

preparations are a mixture of subunits, which differ considerably in sequence and molecular weight.^[5] This, of course, can also effect substrate selectivity and enantioselectivity.

Thus, the application of recombinant PLE now also allows the synthesis, in high optical purity, of compounds which have so far not been accessible by PLE-catalyzed reactions. Furthermore, the successful functional expression now makes the manipulation of enzyme properties by site-directed mutagenesis or directed evolution^[16] feasible.

Experimental Section

Production of recombinant pig liver esterase (rPLE): For expression of rPLE, the yeast *Pichia pastoris*—bearing the genomic-integrated gene that encodes the esterase under the control of the methanol-inducible alcohol oxidase 1 promotor (AOX1)—was grown according to the protocol given by the manufacturer (Invitrogen, Carlsbad, CA, USA), first in BMGY media containing glycerol (1% (v/v)) and then in BMMY media that contained methanol (0.5% (v/v)) as the carbon source and inducer. Induction of rPLE expression was maintained by daily addition of methanol (0.5% (v/v)). After 96 h, the cells were removed by centrifugation and the supernatant was concentrated for 15 min at 4000 g with 20 mL Centricons (NMWL 30000, Ultracel-PL membrane, Millipore). The activity thus obtained was 10 U mL⁻¹ (pNPA-assay), which corresponds to ~500 U mg⁻¹ protein.

Determination of esterase activity: Photometric determination of esterase activity was performed by hydrolysis of *p*-nitrophenyl acetate (pNPA).^[7d] One unit (U) of esterase corresponds to the amount of enzyme that releases 1 μmol of *p*-nitrophenol per min.

The substrate spectrum of PLE was measured with a pH-Stat (Schott, Mainz, Germany) by hydrolysis of different esters (caprylic acid ethylester, acetic acid ethylester, tributyrin, or triolein) at 37 °C and pH 7.5.^[7d] One unit (U) of esterase corresponds to the amount of enzyme that releases 1 μmol of acid per min. The thus-determined highest activity was set as the 100% value.

Esterase-catalyzed kinetic resolution of the acetates: Acetates **1–3** (10 mM) were dissolved in sodium phosphate buffer (pH 7.5, 50 mM) in 1-mL reaction vials and the kinetic resolution was started by addition of esterase (0.5 U, based on the pNPA assay). To stop the reaction, the mixture was extracted with dichloromethane and the organic phase was dried over anhydrous sodium sulfate. The determination of enantiomeric purity and conversion was performed by gas chromatography (column: heptakis(2,6-*O*-methyl-3-*O*-pentyl)-β-cyclodextrin; carrier gas: H₂; flame ionization detector).

Retention times [min]: **1** (100 °C isothermal): (S)-**1** 3.7 min, (R)-**1** 5.8 min, (R)-**1a** 6.7 min, (S)-**1a** 7.6 min; **2** (75 °C isothermal): (S)-**2** 26.5 min, (R)-**2** 42.3 min, (S)-**2a** 32.6 min, (R)-**2a** 34.2 min; **3** (90 °C isothermal): (S)-**3** 17.6 min, (R)-**3** 20.2 min, (S)-**3a** 24.8 min, (R)-**3a** 27.4 min. The absolute configurations given for **1** are based on comparison with commercial (R)-**1a**. In case of **2** and **3** the *R* preference of the lipase Amano PS, as recorded in the literature,^[17] served as the reference.

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Hydrolysis/Polycondensation in the Solid State: Access to Crystalline Silica-Based Hybrid Materials**

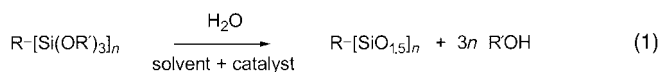
Bruno Boury,* Frédéric Ben, and Robert J. P. Corriu

Silicon-based hybrid materials allow the association at the molecular level of the properties of an organic group with the specific properties of a Si–O–Si network (transparency, chemical and thermal stability).^[1–6] They are generally prepared by hydrolytic polycondensation from organic units covalently bound to trialkoxysilyl groups (Si(OR')₃, R') = Me

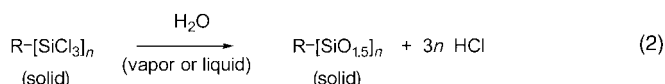
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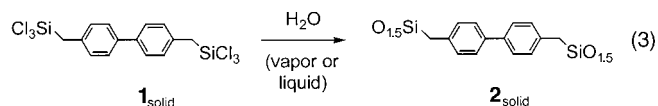
or Et). This sol-gel process is performed under mild conditions in solution and, in most cases, the process leads to formation of amorphous material.^[7] In the case of R-[Si(OR')₃]_n ($n \geq 2$) precursors, the corresponding hybrid materials prepared are organopolysilsesquioxanes (OPS) of the general formula R-[SiO_{1.5}]_n [Eq. (1)]. Moreover, when R is a rigid organic group, a birefringent phenomenon indicates short-range organization at the mesoscopic level.^[8-10]



