

Solid State Hydrolysis/Polycondensation of Alkoxysilane: Access to Crystal-Like Silicon-Based Hybrid Materials

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Solid state reactions frequently correspond to an intramolecular process,^{1,2} but only a few of them concern intermolecular reactions and the formation of materials. Some classical examples are the topological polymerization of diacetylene compounds^{3–5} or polymerization of aromatic compounds such as distyrylpyrazine and phenylenediacyric acid.⁶

This method for the preparation of solids is attractive because a high level of anisotropy can be expected in the resulting solids. Therefore, such a solid-state process could be an alternative to the sol–gel process. The latter enables the preparation of attractive organic–inorganic hybrids but is generally limited by a lack of organization in the case of silicon-based materials.⁷ Hybrid materials made of an organic group and a Si–O–Si network result from the hydrolytic polycondensation of alkoxysilane.^{8,9} Auto-organization in some of these materials R-[SiO_{1.5}]_n (*n* ≥ 2) has been pointed out recently.^{10–13} A short-^{12,14,15} or long-range^{16–18} ordering can be present, depending on the nature of the organic group R and the experimental conditions. Still, there is a need for a general process that leads to materials with a high level of periodicity. We have now found that alkoxysilanes, the most frequently used type of monomer, can be hydrolyzed and polycondensed directly in the solid state (Scheme 1) by a process avoiding the formation of a sol and its further transformation into a gel.

More interestingly, the structures of the materials obtained by such a solid-state process exhibit much higher periodicity than that of a corresponding solid (**3**) that was prepared by the classical sol–gel hydrolytic polycondensation of **1**. This therefore represents a new tool for the preparation of highly anisotropic silicon-based hybrid materials.

The 1,4-bis(5-trimethoxysilyl-1-pentenoxy)biphenyl **1** was used as precursor.¹⁶ First it was melted (mp = 62 °C) under argon and cast in thin films of 20–50 μm deposited on glass slides. When **1** solidified at room temperature, the glass slide was immersed in 1.7 M aqueous HCl for 7 days at 20–25 °C, and no soluble residue was detected in the aqueous solution during or after the process. In a different procedure, a solid/gas reaction was obtained by direct contact of the film with acidic moisture in a desiccator kept at 60–70% humidity provided by 10 M aqueous HCl. In this latter case the reaction takes 12–15 days. In both procedures, a white solid **2** is then collected and washed with solvent to remove any soluble residues.¹⁹

Hybrid material **2** is no longer fusible up to 300°C, and the level of carbon and hydrogen determined by elemental analysis is lower than for **1**. This is in accordance with the expected values. Chemical transformation is confirmed by ²⁹Si NMR (HPDEC sequence) analysis of **2**, which exhibits three signals attributed to T¹ (–48.9 ppm, relative intensity: 22.1, C–Si(OR)₂(O–Si)), T² (–57.8 ppm, relative intensity: 57.0; C–Si(OR)(O–Si)₂), and T³ signals (–67.4

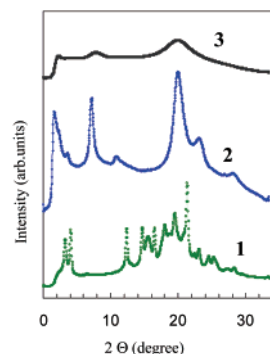
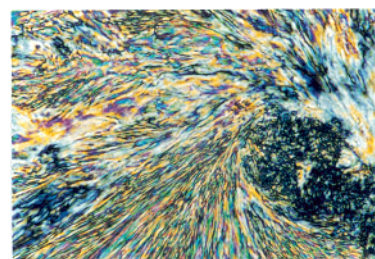
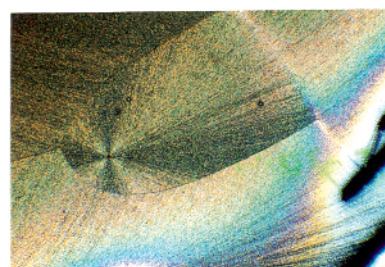


Figure 1. X-ray powder diffraction patterns of precursor **1**, solid hybrid materials **2** and **3**.



