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Evidence for an Organization of Nanostructured Silica-Based Hybrid Materials Prepared by Sol−Gel Polymerization

Frédéric Ben, Bruno Boury,
Robert J. P. Corriu,* and Valérie Le Strat

*Laboratoire de Chimie Moléculaire et Organisation
du Solide, UMR 5637, Université Montpellier II,
Place Eugene Bataillon,
34095 Montpellier Cedex 5, France*

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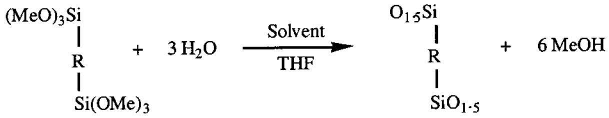
Sol−gel polycondensation is a general route for the preparation of nanostructured hybrid materials of the general formula $[O_{1.5}Si-(R)-SiO_{1.5}]$ by hydrolytic polycondensation of the corresponding molecular building block $(MeO)_3Si-(R)-Si(OMe)_3$, according to the ideal equation below.[1−8]

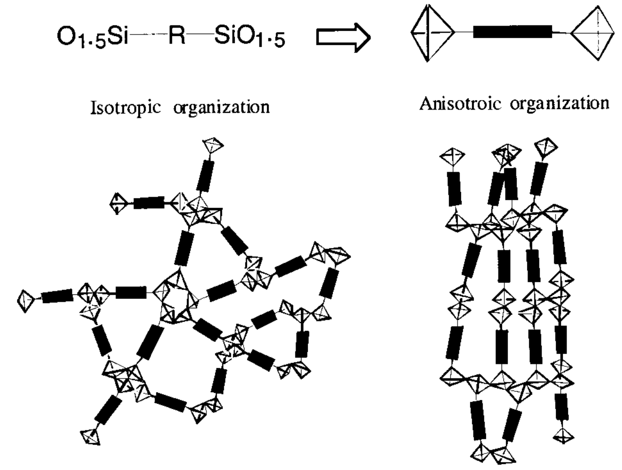


$$\begin{matrix}(MeO)_3Si\\ |\\ R\\ |\\ Si(OMe)_3\end{matrix} + 3\,H_2O \xrightarrow[THF]{Solvent} \begin{matrix}O_{1.5}Si\\ |\\ R\\ |\\ SiO_{1.5}\end{matrix} + 6\,MeOH$$

It has already been demonstrated that the nature of the group R, along with other kinetic parameters (such as water concentration, solvent, or temperature), is a deciding factor for the porosity and surface of the resulting materials,[9−11] as in the case of other materials elaborated by the sol−gel process.[12−14] Previous studies have demonstrated the stability of the Si−C bonds, which are not cleaved under the sol−gel conditions.[15−18]

These materials are frequently considered as amorphous with no preferential orientation of the molecular units (Scheme 1, isotropic organization) because no Bragg diffraction peaks are observed. However, the possibility of local organization in $[O_{1.5}Si-R-SiO_{1.5}]$ hybrid materials has been supported by chemical modification observed in the solid state such as polymerization of the thiophene units of $O_{1.5}Si-(C_4H_2S)-SiO_{1.5}$[15] or the diyne units of $O_{1.5}Si-C{\equiv}C-C{\equiv}C-SiO_{1.5}$.[19]

Scheme 1



Moreover, recently, we have reported experimental X-ray data supporting short-range order on the nanometer scale for a xerogel with the general formula $O_{1.5}Si-C{\equiv}C-C_6H_4-C{\equiv}C-SiO_{1.5}$.[20] In addition, the anisotropic organization of this material was demonstrated by its birefringence properties, which suggested an arrangement such as that depicted in Scheme 1.[21]

Interestingly, this birefringence cannot be associated with a liquid crystal phenomenon as the precursor itself is not a liquid crystal: it behaves as a nonmesogenic compound. Moreover, the final organization of the solid arises from a nonreversible polycondensation in an isotropic solution, occurring at each end of the precursor and resulting in the formation of a three-dimensional Si−O−Si network. This is demonstrated by the ^{29}Si solid state NMR spectrum, which exhibits mainly T^2 $[(SiO)(RO)_2\underline{Si}-C]$ and T^3 $[(SiO)_2(RO)_1\underline{Si}-C]$ units.

This is a completely unreported situation; therefore, it was necessary to determine whether this phenomenon was general or whether it was only related to some special property of the R group $-C{\equiv}C-C_6H_4-C{\equiv}C-$ used in this case.

