

Chloroform Sorption in Nanoporous Crystalline and Amorphous Phases of Syndiotactic Polystyrene

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Received 12 June 2007; revised 18 July 2007; accepted 14 August 2007

DOI: 10.1002/polb.21303

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The transport of chloroform in films of atactic polystyrene and of semicrystalline syndiotactic polystyrene in its nanoporous form (δ -form) has been investigated by gravimetric analysis. Experimental tests have been performed at 35, 49, and 56 °C and at several vapor pressures ranging from 0.5 to 100 Torr. Nonequilibrium lattice fluid prediction of the amorphous sorption behavior was used to enucleate the sorption contribution of the crystalline nanoporous phase from semicrystalline samples. Sorption behavior of the crystalline phase has been interpreted on the basis of Langmuir equation. Moreover, the chloroform sorption at low activities in the crystalline nanoporous phase has been predicted by using Grand Canonical Monte Carlo molecular simulations. Isothermic heats of sorption were also experimentally evaluated for the crystalline phase, and compared with the corresponding prediction of molecular simulation. © 2007 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 46: 8–15, 2008

Keywords: chloroform; Grand Canonical Monte Carlo simulations; isothermic heat of sorption; simulations; syndiotactic polystyrene, transport properties

INTRODUCTION

The sorption behavior of low-molecular weight compounds in semicrystalline polymeric materials is usually assumed to occur only in the amorphous domains; in fact, diffusants are not likely to penetrate and dissolve in the crystalline phase, which is usually denser than the

amorphous one. As a consequence, in most of the cases, solubility in semicrystalline polymers (S) has been assumed to be proportional to the volumetric fraction of the amorphous phase (ϕ_a):¹

$$S = \phi_a \times S_a$$

where S_a is the compound solubility in the totally amorphous polymer. This physical picture, although successful in many cases and simple to handle, is actually oversimplified since the sorption behavior of the amorphous phase is

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Journal of Polymer Science: Part B: Polymer Physics, Vol. 46, 8–15 (2008)
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affected by the constraints imposed by the presence of crystalline domains. Consequently, the behavior of the amorphous phase in a semicrystalline polymer could be generally different from that of a totally amorphous polymer.

Besides constraint effects, the sorption behavior of amorphous domains strongly depends on the physical state of the polymer: significant qualitative and quantitative differences have been evidenced between rubbery (above T_g) and glassy (sub- T_g) states of a polymeric material. Depending on the penetrant and on its activity range, experimental sorption isotherms in rubbery polymers are generally linear or present an upward concavity, if specific interactions are negligible. Accordingly, sorption behavior can be modeled by using different approaches, for example, lattice models²⁻⁴ or van der Waals models.^{5,6} On the other hand, sorption in amorphous glassy polymers is affected by the nonequilibrium nature of macromolecular structure. Several approaches have been proposed which account for this feature, ranging from essentially phenomenological models (e.g., Dual Sorption Model, see reviews by Vieth et al.⁷ and Hopfenberg and Stannett⁸) to the relatively recent nonequilibrium lattice fluid model (NELF).⁹ In the case of glassy polymer, the experimentally observed isotherms are characterized by an initial downward concavity followed, eventually, by an upward concavity which generally sets in when penetrant induced plasticization promotes a sufficient depression of T_g .

There are few cases reported in the literature where the crystalline domain display a non-negligible solubility.¹⁰ In particular, recent studies relative to the complex polymorphic behavior of syndiotactic polystyrene (s-PS) have shown that one of its four crystalline forms (the δ form) is nanoporous and has a density (0.977 g/cm³) significantly lower than amorphous phase in the semicrystalline s-PS (1.051 g/cm³), which is close to that of the atactic polystyrene (a-PS).^{11,12} The monoclinic structure of δ form of s-PS (space group $P2_1/a$; $a = 1.74$ nm; $b = 1.18$ nm; $c = 0.77$ nm; $\gamma = 117^\circ$) has per unit cell two identical cavities fixed on the center of symmetry and bounded by ten phenyl rings (Fig. 1).^{12,13} The volume of these cavities has been evaluated to be about 120 Å³.¹³

Sorption studies from liquid and gas phases, have shown that nanoporous δ -form of s-PS samples are able to absorb suitable guest molecules, even when present at very low concentrations.¹⁴⁻²²

