene comprises a nanoporous crystalline phase where guest molecules can be clathrated. Changes of conformational equilibria of some chlorinated hydrocarbons upon clathration have been rationalized by a molecular mechanics approach. This sheds light on the nature of the host–guest interactions: although the van der Waals interactions are most relevant, the observed conformations for chlorinated guest molecules are essentially associated with electrostatic attractive interactions of quadrupolar conformers with a substantially quadrupolar electrostatic field of the crystalline cavity.

Introduction

Syndiotactic polystyrene (s-PS), whose synthesis was reported about a decade ago,[1,2] is a easily crystallizable and high melting (∼270 °C) stereoregular polymer presenting a very complex polymorphic behavior.[3]

In addition to four different crystalline forms, several clathrate structures, mainly including halogenated or aromatic hydrocarbons as guest molecules, have been described.[3–5]

The crystalline form δ is nanoporous and can be obtained by removal of guest molecules from clathrate samples, by suitable solvent treatments.[6] The corresponding crystal structure[7] is shown in Figure 1A. Sorption studies from liquid and gas phases, into s-PS samples (mainly films) being in this nanoporous δ form, have shown that this thermoplastic material is able to absorb selectively some organic substances from different environments also when present at low concentrations.[6,8,9]

Polymeric clathrates are generally more complex than those with low molecular mass hosts, since the samples generally contain large amorphous fractions (e.g, typical degrees of crystallinity of s-PS samples are not far from 50%). Hence, in general, guest molecules can be included both in clathrate and amorphous phases.

FTIR studies relative to chlorinated hydrocarbons sorption into s-PS films have shown that the *trans* conformation of 1,2-dichloetane (DCE) and 1,2-dichloropropane is largely prevailing in the clathrate phase, while the *trans* and *gauche* conformations are nearly equally populated when both chlorinated compounds are sorbed in the amorphous phase.[9,10] The prevailing presence of the *trans* DCE conformer into the clathrate phase has been confirmed by a recent X-ray diffraction determination of the crystal structure,[11] which for the sake of comparison with the crystal structure of the empty δ form is shown in Figure 1B.

As a preliminary study of host–guest interactions in these polymeric clathrates, an ab initio study of the model complexes benzene/X_2 (X = F, Cl, Br, I) has been recently reported.[12]

In the present paper, conformational equilibria of some chlorinated hydrocarbons in s-PS samples are described and rationalized on the basis of quantitative evaluations of host–guest interaction energies. The aim

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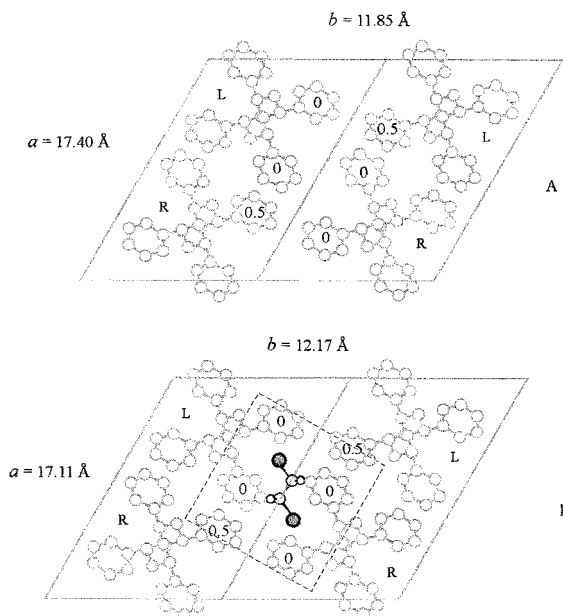
Figure 1. Models of packing and unit cell for the crystal structures of δ form of s-PS: (A) empty and (B) including 1,2-dichloroethane (DCE). Approximate z fractional coordinates of barycenters of phenyl rings are shown. R = right-handed chain; L = left-handed chain. In part B, the calculated minimum energy position for DCE, is shown. The dashed square corresponds to the region considered for the maps of Figure 5.

is to contribute to clarifying the nature of the host−guest interactions into the nanoporous crystalline phase and hence to shedding light onto the origin of the selectivity of these sorbent materials.

