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Gas sorption and transport in syndiotactic polystyrene with nanoporous crystalline phase

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Abstract

In this contribution we analyse sorption and transport of several gases in semicrystalline syndiotactic polystyrene with nanoporous crystalline δ form. Investigation was performed on amorphous samples and on samples characterized by different degrees of crystallinity. Sorption isotherms of carbon dioxide, nitrogen and oxygen in the crystalline phase have been determined starting from experimental results obtained for semicrystalline and amorphous samples. Corresponding isosteric heats of sorption were evaluated for the crystalline and amorphous phase. Permeation tests were also performed to gather information on mass transport properties of semicrystalline samples, evaluating average diffusivities of carbon dioxide and oxygen, in the limit of small concentrations as function of degree of crystallinity.

Keywords: Syndiotactic polystyrene; δ form; Solubility

1. Introduction

Syndiotactic polystyrene (s-PS) is characterized by an elevated melting point (260 °C) and an high crystallization rate. Several structural studies have revealed a complex polymorphic behaviour [1–3]. The various crystalline modifications differ with respect to the chain conformation as well as to the chain packing within the unit cell. Referring to the nomenclature proposed in the literature [2], four main crystalline forms may be distinguished denoted as α, β, γ and δ. The first two, α and β have the chains in the *trans*-planar, zigzag conformation with identity period 5.1 Å [4,5], while the γ and δ forms show a helical s(2/1)2 conformation of the chain with identity period of 7.7 Å [6]. Clathrate structures which include several different guest molecules have also been described [7–9].

Treatments by several volatile organic compounds (mainly halogenated or aromatic hydrocarbons) not only can induce crystallization of amorphous samples but can also transform α and γ crystalline forms into clathrate forms. Only the β form does not give clathrates when contacted with these low molecular weight compounds [10], consistently with its higher density (1.078 g/cm^3) as compared to that of the other crystalline forms.

It has been recently found that, by using suitable extraction procedures [6,11], guest molecules can be removed from the clathrate forms to obtain a nanoporous δ form whose crystalline structure has been recently described [6,12]. The structure of this nanoporous crystalline form of s-PS is reported in Fig. 1, where the dashed area represents volume of the nanocavities located in the crystalline cell as probed by a hard sphere with a 1.8 Å radius. The volume of these cavities has been evaluated [12] to be about 120 Å^3.

Due to the peculiar structure of the crystalline δ form, the corresponding semicrystalline s-PS is characterized by uncommon sorption and transport properties [13–15].

In the following we briefly review some relevant concepts generally accepted for sorption of low molecular weight compounds in amorphous and semicrystalline polymers and discuss them in relationship with peculiarities expected for the polymer under investigation.

The sorption characteristics of amorphous polymers strongly depends on the physical state of the material: in

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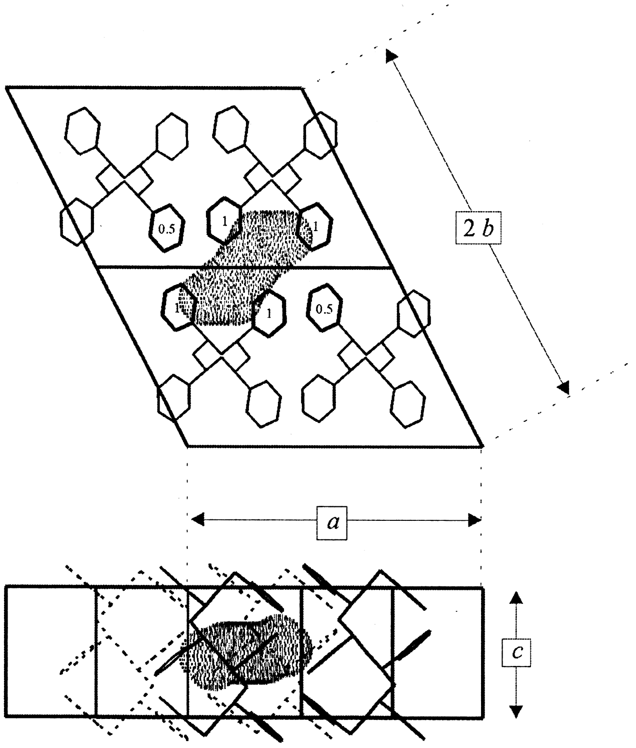

Fig. 1. Molecular chain conformations in the crystalline δ form of s-PS.

fact, significant qualitative and quantitative differences have been evidenced between glassy (below glass transition temperature, T_g) and rubbery (above T_g) states of a polymeric material. In general, sorption in rubbery amorphous polymers can be modeled by using several approaches as, for example, lattice models [16–18] and van der Waals models [19], whereas in the case of amorphous glassy polymers, approaches range from essentially phenomenological models, e.g. Dual Sorption Model [20,21], to a recently proposed Non Equilibrium Lattice Fluid model (NELF) [22]. Sorption theories for glassy polymers take into account the non-equilibrium nature of the macromolecular structure.