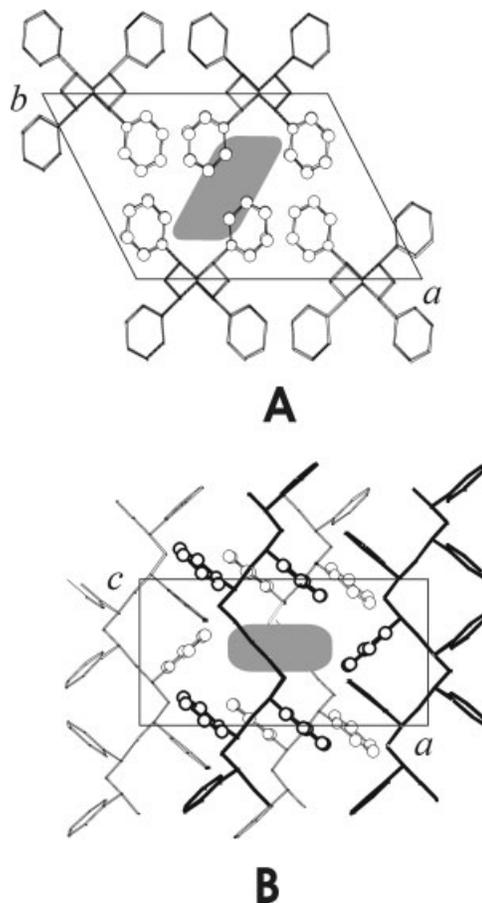


Figure 1. Two different view of the packing of the s-PS δ form: (A) Along the chain axis projection (ab plane) (B) Perpendicular to ac plane. One of the two cavities of the unit cell, confined by 10 phenyl rings (stick and balls represented), are also showed as gray regions.

Guests sorption can eventually lead to the formation of molecular complex phases, being clathrate²³⁻²⁷ or intercalate^{28,29} phases. In particular, clathrate phases are generally characterized by a stoichiometric ratio between guest molecules and s-PS monomer units equal to 1:4, corresponding to one guest molecule per cavity.²³⁻²⁷

When molecules are hosted into the cavities, a distortion of the crystalline lattice can occur depending on the dimension of the guests. For instance, decane or anthracene induce a distortion of the crystalline lattice which corresponds essentially to an increase of the b axis up to 10-15%.^{30,31} Suitable procedures for guest removal, generally involving its replacement by more volatile temporary guests (like acetone, CS₂, or CO₂), allow to easily regenerate the nanoporous form.³²

Previous investigation¹⁵ on vapor chloroform sorption, performed at 35 °C in semicrystalline forms of s-PS has shown that in α , β , and γ form samples sorption occurs, in a small amount, only into the amorphous phase. If the relative pressure of chloroform is high enough, α and γ semicrystalline samples form clathrates while β semicrystalline samples remain unaltered.¹⁵ Moreover, totally amorphous samples are reported to readily form clathrates when exposed to several solvents in vapor phase, including chloroform.^{33–35}

In the case of the nanoporous δ form, a much higher sorption capacity occurs also at low activities. This behavior has been justified by considering a relevant sorption contribution of the crystal nanoporous phase.¹⁵ Experimental analyses of chloroform sorption, performed using *in situ* Fourier transform infrared (FTIR) spectroscopy, have confirmed this hypothesis allowing a quantification of the amount sorbed into the amorphous and nanoporous crystalline phases, respectively.¹⁴

The present investigation is aimed to a deeper analysis of the chloroform sorption behavior in the nanoporous crystalline δ form of s-PS at low vapor activities, where the main sorption contribution derives from the crystalline phase. Gravimetric measurements as well as heat of mixing of chloroform in the nanoporous crystalline and amorphous phases are discussed and compared with prediction of molecular simulations. This study should constitute a useful basis for the development of absorption systems based on this type of material.

EXPERIMENTAL

Materials

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

Film samples of δ form were obtained by a spin coating procedure, at room temperature, from 5 % wt solutions of s-PS in chloroform. The so obtained s-PS semicrystalline films were in a clathrate form which was then transformed into

the nanoporous δ form after treatment by carbon dioxide at 200 bar and 40 °C.³² The residual solvent content in the samples, after these extraction procedures, as evaluated by thermogravimetric measurements, was lower than 0.1%.

