DOI: 10.1002/masy.201150505

Sorption of Pollutant Traces by Nanoporous Crystalline Aerogels: Visualization by a Dye

Christophe Daniel, Fabio Bernardo*

Summary: The influence of the crystalline structure on the pollutant sorption properties of high porosity syndiotactic polystyrene (sPS) aerogels has been made visible by using azulene, a blue dye, capable to form a clathrate phase with sPS. The bluish coloration observed for aerogels with the nanoporous δ-form and the absence of coloration for aerogels with the densely-packed γ-form clearly establish that the crystalline nanopores play a key role for the removal of pollutant traces from water or air.

Keywords: aerogels; azulene; nanoporous crystalline phase; pollutant removal; syndiotactic polystyrene

Introduction

It has been shown recently that high porosity syndiotactic polystyrene (sPS) aerogels can be obtained by supercritical CO_2 extraction of the solvent present in the native sPS physical gels[1–3] or by sublimation of the solvent.[4–5]

The advantage of using a supercritical extraction process to remove the solvent from the gel is the absence of surface tension and in these conditions a supercritical solution is formed between supercritical CO_2 and liquid solvent.[6] Thus, it is possible to extract all the solvent molecules from the gel without collapsing the structure and high porosity monolithic aerogels can be obtained. As an example, Figure 1 shows that the dimensions of a sPS gel prepared in toluene at polymer concentration $C_{pol} = 0.10$ g/g remain substantially unchanged during the supercritical CO_2 extraction and total removal of the solvent initially present in the gel.

Depending on the polymer concentration of the thermoreversible gel, monolithic aerogels with apparent density in the range 0.004-0.5 g/cm^3 can be prepared by solvent extraction with supercritical CO_2.[7]

Qualitatively, the porosity P of the aerogel samples can be expressed as a function of the aerogel apparent density ρ as:[8]

$$P = 100\left(1 - \frac{\rho}{\rho_S}\right)$$

where ρ_S is the density of the polymer matrix (equal to 1.02 g/cm^3, for a semicrystalline δ-form sPS with a crystallinity of nearly 40%).

Thus, depending on the gel polymer concentration, aerogels with porosity in the range 50-99.5% can be easily obtained after solvent extraction.[7]

It has been observed that different crystalline phases and morphologies can be obtained in sPS aerogels depending on the starting gel type (i.e gels with a co-crystalline phase or with the densely-packed β form) and on the supercritical CO_2 extraction temperature.[1] In particular, aerogels with the densely-packed γ [3] and β [1,3]-forms or with the nanoporous δ [1–2] and ε [3]-forms can be obtained.

Of particular interest are the aerogels characterized by the δ and ε crystalline forms which are characterized by the presence of nanocavities in their crystalline unit cells. These areogels are capable to

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Dipartimento di Chimica, Università degli Studi di Salerno, Via Ponte don Melillo, 84084 Fisciano (SA) Italy
E-mail: cdaniel@unisa.it

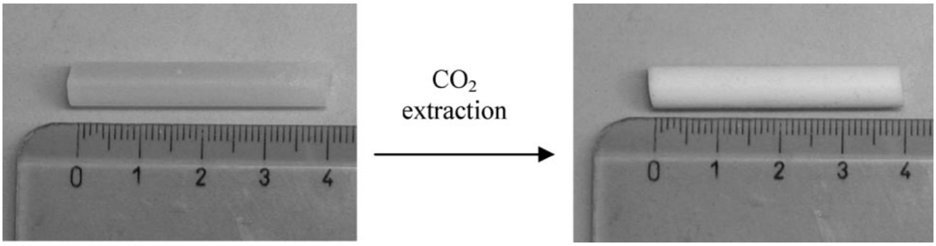


Figure 1.
Photographs of a piece of sPS gel prepared in toluene at $C_{pol} = 0.10$ g/g, before and after total solvent extraction with supercritical CO_2.

absorb rapidly and selectively volatile organic compounds (VOCs) (mainly halogenated or aromatic hydrocarbons) from water and air, also when present at very low concentrations.[1–3] For aerogels with the densely-packed crystalline forms, the VOC uptake is always much lower[1–2] and it becomes negligible for dilute aqueous solutions (i.e. 10ppm).[2] This different behaviour clearly indicates that at low concentrations, the VOC uptake occurs essentially only in the crystalline nanoporous phases and not in the amorphous macropores.

