The Control of Nanostructured Solids: A Challenge for Molecular Chemistry

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Nanostructured hybrid organic-inorganic solids are a class of materials of growing interest because of their great potential in synthesis and possible applications. All organic molecules containing at least two $–Si(OR)_3$ groups can be transformed by hydrolytic polycondensation at silicon into materials in which the $–Si(OR)_3$ groups are changed into $–SiO_{1.5}$. Moreover, the physical properties of the organic units included in the silica matrix are maintained in the solid. This sol-gel-type transformation leads initially to a viscous sol that allows devices to be made (films, matrices and even fibres in some cases). Finally, these materials exhibit both short-range and long-range organisation in the solid when the organic units have a rigid geometry.

I. Introduction

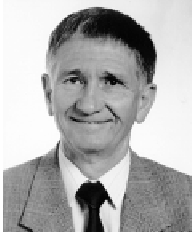
The concept of "Chimie Douce" has been introduced recently in the field of Materials Science.[1,2] This method of obtaining solids represents a breaking down of the preparation of materials and this concept, which is based on inorganic polymerisation, has opened the field of Materials Science to molecular chemistry.

The methodology used in classical solid state chemistry is based on the thermodynamic evolution of the reaction. Whatever the experimental conditions, success is based on the self arrangement of the system leading to stable (or metastable) materials. This approach to the elaboration of materials includes the high temperature methodologies leading to crystals, glasses or ceramics, as well as to other techniques that require lower temperatures such as the synthesis of crystalline aggregates, the preparation of polyanions from solutions, or the hydrothermal synthesis of zeolites.

The properties of the solid materials obtained by these methods are always governed by the general thermodynamic laws represented by the phase diagram.

In contrast, the methodologies encompassed by the phrase "Chimie Douce" are based on kinetic control of the solid synthesis. The solids obtained are not the most thermodynamically stable, but they are the result of a multiparametric chemistry based on mechanistic control of the chemical reactions. One commonly used approach of "Chimie Douce" chemistry is the sol-gel methodology,[3,4] which corresponds to an inorganic polymerisation (Scheme 1). Scheme 2 illustrates the complexity of the hydrolytic polycondensation of $Si(OR)_4$ by showing the possible competitive reactions occurring at the same time.

The preparation of SiO_2 by this route is controlled by the kinetics of the hydrolytic polycondensation that occurs around the silicon atom through nucleophilic substitution at silicon. In this process H_2O acts as a nucleophile and displaces ROH in the first step. The condensation leading to Si−O−Si bonds occurs by hetero or homo condensation (see Scheme 2). This mechanism is a highly complex one because of the four functionalities, the possibility of redistribution, and the formation of chains or rings leading to a



Robert Corriu, born in 1934 in Port-Vendres, France, obtained his Docteur des Sciences Physiques in 1961 from the Université de Montpellier. He became Assistant Professor at the Université de Perpignan in 1963, Associate Professor at the Université de Poitiers in 1964, and Professor at the Université de Montpellier in 1969. His research interests in organometallic chemistry have been focused on organosilicon, organogermanium, and organophosphorus compounds, transition metal complexes, and hypercoordinated silicon and phosphorus compounds. More recently, he has concentrated his research efforts on the elaboration of solids from molecular precursors. His main interest is now connected with hybrid organic-inorganic materials and molecular chemistry permitting solid organisation. He has obtained awards from the French Chemical Society (Prix Sue in 1969 and Prix Lebel in 1985), from the CNRS (silver medal in 1982), and from the American Chemical Society (Kipping Award in 1984). He was elected to the French Academy of Sciences in 1991 and Polish Academy in 1997. He obtained the Alexander Von Humboldt Research Award in 1992, the Max Planck Research Award in 1993, and the Wacker Silicon Award in 1998.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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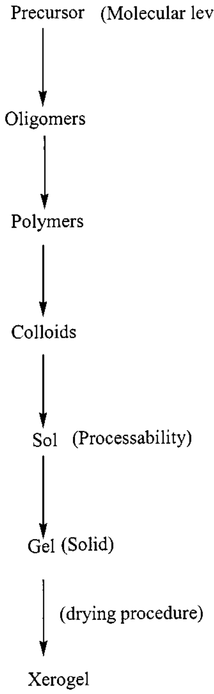
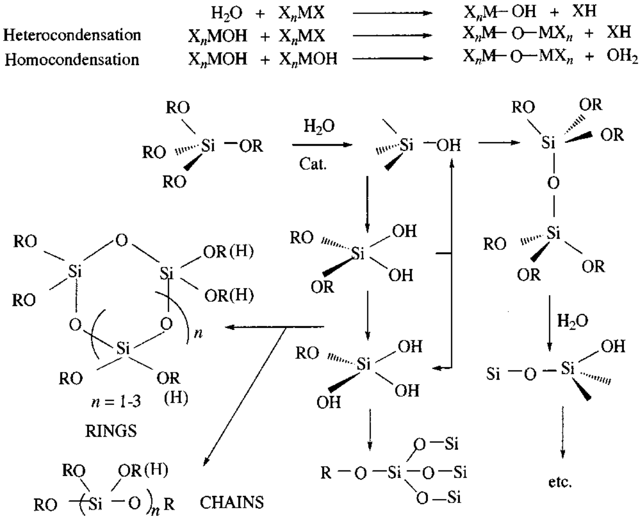


Scheme 1. A general scheme for inorganic polymerisation



Scheme 2. Sol-gel hydrolytic polycondensation of metal alkoxides

highly crosslinked solid. The detailed mechanism for this process is unknown. However, several attempts to elucidate this aspect of the reaction have been made, leading to isolated but interesting results.[5–7]

The use of this chemistry for solid preparation is nowadays strongly connected to polymer science. The physical properties of the highly crosslinked polymers obtained are controlled by the mechanism of the reaction used to build the chains of the resulting macromolecules.[8] In the same manner, the synthesis of the inorganic materials performed by sol-gel corresponds to a kinetically controlled process. The texture of the solid obtained, described in terms of macroscopic properties (specific surface area, porosity, density etc.), is highly dependent on the experimental conditions, a fact that strongly suggests kinetic control of the solid.[9–12] Thus, although it is not possible to predict the texture of the solid, the method is highly flexible because of the great number of parameters that can be manipulated (temperature, concentrations, solvent, catalyst, nature of leaving group etc.) to give experimental control over the texture obtained. It is also important to point out the flexible processability inherent in the formation of the sol. The sol is a viscous liquid that allows devices to be obtained: e.g. films by coating and fibres by spinning, as well as matrices with the possibility of inclusions.

