FEATURE ARTICLE

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Auto-organisation of hybrid organic–inorganic materials prepared by sol–gel process

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Silica-based hybrid organic–norganic materials prepared by sol–gel chemistry exhibit chemical and physical properties revealing their anisotropic organisation. Besides the opportunities that this phenomenon opens for the preparation of new materials, it also provides arguments to the chemist looking for a better comprehension and control of the organisation of solids.

Introduction

The chemistry of organic–inorganic hybrid materials is expanding because of the wide range of possibilities that it opens for the elaboration of new materials. This field of research bridges all the different types of chemistry (organic, inorganic, organometallic and polymer) to material science. It is opening also many interesting possibilities for physical properties.

These materials are prepared by inorganic hydrolytic polycondensation (sol–gel chemistry) using the concept of 'chimie douce'.[1,2] Compared to the classical approach of the synthesis of materials leading to crystallised solids, it is a breakthrough in the use of molecular chemistry to access the design of new materials. Among them, hybrid organic–inorganic materials based on Si–O–Si networks are very attractive. This is due mainly to the relative high stability of the Si–C bond which is generally not cleaved under sol–gel conditions and keep the organic group 'alive'. Moreover, the qualities of the Si–O–Si network is excellent in terms of transparency, thermal and chemical stability, it allows stable materials to be obtained in which the chemical and physical properties are preserved, although they can be modified due to a matrix effect. As a final advantage of the silica-based systems, a great number of synthetic tools developed in organosilicon chemistry allows the access to very different precursors in which organic groups are covalently linked to reactive organosilicon groups that are required for the sol–gel polymerisation (Scheme 1).

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Robert Corriu obtained his Docteur des Sciences Physiques in 1961 from the Université de Montpellier. He became Assistant Professor at the Université de Perpignan (1963), Associate Professor at the Université de Poitiers (1964), and Professor at the Université de Montpellier (1969). His research interests are in organometallic chemistry and hypercoordinated silicon and phosphorus compounds. Now, he is concentrating on the elaboration of solids such as hybrid organic–inorganic materials from molecular precursors. He has obtained the Prix Sue in 1969 and the Prix Lebel in 1985, the silver medal of the CNRS in 1982, the Kipping Award in 1984, the Alexander Von Humboldt Research Award in 1992, the Max Plank Research Award in 1993, and the Wacker Silicon Award in 1998. He is a member of the French Academy of Sciences and the Polish Academy.

Altogether, this has lead to the developments of nanostructured hybrid materials (class II) of the general ideal formula R–$[SiO_{1.5}]_n$ ($n \geqslant 1$) prepared from the corresponding precursors wherein an organic group R is covalently bound to n groups –SiX_3 (X = OMe, OEt, H, Cl,...) (Scheme 1). Such materials are clearly different from the nanocomposites prepared by mixing silica precursors and a doping agent (Scheme 1),[3] such systems will not be considered here.

Compared to other well-known systems with highly organised crystal structures such as for example phosphonates, the silica-based hybrid materials R–$[SiO_{1.5}]_n$ ($n \geqslant 1$) were considered as amorphous materials like all inorganic solids prepared by sol–gel chemistry. The new question of the ability of these systems to auto-organise emerges from the data collected from some polysilsesquioxanes R–$SiO_{1.5}$ and systems such as R–$[SiO_{1.5}]_n$ ($n \geqslant 2$). The latter were initially developed because the presence of at least two –$Si(OR)_3$ group in all cases, allows the formation of a solid even with very bulky organic groups (Scheme 2).[4–8] An organisation at the mesoscopic level of materials R–$[SiO_{1.5}]_n$ ($n \geqslant 1$) by micelle templating has been realised and preparation of hybrid organic–inorganic MCM type materials is achievable; we will not consider these systems here that are frequently reviewed.[9] This paper will focus on the auto-organisation of the molecular units in the nanostructured solids which exists in the absence of any additive or any templating agent for promoting the structure.

From the precursor to silicon-based hybrid organic–inorganic materials by sol–gel chemistry

The process starts from an homogeneous solution of the precursor in a solvent and leads to the formation of oligomers, polymers, cross-linked chains and colloids until a gel is finally formed (Scheme 3). After gelation, syneresis and ageing are important steps where chemical and physical transformations still occur. Finally the xerogel is obtained after elimination of the solvent by a drying step. At this stage, no further crystallisation or purification can be made by any means, in contrast to other materials such as phosphonates that can be crystallized. These different steps of this process are similar to those described for the preparation of silica gel and xerogel by the sol–gel process of silica precursors such as tetraalkoxysilane.[2] The formation of Si–O–Si bonds by hydrolysis/polycondensation of Si–OR groups is the key chemical step, however, the presence of the R group attached to the silicon

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introduces three drastic perturbations. The first is a modification of the reactivity compared to TMOS (tetramethoxysilane) or TEOS (tetraethoxysilane). The second is connected to the loss of the tetrahedral symmetry, which permits anisotropic organisation in such amorphous materials. Finally, the third perturbation corresponds to the interactions between the organic units which can drastically influence the formation of the solid's structure and organisation. Thus, compared to amorphous silica obtained after the sol–gel process and comprised ideally of tetrahedral SiO_2 units, hybrid materials made for exemple of $O_{1.5}Si–R–SiO_{1.5}$ units have the possibility to form either an anisotropic or an isotropic structure (Scheme 4).