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 2. 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 0.6 dL g⁻¹.

The powder and film samples in the δ 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 % solutions in chloroform at room temperature), respectively. Samples in β form were obtained by solution casting from a 5 wt % solution in *o*-dichlorobenzene at 140 °C.

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.

As for the conformational studies, films having thickness of nearly 30 μm have been chosen, so as to maintain the peaks of interest in the range of absorbance linearity (less than 1.2 absorbance units). For the evaluation of the relative population of the conformers of the various guest molecules, according to the method described in refs 9 and 10, the following peaks were used: for dichloroethane, at 1234 cm⁻¹, CH₂ *wagging* of the *trans* conformer; at 1285 cm⁻¹, CH₂ *wagging* of the *gauche* conformer; for dichloropropane, at 1234 cm⁻¹, C−H deformation of the *trans* conformer; at 1264 cm⁻¹, CH₂ *wagging* of the *gauche* conformer; for chloropropane, at 727 cm⁻¹, C−Cl *stretching* of the *trans* conformer; at 650 cm⁻¹, C−Cl *stretching* of the *gauche* conformer.

The sorption measurements have been conducted by immersion of powder samples in aqueous solutions of the chlorinated hydrocarbons. For different sorption and desorption times, the powders were analyzed in the form of KBr pellets by FTIR and the DCE contents have been determined by following the method described in ref 9.

Calculation Methods. The molecular mechanics calculations have been performed with the TINKER package.[13] The AMBER force field of Kollmann and co-workers has been utilized.[14] This force field has been shown to reproduce the geometries and the energies of benzene and toluene dimers reasonably well.[15]

The Cl van der Waals parameters (R_{min} = 2.050 Å and ϵ_{min} = 0.100 kcal/mol) and the charges of chlatrate guest atoms (listed as Supporting Information) were adjusted[16] following the standard approach[15,17,18] to fit molecular mechanics curves to ab initio ones.

With the use of these parameters, the molecular mechanics energy difference between the *trans* and *gauche* DCE conformations amounts to 1.02 kcal/mol, in good agreement with the experimental result.[19] These parameters are close to those developed by Jorgensen and co-workers in their simulations of gaseous and liquid DCE[20] which are able to reproduce experimental conformational results.[19]

All calculations were performed with the s-PS chains fixed to the positions found in the crystal structure of the DCE clathrate.[11] As for chlorinated guests, positions of different conformers have been optimized without any constraint to mimimize overall potential energy.

It is worth noting that the applicability of standard molecular mechanics force fields to the study of host/guest interaction in polymeric materials, is well established.[21−24]

Results

Conformations of Chlorinated Hydrocarbon Guests. Chlorinated hydrocarbons are readily sorbed by the nanoporous crystalline form of s-PS. Just as an example, sorption kinetics of 1,2-dichloroethane (DCE) from saturated (8100 ppm) or diluted (100 ppm) aqueous solutions by powder s-PS samples, characterized by surface areas of nearly 4 m²/g, are shown in Figure 2. In addition to powders in δ form, powders in the β crystalline form, which absorb low molecular mass compounds only into the amorphous phase,[9,25] are also considered. It is apparent that for δ form powders, a few minutes are sufficient to obtain substantial sorption of DCE from water solutions, whereas β form powders sorb DCE more slowly and to a lower extent. Sorption from s-PS samples, which are amorphous or in crystalline forms other than δ, is negligible for low DCE activities as occurs for β form samples. For the considered δ form sample, the equilibrium sorption of DCE from 100 and 10 ppm aqueous solutions is of 7 and 4.5%,

