Journal of Materials Chemistry

Cite this: J. Mater. Chem., 2012, 22, 7712

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COMMUNICATION

Formation of reactive aerogels and their reactivity in aqueous media. Wettability induces hydrophobic *vs.* hydrophilic selectivity[†]

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Received 10th January 2012, Accepted 22nd February 2012 DOI: 10.1039/c2jm30184a

Aerogels were formed from organogels of diamides by a supercritical drying process. The used organogels are composed of selfassembled nanotubes of 29 nm in diameter. SEM studies reveal that the resulting aerogels are made of fibers with diameters comprised between 40 and 200 nm, corresponding to bundles of the starting nanotubes, while WAXS indicated that most of the crystalline structure detected in the self-assemblies of the starting gel is preserved in aerogels. Two different reactive diamides bearing respectively an alkynyl and an azido function were investigated. We have tested the reactivity of the resulting aerogels under coppercatalyzed azide–alkyne cycloaddition in aqueous solution. These aerogels react easily with hydrophobic compounds although reactants are in separate phases. In contrast, they do not react with hydrosoluble compounds, because of their superhydrophobicity.

Aerogels are light materials with an alveolar and macroporous structure.¹ They are formed from gels by replacing the solvent of the gel by air while preserving the structure of the gel network.¹ The principle is very simple, but the removal of the solvent is technically complex. Simple drving does not afford an aerogel since capillary forces collapse the gel fibers. It causes a dramatic shrinkage of the gel network and thus yields a material without a macroporous structure. In order to preserve that structure, the technique of supercritical drying was developed.² This technique consists in immersing the gels in a low critical pressure liquid such as freon, nitrous oxide or carbon dioxide in a sealed vessel. The solvent of the gel is exchanged by this liquid below the critical point, and the temperature is raised above the critical point where the liquid transforms into a supercritical fluid. The release of the fluid lowers the pressure and transforms the supercritical fluid into gas. The overall transformation from liquid to gas is achieved without passing any liquid-gas interface.

Owing to their low density and high porosity, aerogels are attractive materials for applications including acoustic or thermal insulation³ and catalysis.⁴ The range of aerogel applications may be extended by functionalizing them chemically. To address this issue, we have used low molecular weight organogelators.⁵ It has been shown that organogels can be transformed easily into aerogels.⁶ The purpose of this study is to form a reactive organogel, transform it into a reactive aerogel and then study the reactivity of the resulting aerogel in water. It can be anticipated that such aerogels will not return to their initial gel state when brought in contact with water. They are expected to behave like a macroporous solid with high specific area and better mechanical stability than the starting gels. As such, they are good candidates to support catalysis or reactions in aqueous media. However aerogels prepared from organogels and able to undergo reaction have not been reported and their reactivity in water has not been probed.

The present study explores the possibility of functionalizing aerogels with alkynyl or azido groups, then letting them react with external reagents under copper-catalyzed azide–alkyne cycloaddition.⁷ This model reaction was chosen not only because of its efficiency and selectivity, but also because of its effectiveness even in heterogeneous conditions,⁸ including with fibrillar materials, such as in organogels.⁹⁻¹¹ Recent studies on organogels have shown that organogels are able to support other organic reactions.^{9,12} and organic catalysis.¹³ The studied reactions take place at the interface of the gel fibrils and the same solvent in which the gel had been formed. We wondered whether the reactions still occur after replacing the solvent by water. The formation of aerogels allows exploration of this point.

