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The van der Waals induced supramolecular organization of hydrophobic tetrahedral units in the course of hydrolytic polycondensation

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This paper describes the hydrolytic polymerization of a tetrahedral precursor in the four directions. The hydrolytic polycondensation occurring at silicon led to highly polycondensed solids (around 100%). The solids obtained exhibited an organization at the nanometric scale evidenced by X-ray powder diffraction and another at the micrometric scale (birefringence experiments). The optical axis determination which corresponds to the orientation of the cross-linked colloids exhibits an inverse micelle type geometry. Thus the self-organization of the tetrahedral units is controlled by the poor hydrophilicity of the medium.

Introduction

The hydrolytic polycondensation at silicon (sol-gel process[1]) of hybrid organic–inorganic monophasic materials leads to short range organized solids (Scheme 1).

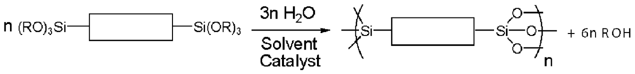
This organization, induced by supramolecular[2,3] van der Waals type interactions between hydrophobic units occurring during polycondensation at silicon, represents an attractive field of investigations. A large variety of precursors containing organic units has been investigated, leading to non-crystalline materials in which the organic and inorganic parts are covalently bound maintaining their physical and chemical properties.[4–6] van der Waals-induced supramolecular organization of these solids is currently under study in our group. In contrast to silica, which is always amorphous when prepared by this route, self-organization in nanostructured hybrid organic–inorganic materials has been evidenced in many examples.[7] Organic units included in the framework, whatever their geometry, exhibit an organization at the nanometric scale, as evidenced by X-ray powder diffraction. They exhibit also an organization at the micrometric scale as shown by birefringence experiments in cross-polarized light microscopy.[7] These results have been observed in the case of rigid-rod linear, twisted, planar and mesogenic organic spacers.[7] Only flexible alkyl organic groups lead to non-birefringent solids.[8] Moreover it has been shown that the hydrophilic conditions are an important factor.

In order to determine the limits of the organization of such systems, we are investigating new precursors with different geometry and connectivity at silicon. We have focused our interest in the case of tetrahedral geometry, expected not to be very favorable to self-organization. In a recent paper[9] we described the surprising results obtained from two precursors presenting such a geometry, tetrakis[4-tris(isopropoxy)silylphenyl]germane and tetrakis[4-tris(isopropoxy)silylphenyl]stannane [Scheme 2(a)].

Both precursors present twelve directions for solid formation, oriented regularly on the four directions of the tetrahedron. Their sol-gel hydrolysis–polycondensation leads to hybrid solids organized from the nanometric scale (X-ray diffraction) to the micrometric (birefringence) and even the millimetric one.[9] This organization occurs during the formation of the Si–O–Si bonds which transforms intermolecular interactions into intramolecular ones corresponding to the weak van der Waals interactions existing between the organic units. These results are noteworthy since it has been recently described that rigid molecules containing Ar_4C and Ar_4Sn as a core, explored as possible mesophases, are not mesogenic in spite of the presence of eight lipophilic long chains [Scheme 2(b) and (c)].[10]

In this paper we describe the case of the formation of polysiloxane polymers obtained from monomers presenting a tetrahedral geometry. The precursors investigated present a germanium or tin tetrahedral central atom and only the four directions of monofunctional silicon atoms for solid formation: tetrakis(4-dimethylisopropoxysilylphenyl)germane **1** and tetrakis(4-dimethylisopropoxysilylphenyl)stannane **2** (Scheme 3).

Furthermore the precursors **1** and **2** were selected because they present the same number of directions and the same tetrahedral geometry as $Si(OR)_4$ which never exhibits any organization when prepared in mild conditions. Indeed, crystals are obtained only after thermal treatment (thermodynamic control). The main difference is the complete hydrophilicity of $Si(OR)_4$ in the hydrolytic polycondensation. In contrast **1** and **2** exhibit a hydrophobic central bulky organic group. Thus in the hydrolytic conditions used for



Scheme 1 Sol-gel process of nanostructured hybrid organic–inorganic materials.