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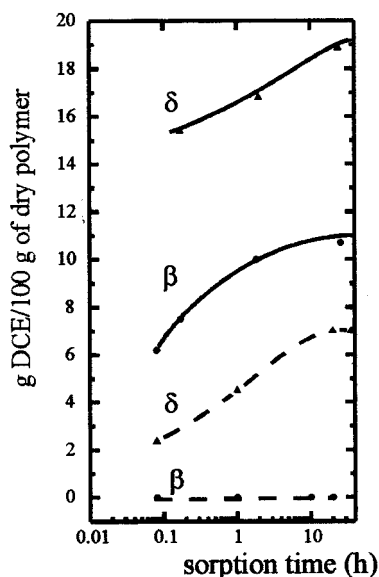
Figure 2. Sorption kinetics of DCE from saturated (8100 ppm; solid lines) or 100 ppm (dashed lines) aqueous solutions by semicrystalline powder s-PS samples: (▲) δ form and (●) β form.

respectively. These results hence indicate the occurrence of high partition coefficients between the polymeric phase and the aqueous phase.

As for the conformational studies, 1,2-dichloroethane (DCE), 1,2-dichloropropane (DCP) and 1-chloropropane (CP) have been chosen as guest molecules, since they present similar and simple conformational equilibria and the different conformations are reasonably populated and readily detectable by spectroscopic means. In fact, the FTIR spectra of these 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.[19,26,27]

A comparison between the conformational equilibria of the three considered chlorinated compounds into s-PS films is presented in Figure 3, as a plot of the fraction of the *trans* conformers (Scheme 1) versus the molar concentration of the chlorinated compounds in the polymer samples. For each set of data, the maximum

Scheme 1
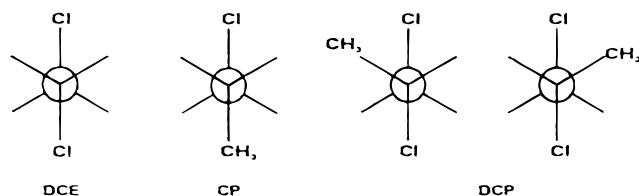
value of the guest molar concentration (the experimental point on the extreme right of each curve of Figure 3) corresponds to that observed immediately after
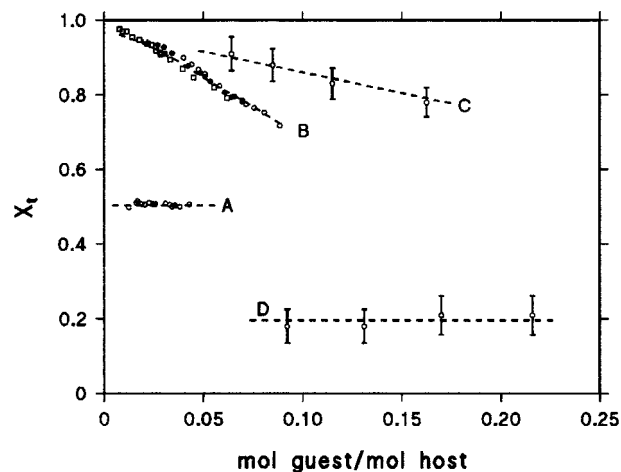
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Figure 3. Plot of the fraction of the *trans* conformers for the three chlorinated hydrocarbons considered (see Scheme 1) as a function of molar concentration of the chlorinated compounds in s-PS semicrystalline films (expressed as mole of guest per mole of styrene monomeric units): (A) DCE absorbed from a 0.5 wt % aqueous solution by a β form film; (B) DCE absorbed from a 0.5 wt % aqueous solution by a nanoporous δ form film; (C) DCP absorbed from pure liquid by a nanoporous δ form film; and (D) CP absorbed from pure liquid by a nanoporous δ form film. The highest molar concentration values for the different curves correspond to those observed immediately after absorption. The other experimental points correspond to the.same samples after different desorption procedures (see text).

sorption. The other experimental points correspond to the same samples after different desorption procedures.

