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Microporous polyacrylate matrix containing hydrogen bonded nanotubular assemblies

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ABSTRACT

We report the straightforward photo-polymerization of polyacrylate films containing bis-urea based self-assembled nanotubes. The obtained materials are characterized by gas adsorption measurements, 129Xe NMR spectroscopy and WAXS. The presence of the bis-ureas is shown by butane adsorption (at 273 K and ambient pressure) to be responsible for the formation of a significant microporosity. This porosity is however not detected by the classical argon adsorption procedure (at 77 K and low pressure). This effect is attributed to the contraction of the material at low temperature and pressure, and may be of general concern for other organic porous materials. One of the potential advantages of the present materials is that the porosity results from the self-assembled nanotubes and should therefore be independent of the matrix mechanical properties. It should in particular be possible to adjust the flexibility of the matrix by changing the monomer composition.

1. Introduction

Most porous materials currently used in commercial applications are inorganic (zeolites, activated carbon, or clays, for example), however porous organic materials provide new opportunities in numerous technological areas, such as gas storage, separation processes or catalysis [1]. Their main potential advantages over inorganic materials are their lower specific weight, dielectric constant, and refractive index, and the virtually unlimited possibilities to functionalize their surface. In this context, several kinds of organic materials have been reported: on one hand, the assembly of well defined molecular building blocks can yield Covalent Organic Frameworks (COF) [2], Metal–Organic Frameworks (MOF) [3–5], or porous organic crystals [6–11], which enable both an exquisite control of the pore dimensions and a possible stimuli responsiveness. On the other hand, microporous materials can be obtained from rigidly crosslinked polymers [12–16]. In this case, a high surface area together with good mechanical properties can be obtained. In an attempt to combine a better control of the pore dimensions and good mechanical properties, it is also possible to polymerize a matrix in the presence of a self-assembled template. This approach has the additional advantage of an easier processability, because the pore formation and the chemical cross-linking steps are decoupled. The template can either remain in the final membrane (if the template presents an intrinsic porosity) [17–23], or it can be removed by dissolution or chemical degradation [24–26]. In the field of ultramicroporous materials (pore width <1 nm), only the former approach is feasible, and therefore, most systems reported consist of microchannels or nanotubes formed by assembly of macrocyclic compounds, where the macrocycle ensures the control of the pore width. In this case, the rigidity of the matrix is not essential, so that elastomeric ultramicroporous membranes can be envisaged.

In fact, self-assembled nanotubes can also be obtained from non-macrocyclic monomers [27–36], with the added advantage of a more direct synthetic accessibility than for macrocyclic compounds. In particular, bis-urea based monomers (Scheme 1) are extremely simple compounds known to form micrometer long nanotubes in non polar solvents [35–40]. We therefore decided to investigate the possibility to use these bis-ureas as template to form ultramicroporous materials.

2. Experimental

2.1. Synthesis of bis-ureas

Bis-urea **1** was prepared from racemic 2-ethylhexylamine and 2,4-toluenediisocyanate as described previously [41]. The synthesis of bis-urea **2** from racemic 2-aminobutanol will be reported later. Synthesis of bis-urea **3**: to a stirred solution of bis-urea **2** (429.5 mg,

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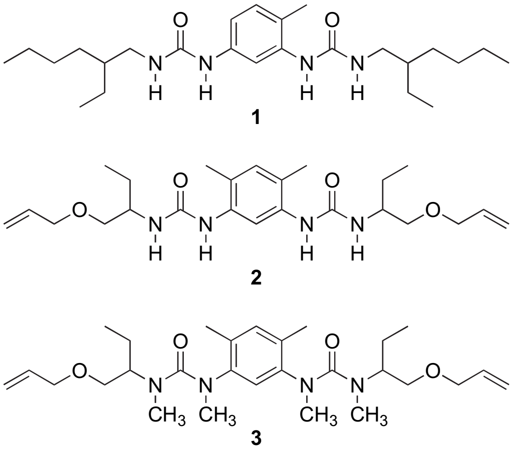

Scheme 1. Structure of hydrogen bonding bis-ureas **1** and **2**, and reference bis-urea **3**.