precursor **1**

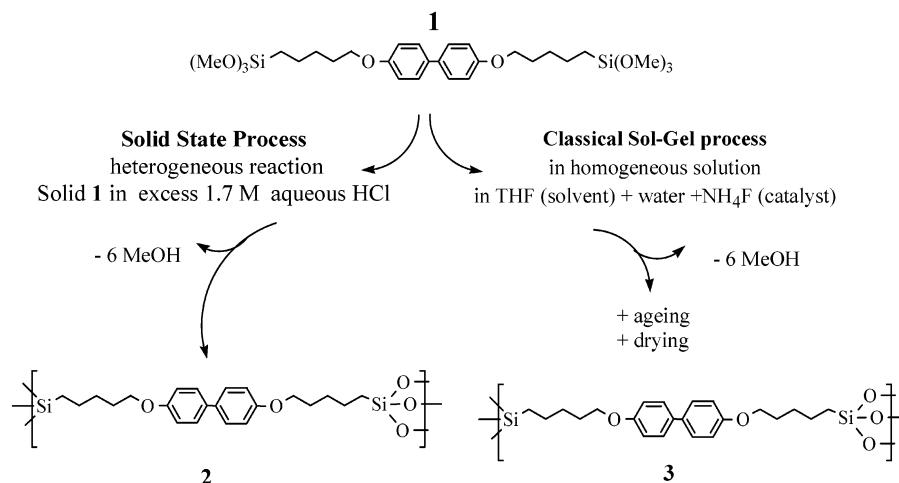


material **2**

Figure 2. Microscopy in polarized light of 50 μm × 50 μm.

ppm, relative intensity: 20.9; C–Si(O–Si)₃ (R = Me or H); no signal at –41.31 ppm related to monomer **1** is observed. Integration of these signals gives a quantitative level of polycondensation of 66%, close to that of solid **3** (70%) prepared by the sol–gel process of **1** (in THF as solvent and ammonium fluoride as catalyst). Therefore, each silicon atom takes part in the Si–O–Si network, but a fully condensed system is not achieved as for most of these materials. For this solid-state process, this is probably because of the increasing difficulty for water to diffuse and the increasing number of Si–O–Si that progressively hinders the movement required for condensation to occur.

Scheme 1. Synthesis of the Silicon-Based Hybrid Material Prepared Either by Solid-State Process (**2**) or Classical Sol–Gel Process (**3**) of the Precursor (**1**)



The presence of a high periodicity for **2** is demonstrated by X-ray powder diffraction (Figure 1). Different Bragg's signals are observed. The one at 24.8 \AA (0.25 \AA^{-1} ; $2\Theta = 3.51^\circ$) could fit with the length of the organic spacer (25.3 \AA) but is not the strongest. On the other hand, a sharp and strong signal at 12.4 \AA (0.25 \AA^{-1} ; $2\Theta = 3.51^\circ$) corresponding to one-half of the length of the organic spacer may for example suggest a layered structure with a tilted angle (estimated here at 30°). In all cases, the diffraction pattern is completely different from that of microcrystallized **1** and suggests a strong reorganization of the solid during the chemical process.

For comparison, the diffraction pattern of **3** exhibits fewer and broader signals suggesting a shorter-range order and a lower level of periodicity than for **2**. Additionally, the birefringence of **3** ($\Delta n = (6.5 \pm 0.5) \times 10^{-3}$) is lower than that of **2** ($\Delta n = (20 \pm 0.5) \times 10^{-2}$) which is itself lower than that of **1** ($\Delta n = >30(\pm 0.5) \times 10^{-2}$) (Figure 2).

The solid-state process that we report is one of the very few requiring the combination of two steps according to the reactivity of the Si–OMe bond toward water: first hydrolysis and second the subsequent intermolecular polycondensation. An important point concerns the elimination of methanol which is the byproduct of the reaction. It might act as a solvent for **1** and would lead to disorganization of the medium. However, this is avoided here, probably because thin films are used and allow either a rapid diffusion into the gas phase or a rapid dilution by the water phase of methanol.

