Shape and Volume of Cavities in Thermoplastic Molecular Sieves Based on Syndiotactic Polystyrene

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The empty space in different crystalline and clathrate phases of syndiotactic polystyrene (s-PS) is evaluated by a numerical procedure. It is shown that the δ form is nanoporous and includes two identical cavities per unit cell, whose shape and volume are characterized. As a consequence of clathration, the unit cell of the δ form is enlarged and the cavity is able to include molecules definitely larger than its starting size. Sorption experiments of nitrogen at 77 K for s-PS powders in different crystalline forms are also presented. These can be interpreted by inclusion of three nitrogen molecules per cavity of the δ crystalline phase and hence give an independent estimate of its volume.

Introduction

Syndiotactic polystyrene (s-PS) presents 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, γ and δ, containing s(2/1)2 helical chains.[1]

Moreover, several clathrate structures, for which the intensities and the precise locations of the crystalline reflections in the X-ray diffraction patterns slightly change with the kind and amount of the included guest molecules, have been described.[2] The crystalline structures of clathrate forms including toluene,[2e] iodine,[2f] and 1,2-dichloroethane (DCE)[2g] have been characterized by X-ray diffraction studies and their unit cell parameters are collected in Table 1.

The clathrate forms can be obtained by solution crystallization as well as by sorption of suitable organic compounds in amorphous or semicrystalline s-PS samples being in the α, or γ, or δ form.[2] The higher density crystalline β-form, instead, is stable in the presence of these organic compounds, which can be absorbed only in the amorphous phase.[3]

Table 1. Crystal Structure Parameters, Guest Volume Fraction, Guest Volume, and Volume of the Cavity for the δ Form and for Three Different Clathrates of s-PS

crystal structure	a (Å)	b (Å)	c (Å)	γ	guest volume fraction[a]	guest volume (Å³)[a]	cavity volume (Å³)[b]
δ form	17.5[c]	11.8[c]	7.8[c]	118°[c]			115
s-PS/DCE	17.1[d]	12.1[d]	7.8[d]	120°[d]	0.22	91	125
s-PS/iodine	17.3[e]	12.9[e]	7.7[e]	120°[e]	0.29	124	151
s-PS/toluene	17.6[f]	13.3[f]	7.7[f]	121°[f]	0.30	132	161

[a] Guest volume fraction = $V_{guest}/(4 \times V_{styrenic\_unit})$. Volume calculations are based on the van der Waals radii. [b] Calculated with the assumption of $r = 1.8$ Å (see text and Figures 1-3). [c] From ref 4a. [d] From ref 2g. [e] From ref 2f. [f] From ref 2e.

The δ form, whose crystal structure has been recently described (unit cell parameters in Table 1),[4a] can be obtained by removal of the guest molecules from clathrate forms, by suitable solvent treatments.[4b−d] It has a density (0.977 g/cm³) lower than that of the amorphous phase (1.05 g/cm³)[4a] and it is readily transformed into clathrate forms upon exposure to suitable volatile organic compounds also when present at very low activities.[5]

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To 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.

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).[6] However, in that case the molecules do not form clathrate structures but dissolve into the crystals at about one-third to one-fourth the level they do in the amorphous phase.

Sorption studies from liquids and vapors have suggested that this thermoplastic material is promising for applications in chemical separations as well as in water purification.[5]

As for molecular separations with these nanoporous polymeric materials, depending on the nature of the molecular mixtures, different mechanisms can operate. For instance, for separation of the azeotropic solution acetone−chloroform, the preferential retention of the halogenated compound[5d] would be essentially enthalpy driven. In fact, for halogenated compounds strong van der Waals and electrostatic interactions involving the host phenyl rings and the guest halogen atoms are present.[7]

On the other hand, for separation of hexane−cyclohexane solutions,[5d] the preferential retention of the cyclic molecules is expected to be associated essentially with an entropic effect. In fact, the enthalpy gains associated with host−guest interactions are expected to be similar for linear and cyclic aliphatic hydrocarbons, while the entropy reduction is expected to be higher for linear hydrocarbons, which, as a consequence of inclusion in the host cavities, should reduce drastically their conformational freedom. Of course, also chemical separations, due to size-exclusion effects, have to be expected.