It is important to stress that there are three different stages in the elaboration of the final hybrid organic–inorganic solid. The first is the formation of soluble species that 'emerge' from a homogeneous solution and results from chemical reactions occurring before the sol–gel transition. The second step is the evolution of the gel once it is formed, its characteristic can be strongly influenced by the chemical and physical transformations occurring during its ageing. The third step is the drying of the gel that leads to the solid (xerogel), this step can still have a deep impact on the characteristic of the residual solid.

In this situation, it is clear that the chemical and physical events occurring during the preparation of the materials will fix its characteristics: porosity, morphology and organisation that can be all considered at the microscopic (<10 nm), mesoscopic (10–1000 nm) and macroscopic level (>1 μm). For a given precursor, the only possibility for changing some of these characteristic relies on the choice of the experimental parameters (temperature,[10–12] solvent,[13] the catalyst and concentration[13,14]) that are chosen for the hydrolytic polycondensation. All these parameters control the kinetics of the reactions, therefore these solids can be considered as kinetically controlled materials.

Experimental data evidencing short-range order organisation of 3-D organized structures in silica-based hybrid organic–inorganic materials

Polysilsesquioxanes R–[$SiO_{1.5}$]$_n$ ($n = 1$)

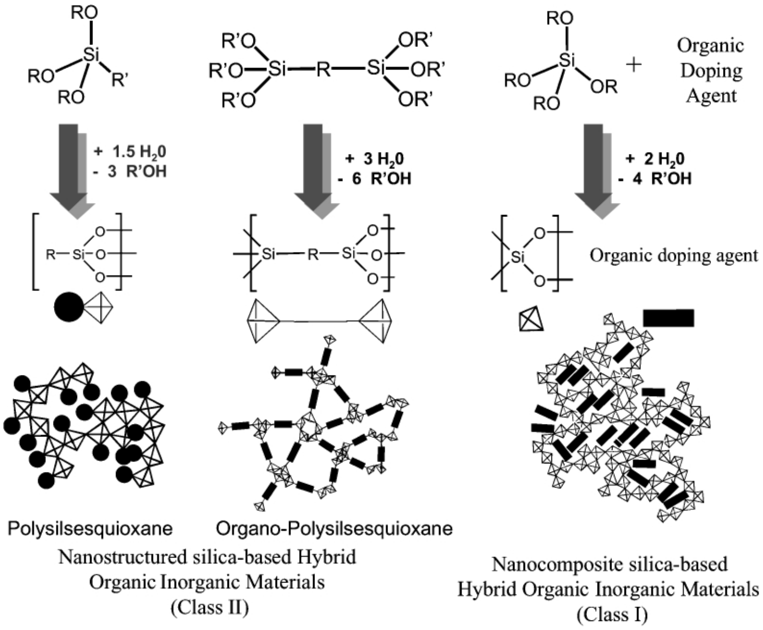
Some of these compounds are generally prepared by hydrolysis/polycondensation of precursors $RSiX_3$ (X = Cl, OR, H).[15] They can be isolated as molecular compounds with cage-like structures such as **XVII** or **XVIII** [Scheme 5(a)] or as resinous high molecular weight solids, this mainly depends on both the nature of the R group and the condition of hydrolysis.[16]

For R = methyl and phenyl,[17,18] a ladder structure has been frequently proposed which represents an intermediate situation between a 1D and a 2D structure, for example with *cis*-syndiotactic **XIX** or *cis*-isotactic configuration [Scheme 5(b)]. For R = propyl, allyl or vinyl there is less evidence of the formation of ladder structures although, as for R = methyl or phenyl, the X-ray data of these resinous compounds may suggest the presence of a short range order between the chains.

In the special case of the octadecyltrichlorosilane $C_{18}H_{37}SiCl_3$, the hydrolysis leads to the formation of flakes of solid **XX** with a highly organized lamellar structure that consists of periodically alternating layers of alkyl chains and siloxy backbones [(Scheme 5(c)].[19] A similar organisation has been reported for materials prepared by hydrolysis/polycondensation of mixtures of octadecyltrimethoxysilane $C_{18}H_{37}Si(OMe)_3$ and tetramethoxysilane.[20,21] In this case, due to the presence of tetramethoxysilane, the lamellar systems are reported to be formed from the packing of alternating layers, one comprised of siloxy backbones and silica to which is covalently attached the other part comprised of octadecyl groups forming the organic layer.

