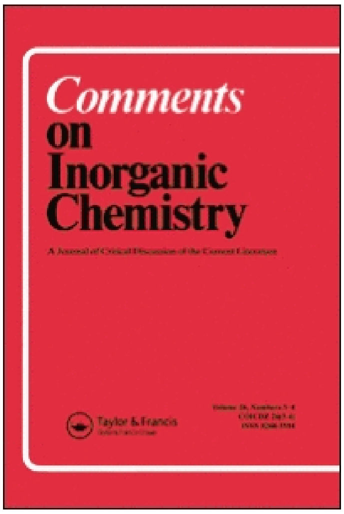


## Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

# Solution Chemistry for the Elaboration of Solids

Robert J. P. Corriu[a]; Dominique Leclercq[a]
[a] Laboratoire des Précurseurs Organométalliques de Matériaux, UMR 44, Case 007, Université Montpellier II, Montpellier, cédex, France

**To cite this Article** Corriu, Robert J. P. and Leclercq, Dominique(1997) 'Solution Chemistry for the Elaboration of Solids', Comments on Inorganic Chemistry, 19: 4, 245 — 262
**To link to this Article: DOI:** 10.1080/02603599708032739
**URL:** http://dx.doi.org/10.1080/02603599708032739

# Solution Chemistry for the Elaboration of Solids

ROBERT J. P. CORRIU and DOMINIQUE LECLERCQ
*Laboratoire des Précurseurs Organométalliques de Matériaux,*
*UMR 44, Case 007,*
*Université Montpellier II,*
*Place E. Bataillon,*
*F-34095 Montpellier cédex 5, France*

Received March 10, 1997

This paper is focused on some aspects of the sol-gel process as a solution chemistry route to the preparation of materials. This field is opening new possibilities for molecular chemistry in the synthesis of metastable solids. Three ways emphasizing these possibilities are presented here: (1) the use of precursors containing functional groups for the preparation of solids with specific chemical reactivity leading to metastable phases; (2) the non-hydrolytic sol-gel process for the synthesis of monocomponent oxides with various structures, and of homogeneous bicomponent oxides; (3) organic–inorganic hybrid solids containing covalent bonds. The chemical reactivity of these solids is used as evidence for the presence of substructures which depend on the geometry of the organic moiety.

**Key Words:** *sol-gel process, metastable phases, non-hydrolytic condensation, monophasic organic–inorganic hybrid materials*

## INTRODUCTION

The preparation of materials has been dominated by the high-temperature reaction of either monocomponent or multicomponent compounds which leads to the most thermodynamically stable products. The solid

*Comments Inorg. Chem.*
1997, Vol. 19, No. 4, pp. 245–262
Reprints available directly from the publisher

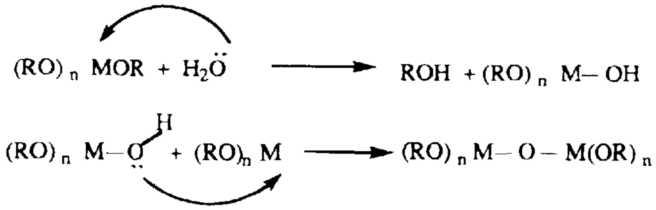
Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science
Publishers
Printed in India

state chemistry involves two steps, the interdiffusion of the reactants and the nucleation of crystalline intermediates and products. Neither interdiffusion nor nucleation are well understood in reacting systems since the reaction mixture is heterogeneous with interfacial diffusion dominating the evolution of the system.[1] The complexity of the system has prevented the development of solid-state reaction mechanisms, or of methods to kinetically control the products. In contrast to solid-state chemistry, synthetic molecular chemistry is based on the kinetic control of the reaction pathway to obtain the kinetic product. Thus, the elaboration of solid materials by molecular chemistry now appears as a wide field of investigation for inorganic chemistry. Inorganic chemists have succeeded in bounding together most of the elements, hence building up very sophisticated structures and developing powerful synthetic tools.

The preparation of silicon carbide fibers, by the Yajima process, is a very good example of elaboration of purely inorganic material from the molecular level by a multi-step procedure which shows the possibilities opened by inorganic chemistry in the field of materials elaboration.[2]

Nowadays sol-gel chemistry[3] is one of the most attractive areas of research for inorganic chemists in the field of chemistry of materials. This method of elaboration of solids is very flexible and permits one pot preparations of solids. Furthermore, it also affords a nice way to bridge organic and inorganic chemistry, by the choice of molecular precursor in which an organic moiety is bound to a metal alkoxide unit.

The sol-gel process has been well studied and developed in materials science. The general method involves the hydrolyses of metal alkoxides as starting precursors. This reaction corresponds to nucleophilic attack of $H_2O$ at the metal, giving metal hydroxide groups. In succeeding steps the metal hydroxide groups react either with alkoxide (hetero-condensation) or with hydroxide groups (homocondensation) giving rise to the M–O–M bridges (Scheme 1).



SCHEME 1

The reactions can be catalyzed by acids, bases or nucleophiles such as $F^-$. The oxide obtained is a highly crosslinked solid which is formed in a one pot procedure by an inorganic polymerization reaction.

Hydrolysis of a solution of alkoxysilane in an organic solvent such as alcohol gives products with silanol functions, which form a sol (a colloidal dispersion of particles in a liquid) by condensation polymerization (Fig. 1).[3] The continuation of the process gives a gel (continuous solid skeleton enclosing a continuous liquid phase). This transformation is designated the sol-gel transition. Gels may exhibit spontaneous shrinkage, called syneresis, on aging. The network is initially supple and allows further condensations, and bond formation induces contraction of the network and expulsion of liquid from pores. Drying of the gel by evaporation under normal conditions gives a dried gel, called a xerogel. Xerogels are interesting materials because of their porosity and high surface area, which make them useful as catalyst substrates, filters, etc. They are also useful in the preparation of dense ceramics by sintering (densification driven by interfacial energy).[3] The advantage of the molecular approach to the synthesis of materials is based on the fact that the precursors can be obtained in the form of monoliths, films, fibres, and monosized powders directly from the gel state.

