Self-Association in Hybrid Organic-Inorganic Silicon-Based Material Prepared by Surfactant-Free Sol-Gel of Organosilane

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Abstract This brief review presents some of the important results obtained in the field of a control of the organisation of hybrid materials prepared by the Sol-Gel process of precursors of the general formula $RSi(O_{1.5})_n$. The different strategies involved are based on the used of weak supramolecular interactions during the hydrolysis/polycondensation process.

1 Introduction: The Sol-Gel Process for Silicon-Based Organic-Inorganic Materials

The Sol-Gel process is a well-known route of inorganic polycondensation now taught at the Master level [1–3]. Using the concept of “chimie douce”, this general approach can be applied to silicon based-material. Indeed, the mild conditions required for the formation of the Si-O-Si framework allows the presence of organic species which can be introduced as a doping agent, then, the material can be assimilated to a nanocomposite (Scheme 1) [4–6]. Alternatively the organic part can be a specific moiety covalently bonded to the silicon with the general formula $R[SiX_3]n$ ($X = Cl$, OR, H,… and $n > 1$). A homogeneous distribution of the organic and inorganic part is always achieved because the covalent bonds linking the Si-O-Si network and the organic parts are introduced via the structure of the monomer [6].

Development of the organosilicon chemistry allows the access to very different monomers for this approach. In all cases, the objective is to combine the qualities of the Si-O-Si network (vitreous structure, transparency, thermal and chemical stability) with those of the organic entities [7].

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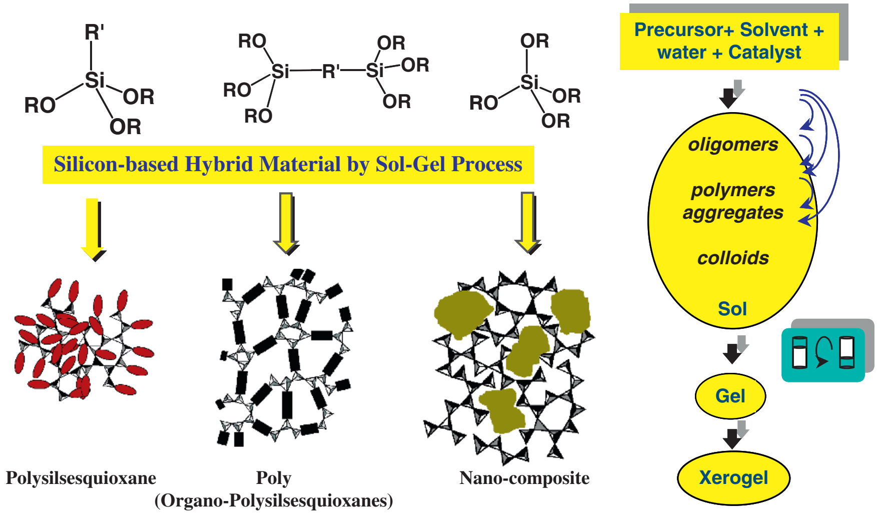
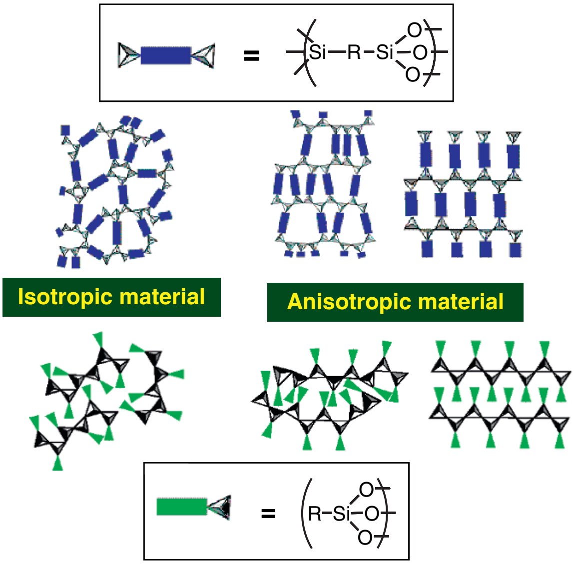