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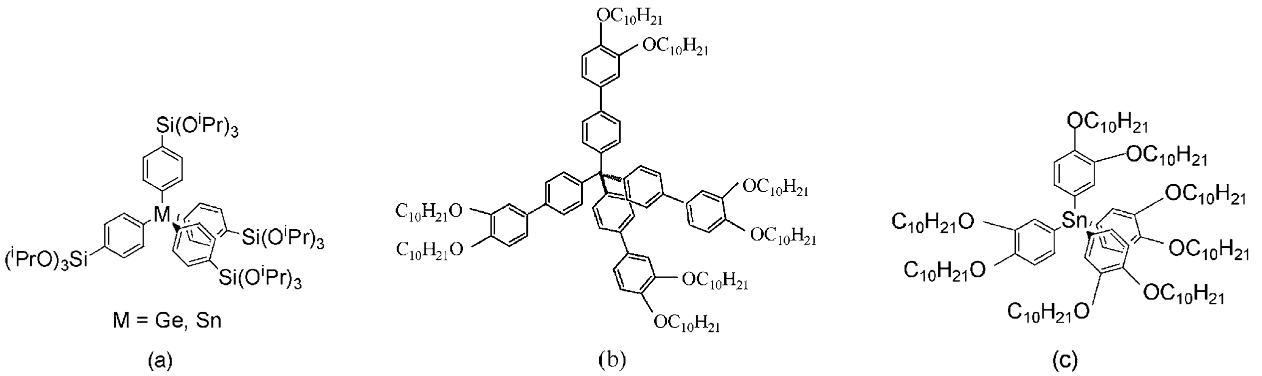


(a) (b) (c)

Scheme 2

polycondensation at silicon, the two precursors behave differently.

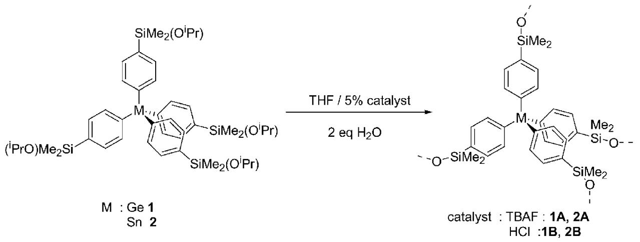
Results and discussion

1 and **2** were prepared by reaction of the Grignard reagent of 4-(bromophenyl)dimethylisopropoxysilane[11] with germanium and tin tetrachloride, respectively. They were isolated as oils in good yields. The hydrolysis was performed in THF (concentration 0.5 M) with a stoichiometric amount of water (2 eq.) in the presence of a nucleophilic (TBAF, tetrabutylammonium fluoride) or acid (HCl) catalyst (5 mol%) (Scheme 3). Opaque monolithic gels formed after a few hours (Table 1). The gels were aged for 6 days, then treated as usual to give insoluble non-porous powders, (S_{BET} < 10 m^2 g^{-1}).

These solids presented similar ^{29}Si CP MAS NMR spectra: only one thin signal at $\delta \sim -0.9$ ppm was observed and attributed to C–Si(Me)$_2$–O– units. This was indicative of almost total polycondensation since no signal appeared at $\delta \sim 5$ ppm (precursor) whatever the catalyst and the precursor, taking into account the accuracy of NMR.

As for all nanostructured hybrid materials reported until now,[12] the X-ray diffraction diagrams did not exhibit any sharp Bragg signal. However broad and intense signals were observed. It is well established that such broad signals correspond unambiguously to the existence of a nanometric scale order in the solid.[12] This point is very important since it means that this tetrahedral precursor is able to induce self-organization at the nanometric scale. As a first approximation, assuming Bragg's law *a priori*, the distances associated with the q values were evaluated ($d = 2\pi/q$). The X-ray powder diffraction diagrams of the solids (Fig. 1) exhibited three broad signals and the shape of the curves was similar whatever the precursor and the catalyst employed.