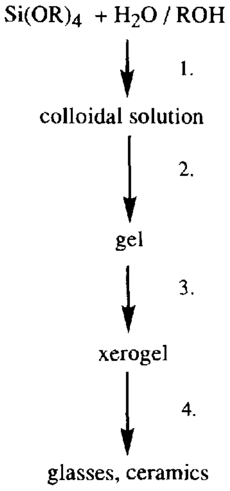


FIGURE 1 Sol-gel process: 1. Hydrolysis/condensation, 2. Sol-gel transition, 3. Drying, 4. Densification.

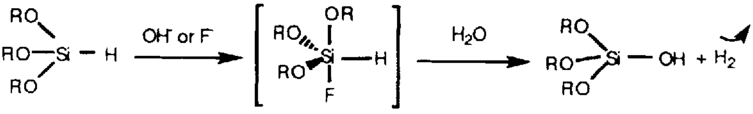
As examples, three sets of results will be presented here:

- (i) the chemistry of metastable systems obtained from precursors with functional groups;
- (ii) a new chemical way to prepare oxides which avoid hydrolytic polymerization;
- (iii) some results concerning hybrid organic–inorganic solids.

## NEW PRECURSORS LEADING TO METASTABLE PHASES

### (a) $HSi(OR)_3$

The hydrolysis of $HSi(OR)_3$ (R = Me, Et, iPr) performed under acidic conditions gives a gel of composition $HSiO_{1.5}$.[4] Under nucleophilic or basic conditions silica is formed with evolution of $H_2$ (Scheme 2),[4] it being known that nucleophilic substitution at hydridosilicates $[HSi(OR)_4]^-$ leads only to cleavage of the Si–H bond.[5]



SCHEME 2

The $HSiO_{1.5}$ gel shows spectroscopic features similar to those of the crystalline octahydrosilsesquioxane $[HSiO_{3/2}]_8$ ($\nu_{Si-H} = 2250\ cm^{-1}$, $\delta_{Si} = -85$ ppm).[6] In contrast to silica gels, these gels are not hydrophilic. This is easily explained by the absence of silanol groups in the gel and by the presence of the hydrophobic Si–H groups at the surface of the gel, instead of hydrophilic Si–OH groups in the case of silica.

The thermal treatment of these solids is interesting. Under an oxidizing atmosphere, as expected, the Si–H bonds are oxidized, leading to an increase in weight (10%) due to the formation of silica.[4,6] Under an $NH_3$ atmosphere silicon oxynitrides are formed with a high content of nitrogen (3 wt.%).[7]

Under argon atmosphere evolution of $H_2$ is detected at temperatures between 450 and 900°C. Taking into account what would be expected in solution, the formation of Si–Si bonds leading to silicon sesquioxide $Si_2O_3$ has been proposed (Scheme 3).[8] At 1600°C X-ray diffraction showed the formation of cristobalite and silicon attributed to disproportionation of $Si_2O_3$.

$$2\ O_{1.5}Si\text{–}H \longrightarrow 2\ O_{1.5}Si\cdot + H\cdot \longrightarrow O_{1.5}Si\text{–}SiO_{1.5} \longrightarrow 0.5 + 1.5\ SiO_2$$

SCHEME 3

ESR spectra between 400 and 1200°C show that the pyrolysed gel contains $O_3Si^{\cdot}$, $O_2SiSi^{\cdot}$, $OSi_2Si^{\cdot}$, $Si_3Si^{\cdot}$ radicals ($10^{17}$ unpaired electrons per g gel).[6] Furthermore, an X-ray absorption near-edge structure (XANES) spectroscopic study reveals that the product obtained by heating at 500°C contains predominantly regions with $Si^{\cdot}$ and those with $Si^{+4}$. Thus, during the thermal dehydrogenation of $HSiO_{1.5}$ between 400 and 900°C, Si–Si bond formation competes with a formal redistribution of Si–Si and Si–O bonds. The ESR signals can thus be assigned to the resulting tetrahedral $Si(Si_xO_{4-x})$ units whose formation can be accounted for by the evolution of reactive sites such as sila radicals $O_{1.5}Si\cdot$ and silylene O–$\underset{\cdot\cdot}{Si}$–O formed in the solid.[6]

(b) $Si_2Cl_6$

The synthesis of a definite compounds $Si_2O_3$ with only one tetrahedral $Si(Si_3O)$ site necessitates formation of Si–Si bonds at low temperature. A simple method has been proposed that employs hexachlorodisilane as a precursor (Scheme 4).[9]

$$Cl_3Si-SiCl_3 \xrightarrow[-95°C]{3H_2O/Et_2O} Si_2O_3 + 6\,HCl$$

SCHEME 4

Neutral or acid hydrolysis does not cleave the Si–Si bonds.[9] The hydrolysis of $Si_2Cl_6$ gives rise to an evolution of HCl, which provides acidic conditions. The reaction affords a white amorphous powder (with a specific surface area of 600 $m^2g^{-1}$) in which most of the Si–Si bonds are preserved (more than 90% of the theoretical ones). The silicon sesquioxide product has been characterized by IR spectroscopy (very weak Si–H stretching band at 2265 $cm^{-1}$, $\nu(SiO_{1.5})$ = 875 $cm^{-1}$), $^{29}Si$ MAS NMR spectroscopy ($\delta = -71$, half height width 954 Hz), and X-ray absorption spectroscopy (absorption edge at 1840.5 eV, those of silicon and silica being at 1836 eV and 1844 eV, respectively).[9] The representation of the average interatomic distances in $Si_2O_3$ in the bulk material obtained by extended X-ray absorption fine structure (EXAFS) spectroscopy is given in Fig. 2.

Thus, $Si_2O_3$, prepared in this way is a defined compound in which each silicon atom is bonded to three oxygen atoms and one silicon atom rather than a random mixture of Si-like and $SiO_2$-like tetrahedra.[9]

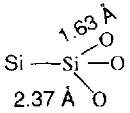


FIGURE 2 Average environment determined by EXAFS spectroscopy of the silicon atoms in $Si_2O_3$ in the bulk material.

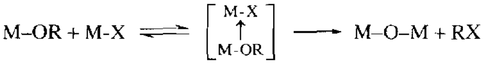
## NEW CHEMICAL ROUTE FOR SOL-GEL PROCESSING

Hydrolysis and condensation of tetraalkoxysilanes $(RO)_4Si$ readily give monolithic gels. However, metal alkoxides are much more reactive toward hydrolysis and condensation, and in general precipitates are formed.[3] Furthermore, due to the different reactivities of metal alkoxides toward hydrolysis and condensation, especially in the case of silicon and transition metal alkoxides, the control of the composition and the homogeneity of binary oxides is difficult to achieve by the sol-gel process.[10]

To counter the extreme hydrolytic reactivity of metal alkoxides, new condensation reactions have been studied. The key point in these reactions is the formation of M–O–M bridges without the hydrolysis step.

