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Syndiotactic Polystyrene Films with Sulfonated Amorphous Phase and Nanoporous Crystalline Phase

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A solid-state sulfonation procedure on syndiotactic polystyrene (s-PS) δ-form films allows an easy and uniform sulfonation of the phenyl rings of the amorphous phase and preserves the nanoporous δ-phase. The high degree of sulfonation of the amorphous phase (up to a molar ratio 2/1 between phenyl rings and sulfonic groups) makes this phase highly hydrophilic, whereas the hydrophobic crystalline phase maintains its guest sorption ability. s-PS films, sulfonated only in the amorphous phase and exhibiting the nanoporous δ-phase, present kinetics of guest sorption from water solutions into the crystalline phase, being markedly higher than those of the corresponding unsulfonated films. For instance, DCE sorption kinetics from 50 ppm aqueous solutions show an unaltered DCE equilibrium uptake (close to 4 wt %) associated with a DCE diffusivity increase of more than 70 times. Moreover, the nanoporous crystalline phase and its sorption ability remain essentially unaffected by water sorption/desorption cycles. The reported results hence indicate that these new materials are particularly suitable for removal of VOC pollutants from water and moist air.

Introduction

Nanoporous crystalline structures, i.e., crystalline phases presenting cavities of nanometric size, are relevant for molecular storage, recognition and separation techniques. They can be achieved for a large variety of chemical compounds and often are referred as inorganic, metal-organic, organic, and polymeric "frameworks".

For syndiotactic polystyrene (s-PS) two nanoporous crystalline phases (δ_1 and ε_2) have been discovered, which can absorb several guest molecules producing clathrate[3] and intercalate[4] cocrystals. In particular, films presenting s-PS/active-guest cocrystals have been proposed as advanced materials, mainly for optical applications (e.g., as fluorescent, photoreactive, and chromophore materials).[5]

Semicrystalline s-PS samples exhibiting the nanoporous δ- and ε-crystalline phases can rapidly and selectively absorb volatile organic compounds (VOC, mainly halogenated and aromatic, e.g., the list in Table 7 of ref 4b) even when present at very low concentrations.[6] The thermoplastic nature of these materials allows easy processing to products suitable for several applications, like films, membranes, and foams, as well as their recycling.

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As a consequence, a number of applications in the field of chemical separations[6] and of molecular sensorics,[7] for these inexpensive and reusable materials has been proposed. Because of their hydrophobic nature, these thermoplastic molecular sieves are particularly suitable for purification and sensorics of water and moist air environments.

Several studies, based on the conformational equilibria of guest molecules,[8] infrared spectra perturbation due to host−guest interactions,[9] linear dichroism of guest molecules in uniaxially stretched host films,[10,5f] and on sorption measurements in s-PS samples presenting different kinds of crystalline phases,[11] have clearly demonstrated that for sorption at low activities, most penetrants are located essentially only as guest into the crystalline phase, whereas their concentration in the amorphous phase can be negligible.

The diffusion kinetics of the guest molecules is strongly dependent on the morphology (and, of course, on the surface area) of the semicrystalline materials. In particular, fine powders present fast guest sorption kinetics but are difficult to handle. On the other hand, morphologies with small surface area (film, sheet) are easier to handle but they display much slower guest sorption kinetics.[6]

As for the films, the guest diffusivity can be slightly increased by imposing a suitable uniplanar orientation of the nanoporous crystalline phase, i.e. one of the three preferential orientations of a crystal plane with respect to the film plane,[12−14] which have been achieved for s-PS films exhibiting a helical crystalline phase.[15,2c] In particular, films presenting the *ac* planes (corresponding to layers of close-packed alternated enantiomorphic helices) preferentially parallel to the film plane[12] (uniplanar $a_{\parallel} c_{\parallel}$ orientation) present minimum guest diffusivities,[16] whereas films presenting the *ac* plane and the *a* axis both perpendicular to the film plane[14] present maximum guest diffusivities (uniplanar $a_{\perp} c_{\parallel}$ orientation).[16] For instance, maximum and minimum diffusivities in desorption experiments, for three different guest molecules (carbon dioxide,[16c] ethylene,[16d] and 1,2-dichloroethane[16b]) roughly differ by 1 order of magnitude.