In this paper, we focus on the precursor's rigidity and report birefringence studies of xerogels obtained with precursors of the general formula $(MeO)_3Si-(R)-Si(OMe)_3$ prepared under similar conditions. We used two families of precursors, either a rigid R group (aryl **1**−**3** or thienyl groups **4**−**5**) or a fully flexible one (alkyl groups **6**−**8**) (Scheme 2).

We have also briefly examined the effect of the film (or coating) that covers the glass slides. We have tested the effect of poly(vinyl alcohol) (PVA) and poly(tet-

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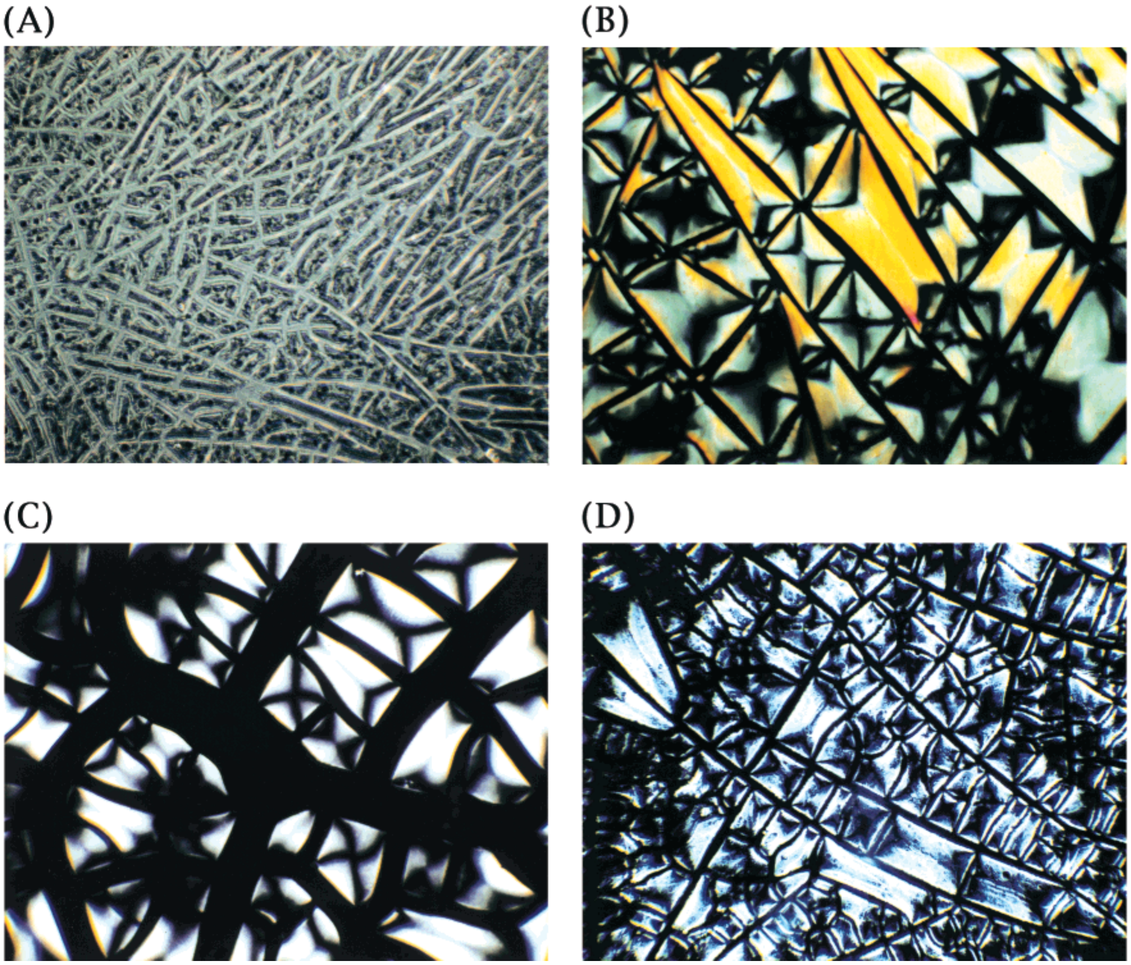
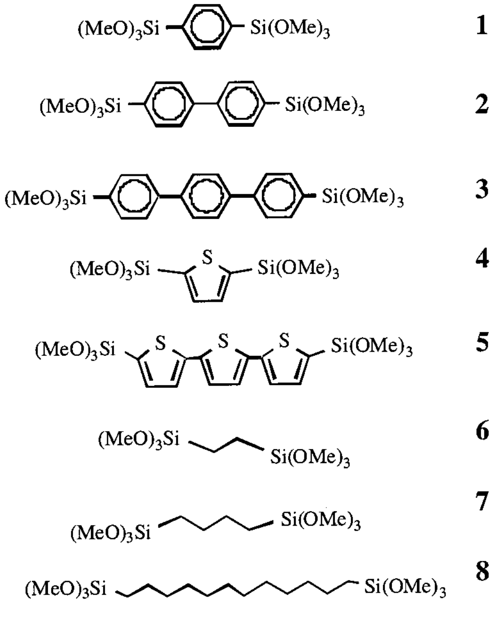