The literature data show that M–O–M may be formed starting from metal halides and different oxygen donors as such as alkoxides, ethers or alcohols. For instance, Gerrard *et al.* showed that silica is formed by heating tetrachlorosilane with tetrabenzyloxysilane or with tertiarybutanol.[11]

The mechanism of the condensation reaction involves the coordination of the oxygen of the metal alkoxide to the metal centre of the metal chloride. This complex reacts further to give MOM bridges (Scheme 5).



$$\text{M–OR} + \text{M-X} \rightleftharpoons \begin{bmatrix} \text{M-X} \\ \uparrow \\ \text{M-OR} \end{bmatrix} \longrightarrow \text{M–O–M} + \text{RX}$$

SCHEME 5

The general principle of this nonhydrolytic process is the induction of cleavage of the carbon–oxygen bond instead of the metal–oxygen one. This nonhydrolytic route has been applied to the preparation of monocomponent as well as bicomponent gels.[12]

# MONOCOMPONENT GELS

## (a) Alumina Gels

Monolithic alumina gels were prepared by heating an equimolar amount of aluminium chloride and aluminium isopropoxide in a mixture of dichloromethane and diethyl ether.[13]

This alumina gel is amorphous up to 750°C, followed by crystallization as γ-alumina at 850°C and as α-alumina at 1200°C. It retains a high specific surface area from 380 $m^2g^{-1}$ at 650°C to 100 $m^2g^{-1}$ at 1000°C. Solid state $^{27}$Al MAS NMR spectroscopy of the xerogel shows a large amount of five-coordinate aluminium sites besides the expected four- and six-coordinate ones. The five-coordinated Al sites are retained in the calcinated samples up to the crystallization of γ-$Al_2O_3$ above 750°C. These sites originate in the structure of the precursor in solution. Indeed, by redistribution reactions, the mixture of aluminium chloride and aluminium isopropoxide gives formation of trimeric aluminium chloroisopropoxides in which one aluminium atom is pentacoordinated and the other two are tetracoordinated.[14] This structure is maintained in solution even after heating for 3/4 of the gelation time.[15] The maintenance of the five-coordinate aluminium sites throughout the gelation supports the belief that the alkoxy bridges are not broken during the aprotic condensation which results from nucleophilic attack of the chloride on the carbon centre adjacent to the oxygen atom (Fig. 3). The example shows that solution chemistry allows the preparation of metastable alumina.

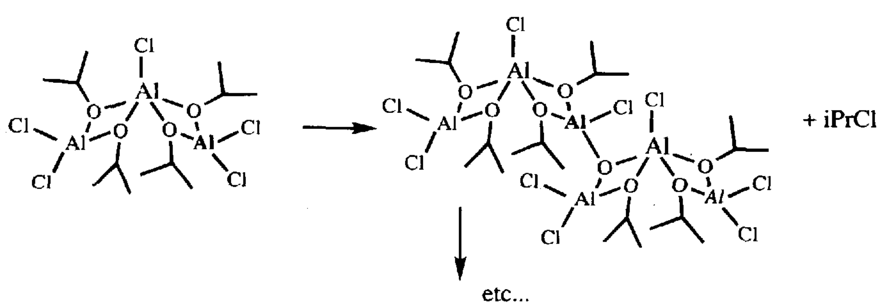


FIGURE 3 Non-hydrolytic condensation of the trimer $Al_3Cl_5(OiPr)_4$.

## (b) Titania Gels

The influence of the oxygen donor on the structure was investigated by reacting titanium chloride either with titanium isopropoxide or with a stoichiometric amount of miscellaneous oxygen donors; ethers: tetrahydrofuran (THF), di(n-propyl)ether, di(isopropyl)ether, diethylether and dimethoxyethane (DME); or alcohol: primary alcohol (ethanol, propan-1-ol, butan-1-ol, ethylene glycol), secondary alcohols (isopropyl alcohol, butan-2-ol) and tertiary alcohols (tert-butyl alcohol and tert-amyl alcohol) without solvent[19] (Scheme 6).

$$\mathrm{TiCl_4 + ROR' \longrightarrow Cl_3Ti{-}OR + R'Cl}$$
$$\mathrm{R' = R \text{ or } H}$$

SCHEME 6

Gelation occurs in all cases at much longer times than under hydrolytic conditions. The gel time depends on the oxygen donor and increases in the order: $t\mathrm{BuOH} \approx t\mathrm{AmylOH} < s\mathrm{BuOH} < i\mathrm{PrOH} \approx n\mathrm{PrOH} < \mathrm{EtOH} < \mathrm{Ti(O}i\mathrm{Pr)_4} \approx i\mathrm{Pr_2O} < \mathrm{Et_2O} < n\mathrm{BuOH} < \mathrm{HOCH_2\,CH_2OH} < \mathrm{THF} < n\mathrm{Pr_2O} < \mathrm{DME}$. The analysis of the syneresis liquid confirms the formation of alkyl chloride as the by-product, except in the case of dimethoxyethane and ethane diol. The absence of dichloro-1,2-ethane as syneresis liquid must be related to weight losses ($\Delta m/m = 47$ and 33%) during calcination. DME and ethane diol react only with the end groups, giving a hybrid organic–inorganic gel (Scheme 7).

$$\mathrm{2\,M{-}Cl + R{-}O{-}CH_2CH_2{-}O{-}R \longrightarrow M{-}O{-}CH_2CH_2{-}O{-}M + 2\,RCl}$$
$$\mathrm{R = CH_3 \text{ or } H}$$

SCHEME 7

After calcination at 500°C titania is no longer amorphous. Usually it crystallizes in the anatase structure. However, for samples prepared with an alcohol, rutile is obtained in the presence of ethanol and tertioamyl alcohol, a mixture of anatase and rutile in the case of secbutanol, and tertiobutanol gives a mixture of rutile and brookite. By heating to 1000°C (without holding time) a proportion of anatase was transformed to rutile. The transformation to rutile was complete for the samples prepared from DME, EtOH, $t$BuOH and $t$AmylOH, whereas for the sample derived from $\mathrm{Ti(O}i\mathrm{Pr)_4}$ the transformation had not yet begun.