Recently, it has been shown that high porosity s-PS aerogels[11b,17] can be obtained by supercritical CO_2 extraction of the solvent present in s-PS physical gels[11b,17a] or by sublimation of the solvent.[17b] Sorption and desorption experiments of guest molecules have shown that the use of δ-aerogels allows us to increase the apparent guest diffusivity of several orders of magnitude (up to 7!), with respect to δ-form films. However, the extremely apparent low density (typically in the range 0.1−0.01 g/cm^3) makes these samples unsuitable for several practical applications.

In this paper, we present a different approach to increase the pollutant sorption kinetics into the nanoporous polymeric crystalline phases consisting of making hydrophilic the amorphous phase, by selective sulfonation of the amorphous s-PS chains. Of course, a hydrophilic amorphous phase is expected to provide a direct contact between the polluted water and the absorbing nanoporous crystalline phase.

Several studies have been reported in the literature relative to the sulfonation of s-PS and to the characterization of the sulfonated polymer.[18] All the studies report sulfonation procedures in solution, leading to random sulfonation of the polymer chains and hence to poor crystallinity, if any. In this paper, a solid-state sulfonation procedure is conducted in a way suitable to preserve not only the polymer crystallinity but also the thermodynamically unstable[19] nanoporous δ-phase. Moreover, it will be shown that s-PS films, sulfonated only in the amorphous phase and exhibiting the nanoporous δ-phase,

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present kinetics of guest sorption definitely higher than those of unsulfonated films.

Experimental Section

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

All δ- and cocrystalline films considered in this paper have been obtained by casting from 0.5 wt % solutions, at room temperature from chloroform (99%, Aldrich).[12b] The films present uniplanar $a_{\|}\, c_{\|}$ orientation of nanoporous and cocrystalline phases and thickness in the range 100−200 μm.

The β-form films (thickness in the range 180−200 μm) have been obtained by compression molding of milled commercial pellets, by using high temperatures ($T_{max} > 320$ °C) and moderate cooling rates (< 20 °C/min), i.e., according to the procedure described in refs 15b and 20.

Sulfonation Procedure. The acyl sulfate sulfonating reagent[18g] was prepared by mixing an excess of dodecanoic acid (lauric acid) over chlorosulfonic acid ($ClSO_3H$) at room temperature

$$CH_3(CH_2)_{10}COOH + ClSO_3H \rightarrow CH_3(CH_2)_{10}COOSO_3H + HCl \qquad (1)$$

In particular,1.6 mol of lauric acid (≥98%, Aldrich) was used per 1.0 mol of $ClSO_3H$ (99%, Sigma-Aldrich), and the reaction time was 1 h. All reagents were used as received.

The sulfonation of sPS films, by the prepared acyl sulfate, was performed at temperature of 40 °C by soaking for a time from 2 to 24 h in a $CHCl_3$ (99%, Aldrich) solution. The same sulfonation procedures were conducted on s-PS films exhibiting the nanoporous δ-phase, as obtained by casting from chloroform solution, or the dense β-phase, as obtained by compression molding.

The sulfonated films have been purified by possible remnants of the sulfonation procedures by extraction with carbon dioxide in supercritical conditions, with a SFX 200 supercritical carbon dioxide extractor (ISCO Inc.) using the following conditions: $T = 40$ °C, $P = 200$ bar, extraction time $t = 180$ min. As well-established in the literature,[21] this procedure also allows complete removal of possible guest molecules from all possible s-PS cocrystalline phases, leading to nanoporous crystalline phases.

The sulfonation degree has been evaluated by elemental analysis on the whole semicrystalline samples and the reported sulfonation degree (thereafter indicated as S) is valued as molar fraction of sulfonated monomeric units.