Scheme 1 General overview of the different possibilities that offers the Sol-Gel process for the preparation of silicon-based hybrid material (See also Plate 17 in the Colour Plate Section)

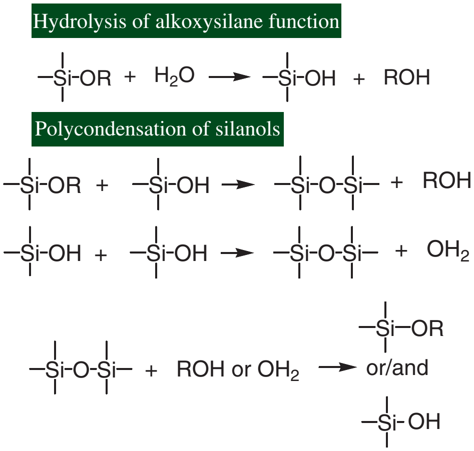
For a given precursor, the characteristics of the solid (composition, structure, porosity and morphology) rely on the choice of the experimental parameters that can control the kinetics of the reactions, therefore these solids are considered as kinetically controlled materials [8–11]. Concerning their organization and structure, it is obvious that the presence of an organic moiety in the precursors has brought into this domain of researches an important dose of supramolecular chemistry. Probably because silica prepared by Sol-Gel chemistry is an amorphous material, these silicon-based hybrid materials were considered initially amorphous too. Meanwhile, the presence of the R group attached to the silicon, not only may introduce important modifications of the reactivity compared to TEMOS or TEOS, it also comes with the possibility of weak interactions between these organic parts. Thus, compared to amorphous silica, the hybrid materials made of R-$[SiO_{1.5}]_n$ units have the possibility to form systems with different organization either anisotropic or isotropic, at a long or a short range order (Scheme 2). This short review focuses on the structure and organization process of such hybrid inorganic-organic materials, and is a non-exhaustive presentation of the progress of the concepts developed in this field. Note that we are talking here of materials prepared in the absence of any surfactant or structure directing agent, this type of materials have been recently reviewed by Inagaki et al [12].

The chemistry involved in the preparation of hybrid materials by the Sol-Gel process is *a priori* similar to the one used to prepare silica gel by the same process (Scheme 3) and it involves necessarily the formation of a Si-O-Si network and silanol groups.

The Si-O-Si linkage has very specific properties. For example, in polysiloxanes [13–16], the structural parameters that determine their general behavior are (a) the relatively high length of the Si-O bond (1.64 Å), (b) an important free volume by segment (c) the conformational flexibility of the polysiloxane bridge (Si-O-Si can vary



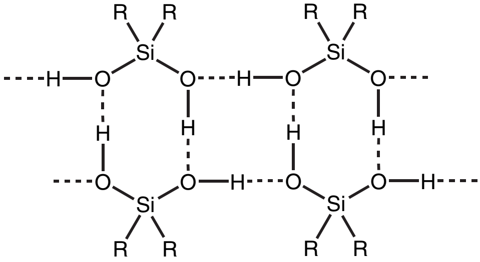
Scheme 2 Various possibilities of organisation and structure for silicon-based hybrid materials (See also Plate 18 in the Colour Plate Section)



Scheme 3 General chemistry at silicon involved during the Sol-Gel process

from 104° to 180°) and (d) the weak interactions between segments (the activation energy for viscous flow is below 40 KJ.mol^{-1}). In this situation, almost all the di-substitued polysiloxanes exhibit thermotropic liquid crystal behavior, revealing their ability to self-organize as mesomorphous phases [17]. This liquid crystal behavior is not only observed when mesogenic groups are used as substituents at the silicon, forming the so-called side-chain and main-chain polysiloxanes. Indeed, it is also observed for these polysiloxanes with "simple" alkyl groups and it is proposed to adopt a columnar structure. On this subject see also the article by Hurduc et al. in this book.