Figure 1. (A) Xerogel $O_{1.5}Si-CH_2-CH_2-SiO_{1.5}$. (B) Xerogel $O_{1.5}Si-(C_4H_2S)_3-SiO_{1.5}$. (C) Xerogel $O_{1.5}Si-(C_6H_4)_2-SiO_{1.5}$. (D) Xerogel $O_{1.5}Si-(C_6H_4)_3-SiO_{1.5}$.

Scheme 2



rafluoroethylene) (Teflon) by comparing their coating effect with the effect of uncovered glass slides. Both film coatings are commonly used to favor the orientation of liquid crystals.

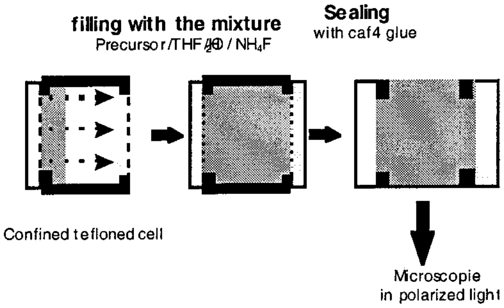
The Effect of the R Group. For both families of precursors $(MeO)_3Si-R-Si(OMe)_3$, polycondensation at the silicon was achieved by the sol–gel process using a homogeneous mixture of precursor/THF/water/ammonium fluoride. The highest possible concentration was used for each precursor depending on the precursor's solubility (concentration in the range of 1.5–3 M).

We used ammonium fluoride as a nucleophilic catalyst (1–4% molar ratio) as hydrolysis/polycondensation of this type of organo(trialkoxysilane) is very low in the absence of any catalyst. We adjusted the experimental conditions to avoid an overly long gelation time, which could lead to some evaporation of the solvent and disturbances of the observations. The solution was introduced by capillarity in a confined glass cell of 12–15 μm thickness; this container was chosen because it allows a clear observation of the birefringence properties at the different stages of the materials' elaboration (Scheme 3). To compare the different precursors, cells with a Teflon coating were always used. After the cell was filled, it was sealed with caf4 glue to limit the elimination of the solvent.

For all of the compounds, the initial solutions were dark when analyzed by polarizing optical microscopy; this observation is characteristic of an isotropic medium. The gelation phenomenon was estimated by the absence of any induced hydrodynamic movement in the domain when gentle pressure was applied to the glass.

All of the gels were initially found to be isotropic. Aging at room temperature produces syneresis, hydrodynamic processes, and slow evaporation of solvent by

Scheme 3



diffusion through the caf4 glue. Altogether and in all cases, these processes result in the cracking and the shrinkage of the gel, both phenomena being similar to those observed for the sol−gel hydrolysis/polycondensation of TMOS or TEOS.[12] However, after a few hours, very different behavior is observed depending on the nature of the precursors. In samples prepared from precursors with a rodlike structure (**1**−**5**), pieces of birefringent gel are separated by an isotropic dark zone, which, in fact, is a crack; examples are given in Figure 1B, C, and D. In each piece of gel we observed under crossed polarizers, the presence of dark and bright regions: in the dark regions the optical axis is parallel to polarizers (Figure 2A). The simultaneous presence of dark and bright zones through the entire pieces of the gels of **1**−**5** demonstrates that the orientation of the optical axis inside each piece is not homogeneous in these materials. All of these observations are similar to those that we reported previously with the $O_{1.5}Si-C\equiv C-C_6H_4-C\equiv C-SiO_{1.5}$ system.[21] Depending on the pieces of gel, the value of the birefringence slightly varies. However, in general, the lowest birefringence is observed for the phenyl precursor **1** [$(1.5-2.0) \times 10^{-3}$], and the highest is measured for the terthienyl precursor **5** [$(8.0-9.0) \times 10^{-3}$].