Accurate knowledge of the distribution of empty space in the δ form and hence of shapes and volumes of possible cavities and channels as well as of their changes as a consequence of guest clathration is a necessary starting point for rationalization of host−guest interactions and of observed separation phenomena.

In this paper, the empty space available for guest molecules in the δ crystalline phase of s-PS has been evaluated starting from the available crystalline structure,[4a] by applying a numerical procedure developed for this purpose.

For the sake of comparison, evaluations of empty spaces have also been applied to crystal structures of α[8] and β[9] forms (in particular, to the limit ordered modifications α'' and β'' of s-PS). Moreover, to estimate possible changes in shape and increases in volume of the cavities as a consequence of guest inclusion, theoretical empty spaces, corresponding to guest removal from available crystal structures of s-PS clathrate forms,[2e−g] have also been evaluated.

With the aim of contributing to the establishment of the size of the crystalline cavity of these nanoporous polymeric materials, sorption experiments of nitrogen at low temperature on semicrystalline and clathrate s-PS samples have also been conducted.

Calculation Method

The implemented procedure for volume evaluations considers, for the different unit cells, grids along the crystallographic axes. As the first step for empty space evaluation, for a given probe sphere radius (r), a set of points is selected that satisfy the inequality

$$d_{min}(i,j,k) \geq r + r_{vdw}(i,j,k)$$

where $d_{min}(i,j,k)$ is the distance between the generic point $P(i,j,k)$ of the unit cell grid and its first-neighbor atom of van der Waals radius $r_{vdw}(i,j,k)$. The empty volume, for a given r, is defined by the envelope surface of a set of spheres, of radius r, centered on this set of points. Calculation of the volume contained in the envelope surface is done by the numerical code GE-POL.[10]

Numerical stability of the computed volumes (± 0.2 Å³) is reached for grid steps lower or equal to 0.4 Å. For the reported calculations, a grid step of 0.3 Å for all the crystallographic directions has been adopted.

Experimental Section

The s-PS sample was supplied by "Istituto Guido Donegani" of Enichem and has been obtained by using as the catalyst $CpTiCl_3$ and methylalumoxane (MAO).[11] The percent of *rrr* tetrads evaluated by the methylene region of ^{13}C NMR spectra is 92%. The molecular weight, determined by GPC analysis on trichlorobenzene, is 7×10^5 (polydispersity = 3.3).

The γ form powder was obtained by treatment at 130 °C of the as-polymerized powder. The s-PS/DCE clathrate powder was obtained by treatment of the γ form powder by boiling DCE for 4 h; the DCE content in the sample, evaluated by thermogravimetric measurements, was reduced to 8%, by leaving the sample in air at room temperature for 1 month. This desiccation procedure produces substantial removal of DCE from the amorphous phase while the clathrate phase is only marginally affected.[5e] The δ form powder was obtained by treatment of the DCE clathrate by supercritical CO_2[4] at 40 °C and 200 bar for 5 h and present a DCE content lower than 1%. Thermogravimetric analyses were carried out by a Mettler TG50 thermobalance in a flowing nitrogen atmosphere at a heating rate of 10 °C/min.

Wide-angle X-ray diffraction patterns of powder samples were obtained with nickel-filtered Cu Kα radiation by an automatic 1710 Philips diffractometer. Degrees of crystallinity

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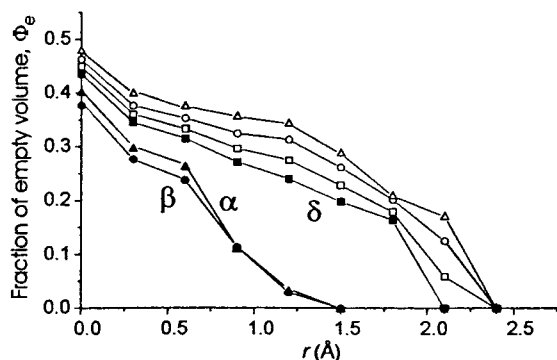(11) Zambelli, A.; Longo, P.; Pellecchia, C.; Grassi, A. *Macromolecules* **1987**, *20*, 2035.

Figure 1. Fraction of empty volume (Φ_e) that can be filled by a hypothetical sphere of radius r, for β (●), α (▲), and δ (■) crystalline forms of s-PS. The theoretical empty volumes relative to the crystalline structures of s-PS clathrates with 1,2-dichloroethane (□), iodine (○), and toluene (△), obtained by neglecting the guest molecules, are also reported as empty symbols.