Molecules with silanol functions are known to form supramolecular arrays in the solid state (linear polymeric chains, 2D-sheets or layers, 3D-networks) based on intermolecular H-bonding between Si-OH groups like the one described in Scheme 4 for dialkyl-silanediol [18].



Scheme 4 Example of H-bonging network in disilanol structure

Recently, the possibility of Si-O-H… phenyl hydrogen-bonds was discovered in arylsilanols [19]. However, the nature and the size of the organic group attached to silicon can limit the development of such networks and lead to an association of a limited number of units forming dimers, trimers,…

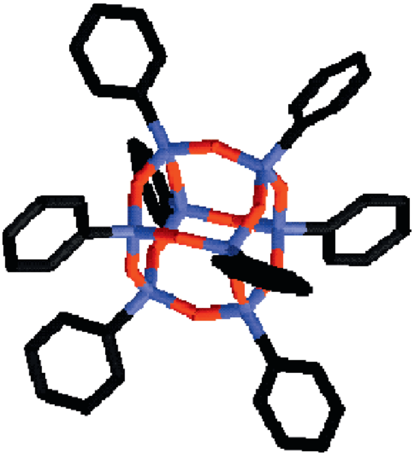
Therefore, silanol species can be a driving force of the resulting organization in the hybrid material. More interestingly, silanols are now used as *reactive supramolecular functions*, that is to say as a synthetic tool allowing the association of molecular units and their further transformation, see below. On the other hand, these self-assembling properties do not appear to be clearly predictable, especially because in the Sol-Gel process other H-bonding species (mainly alcohol, water and sometimes solvent) are present and can disturb the silanol self-association.

2 The case of Polysilsesquioxanes R-$[SiO_{1.5}]_n$ n=1

Polysilsesquioxanes of general formula R-$[SiO_{1.5}]_n$ n=1 are generally prepared by hydrolysis/polycondensation of the corresponding precursors $RSiX_3$ (X=Cl, OR, H). Four basic structures can be envisaged: molecular compound with a cage structure, polymer with a regular ladder structure, polymer with a 3-D disordered structure and lamellar solid.

2.1 Cage-like structures (POSS)

Cage-like structures (POSS) are attractive building blocks (Scheme 5), their organization in the solid is controlled by the shape of these building blocks and mostly by the supramolecular interactions between the organic groups attached to the silicon atoms, some of them exhibiting thermotropic liquid crystal behavior [20,21]. Now

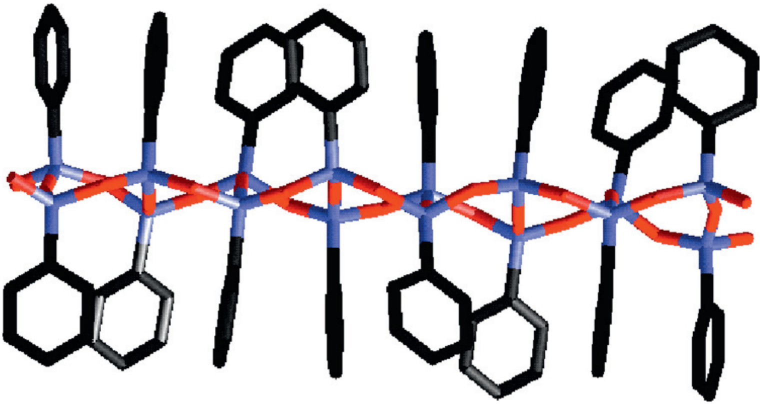


Scheme 5 Cage-like structure of T_8 Cube polysilsesquioxane (See also Plate 19 in the Colour Plate Section)

research in this field is directed towards the preparation of cages with different structures [22] (see also the article of Yoshida et al. in this book).