The signals were centred at 1.61 Å^{-1} (3.9 Å), 1.06 Å^{-1} (5.9 Å) and 0.49 Å^{-1} (12.8 Å) in the case of germanium, and were shifted to slightly longer distances for the tin compound, at 1.49 Å^{-1} (4.2 Å), 1.01 Å^{-1} (6.2 Å) and 0.48 Å^{-1} (12.9 Å). The two signals at 3.9 and 4.2 Å were attributed to the contribution of the Si–O–Si units.[12] The signals at 5.9 and 6.2 Å could correspond to the distance between planes of central metallic (germanium or tin) on one hand and silicon atoms on the other hand. The values obtained by molecular modelling, using Chem 3D pro (MM2 method), were, respectively 6.7 Å and 6.9 Å. The broad signals at 12.8–12.9 Å might correspond to an average organization between the tetrahedrons. However it is difficult to make further comparisons with distances deduced by molecular modelling since we do not know how the tetrahedrons are arranged one to the other. Nevertheless the presence of these X-ray diffraction signals means that there is an organization at the nanometric scale between the tetrahedrons.[13] The irreversible formation of the Si–O–Si bonds induces the auto-organization at the nanometric scale by forcing the molecules to be bonded to each other: the polycondensation at silicon changes irreversibly the intermolecular interactions into intramolecular ones. This process eliminates the main part of the entropy and permits us to understand why very weak van der Waals interactions of tetrahedral units are sufficient for inducing the organization of the solid.



Scheme 3 Hydrolysis–polycondensation reaction of precursors **1** and **2**.

For the birefringence measurements a fraction of the homogeneous solution, containing the precursor, THF, the catalyst and H$_2$O, was introduced by capillarity, a few minutes before sol-gel transition, in a thin Teflon-coated glass cell, which was then sealed. After gel formation (2 hours), the cell was analyzed by microscopy in polarized light. All the solids

Table 1 Some data for solids **1A**, **1B**, **2A**, **2B**

Solid	Catalyst	Gel time (hour)	^{29}Si NMR δ (ppm)	Birefringence Δn ($\times 10^3$)
1A	TBAF	9	−0.91	4.9
1B	HCl	3	−0.93	5.1
2A	TBAF	13	−0.89	6.0
2B	HCl	3.5	−0.90	6.1