In contrast, a completely different situation is found for gels prepared with precursors **6**−**8**, which contain a fully flexible organic group. Initially, the precursor/water/solvent mixture is an isotropic medium that transforms into an isotropic gel. Even many days after gelation (more than 1 month), all pieces of the gels were still isotropic with no birefringence observed, as shown in Figure 1A.[22]

The Gel's Formation and Evolution. An observation of the gel during the aging process indicates that, for the precursors **1**−**5**, the birefringence initially appears as a birefringent zone of 20−40 μm in width on each side of the cracks that cut through the gels, as illustrated by Figure 2B. The birefringence inside these chunks (<100 × 100 μm) apparently results from the addition of the birefringent zone associated with the cracks (Scheme 4).

Coating Effect of PVA and Teflon. We have compared the effect of a coating of the glass cell using PVA or Teflon coating (thickness ≈ 0.02−0.03 μm). Using the $(MeO_3)Si-(C_6H_4)-Si(OMe)_3$ precursor, the intensity of the birefringence was slightly higher forPVA (2.5×10^{-3}) than for polytetrafluroethylene or for the absence of a coating (1.5×10^{-3}). The main difference is the formation of chunks with a spiral shape, in addition to the polygonal-shape chunks (Figure 3). With a PVA coating, the material is difficult to detach from the surface, indicating a possible condensation between the Si−OMe function of the precursor and the −OH group of the PVA. Such behavior was not observed in the case of a Teflon-coated cell.

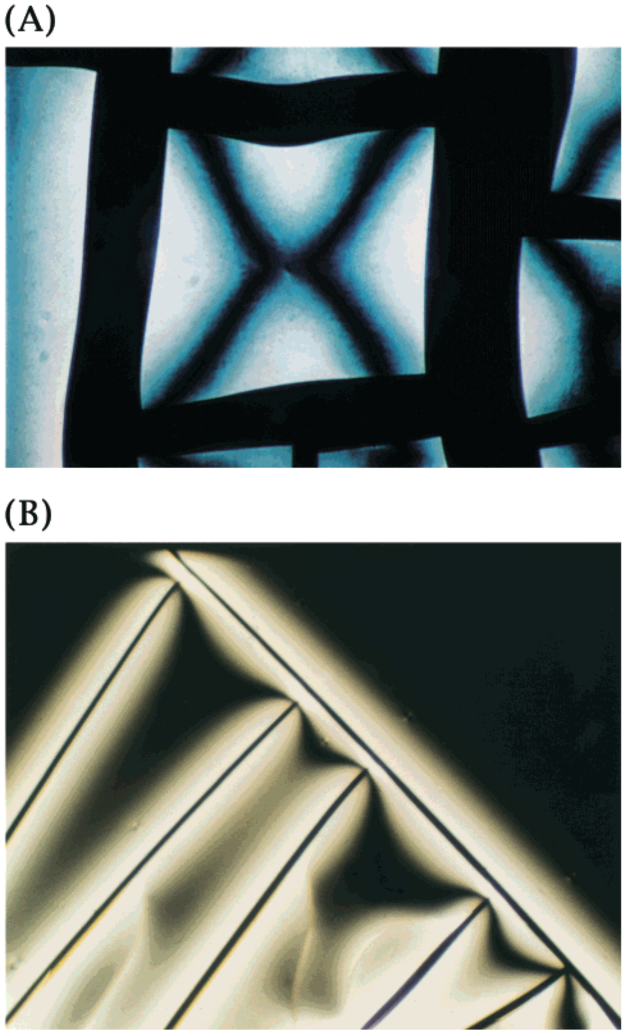
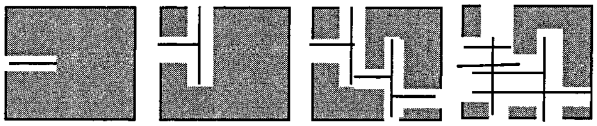


Figure 2. (A) Chunk of xerogel $O_{1.5}Si-(C_6H_4)-SiO_{1.5}$. (B) Propagation of cracks through the gel $O_{1.5}Si-(C_6H_4)_2-SiO_{1.5}$.

