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# Communications to the Editor

## Multiporous Material from Fibrillar Syndiotactic Polystyrene Intercalates

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The study of porous networks prepared from organic molecules or from polymers has aroused considerable interest among material scientists this past decade with the aim of devising materials with tailor-made properties. One aspect of material science dealing with large scale structures, with wide industrial applications, is the preparation of porous materials such as filtering membranes for the purification of water. So far, however, the range of pore sizes of these membranes is restricted: when porosity at the nanoscale level (*nanoporosity*) is obtained (zeolites, urea chlathrates, ...) porosity at the mesoscale level (*mesoporosity*) is absent, and vice versa. In the aim of preparing porous materials with pores ranging from the nano to the micro size, polymer/solvent intercalates[1] can be of interest, and particularly those obtained from syndiotactic polystyrene (sPS). It has been shown by Guerra et al.[2] that in some sPS intercalates the intercalated solvents can be removed from the crystalline lattice while its size and the chain structure remain unaffected (namely a $2_1$ helical form). These systems, designated as emptied clathrates, possess therefore nanocavities that have been shown to reabsorb solvent molecules of a wide range of molar volumes. The first materials produced by Guerra et al.[3] were powder as they were obtained from sPS systems of spherulitic morphology. Recently Guenet et al.[4] have suggested the use of sPS/solvent intercalates for which the morphology is fibrillar rather than spherulitic. Such a fibrillar morphology can be obtained through the formation of a thermoreversible gel. These systems could then be used directly as filtering membranes as liquids are allowed to go through thanks to the connected macropores. Also, such membranes would offer a specific area far larger than powderlike systems. In a recent paper Guerra's group[5] have shown that by preparing a thermoreversible gel and replacing the solvent through supercritical carbon dioxide extraction technique they could achieve this goal.

In this communication, we present another technique which is based on the sublimation of the solvent rather than its replacement. Results presented have been obtained with sPS/naphthalene systems because naphthalene is a sublimable solvent which is solid at room temperature.

Recently, our group has reported that sPS forms molecular compounds with naphthalene.[6] The number as well as the "thermodynamic" stoichiometry of the complex were determined by mapping out the temperature−concentration phase diagram coupled with a Tamman's type diagram. This study has revealed a domain of concentration and a temperature range wherein the intercalates of the type described by Chatani and co-workers[7] are produced. The representative morphology of the materials as observed by AFM after removing the solvent through sublimation is shown in Figure 1. As can be seen an appropriate fibrillar network structure is obtained with fibrils cross sections of about 50 nm.

The pore size distribution function of this network was determined by Mercury Intrusion porosimetry. Figure 2 shows that the specific surface depends on polymer concentration for the smallest pores. Of particular interest in the concentration $C_{pol} = 0.3$ (w/w) for which the specific area is the largest. Figure 3 presents a histogram of a system prepared at a concentration $C_{pol} = 0.3$ g/g. There are typically two ranges of mesoporosity, centered around diameters of about 0.05 and 8−10 $\mu$m. The question remains as to the presence of nanocavities (nanoporosity) after naphthalene removal. This cannot be answered (or accessed) only through mercury porosimetry and a series of further investigations by spectroscopic techniques were carried out.

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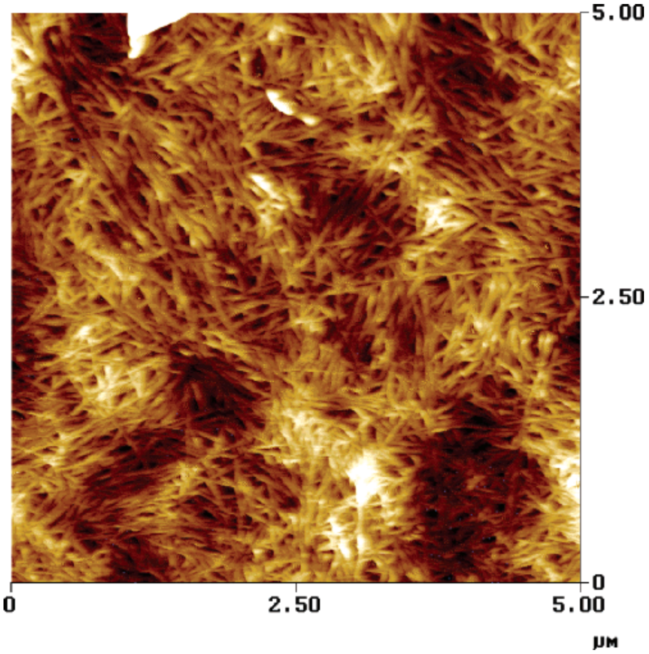

**Figure 1.** AFM picture taken from a sPS/naphthalene system ($C_{\mathrm{pol}}$ = 0.30 g/g) after sublimation of naphthalene through vacuum extraction for 10 days.

