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A simple access to ω-aminoalkyltrialkoxysilanes: Tunable linkers for self-organised organosilicas

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Abstract

A simple route to ω-aminoalkyltriethoxysilanes with variable alkylene chain lengths, $(EtO)_3Si(CH_2)_nNH_2$ ($n = 5, 11$) is described. These silyl linkers have been used to prepare urea-based compounds with H-bonding and hydrophobic interactions which enable the self-assembly of the molecules. These molecular precursors are suitable for the obtention of nano-structured hybrid silicas.

Keywords: Aminoalkytriethoxysilane; Coupling agent; Organosilica; Self-organisation; Sol–gel

1. Introduction

We are currently interested in the synthesis of bulk nano-structured hybrid silicas. In this context, sol–gel chemistry constitutes a simple and easy approach for hybrid silica materials synthesis [1–3]. Bridged silsesquioxanes [4,5] composed of an organic fragment covalently bonded to a silica network, are receiving much attention owing to the possibility to introduce a large variety of organic fragments leading to hybrids for diverse applications [6–9]. Efforts are being made to synthesize well-defined structured hybrid materials. Using external supramolecular templates or taking advantage of intermolecular interactions between organic fragments allowed the formation of nano-structured materials [10,11]. We showed that hydrogen bonds interactions between urea groups [12] attached to the organic fragment permit to direct the organisation in the silica network and the transcription of a designed supramolecular architecture within the solid material. An essential step for the creation of nano-structured hybrid with various functionalities, consists in the synthesis of appropriate precursors containing both functional organic groups and hydrolysable trialkoxysilyl moieties. We already emphasised the interest of new trialkoxysilyl reagents for the synthesis of the required precursors [5a,13].

Numerous trialkoxysilanes functionalised by organic groups are now commercially available and are used for many applications such as surface modifiers, coupling agents and cross-linkers [14]. Aminoalkyl functional silanes are of particular interest and offer a broad array of applications owing to their chemical activity, their ability to form hydrogen bonds and also to complex metallic species. Among these, 3-aminopropyltriethoxysilane represents one of the most versatile functional silane which is used as coupling agent for surface treatments. It has been used for the derivatization of solid support media for covalent bonding on DNA-microchips [15], as side groups for the molecular imprinting of bulk, mesoporous silica [16] and also for the formation of self-assembled monolayers (SAM) on a surface active reagent [17]. However in the latter case, the formation of monolayers was not always reproducible. A better self-assembly of the organics was obtained with longer alkyl chains of the aminoalkylsilane facilitating the controlled deposition of self-assembled monolayers [18]. This observation shows that additional organic groups

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with self-association properties such as long alkylene chain favor the self-assembly and hence the organisation of the organic functionalities in the solid materials.

Our current interest in self-assembled organo-bridged silicas [12] led us to use alkylene chain with various lengths as linker to generate bisureido units for forming organogels the structure of which was then transcribed into hybrid silicas [19]. Appropriate tuning of the self-organisation properties can result by use of hydrogen bonding or hydrophobic interactions. This led us to envisage a direct and simple route to ω-aminoalkyltrialkoxysilanes $(EtO)_3Si(CH_2)_nNH_2$, with variable chain length ($n = 5, 11$) suitable to synthesize molecular precursors of self-organised hybrids. The triethoxysilyl group undergoes the hydrolysis-condensation reaction and the amino group allows the attachment to organic molecules which will bring intrinsic properties to the material.

2. Results and discussion

ω-Aminoalkyltrialkoxysilanes [20,21] have already been described but the synthetic route involved a protecting-deprotecting strategy with multiple steps leading to a moderate over-all yield [21]. With the aim to improve the over-all yields and to reduce the number of steps, we looked for a general method using commercially available 1-bromo-ω-alkenes, $CH_2{=}CH(CH_2)_mBr$ ($m = 3, 9$) (**1**) as starting compounds (Scheme 1).