Data corresponding to DCE sorption from a 0.5 wt % aqueous solution followed by isothermal desorption at 40 °C (empty circles), 60 °C (filled circles), and 80 °C (squares) relative to β and δ form s-PS samples are labeled A and B, respectively, in Figure 3. It is apparent that, the *trans* and *gauche* conformations are nearly equally populated for DCE molecules sorbed in the amorphous phase of samples including the dense and impermeable β crystalline phase[25] (data set A in Figure 3). The observed X_t values are intermediate between those observed for pure liquid ($X_t = 0.35$) and for vapor ($X_t = 0.75$) DCE[19] and close to those previously observed for DCE sorption experiments into s-PS amorphous films from aqueous solutions of different concentrations.[9] For equal sorption conditions, the DCE concentration is higher and the fraction of its *trans* conformer is larger when DCE is sorbed into δ form crystalline samples (cf., e.g., data points on the extreme right of curves B and A of Figure 3). Moreover, the X_t value increases up to 0.94 as DCE concentration in the polymer is reduced by desorption (curve B in Figure 3), that is to the same value obtained for DCE sorption into nanoporous polymer samples from very diluted aqueous solutions (10 ppm).[9]

A similar behavior is observed for DCP. For instance, sorption experiments into a nanoporous s-PS film from pure liquid, followed by desorption at room temperature (data set C in Figure 3), show large X_t values, larger than those measured for diluted DCP solutions in benzene ($X_t = 0.65$)[26] or for liquid DCP ($X_t = 0.62$),[10] which increase as desorption proceeds.

In contrast the CP behavior is completely different, in fact the population of the *trans* conformer is not
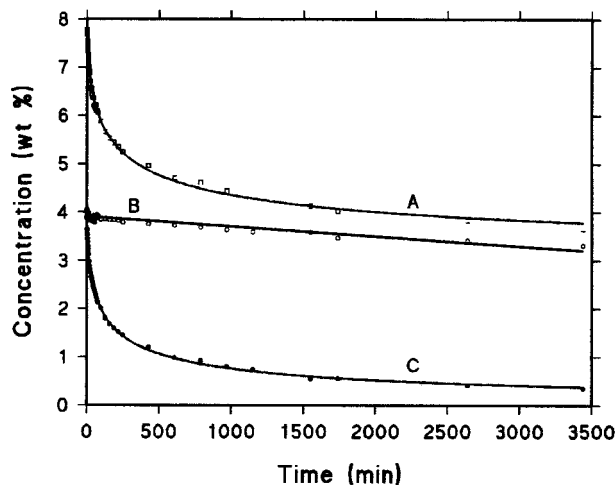
Figure 4. Desorption kinetic of DCE at 40 °C from a s-PS film, after sorption from a 0.5 wt % aqueous solution: (A) overall; (B) for the clathrate phase; (C) for the amorphous phase. Data of curves B and C have been calculated on the basis of X_t variations (see text).

increased by clathration into s-PS. Take for example CP sorbed from pure liquid at room temperature by a nanoporous s-PS sample: although the clathration phenomenon is confirmed by the typical changes in the X-ray diffraction patterns,[7] X_t remains close to 0.2 (data set D of Figure 3), which is not far from the value observed for liquid (0.27) and vapor (0.38) CP.[27]

These results, therefore, indicate that the conformational equilibria of the chlorinated compounds are poorly affected by sorption into the amorphous polymer phase. Moreover, the conformational equilibrium of CP is poorly affected also by inclusion into the s-PS nanoporous phase. On the contrary, for DCE and DCP, the conformers presenting two *trans* chlorine atoms are largely prevailing into the clathrate phases.

The observed increases of the X_t values during guest desorption procedures can be rationalized in terms of faster desorption kinetics from the amorphous phase. In particular, by assuming X_t values for both phases independent of guest concentration, guest contents into clathrate and amorphous phases can be evaluated from the above-described FTIR peak intensities. For instance, X_t for DCE sorbed into the amorphous phase can be reasonably assumed equal to 0.51, which is equal to the experimental value observed for different amorphous and semicrystalline samples sorbing DCE only into the amorphous phase (see, e.g. curve A of Figure 3 and ref 9). As for the clathrate phase, X_t can be assumed close to 0.94, i.e., the highest experimental value observed for δ-form s-PS samples after substantial guest desorption (see curve B in Figure 3) as well as after DCE absorption from diluted solutions.[9]

In these assumptions, separate desorption kinetics from the amorphous and clathrate phases of s-PS can be evaluated.[28] Just as an example, desorption kinetics at 40 °C from amorphous and clathrate phases of a s-PS film after DCE sorption from a 0.5 wt % aqueous solution (based on the X_t values corresponding to the empty circles of curve B of Figure 3) are shown in Figure 4. Initially, in the considered sample, DCE is partitioned

almost evenly in the amorphous and the crystalline phases, while the difference in the desorption rates between the two phases is dramatic. For istance after about 60 h the DCE content in the amorphous phase has decreased by about 90% of its initial value, while, in the crystalline phase, the reduction is close to 10%.