Figure 2. Difference between fractions of empty volume (Φ_e, taken from Figure 1) of different crystalline forms, with respect to those of the most dense (β) crystalline form, plotted as a function of r. Values relative to the crystalline structures of s-PS clathrates with 1,2-dichloroethane (□), iodine (○), and toluene (△), obtained by neglecting the guest molecules, are also reported as empty symbols.

(X_c) have been determined resolving the diffraction patterns, in the selected 2θ range (4°−40°), into two areas, A_c and A_a, that can be taken as proportional to the crystalline and amorphous fractions of the copolymer, respectively, and calculated through the expression $X_c = 100A_c/(A_c + A_a)$.

The shape of the amorphous halo has been obtained by a wide-angle X-ray diffraction pattern of a compression moulded s-PS sample quenched into a water−ice mixture and then milled to remove possible molecular orientation.

Nitrogen adsorption experiments were conducted by a Thermoquest Sorptomatic 1990. Powder samples (70−100-mesh size) were outgassed (10^{-4} Torr) at ambient temperature. For specific surface area calculation, the two-parameters BET method in the range 0.05−0.30 p/p^0 was used.

Results and Discussion

Empty Volume in Crystalline Phases of s-PS. Crystal structure data contain all the information necessary to evaluate the empty volume fraction as well as the shapes and sizes of possible empty spaces (cavities and/or channels).

In principle, the fraction of empty volume of the crystalline phase could be evaluated as the difference between the volume of the unit cell and the volume occupied by the van der Waals spheres of the host atoms. However, such evaluation considers as empty space also regions too small to include the smallest atoms and would lead to high values of empty volume fractions for all the crystalline structures. For instance, by these evaluations the empty volume fraction would be equal to 0.38, 0.40, and 0.48 for the crystalline structures proposed for the β,[8] α,[9] and empty δ[4a] forms of s-PS, respectively.

The fraction of empty volume (Φ_e) can be more significantly defined on the basis of the volume that can be filled by a hypothetical sphere of radius r, as described in the section devoted to the calculation methods. For β ($\rho = 1.078$ g/cm³), α ($\rho = 1.033$ g/cm³), and δ ($\rho = 0.977$ g/cm³) crystalline forms of s-PS, the fractions of empty volume, calculated as a function of r, are reported in Figure 1.

The differences between the curves of Figure 1 are relatively small for low values of r (<0.5 Å) while becoming large for r values in the range 1−2 Å, corresponding to van der Waals radii of common atoms.
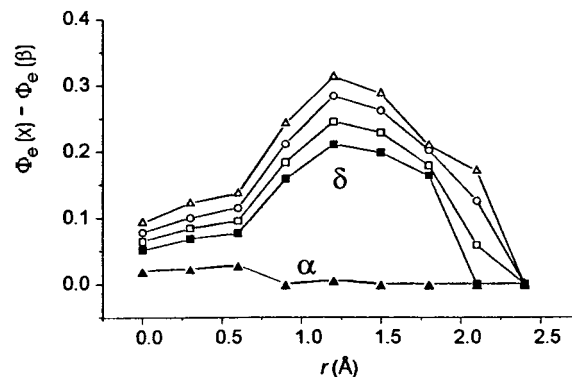
This is more clearly shown in Figure 2, where the difference between the Φ_e values of the different crystalline forms with respect to the Φ_e values of the most dense crystalline (β) form is plotted as a function of r.

The plot of Figure 2 suggests that the fraction of empty space in the δ form, available to the guest molecules, can be as high as 0.20.

The theoretical empty volumes relative to the crystalline structures of clathrates with 1,2-dichloroethane,[2g] iodine,[2f] and toluene,[2e] obtained by neglecting the guest molecules, are also reported as empty symbols in Figures 1 and 2.[12] These volumes are only hypothetical empty spaces because in reality the guest removal from the filled clathrates leads to the δ form. However, these hypothetical empty spaces give a measure of possible expansions of the cavity of the nanoporous crystalline structure as a consequence of clathration. It is apparent from Figure 2 that, as a consequence of guest clathration, an expansion of the crystalline structure occurs and the volume fraction of the crystalline phase available to guest molecules can become substantially larger (up to nearly 0.30).