The crystallinity of semicrystalline films of δ forms was evaluated to be around 51% by volume through density measurements performed by flotation method at 45 °C, assuming for the amorphous phase a density equal to 1.051 g/cm³ and for the crystalline phase a density of 0.977 g/cm³.¹²

Amorphous samples of a-PS were prepared and used as a reference for sorption into the amorphous phase. These samples were obtained through a casting from a chloroform solution to mimic the protocol adopted to process s-PS. The measured density of such samples was equal to 1.051 g/cm³. We did not use as a reference s-PS amorphous samples for two main reasons. First, amorphous s-PS can only be obtained by quenching from the melt phase, which is expected to induce a much greater amount of frozen excess free volume and, in turn, an increased sorption capability as compared with the amorphous phase of the semicrystalline s-PS δ form. Second, amorphous s-PS samples, when exposed to chloroform vapors, are likely to change structure forming a clathrate.³³ The use of a-PS should not affect the conclusions drawn in the present investigation since the tacticity does not influence significantly the density of polystyrene chains in the amorphous state, as reported in the literature.^{36,37}

All films considered in this article had a squared shape (1×1 cm²) with a thickness ranging from 30 to 40 μ m.

Grand Canonical Monte Carlo Simulation of Chloroform Sorption Gravimetric Analysis

A Grand Canonical Monte Carlo (GCMC) procedure was adopted to simulate chloroform sorption properties of crystalline cell of s-PS at equilibrium. The initial structure of the single crystal of the δ form was generated on the basis of an X-ray diffraction experiment¹² using the Crystal Builder of Materials Studio (v. 4.0; Accelrys, San Diego, CA). The space group is $P2_1/a$, and the main chain conformation is TTGG. According to the space group symmetry, the atomic coordinates were generated from the fractional coordinates of atoms in an asymmetric unit, which are listed in the literature.¹² After

energy relaxation, the cell parameters obtained were the following: $a = 1.76$ nm, $b = 1.33$ nm, $c = 0.77$ nm, $\gamma = 116.8^\circ$, with a density of 0.994 g/cm³. It is worth noting that the unit cell parameters are slightly different from the ones obtained experimentally.¹² This small discrepancy could be attributed to the metastability of the δ crystalline form and to the dependence of related cell parameters on processing procedures.

The Monte Carlo method is a well-known stochastic strategy that relies on probabilities. To simulate a system, transitions between different system states or configurations are achieved by (i) generating a trial configuration randomly; (ii) evaluating an acceptance criterion by calculating the change in energy and other properties in the trial configuration; (iii) comparing the acceptance criterion with a random number, and (iv) either accepting or rejecting the trial configuration. In MC molecular simulations, a new configuration is obtained typically by displacing, exchanging, removing, or adding a molecule. The exact nature of the transition probability depends on the statistical ensemble chosen but it always involves evaluating the energy of the new configuration and comparing it with the energy of the existing (old) configuration. One of the distinctive features of Grand Canonical ensemble is that the number of particles fluctuates while maintaining a constant chemical potential, volume, and temperature. The algorithm for the GC ensemble can be devised as consisting of three attempted moves: particle displacement, particle insertion, and particle removal. Accordingly, a molecular creation attempt is accepted with probability:

$$P_c = \min[1, (V/(N+1)\Lambda^3) \exp(-\Delta U + \mu/k_B T)]$$

where N is the number of molecules in the simulation box before the creation attempt, ΔU is the change in the potential energy accompanying the creation attempt, μ is the chemical potential and Λ is the thermal de Broglie wavelength. The attempt to destroy a molecule, randomly selected from the N existing molecules, is accepted with probability:

$$P_d = \min[1, (N\Lambda^3/V) \exp(-\Delta U + \mu/k_B T)]$$

In the GC ensemble, the chemical potential of the adsorbed molecules equals the chemical potential of molecules in the bulk phase, which

can be written as a function of temperature and fugacity f :

$$\mu = k_B T \ln(f\Lambda^3/k_B T)$$

which can be substituted in the previous expressions for P_c and P_d . At very low pressure, such as those considered in this work, ideal behavior can be assumed, and f can be replaced by gas pressure P . Finally, molecular displacements and rotations are accepted with probability:

$$P = \min[1, \exp(-\Delta U/k_B T)]$$

The total potential energy U of the polymer lattice and adsorbed molecules is written as the sum of the interaction energy between the adsorbate and the polymeric matrix, U_{AB} and that between the adsorbates, U_{AA} . In this work, U_{AB} and U_{AA} are both given by the COMPASS force field expression.³⁸ Periodic boundary conditions were applied to three-dimensions. The van der Waals interactions for the adsorbate–polymer interactions and both the dispersive and electrostatic (Coulombic) terms of the adsorbate–adsorbate interactions were calculated using the minimum image convention, with consistent potential cutoffs. The Coulombic term for the adsorbate–polymer interactions were evaluated using the Ewald summation method. All calculations of ΔU were preceded by a check for overlapping interaction sites. The distance used for the criterion of overlap was set equal to half the sum of the van der Waals radii for the two sites. Any attempt to create, displace, or rotate a molecule accompanying an overlapping of site was not accepted. To achieve system equilibration, the length of the simulation was 1×10^7 Monte Carlo steps. The first 5×10^6 steps were used for equilibration and the last 5×10^6 ones were used for thermodynamic property averaging. The Sorption modulus, as implemented in the Materials Studio platform, was employed for all GCMC calculations.

Gravimetric Analysis

The equipment used to determine weight gain of samples exposed to a chloroform vapor is analogous to that described in a previous contribution³⁴ and is based on a controlled atmosphere electronic microbalance, CAHN D200, with sensitivity equal to 0.1 μ g.

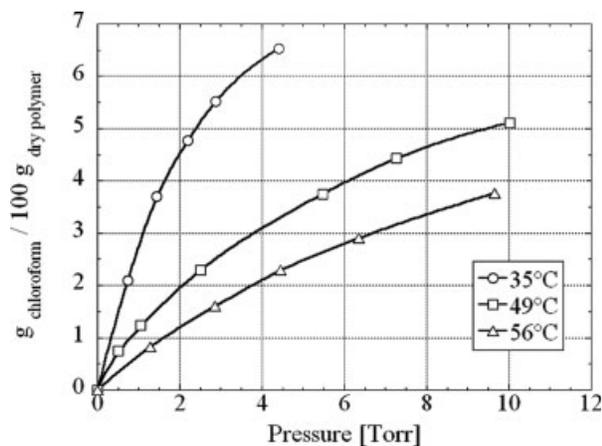


Figure 2. Chloroform sorption isotherms in semicrystalline s-PS δ -form films. The interpolation lines are only used to guide the eye.

Langmuir Equation

The equation originally developed by Irving Langmuir in 1916 relates the coverage or adsorption of molecules on a solid surface to the gas activity of the medium above the solid surface at a fixed temperature. The relationship which has found wide application in amorphous and semicrystalline polymers,^{22,38,39} states that:

$$C = \frac{C'_H bP}{1 + bP}$$

where C is the concentration of the specie adsorbed on the solid surface, P is the gas pressure, and C'_H and b are typical Langmuir constants. In particular C'_H can be related to the saturation level of the gas adsorbed, while b is usually associated to the affinity constant between the polymer and the dissolved gas molecules.

RESULTS AND DISCUSSION

Chloroform sorption isotherms have been experimentally evaluated at three different temperatures (35, 49, and 56 °C) on semicrystalline s-PS δ form films. The results, reported in Figure 2, witness the exothermic nature of the sorption process which is related to the relevant adsorption contribution in the crystalline nanocavities, as will be discussed in the following.

To enucleate the contribution of the crystalline phase, sorbed amount of chloroform in the amorphous phase must be subtracted. To this aim,

sorption experiments have been performed on a-PS samples with a density equal to 1.051 g/cm³ assuming that the behavior of a-PS is equivalent to that of the amorphous phase of semicrystalline s-PS.

Sorption isotherms for a-PS are reported in Figure 3 in the same range of pressures as for the semicrystalline s-PS. A good agreement was found between experimental data and predictions based on NELF model (see Fig. 3), which has been used to produce reliable continuous curves through experimental data to allow data subtraction at the needed pressure values. In evaluating NELF prediction, the density of polymer phase in the mixture has been assumed to be identical to that of pure glassy polymer: this assumption can be safely made when dealing with low sorbed amounts.^{9,40–43}

Sorption contribution of the crystalline phase was then evaluated by performing the subtraction procedure. In Figure 4 are reported the results at the three investigated temperatures.