It is worth adding that as sPS aerogels are hydrophobic they seem particularly suitable for applications in chemical separation and in air/water purification.

In this contribution, the sorption of azulene (a blue organic dye) from diluted aqueous solutions has been studied for aerogels with the nanoporous δ crystalline form and the densely-packed γ crystalline form. Azulene is a molecule capable to form a clathrate phase with sPS by soaking δ sPS films in concentrated acetone solutions containing azulene or by exposing the films to azulene vapor for several days.[9]

The principle aim of this work was to make visible to the naked eye the influence of the aerogel crystalline nanopores on the sorption of pollutant traces from aqueous solutions.

In particular, it will be shown that in presence of the nanoporous δ-form the aerogel takes an intense blue coloration which indicates the sorption of azulene molecules while with the densely-packed γ crystalline form the aerogel maintains its white color. Moreover by taking advantage of the dye it is possible to follow the variation of the pollutant in the diluted aqueous solution by UV-Vis spectroscopic measurements.

Experimental Part

The syndiotactic polystyrene used in this study was manufactured by Dow Chemicals under the trademark Questra 101. ^{13}C nuclear magnetic resonance characterization showed that the content of syndiotactic triads was over 98%. The mass average molar mass obtained by gel permeation chromotography (GPC) in trichlorobenzene at 135°C was found to be $M_w = 3.2 \cdot 10^5\,g\,mol^{-1}$ with a polydispersity index $M_w/M_n = 3.9$. Solvents used to prepare the gels were purchased from Aldrich and used without further purification.

All sPS gel samples were prepared in hermetically sealed test tubes by heating the mixtures above the boiling point of the solvent until complete dissolution of the polymer and the appearance of a transparent and homogeneous solution had occurred. Then the hot solution was cooled down to room temperature where gelation occurred.

δ-form aerogels were obtained by treating sPS gels with a SFX 200 supercritical carbon dioxide extractor (ISCO Inc.) using the following conditions: $T = 40°C$, $P = 200$ bar, extraction time $t = 60$ min. γ-form aerogels were obtained with the same apparatus by treating gels using the following conditions: T = 130°C, P = 200 bar, extraction time t = 120 min.

X-rays diffraction patterns were obtained on a PW1710 Philips automatic diffractometer operating with a nickel-filtered Cu K_α radiation.

UV-Vis spectra were measured using a Perkin Elmer Lambda 800 spectrophotometer.

δ-form aerogel sorption kinetics with the azulene aqueous solution was obtained by gravimetric measurements. The weight gain of samples was determined with an analytical balance (0.01 mg precision) after wiping of the aerogels.

Results and Discussion

In Figure 2 are shown the photographs of a piece of δ-aerogel and γ-aerogel with a porosity P = 90% taken at different soaking times in a 1 liter aqueous solution of azulene at 10 ppm.

