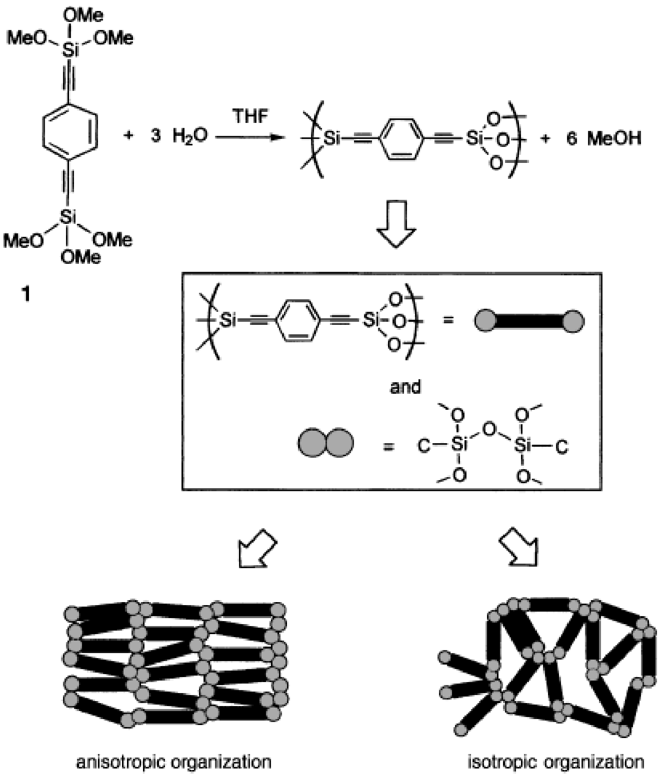
Nanostructured Silica-Based Organic–Inorganic Hybrid Materials—Evidence for Self-Organization of a Xerogel Prepared by Sol–Gel Polymerization**

Bruno Boury, Robert J. P. Corriu,* Valérie Le Strat, Pierre Delord, and Maurizio Nobili

The sol–gel polycondensation is a very convenient method for the preparation of amorphous oxide.[1] Recently this method was also developed for the preparation of organic–inorganic hybrid materials such as nanocomposites (non-covalently bonded organic groups) and nanostructured hybrid solids (covalently bonded organic groups).[2–11] The latter can be prepared using a building block of the general formula $(MeO)_3Si{-}R{-}Si(OMe)_3$. Their purity is greatly dependent on both the nature of the organic group and the experimental procedure used to form the gel.[12–16] These materials are generally considered as amorphous and their organization is still unclear. Two extreme situations can be considered (Scheme 1): a complete isotropic organization with no preferential orientation of the molecule, and the opposite situation with an ordered organization of the organic group that locally mimicks the organization in a liquid crystal.

Chemical evidence of a short-range order in these materials was found when precursors with a rigid, organic core, such as aryl, acetylenic, or thienyl groups, were used. For example, it is possible to induce a selective reaction in these solids, as demonstrated for the electrochemically and chemically induced polymerization of thiophene units in $(O)_{1.5}Si{-}(C_4H_4S){-}Si(O)_{1.5}$,[17] or the thermal crosslinking reaction of acetylenic units in $(O)_{1.5}Si{-}C{\equiv}C{-}C{\equiv}C{-}Si(O)_{1.5}$.[18] These results demonstrated that the organic groups are in a favorable situation for reaction with each other. Moreover, small-angle X-ray scattering (SAXS) analysis showed a signal at 150 pm in the case of the xerogel $(O)_{1.5}Si{-}(C_6H_4)_3{-}Si(O)_{1.5}$, which, on the basis of a Bragg assumption, was tentatively related to the size of the spacer.[19] In this case, the formation of aggregates was proposed and modeled in accordance with the ^{29}Si NMR data.[20]

More recently we reported the use of 1,4-bis[(trimethoxysilyl)ethynyl]benzene (**1**) as a rigid-core precursor for the preparation of such organic–inorganic xerogels.[21] This precursor was initially chosen because of its well-defined size and geometry and also because of the possibility of selectively hydrolyzing the fragile $Si{-}C_{sp}$ bond using a F^- catalyst.[22–24] This property allows organic–inorganic xerogels based on silicon to be prepared, and leads to silica with a narrow pore size distribution after hydrolysis and removal of the organic group.[21,25,26] The rigidity of the organic group in this precursor has motivated the investigation of the organization of the corresponding gels and xerogels.