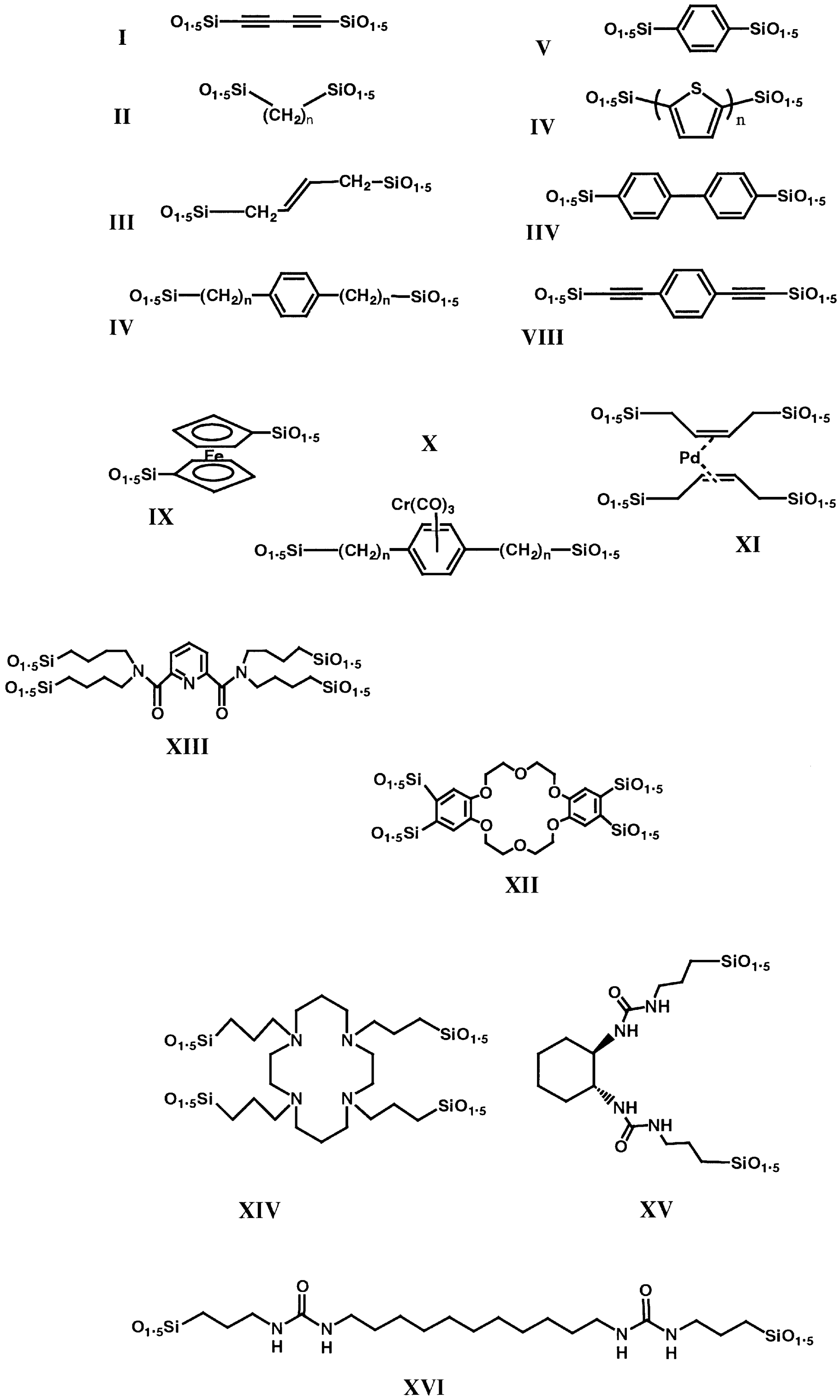
Organo-polysilsesquioxanes R–[$SiO_{1.5}$]$_n$ ($n > 1$)

Initially, chemical reactivity of some of the nanostructured solids suggested the possibility of a short range order in these materials (Scheme 6).[7] There is for example the case of a very easy polymerisation between the thiophene units of solid prepared from **VI** and leading to a silica–polythiophene composite **XXI**,[22,23] or the example of the polymerisation of the butadiyne units of solid prepared from **I**, by thermal treatment at low temperature (200 °C) leading to the polydyine–silica composite **XXII**.[24] Another example is the specific properties of chelating units of solid prepared from **XIV** that complexes $CuCl_2$. Beside the expected paramagnetic signals of Cu^{2+}, antiferromagnetic Cu–Cu interactions have been also observed in the EPR spectrum. These interactions can be represented by the possible structure **XXIII** and only be explained by an initial

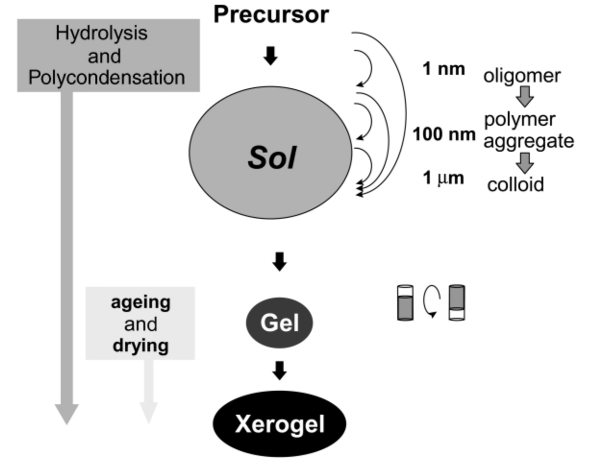


Scheme 1 Overall process of the hydrolysis polycondensation of precursors of silica-based hybrid organic–inorganic materials.