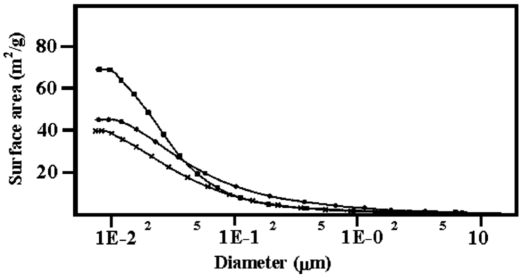

**Figure 2.** Specific surface area vs diameter of pores of sPS/naphthalene systems: (■) for $C_{\mathrm{pol}}$ = 0.30, (●) for $C_{\mathrm{pol}}$ = 0.20, and (×) for $C_{\mathrm{pol}}$ = 0.05 g/g.

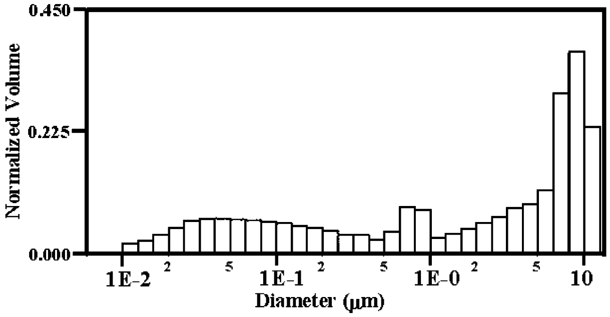

**Figure 3.** Normalized volume vs pore diameters of sPS/naphthalene systems for $C_{\mathrm{pol}}$ = 0.30 after sublimation of naphthalene through vacuum extraction for 10 days.

Typical X-ray diffraction pattern of the sPS/naphthalene system shown in Figure 4 is consistent with Chatani's lattice and therefore the presence of the $2_1$ helical conformation. Typical reflections for this lattice are at $q = 5.5$, 7.4, 10.8, 12.3, and 14.2 nm$^{-1}$ ($d = 1.14$, 0.85, 0.58, 0.51, 0.44 nm). Reflections from pure naphthalene crystals are at $q = 8.8$, 13.9, 14.3, and 15.7 nm$^{-1}$ ($d = 0.71$, 0.45, 0.44, and 0.43 nm). Extracting naphthalene through sublimation under vacuum shows the disappearance of all the naphthalene crystal reflections. However, this does not necessarily mean that naphthalene has been removed from the crystalline lattice. At this stage what can be said is that after naphthalene extraction the diffraction by sPS is still that of the $\delta$ form.[7]

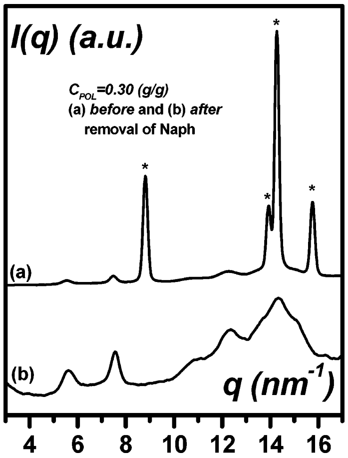

**Figure 4.** X-ray diffraction pattern of a sPS/naphthalene system ($C_{\mathrm{pol}}$ = 0.30 g/g): (a) before and (b) after sublimation of naphthalene through vacuum extraction for 10 days. Key: (∗) strong reflections coming from naphthalene.

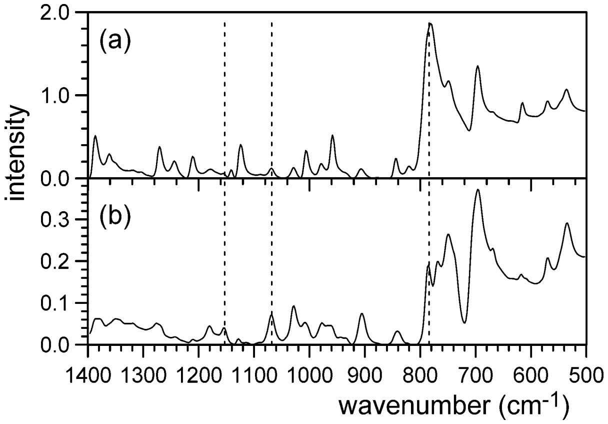

**Figure 5.** FT-IR spectra of (a) before and (b) after removal of naphthalene from sPS/naphthalene system after sublimation of naphthalene through vacuum extraction for 10 days. The vertical dotted lines stand for the bands at 1068 cm$^{-1}$ and at 1153 cm$^{-1}$ characteristic of sPS and at 783 cm$^{-1}$ characteristic of naphthalene.