In the case of NELF, a pseudoequilibrium conditions for sorption of gases in amorphous glassy polymers is imposed by equating the penetrant chemical potential in the gas phase to that in the solid polymer mixture. In particular, the penetrant chemical potential in the polymer mixture takes the form:

$$\mu_1^{(S)}(T,p,\rho_2,\omega_1) = \left(\frac{\partial G^{(S)}}{\partial n_1}\right)_{T,p,\rho_2,n_2}$$
$$= RT\ln(\tilde{\rho}\phi_1) - RT[r_1^0 + (r_1 - r_1^0)/\tilde{\rho}]\ln(1-\tilde{\rho}) - r_1$$
$$- \tilde{\rho}[r_1^0 v_1^*(p_1^* + p^* - \phi_2^2\Delta p^*)]$$

where ω_i and ϕ_i are, respectively, the weight and volume fraction of component ‘i’ (subscript 1 stands for the gas and subscript 2 stands for the polymer), r_1^0 and r_1 are, respectively, the number of lattice sites occupied by a gas molecule in the pure state and in the solid mixture, $\tilde{\rho}$ is the dimensionless mixture density ($\tilde{\rho} = \rho/\rho^*$, where ρ is the density of the mixture and ρ^* is a mixture parameter), p_i^* and v_i^* are equation of state parameters for pure component ‘i’.

The characteristic pressure, p^* of the polymer mixture is related to p_1^* and p_2^* through the following expression:

$$p^* = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1\phi_2\Delta p^*$$

where $\Delta p^* = \psi(\sqrt{p_1^*} - \sqrt{p_2^*})^2$ with ψ the mixing parameter, which measures the deviation from the empirical geometric mean combination rule.

In order to evaluate the chemical potential, one needs to know the appropriate value of the mixture density, ρ, or, alternatively, the value of polymer density, $\rho_2 = \omega_2\rho$. The polymer density, is the internal state variable for the system describing the distance from equilibrium. The value of ρ_2 could be obtained, in principle, from the knowledge of bulk rheology of the system or from direct value of dilation data. However, for the case of low penetrant pressure, one can adopt the density value of the pure unpenetrated glassy polymer [23].

NELF approach has been proved to satisfactorily predict sorption isotherms of several gases in different amorphous glassy polymers [23–26]. Data fitting can be optimised by properly fixing the value of the binary parameter (ψ) which takes into account the deviation of the gas/polymer pair energy of interaction from geometric mean of the values for pure components [17].

In semicrystalline polymers it is usually assumed that low molecular weight compounds are absorbed only in the amorphous domains and cannot penetrate and dissolve in the crystalline phase, which is generally denser than the amorphous one. As a consequence, in most of the cases, solubility in semicrystalline polymers (S) can be expressed as [27]:

$$S = \phi_a S_a$$

where ϕ_a is the volume fraction of amorphous phase and S_a is the compound solubility in the amorphous phase.

This physical picture, although substantially correct in many cases and simple to handle, is actually oversimplified since the sorption behaviour of the amorphous phase can be affected by the constraints imposed by the presence of crystalline domains distributed in the sample and to the peculiar behaviour of interphases [28]. Moreover, few notable exceptions have been reported to the generally observed impermeability of the crystalline phase. One of these exceptions is the semicrystalline poly(4-methyl-1-pentene), for which a non negligible gas solubility has been measured in the crystalline phase [29,30]. However, it is worth of note that the solubility coefficients of CO_2 and CH_4 for the crystalline region of poly(4-methyl-1-pentene) are still four to five times smaller than that those of the amorphous phase [29].

In the case of the nanoporous crystalline phase of s-PS, sorption is expected to occur in localized sorption sites (the nanocavities) where guest molecules can be hosted. Each cavity has a well defined structure and dimension. As a consequence, the crystalline phase can be envisaged as a collection of identical specific interaction sites and a Langmuir-type equation can be adopted to interpret sorption isotherms. Langmuir equation is expressed as:

$$C = \frac{C'_{\mathrm{H}} bp}{1 + bp}$$

where C is the equilibrium concentration of low molecular weight molecule in the crystalline phase, p is the pressure of gas or vapour in contact with the polymer and C'_{H} is the saturation sorption capacity and b is the host–guest affinity constant.