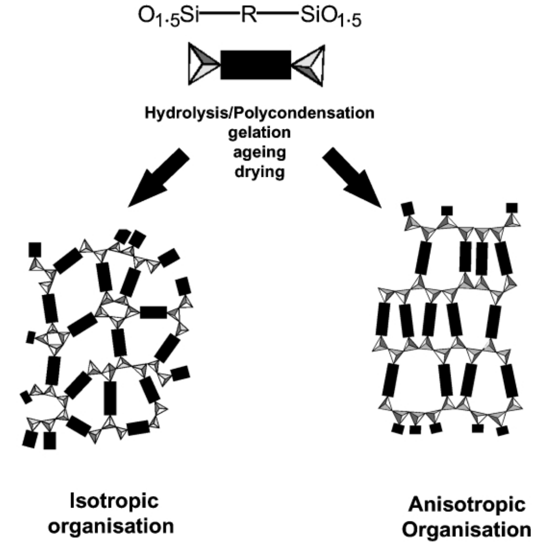
organisation of the cyclam units in the solid made from **XIV**.[25] In agreement with this explanation, the same EPR spectra indicating Cu···Cu interactions are observed in solution with cyclam-basket type molecules where two cyclam units are linked to each other. The organisation of the cyclam units in the framework has been also evidenced by the ability of these materials to complex Eu^{3+} in the ratio Eu^{3+}: cyclam unit being equal to 1 : 2. Interestingly the cyclams do not complex Eu^{3+} in solution. This complexation of one Eu^{3+} between two cyclam units is in good agreement with the Cu···Cu interactions due to the organisation of the cyclam in the framework. Similarly, quantitative complexation of Eu^{3+} or Gd^{3+} by solid prepared from precursor **XIII** requires a special positioning of the organic units to achieve the formation of a hexacoordinated complex as illustrated in **XXIV**.[26,27] As a final example, the difference of reactivity of **IV** and **V** towards complexation with $Cr(CO)_6$ suggests a difference of organisation of the molecular units in each of these solids (Scheme 7).[28–30] Such a difference of organisation and reactivity was confirmed by TOF SIMS measurement (mass spectrometry). All these chemical trans-



Scheme 2 Examples of different organic groups that can be used in precursors to form silica-based hybrid organic–inorganic materials by the sol–gel process.



Scheme 3 Main steps of the elaboration of silica-based hybrid organic–inorganic materials by the sol–gel process.



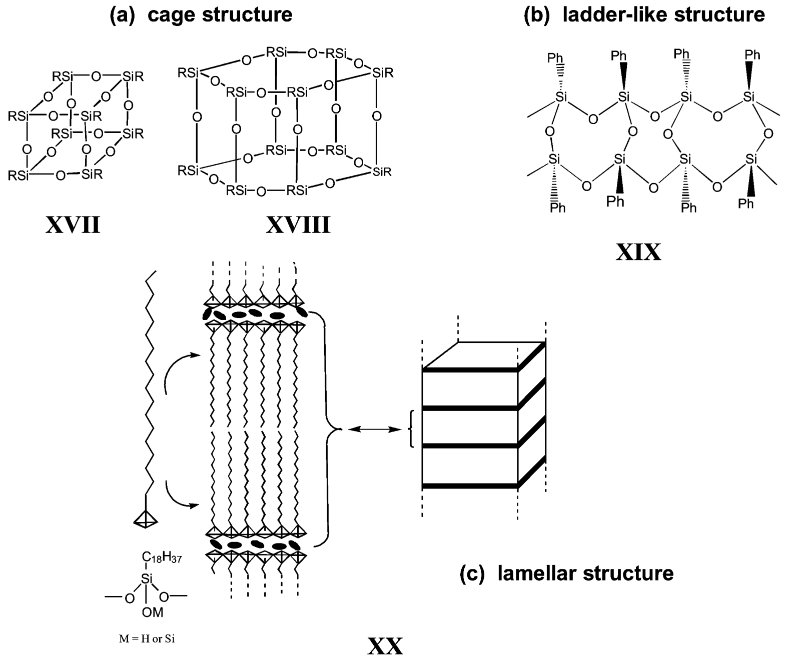
Scheme 4 Possible anistropic and isotropic organisation in silica-based hybrid organic–inorganic materials with a rigid rod-like organic group in the precursor.

formations are indicative of a short-range order in the solid since they require the proximity of the organic groups to react either with each other or to organise around a transition metal.

