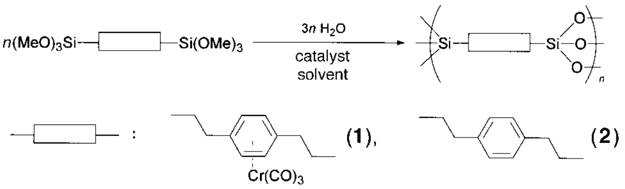
Nonrelaxable Anisotropic Organization of Organic – Inorganic Hybrid Materials Induced by an Electric Field**

Geneviève Cerveau, Robert J. P. Corriu,* Eric Framery, Shubhajit Ghosh, and Maurizio Nobili

Hydrolytic polycondensation (sol – gel-type process)[1] is a general route for the preparation of organic – inorganic hybrid materials.[2–8] Nanostructured hybrid solids[3] (class II)[9] obtained from bis(trialkoxysilyl) precursors $(MeO)_3Si{-}R{-}Si(OMe)_3$ can be regarded as amorphous, since their X-ray powder diffraction diagrams exhibit no Bragg diffraction peaks. Only two or three broad diffraction bands are observed, which could be indicative of a short-range organization of the organic units, consistent with the chemical reactivity between the organic moieties in these solids.[10, 11] In the case of precursors containing rigid, rodlike organic units, highly cross-linked materials that form a new kind of mesophase were observed in birefringence experiments.[12, 13] Moreover, formation of this micrometer-scale organization was observed to take place after the sol – gel transition, during ageing of the solid.[14] This permanent transition from short- to long-range organization in highly cross-linked materials is very attractive with regard to the possibilities opened up by the physical properties which can be afforded by the organic units.

Here we describe the effect of electric field as a controlling factor for the self-organization of organic groups attached to a hybrid material. The hydrolytic polycondensation of precursor **1**,[15] which has a dipole moment and is silylated in the α and ω positions to prevent relaxation of the solid formed, was performed in an electric field. The dipole moment was calculated by ZINDO/1 simulation with the program Hyperchem to be 2.37 D. The dipole moment is introduced by a $Cr(CO)_3$ group, and for comparison experiments were performed with **2**, which lacks the $Cr(CO)_3$ group (Scheme 1). Birefringence was selected for testing for the presence of organization, since it evidences an anisotropic order on the micrometer scale corresponding to the wavelength range used for its measurement (visible light). We therefore studied the formation of solids in glass cells coated with transparent indium tin oxide (ITO), which allow the visualization of optical properties under a polarizing microscope. Since a strong electric field ($1\,V\,\mu m^{-1}$) is necessary, we selected experimental conditions that avoid electrolysis of reagents. Hence, we replaced the nucleophilic (NBu_4F or NH_4F) or acid catalyst (HCl) by the neutral nucleophile *N*-methylimidazole (NMI), the catalytic efficacy of which was recently demonstrated.[16] To minimize the amount of water present in the cell we used water vapor as reagent.



Scheme 1. Polycondensation of bis(trialkoxysilyl) precursors **1** and **2**.

The following procedure was used: a homogeneous mixture of precursor, THF, and NMI was introduced by means of capillarity into the cell, which was placed in a closed glass apparatus providing an atmosphere with 60 % humidity (vacuum/NaBr solution). Thus, the gel formed by slow diffusion of gaseous water. In all cases, the cells were inspected at different stages of the hydrolysis process by optical microscopy with polarized light. The observations were made in the direction of the field. In the case of precursor **1**, the initial **1** – THF – NMI mixture was dark when analyzed by polarizing optical microscopy; this observation is characteristic of an isotropic medium. Interestingly, when a dc electric field was applied ($1\,V\,\mu m^{-1}$) normal to the glass plates, hydrodynamic movement was observed in the entire cell. Gelation occurred after 22 – 24 h. The electric field was switched off at this stage. Analysis of the cell by polarizing optical microscopy revealed the presence of bright regions corresponding to a birefringent medium (1.70×10^{-3}). The optical axis and the birefringence were not homogeneous throughout the cell (Figure 1). However, it was possible to observe complete light extinction at each point in the cell when the sample was rotated through 45°. We checked that the integrity of the organic unit was preserved under the electric field by using a thicker cell (100 μm), which allowed enough material to be collected for IR analysis. This cell was subjected to a field of $0.2\,V\,\mu m^{-1}$ and then opened. The product exhibited the same IR spectrum as that previously reported.[15] We also studied the evolution of birefringence with time and observed great stability, since no change was observable after two years. A similar experiment performed

Figure 1. Birefringent gel obtained from **1** in an electric field.