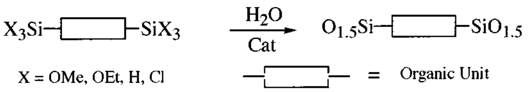
In materials science the gels are described as unstable solids.[4] They cannot be classified as metastable since their stability can be dependent on experimental conditions. This fact has led to difficulties as far as reproducibility is concerned. However, after extensive studies performed on silsesquioxanes and nanostructured hybrid organic-inorganic materials, we have shown that *reproducibility is attained when the experiments are carefully performed with the precision that is necessary for physical chemistry experiments or analytical measurements.*[8–11] Moreover, the stability of these solids is very good when they are stored under very strictly controlled conditions that exclude the presence of reagents such as air humidity.[13]

The sol-gel methodology is an alternative to the classical thermodynamic routes for the synthesis of solids. It allows materials to be obtained by "step-by-step" chemistry starting from molecular precursors at low temperatures. The preparation of the solids through "Chimie Douce" processes is the natural bridge between molecular and solid state chemistry. There is a wonderful way to obtain, in one step, new materials in which organic, inorganic, organometallic molecules or polymers can been included or chemically bound to inorganic matrices. A wide field of research is now open to chemists, including the possibility of designing the organisation of the porosity of the inorganic matrix using templates or micellar media.[14–27]

This paper focuses on the organic-inorganic hybrid materials obtained from molecular precursors. However, it is important to make the distinction between nanocomposites and the nanostructured hybrid materials[28–40] that are the topic of this paper.

The polycomponent solids corresponding to nanocomposites are obtained by hydrolytic polymerisation of a metal alkoxide previously mixed with organic molecules (or polymers). These solids can be separated into two phases by washing with an organic solvent. However, it is important to point out that this approach to the synthesis of materials is the simplest and most efficient. The method allows interesting devices to be obtained very quickly in order that their properties can be studied. The method also provides a very flexible way to obtain new materials and to include organic units, with desirable physical properties, within inorganic matrices. Silica is currently the most useful oxide matrix because of its physical and chemical properties and also due to its ease of preparation and processability by the sol-gel methodology. The number of possibilities open is vast and includes, amongst others, the preparation of controlled mesoporous materials, molecular imprinting and foot printing, and optical devices. etc. Indeed, in this area a large number of papers[21−31] have been published that describe numerous very interesting materials.

In contrast, the nanostructured hybrid materials that form the topic of this paper are obtained by hydrolytic polycondensation of a molecular precursor in which trifunctional silicon atoms SiX_3 are covalently bound to the organic moiety (Scheme 3).



Scheme 3. Elaboration of organic-inorganic hybrid solids from bis-silylated precursors

The hydrolytic polycondensation allows the $SiO_{1.5}$ groups to be crosslinked around the organic unit to give to monophasic solids. These solids correspond to nanostructured materials. This aspect will be developed in more detail later in the paper.

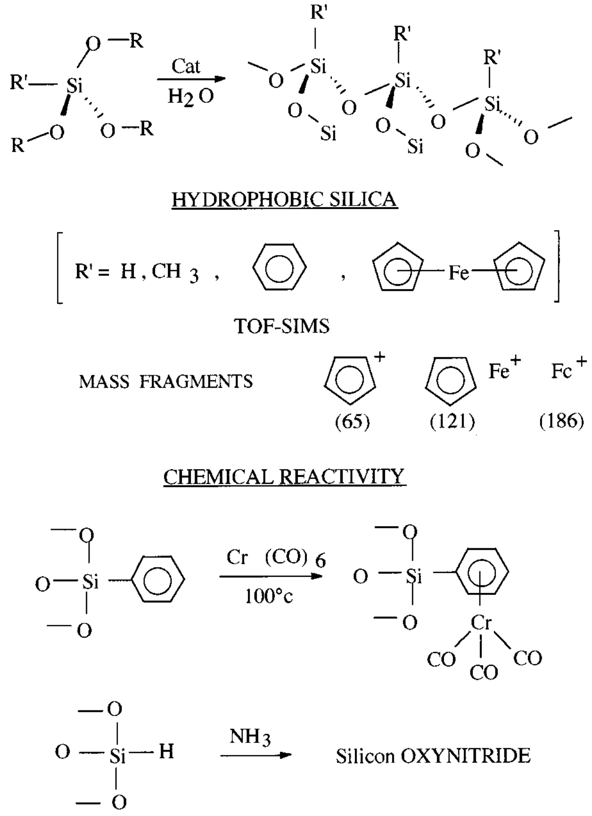
II. Monophasic Hybrid Organic-Inorganic Materials: Scope and Limitations

Scheme 3 outlines the principle used in the synthesis of these materials. It is important to summarise the main results obtained in this field to date and to point out the main features of this class of materials.

The main prerequisite is the presence of non-hydrolysable and non-oxidisable bonds between the organic unit and the oxide matrix. The second requirement is the presence of groups that permit the formation of the oxide matrix by a hydrolytic polycondensation ("Chimie Douce" process). Trifunctional silicon groups (SiX_3) are very convenient for this purpose and trialkoxysilyl groups [$-Si(OR)_3$ (R = Me, Et, *i*Pr)] are commonly used.[32−40] However, $-SiCl_3$ [41] and $-SiH_3$ [42] groups can also lead to silica matrices. Moreover, Si−C bonds are highly stable towards hydrolysis and oxidation and many routes have been found for the introduction of a silicon group into an organic molecule.

II.a. Materials Obtained from Mono-silylated Precursors

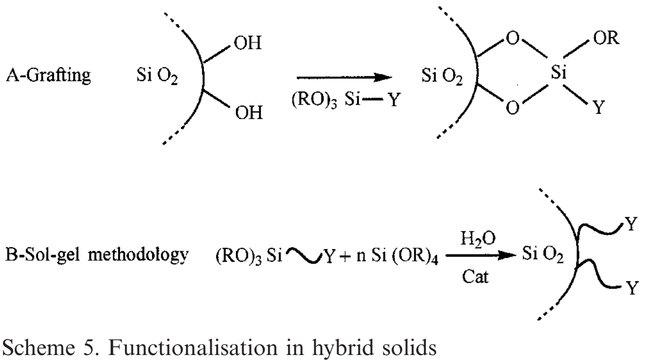
The focus of this paper is on nanostructured materials obtained from precursors containing at least two Si−C bonds.[34−40] The case of monocomponent hybrids with only one Si−C bond has been reviewed recently.[32,33] Monocomponent systems are particularly interesting since they open the way to functionalised surfaces. It has been demonstrated that the hydrolytic polycondensation of $R-SiX_3$ leads to solids in which the organic part is mainly located at the surface of the material, as evidenced by TOF-SIMS (Time of Flight Secondary Ion Mass Spectrometry),[43] by the hydrophobicity of the material obtained, and by the reactivity of the functionalities attached to the organic group R[44,45] (Scheme 4).



Scheme 4. Hybrid materials obtained from mono-silylated precursors

The characteristics of the materials obtained for catalysis, separation, its physical properties or other purposes are related to the accessibility of the functional groups in the solid.

The location of the functionalities at the surface is a very important feature and two routes are used for the preparation of these materials: grafting of an oxide surface (generally SiO_2) (route A) or preparation by the sol-gel methodology (route B) (Scheme 5).