Characterization Methods. The films were examined with a scanning electron microscope (SEM) (Leica Cambridge Stereoscan S440) coupled with a probe for energy-dispersive scanning (EDS), to evaluate the sulfonation degree at different depths throughout the sample thickness, as e.g. reported in Figure 1. The films were cryogenically fractured in liquid N_2 for the SEM-EDS examinations. All films were coated with Au prior to EDX analysis. For the calibration of EDX, the following standards were used: $CaCO_3$ (carbon standard), SiO_2 (oxygen standard), FeS_2 (sulfur standard).

Wide-angle X-ray diffraction patterns with nickel-filtered Cu Kα radiation were obtained, in reflection, with an automatic Bruker D8 Advance diffractometer. The spectra are reported as a function of 2θ diffraction angles (bottom scale) as well as of q values ($q = (4\pi/\lambda)\sin(\theta)$, upper scale).

The correlation length of the crystalline domains D_{010}, perpendicular to the (010) crystal planes (i.e., perpendicular to the layers of close-packed alternated enantiomorphous s-PS helixes), was evaluated using the Scherrer formula

$$D_{hkl} = 0.9\lambda/\beta_{hkl}\cos\theta_{hkl}$$

where β_{hkl} is the full width at half-maximum expressed in radiant units, λ is the wavelength, and θ_{hkl} the diffraction angle.

Infrared spectra were obtained at a resolution of 2.0 cm^{-1} with a Tensor 27 Bruker spectrometer equipped with deuterated triglycine sulfate (DTGS) detector and a Ge/KBr beam splitter. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He−Ne laser. Sixteen scans were signal-averaged to reduce the noise.

The degree of crystallinity (X_c) has been evaluated by the FTIR spectral subtraction procedure, as described in refs 22. In particular, for semicrystalline samples presenting helical crystalline phases, the choice of the 1379 cm^{-1} amorphous peak is the most suitable for crystallinity evaluation.[22b] This amorphous peak selection has also the advantage that the spectral region between 1450 and 1250 cm^{-1} is the only one for which, for high solfonation levels, the peak absorbances remain in the range of absorbance linearity (< 1.2 absorbance units).

The water-uptake of the polymers was investigated by a Q5000 SA thermogravimetric analyzer from TA Instruments, containing a microbalance in which the sample and reference pans were enclosed in a humidity and temperature controlled chamber. The temperature in the Q5000 SA was controlled by Peltier elements. Dried N_2 gas flow (200 mL min^{-1}) was split into two parts, of which one part was wetted by passing it through a water-saturated chamber. The desired relative humidity (RH) for the measurements could subsequently be obtained by mixing proper proportions (regulated by mass-flow controllers) of dry and wet stream.

Results and Discussion

Sulfonation of s-PS Films Exhibiting the Nanoporous $\boldsymbol{\delta}$- or the Dense $\boldsymbol{\beta}$-Crystalline Phases. The sulfonation procedure, described in detail in the experimental section, utilizes as sulfonating agent the lauroyl sulfate, that is a bulky molecules (molar volume of 0.289 L/mol, molecular volume 0.41 nm^3), which is not included as guest of the nanoporous δ phase. In fact, the maximum volume of possible guest molecules of s-PS clathrate phases is generally close to 0.25 nm^3.[4b] This choice was motivated by the will of pursuing phenyl ring sulfonation only in the amorphous phase, possibly without disturbing the polymer crystallinity. In fact, procedures involving smaller sulfonating agents, e.g., chlorosulfonic acid, generally lead to more rapid decline of polymer crystallinity.[18e]