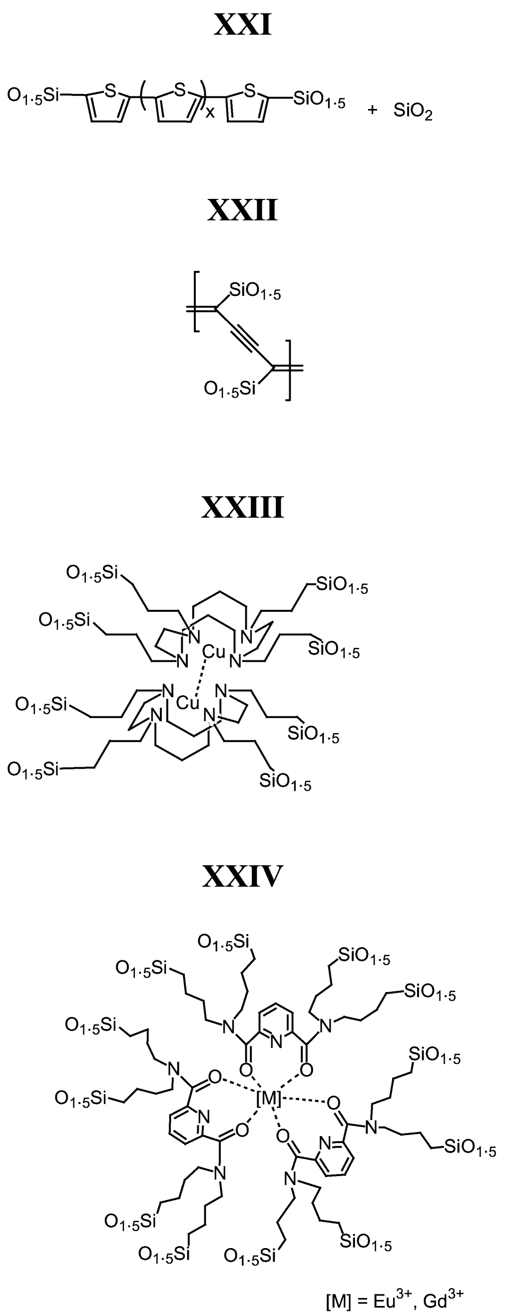
At the microscopic level, the X-ray diffraction of nanostructured solids of the general formula $R[SiO_{1.5}]_n$ ($n \geqslant 2$) do not exhibit any sharp Bragg signals. However, broad signals, the position and intensity of which depend on the nature of the precursors, are frequently observed along with a signal attributed to the Si–O–Si contribution (q = 1.7 Å^{-1} corresponding to 3.5–3.7 Å). These peaks are too large to be interpreted in terms of crystalline periodicity on a long-range order, however a short-range order can be considered. Indeed when R is a rigid organic unit as in **VIII**, the distance associated with the first peak at q_1 = 0.55 Å^{-1} corresponds to a distance d = 11.4 Å (assuming Bragg's law), close to the Si···Si distance estimated in the precursor [d(Si···Si) = 11.45 Å] (Fig. 1).[31] A similar close correspondence is observed in other cases where R is a rigid-rod like molecule.[7]

For **VIII**, when co-polymerised with various amount of TMOS, fluctuations in the position and intensity of the peaks is in accord with the behaviour of a lamellar structure partially swelled unidimensionally (Fig. 1). This supports the hypothesis that the TMOS is partially inserted in the hybrid xerogel architecture during the sol–gel process.[32] Consequently, such a lamellar structure can be assumed for **VIII** alone and gives experimental support to lamellar organisation as was predicted by modelling in the case of xerogels with rigid aromatic organic groups (Scheme 8).[33] A more complete description of these phenomena will be given below (*vide infra*).

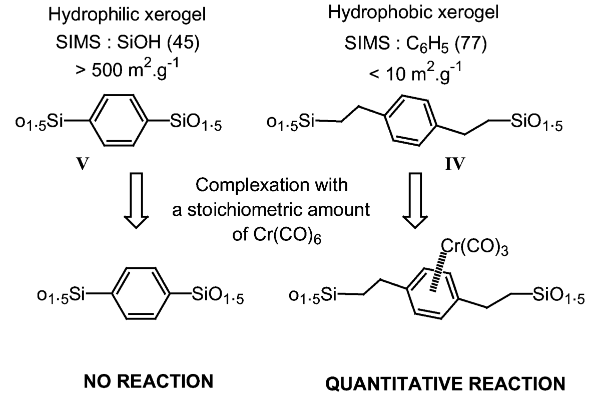
At the meso- and micro-scopic level, a clear demonstration of the anisotropic organisation of these hybrid xerogels is the birefringence of the solid xerogels when observed by microscopy in cross-polarised light as exemplified by solid **VII** in Fig. 2.[31] It has been demonstrated that this birefringence is highly dependent upon three phenomena. The first factor is the nature of the organic group; a rigid rod-like group appears to be a requirement in order to achieve such highly birefringent anisotropic organisation. In contrast, when a flexible alkyl organic group is used, a non-birefringent solid is obtained.[34,35] The second parameter that governs the birefringence phenom-



Scheme 5 Structures of some polysilsesquioxanes $RSiO_{1.5}$.