The data of Figure 2 compare well with simple evaluations of volume fractions of guest molecules into the clathrate crystal structures, based on the van der Waals encumbrances of host and guest atoms in the unit cell, which are in the range 0.22−0.30 (sixth column of Table 1).

Shape and Volume of the Cavities in the Nanoporous Crystalline Phase. The region of empty space calculated for the δ form, by assuming $r = 1.8$ Å, that is a typical van der Waals radius of chlorine atoms or methyl groups[13] is shown as a dotted region for three different views of the unit cell, along c and perpendicular to ac and bc planes, in Figure 3. The figure shows that this empty space corresponds to finite cavities (two per unit cell) centered on the center of symmetry of the crystal structure, whose boundary is essentially defined by 10 phenyl rings. By considering, for instance, the

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(12) It is worth recalling that for the clathrate s-PS/iodine two I_2 molecules per cavity, while for the other considered clathrates only one molecule per cavity, are included.

(13) See e.g.: Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1996**, *118*, 11225.
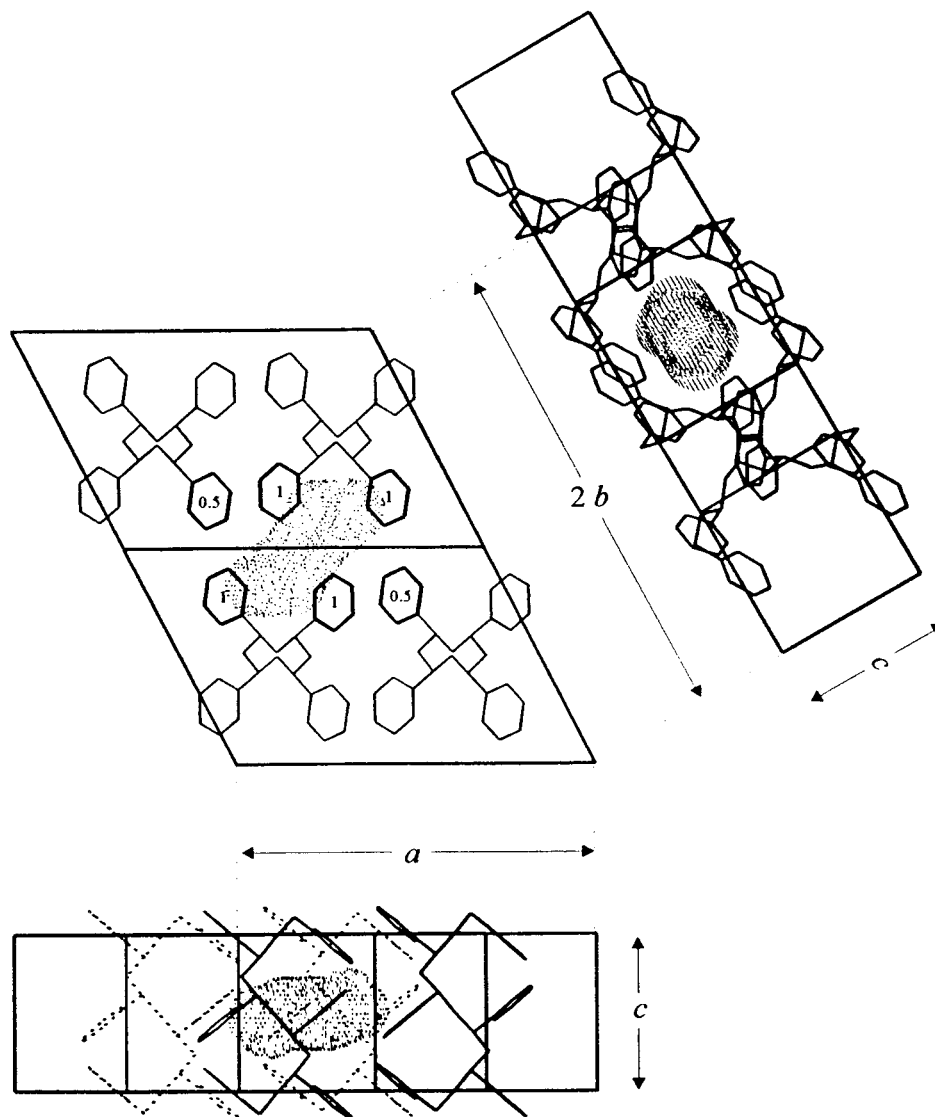
Figure 3. Region of empty space (dotted) calculated for the δ form, by assuming $r = 1.8$ Å (that is a typical van der Waals radius of chlorine atoms or methyl groups) shown for three different views of two unit cells: along c and perpendicular to ac and bc planes. Along the c view, the phenyl rings that define the boundary of the cavity are bolded and labeled by heights (expressed as fractions of $c = 7.7$ Å).