In this contribution we analyse the equilibrium sorption behaviour and permeation of three permanent gases (carbon dioxide, nitrogen and oxygen) in semicrystalline s-PS with nanoporous crystalline phase. The sorption and mass transport properties evaluated for samples with different degrees of crystallinity are discussed in terms of crystalline structure.

2. Materials

Semicrystalline s-PS films with a nanoporous crystalline form have been obtained by following the protocol reported below. The starting s-PS pellets, supplied by DOW Chemical (Questra 101), were extruded to obtain films with thickness ranging from 80 to 120 μm. The resulting mesomorphic s-PS films have been then crystallised by exposure to boiling THF at atmospheric pressure, for about 2 h. Characterization of the films by X-ray and FTIR spectroscopy confirmed the presence of the s-PS clathrate form containing THF molecules.

Formation of the nanoporous δ form was hence induced removing the THF by exposition of the films to CS_2 vapour. In fact, CS_2 replaced the THF molecules inducing the formation of a CS_2 clathrate characterized by a weak host–guest interaction. CS_2 was then easily removed by keeping the films in air at atmospheric pressure. The presence of a nanoporous crystalline δ form has been assessed through X-ray spectroscopy on the prepared samples. Fig. 2 displays a diffraction pattern of one of the semicrystalline samples (the sample with 18% crystallinity referred in the following as s-PS18), where the peak positions are those peculiar of the s-PS δ form [6]. In fact, the δ form, as compared to clathrate forms (see for instance the THF clathrate reported as well in Fig. 2), is characterized by reduced intensity of $\bar{2}10$ reflection and enhanced intensity of $\bar{1}11$ reflection, which are located for Cu Kα radiation at $2\theta \cong 10°$ and 13° respectively. The low intensity ratio between 010($2\theta \cong 8°$) and $\bar{1}11$ reflections (compare patterns 'a' and 'b' in Fig. 2) indicate the occurrence of a low degree of perpendicular orientation of chain axis of the crystalline phase with respect to the film surface [31]. In particular the degree of orientation of the crystalline phase, evaluated through the Hermans' orientation function [32], for all the considered samples, is lower than 0.5.

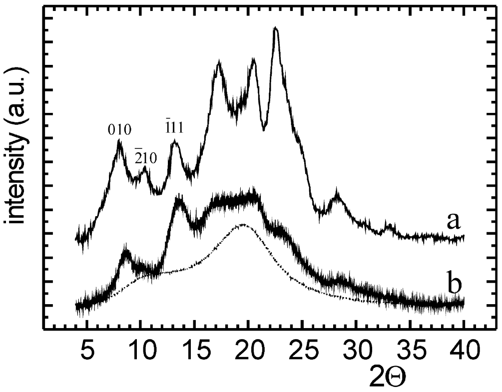

Fig. 2. X-ray diffraction pattern (Cu Kα) of a THF clathrate (pattern 'a') and of the sample s-PS18 in δ form (pattern 'b'). Dotted pattern represents the amorphous halo.

Changing the contact time with THF, different degrees of crystallinity were obtained. Samples characterized by volumetric crystallinity equal to 5, 9.5 and 18% were prepared. In the following these samples will be referred to as s-PS5, s-PS10 and s-PS18, respectively. Crystallinity was evaluated through density measurements performed by flotation method at 45 °C, assuming for the amorphous phase a density equal to 1.051 g/cm^3 and for the crystalline phase the density of 0.977 g/cm^3, typical of the δ crystalline form [6]. In the gas sorption and permeation analysis performed in this investigation, we have neglected changes of polymer density in the range of investigated temperatures. Amorphous samples of atactic PS (referred in the following as a-PS) were used as a reference. These samples were obtained through a casting from a THF solution to mimic the protocol adopted to process s-PS. The measured density of such samples was equal to 1.051 g/cm^3.

We did not use as a reference s-PS amorphous samples since these can only be obtained by quenching from the melt phase, which is expected to induce a much greater amount of frozen excess free volume. 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 [33,34].

3. Experimental methods

3.1. Sorption tests

An electronic microbalance, CAHN D200, with a sensitivity equal to 0.1 μg, equipped with a controlled environment cell, has been used to perform gas sorption tests at sub-atmospheric pressures (from 80 to 760 Torr).

The head of the balance was kept at a constant temperature (35 °C) while the temperature of the sample pan was controlled by means of a water jacket. The microbalance was connected through service lines to the rest of the apparatus equipped with a pressure transducer, a 'Pirani' vacuometer, a glass flask and connected to the gas cylinder and a turbomolecular vacuum pump.