2.2 Ladder silsesquioxane polymers

Ladder silsesquioxane polymers are very unique in the polymer family since they can be considered as an intermediate structure between a 1D macromolecular chain and a 2D lamellar structure (Scheme 6). Indeed, theoretically, polysilsesquioxanes can adopt such structures. However, their preparation in high yield and leading unambiguously to the precise ladder structure is very recent although they have been postulated frequently in the past. Matsumoto et al. succeeded in their



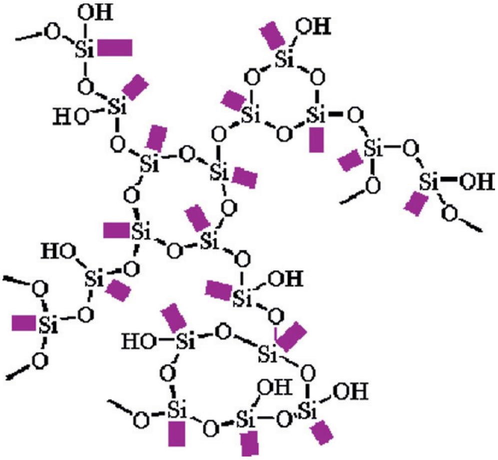
Scheme 6 Ladder-like structure of polysilsesquioxane (See also Plate 20 in the Colour Plate Section)

preparation by oxidation of polysilanes [23] or by a step by step process [24]. They have also reported the possibility to take advantage of the reactivity of silanol-containing precursors whose silanol functions are condensed [25].

Zang et al used such a reactivity of the silanols but while also taking advantage of the self-organization promoted by this function in the solid-state structure of the precursor. Combined with the presence of organic groups with strong self-organization ability at silicon, they obtained the solid-state condensation of the pre-organized precursor leading directly to the formation of the ladder structure [26].

2.3 Polymers with a 3-D disordered structure

Polymers with a 3-D disordered structure are systems described as resins with a disordered cross-linked polymeric structure (Scheme 7).

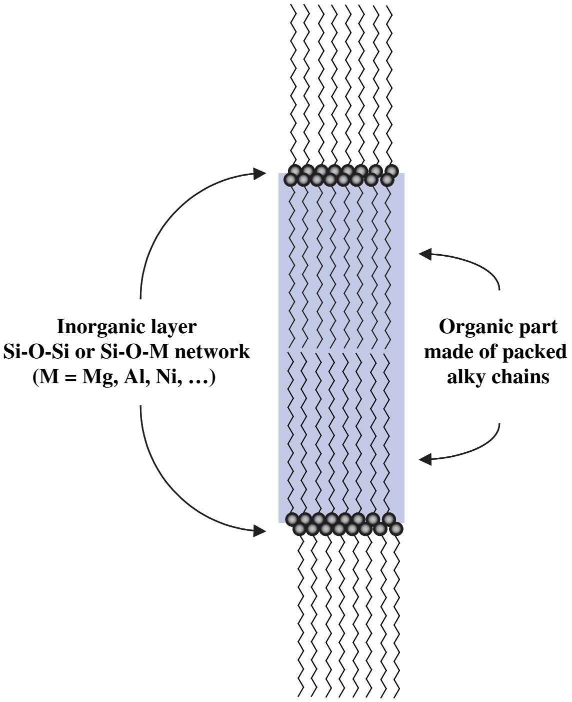


Scheme 7 Idealized structure for polysilsesquioxane resin (See also Plate 21 in the Colour Plate Section)

Such high molecular weight solids like phenylpolysilsesquioxanes or methylpolysilsesquioxanes are often used for matrix of nanocomposites or as resins [27–30]. Brown et al. were the first to consider a ladder structure for phenylpolysilsesquio xanes $C_6H_4SiO_{1.5}$ based on macromolecular and X-ray analysis [31–33]. Methylp olysilsesquioxanes $MeSiO_{1.5}$ was also proposed to present such a ladder structure. For hydro [34], and propyl [28] polysilsequioxanes only the presence of a short range order may be proposed based on the X-ray data that exhibit a set of few broad signals for these products [30]. Other experimental data supporting the formation of these laddered structures are still under debate. In addition the preparation of these products require some chemical treatment and "equilibration" reactions. It suggests that a reorganization process is required and the mixture of macromolecular species associating cage and ladder structures is apparently always obtained [28]. Loy et al. have extensively studied the ability of this system to form gels, resins or crystals [36].