view along the c axis, there are four phenyl rings below the cavity (average height 0), four phenyl rings above the cavity (average height $c = 7.7$ Å), and two phenyl rings whose average height is equal to the average height of the cavity ($c/2$) (bolded rings in Figure 3). For a probe sphere with $r = 1.8$ Å, the cavity has a volume of nearly 115 Å^3 and its maximum dimension is nearly 8.1 Å (essentially along the $a-b$ direction) while its minimum dimension is nearly 3.4 Å (essentially along the c axis).

Following the same procedure, the shapes and volumes of the hypothetical cavities generated by ignoring the presence of the guest molecules have been evaluated for the clathrate structures and the relative cavity volumes are reported in the last column of Table 1.

It is apparent that, for the case of inclusion of two molecules per cavity (s-PS/iodine clathrate) or of a bulky guest molecule (s-PS/toluene clathrate), the volume available to the guest molecules can be substantially larger (up to 160 Å^3) than the volume of the cavity of the δ form. However, independently of the size and shape of the guest molecule, the calculated cavities present shapes and orientations similar to those found for the empty δ form (Figure 3).

The crystal structure data, collected in columns 1−5 of Table 1, show that, as the volume of the guest molecule increases, substantial increments of the b axis (up to 15%), with respect to the values observed for the δ form, are observed. Correspondingly, not only the c axis (corresponding to the chain repeating unit) but also the a axis remains essentially constant.

In the simplifying assumption that inclusion of guest molecules into the δ form would produce substantially only an increase of the b value, leaving nearly unaltered all the other unit cell parameters as well as the s-PS chain fractional coordinates, the dependence of the volume of the cavity on the b value has been calculated and shown by a continuous curve in Figure 4. The approximate validity of this assumption is confirmed by a satisfactory fitting of the values of cavity volumes calculated on the basis of the true crystal structures for the three clathrate structures (listed in Table 1 and shown by stars in Figure 4).
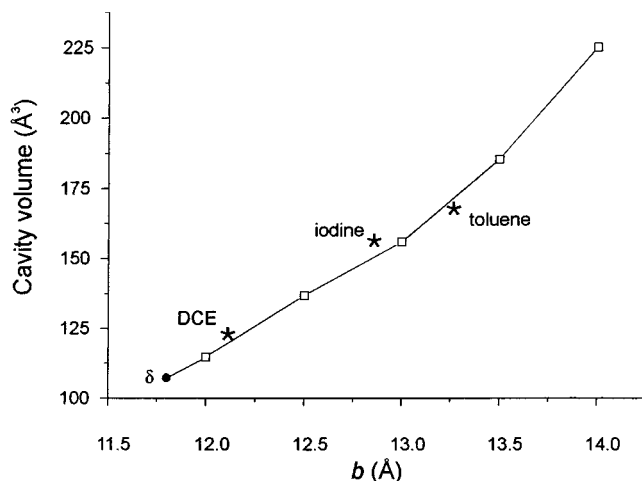
Figure 4. Volume of the cavity calculated as a function of the unit cell parameter b (□), calculated in the simplifying assumption that inclusion of guest molecules into the δ form leaves unaltered the other unit cell parameters as well as the s-PS chain fractional coordinates. Cavity volumes calculated on the basis of true crystal structures for three clathrates (listed in Table 1) are shown by stars. All calculations assume $r = 1.8$ Å.

The data of Table 1 and Figure 4 suggest that molecular modeling studies of host−guest interactions, like those reported in ref 7c, can be reasonably extended to other guest molecules, also in the absence of crystal structures of the corresponding clathrates.