Before performing sorption tests, the samples were first desiccated into the microbalance at 60 °C under vacuum until the attainment of a constant weight. Consecutive sorption–desorption cycles were performed at three temperatures (35, 45 and 55 °C) on samples s-PS10, s-PS18 and on a-PS. Pressure was monitored by means of a MKS Baratron 121 pressure transducer with a full scale of 1000 Torr, a sensitivity of 0.1 Torr and an accuracy of ± 0.5% of the reading.

3.2. Permeation tests

Permeation tests were performed in gas-membrane-gas configuration apparatus based on the measurement of the pressure increase of the downstream side, while maintaining a constant upstream side driving pressure. The apparatus and experimental procedure were similar to those reported elsewhere [35]. In each experiment sufficient time was allowed to ensure attainment of steady state permeation. The permeability was computed from the slope of the linear, steady state part of the curve representing the permeated gas volume as a function of time. All the tests were performed at a vanishingly small downstream pressure which was assumed to be equal to zero. The use of a very accurate transducer on the downstream side (MKS Baratron 121 pressure transducer with a full scale of 10 Torr, a sensitivity of 0.001 Torr and an accuracy of ± 0.5% of the reading) allowed reliable measurement of permeability even though the downstream side pressure never exceeded 0.25% of the upstream side value. The experiments were performed at upstream pressures equal to 250 and 750 Torr. In the following the discussion is based on the data collected at 250 Torr. Experiments were performed at three temperatures: 35, 45 and 55 °C.

4. Results and discussion

4.1. Gas sorption isotherms

Sorption of gases at low pressures in semicrystalline s-PS samples (s-PS10 and s-PS18) evidenced the high sorption capacity of the nanoporous crystalline phase, which is able to host gas molecules in its nanocavities. The sorption values, as shown in the following, are much higher than those typically observed in the case of the totally amorphous samples [36,37]. These results are consistent with the lower density values of the δ crystalline form (0.977 g/cm^{3}for δ form) as compared to that of the amorphous phase. In Fig. 3(a)–(c) are reported the sorption isotherms at several temperatures for the three investigated gases in the case of semicrystalline sample s-PS18.

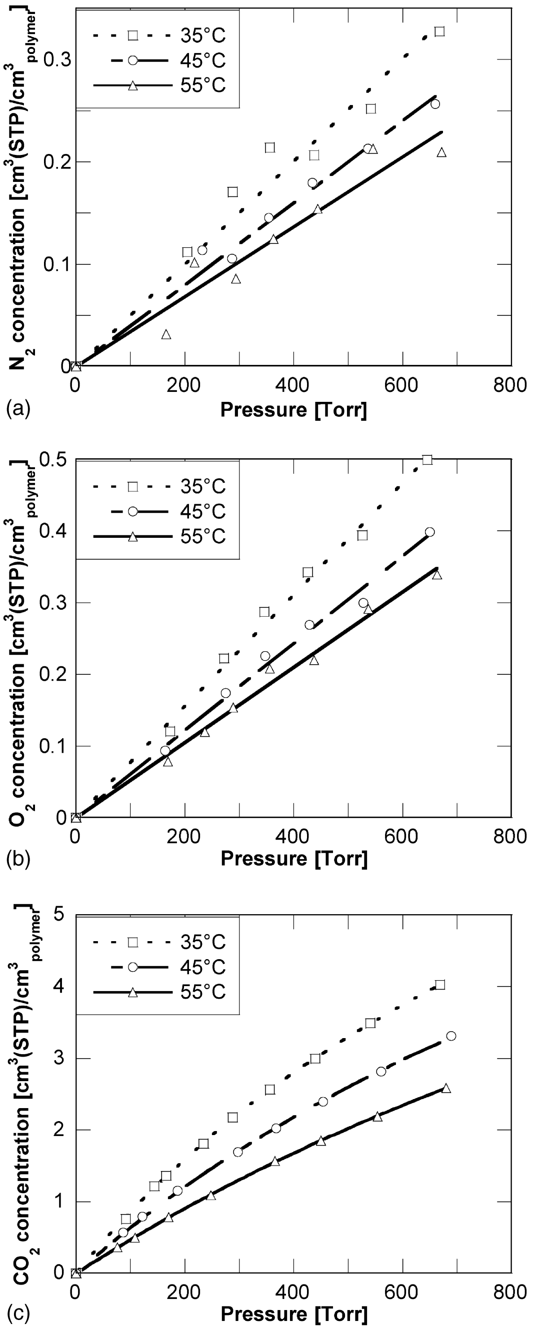

Fig. 3. Sorption isotherms at 35, 45 and 55 °C for sample s-PS18 for (a) nitrogen, (b) oxygen and (c) carbon dioxide.