Scheme 1. Possible organization of the molecules in the organic–inorganic xerogel prepared from the rigid rodlike precursor 1,4-bis[(trimethoxysilyl)-ethynyl]benzene (**1**).

These organic–inorganic xerogels are generally obtained by mixing the precursor with solvent in a Schlenk tube in an atmosphere of nitrogen and adding a stochiometric amount of water. Hydrolysis and polycondensation of the Si-OMe bonds result in the formation of the Si-O-Si network without cleavage of the $Si{-}C_{sp}$ bond. In an ideal case the polycondensation reaction corresponds to that presented in Scheme 1. In the present case, the gelation occurs within 5 to 10 min without the addition of any catalyst. After aging, washing, and drying, chunks of this xerogel are slightly birefringent when analyzed by polarizing optical microscopy, which indicates a possible self-organization of the organic spacers in the xerogel. We saw the possiblity to enhance the birefringence of the xerogel and to better visualize its optical properties by preparing it in closed cells. This procedure is used to study the textures of liquid crystals by promoting the formation of self-organized structures.[27] Herein we report the preparation of a highly birefringent xerogel by hydrolysis of **1** in closed glass cells treated with oriented teflon.

Two different experimental procedures were used to prepare the xerogel in the cells. The first method (A) is a “static” observation: a homogeneous solution of **1** in THF with a stochiometric amount of water was prepared and then

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[*] Prof. R. J. P. Corriu, B. Boury, V. Le Strat
Laboratoire de Chimie Moléculaire et Organisation du Solide
UMR 5637, Université Montpellier II
Place E. Bataillon, 34095 Montpellier Cedex 5 (France)
Fax: (+33) 4-67-14-38-52
E-mail: boury@crit.univ-montp2.fr

P. Delord, M. Nobili
Groupe de Dynamique des Phases Condensées
UMR 5581 Université Montpellier II
Place E. Bataillon, F-34095 Montpellier Cedex 5 (France)

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quickly introduced by capillarity into the cell which is then sealed. The second method (B) is a "dynamic" study: the pure precursor **1** (m.p. = 36 °C) was melted in a nitrogen atmosphere and introduced into the cell by capillarity. The cell was then cooled and the precursor **1** solidified as a microcrystalline solid after a few minutes. The sides of the cell were not sealed and the gelation of **1** was promoted by placing the cell in a dessicator with a 70 % humidity level. This experimental procedure was chosen to limit the dynamics of the gel formation by using a slow diffusion of gaseous water. In both cases, the cells were observed at the different stages of the hydrolysis process by optical microscopy using polarized light.

The **1**:THF:H_2O mixture used in method A is initially an optically isotropic solution that always appears dark, no matter what the angle of the crossed polarizer. Gelation occurred a few minutes after the cell was filled. The absence of any induced hydrodynamic movement in the domain when gentle pressure was applied to the glass plate indicated that these bright regions are solid. The gelation time of 7 to 10 mins is similar to the gelation time of the same solution in the Schlenk tube. After a few hours the gel occupied the whole cell and we observed the formation of retracts and cracks, which were attributed to a hydrodynamic process similar to the syneresis process generally observed during sol–gel polycondensation.[1] This process leads to the formation of birefringent pieces of gel, which are separated by optically isotropic dark cracks (Figure 1 a). In each piece of gel we observed simultaneously the presence of dark and bright regions, with the bright zones changing with the orientation of the sample in the polarized light.[28] The absence of complete light extinction in the whole piece of gel when using crossed polarizers proves that the orientation of the optical axis inside each piece is not homogeneous. We found from birefringent measurements that in each case the optical axis is parallel to the edge of these pieces. Therefore, the distortion of the optical axis arises from the shape of the piece and its morphology. The birefringent phenomenon suggests a self-organization of the highly polarizable organic spacers. After 48 h, final aging and evaporation of the solvent (THF and methanol produced by the reaction) led to an increase in both the number and the size of the cracks that cut through the gel as it is progressively transformed into a xerogel with similar birefringent properties.