0.963 mmol) in 5 mL of anhydrous dimethylformamide was added NaH (143.2 mg, 5.778 mmol) at 0 °C. After 30 min, iodomethane (820.1 mg, 5.778 mmol) was added to the solution under nitrogen, at 0 °C. The mixture was stirred at room temperature for 14 h. The solution was diluted with 10 mL of dichloromethane, washed with water, dried over magnesium sulphate and evaporated to dryness. The product was purified by silica gel column chromatography (*n*-hexane/ethylacetate, 3/1) to give bis-urea **3** as a viscous oil (54% yield). ^{1}H NMR (200 MHz, DMSO): δ (ppm) = 0.87 (t, 6H, CH_3); 1.34 (m, 4H, CH_2); 2.05 (s, 6H, Ar-CH_3); 2.46 (s, 6H, N—CH_3); 3.05 (s, 6H, N—CH_3); 3.29 (m, 4H, CH_2—O); 3.65 (m, 2H, CH); 3.96 (d, 4H, CH_2—O); 5.14 (m, 4H, CH_2=CH); 5.82 (m, 2H, CH=CH_2); 6.83 (s, 1H, Ar-H); 8.03 (s, 1H, Ar-H).

2.2. Polymerization

The bis-urea (**1**, **2** or **3**) was dissolved under stirring in a mixture of isobornylacrylate (Aldrich) and divinylbenzene (Aldrich) (95/5 by weight) at 60 °C. In the case of bis-ureas **1** and **2**, a viscoelastic gel was obtained. The photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba) (1% by weight/isobornylacrylate) was added to the mixture. The solution was placed between two glass slides separated by a 1 mm thick spacer, and then photo-polymerized under a DYNAX UV light curing system (2000 Flood Model, 400 W) for 5 min. The obtained film was dried under vacuum for several days.

2.3. Porosity measurements

The polymer samples were first ground for 10 min, while cooled with liquid nitrogen, to yield a fine powder. The surface area and the porosity were measured by volumetry, with an ASAP 2020 Micromeritics apparatus using either argon at 77 K or butane at 273 K as adsorbent. The surface areas were calculated following the Brunauer, Emmet and Teller method (BET surfaces) and the microporous volumes were estimated from the point B, point from which the adsorbed quantity of adsorbent begins to vary linearly with the relative pressure of the gas. It corresponds to the filling of micropores [42].

2.4. Xe NMR

It has been proved that xenon NMR of adsorbed xenon is a very good tool to probe the micro and ultra-microporosity of porous materials [43]. Typically 300–500 mg of powdered polymer are placed in a cell. After treatment under vacuum at 60 °C, the cell is connected to a home-made volumetric apparatus. Xenon is introduced in the manifold and condensed in the cell at liquid nitrogen temperature. The cell is then sealed and brought back to the ambient temperature. The pressure of xenon in the manifold is determined so that the pressure in the cell after sealing is about 10 bar. Spectra are recorded with an AMX 300 Bruker spectrometer at the frequency of 83 MHz. The correct value of the pressure in the cell can be obtained from the chemical shift of the gas signal, which varies linearly with the xenon gas pressure.

3. Results and discussion

3.1. Design of the system

Due to strong hydrogen bonding between urea groups, bis-urea **1** spontaneously forms long and rigid nanotubes in a wide temperature and concentration range. The inner diameter of the nanotubes is fixed by the supramolecular architecture and has been shown by host-guest studies and molecular simulations to be close to 7 Å [36,38]. Our aim is to dissolve the bis-urea in a suitable monomer where the nanotubes can self-assemble, and then to polymerize the monomer. Our assumption is that the monomers present inside the cavity of the nanotubes do not have enough conformational freedom to polymerize, so that it should be possible to evaporate them after polymerization of the matrix, and thus to obtain porous channels of 7 Å diameter.

In low polarity solvents, bis-urea **1** nanotubes are isotropically dispersed and entangled, thus yielding gels. The viscoelastic nature of these gels proves that the nanotubes can break and recombine on the time-scale of seconds [44–46]. The dynamic character of the nanotubes has also been confirmed by isothermal titration calorimetry experiments, which show that dilution of the solution is responsible for a fast shortening of the nanotubes [37,47]. In some cases, the fast dynamics of this system is an advantage, because it ensures that a thermodynamic equilibrium is reached and that the self-assembled structures are stable over unlimited periods of time. In the present case however, the fast dynamics may allow the assemblies to reorganize during polymerization. To limit this potential issue, we need to use a fast polymerization process. Moreover, because a high polymerization temperature may destabilize the nanotubes, we selected a photo-polymerization process. Photo-initiated free radical polymerization has been widely used to polymerize a matrix containing non-dynamic self-assemblies [25,48–51]. We therefore sought to investigate if the same approach can be used in the case of a more dynamic system.