Nevertheless, a truly precise control of the organization of such materials would certainly represent an additional advantage in cases where the organic group R could provide chemical or physical properties to the material (optical, magnetic, etc...). Here we report an alternative way to achieve the formation of Si-O-Si three-dimensional networks using crystallized alkylchlorosilanes as precursors. Chlorine atoms as leaving groups allow a chemical transformation and we found that their hydrolisis/polycondensation can be performed in the solid state, according to the ideal situation shown in Equation (2), by direct contact of the insoluble compound in an excess of water (gaseous or liquid).



To demonstrate the potential of this approach we have used bis(trichlorosilyl)dibenzyl **1** as a precursor and obtained the corresponding hybrid material **2**, according to the ideal situation represented in Equation (3). Compound **2** was



prepared by a Benkeser reaction,^[11, 12] it is crystalline, with a high melting point, and the bulky and hydrophobic aryl group prevents any solubility in water. The precursor **1** is melted and cast as a film with a thickness of 0.5 mm. When cooled back to room temperature, the white pieces of precursor are directly put into water ($8 < \text{pH} < 9$) where they remain insoluble and white. The chemical transformation occurs in the solid by a solid/liquid reaction and a slightly exothermicity is evidenced by the temperature increase (up to $30\text{--}32^\circ\text{C}$). After 8 days, a white solid is filtered off, washed with solvents (diethyl ether and acetone), and dried. Chemical transformation is readily evident from elemental analysis, which reveals a level of chlorine of 47.5 % in **1** and of less than 0.6 % in **2**. (The lower value of the actual carbon content, compared to the theoretical one, may be ascribed to noncondensed Si–OH groups.)

The ^{29}Si CP MAS NMR spectroscopic experiment agrees with complete hydrolysis of Si–Cl bonds and partial polycondensation of the Si–OH bonds (Figure 1). Compound **1** presents a signal at $\delta = 8.06$, while three signals are observed

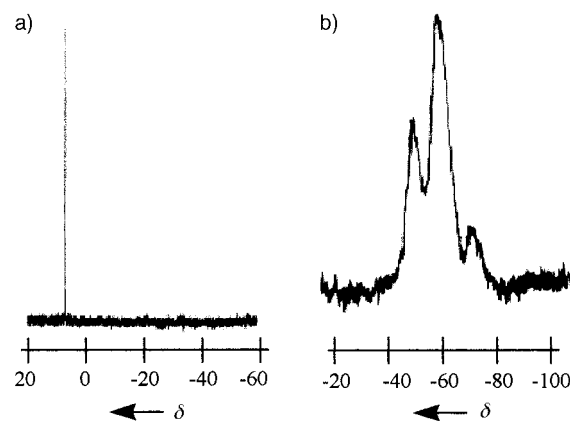


Figure 1. ^{29}Si NMR spectra of **1** (in CDCl_3) and **2** (by solid-state CP MAS NMR analysis).

for **2** and are attributed, respectively, to T^1 ($\delta = 50.8$, $CSi(OH)_2(OSi)$), T^2 ($\delta = 59.5$, $CSi(OH)(OSi)_2$), and T^3 signals ($\delta = 68.8$, $CSi(OSi)_3$) where T^y is the level of condensation at a particular center. Although the level of polycondensation achieved is not the highest possible, no signal from T^0 ($\delta = 41.5$, $CSi(OH)_3$) is observable; this indicates that each silicon atom is linked by at least one Si–O–Si bond to the rest of the solid. The relative intensity of the $T^1/T^2/T^3$ signals is 34/56/10 and corresponds to an overall level of polycondensation of 59%. Apparently a fully condensed system is difficult to achieve in this case, either because of the increasing difficulty in the diffusion of water through the cross-linked solid or because, with consideration of the relative position of the Si–Cl bond in the molecular packing, increasing the Si–O–Si units would require a too great distortion of the initial crystal structure. Both elemental and NMR spectroscopic analyses demonstrate the formation of the Si–O–Si network without the cleavage of Si–C bonds and the elimination of the organic groups that would result.

We have looked at the X-ray powder diffraction of the precursor **1** and the hybrid material **2** to investigate the presence of a well-defined organization. For **1**, a set of Bragg's rings is observed in a two-dimensional (2D) experiment, which reveal the microcrystallized structure of the starting chlorosilane **1** (Figure 2). Such signals are not preserved by the hydrolysis step; analysis of **2** indicates totally different Bragg's rings and suggests an important transformation of the initial organization. However, although the initial structure is lost, Bragg's rings are present for **2** and they evidence a high level of organization. The difference between the X-ray powder diffraction results for **1** and **2** shows that the linking of **1** by Si—O—Si bonds results in an important modification of distances, orientation, and general organization of the molecular units.