In this respect, the calculated curve of Figure 4 can be helpful in getting approximate evaluations of the volumes of cavities for clathrate forms whose crystalline structures are unknown. In fact, the b value can be easily obtained already from X-ray diffraction patterns of unoriented samples by just measuring the precise 2θ position of the 010 reflection ($b = \lambda/2 \sin \theta_{010}$), nearly located at 8° for the case of the Cu Kα radiation.

Nitrogen Sorption by Semicrystalline s-PS Samples. Following a standard procedure for porosity evaluation of powders,[14] nitrogen sorption experiments at low temperature (77 K) on amorphous and semicrystalline s-PS samples have been conducted. In particular, as for semicrystalline samples s-PS powders in the γ form or in the DCE clathrate form or in the nanoporous δ form, whose X-ray diffraction patterns are shown in Figure 5A, B, and C, respectively, have been considered.

The δ form sample was obtained by CO_2 treatment of the clathrate sample, which in turn was obtained by DCE treatment of the γ form sample (see Experimental Section). The three samples present similar morphologies and their crystallinity indexes, evaluated on the basis of the patterns of Figure 5, are all in the range 30−43%.

Sorption and desorption isotherms of γ and δ form samples are compared in Figure 6, where the sorption is expressed as cm^3 of nitrogen in normal conditions (1 atm, 0 °C) per gram of polymer. The sorption behavior of a s-PS/DCE clathrate is essentially coincident with that of the γ form and is not reported.

It is worth noting that the sorption by amorphous samples is also smaller than the sorption by γ phase
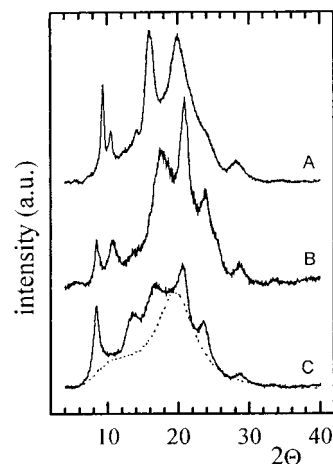
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Figure 5. X-ray diffraction patterns of s-PS samples used for nitrogen sorption experiments: γ form (A), DCE clathrate (B), and δ form (C) powders. The dashed line shows the amorphous halo used for crystallinity index evaluations.
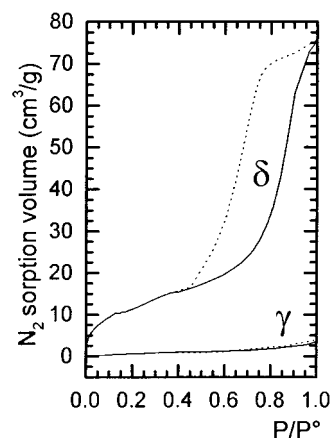

Figure 6. Sorption (continuous curves) and desorption (dashed curves) isotherms of nitrogen at 77 K into s-PS powder samples, including γ and δ crystalline phases. The sorption is expressed as cm^3 of nitrogen in normal conditions (1 atm, 273 K) per gram of polymer.

samples, possibly due to lower surface areas, generated by the melt processing.

Sorption of the nanoporous form is already higher for low nitrogen activities: for instance, at $p/p^0 = 0.4$, the sorption is close to 15 cm^3/g for the δ form while it is only 2 cm^3/g for the γ form. The specific surface area, as evaluated in the range 0.05−0.30 p/p^0, is 4 m^2/g for the DCE clathrate and γ form samples.

Moreover, starting from $p/p^0 \approx 0.6$, there is a steeper increase of sorption of the δ form up to $p/p^0 \approx 0.9$. This makes the sorption difference between the δ form and the other semicrystalline samples particularly large (nearly 70 cm^3/g) at $p/p^0 = 0.98$. It is also worth noting that for the δ form powder there is a remarkable hysteresis in the sorption−desorption phenomenon.

Because the three samples present similar crystallinities, it can be reasonably assumed that the sorption increase observed for the δ form sample is essentially associated with condensation of nitrogen molecules into the crystalline nanoporous phase and that the observed hysteresis is due to the formation of polymer−gas intercalates.

A Possible Evaluation of Volume of the Crystalline Cavities by Nitrogen Sorption Experiments.