Scheme 6 Examples of materials resulting from chemical transofrmation in the solid state of hybrid materials.



Scheme 7 Illustration of the difference of reactivity of two solids with similar phenyl groups that can react by complexation with chromium hexacarbonyl.

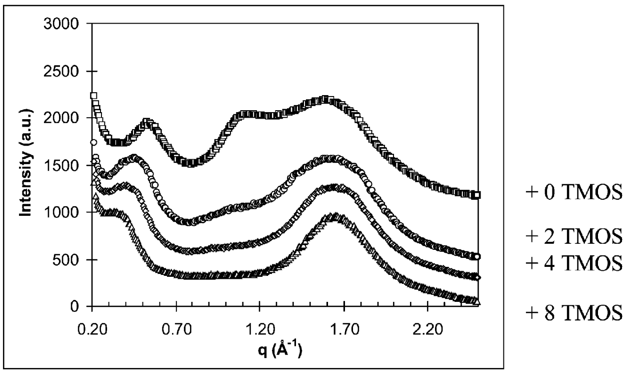
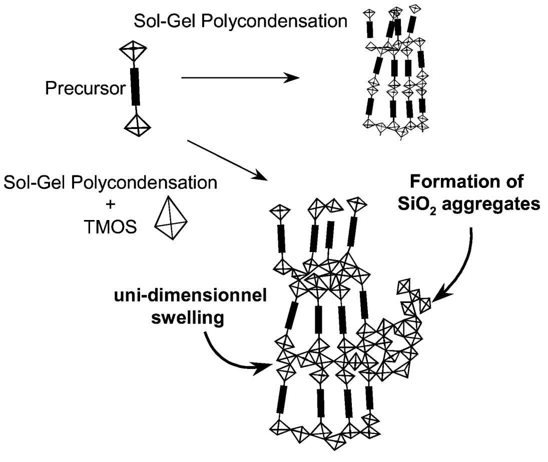


Fig. 1 Diffractogram of **VIII** by X-ray powder diffraction analysis and of **VIII** copolymerised with various amounts of TMOS (stochiometric ratios).



Scheme 8 Comparison of the organisation of hybrid materials with a rigid rod-like precursor, prepared by sol–gel polycondensation or by co-polycondensation with TMOS.

ena is the choice of the experimental conditions showing that the organisation in these systems is also under the control of the kinetics of the chemical process. For example, the solvent and the catalyst can influence the values of the birefringence for solids such as **VII**. Birefringence of 1.5 to 3.5 × 10^{-3} can be obtained depending on the solvent. The catalyst effect is even greater, since solids **VII** can be either isotropic if prepared with NaOH as catalyst, or birefringent (3.5 × 10^{-3}) if prepared with HCl as catalyst.[36] The reason for such a difference may be due to the catalytic cleavage of Si–O–Si bonds by NaOH,[14] it can also be due to the difference between the architecture of the solids due to the relative kinetics of the hydrolysis and the polycondensation reaction, depending on the catalyst, HCl or NaOH for example.

Finally, an important parameter for the birefringence to appear is the propagation of cracks through the gels. This process occurs from few minutes to several hours after gelation depending on the experimental parameters. As mentioned above, at the ageing step, contraction of the Si–O–Si network and expulsion/evaporation of the solvent generates stress that is released by a cracking phenomenon. Fig. 3 illustrates these observations showing a bright birefringent zone on each side of a crack propagating through the isotropic dark gel. This is a sign of the reorganisation and reorientation in the solid during the ageing and cracking of the gel.

Further evidence of the auto-organisation of the solids is their morphological aspect revealed by TEM observations. In some cases, material with a helical fiber-like structure assembled in bundles with widths within the range 0.3–1 μm can be observed

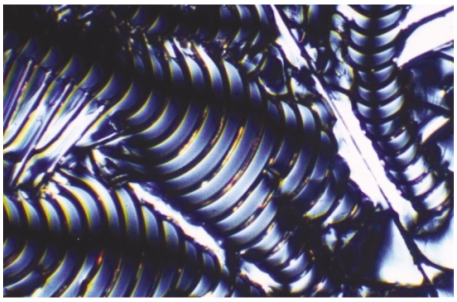


Fig. 2 Hybrid material **VII** analysed by optical microscopy in polarised light after the ageing process and partial drying.

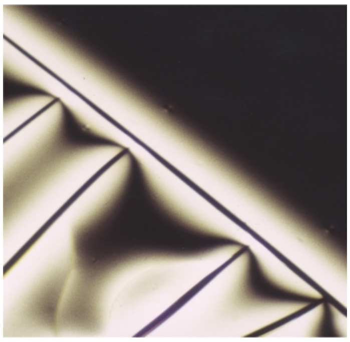


Fig. 3 Hybrid material **VIII** analysed by optical microscopy in polarised light during the propagation of the cracks in the gel.