These examples highlight the capability of molecular chemistry in the synthesis of $\mathrm{TiO_2}$ precursors with various ultrastructures which in turn induce various crystallisation behaviours. Thus it is possible to delay the anatase–rutile transformation up to ca. 950°C, or to obtain the rutile phase directely as well. Even brookite, which is very uncommon in synthetic products, may be prepared.

## BICOMPONENT GELS

### (a) General Aspect

When bicomponent oxides are prepared by high temperature solid state chemistry, only thermodynamically stable compounds are obtained. On the other hand, molecular chemistry may lead to metastable compounds when a high level of homogeneity is achieved in the precursor oxide and when diffusion is restricted at low temperature.[17]

In the synthesis of bicomponent gels by the sol-gel process, the composition and the homogeneity of gels are the two problems which have to be circumvented due to the difference in the rates of hydrolysis and condensation of the various metal alkoxides used.

The nonhydrolytic sol-gel process appears well suited to the preparation of binary oxides, due to the mechanism of its mode of condensation.[18] Furthermore, any composition is theoretically attainable by several chemical combinations, provided that the number of chloride groups (Cl) is equal to the number of alkyl groups (R) (in the alkoxides $M(OR)_n$ or in the ether $R_2O$). However, redistribution reactions between metal chlorides and metal alkoxides could give rise to heterogeneous gels, the compositions of which may be difficult to control.

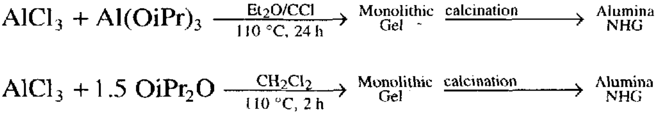
### (b) Aluminium Silicate Gels

Different compositions in the system $SiO_2/Al_2O_3$ were prepared from metal chlorides and an ether or from metal chlorides and metal alkoxides, the ratio Al/Si varying from 0.39 to 10.52. For all the compositions, monolithic gels were obtained. The overall yields in binary oxide, determined after calcination in air, are very large (from 92 to 100%). Based on X-ray diffraction patterns, the gels remained amorphous after calcination up to 700°C. Their specific surface areas determined by the BET method in the amorphous state, are large, from 230 to 700 $m^2g^{-1}$. As expected from the high yields (>90%), the compositions of the calcinated gels, determined by energy-dispersive X-ray spectroscopy analysis (EDAX), are rather close to those of the initial solution. Thus, in this process, the composition of the binary oxides is controlled by the stoichiometry of the starting solution.

The homogeneity of the binary oxides has been investigated by means of $^{29}Si$ solid-state MAS NMR spectroscopy. The $^{29}Si$ chemical shifts are quite sensitive to the number of further silicon atoms attached at the vertices of a given $SiO_4$ tetrahedron. Thus, a Ca. 5 ppm downfield shift from the silica resonance is observed for each substitution of a Si atom by an Al atom, generating the five possible local environments of silicon Si[4Si], Si[Al, 3Si], si[2A1, 2Si], Si[3Al, Si] and Si[4A1].[19]

The $^{29}Si$ NMR spectra of the various silicoaluminates prepared show a large chemical shift distribution (Fig. 4). The regular downfield shift of chemical shifts observed from the Si rich oxide (gel 1, $\delta$ centered at $-102$ ppm) to the Al rich oxide (gel 4, $\delta$ centered at $-84$ ppm) shows that Si–O–Al bonds are formed and corresponds to an increase in the number of Si–O–Al bridges as expected for a random distribution of Si and Al atoms in the oxides.

Another means of determining the homogeneity of bicomponent gels is the study of their crystallization. When a definite bicomponent oxide is known, its crystallization temperature strongly depends on the homogeneity of the starting gel. For example, in the $Al_2O_3$–$SiO_2$ system, the only definite compound is mullite with a composition 3 $Al_2O_3$, 2 $SiO_2$. The crystallisation of pre-mullite gels is known to be affected by ultrastructure, giving a clear insight into the scale of mixing between aluminium and silicon.[20] When the homogeneity is achieved at the atomic level, crystallization of tetragonal mullite occurs at 980°C. When the gel is homogeneous only at the nanometer scale, a spinnel phase crystallizes at the same temperature (980°C), mullite being obtained at 1200°C. The homogeneity of nonhydrolytic gels with stoichiometric mullite composition was investigated.[21] Two gels of this composition were studied. In the first diisopropyl ether and in the second aluminium isopropoxide were used as oxygen donor (Scheme 8).



$$AlCl_3 + Al(OiPr)_3 \xrightarrow[110\ ^\circ C,\ 24\ h]{Et_2O/CCl} \begin{array}{c}\text{Monolithic}\\ \text{Gel}\end{array} \xrightarrow{\text{calcination}} \begin{array}{c}\text{Alumina}\\ \text{NHG}\end{array}$$

$$AlCl_3 + 1.5\ OiPr_2O \xrightarrow[110\ ^\circ C,\ 2\ h]{CH_2Cl_2} \begin{array}{c}\text{Monolithic}\\ \text{Gel}\end{array} \xrightarrow{\text{calcination}} \begin{array}{c}\text{Alumina}\\ \text{NHG}\end{array}$$