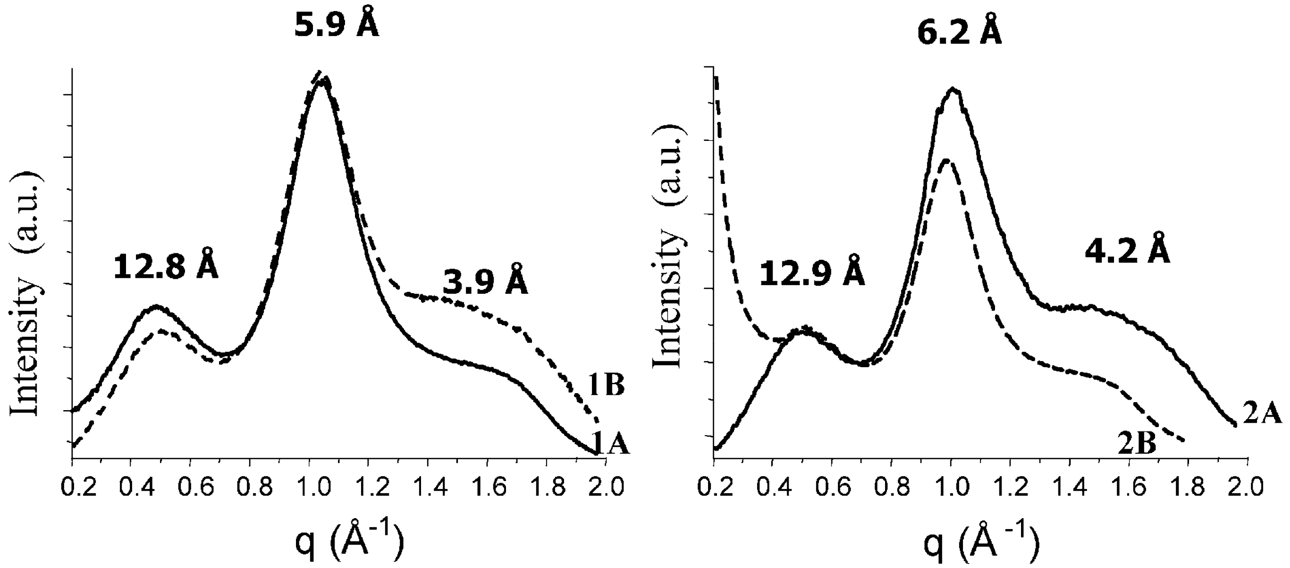


Fig. 1 X-Ray diffraction diagrams of solids **1A** (plain), **1B** (dotted), **2A** (plain) and **2B** (dotted).

presented birefringence properties after 24 hours. The higher values were found for the tin compounds **2A** and **2B**. The birefringence intensities are given in Table 1. They correspond to an average of 10 measurements recorded at different locations of the cell. The morphologies of the solids in the cells were very similar whatever the precursor and the type of catalyst. Many circular nodules of various size were observed. These isotropic zones corresponded to bubbles formed during the polycondensation. They were empty of material since only Teflon coating is observed in their center, as confirmed by Raman experiments.[14] The other parts of the solid around the bubbles were anisotropic, the higher birefringence values being observed in the near environment of the bubbles (Fig. 2).

The orientation of the optical axis was determined using a Berek compensator (Fig. 2). It corresponds to the orientation of anisotropy at the micrometric scale. Interestingly we observed the formation of empty bubbles instead of the cracks that are usually formed under equivalent conditions with rigid-rod linear, planar and even tetrahedral spacers.[7,9] We have previously evidenced that reorganization within hybrid solids occurs during the ageing step, that is when densification of the Si–O–Si bridges and solvent evaporation generate stress and shrinkage, forming empty spaces in the cell as shown in Scheme 4(a).

In other words, the organization of aggregates of matter at the micrometric scale occurs with an anisotropic orientation around the empty bubbles in the case of polycondensation of precursors **1** and **2** containing monodimensional $Me_2Si(OR)$ groups. This situation is completely different from the orientation observed in the case of the hydrolysis–polycondensation of tetrahedral precursors containing tridimensional $Si(OR)_3$ units (Scheme 2a).[9] In this case, regular parallel rectangular chunks are always observed and the orientation of the optical axis was always found perpendicular to the edges of the chunks (Scheme 4b). This difference of birefringence figures and the orientation of the optical axes towards the centre of the bubbles suggested the geometry of an inverse micelle: the cross-linked hydrophobic polymer is oriented towards the hydrophilic centre.