A second bis-urea (**2**) was also considered, to test the versatility of our approach. The xylene spacer in **2** (compared to the toluene spacer in **1**) is expected to stabilize the nanotube structure due to a better preorganization of the monomer [39]. Moreover, the allylether side-chain was introduced to improve the solubility in moderately polar monomers. The solubility of both bis-ureas was then tested in a range of monomers (Table 1). Unexpectedly, bis-urea **1** does not form viscoelastic gels in any styrene-based monomers, although it was previously shown that **1** forms viscoelastic gels in a wide range of aromatic solvents (such as toluene, xylenes or ethylbenzene) [36]. In fact, **1** is insoluble in most styrene-based monomers; the only exceptions being 2-substituted styrene derivatives. Unfortunately, these monomers are too large to fit inside the nanotubes and therefore destabilize them [36]. Among the acrylic monomers tested, isobornylacrylate is the only monomer, which yields viscoelastic gels for both bis-ureas. This monomer was thus selected for further study. In particular, it was checked by FTIR that the characteristic signature of nanotubes is indeed obtained at room temperature (see Fig. S1 in Supporting

Table 1
Solubility at room temperature of bis-ureas **1** and **2** in vinylic monomers (1% solutions) (F: fluid solution; G: viscoelastic gel; P: precipitates at room temperature after dissolution at 70 °C; I: insoluble; nt: not tested).

Monomer	Bis-urea **1**	Bis-urea **2**
Styrene	I	I
Divinylbenzene	I	I
2-Methylstyrene	F	nt
3-Methylstyrene	P	nt
4-Methylstyrene	P	nt
2,5-Dimethylstyrene	F	nt
2,4-Dimethylstyrene	P	nt
2,4,6-Trimethylstyrene	F	nt
4-Isopropylstyrene	P	nt
4-Tert-butylstyrene	P	nt
4-Chlorostyrene	I	nt
4-Fluorostyrene	P	nt
4-Chloromethylstyrene	I	nt
Vinylcyclohexane	G	nt
Methylmethacrylate	I	G
Butylacrylate	I	G
Isobornylacrylate	G	G
Butanedioldiacrylate	I	I

Information) [35]. The thermal stability of the nanotubes was then checked by high sensitivity DSC: for **1** in isobornylacrylate, a transition temperature of 38 °C was detected (see Fig. S2 in Supporting Information), whereas no transition was detected for **2** in isobornylacrylate (up to 80 °C), thus confirming the improved stability of the nanotubes in the case of bis-urea **2**.

Finally, samples were prepared by photo-polymerization of mixtures containing a bis-urea, isobornylacrylate, divinylbenzene (as cross-linker) and DMPA (as photoinitiator). Here, two samples are described, the first (**P1**) is composed of 10% **1** and 90% monomer (isobornylacrylate + divinylbenzene) (95/5). The second sample (**P2**) is composed of 10% **2** and 90% monomer (isobornylacrylate + divinylbenzene) (95/5). It was checked by WAXS on the final samples that no phase separation occurred during polymerization (see Fig. S3 in Supporting Information).

3.2. *Characterization of porosity by gas sorption*

In order to evaluate the microporosity, argon adsorption and desorption of **P1** and **P2** were measured at 77 K, and the results are shown in Fig. 1. In both cases, the obtained isotherm can be classified as type II and is consistent with a non-microporous material [42]. The apparent Brunauer–Emmett–Teller (BET) surface areas for **P1** (1.1 m^2/g) and **P2** (0.73 m^2/g) are very low. Moreover, the model of Horvath-Kawazoe [52] indicates a low microporous volume (0.0005 cm^3/g for **P1** and 0.0004 cm^3/g for **P2**) and the complete absence of micropores with diameter lower than 1 nm. This negative result obtained with conditions classically used to characterize inorganic materials may in fact be an artefact due to the experimental conditions of the adsorption and desorption measurement. Indeed, during the experiment the sample is placed under vacuum and at a very low temperature (77 K), which may cause a change in the supramolecular structure of the nanotubes. Knowing that the hydrogen bonds that maintain the tubular structure of bis-ureas are very sensitive to temperature and pressure, it is possible that if nanopores are present at room temperature and ambient pressure, they may reorganize and get obstructed at low temperature and low pressure. A similar contraction phenomenon has been observed in the case of nanoporous polyamides [15].

To confirm this hypothesis, we conducted new measurements of adsorption and desorption, but with a gas that can be condensed at a temperature close to room temperature and ambient pressure.