To estimate the sorption capability of the pure crystalline phase from data on semicrystalline sample s-PS18, the sorption contribution of the amorphous phase of s-PS must be subtracted. To evaluate this contribution, the relevant assumption has been made that the sorption capability of the amorphous phase of semicrystalline s-PS is the same as displayed by amorphous atactic PS with a density equal to 1.051 g/cm^3. To this aim, sorption experiments with investigated gases were performed also on a-PS samples. Results were obtained experimentally only at the highest investigated pressures (around 700 Torr) due to the low solubility of gases into a-PS. These experimental findings are close to results of analogous tests on a-PS reported in the literature [36,37].

Estimation of sorption capabilities in the full range of pressures were obtained by using the NELF model. The adopted NELF parameters for pure components (T^*, P^*, and ρ^*) were taken from the literature. In particular data for nitrogen, oxygen and carbon dioxide were taken from Ref. [38], while data for PS were taken from Ref. [39]. The interaction parameter (ψ) have been calculated through best fitting of the experimental values obtained at the higher pressures. The values of the parameters are reported in Table 1. It is worth noting that for the three gases in the pressure range of interest, sorption isotherms predicted for a-PS are essentially linear.

In Fig. 4(a)–(c) are reported the sorption isotherms for nitrogen, oxygen and carbon dioxide, respectively for the pure δ crystalline phase of s-PS, as evaluated through the subtraction procedure, along with sorption isotherms for the totally amorphous sample, as evaluated using NELF. For all investigated gases, sorption capacity of crystalline δ form is much higher than for the amorphous phase, qualitatively consistent with results of molecular dynamics simulation for the case of carbon dioxide and oxygen performed by Tamai and Fukuda [40].

It is worth noting that measured CO_2 sorption capacities of the crystalline phase at one atmosphere is roughly 20 times larger than that of the amorphous phase and around two order of magnitude, or even more, larger than that of the crystalline ordered α form of s-PS [34,41] (the values of solubility for the pure ordered α form reported in the literature [34,41] depend on the experimental method adopted to evaluate the crystalline fraction of investigated samples). In similar conditions the crystalline phase of poly(4-methyl-1-pentene) [29] displays a sorption capacity, which although not negligible, is much lower than its corresponding amorphous phase.

Analogous results were obtained by applying the above subtraction procedure to a semicrystalline sample (s-PS10), characterized by a lower degree of crystallinity.

Sorption isotherms for carbon dioxide in the nanoporous crystalline phase obtained using this procedure were well fitted by using Langmuir equation. In Table 2 are reported

Table 1
NELF parameters for the pure components along with the binary parameter Ψ

	T^* (K)	P^* (MPa)	ρ^* (kg/L)	Ψ
a-PS	750	360	1.099	–
N_2	145	160	0.943	1
O_2	180	214	1.25	0.9
CO_2	300	630	1.515	1