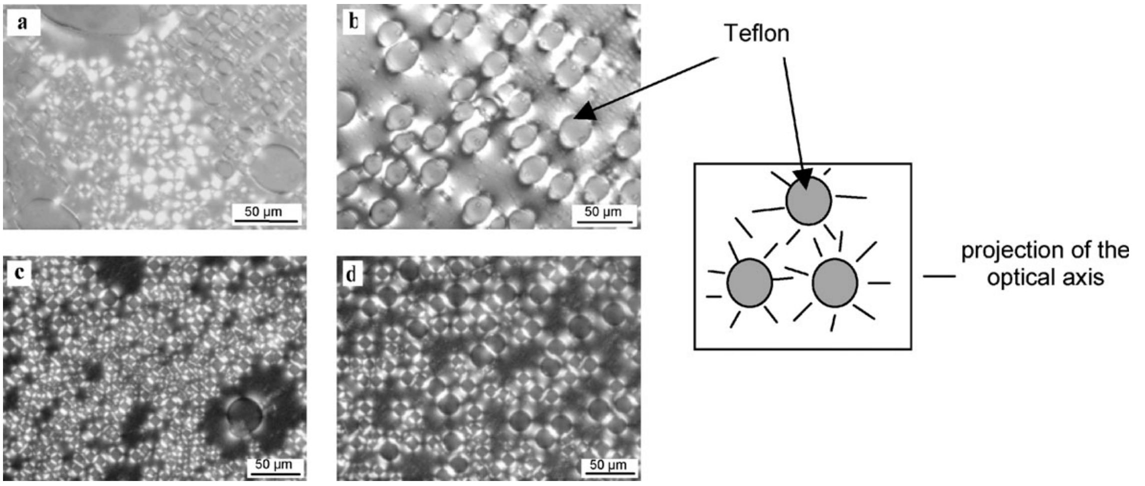
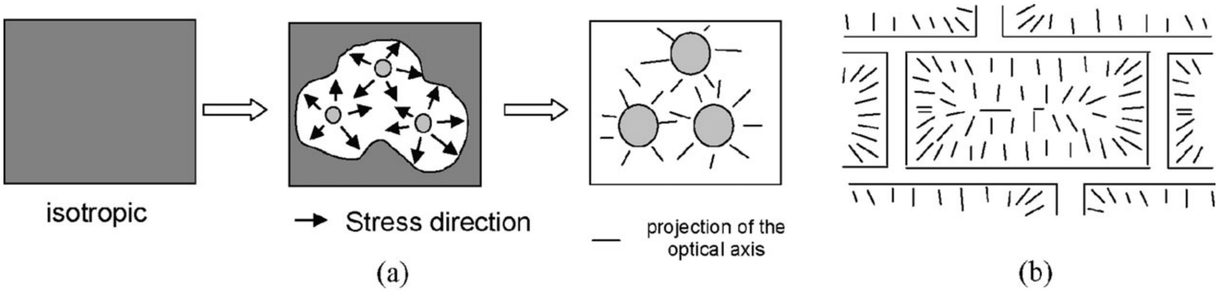


Fig. 2 Birefringence pictures of: (a) **1A**, (b) **1B**, (c) **2A**, (d) **2B** and schematic representation of a gel picture.



Scheme 4 (a) Schematic representation of stress and shrinkage during ageing step, and orientation of optical axis in a chunk of solid **1A**, **1B**, **2A** or **2B**; (b) cracks and orientation of optical axis in a chunk of solid obtained from tetrahedral precursor with Si(OR)$_3$ groups *cf.* Scheme 2(a).

In fact the work-up always employed involves the use of a solution corresponding to the stoichiometric amount of H_2O necessary for the hydrolysis–polycondensation. In the present case, the amount of H_2O is 1 mole of H_2O for 13.4 moles of hydrophobic species (precursor and THF) whereas in the general cases and particularly in the case of the tetrahedral precursors shown in Scheme 2(a), this molar ratio was $\sim 1/4$. The polycondensation goes on with the elimination of hydrophilic isopropanol molecules in a geometry similar to that of an inverse micelle. It is possible to explain this organization considering that the polycondensation begins to induce the organization of the oligomers at the nanometric scale by van der Waals interactions. The growth of the oligomers is then controlled by the structure of the inverse micelle existing in the medium owing to the presence of a low amount of hydrophilic entities (H_2O, isopropanol).

These observations show that it will certainly be possible to obtain different orientations by varying the amount of H_2O employed. Work is in progress in this direction.

Conclusions

In conclusion tetrahedral precursors led to the formation of long range ordered solids. This particular example shows the degree of generality of the auto-organization phenomenon since systems presenting four directions for polycondensation regularly distributed in space led to highly polycondensed ordered solids. The results reported here clearly illustrate the fact that the micrometric organization takes place during Oswald ageing and is governed by completely different parameters than the nanometric one.