In the assumption of formation of s-PS/nitrogen intercalates, the number of N_2 molecules per crystalline cavity can be approximately evaluated. In fact, if n_{N_2} and n_{cavity} are moles of nitrogen and cavities, respectively, for a given mass of polymer M_{pol}, then

$$\frac{n_{N_2}}{n_{cavity}} = \frac{(PV_{N_2}M_{pol})/RT}{(M_{pol}X_c)/4M_{styr}} = \frac{4PV_{N_2}M_{styr}}{RTX_c} = 0.0186\,V_{N_2}/X_c$$

$$(1)$$

where V_{N_2} is the volume of nitrogen (for $P = 1$ atm and $T = 273$ K) sorbed in the crystalline phase per gram of polymer, M_{styr} is the molecular mass of the styrenic unit, X_c is the crystalline fraction of the δ form polymer sample, and 4 is the number of styrene units per cavity in the δ crystalline phase.

A possible evaluation of the degree of crystallinity of δ form samples can be taken from X-ray diffraction paths of Figure 5C (as described in the Experimental Section).[15]

On the basis of eq 1, by taking $V_{N_2} = 70$ cm^3/g (from Figure 6), and $X_c = 0.43$ (from the X-ray diffraction pattern of Figure 5C), the number of nitrogen molecules per crystalline cavity is calculated to be close to 3.

Two possible limit evaluations of the space occupied by the molecule of N_2 can be obtained considering the space occupied by three molecules in the two possible nitrogen crystalline structures (cubic and hexagonal):[16] 137 and 163 Å^3, respectively.[17] In our assumptions these volumes can be taken as a rough evaluation of the volume of the cavity of the crystalline phase. This independent evaluation is in satisfactory agreement with the calculated volumes of column 8 in Table 1.

Conclusions

Shape and volume of empty space of the nanoporous crystalline phase of syndiotactic polystyrene have been evaluated by considering the space available to probe spheres of given radii into crystalline structures of different polymorphic forms of this polymer.

This kind of analysis, for probe sphere radii higher than 1.3 Å, shows that the empty space into the nanoporous form corresponds to cavities (two per unit cell) centered on the center of symmetry of the crystal structure, whose boundary is essentially defined by 10 phenyl rings. The volume of these cavities, evaluated for probe spheres with a radius of 1.8 Å, is close to 115 Å^3.

Analogous calculations relative to clathrate forms of this polymer show that, as a consequence of clathration, the unit cell (mostly the b axis) is enlarged and its cavity becomes able to include molecules that are definitely larger than its starting volume (e.g., see Table 1). Correspondingly, the size, shapes, and number of included guest molecules poorly affect shape and orientation of the cavity. This suggests that molecular modeling studies of host−guest interactions can be reasonably performed also in the absence of specific crystal structure data of corresponding clathrates.

Sorption experiments at low temperature show that the nitrogen sorption by nanoporous δ form samples is much higher than that by amorphous as well as other semicrystalline and clathrate s-PS samples.

This kind of sorption cannot be treated by the widely accepted physical models of transport in semicrystalline materials, which assume that the crystalline phase is impenetrable.[18] In fact, for these materials, the sorption from the amorphous phase is substantially negligible with respect to the sorption from the crystalline phase.

In the assumption of the formation of s-PS/N_2 intercalates the experimental data can be interpreted by sorption of three nitrogen molecules per crystalline cavity. This allows an independent evaluation of the volume of the cavity, which is in fair agreement with the evaluation based on structural considerations.

Experiments are in progress to explore possible applications of this kind of nanoporous material for chemical separations based on size exclusion.

(15) Calorimetric measurements are not helpful for crystalline degree evaluations because the δ phase upon heating is transformed into the γ phase and only a weak exothermic peak (also superimposed with the variation of the specific heat typical of the glass transition) is observed. Also, crystallinity evaluations based on density measurements by flotation are difficult because of the high tendency of these nanoporous samples to absorb several molecules also when present only in traces.

(16) Wyckoff, R. W. G. In *Crystal Structures*; J. Wiley & Sons: New York, 1963.

(17) The space occupied by three N_2 molecules is considered as three-halves and three-fourths of the volumes of the dimolecular cubic and tetramolecular hexagonal unit cells, respectively.

(18) Michaels, A. S.; Bixler, H. J. *J. Polym. Sci.* **1961**, *50*, 393.