The anisotropy of the solid has also been investigated at the mesoscopic range by examining the birefringence of the material before and after hydrolysis/polycondensation. This is performed by filling a glass cell of 30 mm thickness with pure melted precursor **1** by capillarity. When cooled to room temperature, compound **1** solidifies as white, shiny, long needles (Figure 3a). The hydrolysis/polycondensation of **1** is promoted by placing the cell in a dessicator with a 70 %

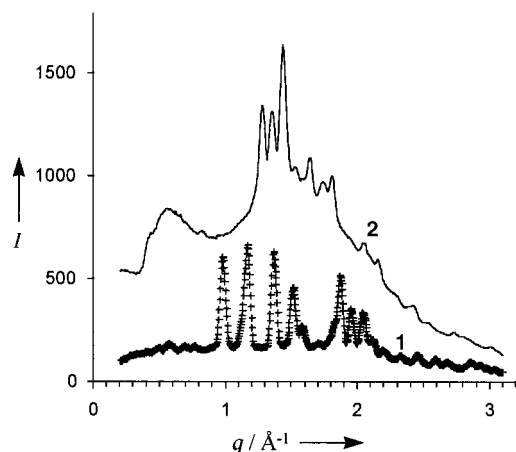


Figure 2. X-ray powder diffraction patterns of solids **1** and **2**. I = intensity.

relative humidity (at 20–22 °C) so that diffusion of water vapor occurs through the cell.^[8] At this stage the reaction is a solid/gas reaction occurring between the vapor of water and the solid chlorosilane **1**. After 8 days, the chemical transformation is evidenced by the lack of melting when the solid is heated up to 200 °C. Pictures of the same region of the cell

were taken before and after hydrolysis/polycondensation (Figure 3 a and b).

Firstly, it appears that the transformation occurs without dramatic destruction of the solid as the shape of the initial crystalline needles remains after the chemical transformation. Secondly, as for the starting compound **1**, a very high birefringence is measured in the resulting hybrid material: 25×10^{-3} for **1**, 20×10^{-3} for **2**. The preservation of the anisotropy confirms the X-ray dif-

fraction analysis. As an example, a gel of **1** prepared by the classical sol–gel process with THF as the solvent exhibits a birefringence of 2.5×10^{-3} , that is ten times lower than **2**, and this demonstrates the higher degree of anisotropy achievable with the solid-state hydrolysis/polycondensation process. Therefore a high level of organization is present at the microscopic level (as demonstrated by X-ray analysis) and also at the mesoscopic level (as demonstrated by the high birefringence). In addition, organization is also present at the macroscopic level, as evidenced by the conservation of the needle shapes of the material in the micron range.

From a general point of view, some solid-state reactions in molecular compounds are known,^[13, 14] but they generally correspond to a transformation of the molecular compound or to intermolecular reactions. Very few concern polymerization—the most well-known examples are topological polymerization of diacetylene compounds^[15–17] or polymerization of aromatic compounds like distyrylpyrazine and phenyl-

enediacrylic acid.^[18] To our knowledge, this is the first example involving chlorosilane, and here we have observed a solid-state chemical process that combines the hydrolysis of a molecular compound and the subsequent intermolecular polycondensation reaction.

The process relies on the reactivity of the Si–Cl bond toward water. This reactivity is high and well-established in previous organosilicon chemistry,^[19] and it allows transformation by a solid/liquid or a solid/gas reaction. The chemical pathway certainly relies on the diffusion of water through the solid and the hydrolysis of the Si–Cl bonds. Thus, the Si–OH bond that forms can quickly react by polycondensation with the Si–Cl group of neighboring molecules to form the Si–O–Si network. In turn, elimination of HCl occurs by diffusion through the solid to the water phase, as evidenced by a decrease in the pH value of the water. This process does not need any catalyst, however it requires a molecular packing where the Si–Cl bonds are close enough to react. Formation of the Si–O–Si network may also occur by polycondensation of neighboring Si–OH groups; such a process is facilitated by the acidity of the medium, which permits the formation of $\text{Si}[\text{OH}_2]^+$ intermediate species.