2.4 Lamellar structures

Lamellar structures (Scheme 8) obtained by hydrolysis/polycondensation of organosilicon precursors are generally the result of a segregation between polar and non polar part of a precursor already set up in it: hybrophobic alkyl chain on one hand and alkoxy or halogeno as “masked-silanol” on the other hand. That was the case with the first polysilsesquioxane organized on a long-range order reported by Allara et al. using liquid octadecyltrichlorosilane $C_{18}H_{37}SiCl_3$ [37].



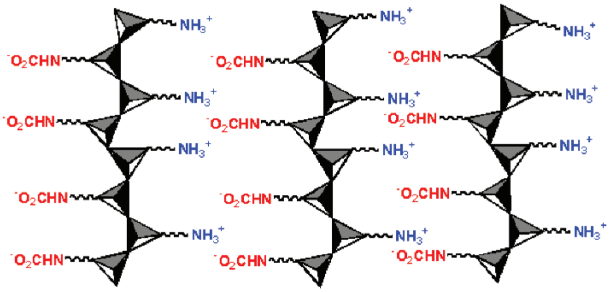
Scheme 8 Idealised lamellar structure of polysilsesquioxanes (See also Plate 22 in the Colour Plate Section)

Its hydrolysis in the absence of solvent by direct contact with water leads to the formation of flakes of octadecylpolysilsesquioxane with a highly organized lamellar structure. It consists of periodically alternated layers, an“organic” one made of alkyl chains and an “inorganic”one made of siloxy backbones plus residual silanols and physi-sorbed water. The high level of organization in these solids is proven by the positioning of the alkyl chains between each other in the “organic layers”, this packing is close to the one reported for alkyl chains of crystallized octadecane. Similarly, Da Fonseca et al demonstrated that layered structures based on a polysilsesquioxane of the formula R-$SiO_{1.5}$ but combined with Si-O-M network, (M = Mg [38–41], Al [38,39], Cu [41] or Ni [42]), can be obtained by mixing the organosilane precursor with metal salts.

Numerous contributions by Kuroda et al. have established that a layered 2D-network can be obtained by hydrolysis/polycondensation of a trialkoxysilane with long alkyl chains [43–50]. Like for other layered structures, the architecture of the solid consists of a packing of alternated layers, one made of a siloxy backbone to which is covalently attached the other one, the "organic layer", made of octadecyl groups. Here again, we found the silanols as one of the driving force of the organization of the system. The formation during the hydrolysis/polycondensation process leads to $RSiX_n(OH)_{(3-n)}$ (X = OMe or Cl) entities with a "surfactant" character that is at work for promoting the resulting structure. The formation of a layered structure is assumed to occur either before or simultaneously with the polycondensation of the silanol group. Kuroda's group is currently working on this approach.

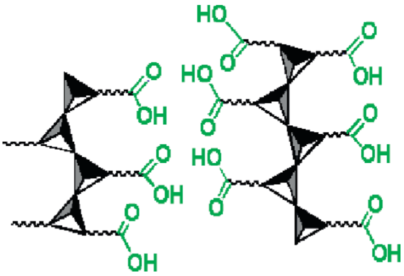
Layered materials can also be prepared from more functional precursors of the general formula $A\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Si(X)_3$ (X = Cl or OR) where A can be for example amino groups. White et al reported the formation of fibrous materials using $H_2N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Si(OEt)_3$ (APS) [51]. The formation of carbamates by reaction with CO_2 from air and their association with Na^+ ions is assumed to result in the observed lamellar structure.

Based on the formation of ammonium carbamate salts, Corriu et al. have obtained the formation of layered material by self-assembling of monosilylated monomers. Starting from $H_2N\text{-}(CH_2)_n\text{-}Si(OMe)_3$, the method consisted of using the reversible reaction between CO_2 and amines groups giving rise to ammonium carbamate salts. The hydrolytic sol–gel process of these carbamates provided hybrid materials with lamellar structure containing ammonium carbamate salts (Scheme 9). Subsequently, the elimination of CO_2 upon heating generated materials with free amino groups in which the long-range order was maintained. The structuration appears dependent on both the ionic interaction between ammonium carbamate pairs and also on van der Waals interactions between the long alkylene chains [52,53].