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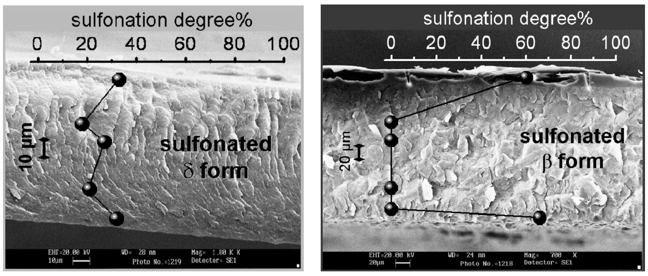

A B

Figure 1. Scanning electron microscopy images of the section of s-PS films exhibiting the (A) nanoporous δ- and (B) β-crystalline phases. The black dots indicate the sulfonation degrees (S), as evaluated by EDS profiling analysis. The lines are only used to guide the eye.

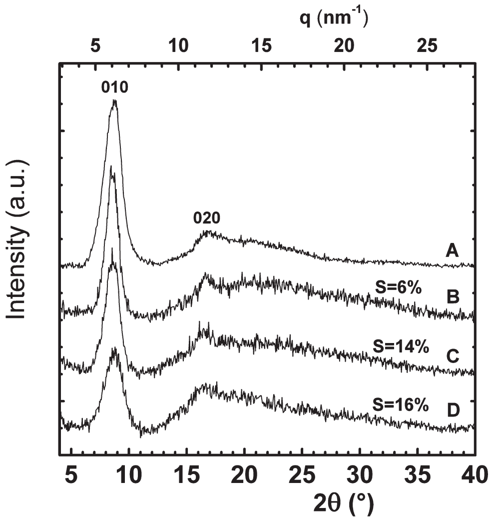

Figure 2. X-ray diffraction patterns (Cu Kα) of s-PS films with $a_{||}$ $c_{||}$ uniplanar orientation of the nanoporous crystalline δ-phase, (A) before and (B−D) after sulfonation procedures. Close to the curves, the sulfonation levels as determined by elemental analyses are indicated.

The same sulfonation procedures have been applied on s-PS semicrystalline films, presenting degree of crystallinity in the range 40−50% and having a thickness in the range of 100−200 µm, which exhibit as the crystalline phase the nanoporous δ-phase or the dense and thermodynamically stable β phase. Our results indicate a completely different response of s-PS films exhibiting different crystalline phases. In particular, by depth profiling analysis, the observed sulfonation degree is high (in the range 15−35%) for the entire thickness of the nanoporous δ-form film (Figure 1A) already after 2 h of sulfonation treatment. For the β-form films, also after 24 h of treatment, the sulfonation degree is negligible for measurements at any depth from the surface higher than 30 µm (Figure 1B), whereas that close to the film surface is high (close to 60%).

The reported results clearly suggest that the nanoporous crystalline phases, being highly permeable to the solvent (chloroform)[6a,6f,9] used for the sulfonation procedure, makes the plasticization of the amorphous phase faster and hence facilitates the diffusion of the reactants and as a consequence the uniformity of the solid-state sulfonation.

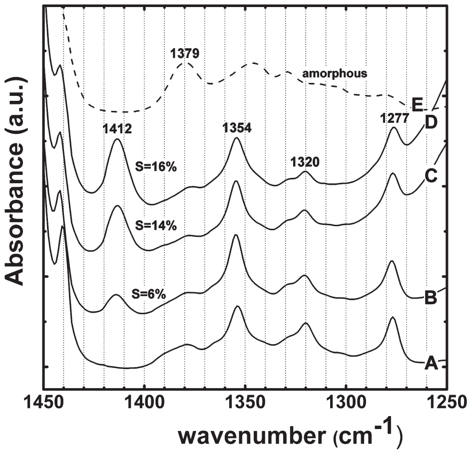

Figure 3. FTIR spectra in the wavenumber range 1450−1250 cm^{-1} of s-PS films with $a_{||}$ $c_{||}$ uniplanar orientation of the nanoporous crystalline δ-phase, (A) before and (B−D) after sulfonation procedures. The spectrum of an amorphous sPS film (E, dashed line) is added for comparison. Close to the curves, the sulfonation levels as determined by elemental analyses are indicated. Relevant absorbance peaks associated with the crystalline (1354, 1320, and 1277 cm^{-1}) and amorphous (1379 cm^{-1}) phases, or with the sulfonation level (1412 cm^{-1}) are also indicated.