Fourier transformed infrared (FT-IR) spectroscopy is unique tool to obtain information about the conformation of sPS in the intercalates as well as the presence and absence of the solvent within the crystalline lattice.

In the region 1400−500 cm$^{-1}$, Figure 5 shows the presence of strong naphthalene bands[8] along with the characteristics bands of sPS[9] some of which are characteristic of the $2_1$ helical conformation (in particular 571 cm$^{-1}$). Conversely, the characteristic bands of planar zigzag conformation[10] (1350, 1333, 1222, 1090, 542 cm$^{-1}$) are conspicuously absent. Of interest are three bands of which two are exclusively characteristic of sPS (at 1068 cm$^{-1}$ characteristic of polystyrene and at 1153 cm$^{-1}$ characteristic of the amorphous material), on one hand, and one exclusively characteristic of naphthalene (783 cm$^{-1}$), on the other hand. As shown recently by Albunia et al.[9d] the intensity of the band at 1068 cm$^{-1}$ is virtually unaffected by solvent removal while that at 1153 cm$^{-1}$ tends to increase by about 10%. Therefore, by determining through curve fitting analysis the relative ratio of the intensities of these two bands before and after naphthalene sublimation we are in a position of calculating the remaining amount of naphthalene in the whole sample and in the amorphous phase. This can be done by considering that the following ratio of the IR integrated intensities:

$$r_o = \frac{I^o_{sPS}}{I^o_{naph}} \propto \frac{F^o_{sPS}}{1 - F^o_{sPS}} \quad \text{and} \quad r_d = \frac{I^d_{sPS}}{I^d_{naph}} \propto \frac{F^d_{sPS}}{1 - F^d_{sPS}}$$

where $I_{sPS}$, $I_{naph}$ are the intensities of the band related to sPS, to naphthalene and $F_{sPS}$ the molar fraction of sPS, the superscripts o standing for the initial sample and d for the sample after extraction through sublimation. As $F^o_{sPS}$ is known, and $r_o$ and $r_d$ are derived from the FTIR spectra, then $F^d_{sPS}$ can be calculated. This yields 8 sPS monomers for 1 naphthalene molecule by considering the band at 1153 $cm^{-1}$, and 9 sPS monomers for 1 naphthalene molecule by considering the band at 1068 $cm^{-1}$, which figures stand for about half the stoichiometric composition of the compound (4/1). Clearly, if naphthalene molecules would not have been removed at all from the sPS/naphthalene compound crystalline lattice but only from the amorphous phase, then these two figures should significantly differ. We therefore conclude that the naphthalene content of the compound phase has been drastically reduced.

We have also used another method which simply consists of weighing a disk-shaped sample of about 2 cm diameter and 0.1 mm before and after sublimation. In this case the calculation yields 10 sPS monomers for 1 naphthalene molecule.

The fact that the three figures are about the same (typically 9 ± 1 sPS monomers for 1 naphthalene molecule) implies that naphthalene molecules have been removed from the crystalline lattice well beyond the compound stoichiometry (4/1). We, however, note that despite a large specific surface of the sPS/naphthalene fibrillar morphology, which should favor removal from the naphthalene molecules belonging to the compound phase, naphthalene molecules are still trapped in this phase. This is in contradiction with results reported by Venditto et al.,[11] who report that they produce totally emptied chlathrates from this solvent.

We suspect that the remaining naphthalene molecules play a role in preventing the crystalline lattice from collapsing to the $\gamma$ form while nanocavities are created due to the significant deficit of naphthalene molecules with respect to the stoichiometry of the compound.

In conclusion, we have shown that multiporous materials, with porosity ranging continuously from the nano to the micro range, can be prepared through the sublimation of the preparation solvent. This procedure offers an alternative route for the making of filtering membranes possessing properties of capturing small pollutants from water wastes.

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**Supporting Information Available:** Text describing the materials and experimental techniques used. This material is available free of charge via the Internet at http://pubs.acs.org.

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