Scheme 4



Origin of the Birefringence. The value that we measure for the birefringence in the case of **1**−**5** is high and reveals the anisotropic organization of the material. All of these materials are highly polycondensed, as evidenced by the presence of T^1, T^2, and T^3 signals at each end of each molecular unit and the absence of a T^0 signal in the ^{29}Si NMR spectrum of the xerogels with **4** and **5**[15] and with **1**−**3**.[16,23,24] The present results

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[22] For technical reasons, the picture is overexposed in order to distinguish the pieces of xerogel that are dark and isotropic.

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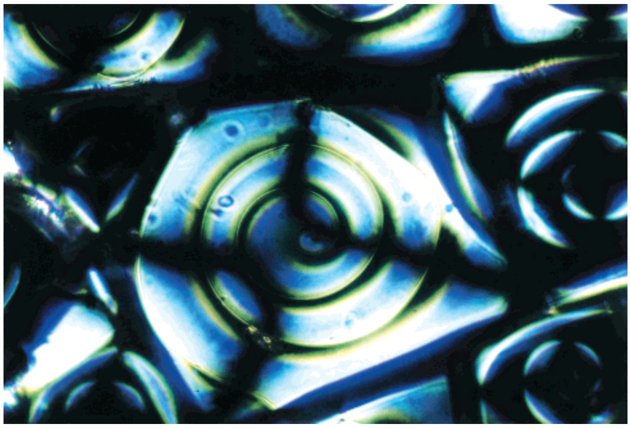

Figure 3. Chunks with a spiral crack of $O_{1.5}Si-(C_6H_4)-SiO_{1.5}$ in cell with glass slides coated with PVA.

demonstrate that an anisotropic organization is generally achieved in silica-based materials prepared by sol–gel polycondensation of rigid precursors, but not in the case of flexible precursors.

These results are corroborated in the case of **4** and **5** by the xerogel's reactivity: electrochemical- or chemical-induced polymerization of the thiophene units[16] because of a favorable and specific organization of the precursor units in the solid. Similarly, the anisotropy of the xerogels of **1**, **2**, and **3** confirms the possibility of short-range order, supported by the signals observed by X-ray analysis of $O_{1.5}Si-(C_6H_4)-SiO_{1.5}$[16] (7.5 Å) and $O_{1.5}Si-(C_6H_4)_3-SiO_{1.5}$[25] (15 Å) and by the chemical reactivity of the aromatic groups in **1**.[26]

The nature of the organic group appears to be one of the key parameters. The presence of a rigid aromatic group is a requirement for the achievement of such anisotropic organization, whereas an isotropic organization is obtained when using a flexible alkyl group. Therefore, auto-association during the chemical transformation is possibly the driving force of the resulting organization at the microscopic level. However, mechanical deformation during the aging and the drying of the gel might play an important role for the propagation of this effect on a macroscopic scale. Studies are in progress in these directions.

Table 1

precursor	conc[b]	catalyst (%)[a]	gelation time (h)
1	3	1	0.5
2	3	1	24
3	2	2	36
4	3	1	0.2
5	3	1	1.5
6	1.5	4	2
7	1.5	4	96
8	1.5	4	120

[a] NH_4F/precursor molar ratio. [b] In THF as the solvent.

Experimental Section

The precursors were prepared according to the previous literature procedures: **1**–**3**,[16] **4** and **5**,[15] **6**–**8**.[18]

Preparation of the Gel Precursor Mixture. In a typical experiment, a homogeneous solution of precursor is prepared by adding, to a Schlenk tube under argon, precursor **1** (0.49 g, 1.54 mmol) in THF (0.52 mL) and 1% NH_4F aqueous solution (0.085 mL, 3.72 mmol). The gelation times of the mixtures are given in Table 1.

Preparation of the Cell. The cell's glass is cleaned using ethanol, acetone, sulfochromic acid, and finally water. A thin film of Teflon is deposited on one side of each slide by gently applying (2 kg pressure) and rubbing a Teflon roller heated at 285 °C onto it. Then, the slides are assembled with a caf4 glue using two Mylar stripes (12 μm thickness) as spacers. The typical cell thickness is 15 ± 2 μm as measured by UV–vis spectroscopy. The amount of xerogel prepared under these conditions (<50 mg) is too low to permit other analyses (size of the cell = 20 mm × 20 mm).

Optical properties of the material were observed with a Laborlux12POLS polarizing microscope. Photographs were taken using a Leica wild MPS28 camera. The gel birefringence Δn is obtained from the expression $\Delta l = (\Delta n)d$, where Δl is the optical path difference and d is the cell thickness. Δl is measured by a Berek compensator.

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(26) These distances were calculated according to the Bragg's assumption.