SCHEME 8

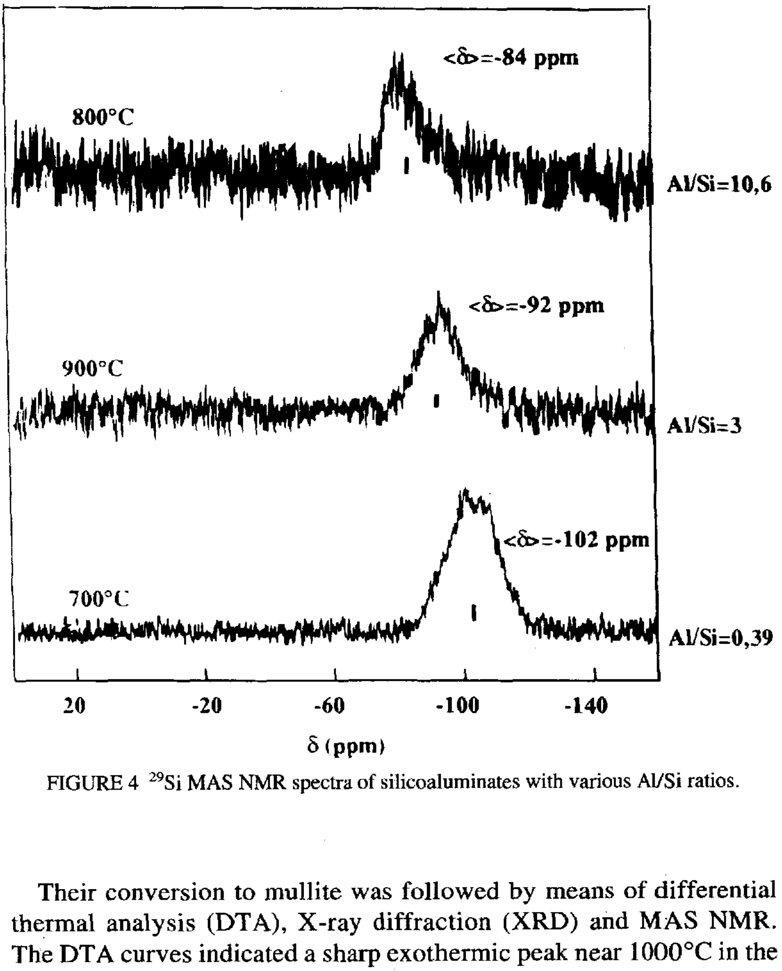


FIGURE 4 $^{29}$Si MAS NMR spectra of silicoaluminates with various Al/Si ratios.

Their conversion to mullite was followed by means of differential thermal analysis (DTA), X-ray diffraction (XRD) and MAS NMR. The DTA curves indicated a sharp exothermic peak near 1000°C in the case of the first gel corresponding to the crystallisation of tetragonal mullite, and for the second a broad peak near the same temperature due to the appearance of spinel. The $^{29}$Si MAS NMR spectra of both samples calcined at 900°C are very similar. The broad signal centered at ca. –92 ppm corresponds to that expected for a random distribution of Al and Si in the oxides. Thus the crystallization behaviour appears to be a more accurate probe for homogeneity of pre-mullite gels than is solid-state NMR spectroscopy.

### (c) Aluminium Titanate

The domain of stability of $Al_2TiO_5$ exceeds 1180°C. At lower temperatures, separation into its constituents $Al_2O_3$ and $TiO_2$ occurs. The samples prepared by classical sol-gel crystallize to aluminium titanate at temperatures over 1200°C, after crystallization of $TiO_2$ and corundum.[22] However, upon heating homogeneous gels, prepared by slow hydrolysis of aluminium and zirconium alkoxides, $\beta$-$Al_2TiO_5$ crystallizes at 800°C.[23] This metastable phase separates into titania and alumina when the temperature increases. Thus crystallization of this metastable phase at low temperature is a criterion of homogeneity of the starting gel. We have prepared aluminium titanate gels by the nonhydrolytic sol-gel process according to Scheme 9.

$$1.72\,AlCl_3 + 0.38\,Al(O^iPr)_3 + Ti(O^iPr)_4 \xrightarrow{CH_2Cl_2} Al_2TiO_5 + 5.16\,{}^iPrCl$$

$$2\,AlCl_3 + TiCl_4 + 5\,{}^iPr_2O \xrightarrow{CH_2Cl_2} Al_2TiO_5 + 10\,{}^iPrCl$$

SCHEME 9

Gelation occurs in less than 10 hours heating at 110°C. The condensation degree of the gels is rather low, around 50%. Figure 5 shows the XRD pattern of the sample annealed 5 h at 600, 850, 1000 and 1200°C. At 600°C, the sample is rather amorphous with broad peaks corresponding to the beginning of the crystallization of $\beta$-$Al_2TiO_5$. At 850°C, crystallization of the pseudo brookite $\beta$-$Al_2TiO_5$ occurs without formation of $TiO_2$ and $Al_2O_3$. At 1000°C, only lines of $\beta$-$Al_2TiO_5$ are present. At 1200°C, a small amount of rutile may be detected besides $\beta$-$Al_2TiO_5$. The direct crystallization of the metastable phase $\beta$-$Al_2TiO_5$ at temperatures below its stability domain results from the homogeneity of the starting gels which favours short range ordering instead of long range diffusion which would give the thermodynamic products rutile and $\alpha$-$Al_2O_3$.

## ORGANIC–INORGANIC HYBRID SOLIDS

### (a) Generalities

Inorganic chemistry is opening the field of organic–inorganic hybrid materials thanks to the possibility of forming metal–carbon bonds by many chemical routes. Organic–inorganic hybrid materials are a very wide field of growing interest.[24,25] They encompass inorganic oxides that

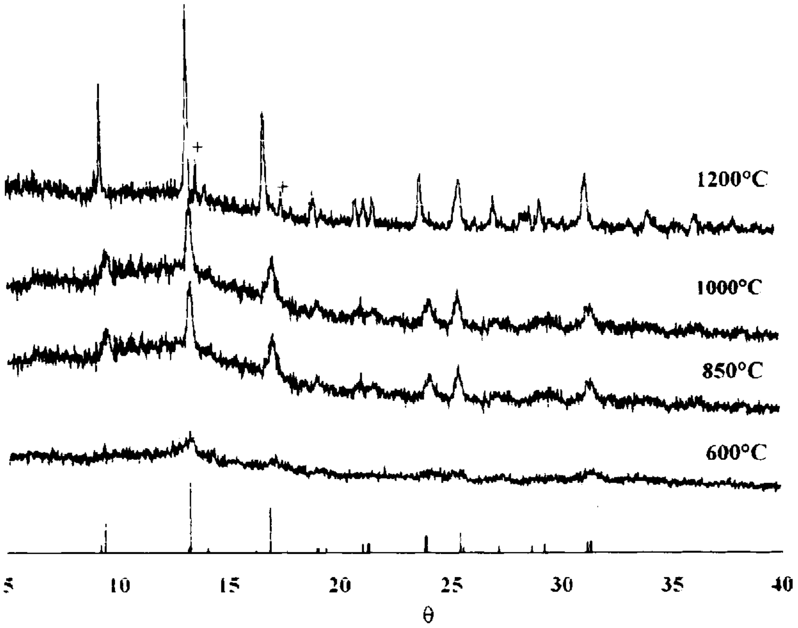


FIGURE 5 XRD pattern of aluminium titanate and of gel annealed 5 h at 600, 850, 1000, and 1200 °C (+ $TiO_2$-rutile).

function as fillers in organic polymers, and also solids consisting of polymers or organic molecules, including inorganic oxide networks.