In the experimental procedure used in method B, the whole cell is filled with the crystalline solid precursor, which is easily identified by both its texture and anisotropy. Investigations into the liquid crystalline properties of the precursor have demonstrated that this compound is not mesomorphous. It is a crystalline solid that melts into an isotropic liquid without formation of any mesophases.[29] The precursor solidified after cooling back to room temperature, and then the cell was placed in the humid atmosphere. In this case, the gelation is closely dependent on the possibility of water reaching and reacting with the crystalline precursor. We observed a slow and continuous process that can be broken down into four steps (Scheme 2).

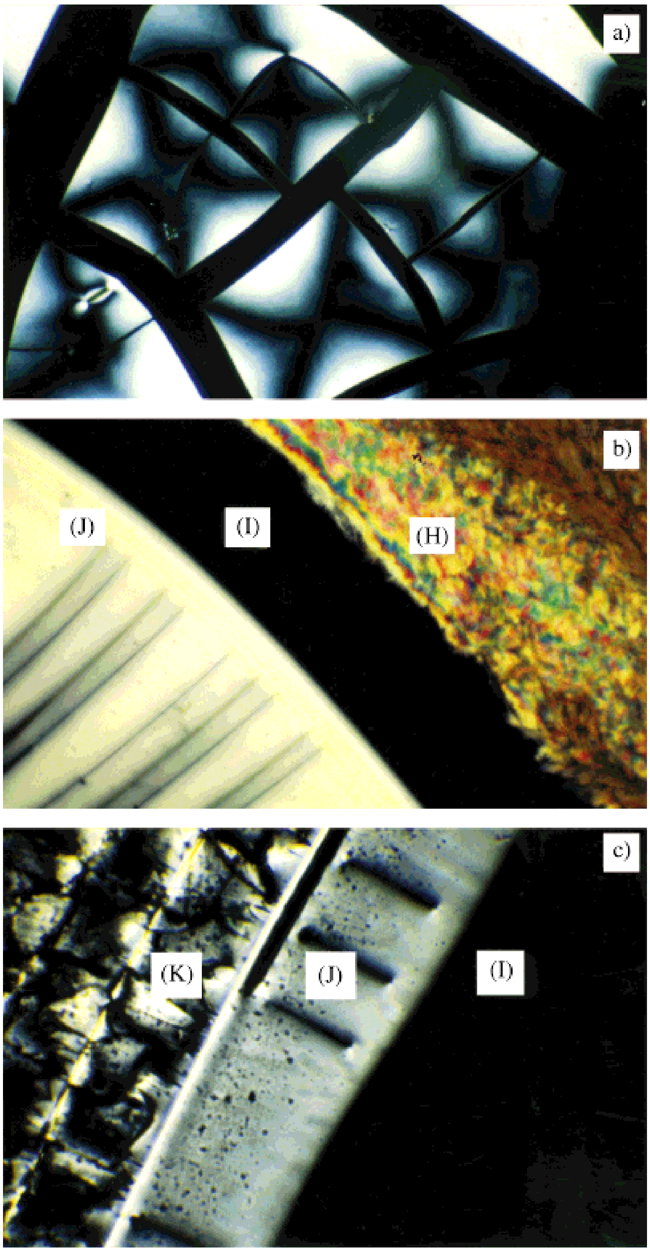
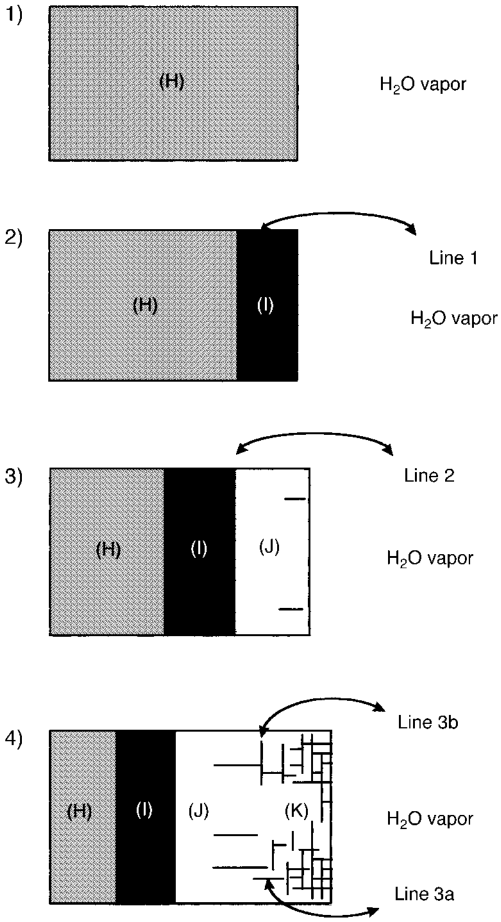


Figure 1. Pictures of the cells of experiment A(a) and experiment B(b, c).