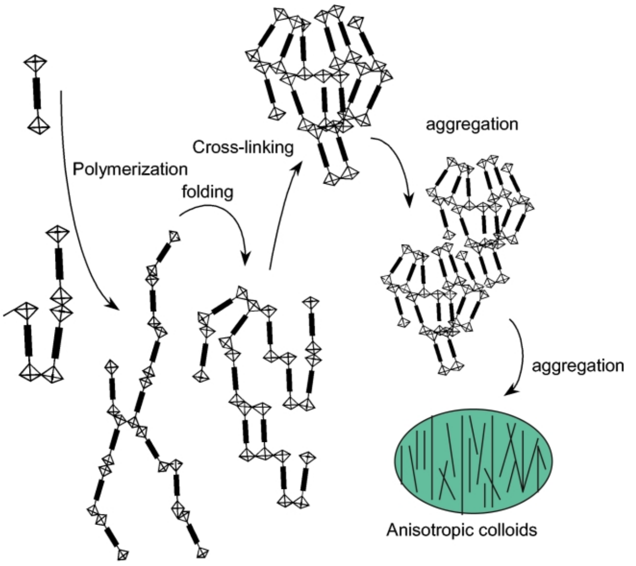
for solid **XV**. The helices are right-handed for materials prepared from the (*R*,*R*) precursor and left-handed in the case of the (*S*,*S*) precursor.[37] Following this approach, a solid with a long range ordered layered structure was obtained and characterized by X-ray diffraction and microscopy using the α,ω-bis-silylated molecule **XVI**.[38] These two last cases suggest a self-organised hybrid material by reference to other supramolecular architectures with helical morphologies driven by H-bonding interaction of auto-associated chiral structures.[39]

Finally, it can be mentioned here, that the formation of such material in a more crystallized form was achieved by a new approach using a solvent-free reaction and performing the hydrolysis/polycondensation of chlorosilane in the solid state.[40]

Possible mechanisms for auto-organisation

The sol–gel process leads from a homogeneous mixture (precursor/water/solvent) to a solvent-free solid. As shows in Scheme 3, the turning point is the sol–gel transition. A tentative description of the process must consider what happens before and after the gel point and especially the evolution occurring after it, in the gel and solid state. Let us consider these two steps separately.

In the first stage the polycondensation process is kinetically controlled and clearly depends on all the experimental parameters. During this processes in which the Si–O–Si bonds are *irreversibly* formed, organisation of the hybrid network is occurring. We propose that steric and van der Waals type interactions between the organic units are the driving forces of the organisation during this step of the elaboration of the solid. Here, the formation of the Si–O–Si brings the molecular units close to each other, allowing interactions that may force the self-organisation of the polysilsesquioxanes cross-linked polymer. This organisation step is controlled by the nature of the organic group (size, geometry and atoms). Scheme 9 is an illustration of this possible pathway and of the formation of a short-range organisation on domain ranging from the size of oligomers to polymers and colloids.



Scheme 9 Illustration of a possible organisation at the molecular level by self-organisation of the precursor units and formation anisotropic colloids and aggregates.

The self-organisation at the nanometric level experimentally evidenced by chemical reactivity and physico-chimical characterisations, can result of this process occurring during the polycondensation step. Thus in this hypothesis the kinetics of the hydrolysis/polycondensation reactions can definitively fix the organisation of the aggregates.

An experimental confirmation of such organisation is the co-polycondensation of **VIII** with various amounts of TMOS.[32] This study evidenced a partially mono-dimensional swelling phenomenon. In other words, increasing the amount of TMOS in the starting mixture leads only to a partial incorporation of silica units in the structure of the solid. A complete and general reaction of TMOS with the precursor of **VIII** should lead to a complete 3D swelling phenomenon and would be correlated with the cube root of the volume fraction of silica introduced by the amount of TMOS. Because the kinetics of the hydrolysis/polycondensation of **VIII** is much faster than that of TMOS, it reacts firstly with itself and less so with TMOS. Then, residual TMOS can react with itself to form aggregates of silica. Here again, the nature of the organic group and the reactivity of the precursor are deciding parameters that demonstrate the kinetic control of the system in the initial steps. Self-organisation of molecular units containing hydrophobic regions forces them to react with each other, apart from TMOS.

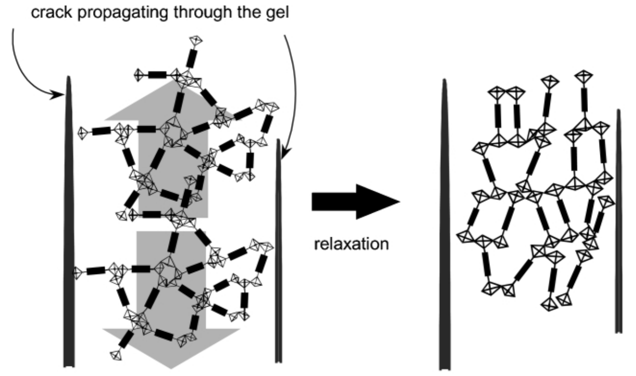
As a support for the drastic influence of the hydrophobic interaction between organic units for the self-organisation in silica-based materials the great ability of polysiloxanes to self-organise even when non-mesogenic groups are used can be noted.[41–43] Simultaneously, it is also important to take into account the presence of silanols[44] (intermediates in the chemical process), their association by hydrogen bonding can lead to an organisation of the precursor units.