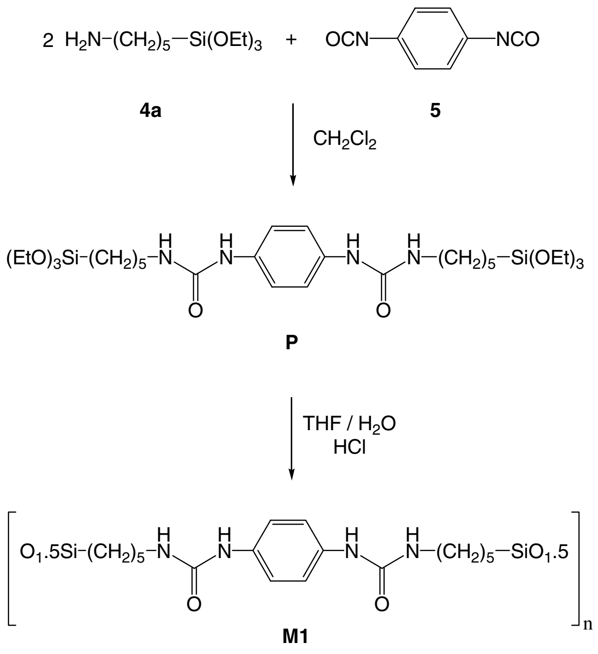
The corresponding ω-bromoalkyltrialkoxysilanes **2** were synthesized by hydrosilylation of **1** with $HSi(OEt)_3$ using Karstedt platinum catalyst at room temperature under N_2 atmosphere. **2** were isolated by distillation under reduced pressure in good yields. The synthesis of the corresponding ω-aminoalkyltrialkoxysilanes **4** was achieved via an azide intermediate **3**. This approach permits the synthesis of the amino group under dry medium to preserve the triethoxysilane group from hydrolysis. The bromine substitution by an azide was realised upon treatment of **2** with 2.5 equiv. of sodium azide in dry acetonitrile. Reduction under hydrogen atmosphere in the presence of palladium activated on charcoal catalyst led to an amine function. This simple approach avoids the protection–deprotection strategy and the final products are obtained in less steps with excellent over-all yields.

The treatment of these silylated compounds with organic molecules consisting of isocyanato groups can lead to hybrid silsesquioxanes molecular precursors with urea functions capable of self-assembling through the hydrogen bonding interactions. To illustrate this approach we synthesize precursor **P** by the reaction of 5-aminopentyltriethoxysilane **4a** with 1,4-diisocyanatobenzene **5** in dichloromethane (Scheme 2).

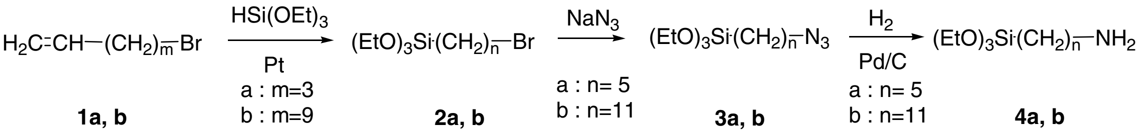
The hydrolysis of **P** was performed in solution in the presence of HCl in a 1:1 (v:v) mixture of THF and water. After few minutes a white precipitate appeared. The reacting mixture was left standing for 2 days at 60 °C under static conditions. The material **M1** was obtained after elimination of solvents followed by filtration and washing with water and ethanol. The white solid was then air-dried at 110 °C. The solid state ^{13}C and ^{29}Si NMR spectra showed that the silica network is covalently bonded to the organic fragment. The ^{29}Si NMR indicates peaks corresponding to T^1 ([C–Si(OSi)(OR)$_2$], 8%), T^2 ([C–Si(OSi)$_2$(OR)], 59%) and T^3 ([C–Si(OSi)$_3$, 33%) units showing **M1** to be a highly condensed solid material. The scanning electron microscopy (SEM) image (Fig. 1) shows **M1** to consist of entangled fibers (length up to 2 μm, width up to 0.15 μm).

Fig. 2 represents the X-ray powder diffractogram of **M1** with sharp peaks corresponding to a long range-ordered structure.

The two peaks at long distances (12.6 and 8.4 Å) can be assigned respectively to the second and the third order of a lamellar structure with *d* spacing of 25.2 Å. This distance is related to the bridging organic group between the two silicon atoms [12a,12b,12e]. The *d* spacing of the lamellar



Scheme 2. Synthesis of precursor **P** and hybrid material **M1**.



Scheme 1. Synthesis of ω-aminoalkyltrialkoxysilanes ($n = 5, 11$).