The first topic is an important part of polymer science, and the second one is now developing very quickly because of the wide possibilities for building up new materials.

The preparation of monophasic hybrid materials in which organic molecules are covalently bound to silica is a field of interest which has begun very recently. It is opening interesting perspectives for chemists. The organic moieties can be located inside the solid or only at its surface.[26–29] When only one organic substituent in the silicon alkoxide precursor is linked by a C–Si bond, the hydrolysis of the $Si(OR)_3$ group leads to a crosslinked solid in which most of the organic groups are located at the surface.[29] The incorporation of an organic spacer inside an inorganic matrix can be achieved when at least two covalent bonds are formed between the organic molecule and the solid. The organic spacers used are given in Fig. 6.

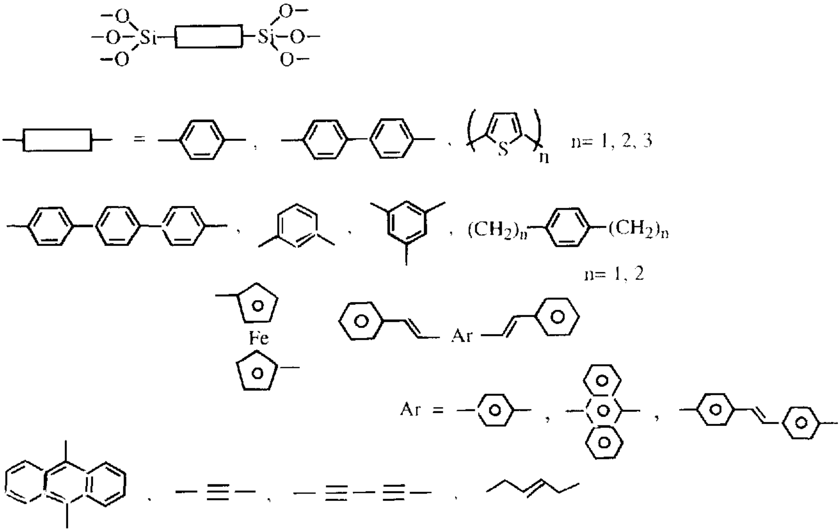


FIGURE 6 Organic spacers in polysiloxane hybrid gels.

### (b) Nano Structures of Solids

The case of ferrocene is a good example for illustrating the difference in microstructure between solids in which the organic moiety can be located either at the surface (monosilylated ferrocene) or in the core of the solid (bis-silylated ferrocene).[28] In this latter case, cyclic voltametry shows the classical reversible apparently diffusive limited pattern: the peak currents scale linearly with the square root of scan rate.[28] Furthermore, it is impossible to perform complete oxidation of the $Fe^{II}$ into $Fe^{III}$ in a macroelectrolysis performed on a suspension of the hybrid solid in ($CH_3CN/TBABF_4$). Mössbauer spectroscopy indicates the coexistence of signals corresponding to the two oxidation states of iron. In the case of monosilylated ferrocene, the macroelectrolysis performed under the same conditions exhibits complete oxidation as shown by Mössbauer spectroscopy.

These experiments show that in the case of the monosilytated ferrocene, most of the iron atoms are accessible, in agreement with a structure of the solid in which the ferrocene units are bound to the silica surface.

In the bis-silylated ferrocene, the micro-organisation does not permit the location of the ferrocene at the surface. These units are embedded inside the silica, and only some of them are accessible for electrochemical reactions.

The same kind of observation has been made in the case of complexation reactions of solids containing mono or bisilylated phenyl groups attached to a silica matrix.

In the case of monosilylated phenyl systems, the introduction of $Cr(CO)_3$ in gels is possible since most of the phenyl groups located at the surface of silica are accessible.[29] The presence of the phenyl groups at the surface also explains the high hydrophobicity of these solids.

It is also possible to prepare gels containing $Cr(CO)_3$-complexed phenylene groups from bis-silylated phenylene compounds,[26,27] when the complexation takes place prior to gelation (Fig. 7).[29] When the gelation is performed first, it is impossible to introduce the $Cr(CO)_3$ moieties to the phenylene ring. It has been concluded that most of the phenylene groups are located in the core of the solid and are thus not accessible for chemical reactions. This is consistent with the high hydrophilicity observed for gels containing p-phenylene units.[29] Interestingly, the structure of the organic moiety is important. With non-rigid systems complexation by $Cr(CO)_6$ is possible, showing an accessibility of phenyl groups due to the location of these groups at the surface of the solid, in agreement with the very low hydrophilicity observed.

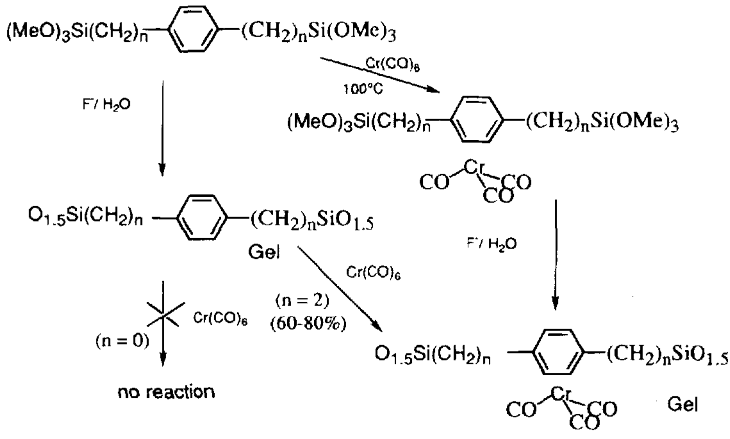


FIGURE 7 Reactions of gels containing bis-silylated phenylene groups.

### (c) Solids Containing Charge Transfer Complexes

The importance of the interactions between the organic units on the microstructure of the solid obtained during the gelation process is illustrated by the inclusion of charge transfer complexes in gels (Fig. 8).[30]

These kinds of complexes formed between bis-silylated terthiophenes and TCNQ can be included in silica. They remain unchanged after gelation as shown by absorption spectroscopy ($\lambda = 855$, 752 and 684 nm) and by conductivity measurements ($x = 10^{-6}$ $\mathrm{Scm^{-1}}$). Although these interactions are very weak, they are strong enough to control the structure in the amorphous solid as indicated by the conductivity observed.