The above-described process would occur during the polycondensation in solution and lead to the formation of short-range order. Moreover, it has been shown that micrometric scale organisation is observed after the sol–gel transition; during ageing of the solid when birefringence is observed.[31] Thus we can propose a sub-micrometric size for the domain.

At the gel point, the main phenomenon is certainly the anchoring of the colloids to each other by Si–O–Si bond formation. At the moment, we do not know to which extent the sol–gel transition influences the organisation of the precursor units in the materials. However, this step is certainly of great importance for the porosity and morphology of the materials.

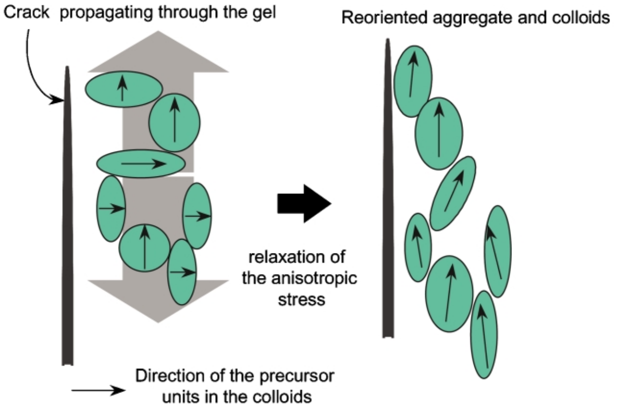
The second important moment in the history of the solid concerns the changes which occur in the gel, during the ageing, a determining step for the birefringence. Extension of the short range order to a larger domain (several μm) is revealed by microscopy and is related with the crack formation process. This phenomenon occurs only in the case of specific organic groups, generally those with a rigid rod-like shape. It must be clearly stated that this birefringence cannot be related to any type of liquid crystal behaviour since the precursor units, here, are linked to each other irreversibly by Si–O–Si bonds and not by van der Waals forces between independent units as in liquid crystals. Moreover the organisation observed here is kinetically controlled instead of the thermodynamical control of liquid crystal structures.

During the ageing, a reorganisation of the solid occurs and leads to important transformations, this fact has been largely demonstrated in silicas[2] and in hybrids particularly with the formation of a monodisperse porosity with a drastic decrease of micropores.[12] From the organisational point of view, densification of the Si–O–Si framework, evaporation of solvent and by-products, and chemical reorganisation of the Si–O–Si network generate stress and finally lead to cracks. The propagation of these leads to birefringence caused by the extension of the short-range order to larger domains. As for any polymeric materials, such processes can lead to the orientation of the precursor units as depicted in Scheme 10,[45] the value of birefringence being in the same range as those of stretched polymers. Such reorientation is certainly facilitated because of the 'flexibility' of the Si–O–Si bridges, with deformation of the Si–O–Si angle being of low energy.[46] Secondly, the level of condensation is not necessarily very high when gelation and cracking occur. Finally, this reorientation/reorganisation is linked to the ability of the system (level of condensation, rigidity of the molecular units) to transmit the stress produced by the cracking.



Scheme 10 Illustration of the relaxation process of molecular units when a crack propagates through a polymeric material.

In the present case, taking into account the above consideration, it can be proposed that here this process occurs in a cooperative manner leading to orientation of anisotropic domains linked to each other and relaxing the stress orthogonal to the cracks as depicted in Scheme 11.



Scheme 11 Illustration of the relaxation process at work when a crack propagates through the gel.

Conclusion

Hybrid materials in which the organic part is chemically bound to the siloxane matrix can exhibit an organisation resulting from two separate steps. The first, which is kinetically controlled, occurs in solution, before the sol–gel transition. It depends strongly on the experimental parameters and is evidenced by the chemical reactivity in the solid and by X-ray diffraction. This organisation occurring before the sol–gel transition could be controlled by the van der Waals interactions between the organic units during the polycondensation at silicon. This polycondensation leads to aggregates possibly exhibiting an organisation between the organic units at the nanometric scale (10–100 nm).

After the sol–gel transition, during the ageing of the solid the development of a short-range organisation on micrometer size domains is evidenced by birefringence. Physical and chemical process occurring during the ageing of the material are the driving forces leading to the extension of the short-range order to larger domains. At this step, the chemical evolution (formation and redistribution of Si–O–Si bonds) and solvent evaporation induce stress and formation of cracks through the gel leading to reorientation and anisotropic organisation on the micrometer size level.

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