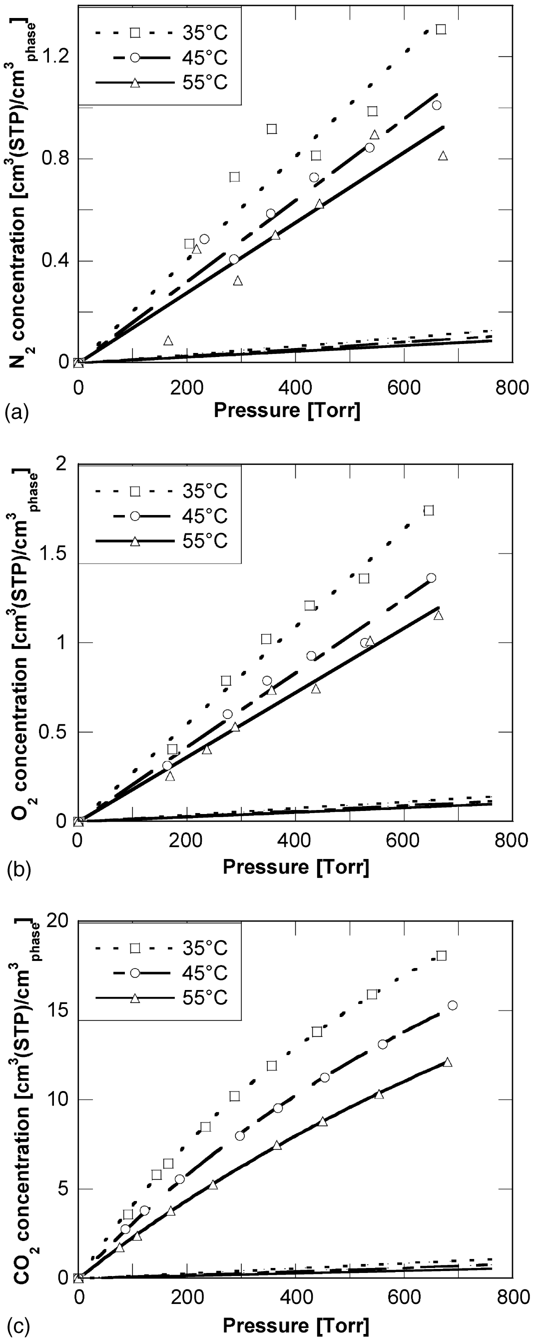

Fig. 4. Sorption isotherms at 35, 45 and 55 °C in the crystalline phase (upper curves) of sample s-PS18 and in the amorphous a-PS (lower curves) for (a) nitrogen, (b) oxygen and (c) carbon dioxide.

Table 2
Langmuir parameters for crystalline phase

	C'_H (cm^3(STP)/cm^3)	b ($Torr^{-1}$)
35 °C	45.3	9.98×10^{-4}
45 °C	45.2	7.33×10^{-4}
55 °C	47.2	5.08×10^{-4}

the values of Langmuir parameters evaluated at each temperature. As can be noted, C'_H, which represents the saturation capacity of the nanoporous crystalline phase, is roughly independent of temperature and, on the average, is equal to about 45.9 cm^3(STP) per cm^3 of crystalline phase. This value corresponds to 2.06×10^{-3} mol of carbon dioxide per cm^3 of crystalline phase (i.e. a stoichiometric ratio between styrene monomeric units of the crystalline phase and CO_2 guest equal to 4.56). Since the moles of cavities per cm^3 of crystalline phase are about 2.44×10^{-3} (which corresponds to the stoichiometric ratio of 4, typical of most s-PS clathrate phases [6–9]) the obtained results suggest that nearly one molecule of CO_2 is hosted per crystalline cavity.

In the case of oxygen and nitrogen it has not been possible to perform a similar analysis since in the range of investigated pressures, there was no significant deviation of the isotherm from a linear shape, hence reliable value for Langmuir parameters could not be obtained from data fitting.

A significant parameter characterizing the interaction between the polymer matrix and the penetrant is the isosteric heat of sorption. In the hypothesis that the enthalpy change for the polymer is negligible, isosteric heat (q_{st}) is defined as:

$$q_{st} = (\bar{H}_2^s - h_2^g)_{n_1/n_2}$$

where h_2^g e $\bar{H}_2^s$ represent the partial molar enthalpy of the component '2' in the gas and polymer solution phase, respectively. The ideal process considered here consists in transferring a mole of component '2' from the mixture with the polymer ($\bar{H}_2^s$) to the gas phase (h_2^g), at constant p and T. By using Gibbs–Duhem equation and making the assumption that both polymer volume change on mixing and penetrant volume in the mixture are negligible, q_{st} can be evaluated operatively as:

$$q_{st} = R\left(\frac{\partial \ln(p)}{\partial(1/T)}\right)_{n_1/n_2} \qquad (1)$$

where the partial derivation is performed at constant composition of the gas polymer mixture (n_1 and n_2 represent, respectively, the number of moles of dissolved gas molecules and of polymer repeating units), and p is the equilibrium pressure evaluated at different temperatures.

If sorption isotherm follows Langmuir equation with a C'_H value independent of temperature, the isosteric heat of sorption can be directly evaluated from the dependence of 'b' on the temperature according to the expression:

$$q_{st} = -\frac{\partial \ln(b)}{\partial\left(\frac{1}{T}\right)} \qquad (2)$$

Isosteric heats of sorption for the crystalline phase were evaluated from sorption isotherms at three different temperatures and are reported in Table 3 along with the corresponding values for the amorphous one. In the case of oxygen and nitrogen isosteric heats were evaluated through Eq. (1), while in the case of carbon dioxide, due to invariance of C'_H with temperature, it was directly evaluated through Eq. (2).