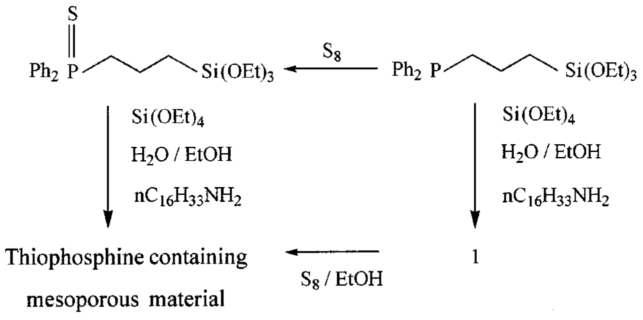


Scheme 5. Functionalisation in hybrid solids

Although grafted silica with interesting applications has been prepared by route A, route B is generally a more efficient way to obtain materials than route A. A similar trend is observed in the case of the mesoporous materials prepared using a micellar medium.[46,47] The sol-gel polycondensation of $Si(OR)_4$ in the presence of a surfactant solution in H_2O leads to a hybrid material with a regular hexagonal distribution of the surfactant. After elimination of the surfactant it is possible to obtain a mesoporous SiO_2 in which the pores are regularly distributed within the material.[22]

Functionalisation of mesopores can be achieved by grafting (route A) using the reactive groups located inside the mesopores.[21,48−52] However, it is possible to obtain directly a mesoporous silica that has a narrow and organised porosity and contains chemical functionalities located inside the pores. The methodology used is similar to that shown in route B, but is performed in presence of surfactant. The lipophilicity of the precursor permits its inclusion in the surfactant. Thus, during the formation of SiO_2, the polar $Si-OH$ head is at the surface and the lipophilic and functional tail is included in the micelle.[21,47,53−56]

Scheme 6 illustrates the synthesis of thiophosphane-containing materials either by direct preparation using method B in presence of a micellar medium, or by reaction of S_8 on the phosphane-containing material prepared by the same method.[53] The materials obtained by the two methods exhibit the same characteristic features in terms of ^{31}P, ^{13}C, ^{29}Si NMR, porosity etc.



Scheme 6. A phosphane-containing material elaborated in micellar media

II.b. Bis-Silylated Precursors

The main features of these systems are summarised by four key points, which will be discussed in greater depth in the following sections.

(1) Processability. (2) Wide range of synthetic possibilities. (3) Inclusion in the oxide matrix of the desired physical properties using appropriate organic moieties. (4) Inclusion of the desired chemical properties.

II.b.1. Processability

In all cases the sol-gel methodology allows processable materials to be obtained since the inorganic polymerisation occurs with formation of a highly viscous sol. Thus, it is always possible to obtain films (by coating), matrices, and also fibres (by spinning).

II.b.2. Wide Range of Possibilities

The wide range of possibilities for the synthesis of materials is exemplified by the fact that, in all cases studied to date, the organic unit is included within the silica matrix without any transformations. The hydrolytic polycondensation occurs under mild conditions and it does not induce any rearrangement or bond breaking in the organic compound: the ^{13}C NMR spectra of the organic units are almost identical in solution and in the oxide matrix. ^{29}Si NMR spectroscopy, which is sensitive to the first and second nearest neighbours, allows easy discrimination between the T ($C-SiO_3$) and the Q (SiO_4) units.[57][58] The cleavage of the $Si-C$ bonds corresponds to the formation of Q units whose signals are located in the range $\delta = -90$ to -110, and are shifted to higher field in comparison to the T units ($\delta = -40$ to -80) depending on the nature of the organic group. The only exception is the case of the $Si-C\equiv C$ bond, which can be cleaved by H_2O when fluoride ions are used as the catalyst.[17−20,59−73] Scheme 7 shows, as an example, the ^{29}Si NMR and IR spectra observed before and after cleavage of $Si-C$ bonds in the case of the tetraethynylbenzene hybrid material.[61] The solid (I) is obtained from the corresponding precursor by hydrolysis. Treatment with NH_4F/H_2O in MeOH leads to $Si-C\equiv C$ cleavage. However, the tetraethynylbenzene formed (II) cannot be separated from SiO_2. It is possible to show by spectroscopic analysis that the reaction is complete, as illustrated in Scheme 7.

Any organic molecule containing at least two SiX_3 units can be transformed into a nanostructured hybrid material by hydrolytic polycondensation (Scheme 8). Thus, this very flexible synthetic route does not suffer from any limitation in terms of access to materials. In this way chemists have the opportunity to include in a solid material any organic molecule that has a desirable physical property in solution. It also offers an alternative to the thermodynamic approach to the preparation of materials since is allows all the possibilities available by molecular chemistry to be combined in the design of new kinds of materials (Scheme 8).

II.b.3. Physical Properties in the Hybrid Materials

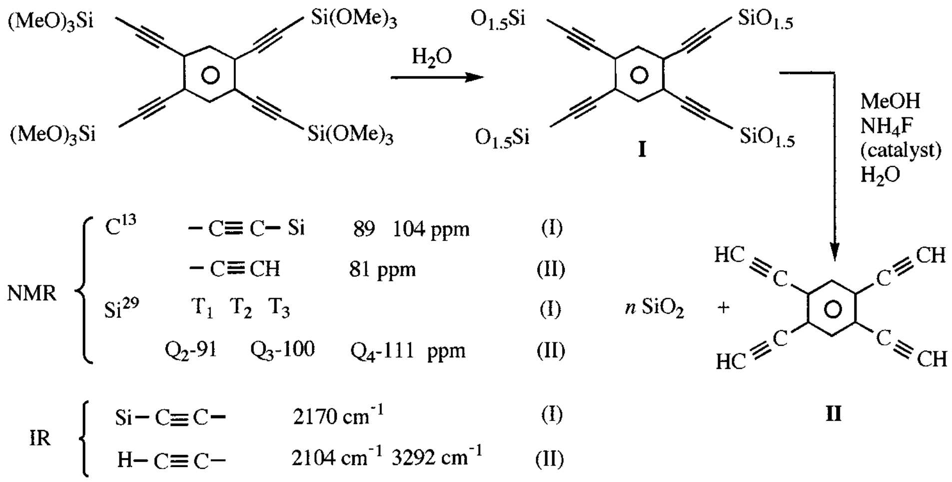
Generally speaking the physical properties of the organic part are maintained in the hybrid solid. However, these properties can be different depending on whether the location of the organic part is at the surface or in the core of the material. Moreover, possible strains induced by the rigidity of the solid can lead to some distortion of the physical properties of the organic compound. A few examples are given below.