We have previously shown that compound 1 (Scheme 1) forms organogels in alkanes.¹⁴ These gels are obtained simply by dissolving a small amount of the compound in hot solvent and letting it cool down to 25 °C. Freeze fracture electron microscopy and small angle neutron scattering show that the gel is composed of nanotubes with an external diameter of 29 nm. The compound self-associates through non-covalent bonds: H-bonds between the amides and π - π stacking between the aromatic units. Insertion of an alkynyl or an azido group at the end of the ester chain of compound 1 preserves the properties of forming nanotubes.¹⁰ Freeze fracture TEM (Fig. 1A) or SAXS¹¹ shows that 2 and 3 self-assemble into tubes with diameters





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[†] Electronic supplementary information (ESI) available: Experimental details for the formation of the aerogels, reaction with the aerogels, and analysis of the products. See DOI: 10.1039/c2jm30184a



comparable with those of 1 (25.3 \pm 3 nm for 2 and 26.5 \pm 0.3 nm for 3).

Gels of 1, 2 or 3 were formed in cyclohexane and the solvent was removed by supercritical drying with CO_2 . A white and cotton-like material was obtained; its volume is about 80% of that of the starting organogels, indicating a partial collapse of the structure. SEM microscopy shows that the fibrillar network is preserved (Fig. 1C and D).

Large field micrographs show some fluctuation in the fiber density and some spherical areas where fibers are more compact (Fig. 1B). The volume loss cannot be attributed to those dense areas since such areas are also observed in the gels before drying. The thicknesses of the observed fibrils are polydisperse, between 40 nm and 180 nm, with an average value of 60 nm. It is clear that fibers in aerogels arise from the association of several starting nanotubes. The aerogels of three compounds have the same morphology especially the same alveolar structure and fiber size. This structural homogeneity reflects that of the organogels as observed by freeze fracture-TEM.

WAXS measurements have been performed on the studied compounds in different states. Fig. 2 compares the diffraction pattern from 1 in aerogels, organogels and solid state. The latter corresponds to the powder obtained from synthesis, without any self-assembly or heating/cooling cycle in organic solvent. The spectrum of the aerogel is similar to that of the organogel (after subtraction from the solvent 1, 2 and 3 are water insoluble and the corresponding aerogels are hydrophobic. Especially, they do not reform any gel when being in contact with water. After its removal from water, the aerogel dewets instantaneously and there is no need to proceed with a new supercritical drying process. This advantage makes them useful as a catalytic support for reaction in aqueous solutions. In contrast, when the aerogel is brought in contact with the organic solvent, the organogel reforms.

The reactivity of aerogels has been tested first with reagents soluble in water. The aerogels of 2 and 3 were reacted with an aqueous solution of CH₃(OCH₂CH₂)₃N₃ or propargyl alcohol (15 equiv.) respectively in water in the presence of CuSO₄ and ascorbic acid (0.2 and 0.8 equiv. resp.) (Scheme 2). Because of their low density and hydrophobicity, aerogels float above the solution and thus have limited contact with the reaction medium. In order to increase this surface, they have been trapped in a heavy wire mesh holder immersed in the reaction medium and the air trapped in the aerogel was removed under vacuum. The resulting aerogels were analyzed (after dissolution and extraction in dissociating solvents) with standard chromatographic and spectroscopic methods. Under the described conditions, no reaction occurs with aerogels of 2 and 3 (Table 1). Surprisingly, as a comparison, solid powders of 2 and 3 can react with those reagents under the same conditions to afford the desired products (resp. 4 and 6) in good yields.

The reactivity of aerogels *vs.* hydrophilic reagents was compared on the same self-assemblies but in the organogels *i.e.* still in the organic solvent. We have reported¹¹ that self-assembled gels of **2** and **3** react with $C_{10}H_{21}N_3$ and propargylic alcohol to afford **5** and **6** with a yield of 61% and 70% respectively. Since the reactions were conducted in the organic gelled solvent, a different catalyst, the organosoluble Cu(PPh₃)₃Br, was used. Although quantitative comparison cannot be done, the formation of the final compound observed only in the case of organogel shows the difference in reactivity of gels and aerogels.