The solid (IV′) obtained by the direct co-hydrolysis of (I) and four equivalents of $Si(OMe)_4$ is different from the solid (IV) obtained by the charge transfer complex route after washing. The two solids exhibit the same $^{13}C$ NMR spectrum and very similar $^{29}Si$ NMR spectra. However, the macroscopic data are different. For instance, the specific surface area observed for (IV′) is high (566 $m^2$ $g^{-1}$), whereas a poor one is obtained

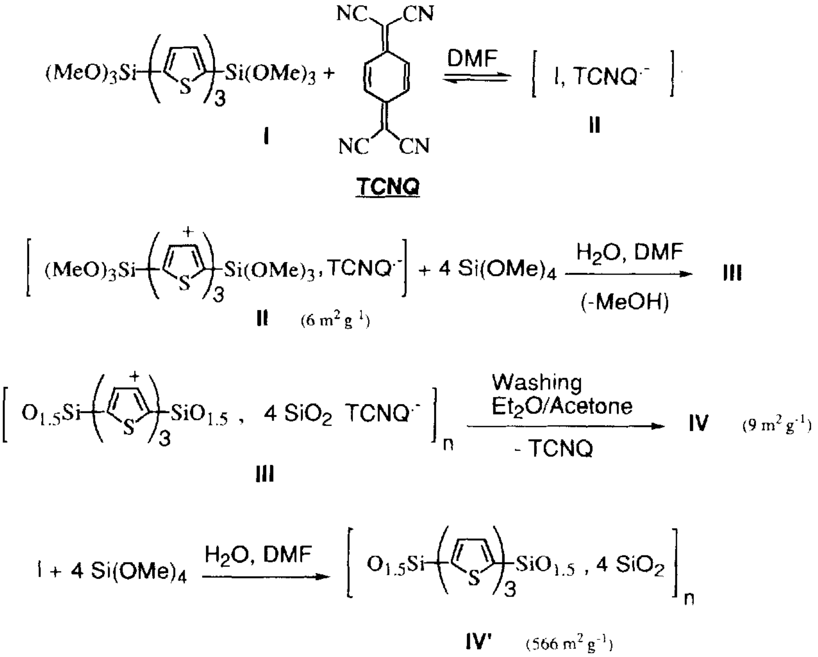


FIGURE 8 Charge transfer complex from terthiophene and TCNQ in a polysiloxane gel.

for IV (9 $m^2$ $g^{-1}$). The charge transfer interactions between (I) and TCNQ modify completely the kinetic parameters which control the formation of the hybrid solid during the hydrolytic polycondensation.

In conclusion, this short presentation is only an illustration of the wide possibilities opened by inorganic chemistry in the field of solids elaboration, since only a few aspects have been indicated. Many other possibilities are of great interest: chemical vapour deposition from organometallics (OMCVD),[31] the synthesis of materials with a controlled porosity,[32] inorganic membranes,[33] etc., which were not covered in this paper.

## References

1. (a) T. Noret, D. C. Johnson, *J. Am. Chem. Soc.* **113**, 3398 (1991). (b) L. Fister, D. C. Johnson, *J. Am. Chem. Soc.* **114**, 4639 (1992) (c) L. Fister, D.C. Johnson, R. Brown, *J. Am. Chem. Soc.* 629 (1994).
2. (a) S. Yajima, J. Hayashi, M. Omori, *Chem. Lett.* 931 (1975). (b) S. Yajima, K. Okamura, J. Hayashi, *ibid.*, 1209 (1975). (c) M. Birot, J. P. Pillot, J. Dunogues, *Chem. Rev.* **95**, 1443–1477 (1995). (d) R. M. Laine, F. Babonneau, *Chem. Mater.* **5**, 260 (1993). (e) M. Verbeek, G. Winter, *German Patent* 2236078 (1974), *Chem. Abstr.* **81**, 50911 (1974).
3. (a) S. Sakka, K. Kamiya, *J. Non-Cryst. Solids* **42**, 403 (1980). (b) C. J. Brinker, G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego (1990). (c) L. C. Klein, *Ann. Rev. Sci.*, 227 (1985); *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Specialty Shapes*, Noyes Publications, Park Ridge, NJ (1988). (d) L. L. Hench, J. K. West, *Chem. Rev.* **90**, 33 (1990). (e) C. D. Chandler, C. Roger, M. J. Hampden-Smith, *Chem. Rev.* **93**, 1205 (1993). (f) R. K. Iler, *Chemistry of Silica*, J. Wiley & Sons, New York (1979). (g) J. Livage, M. Henry, C. Sanchez, *Prog. Solid State Chem.* **18**, 259 (1988). (h) R. Corriu, D. Leclercq, *Angew. Chem. Int. Ed. Engl.* **35**, 1420–1436 (1996).
4. M. Pauthe, J. Phalippou, R. J. P. Corriu, D. Leclercq, A. Vioux, *J. Non-Cryst. Solids* **113**, 21 (1989).
5. (a) R. Corriu, C. Guerin, B. Henner, Q. Wang, *Inorg. Chim. Acta* **705**, 198–200 (1992).
6. V. Belot, R. Corriu, D. Leclercq, P. Lefèvre, P. H. Mutin, A. Vioux, A. M. Flanck, in *Chemical Processing of Advanced Materials*, (Eds.: L. L. Hench and J. K. West), J. Wiley & Sons, p. 143 (1992). (b) V. Belot, R. Corriu, A. M. Flanck, D. Leclercq, P. Lefèvre, P.H. Mutin, A. Vioux, in *Eurogel'91*, (Edt: S. Vilminot, R. Nass & H. Schmidt), Elsevier Science Publishers B. V., p. 77 (1992). (c) V. Belot, R. Corriu, D. Leclercq, P. H. Mutin, A. Vioux, *Chem. Mater.* **3**, 127 (1991).
7. M. Pauthe, J. Phalippou, R. J. P. Corriu, D. Leclercq, A. Vioux, *J. Non-Cryst. Solids* **125**, 187 and 195 (1990).
8. G.H. Wagner, A.N. Pines, *Ind. Eng. Chem.* **44**, 321 (1952).
9. V. Belot, R. Corriu, D. Leclercq, P. Lefèvre, P. H. Mutin, A. Vioux, A. M. Flanck, *J. Non-Cryst. Solids* **127**, 207 (1991).
10. K. Kamiya, S. Sakka, Y. Tatemichi, *J. Mater. Sci.* **15**, 1765 (1980).
11. W. Gerrard, J. V. Jones, *J. Chem. Soc.*, 1690 (1952).
12. R. J. P. Corriu, D. Leclercq, P. Lefèvre, P. H. Mutin, A. Vioux, *J. Non-Cryst. Solids* **146**, 301 (1992); *J. Mater. Chem.* **2**, 673 (1992); *Chem. Mater.* **4**, 961 (1992).