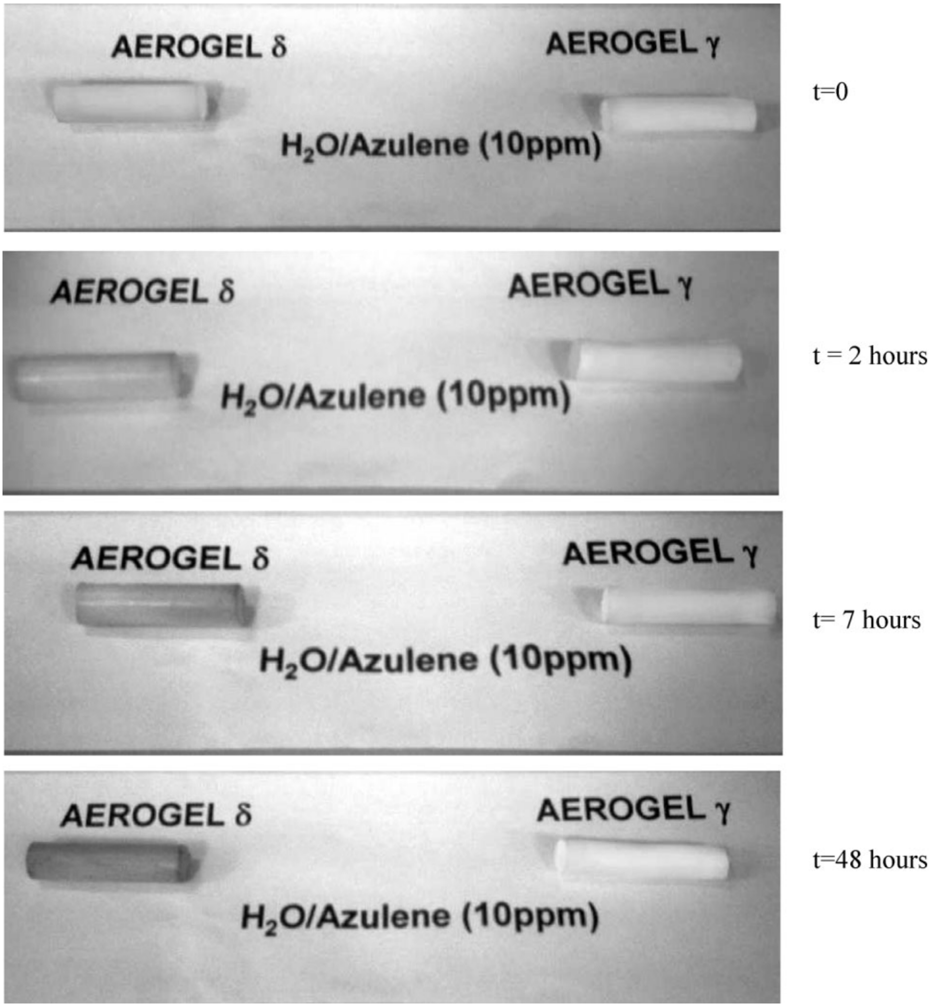


Figure 2.

Photographs of a piece of δ-form aerogel and γ-form aerogel taken at different soaking times in an aqueous solution of azulene prepared at 10 ppm.

The photographs reported in Figure 2 clearly show the different sorption properties of the two types of aerogels. The δ-form aerogel presents a blue coloration due to azulene sorption which becomes deeper with time while the white colour of the γ-form aerogel remains substantially unchanged. This result indicates that the azulene uptake occurs essentially only in the aerogels characterized by nanopores.

It is worth adding that the aqueous solution keeps its bluish colour with the γ-form aerogel while with the δ-form aerogel the solution becomes transparent.

The azulene sorption kinetics from a 10 ppm solution for a δ-form aerogel with a porosity P = 90% as obtained by gravimetric measurements is reported in Figure 3A while the UV-Vis spectra of the solution measured at different soaking times are reported in Figure 3B.

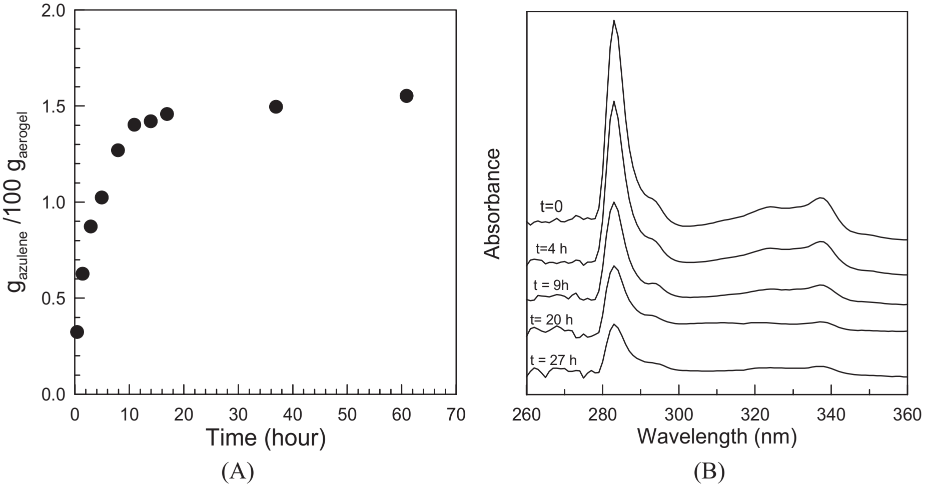
We can observe in Figure 3A that although the macroscopic dimensions of the aerogel are large (see Figure 1), the sorption kinetics of azulene proceeds very rapidly and after ca. 20 hours, the sorption equilibrium uptake has been reached. This fast sorption kinetics which is typical of the aerogels is due to the presence of macropores in addition to the nanopores of the δ-form.