Experimental

All reactions were carried out under argon using a vacuum line and Schlenk techniques. Solvents were dried and distilled just before use. The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-200 spectrometer and the ^{29}Si NMR spectra were recorded on a Bruker WP-200 SY spectrometer. The ^{29}Si CP MAS NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 59.6 MHz using a recycling delay of 10 s and a contact time of 5 ms. The spinning rate was 5 kHz. Chemical shifts are given relative to tetramethylsilane. The nitrogen adsorption–desorption isotherms at 77.35 K were recorded on a Micromeritics Gemini III 2375 apparatus. The specific surface area was determined using the BET equation. The X-ray experiments were performed on powders of solids in a Lindeman tube with an imaging plate two-dimensional detector (Marresearch 2D "Image-Plate") with a rotating anode apparatus (Rigaku RU 200). The radiation used was Cu Kα (λ = 1.5418 Å). Optical properties of the materials were observed with a Laborlux12POLS polarizing microscope. Photographs were taken using a Leica wild MPS28 camera. The birefringence Δn of the gels was obtained from the expression $\Delta l = (\Delta n)d$, where Δl is the optical path difference and d is the cell thickness which is evaluated by UV-Vis spectroscopy ($\sim$15 µm). Δl was measured by a Berek compensator. Elemental analyses were carried out by the "Service Central de Micro-Analyse du CNRS".

Syntheses

Tetrakis(4-dimethylisopropoxysilylphenyl)germane 1. The Grignard reagent of 4-bromophenyldimethylisopropoxysilane was prepared in THF from 7.3 g (26.72 mmol) bromo compound and 0.78 g (32.10 mmol) of magnesium according to a literature procedure.[11] The greenish mixture was stirred during 3 hours at room temperature, then 0.71 mL (6.07 mmol) of tetrachlorogermane were added. After 12 additional hours of stirring, THF was evaporated and the solid residue was taken up in hexane. After filtration it was evaporated under vacuum to give **1** as a translucent thick oil: 3.85 g (4.55 mmol), yield 75%. ^1H NMR (CDCl$_3$) δ: 0.42 (s, 24H), 1.17 (d, J = 6.0 Hz, 24H), 4.02 (hept, J = 6.0 Hz, 4H), 7.53 (dd, J = 7.6 Hz, 16H); ^{13}C NMR (CDCl$_3$) δ: −0.7 (CH$_3$), 26.1 (CH$_3$), 65.9 (CH), 124.7 (Ar), 131.4 (Ar), 135.5 (Ar), 137.8 (Ar); ^{29}Si NMR (CDCl$_3$) δ: 4.94; elemental analysis: calcd for $C_{44}H_{68}O_4GeSi_4$: C 62.47, H 8.10, Ge 8.58, Si 13.28. Found: C 62.14, H 8.06, Ge 8.21, Si 13.42%.

Tetrakis(4-dimethylisopropoxysilylphenyl)stannane 2. **2** was prepared similarly from 10.3 g (37.69 mmol) of 4-bromophenyldimethylisopropoxysilane, 1.10 g (45.23 mmol) of magnesium and 1.00 mL of tin tetrachloride. **2** was obtained as a translucent thick oil: 5.37 g (6.02 mmol), yield 72%. ^1H NMR (CDCl$_3$) δ: 0.45 (s, 24H), 1.20 (d, J = 6.0 Hz, 24H), 4.08 (hept, J = 6.0 Hz, 4H), 7.68 (dd, J = 7.6 Hz, 16H); ^{13}C NMR (CDCl$_3$) δ: −0.7 (CH$_3$), 26.2 (CH$_3$), 65.8 (CH), 124.7 (Ar), 133.9 (Ar), 137.1 (Ar), 139.8 (Ar); ^{29}Si NMR (CDCl$_3$) δ: 5.18; elemental analysis: calcd for $C_{44}H_{68}O_4Si_4Sn$: C 59.24, H 7.68, Si 12.59, Sn 13.30. Found: C 59.12, H 7.96, Si 12.14, Sn 12.94%.