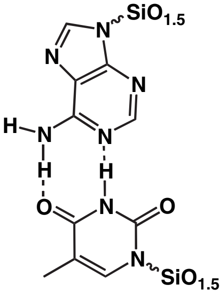
Scheme 9 Idealised structure of the assembly of polysilsesquioxanes layers through carbamate/ammonium interactions (See also Plate 23 in the Colour Plate Section)

Corriu's group has reported another possibility to form layered materials by direct hydrolyis/polycondensation of functional monosilylated organosilanes. In the case of $CN\text{-}(CH_2)_n\text{-}Si(OEt)_3$ hydrolysis/polycondensation of the ethoxy groups simultaneously with the formation of the carboxylic functions from the cyano groups lead to a 2D lamellar structure (Scheme 10) [54]. Strong hydrogen-bonding between carboxylic groups along with the Sol-Gel process is assumed to promote the structuration. Similar systems have been developed that combined the presence of diazogoups **[55]**.



Scheme 10 Idealised structure of the assembly of polysilsesquioxanes layers through H-bonds between carboxylic acid groups (See also Plate 24 in the Colour Plate Section)

Moreau et al. took advantages of hydrophobic interactions and hydrogen-bonding between adenine-containing and thymine-containing monosilylated precursors (Scheme 11). Lamellar structures are obtained with an interlayers distance in agreement with the length of the sum of the organic moieties [56].



Scheme 11 Self association through H-bonds between adenine-containing and thymine-containing monosilylated precursors

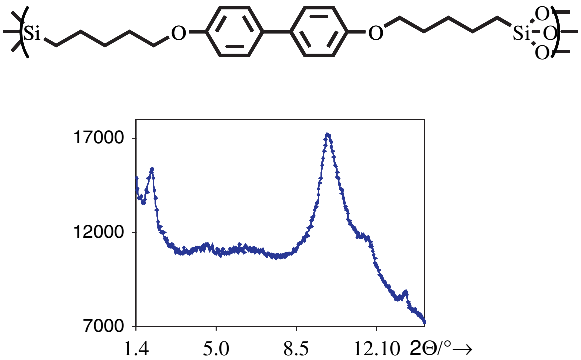
By a similar approach based on H-bonding supramolecular interaction between an adenine- and an uracil-containing precursors, Barboiu et al obtained materials with a micrometric plate-like morphology with a 1-dimensional periodicity of 3.5 Å [57].

3 Organo-Polysilsesquioxanes R-$[SiO_{1.5}]_n$ n>1

The organo-polysilsesquioxane solids have a polysilsesquioxane-based structure. These systems with precursor containing at least 2 $-SiX_3$ groups were first developed by Shea et al.[58], and by Corriu et al [59]. and many reviews have covered the topic of their synthesis and reactivity [7, 60–62].

Initially, the anisotropic organization in these materials was evidenced by three main sets of data. Organization in some of these solids was suggested by their reactivity in the solid state (polymerization [63–65] or complexation [66–72]).

Secondly, the broad signals observed by X-ray powder diffraction of the xerogel support the idea of an anisotropic organization of $R[SiO_{1.5}]_n$ $(n>1)$, whose position and intensity depend on the nature of the precursors (Scheme 12) [73–75].



Scheme 12 X-ray diffraction patern of a powder of bridged-polysilsesquioxane with mesogenic group as a bridge

Finally, at the mesoscopic level, we reported the birefringence observed by microscopy in polarized light of these xerogels that demonstrates unambiguously the anisotropic organization of the medium as exemplified by Fig. 1 [73, 76–78].

A rather high level of organization can be achieved this way in certain cases, for example when carborane-containing precursors are used [79], or with biphenyl-containing precursors [78,80]. However, an organization at the long-range order in these solids requires a better control of the supramolecular forces than can self-associate the precursor during the Sol-Gel process to be achieved. For this, two points are important, first to avoid the use of an organic solvent as much as possible in order to favor any type of hybrophobic or aromatic interactions and secondly to introduce as much as possible a strong interaction between precursors.