Initially, the highly birefringent solid **1** (H) occupies the whole cell domain (step 1). After a few minutes the solid (H) at the edge of the cell was converted into an isotropic liquid (I) that is separated from the pure precursor by line 1 (step 2). In step 3 (I) is formed deeper in the cell at the expense of (H), and at the same time a new birefringent solid (J) appears. This process is initiated at the edges of the cell and leads to the successive transformation of each part of (H) into (I) and then into (J). We also designated a fourth domain (K) related to the evolution of (J) by aging. This domain is characterized by the appearance of dark isotropic lines either perpendicular (line 3 a in Scheme 2) or parallel (line 3 b) to the fronts of hydrolysis (line 1) and gelation (line 2). These cracks are related to the syneresis and hydrodynamic processes that occur during the aging of the gel. The kinetics of the whole process decreases through time because the water vapor has to diffuse progressively deeper into the cell. After one week,



Scheme 2. Evolution of a part of a cell during the polycondensation process of the pure precursor **1**.

only a small part of the precursor remained in the center of the cell surrounded by birefringent pieces of xerogel that occupyied the rest of the cell.

Photographs of the cell give a steady image of the system's evolution (Figure 1b, c). The pictures obtained using crossed polarizers revealed the four different regions, which could be easily distinguished by their optical properties and morphology. Going from the center of the cells towards the edge we found a microcrystalline birefringent solid (H), an isotropic liquid domain (I), a birefringent gel (J), and a cracked birefringent xerogel (K).

This experimental procedure enables us to trace the history of the xerogel formation through the successive four states: precursor, sol, gel, and xerogel. We assume that hydrolysis and polycondensation reactions of **1** start in domain (I) and produce methanol. The methanol can in turn act as a solvent for the small amount of precursor and partially hydrolyzed precursor. Both species are free to move easily and this accounts for the liquid and isotropic properties of this domain. In this case, this domain can be assimilated to the sol formed during the sol–gel polycondensation of an alkoxysilane.[1] When reactive species of domain (I) polycondense with Si-OH groups at the surface of the gel (J) their mobility becomes restricted and finally completely suppressed when the aggregate is linked by several Si-O-Si linkages. However, their position is not statistical but occurs with respect to an organization that leads to the birefringent solid (J). The aging of (J) leads to a syneresis process that is related to the polycondensation, the shrinkage of the xerogel's network, and the expulsion of methanol. The regularity of the dark lines produced, either parallel or perpendicular, to the gel's growth front reinforces the idea of the formation of an organized material by a progressive and diffusive process.

Pieces of the xerogel obtained with method A were powdered and placed in a Lindemann tube for X-ray analysis. A preliminary measurement using a 2D detector showed Bragg's spots forming a ring at $q = 1.5$ Å^{-1} ($d = 4.16$ Å). Other isolated Bragg's spots were found at $q = 1.67$ Å^{-1} ($d = 3.76$ Å), $q = 1.87$ Å^{-1} ($d = 3.36$ Å), and $q = 2.0$ Å^{-1} ($d = 3.04$ Å). These signals clearly indicate the presence of a crystal order within the material.

This experiment enables us to follow the different steps of the gelation process at a macroscopic scale. In addition, the flat geometry of the pieces of xerogel permits their optical study. In the present case, the formation of a highly cross-linked anisotropic material with a crystal order is observed from a nonmesomorphous precursor. The material's organization is unexpected since neither the precursor nor the oligomeric materials obtained in the first step of the hydrolysis (I) exhibit birefringence. The formation of organized structures from a nonmesomorphous precursor has already been reported in the case of polymeric materials in which the polymeric chains lead to mesophases. As an example, several polysiloxanes with no mesogenic groups[30–33] are known to form liquid crystalline polymers with smectic structures. However the present case is completely different since the organization of the solid arises from a nonreversible polycondensation in an isotropic solution.

In conclusion, we can state that the formation of a microstructure occurs during the sol–gel polycondensation of a nonmesomorphous precursor. There is an extension from the nanostructure scale previously reported and is certainly the result of the rigid, rodlike structure of the precursor and/or the formation of the siloxane network. However, the influence of the surface treatment also has to be considered.