(i) Electrochemistry

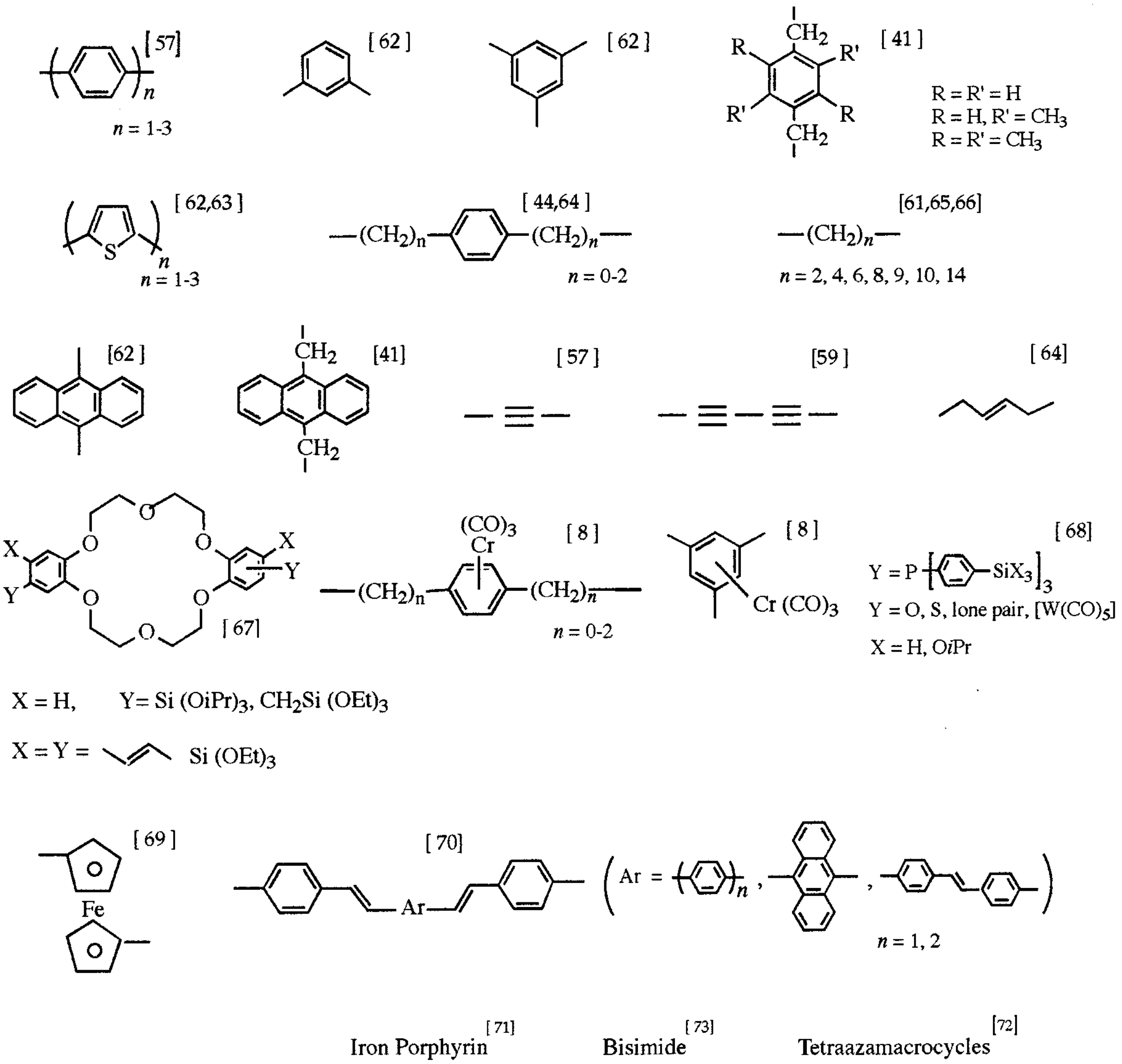
Ferrocene is a good example because of its high stability and precise electrochemical behaviour.[74] The electrochemistry observed is very different in the cases of mono- and bis-silylated ferrocene.[75]

Gels III and IV, respectively formed from trimethoxysilylferrocene and 1,1′-bis(trimethoxysilyl)ferrocene copolymerized with tetramethoxysilane and deposited onto platinum, allow modified electrodes to be built and these systems have interesting electrochemical properties (Scheme 9).[75]

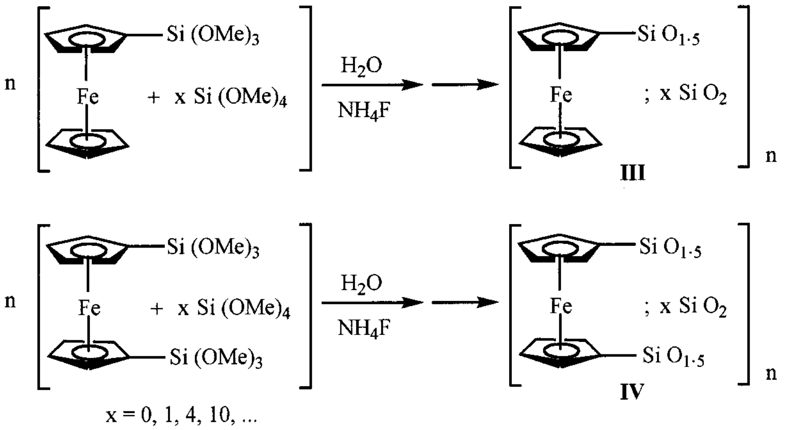
Solid IV, obtained from the bis-silylated ferrocene, displays a Cottrelian diffusion of charge transfer and exhibits



Scheme 7. Cleavage of the Si−C≡C bond catalysed by fluoride ions; spectroscopic characterisation



Scheme 8. Examples of organic units included in nanostructured materials



Scheme 9. Gels obtained from mono and bis-silylated ferrocene

classical reversible cyclic voltammograms: the peak current scales in a linear way with the square root of the scan rate (Figure 1).

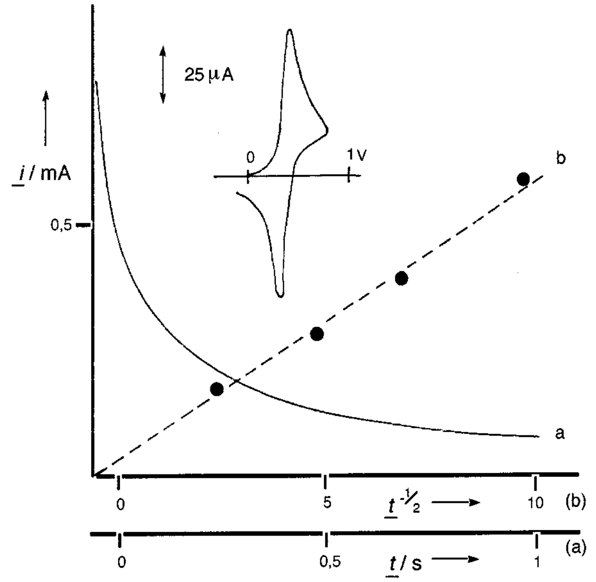


Figure 1. Typical chronoamperometric and linear Cottrell curves of a gel prepared from a bis-silylated ferrocene precursor: (a) plot of current i versus time t, (b) plot of current i versus $t^{-1/2}$

Furthermore, it proved impossible to perform complete oxidation of Fe^{II} into Fe^{III} in a macroelectrolysis carried out on a suspension of IV.[76] The process is, however, reversible (Figure 2). Such behaviour is due to the fact that some ferrocenyl units are embedded in the core of the solid and do not participate to the electrochemical process.

In the gels III (Scheme 9), derived from the mono-silylated ferrocene, the charge transfer follows a law with a fractional exponent. This unique behaviour is indicative of a particular substructure in the gels. Moreover in this case, complete and reversible oxidation of Fe^{II} into Fe^{III} is observed in macroelectrolysis, as evidenced by Mössbauer spectroscopy[76] (Figure 2).

(ii) Optical Properties

Molecular precursors containing 1−4 phenylene vinylene units have been prepared.[70] These organic units are known for their photoluminescence properties.[77]

Solid materials containing these organic fragments have been easily prepared by sol-gel from the appropriate precursors. These materials provide examples of the inclusion of chromophores into silica frameworks (Scheme 10).