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[*] Prof. R. J. P. Corriu, G. Cerveau, E. Framery, S. Ghosh
Laboratoire de Chimie Moléculaire et Organisation du solide
UMR 5637, Université Montpellier II, cc 007
Place E. Bataillon, 34095 Montpellier Cedex 5 (France)
Fax: (+33) 4-67-14-38-52
E-mail: cmos@crit.univ-montp2.fr

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

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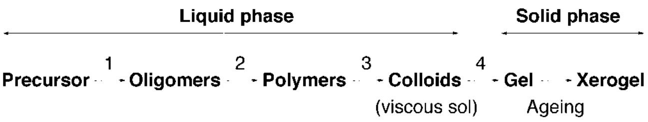
without an electric field led after 5 d to a gel which did not exhibit any birefringence.

The precursor **2**, which has no dipole moment, was treated under the same conditions: initial precursor–THF–NMI mixture, electric field of about 1 V μm^{-1}. A hydrodynamic movement was observed for a fraction of a second, and a gel formed after 32 h, instead of 72 h without an electric field. However, in both cases, no birefringence was observed. Moreover, as **1**, too, does not exhibit any birefringence when the polycondensation at silicon is performed in a cell without an electric field, we can conclude that the micrometer-scale organization we have observed in the case of **1** is induced by the electric field, which imposes the orientation of the dipole moments.

Besides the observation of birefringence, the effect of the electric field on the gelation time is noteworthy. For both organic precursors **1** and **2** a shorter gelation time is always observed in an electric field. This might be due to the hydrodynamic movements that it induces.

This observation prompted us to perform experiments with plates that were half-coated by transparent ITO. This made it possible to observe **1** in the same cell with (ITO coating) and without an electric field (no coating). In the ITO-coated part we observed the formation of birefringent gel after 22–24 h. In the other part of the cell neither birefringence nor formation of a solid was observed. Surprisingly, however, 2 d after switching off the electric field a birefringent gel also appeared in this part of the cell. Moreover, this birefringence had the same characteristics as that observed in the part under the electric field, and rotation of the sample under the polarizing microscope led to the same observations in the two parts of the cell in terms of organization or birefringence. This observation was completely unexpected: although, in the absence of electric field the solid derived from **1** did not exhibit any birefringence. The micrometer-scale organization in the second experiment occurred in that part of the cell that was not subjected to the controlling factor of organization. Furthermore, this organization was observed 2 d after the electric field had been switched off. Experiments were performed in which the intensity of the field was varied from 0.2 to 1 V μm^{-1}. In all cases, a gel formed in the ITO-coated part of the cell after 20–24 h, whereas gelation occurred in the other part 2 d after the electric field had been switched off. At 0.2 and 0.4 V μm^{-1}, no birefringence was observed in any part of the cell. In contrast, at 0.6 and 1 V μm^{-1}, the phenomenon described above was evident under polarized light. These results confirm the crucial importance of the electric field as a controlling factor that induces organization not only in the first part but also in the second, which was not subjected to the electric field.

We propose an explanation that takes into account the hydrodynamic movement induced by the electric field. Let us consider the general equation of sol–gel transition (Scheme 2). During steps 1–3, exchange of matter is occurring between the two parts of the cell, since the material is a liquid. At this moment the two parts have the same composition. This means that the polycondensation at silicon, which transforms the molecular precursor into a cross-linked material, is more or less at the same level in the two parts of the cell. The organization induced by the electric field is permanently exchanged with the second part of the cell. In other words, the degree of organization induced by polymers in which the dipole moments of the cross-linked organic units are oriented is the same in the two parts of the cell during polycondensation in the liquid phase. However this exchange becomes slower when the viscosity increases with the formation of colloids in the viscous sol. Under these conditions the part of the cell that is subjected to the electric field becomes more organized. Thus, the sol–gel transition and the ageing step permit the formation of birefringence at first in the part submitted to the field and after some time in the other part of the cell.



Scheme 2. General scheme of the sol–gel process.

To explain the presence of birefringence in the second part we considered earlier results which indicated that both texture (specific surface area, porosity, etc.) and self-organization of the organic units in the solid are controlled not only by polycondensation in solution (steps 1–3), but also during ageing in the solid state.[17] Thus, formation of this new type of birefringent, highly cross-linked material starts during the ageing step when the solid is already formed, since the highly cross-linked solid formed just after the sol–gel transition does not exhibit any birefringence.

In the liquid phase the two parts of the cell contain the same amount of colloids in which the organic units have been orientated by the electric field. After the sol–gel transition these colloids are linked to each other, and the reorganization of Si–O–Si bonds that occurs at the surface of colloids in the parts of the cell with and without electric field lead to the same birefringent material. These experiments show that the formation of self-organized domains in solution is a sufficient condition for inducing micrometer-scale organization during ageing. The electric field does not make any significant difference during this step of long-range ordering of domains with short-range order.