Experimental Section

Compound **1**, was prepared according to literature methods.[21, 25] In a typical experiment a homogenous solution was prepared from **1** (0.45 g, 1.24 mmol), THF (0.413 mL), and H_2O (0.67 mL, 3.72 mmol). When the reaction was performed in a Schlenk tube, the gelation time of this mixture was 5–10 min.

The cell's glass was cleaned using ethanol, acetone, sulfochromic acid, and finally water. A thin film of teflon was deposited on one side of each slide by gently applying and rubbing a teflon roller heated at 285 °C onto it. The slides were then assembled with a cellulose acetate glue (CAF4) and using two mylar stripes as spacers; size of the cell 20 × 20 mm. The typical cell thickness was 40 ± 5 μm as measured by UV/Vis spectroscopy. The amount of xerogel prepared in this condition (< 50 mg) was too low to permit other analyses.

Liquid crystalline properties of the precursor **1** were investigated by heating a teflon-lined cell filled by pure precursor. The melted precursor was introduced into the cell under an atmosphere of nitrogen. The four sides of the cell were sealed with cellulose acetate glue (CAF4). The precursor recrystallized on cooling to room temperature. The cell was then put in an oven (Mettler) and heated from 22 °C to 50 °C at a rate of 0.1 °C min^{-1}. At around 36 °C the crystalline precursor started to break up and turn into an isotropic liquid without showing any mesophase. When this liquid was cooled at the same rate, the crystal slowly appeared, but formation of mesophase was still not observed.

Optical properties of the material were observed with a Laborlux12POLS polarizing microscope. Photographs were taken with a Leica camera (MPS28). The imaging plate apparatus Rigaku RU 200 equipped with a Marresearch 2D detector was used for the X-ray analysis (the radiation was $\mathrm{Cu}_{K\alpha}$; $\lambda = 1.542$ Å).

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[28] See the photographs in the Supporting information. Pictures (a) to (f) were taken with crossed polarizers at every 30° rotation of the sample. Picture (a′), also given in the Supporting information, shows other examples of birefringent pieces of xerogel.
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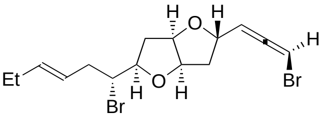
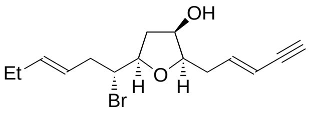
Enantioselective Total Synthesis of the Nonisoprenoid Sesquiterpene (−)-Kumausallene**

P. Andrew Evans,* V. Srinivasa Murthy,
Jamie D. Roseman, and Arnold L. Rheingold

(−)-Kumausallene (**1**) was isolated by Kurosawa and coworkers in 1983 from the red algae *Laurencia Nipponica* Yamada[1] indigenous to the coast of Hokkaido in Japan, and is a member of a class of halogenated nonisoprenoid sesquiterpenes that contain a *cis*-2,5-disubstituted tetrahydrofuran unit halogenated or oxygenated at C3.[2–4] In a program directed towards the construction of *cis*-2,5-disubstituted tetrahydrofuran-3-ones using acyl radical cyclizations,[5–7] we decided to apply this methodology to the enantioselective total synthesis of kumausallene (**1**) and thus confirm the absolute configuration of the bromoallene moiety, which had previously been assigned on the basis of optical rotation data (Lowe's rule).[1, 8] Furthermore, the proposal that kumausallene (**1**) is biomimetically related to (+)-*trans*-deacetylkumausyne (**2**)[9] through an electrophilic cyclization of the C3 hydroxy group onto the enyl side chain[10] provided an additional incentive to incorporate this feature into the synthetic sequence and determine the suitability of the bromoallene to multistep synthesis. Herein, we describe the first enantioselective synthesis of (−)-kumausallene (**1**) by a



(−)-Kumausallene **1**



(+)-*trans*-Deacetylkumausyne **2**

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[*] Dr. P. A. Evans, Dr. V. S. Murthy, J. D. Roseman,
Dr. A. L. Rheingold
Brown Laboratory, Department of Chemistry and Biochemistry
University of Delaware, Newark, DE 19716 (USA)
Fax: (+1)302-831-6335
E-mail: paevans@udel.edu

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