Analogous conformational studies, applied to sorption kinetics relative to δ form s-PS samples, have indicated that the absorption of the considered chlorinated compounds from aqueous solutions occurs preferentially into the clathrate phase and essentially only into the clathrate phase for low guest concentrations.[9]

Gas sorption (CO_2 and CH_4) and transport into a polymeric crystalline phase have already been observed for isotactic poly(4-methyl-1-pentene).[29,23] However in that case the molecules do not form clathrate structures but dissolve in the crystals at about $1/3$ to $1/4$ the level they do in the amorphous phase.

In our knowledge, this is the first case of polymeric semicrystalline material whose sorption ability is higher for the crystalline phase than for the amorphous phase.

Nature of the Host–Guest Interactions. As for the nature of the host–guest interactions, the occurrence for DCE and DCP (but not for CP) of conformational selectivity, favoring the *trans* conformers in the cavities of the δ form of s-PS, indicates the presence of specific attractive, rather than van der Waals repulsive, interactions involving the *trans* chlorine atoms. In fact, since chlorine atoms and the methyl groups present similar van der Waals radii (close to 1.8 Å[30]), if the conformational selectivity had been due to repulsive nonbonded interactions, it would have been observed also for CP (see Scheme 1).

Furthermore, for all the chlorinated compounds considered, FTIR spectra both into polystyrene samples and into aromatic solvents show shifts of C–Cl stretching bands (of nearly 3–4 cm^{-1}), with respect to the same bands into solutions in non interacting solvents.[10] These band shifts correspond to a reduction of the force constant of the C–Cl bonds into the PS environment close to 1% and indicate the occurrence of attractive interactions, possibly established between chlorine atoms and aromatic rings, both into amorphous and into clathrate phases of s-PS. It is reasonable to assume that the specific locations of the phenyl rings delimiting 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.

A molecular mechanics approach is used in the following to rationalize the previously described experimental conformational results. This can contribute to elucidating the nature of the host–guest interactions into s-PS clathrate compounds.

As for the polymeric host, separate van der Waals and electrostatic potential maps, relative to the region of the unit cell of the clathrate form of s-PS indicated by a dashed square in Figure 1B, at a quote of $1/2c$, obtained by ignoring the guest molecule, are shown in Figure 5, parts A and B, respectively.[31]