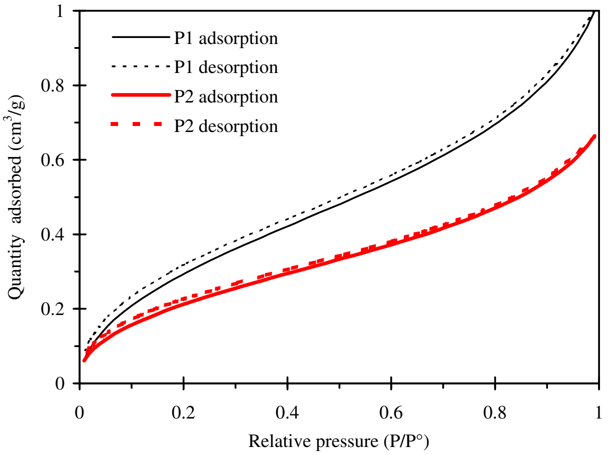

Fig. 1. Argon adsorption and desorption isotherms at 77 K, for **P1** and **P2** samples.

Butane is ideally suited for this, because it can be condensed at 273 K under atmospheric pressure, and it is characterized by a small enough encumbering surface area (0.47 nm^2). The adsorption isotherms of butane at 273 K and argon at 77 K of **P1** and **P2** are compared in Fig. 2. Remarkably, the adsorbed quantity of butane by **P1** and **P2** is more than 20 times higher than that for argon (in the relative pressure range $0 < P/P_0 < 0.4$). The BET surface areas for **P1** and **P2**, calculated using butane as adsorbate at 273 K, are respectively 65.4 m^2/g and 111 m^2/g. These values of surface area are much higher than that obtained with argon as adsorbate at 77 K. These results show clearly the high sensitivity of the microporous properties of **P1** and **P2** to the measuring conditions. Moreover, if we consider that the volume adsorbed at point B (Fig. 2) corresponds to the filling of the micropores, we find microporous volumes of 0.0095 and 0.015 $cm^3\ g^{-1}$, for **P1** and **P2** respectively. If we assume that all bis-ureas in the samples form nanotubes of 7 Å inner diameter, we can estimate a maximum microporous volume of 0.01 $cm^3\ g^{-1}$ (see Supporting information). The experimental values are therefore of the correct order of magnitude. The higher microporous volume and surface area of sample **P2** compared to sample **P1** may be related to the better stability of nanotubes in the case of bis-urea **2**. It is indeed possible that a larger fraction of bis-ureas are involved in the nanotubes in the case of bis-urea **2**.

To confirm that the large quantity of butane adsorbed in the samples is due to the presence of porosity, and not to swelling of

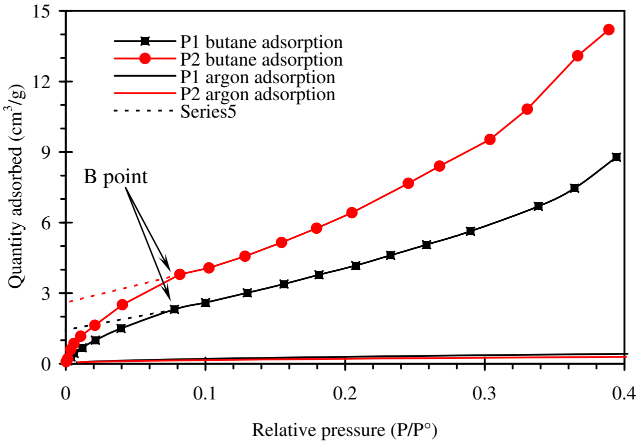

Fig. 2. Comparison between argon adsorption isotherm (obtained at 77 K) and butane adsorption isotherm (obtained at 273 K), for **P1** and **P2** samples.

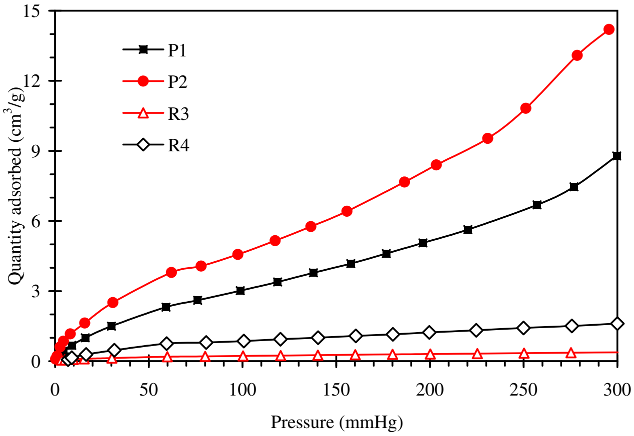

Fig. 3. Butane adsorption isotherms at 273 K, for **P1**, **P2**, **R3** and **R4** samples.