The absorption and fluorescence spectra of the gels exhibit maxima at 495−496 nm, which are similar to the values observed with the corresponding precursors in the solid state. However, the high energy emission of the precursor at 466 nm is absent (Figure 3). The optical properties of the chromophores are retained in the solid and they lead to materials with potential optical and electro-optical applications. Moreover, it was observed that upon formation of the solid the position and form of the photoluminescence spectra changes. The modifications observed are different depending on the nature of the aromatic fragment Y.

II.b.4. Chemical Properties of the Hybrid Materials

The chemistry in the solid state is essentially the same as the chemistry occurring in homogeneous phases (liquid or gas). However, working with the solid does cause some very important changes, the first one being due to the highly restricted mobility of the compound in question. At room or moderate temperatures the motions of the atoms are limited to vibration and to a very low conformational flexibility. This restricted mobility is connected with a large decrease of the entropy. The second change in the chemistry involves the location of the organic part either at the surface or in the core of the solid. Thus, the accessibility of the reactive sites towards a particular reagent will be different depending on the texture (mainly specific surface area and porosity) and the structure of the solid: the structure corresponds to the relative arrangements of the organic units within the material.

A few examples are given in order to illustrate the chemical reactivity of such solids.

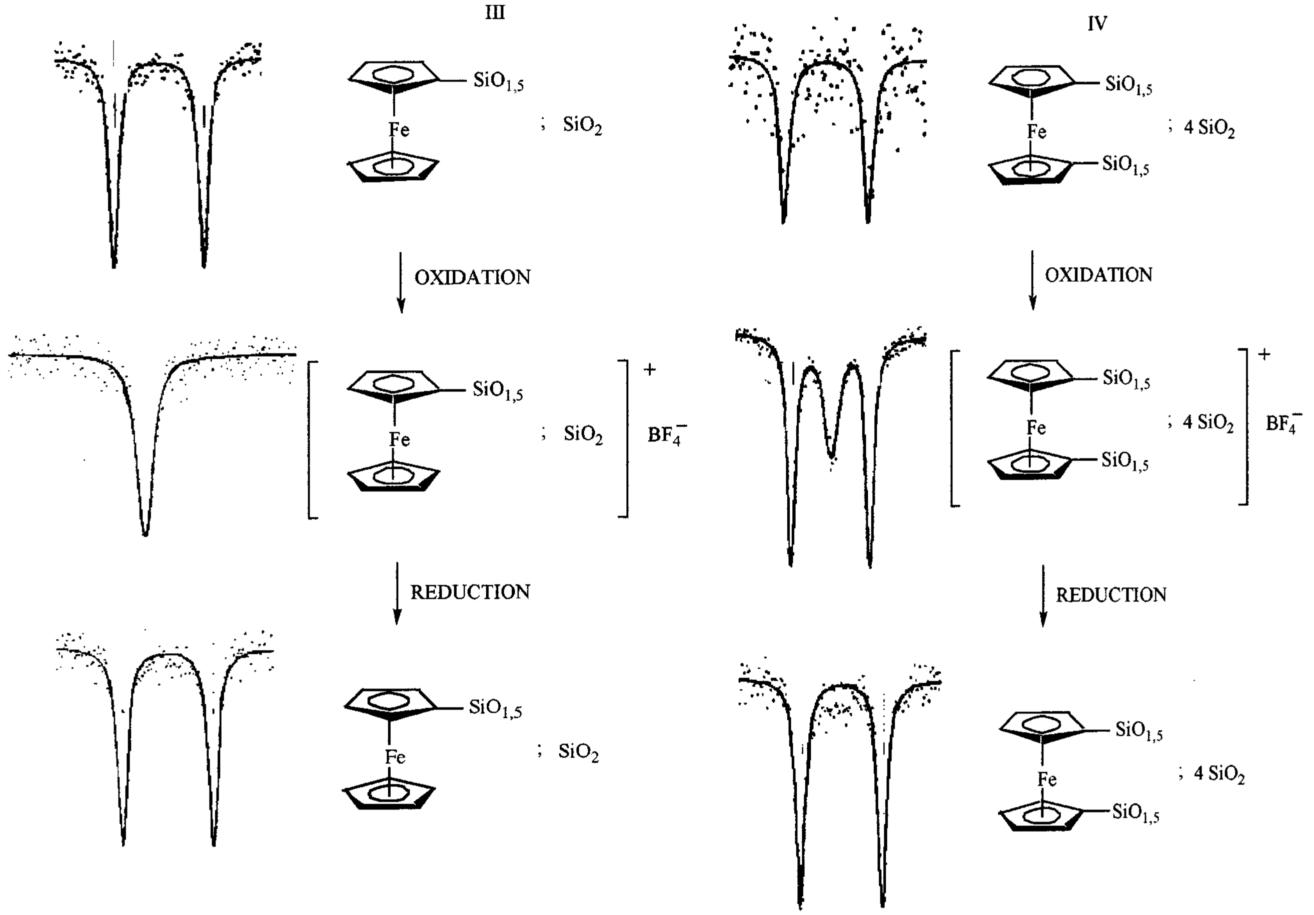
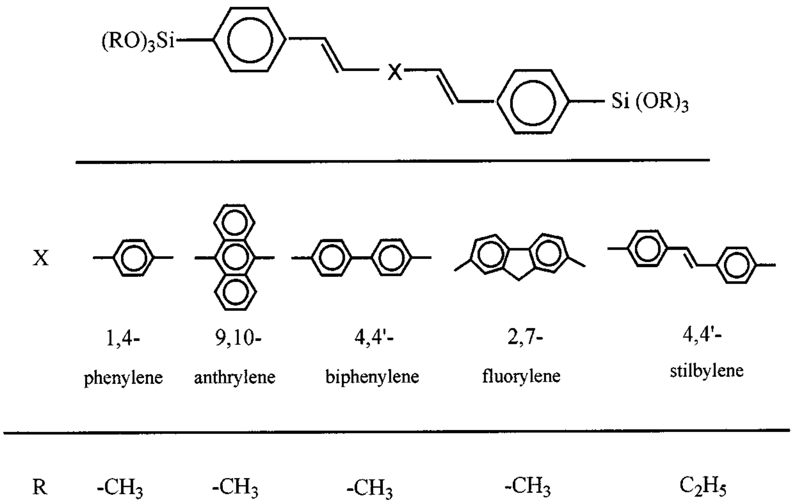


Figure 2. Mössbauer spectra of hybrid solids with ferrocenyl units



Scheme 10. Precursors with oligo-1,4-phenylene vinylene precursors

(i) Chemical Accessibility at Phosphorus and Crosslinking Ratio

The phosphorus atom is a good probe for the study of the chemical accessibility due to the fact that it has a wide range of reactivity towards both uncrowded (O_2, S_8, CH_3I etc.) and more crowded reagents (alkyl halides or transition metals). Moreover, its very high NMR sensitivity (^{31}P) permits a very reliable measurement of chemical changes at phosphorus.[78]