These results confirm the prominent role of the crystalline phase in the chloroform sorption process at low activities. Further evidence of these findings is offered by results obtained through *in situ* FTIR spectroscopy performed in transmission mode on thin films of s-PS nanoporous δ form during sorption at activities ranging from 0 to 0.16.¹⁴

Chloroform sorption process in the nanoporous crystalline phase can be fitted on the basis of Langmuir equation, assuming that the crystalline phase consists of a collection of adsorption sites. This approach has been already used

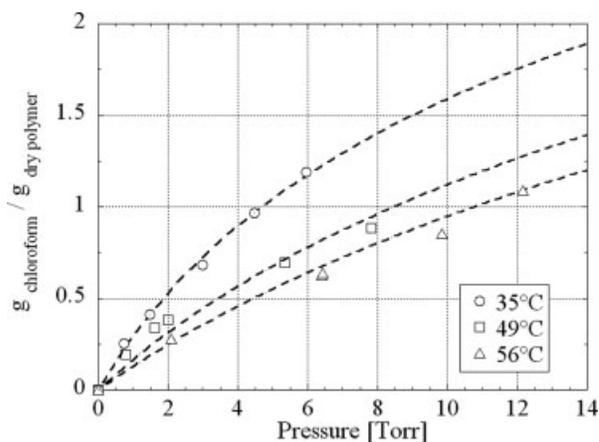


Figure 3. Chloroform sorption isotherms in glassy a-PS films. Dashed lines represent sorption prediction based on NELF model.

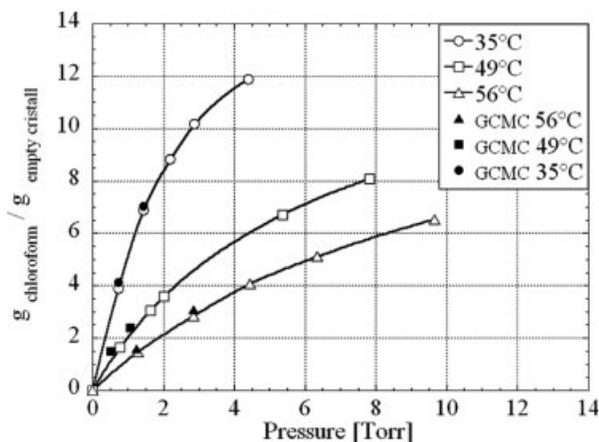


Figure 4. Chloroform sorption isotherms in crystalline s-PS δ -form films. Lines represent fitting by Langmuir equation. Full marks are simulation values by GCMC.

with success in the case of gas sorption data in semicrystalline s-PS δ form films.²²

To get reliable value of the sorption capacity (C'_H), an extended range of pressures has been considered at 35 and 56 °C (see Fig. 5); the corresponding Langmuir parameters are reported in Table 1. It is worth noting that the values of Langmuir adsorption capacity are very close to that one would evaluate theoretically assuming that in each nanocavity can be hosted only one molecule of chloroform (i.e., 28.4 g_{chloroform}/100 g_{crystal}).

Chloroform sorption at extremely low activities in the corresponding crystalline cell was predicted by using GCMC simulations. On the basis of the results reported in Figure 4, a good agreement has been observed between deduced

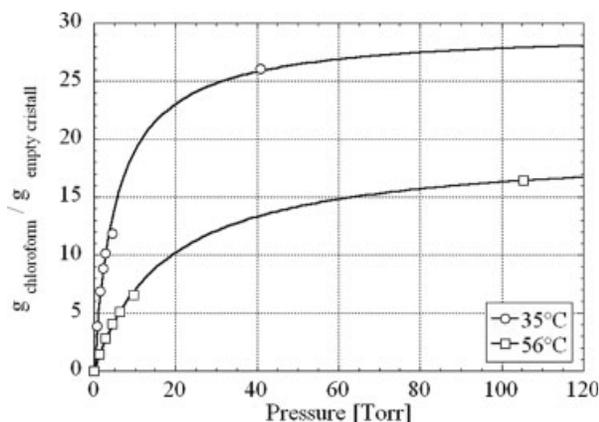


Figure 5. Chloroform sorption isotherms on an extended range of pressure. Lines represent fitting by Langmuir equation.