X-ray Diffraction and Infrared Characterization of Sulfonated δ-Form sPS Films. The X-ray diffraction pattern and the FTIR spectrum of a s-PS film cast from chloroform solution are shown in Figures 2A and 3A, respectively. The X-ray diffraction pattern of Figure 2A shows only (010) and (020) peaks at 2θCu Kα ≈ 8.4 and 17° (d = 1.05 and 0.52 nm), typical of the nanoporous δ-phase and indicating a high level of uniplanar orientation ($f_{010} \approx 0.7$) with both a and c axes preferentially parallel to the film plane (uniplanar $a_{||}$ $c_{||}$ orientation).

The FTIR spectrum of Figure 3A shows typical peaks of the δ-crystalline phase (e.g., those located at 1354, 1320, and 1277 cm^{-1}) and allows us to evaluate a degree of crystallinity of nearly 50%, by subtracting the spectrum of a fully amorphous s-PS film (Figure 3E) and by reduction close to the baseline the 1379 cm^{-1} "amorphous" peak.[22b]

The X-ray diffraction patterns and the FTIR spectra of the cast film of Figures 2A and 3A, after sulfonation at different levels by following the procedure described in this paper, are reported in Figures 2B−D and 3B−D, respectively.

The X-ray diffraction patterns of Figure 2A−D indicate a progressive increase in the intensity of the amorphous halo with the increase in sulfonation degree. However, the position and the intensity of the (010) peak clearly show that both the nature of the crystalline phase (δ) and its uniplanar orientation are essentially unaffected by our sulfonation procedure. The broadening of this peak only indicates a slight reduction of the order of the crystalline phase. In particular, the full width at half-maximum of the (010) peak (β_{010}) is close to 1.2° for the unsolfolnated film and increases up to 1.9° for the film with a degree of sulfonation of 16%. This corresponds to a reduction of the correlation length (D_{010}) of the crystalline domains from 6.6 to 4.3 nm.

Very informative also are the FTIR spectra of Figure 3B−D, clearly showing the progressive increase of a 1412 cm^{-1} peak due to the sulfonation procedure and a degree of crystallinity only slightly reduced. Spectral

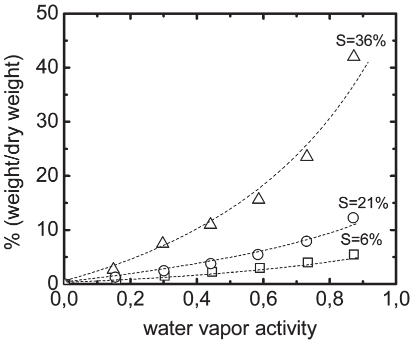

Figure 4. Water sorption, as a function of water vapor activity, from sulfonated s-PS δ-form where the sulfonation has occurred in the sole amorphous phases. Close to the curves, the sulfonation levels, referred to the monomeric units, are indicated.

subtraction procedures, analogous to that one described in ref 22b, show that a degree of crystallinity $X_c > 20\%$ is observed for a molar fraction of sulfonated monomeric units as high as 40%.

Water Sorption. The used sulfonation procedure allows us to reach high degrees of sulfonation of the amorphous phase (up to 50%), whereas the δ-crystalline phase is maintained with only a partially reduced degree of crystallinity ($X_c > 20\%$).

The high sulfonation levels make hydrophilic films, which were formerly completely hydrophobic. For instance, the equilibrium water uptake from δ-form s-PS films, as sulfonated at three different degrees ($S = 6$, 21, and 36%) according to the above-described procedure affecting essentially only the amorphous phase, are reported versus the water vapor activity in Figure 4.