In conclusion, we previously observed self-organization due to van der Waals-type interactions between the organic units[12] during the polycondensation at silicon. In the case of rigid, rodlike organic groups, short-range order was indicated by X-ray diffraction peaks that were related to the length of the organic spacer. The short-range order was also confirmed in experiments performed with dilution by $Si(OMe)_4$ in the solid.[18] In the present study, the short-range order is induced by the electric field, which imposes vectorial orientation on the $Cr(CO)_3$ groups in the same direction and leads to a microscale order. Moreover, the experiments presented here showed that the existence of self-organized domains in solution is a sufficient condition for the formation of this microscale ordering in the solid phase during ageing. Finally, the stability of birefringence over the time (two years without change) demonstrates that the dipole moments do not relax after switching off the electric field, and this suggests the possibility of nonlinear optical properties.[19, 20] This behavior is certainly due to the high degree of cross-linking and to the appropriate α,ω arrangement of the silicon-containing groups in the precursor, which prevents any relaxation.

Experimental Section

Preparation of the cells: The ITO-coated and normal glass plates (20 × 20 mm) were cleaned with ethanol, acetone, sulfochromic acid, and finally water. Two plates were then mounted on each other and attached with UV-sensitive glue at four corners. The parallelism of the glass plates and the cell thickness were checked by measuring the interference fringes. The cell was then placed under a UV lamp for 10 min. Thickness was measured by UV/Vis spectroscopy and was (10 ± 2) µm. The wires on each cell were soldered with indium pellets (15 mm, 99.99 % pure).

Preparation of the gels: A solution of NMI (35 mol %, 0.205 mmol) in THF (277 µL) was added to a solution of the precursor (0.587 mmol) in THF. The homogenous solution was introduced into the cell, which was filled by capillarity. The cell was then placed inside a glass apparatus with a chamber for saturated NaBr solution, and vacuum was then applied to give an atmosphere with 60 % humidity. Finally, a potential difference of 10 V, which corresponds to a dc electric field of about $1\,\mathrm{V\,\mu m^{-1}}$, was applied across the two plates of the cell. The evolution was constantly monitored under the microscope during condensation. The optical properties of the material were observed through a Laborlux 12 POLS polarizing microscope. Photographs were taken with a Leica MPS28 camera.

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[1] C. J. Brinker, G. W. Scherer, *Sol–Gel Science*, Academic Press, London, **1990**.

[2] G. Cerveau, R. J. P. Corriu, *Coord. Chem. Rev.* **1998**, *178–180*, 1051, and references therein.

[3] R. J. P. Corriu, *Angew. Chem.* **2000**, *112*, 1432; *Angew. Chem. Int. Ed.* **2000**, *39*, 1376, and references therein.

[4] P. Judenstein, C. Sanchez, *J. Mater. Chem.* **1996**, *6*, 511.

[5] D. A. Loy, K. J. Shea, *Chem. Rev.* **1995**, *95*, 1431.

[6] U. Schubert, N. Hüsing, A. Lorenz, *Chem. Mater.* **1995**, *7*, 2010.

[7] *New J. Chem.* special issue, **1994**.

[8] E. Lindner, T. Schneller, F. Auer, H. A. Mayer, *Angew. Chem.* **1999**, *111*, 2288; *Angew. Chem. Int. Ed.* **1999**, *38*, 2154.

[9] C. Sanchez, F. Ribot, *Comment Inorg. Chem.* **1999**, *20*, 327.

[10] R. J. P. Corriu, J. J. E. Moreau, P. Thépot, M. W. C. Man, C. Chorro, J. P. Lereporte, J. L. Sauvajol, *Chem. Mater.* **1994**, *6*, 642.

[11] R. J. P. Corriu, J. J. E. Moreau, P. Thépot, M. W. C. Man, *Chem. Mater.* **1996**, *8*, 100.

[12] B. Boury, R. J. P. Corriu, V. Le Strat, P. Delord, M. Nobili, *Angew. Chem.* **1999**, *111*, 3366; *Angew. Chem. Int. Ed.* **1999**, *38*, 3172.

[13] F. Ben, B. Boury, R. J. P. Corriu, V. Le Strat, *Chem. Mater.* **2000**, *12*, 3249.

[14] M. Nobili, P. Delord, A. Vergnes, F. Ben, B. Boury, R. J. P. Corriu, 11th International Workshop on Glasses, Ceramics, Hybrids and Nanocomposites from Gels, Abano Terme, Italy, **2001**.

[15] G. Cerveau, R. J. P. Corriu, C. Lepeytre, *Chem. Mater.* **1997**, *9*, 2561.

[16] G. Cerveau, R. J. P. Corriu, E. Framery, *Polyhedron* **2000**, *19*, 307.

[17] G. Cerveau, R. J. P. Corriu, E. Framery, *Chem. Mater.*, **2001**, *13*, 3373.

[18] B. Boury, R. J. P. Corriu, P. Delord, V. Le Strat, *J. Non-Cryst. Solids* **2000**, *265*, 41.

[19] B. Lebeau, S. Brasselet, J. Zyss, C. Sanchez, *Chem. Mater.* **1997**, *9*, 1012, and references therein.

[20] F. Chaumel, H. Jiang, A. Kakkar, *Chem. Mater.* **2001**, *13*, 3389, and references therein.

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