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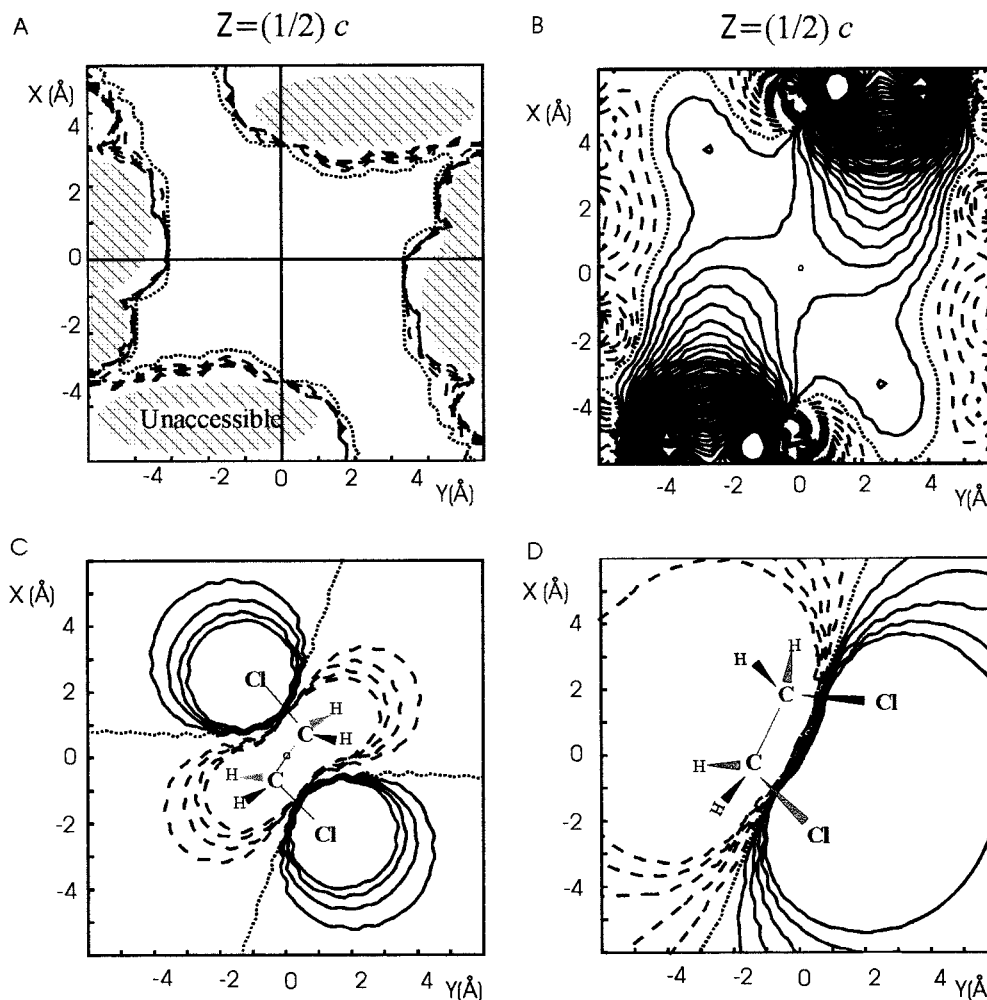
Figure 5. Potential maps, relative to the region of the unit cell of the clathrate form of s-PS indicated by a dashed square in Figure 1B, at a quote of $^1/_2c$, when the guest molecule is ignored: (A) van der Waals interactions of a probe carbon atom with the cavity and (B) electrostatic potential of the cavity. Electrostatic potential maps relative to the *trans* (C) and *gauche* (D) conformers of DCE positioned with respect to the cavity in the way suitable to minimize the overall potential energy. For all maps; the origin of *x* and *y* axes has been located on the center of symmetry of the unit cell of the nanoporous crystalline form. The zero energy curve is dotted and positive and negative curves are dashed and continuous, respectively. The difference between the curves is of 1 kcal/mol. A good electrostatic fit between the cavity (B) and the *trans* conformer (C) is immediately apparent.

In particular, the map of Figure 5A shows the van der Waals interactions of a probe carbon atom with the cavity. The dotted zero energy curve includes the region of attractive nonbonded interactions for a carbon atom and can be considered as a section of the surface delimiting the empty space available for the guest molecules. This section presents a maximum area at quote $^1/_2c$ and is substantially absent at quote 0 (or, c = 7.7 Å). It is apparent that the cavity is centered on the symmetry center of the unit cell, which is also indicated in Figure 5.[32]

The electrostatic potential map of Figure 5B shows (by comparison with the map of Figure 5A) that the electrostatic potential is essentially negative in the central part of the cavity while it is prevailingly positive in some regions which are external to the cavity.

As for the chlorinated guests, *trans* and *gauche* conformers of DCE, positioned with respect to the cavity in the way suitable to minimize overall potential energy,

are shown in Figure 5, parts C and D, respectively. For comparison with electrostatic potential of the cavity (Figure 5B), the electrostatic potential of both conformers of DCE is also shown.