The X-ray diffraction patterns (Cu Kα) of a highly sulfonated film ($S = 30\%$), before (A), after equilibrium water uptake (50 wt %, B) and after complete water loss (C) are compared in Figure 5.

The pattern of Figure 5B, beside the intense and broad water diffraction halo (in the 2θ range 12−35°), shows a well-defined crystalline peak for $2\theta \approx 8.5°$, clearly indicating the maintenance of some amount of nanoporous δ-crystalline phase, also after the large water uptake.

The pattern of the film after the water sorption/desorption procedure, in Figure 5C, is extremely similar to that one of the starting sulfonated film (Figure 5A). This clearly indicates that the nanoporous δ-phase is maintained after water removal without significant crystallinity reduction (the crystallinity remains close to 30%).

These results clearly confirm that our solid-state sulfonation procedure involves essentially only the amorphous phase, becoming highly hydrophilic, while leaves essentially unaltered the crystalline phase, which remains hydrophobic and unaffected by the high water uptake in the amorphous phase.

Sorption Kinetics of Pollutants from Water. The equilibrium uptake of 1,2-dichloroethane (DCE) from diluted aqueous solutions has been investigated for several s-PS samples.[8a,8b,10a,16b] The choice of DCE was motivated by the additional information, which comes from its conformational equilibrium. In fact, as described in detail in previous papers,[8a,8b] because essentially only its trans conformer is included into the clathrate phase while both trans and gauche conformers are included in the amorphous phase, quantitative evaluations of vibrational peaks associated with these conformers allow us to evaluate the amounts of DCE confined as guest in the clathrate phase or simply absorbed in the amorphous phase. The choice of DCE was also motivated by its presence in contaminated aquifers and by its resistance to remediation techniques based on reactive barriers containing Fe^0.[23]

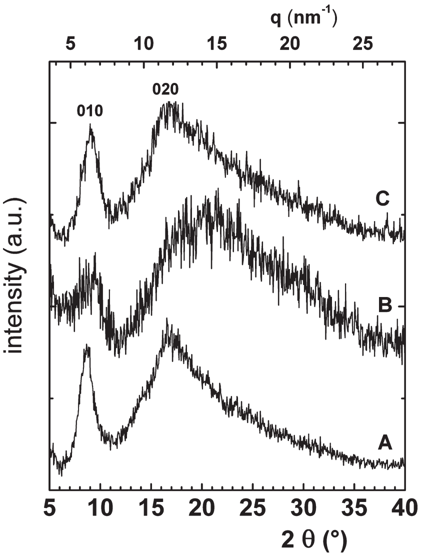

Figure 5. X-ray diffraction patterns (Cu Kα) of s-PS films with $a_{||}$ $c_{||}$ uniplanar orientation of the nanoporous crystalline δ-phase, exhibiting a degree of sulfonation of 30% (A) before, (B) after equilibrium (50 wt %) water sorption, and (C) after a complete water sorption/desorption procedure.

Sorption kinetics from 50 ppm aqueous solutions of DCE, based on the absorbance of its 1234 cm^{-1} trans peak, in three films presenting the $a_{||}$ $c_{||}$ uniplanar orientation of the δ-nanoporous phase and different degrees of sulfonation are compared in Figure 6, where M_t is the amount of penetrant absorbed at time t, M_{inf} is the amount of penetrant absorbed at equilibrium, and L is the thickness of the films. The equilibrium guest uptake is nearly independent of the sulfonation degree and not far from 4 wt %. As already established in previous papers,[8,9,16b−16d] the kinetic curves for guest absorption from the nanoporous δ-phase are formally fitted by means of Fick's model (Figure 6). The apparent diffusivities (D_{abs}) obtained by the slopes of the lines substantially increase with the degree of sulfonation. In particular, for the film with a degree of sulfonation $S = 14\%$, there is an increase in DCE sorption diffusivity of more than 70 times.