13. S. Acosta, R. J. P. Corriu, D. Leclercq, P. Lefèvre, P. H. Mutin, A. Vioux, *J. Non-Cryst. Solids* **170**, 234 (1994).
14. A. I. Yanovskii, V. A. Kozunov, N. Ya. Turova, N.G. Furmanova, Yu. T. Stuchkov, *Dokl. Chem.* **244**, 119 (1979).
15. S. Acosta, R. J. P. Corriu, D. Leclercq, P. H. Mutin, A. Vioux, *J. Sol-Gel Sci. Tech.* **2**, 25 (1994).
16. P. Arnal, R. J. P. Corriu, D. Leclercq, P. H. Mutin, A. Vioux, *Mat. Res. Soc. Symp. Proc.* **346**, 339 (1994); *J. Mater. Chem.* **6**, 1925 (1996).
17. P. Barboux, P. Griesmar, F. Ribot, L. Mazerolles, *J. Solid State Chem.* **117**, 343 (1995).
18. (a) S. Acosta, P. Arnal, R. J. P. Corriu, D. Leclercq, P. H. Mutin, A. Vioux, *Mat. Res. Soc. Symp. Proc.* **346**, 43 (1994). (b) M. Andrianainarivelo, R. J. P. Corriu, D. Leclercq, P. H. Mutin, A. Vioux, *J. Mater. Chem.* **6**, 1665 (1996).
19. C. Engelhart, D. Michel, in *High-Resolution Solid-State NMR of Silicates and Zeolites*, J. Wiley & Sons, New York, pp. 147–149 (1987).
20. B. E. Yoldas, *J. Mater. Sci.* **27**, 6667 (1992); and ref. therein.
21. S. Acosta, R. J. P. Corriu, D. Leclercq, P. H. Mutin, A. Vioux, *Mat. Res. Soc. Symp. Proc.* **346**, 345 (1994).
22. T. Woignier, P. Lespade, J. Phalippou, R. Rogier, *J. Non-Cryst. Solids* **100**, 325 (1988).
23. L. Bonhomme-Coury, N. Lequeux, S. Mussotte, P. Bloch, *J. Sol-Gel Sci. Tec.* **2**, 371 (1994).
24. For a general survey see *Hybrid Organic-inorganic Composites*, Ed. *ACS Symp.*, ser.n°585, American Chemical Society, San Diego, DC (1994); *New J. Chem.* **18**, 989–1117 (1994).
25. (a) P. Judenstein, C. Sanchez, *J. Mater. Chem.* **6**, 511–525 (1996). (b) H. K. Schmidt, *Mater. Res. Soc. Symp. Proc.* **32**, 327 (1984). (c) H. K. Schmidt, *Inorganic and Organometallic Polymers, ACS Symp.*, ser.n°360, American Chemical Society, Washington, p 333, DC (1988). (d) H. K. Schmidt, *Mater. Res. Soc. Symp. Proc.* **180**, 961 (1990); and references therein. (e) J. D. Mackenzie, *J. Sol-Gel Sci. Tech.* **2**, 81 (1994); and references therein. (f) U. Schubert, N. Hüsing, A. Lorenz, *Chem. Mater.* **7**, 2010 (1995).
26. (a) D. A. Loy, K. J. Shea, *Chem. Rev.* **95**, 1431 (1995). (b) K. J. Shea, D. A. Loy, O. W. Webster, *Chem. Mater.* **1**, 574 (1989). (c) K.J. Shea, D.A. Loy, O.W. Webster, *J. Am. Chem. Soc.* **114**, 6700 (1992), and references therein. (d) K. M. Choi, K. J. Shea, *ibid.* **116**, 9052 (1994). (e) K. M. Choi, K. J. Shea, *J. Phys. Chem.* **98**, 3207 (1994). (f) K. M. Choi, J. C. Hemminger, K. J. Shea, *ibid.* **99**, 4720 (1995). (g) H. W. Oviatt, K. J. Shea, S. Kalluri, Y. Shi, W. H. Steier, L. R. Dalton, *Chem. Mat.* **7**, 493 (1995).
27. R. J. P. Corriu, J. J. E. Moreau, P. Thepot, M. Wong Chi Man, *Chem. Mater.* **4**, 1217–1224 (1992); *J. Sol-Gel Sci. Tech.* **2**, 87 (1994).
28. (a) P. Audebert, P. Calas, G. Cerveau, R. J. P. Corriu, N. Costa, *J. Electroanal. Chem.* **372**, 275 (1994). (b) G. Cerveau, R. J. P. Corriu, N. Costa; *J. Non-Cryst. Solids* **163**, 226 (1993). (c) P. Audebert, G. Cerveau, R.J.P. Corriu, N. Coste, *J. Electroanal. Chem.* **413**, 89 (1996).
29. G. Cerveau, R. J. P. Corriu, C. Lepeytre, *J. Mater. Chem.* **5**, 793 (1995).
30. R. J. P. Corriu, J. J. E. Moreau, P. Thépot, M. Wong Chi Man, C. Chorro, J. P. Lère-Porte, J. L. Sauvajol, *Chem. Mater.* **6**, 640 (1994).
31. G.B. Stringfellow, *Organometallic Vapour Phase Epitaxy: Theory and Practice*, Academic Press, New York (1989).
32. See for instance Chemistry of Materials (Special Issue) *Nanostructurated Materials*, vol. **8**, 1571–2193 (1996).
33. A. W. Baker, E. L. Cussler, W. Eykamp, W. J. Koros, R. L. Riley and H. Strathmann, *Membrane Separation Systems. Recent Developments and Future Directions*, Noges Data Corporation, New Jersey (1991).