The comparison between gels and aerogels proves that the lack of reactivity of aerogels is not the result of a reduced mobility of the reactants inside a tight network structure. As a matter of fact, it has been shown by conductimetry,¹⁵ fluorescence quenching¹⁶ and NMR¹⁷ that transport within gels is the same as in pure solvents. Organogels have been used as a reagent⁹⁻¹² or as a selective binding



1

q [Å

1.5

2

0.5

Log(Intensity) [a.u.]

0



2.5



Scheme 2 Reactions tested with aerogels.



Table 1 Yields of reactions of 2 and 3 in different states

-	Aerogel ^a	Gels ^b	Powder
$2 + N_3(CH_2CH_2O)_3CH_3$	0	_	80 (60 ^c)
3 + Propargylic alcohol	0	70	Quant. (50°)
$2 + C_{10}H_{21}N_3$	63	61	$54(30^{\circ})$

 a Yields in purified compounds. b In $\rm C_6H_{12},$ catalyst Cu(Ph_3)_3Br. c Yields without stirring.

medium¹⁸ and diffusion never prevents reactions. However since the reactions with the organic gels were carried out without stirring, the complete matter transport through the whole volume is slow (typically 1 week for a 2 cm³ gel). Therefore, we have conducted blank experiments with powders without stirring in order to mimic the unfavorable conditions of the reactions in organogels and in aerogels. In this case, the yield is lower but is still significant (Table 1).

The low reactivity of aerogels toward hydrosoluble reagents is clearly not due to an intrinsic lack of reactivity. In order to study the role of reagent hydrophilicity, we have conducted a reaction between aerogels of **2** and hydrophobic reagents such as $C_{10}H_{21}N_3$, in water under the same conditions as described for hydrosoluble compounds. The azido compound is a water-insoluble oil and the three components of the reaction (alkyne, azide and catalyst) were thus in separate phases. Despite these unfavorable conditions, the reaction proceeds in good yield (63%). The morphology of the aerogels, checked by SEM, before and after reaction shows no change in the macroporous architecture as well as in the diameters of the fibers.

The reactivity of the aerogel with a hydrosoluble reactant is null, whereas it is significant with hydrophobic species. Hydrophobicity of the aerogels can explain this phenomenon: the hydrophobic reagents tend to adsorb on the fibers of aerogels. The porous structure of aerogels favors the adsorption via capillary force. On the other hand, hydrophobicity of aerogels cannot explain their low reactivity with hydrosoluble species, since the powders react with good yields. The most relevant property to explain the difference of reactivity between aerogels and powder is the superhydrophobicity of the aerogels. This property is the magnification of the hydrophobicity of a surface by its roughness.¹⁹ This property is observed in nanopatterned surfaces,¹⁹ fibrillar materials such as electrospun mats²⁰ and porous materials like foams.21 Laplace's law can be used to derive the pressure difference between the air and the liquid necessary for the liquid to penetrate into pores: $\Delta P = \Gamma/2r$, where Γ is the superficial tension of water (72 mN m^{-1}) and r the radii of the pores, assuming that they are spherical. After removal of the air under vacuum, ΔP cannot exceed 1 bar under the experimental conditions, which allows the penetration of pores of radii larger than 1.5 µm. The pores of the studied aerogels have radii of this order or below and cannot be wetted by water at room pressure.

In summary, we have been able to prepare reactive aerogels from organogels. The morphology of the aerogel reflects that of the organogel. The hydrophobicity of the aerogel severely screens the reactants: it is inert toward hydrosoluble reactants, but highly reactive toward liposoluble reactants. This selectivity is explained by the superhydrophobic nature of the material. Further studies will be conducted to explore the reactivity with binary mixtures of solvents and with higher pressures.

Acknowledgements

This project was funded by the International Center for Frontier Research in Chemistry (icFRC), Strasbourg and by the Région Alsace. We thank J. Faerber for the SEM experiments, B. Heinrich and F. Schnell for the WAXS measurements. We acknowledge Dr T. Ondarçuhu for the fruitful discussions.

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