All atoms of both conformers are included into the zero energy surface of the cavity (whose projection on the $x-y$ plane is shown in Figure 5A). It is apparent on inspection that there is a good electrostatic fit between the quadrupolar *trans* conformer and the substantially quadrupolar cavity. In particular, the positive electrostatic region of the DCE *trans* conformer, corresponding to the carbon and hydrogen atoms (Figure 5C), presents a good superposition with the negative electrostatic nature of the cavity (Figure 5B). The electrostatic fit between the cavity and the substantially dipolar *gauche* conformer (cf. Figure 5D with Figure 5B) is instead poor. Strictly analogous considerations hold for DCP. On the contrary, CP is dipolar and its electrostatic field is essentially independent of its conformation, as a consequence its electrostatic interaction with the cavity is similar for all conformers.

Results of minimizations of the host−guest interaction energies for the different guest conformers, into the

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(32) There are two of these cavities per unit cell, and the volume of each cavity, evaluated as the space available to probe rigid spheres of radius of 1.8 Å, is close to 120 Å^3. The corresponding volume fraction of empty space is close to 20%(see ref 33).

Table 1. Host−Guest Interaction Energies[a]

| | guest molecule by conformation | | | | | |
| | DCE | | DCP | | CP | |
	T	G	T	G	T	G
van der Waals	−12.8	−12.9	−16.0	−16.1	−13.5	−13.6
electrostatic	−1.1	0.0	−0.8	0.2	−0.8	−0.6
total	−13.9	−12.9	−16.8	−15.9	−14.3	−14.2

[a] Results of minimization of the interaction energies (kcal/mol) with the cavity of Figure 5 for *trans* and *gauche* conformers of chlorinated guests.

cavity of Figure 5, parts A and B, are reported in Table 1. For the sake of simplicity, only the absolute energy minimum situations of both conformers are listed. It is apparent that for all the considered chlorinated guests the main attractive contribution (up to 16 kcal/mol) is of van der Waals type, being however poorly dependent on the guest conformation. The electrostatic attractive contribution is smaller for all the considered chlorinated compounds; however, it is nearly 1 kcal/mol larger for the *trans* conformers, with respect to the *gauche* conformers, for both DCE and DCP. On the other hand, the electrostatic contribution to the minimum energy values is poorly dependent on the CP conformation. Hence, the calculations of Figure 5 and Table 1 are able to rationalize the absence of conformational selectivity for CP and the preference toward *trans* conformers for DCE and DCP, in the cavities of the δ form s-PS.

Conclusions

Nanoporous crystalline structures, obtained by guest removal from clathrate structures, are well-known for some inorganic materials (e.g., zeolites) and have found wide applications as molecular sieves.

Several clathrate structures with polymeric hosts have been described[34−38] which however are generally unstable after guest removal. To our knowledge this is the first case of a complete guest removal from a polymeric clathrate phase, which leaves the structure of the polymeric host substantially unchanged and leaves cavities in the crystalline locations previously occupied by guest molecules.

The reported results indicate that nanoporous crystalline samples of s-PS can be suitable for water purification from some chlorinated hydrocarbons. The occurrence of different conformational equilibria of some guest molecules, into amorphous and clathrate phases of s-PS, allows evaluation of the guest contents into both phases. On this basis, it is established that sorption involves preferentially the clathrate phase and that desorption from clathrate phase is much slower than desorption from amorphous phase.

Moreover, on the basis of conformational studies relative to chlorinated guest molecules, the nature of the host−guest interactions of these sorbent materials has been elucidated: van der Waals interactions are most relevant; however, the conformational selectivities observed for DCE and DCP are essentially associated with electrostatic attractive interactions, involving their quadrupolar conformers presenting two chlorine atoms in the *trans* arrangement.

A number of applications in the field of chemical separations and in particular of water and air purification from volatile organic compounds of these inexpensive and reusable thermoplastic molecular sieves is foreseen. In fact, the thermoplastic nature of this material should allow an easy processing to suitable products, like films, membranes, and foams as well as their recycling. Possible advantages of clathration into a crystalline phase with respect to sorption into an amorphous polymeric phase could be higher selectivity as well as stability (e.g., see Figure 4).

It is also worth noting that the size and the shape of the crystalline cavities could be modified, and tailored, by using syndiotactic copolymers of styrene[39] and possibly homopolymers of substituted styrenes,[40,41] which also can present clathrate forms.

Supporting Information Available: Table of atomic type and atomic charges utilized in the molecular mechanics calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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