The UV-Vis spectra reported in Figure 3B show a progressive decrease of the azulene absorbance with time. This decrease if of course due to the sorption of azulene in the aerogel and after 1 day, ca. 80% of the azulene molecules initially present in the solution have been absorbed.

It is worth adding that the use of UV-Vis spectroscopy and pollutant dyes makes possible the evaluate the efficiency of nanoporous sPS aerogels in removing pollutants from sub ppm aqueous solutions.

In Figure 4 are reported the x-ray diffraction patterns of the δ-form aerogel before (curve A) and after (curve B) immersion in the 10 ppm azulene aqueous solution.

After soaking in the solution, we can clearly observe some changes in the diffraction pattern of the aerogel sample. In particular the (-210) reflection at $2\theta = 10.1°$characteristic of the δ-clathrates is present while the intensity of the (-111) reflection at $2\theta = 13.4°$ which is typical of the nanoporous δ-form decreases. Moreover, the shift of the (010) reflection from $2\theta = 8.2°$ to 8.0° corresponds to an increase



(A) (B)

Figure 3.
(A) Sorption kinetics of azulene from a 10 ppm aqueous solution for a δ-form aerogel with a porosity P = 90%.
(B) UV-Vis spectra of the aqueous solution of azulene measured at different soaking times.

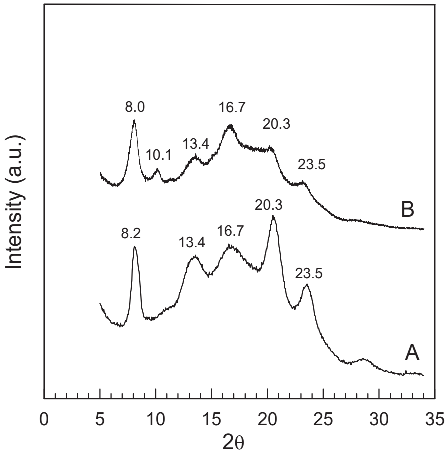


Figure 4.
X-ray diffraction patterns of a δ-form aerogel (P = 90%) before (A) and after (B) soaking for 24 hours in a 10 ppm azulene aqueous solution.

of the spacing between the *ac* layers. These variations indicate that sorption of azulene occurs in the nanoporous δ-form leading to the formation of a co-crystalline phase.

Conclusion

In this paper the sorption of azulene, a blue organic dye, from a 10 ppm aqueous solution has been studied for sPS aerogels with the nanoporous δ crystalline form and the densely-packed γ crystalline form.

A simple observation of the color variation of these two types of aerogels during their soaking in the aqueous solution has clearly established that the sorption of pollutant traces occurs in the nanopores of the aerogel crystalline phase.

Aerogel weight variation and UV-Vis spectroscopy measurements of the aqueous solution have also shown that azulene sorption kinetics is fast and after 1 day ca. 80% of the azulene molecules initially present in the solution have been removed from water.

Acknowledgements: Financial support of the ‘‘Ministero dell’Istruzione, dell’Università e della Ricerca’’ (PRIN07) and of ‘‘Regione Campania’’ (Legge 5 and Centro di Competenza per le Attività Produttive) is acknowledged. We thank Prof. Gaetano Guerra of University of Salerno for useful discussions.

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