Preparation of the solids 1A, 1B, 2A and 2B. The preparation of the gels was carried out according to the following general procedure. The preparation of **1A** is given as an example: in a Schlenk tube, 946 μL of a solution containing 47 μL (47 μmol) of TBAF (1 mol L^{-1} in THF), 34 μL (1.89 mmol) of H_2O and 865 μL of dried THF, were added to a solution of 0.800 g (0.946 mmol) of **1** in 946 μL of dried THF. After homogenization the mixture was kept in the Schlenk tube. A few minutes before the sol-gel transition, a part was introduced by capillarity into a Teflon-coated cell for birefringence measurements. The gel obtained after 9 h in the Schlenk tube was aged for 6 days, then crushed and washed twice with acetone, ethanol and diethyl ether, and the resulting solid was dried at 120 °C *in vacuo* for 3 hours yielding a white powder.

1A: 0.587 g (0.915 mmol); yield 97%. ^{29}Si CP MAS NMR (δ ppm): −0.91. $S_{\mathrm{BET}} < 10\ \mathrm{m^2\ g^{-1}}$.

1B: 0.800 g (0.946 mmol) of **1** in 1.892 mL of THF containing 47 μL (47 μmol) of HCl and 34 μL (1.89 mmol) of H_2O gave a gel after 3 h. **1B**: 0.565 g (0.880 mmol); yield 93%. ^{29}Si CP MAS NMR (δ ppm): −0.93. $S_{\mathrm{BET}} < 10\ \mathrm{m^2\ g^{-1}}$.

2A: 0.500 g (0.560 mmol) of **2** in 1.120 mL of THF containing 28 μL (28 μmol) of TBAF and 20 μL (1.12 mmol) of H_2O gave a gel after 13 h. **2A**: 0.378 g (0.550 mmol); yield 98%. ^{29}Si CP MAS NMR (δ ppm): −0.89. $S_{\mathrm{BET}} < 10\ \mathrm{m^2\ g^{-1}}$.

2B: 0.500 g (0.560 mmol) of **2** in 1.120 mL of THF containing 28 μL (28 μmol) of HCl and 20 μL (1.12 mmol) of H_2O gave a gel after 3.5 h. **2B**: 0.365 g (0.531 mmol); yield 95%. ^{29}Si CP MAS NMR (δ ppm): −0.90. $S_{\mathrm{BET}} < 10\ \mathrm{m^2\ g^{-1}}$.

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References

1 C. J. Brinker and G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego, 1990.
2 J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1st edn, 1995.
3 M. W. Hosseini, *Coord. Chem. Rev.*, 2003, **240**, 157.
4 D. A. Loy and K. J. Shea, *Chem. Rev.*, 1995, **95**, 1431.
5 R. J. P. Corriu, *Angew. Chem., Int. Ed.*, 2000, **39**, 1376, and references cited.
6 G. J. de Soler-Illia, C. Sanchez, B. Lebeau and J. Patarin, *Chem. Rev.*, 2002, **102**, 4093.
7 B. Boury and R. J. P. Corriu, *Chem. Rec.*, 2003, **3**, 120, and references cited.
8 B. Boury, F. Ben, R. J. P. Corriu, P. Delord and M. Nobili, *Chem. Mater.*, 2002, **14**, 730.
9 F. Lerouge, G. Cerveau and R. J. P. Corriu, *J. Mater. Chem.*, 2006, DOI: 10.1039/b509017b.
10 A. Pegenau, T. Hegmann, C. Tschierske and S. Diele, *Chem.–Eur. J.*, 1999, **5**, 1643.
11 J.-P. Bezombes, C. Chuit, R. J. P. Corriu and C. Reye, *J. Mater. Chem.*, 1998, **8**, 1749.
12 B. Boury and R. J. P. Corriu, in *Supplement Si: The Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley & Sons, Chichester, 2001, ch. 10, p. 565, and references cited.
13 B. Boury, R. J. P. Corriu, P. Delord and V. Le Strat, *J. Non-Cryst. Solids*, 2000, **265**, 41.
14 Raman experiments were performed by Dr Jean-Francois Bardeau from University of Maine, Le Mans.