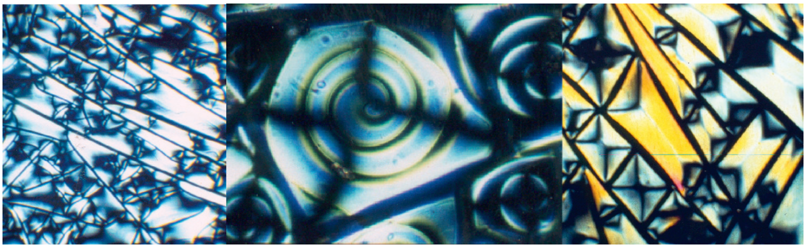
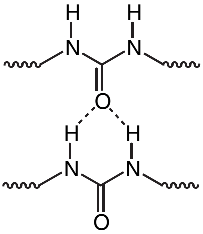


Fig. 1 Images by microscopy in polarized light of three bridged-polysilsesquioxanes (See also Plate 25 in the Colour Plate Section)

In this idea, hydrophobic interactions alone require long alkyl chains to be efficient enough. Corriu et al have shown the effect of C12 to C20 chains on the formation of lamellar structures and the ability to achieve 2D hexagonal structures with C30 chains [81,82].

Other weak interactions like ππ-stacking interactions between aromatic groups can be used to promote self-association between precursor units, as such or as subunits of a mesogenic organic group [76]. In the case of an aromatic moiety exhibiting photophysical properties the organization of the solid after Sol-Gel process can result in preservation or very important modification of such properties compared to the monomer [83–85].

Obviously, H-bonds are also very efficient weak interactions to promote the self-association during the Sol-Gel process. Ureido groups appeared very efficient in doing this job as demonstrated by Moreau et al. [86–91] or Brinker et al. [92] The self-organization of the ureido-containing precursors (Scheme 13) during the Sol-Gel process leads to lamellar structured materials whose proposed structures are in agreement with MEB and X-ray powder diffraction analyses.



Scheme 13 H-bonds between subunits in an ureido-containing bis-silylated precursor or material

Alternatively, formation of highly organized materials is achievable by a new approach using a solvent-free reaction and taking advantage of the crystalline structure of the precursor. We investigated that approach by considering the hydrolysis/polycondensation of bis(trichlorosilyl)bibenzyle in the solid state by direct contact with water vapour (or liquid) [93]. The high reactivity of the Si-Cl function and the formation of HCl as a by-product prevent dissolution during the process. The crystalline structure of the precursor is not preserved during the process but it apparently serves as a scaffold for the building of the crystalline structure of the hybrid material. This is also achievable with crystallized alcoxysilanes [94].

Such approach of the synthesis by solid-state reaction is especially attractive with precursors that present silanol functions. Here again, the supramolecular association promoted by these functions combined with their reactivity allows to directly transform by a simple thermal treatment a molecular precursor to a polymeric hybrid material. Liu, et al. have reported on the possibility to polycondense silanols in the solid state [95], and Corriu et al. have obtained the formation of layered materials by condensation of bis-trisilanol precursors [96,97].

4 Conclusion

At the crossover between supramolecular and synthetic chemistry the hybrid materials represent a major field of science exploration and applications. In contrast with pure silica, the presence of the organic groups in R-$[SiO_{1.5}]_n$ (n>1) systems questions the possibility to have organization based on the presence of hydrophobic and hydrophilic parts.

The key to control the organization of the solid during the Sol-Gel process, i.e.: the design of the monomeric building blocks and the conditions in which they are assembled, are in the hands of the chemist. In these materials prepared in the absence of any template or structure directing agent, weak forces (H-bond, ππ-stacking, hydrophobic …) are the driving forces of the organization of the materials. Similarly, these forces are also at work in mesoporous hybrid materials prepared by Sol-Gel process of organosilanes [98,99].

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