From a structural point of view, a Riedvelt procedure cannot be expected for **2** due to the low quality of the X-ray diffraction pattern. For compound **1**, a packing of the molecular units based on π – π interaction can be proposed from the crystal structure of similar bis(trichlorosilyl)benzyl compounds.^[12] However, halogen–halogen interaction may also play an important role, as pointed out for supramolecular crystal engineering.^[20]

Those results show the possibility of hydrolyzing and polycondensing a chlorosilane with the architecture of the molecular solid as a scaffold, to form a highly organized covalent solid. We note that the polycondensation level is high and of a similar level to those generally obtained for this type of material prepared by sol–gel processes.^[21] Indeed, the high level of Si–O–Si bonds is achieved without an “amorphisation”. The formation of the solid is not related to the formation of aggregates and colloids, which are generally described as intermediates in the sol–gel process.^[7] By this approach, a “crystallized” silica-based hybrid material can be prepared from a molecular solid directly, by hydrolysis/polycondensation in the solid state without any solvent or catalyst.

Experimental Section

Preparation of the cell has been reported previously although, in this case, cells were not coated with any polymer.^[10] Preparation of precursor **1** was carried out as described in the literature.^[12] Optical properties of the materials were observed with a Laborlux 12POLs polarizing microscope. Photographs were taken with a Leica MPS28 camera. The birefringence was 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. ^{29}Si NMR spectra were recorded on a Bruker AM300 spectrometer at 59.620 MHz (acquisition time: 10 s, contact time: 2 ms, scans: 7400, rotating speed: 5000 Hz, internal standard: tetramethylsilane). Elemental analyses were performed by the “Service Central de Micro-analyse du CNRS” in Vernaison (France). The X-ray experiments were performed on a 2D detector with a rotating anode apparatus (radiation: $\text{Cu K}\alpha$, $\lambda = 1.542 \text{ \AA}$). The samples were ground in an agate mortar under nitrogen and put in a 1-mm diameter, 8-mm length glass Lindeman

capillary. For the imaging-plate apparatus the acquisition time was 3600–7200 seconds (distance between source and detector: 150 mm, diameter of plate: 300 mm).

Precursor **1**: m.p.: 151.5 °C; ^{29}Si NMR (CP MAS): $\delta = 8.06$.

Hybrid material **2**: ^{29}Si NMR (CP MAS): $\delta = -50.8(\text{T}^1)$, $-59.5(\text{T}^2)$, $-68.8(\text{T}^3)$; CP MAS NMR spectroscopy is not always quantitative, however, single-pulse experiments did not reveal any significant variation in relative peak intensity from the CP MAS NMR spectra in the case of alkylene-bridged polysilsesquioxanes with structure similar to **2**.^[21, 22] Elemental analysis calcd for $\text{O}_{1.5}\text{SiCH}_2(\text{C}_6\text{H}_4)_2\text{CH}_2\text{SiO}_{1.5}$: C 59.1, H 4.2, Cl 0%; found: C 55.2, H 4.9, Cl 0.66%.

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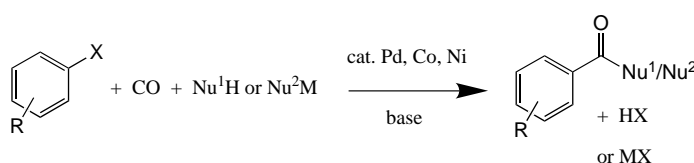
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A More Efficient Catalyst for the Carbonylation of Chloroarenes**

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Dedicated to Professor K. Barry Sharpless on the occasion of his 60th birthday

Palladium-catalyzed C–C bond formation with aryl halides is, at the moment, one of the most important organometallic reactions used in synthetic organic chemistry.^[1] However, the palladium-catalyzed carbonylation^[2] has been investigated far less intensively than the well known Heck, Suzuki, or Stille reactions, although it offers the practical preparation of a broad spectrum of aromatic carboxylic acid derivatives from simple, commercially available building blocks (Scheme 1).^[3]



X = I, Br, Cl, N_2^+ , $\text{OSO}_2\text{R}'$, ArI^+ , IO_2 , SO_2Cl

M = Na, K, BR'_2 , AlR'_2 , SnR'_3 , SiR'_3

$\text{Nu}^1 = \text{OH}$, OR' , NR'_2 , F, Cl, SR' ; $\text{Nu}^2 = \text{H}$, alkyl, aryl, CN, alkenyl, alkynyl, $\text{R}'\text{CO}_2$

Scheme 1. Carbonylation of aryl-X compounds.

Of the aryl halides aryl chlorides, because of their ready availability and low cost, are particularly interesting starting materials for “refinement”. These substrates are, however, comparatively inert towards conventional palladium–aryl phosphane catalysts because the dissociation energy of the $\text{C}(\text{sp}^2)\text{--Cl}$ bond is relatively large (402, 339, and 272 kJ mol^{-1} for PhCl, PhBr, and PhI, respectively, at 298 K). Whereas significant progress has been made in recent years in the activation of chloroarenes for Suzuki, Heck, and other similar reactions,^[4, 5] the efficient carbonylation of chloroarenes remains a problem without a general solution. The crux of the problem is the coordination of CO to the metal center, the π -acceptor character of this ligand reduces the activity of the

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