Table 3
Isosteric heat of sorption (kcal/mol) at 45 °C

	O_2	N_2	CO_2
Crystal phase	−4.16	−3.89	−6.77
Amorphous phase	−3.45	−3.87	−6.67

The isosteric heat of sorption for both carbon dioxide and nitrogen in the case of crystalline phase are very close to the values found for the amorphous one. This result suggests that the average interactions experienced by the gas molecules in the amorphous and crystalline environment are very similar. In fact, at the low investigated pressure, it is expected that gas molecules present in the amorphous phase are mainly adsorbed in pockets of excess free volume present in the glassy polymer similarly to what happens to gas molecules hosted in the nanocavities of the crystalline phase.

In the case of oxygen, the isosteric heat of sorption is more exothermic for the case of the crystalline phase. This finding could be rationalized by considering that oxygen is able to form a complex with the aromatic rings [42], which for the cavities of the crystalline phase have a well defined arrangement [6,12].

4.2. Gas diffusivities

Carbon dioxide and oxygen diffusivities have been evaluated by combining results from permeation and sorption experiments on the basis of the following expression:

$$\tilde{D} = P/S$$

where P is the permeability evaluated for an upstream pressure (p^{up}) equal to 250 Torr and a negligible downstream

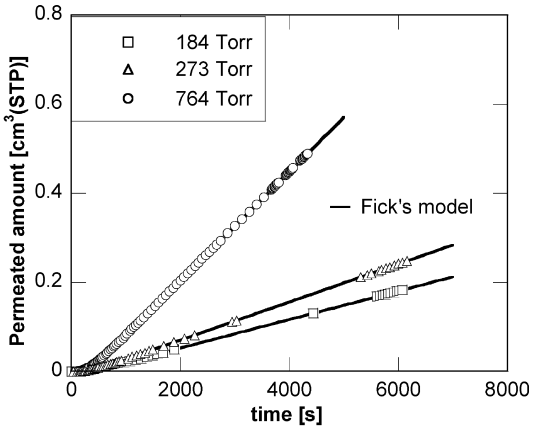

Fig. 5. Permeation curves of CO_2 in semicrystalline s-PS18 vs. time at upstream pressures of 184, 273 and 764 Torr. Temperature 45 °C.

pressure ($p^{\text{down}} \cong 0$), while S is the solubility evaluated at pressure p^{up}. As an example in Fig. 5 are reported some raw permeation curves for sample s-PS18 in the case of carbon dioxide at 45 °C and several upstream pressures, along with best fitting curves based on Fick's model. Predictions of permeation curves founded on the assumption of Fickian behaviour [43] supply a good fitting of experimental data.

Since diffusivity has been found to be concentration dependent (mainly in the case of carbon dioxide), the analysis of transport behaviour has been performed at a value of the upstream pressure (250 Torr) which guaranteed at the same time a reliable measurement and a good estimate of the zero concentration limit.

In Fig. 6(a) and (b) are reported the diffusivities of the two gases at three temperatures as a function of the degree of crystallinity. For both gases diffusivity decreases as the degree of crystallinity increases.

Data have been interpreted by using the Maxwell model [44]. This model was originally developed for steady state permeation in an heterogeneous system made of uniform and dilute dispersion of isotropic spheres in an isotropic surrounding matrix. In the case at hand, the amorphous phase of s-PS has been envisaged as the isotropic matrix while crystalline domains as the dispersed spheres. Actually, nanoporous crystallites are characterized by non isotropic diffusional properties (see molecular dynamics studies reported in Ref. [40,45]) and the assumption of uniform distribution of crystalline domains could also be questioned (see the adopted protocol for sample preparation). However, with regard to the first point, we have hypothesized that, on the average, crystals can be modelled as being isotropic due to the random orientation of crystalline domains. While, with regard to the second point, we did not take into account in our analysis a non uniform distribution of crystallinity, which could eventually derive from occurrence of diffusion controlled regime in THF induced crystallization [46]. As a matter of fact, the Maxwell model supplied a good data fitting for both CO_2 and O_2.