In the rapidly developing area of auto-organized systems,²⁰ these results point out that it is possible to hydrolyze and polycondense into solid state alkoxy silane, taking advantage of the crystalline structure of the precursor. The architecture of the molecular solid is apparently not preserved but serves as a template or a scaffold. These data are representative of our current efforts to find new methods for the control of the organization of silicon-based hybrid organic–inorganic materials.²¹

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Supporting Information Available: General experimental procedures and preparation of compound **3** by the classical sol–gel process (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025.
- (2) Ramamurthy, V.; Venikatesan, K. *Chem. Rev.* **1987**, *87*, 433.
- (3) Kato, J.; Nakamura, K.; Yamasaki, S.; Tokushige, K.; Amano, T. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 1853.
- (4) Adler, G. *Cryst. Liq. Cryst.* **1983**, *93*, 1.
- (5) Wegner, G. *Pure Appl. Chem.* **1977**, *49*, 443.
- (6) Nakanishi, M.; Hasegawa, M.; Sasada, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1972**, *10*, 1537.
- (7) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science*; Academic Press Inc.: Boston, 1990; and references therein.
- (8) Sanchez, C.; de A. A. Solla-Illia, G. J.; Ribot, F.; Lalot, F.; Mayer, C. R.; Cabuil, V. *Chem. Mater.* **2001**, *13*, 3061.
- (9) Livage, J.; Sanchez, C.; Babonneau, F. In *Chemistry of Advanced Materials: An Overview*; Interrante, L. V., Hampden-Smith, M. J., Eds.; VCH: New York, 1998.
- (10) Chaumel, F.; Jiang, H.; Kakkar, A. *Chem. Mater.* **2001**, *13*, 3389.
- (11) Corriu, R. J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 1376.
- (12) Boury, B.; Corriu, R. J. P. In *Supplement Si: The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley & Son: Chichester, 2000; Vol. 3, p 565.
- (13) Shea, K. J.; Loy, D. A. *Chem. Mater.* **2001**, *13*, 3306.
- (14) Boury, B.; Corriu, R. J. P.; Delord, P.; Nobili, M.; Le Strat, V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3172.
- (15) Boury, B.; Corriu, R. J. P.; Delord, P.; Le Strat, V. *J. Non-Cryst. Solids* **2000**, *265*, 41.
- (16) **1** was used in precedent studies on self-organization of the hybrid organic–inorganic materials mentioned before, see Boury, B.; Ben, F.; Corriu, R. J. P. *Adv. Mater.* **2002**, *14*, 1081.
- (17) Moreau, J. J. E.; Vellutini, L.; Wong Chi Man, M.; Bied, C. *J. Am. Chem. Soc.* **2001**, *123*, 1509.
- (18) Moreau, J. J. E.; Vellutini, L.; Wong Chi Man, M.; Bied, C.; Batignies, J.-L.; Dieudonné, P.; Sauvajol, J.-L. *J. Am. Chem. Soc.* **2001**, *123*, 7957.
- (19) Preparation of **2**: Films of **1** (0.89 g 1.57 mmol) were prepared by melting the pure compound under argon on glass slides, cooling back to room temperature, and solidifying. The glass slides were immersed in 1.7 M aqueous HCl for 7 days at room temperature. The resulting white solid was peeled from the glass slide, crushed in a mortar, and then washed with $3 \times 20 \text{ mL}$ of ethanol and $2 \times 20 \text{ mL}$ of diethyl ether and finally vacuum-dried in an oven at $120 \text{ }^\circ\text{C}$ for 12 h (1 mmHg). The resulting solid **2** is a white powder, 0.70 g (102% yield according to a complete polycondensation reaction) Elemental analysis: theoretical for $\text{O}_{1.5}\text{Si}-(\text{CH}_2)_5-(\text{C}_6\text{H}_4)_2-(\text{CH}_2)_5-\text{SiO}_{1.5}$: C 61.7%; H 6.6%; experimental: C 60.9%; H 6.9%.
- (20) Förster, S.; Plantenberg, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 689.
- (21) Boury, B.; Corriu, R. J. P. *Chem. Commun.* **2002**, 795.

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