We have considered the reactivity on the solids V to VII, which were obtained by hydrolytic polycondensation from the corresponding $Si(OiPr)_3$ precursors. The reagents H_2O_2, S_8, CH_3I, φCH_2Br, THF/$W(CO)_5$, and BH_3 were used (Scheme 11).[79]

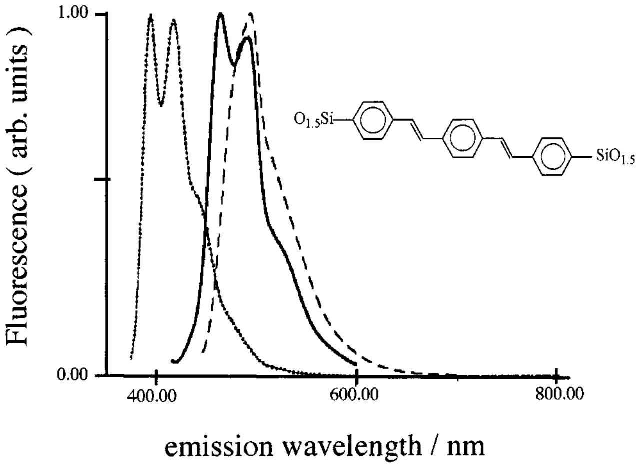
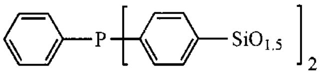
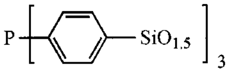


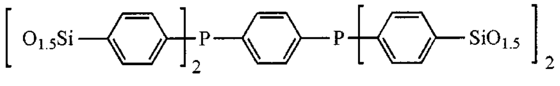
Figure 3. Photoluminescence spectra of gels with 1,4-phenylene vinylene units (precursor in THF (····) and KBr (— —) and the corresponding gel (---)



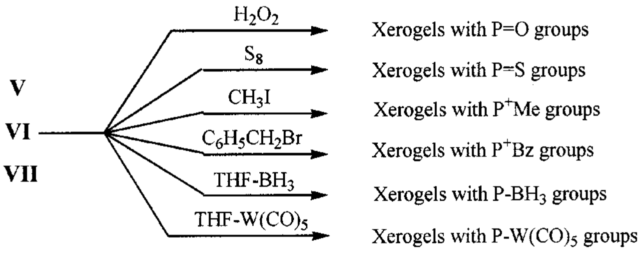
V



VI



VII



Scheme 11. Chemical accessibility of phosphorus atoms in hybrid solids incorporating phosphane units

Table 1 shows that all the phosphorus atoms are accessible to uncrowded reagents (H_2O_2, S_8, CH_3I), regardless of the specific surface area and the degree of crosslinking of the solid measured by the number of functionalities. (The degree of polycondensation at silicon has a similar magnitude for all the solids prepared.)

Table 1

Solid	S[a]	f	H_2O_2 or S_8[b]	CH_3I[b]	THF/W(CO)$_5$ [b]
V	<10	6	100	100	100
VI[c]	30	9	100	95	5
VI[d]	400	9	100	100	80
VII	460	12	100	100	20

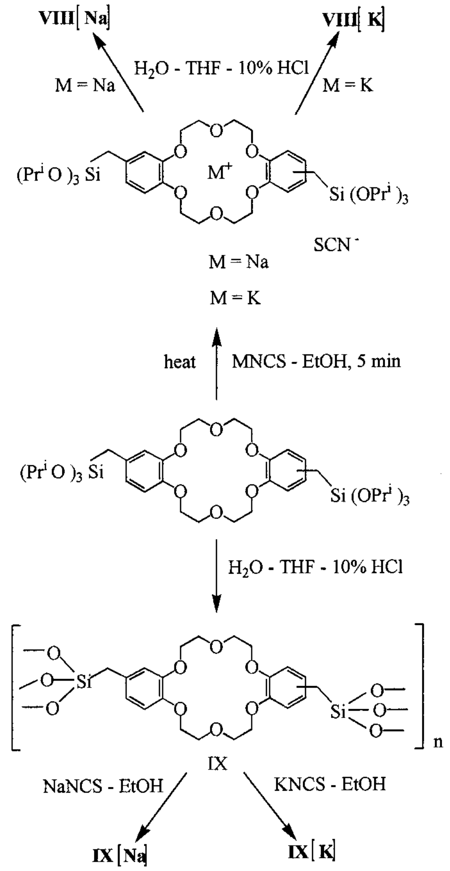
[a] Specific surface area (BET) [m^2 g^{-1}]. – [b] Reaction yield obtained from NMR spectroscopy on solids; f = number of functionalities at silicon. – [c] Solids obtained with *p*-toluene sulfonic acid (1%) as catalyst. – [d] Solids obtained with HCl (10%) as catalyst.

In contrast, the reactivity of the crowded reagent THF/W(CO)$_5$ is highly dependent on the crosslinking of the solid, which appears to be the dominant parameter. The specific surface area also plays a role, but to a lesser extent.

The steric hindrance of the reagent involves drastic requirements and the most rigid materials are not mobile enough to allow access to phosphorus. Thus, solid VII, which has twelve condensation directions, exhibits poor reactivity.[79]

(ii) Influence of the Solid on Crown-Ether Properties

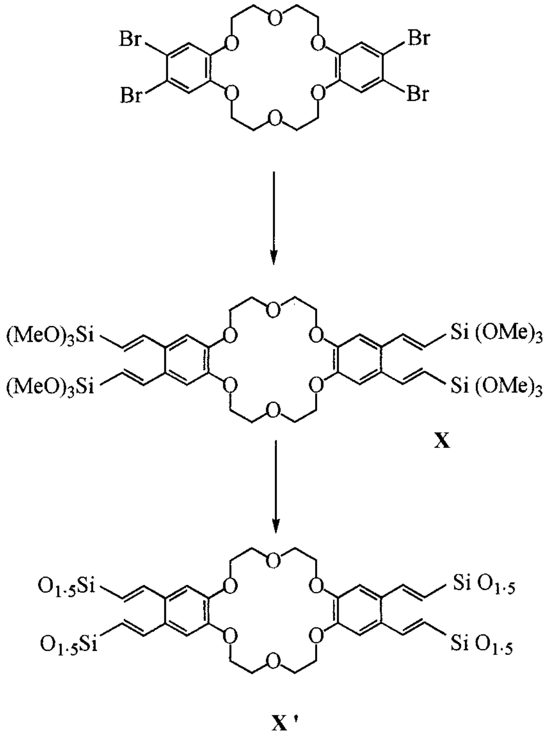
Hybrid materials incorporating crown ethers have been prepared as shown in Scheme 12.[67]



Scheme 12. Hybrid materials incorporating crown ether units from bis-silylated precursors

We prepared the gels VIII [Na] and VIII [K] by hydrolysis of the complexes of crown ethers with Na$^+$ and K$^+$. These solids were compared to the materials obtained by treatment of the solids IX with Na$^+$ and K$^+$, which gave IX [Na] and IX [K]. The degree of complexation of VIII [Na] and VIII [K] is high (95%), suggesting that the polycondensation at silicon does not induce a strong distortion of the geometry of the crown ether, a situation that could lead to the elimination of complexed salts. In contrast, IX [Na] and IX [K], obtained by direct complexation of the solids, are totally different: only 45% of the sites are complexed by Na$^+$ (IX [Na]) and 73% by K$^+$ (IX [K]). These observations suggest that during the polycondensation of the non-complexed precursor, a distortion occurs that restricts the conformational aptitude of the crown ether ring for complexation of Na^+ and K^+. In this case, the use of complexed and non-complexed crown ethers as precursors leads to different materials. In order to verify this hypothesis we prepared the precursor X, which can lead to more crosslinked solids by increasing the number of functionalities.