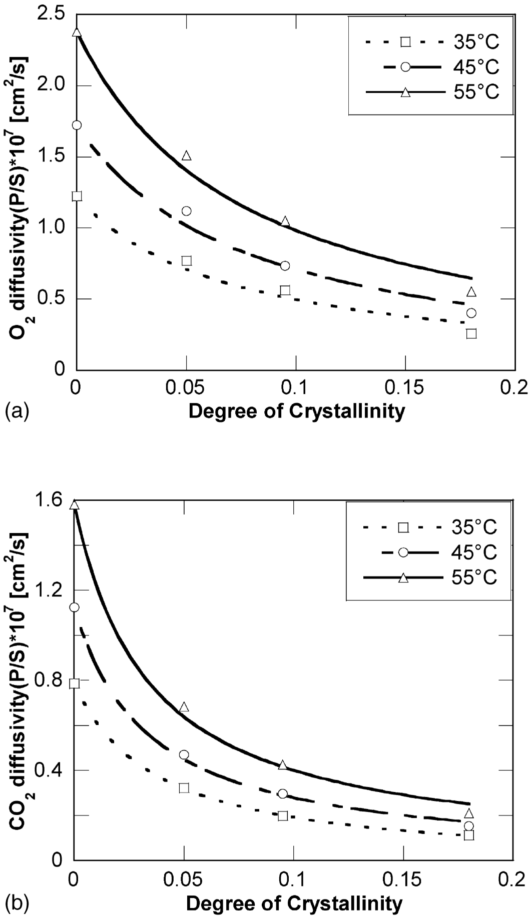

Fig. 6. Diffusivities as function of degree of crystallinity at 35, 45 and 55 °C for (a) oxygen and (b) carbon dioxide.

The Maxwell model, expressed in terms of diffusivities and solubilities, takes the following form:

$$\tilde{D} = \frac{D_a}{\phi_a + S_{ab}\phi_b} + 3D_aS_a\phi_b\left[\frac{D_b/D_aS_{ab} + 2}{D_b/D_aS_{ab} - 1} - \phi_b\right]^{-1} \qquad (3)$$

where subscripts 'a' and 'b' refer to the continuous phase and the disperse one respectively, D_i represents the diffusivity of the examined gas into the i-th phase, S_a represents the penetrant solubility in the continuous phase, S_{ab} is the ratio between the solubility in the continuous and dispersed phase and ϕ_i is the volumetric fraction of the i-th component. As evident from Fig. 6(a) and (b) a good data fitting has been obtained by using Eq. (3), from which estimates of the gas diffusivities in the crystalline phase have been obtained and reported in Table 4. It is worth of note that the diffusivity in the crystalline phase, although being about two order of magnitude lower than that in the amorphous phase, is however non negligible.

The present analysis, which is limited to samples characterized by a low degree of crystallinity and low degree of orientation, does not fully embrace the complexity of physical phenomena involved in. In fact, the anisotropy of transport properties of the crystalline phase [40,45], and the dependence of mass transport behaviour on the morphology of the samples and, mostly, on the kind and degree of orientation of the crystalline phase should be further analysed.

Table 4
Diffusivities in the totally amorphous phase (experimental) and in the totally crystalline phase δ form of s-PS (obtained through best fitting with Eq. (3)) for (a) oxygen and (b) carbon dioxide

	$D_{\text{Amorphous}}$ (cm^2/s) (experimental)	D_{Crystal} (cm^2/s)
(a) O_2		
35 °C	1.22×10^{-7}	6.3×10^{-9}
45 °C	1.72×10^{-7}	5.3×10^{-9}
55 °C	2.38×10^{-7}	9.2×10^{-9}
(b) CO_2		
35 °C	7.80×10^{-8}	6.2×10^{-10}
45 °C	1.12×10^{-7}	3.1×10^{-9}
55 °C	1.58×10^{-7}	5.3×10^{-9}

5. Conclusions

Sorption and transport of several gases in semicrystalline syndiotactic polystyrene with nanoporous crystalline phase has been analysed.

Investigated semicrystalline s-PS is characterized by a gas solubility which is much higher than in the case of totally amorphous samples. This behaviour has been attributed to the circumstance that the sorption capacity of the well ordered nanoporous crystalline phase is around one order of magnitude higher than in the amorphous domains, due to the very low density of the crystalline phase (0.977 g/cm^3 for the crystalline δ form as compared to 1.051 g/cm^3, which is typical for amorphous samples). This rather uncommon behaviour, related to adsorption of penetrant molecules inside the crystalline nanocavities, is further confirmed by the analysis of carbon dioxide sorption isotherms. In fact, these sorption isotherms clearly display, in the investigated pressure range, a Langmuir type behaviour whose maximum sorption capacity is very close to the 4/1 stoichiometry of most s-PS clathrate phases.

Analysis of gas permeation properties for the case of carbon dioxide and oxygen allowed the determination of gas diffusivities in the limit of small concentrations. The dependence of diffusivity on the amount of crystalline phase, was well fitted by using a biphasic Maxwell model. From this analysis, it emerges that the diffusivity in the crystalline phase is not negligible. Further analysis of diffusion behaviour is desirable taking in proper account the anisotropy as well as the possible disorder of the nanoporous crystalline phase.

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