These results also suggest that at low pollutant activity, the slow sorption kinetics observed for s-PS semicrystalline nanoporous (unsolfonated) films would be mainly due to

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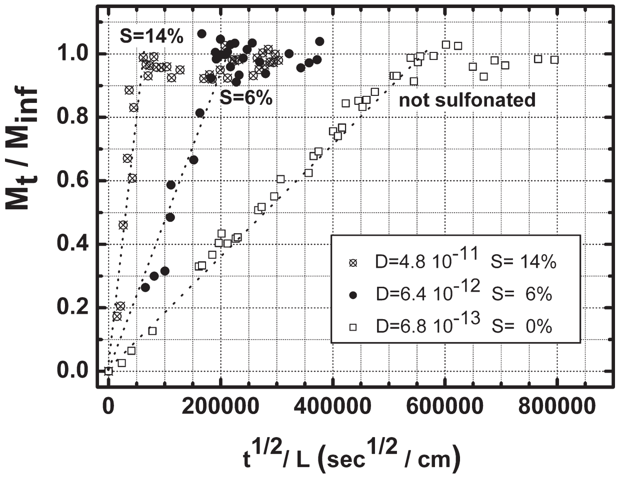

Figure 6. Sorption kinetics at room temperature of DCE from 50 ppm DCE aqueous solutions, based on the absorbance of its 1234 cm^{-1} trans peak, for δ-form s-PS films presenting different degrees of sulfonation of the amorphous phase: (□) not sulfonated; (●) $S = 6\%$ and 6% water uptake; (⊗) $S = 14\%$ and 15% water uptake.

Table 1.

sulfonation degree %	H_2O uptake (wt %)	DCE uptake (wt %)	diffusivity (cm^2/s)
0	0	5	6.8×10^{-13}
6	6	4.8	6.4×10^{-12}
14	15	4.7	4.8×10^{-11}

the poor solubility of organic pollutants in the polymer amorphous phase. This low guest solubility of the amorphous phase would be not compensated by the higher guest diffusivity, which has been clearly established by sorption and transport studies with several gases[6e] as well as by solid-state ^{2}H NMR spectra of deuterated aromatic guest molecules.[24]

Conclusions

The paper presents a solid-state sulfonation procedure, which when applied to syndiotactic polystyrene samples exhibiting the nanoporous δ-crystalline phase allows an easy and uniform sulfonation of the phenyl rings of the amorphous phase.

In fact, X-ray diffraction and Fourier Transform Infrared measurements clearly show that the proposed sulfonation procedure is able to preserve the thermodynamically unstable nanoporous δ-phase, essentially also preserving its degree of crystallinity (generally in the range 30−40%). Elemental analysis of S and C content of the prepared films, combined with data of degree of crystallinity (as obtained by FTIR), indicate that the sulfonation degree of the polymer amorphous phase can be high (at least up to 50%, i.e., 1 sulfonic group per 2 phenyl rings of amorphous phase).

The high degree of sulfonation makes the amorphous phase highly hydrophilic. However, the presence of a hydrophobic crystalline phase makes crystallinity, and related physical properties, essentially independent of water sorption/desorption cycles.

s-PS films, sulfonated only in the amorphous phase and exhibiting the nanoporous δ-phase, present fast kinetics of guest sorption from water solutions into the nanoporous crystalline phase. These sorption kinetics are markedly higher than those of the corresponding unsulfonated films, which are already extremely efficient in removal of VOC from water. For instance, DCE sorption kinetics from 50 ppm aqueous solutions, as measured for films with a degree of sulfonation $S = 14\%$, when compared with the corresponding unsolfonated film, show an essentially unaltered DCE equilibrium uptake (close to 4 wt % and only as guest of the δ-nanoporous crystalline phase) associated with a DCE diffusivity increase of more than 70 times.

These results indicate that s-PS samples, being sulfonated only in their amorphous phases and exhibiting the nanoporous s-PS crystalline δ-phases, can be particularly suitable to remove VOC pollutants from water and moist air.

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