In this case the possibility of direct complexation of the solid X′, obtained after hydrolytic polycondensation, is very low: 12% for Na^+ and 37% for K^+ (Scheme 13) and, in addition, ≈ 40% of the crown ether units do not exhibit the appropriate geometry for complexation with Na^+ or K^+. The rigidity of the crown ether in the solid prevents the conformational mobility necessary for complexation.



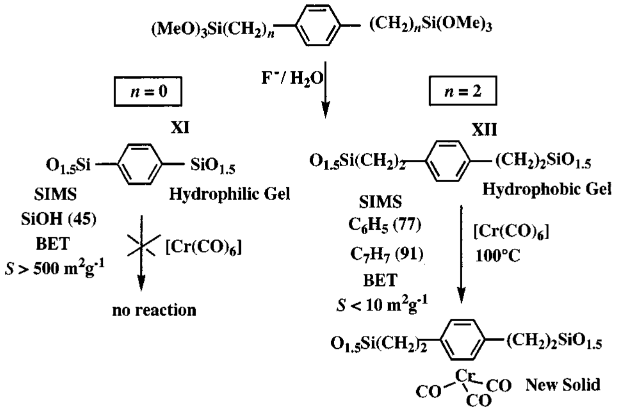
Scheme 13. Hybrid material incorporating crown ether units from tetra-silylated precursors

(iii) Chemical Reactivity Connected with Solid Organisation

A number of previous observations have shown that the molecular geometry is a very important parameter in controlling solid organisation. The example presented here illustrates the drastically different behaviours observed between the solids obtained from two similar precursors.[8,44]

Despite the fact that the two precursors are very similar, materials XI and XII, obtained using the same experimental conditions, exhibit completely different chemical and physical properties (Scheme 14).

XI is a hydrophilic solid with a high specific surface area ($550\ m^2\ g^{-1}$) for which the TOF-SIMS does not exhibit any fragment arising from C_6H_4. Indeed, only Si−OH fragments can be detected. Interestingly, XI does not react with $Cr(CO)_6$, which is consistent with the fact that the organic groups are embedded in the core of the solid.



Scheme 14. Influence of the molecular geometry of the precursor on chemical and physical properties of the solid

In contrast, XII is a hydrophobic resin that has a very low specific surface area and the TOF-SIMS mass fragments exhibit phenyl (m/z = 77) and tropylium (m/z = 91) units. Moreover, Si−OH fragments cannot be detected.[43] These results suggest strongly that the organic groups are located at the surface of the solid. This fact is evidenced by the good yield observed in the reaction with $Cr(CO)_6$ (about 80%).

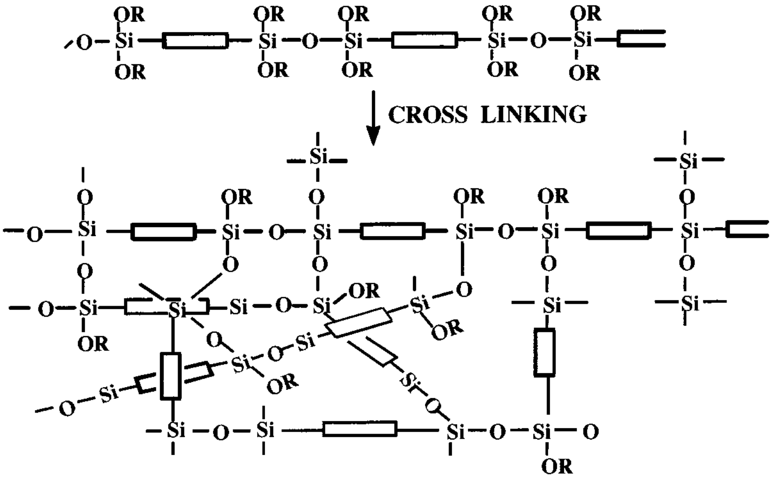
These two examples illustrate very well the significance of the organic unit in controlling the solid arrangement under identical experimental conditions. The rigid precursor leads to a solid with a completely different chemical reactivity to that of the solid obtained by polycondensation of a more flexible precursor.

III. Organisation of Hybrid Materials

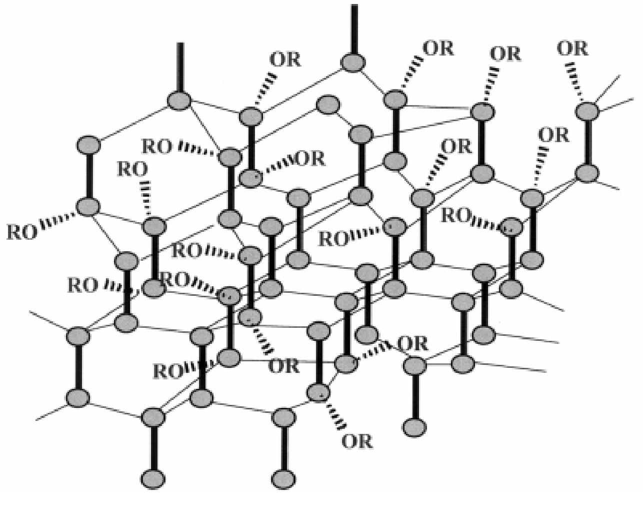
All the hybrid materials reported in the literature to date are described as amorphous materials. Their XRD patterns are generally similar to those of amorphous silica. However, it is known that the XRD patterns can only be observed in solids with a long-range organisation. Moreover, at the moment a physical method that permits the study of short-range organisation in the solids is not available, with the exception of SAXS (Small Angle XR Scattering).[77]

(i) Preliminary Reports: Local Order in the Solid

The possibility and the nature of organisation were chemically assessed chemically. In section II.b.4(iii), we discussed the results obtained with XI and XII, which suggest that the arrangements of their organic units in the solid are completely different.[9,44] The hydrophobic material XII, in which the aromatic groups are at least partly located at the surface (detection by SIMS) and are also chemically accessible with good yield, can be more or less described as a solid in which molecular chains are crosslinked. Thus, $Cr(CO)_6$ dissolved in an organic solvent is able to pass through the material and react with the aromatic groups (Schemes 15 and 16).



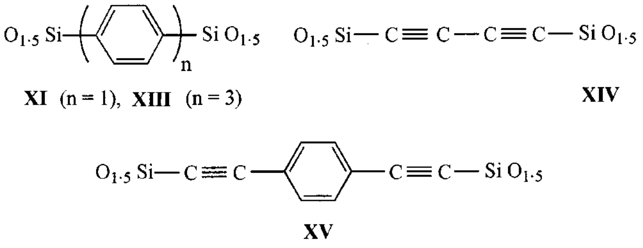
Scheme 15. Short-range organisation in the solid



Scheme 16. Short-range organisation in the solid

In the hydrophilic material, XII, the aromatic groups are not detected by TOF-SIMS and they are not chemically accessible.