the polymer matrix by butane, the following blank experiments were performed. The first reference sample (**R3**) contains the methylated bis-urea **3** (Scheme 1), which cannot self-assemble into nanotubes, and the second reference sample (**R4**) is the crosslinked polyisobornylacrylate matrix containing no bis-urea. The four samples (**P1**, **P2**, **R3** and **R4**) were prepared strictly under the same conditions. The reference samples were also analyzed by BET with butane as adsorbent at 273 K. The obtained isotherms of adsorption are compared in Fig. 3, and show that **R3** and **R4** adsorb much less butane than **P1** and **P2**. The calculated BET surface area for **R3** and **R4** are 3.1 m^2/g and 13 m^2/g, respectively. The origin for the difference in butane adsoption between **R3** and **R4** is presently unknown, but the results clearly show that swelling of the matrix by butane cannot account for the large adsorption measured for **P1** and **P2**. This therefore confirms the porosity of **P1** and **P2** samples.

3.3. Xenon NMR measurements

It is well known that 129Xe NMR of adsorbed xenon is a useful technique to probe the microporosity of solids. Initially, this technique has been successfully used in the case of zeolites and then extended to others microporous materials (such as porous silica, pillared clays, activated carbons, coals, or polymers…) [43]. In this latter case, it is generally necessary to work at fairly high xenon pressures (10 bar) and with pulse delays of several seconds. We tried to use xenon NMR to confirm the existence of a microporosity in the samples. Fig. 4 presents xenon spectra adsorbed under about 10 bar on **P2** and its **R3** reference. In both cases, we observe two well defined signals: one near 4 ppm which is due to the xenon gas (the value of the chemical shift allows us to determine the equilibrium pressure of xenon over the solid) and a second strongly shifted near 220 ppm that we attribute to xenon in the polymer, in agreement with the literature [43]. Unfortunately the limited shift difference between the high field peaks in **P2** and **R3** does not allow to distinguish xenon adsorbed in the bis-urea nanotubes from xenon adsorbed in the polymer matrix. The reason is probably due to the similar chemical nature of the walls of the nanotubes and the polymer matrix and to the low microporous volume of the materials. However, the moderately larger peak width for **P2** (680 Hz), compared to **R3** (550 Hz) may be an indication of a more heterogeneous environment in the case of **P2**, i.e. with xenon adsorbed either in the bis-urea pores or in the polymer matrix.

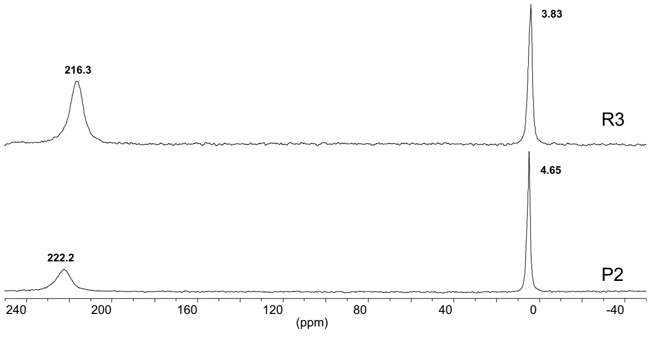

Fig. 4. Xenon NMR spectra of adsorbed xenon under 10 bar, for **P2** and **R3** samples.

4. Conclusion

We report the straightforward photo-polymerization of polyacrylate films containing bis-urea based self-assembled nanotubes. The presence of the bis-ureas is shown by butane adsorption (at 273 K and ambient pressure) to be responsible for the formation of significant microporosity. This porosity is however not detected by the classical argon adsorption procedure (at 77 K and low pressure). This effect, attributed to the contraction of the material at low temperature and pressure, may be of general concern for other organic porous materials. One of the potential advantages of the present materials is that the porosity results from the self-assembled nanotubes and should therefore be independent of the matrix mechanical properties. It should in particular be possible to adjust the flexibility of the matrix by changing the monomer composition.

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Appendix. Supporting information

Supplementary data associated with this article can be found in the on-line version, at doi:10.1016/j.polymer.2010.05.047.

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