Table 1. Langmuir Parameters

Temperature (°C)	C'_H	b
35	34.4	0.027
56	29.4	0.182

crystalline sorption curves and the results of simulations performed on the crystalline cell (full marks).

Using sorption isotherms, net isosteric heat of sorption can be evaluated for the case of the amorphous phase, crystalline phase, and for the semicrystalline sample as a whole, by using the following equation:

$$\Delta H = - \left[\frac{\partial(\ln a)}{\partial(1/T)} \right]$$

where the derivation is performed at a constant chloroform loading. The results are reported in Figure 6. The three curves, which report the change of isosteric heat as a function of the chloroform concentration, display a very different behavior reflecting specific morphological peculiarities of the two phases. As for the amorphous phase behavior, physical picture generally assumes a distribution of sorption sites characterized by different heat of mixing: adsorption on excess free volume (exothermic contribution) and absorption in the bulk (endothermic contribution to “create” a hole into the bulk of polymer). This gives raise to the reported dependence of heat of sorption on sorbate concentration. Instead, sorption in the regular array of crystalline nanocavities is strongly exothermic

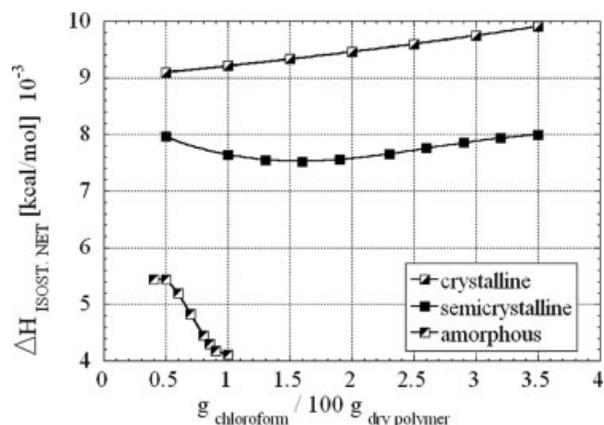


Figure 6. Isosteric heat of sorption as function of chloroform concentration at the average temperature of 45.5 °C.

Table 2. Isothermic Heat of Crystalline Phase

Temperature (°C)	Isothermic Heat (kcal/mol)	
	Simulation	Experimental
35.0	-9.32	
49.0	-9.14	-9.32
55.8	-9.13	

and ideally independent on the penetrant concentration, since only adsorption on cavities surfaces occurs.

Because of the homogeneity of the adsorption sites, isothermic heat should remain constant as a function of concentration. Actually, the calculated values show a slight increase of the heat of sorption which; however, could be related to the intrinsic uncertainty of the calculation procedure. The values for the crystalline phase, as evaluated experimentally, compare well, see Table 2, with the result obtained from molecular simulation. It is also worth noting that the order of magnitude of the isothermic heat of mixing is close to the values detected in the case of activated carbon and of hypercrosslinked polystyrene^{38,39} which are both characterized by nanocavities (although with broad size distributions).

CONCLUSIONS

The gravimetric analysis of the chloroform sorption behavior in the nanoporous crystalline δ form of s-PS, at low vapor activities, has confirmed the high sorption capacity of the crystalline phase. The crystalline phase contribution to the chloroform sorption was obtained by subtraction of the amorphous phase contribution from the experimental chloroform sorption isotherm on semicrystalline s-PS δ form films.

The chloroform sorption isotherms of the s-PS δ form can be satisfactorily fitted with the Langmuir equation. The success of the Langmuir equation can be attributed to the similarity of the process described by the equation with the one occurring during adsorption into the cavities of the nanoporous crystal lattice. The obtained values of the adsorption capacity correspond to one chloroform molecule per cavity.

GCMC simulation of the equilibrium sorption capacities in the crystalline phases at different vapor pressures and temperatures are in good

agreement with the experiments. Similar agreement has been obtained between experiments and molecular simulation for the isothermic heat of sorption of the crystalline phase of s-PS δ samples.

Financial support of “Ministero dell’Istruzione, dell’Università e della Ricerca” (PRIN 2004) and of “Regione Campania” (Legge 5 and “Centro di Competenza per le Attività Produttive”) is acknowledged. The authors thank Dr. Pellegrino Musto and Dr. Giuseppe Milano for useful discussion.

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