Moreover, a local order in the material is evidenced by the presence of a broad XR diffraction signal in SAXS.[80] Besides XII, this kind of XR diffraction signal has been observed in the case of three hybrids (XIII, XIV, XV), which were synthesized from precursors that also have a rigid geometry[81] (Scheme 17).



XI (n = 1), **XIII** (n = 3)

XIV

XV

Scheme 17. Hybrid solids from precursors with a rigid geometry

We propose the formation of local order (Scheme 16) in which the organic units are regularly alternated. The representation proposed here allows us to explain the presence of OCH_3 and OH fragments in TOF-SIMS and the absence of aromatic units since only one Si−C bond is located at the surface. This model also explains the hydrophilicity. The lack of flexibility accounts for the very poor reactivity towards $Cr(CO)_6$ and the regularity of the arrangements is in agreement with the SAXS results, which show a diffraction peak for a distance close to the size of the organic spacer.

In the case of XIII, a diffraction signal was observed at 15 Å.[82]

These values are estimated from the q values using the Bragg law as a first approximation. They provide evidence for the existence of a short-range order in the solid. However, the distance is only indicative, since the Bragg law is valid only for narrow diffraction signals. In the case of the two other materials, we reported the scattering peaks at 8.1 Å for XIV[59] and two signals at 11.4 Å and 5.5 Å for XV.[81] In this case, it was observed that the order demonstrated by the XR diffraction signal is independent of experimental parameters like the solvent, concentration, or catalyst. Moreover, the study of the copolymerisation between the precursor XV and TMOS shows a unidimensional swelling. The q values vary in a linear manner with the volumic fraction of added silica:

$q_{1,n} = q_{1,0}\ (1 - 0.48\ \ SiO_2)$ (n = mol number of TMOS, = volumic fraction), indicating the unidimensional swelling of a short-range organised solid.[83]

All these facts are in agreement with a local order in the solid that arises during its formation.

(ii) Physical Evidence of Long Range Organisation

We have obtained some physical evidence of long-range organisation in the solid by birefringence experiments performed with the solid derived from the precursor XV.[83]

A homogeneous solution of XV in THF with an equimolecular amount of H_2O was introduced into a confined cell made of glass plates treated with oriented Teflon. In the sealed cell the isotropic solution always appeared dark regardless of the angle of the crossed polarizers. After a few minutes bright domains appeared in different places due to

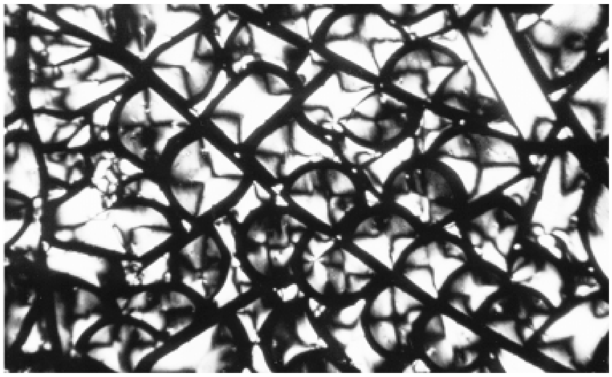
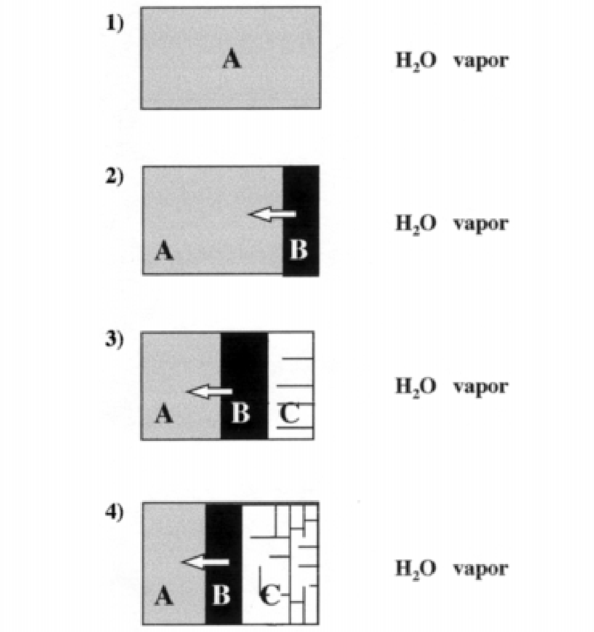


Figure 4. Physical evidence for long-range organisation by birefringence experiments



Scheme 18. Birefringence experiments: evolution of a part of a cell during the polycondensation process: A = precursor; B = liquid-to-gel isotropic medium; C = anisotropic gel and xerogel (dark lines: cracks)

birefringence. A few hours later the whole field of view the cell was birefringent and some cracks appeared (Figure 4).

Another set of experiments was performed with a controlled partial pressure of water using open cells containing the pure crystalline precursor. The results are represented in Scheme 18.

The microcrystalline precursor XV is birefringent and was converted into an isotropic liquid from which a birefringent solid formed. The birefringence subsequently increases upon ageing the gel and birefringent cracks were observed. This experimental procedure allows the history of the xerogel formation to be traced through the successive states: precursor, oligomers, polymers, sol, gel and cracks.

Thus, birefringence that corresponds to a micrometric scale organisation is observed when the polycondensation at silicon occurs to give crosslinked solids. Interestingly, the driving force for the organisation in the material during the polycondensation appears to be the rigidity of the organic unit included in the silica matrix.

IV. Conclusion

This short review has briefly covered only a few aspects of the wide possibilities opened up by the combination of Molecular Chemistry and "Chimie Douce" for the preparation of new kinds of materials.

Both approaches are based on kinetic control of the synthesis and their wedding has opened the way to materials that combine organic, inorganic and also macromolecular chemistry with inorganic polymerisation.

These new avenues are made accesible by the flexibility of "Chimie Douce", which permits the elaboration of oxides by a hydrolytic polycondensation mechanism. This low temperature polymerisation is compatible with the existence of covalent bonds between the oxide and organic, inorganic or macromolecular units. These hybrid materials combine the properties of the oxide matrix and the physical and chemical properties of the units included in the solid material. In the case of silica, the physical properties are restricted. However, this matrix has the great advantage of having a very wide chemical flexibility, good stability and excellent processability in the viscous sol state. The matrix allows the organic or organometallic partner to jump from its molecular state to the solid material. In this state the molecule becomes a part of the whole and the properties cannot be described in terms of isolated systems but as the properties of the material. For instance, the possible organisation of the organic or organometallic groups may enhance the physical properties in comparison to the isolated units. It is also possible to modify the chemical properties. A good example is the case of mesoporous materials obtained by the MCM-type route. These materials, called catalytic materials, have interesting possibilities in polyfunctional catalysis as well as for selective separation and purification.

The new horizons provided by hybrid organic-inorganic materials appear very wide and the future offers the prospect of many developments as chemists explore new routes to other oxides and to other kinds of matrices.

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