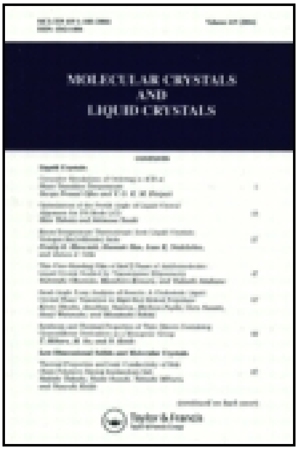

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Design of Hybrid Organic-Inorganic Nanocomposites Synthesized Via Sol-Gel Chemistry

C. Sanchez [a] , F. Ribot [a] , L. Rozes [a] & B. Alonso [a]
[a] Chimie de la Matière Condensée, UMR CNRS 7574, Université Pierre et Marie Curie, 4, place Jussieu, 75252, Paris, France

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Design of Hybrid Organic-Inorganic Nanocomposites Synthesized Via Sol-Gel Chemistry

C. SANCHEZ*, F. RIBOT, L. ROZES and B. ALONSO

Chimie de la Matière Condensée, UMR CNRS 7574, Université Pierre et Marie Curie. 4, place Jussieu, 75252 Paris, France

Among other soft chemistry processes, sol-gel chemistry offers a versatile access to chemically designed new hybrid organic-inorganic materials. Two approaches to synthesize hybrids are presented: the hydrolysis of organo functional metal alkoxides or the assembly of nanobuilding blocks.

Keywords: Hybrid Organic-inorganic; Sol-Gel; Nanobuilding Blocks; Optic

INTRODUCTION

The possibility to combine properties of organic and inorganic components in an unique material is an old challenge starting with the beginning of the industrial era. Some of the oldest and most famous organic-inorganic representatives are certainly coming from the paint industries, where inorganic pigments (i.e. TiO_2) are suspended in organic mixtures (solvents, surfactants...). While the concept of "hybrid" materials was not evoked at that time, the wide increase of work on organic-inorganic structures was pursued with the development of the polymer industry. The concept of "hybrid organic-inorganic" materials exploded only very recently, when the research shifted to more sophisticated materials with an higher added value[1-5]. The mild characteristics offered by the sol-gel process[1,2], allowing the combination of inorganic and organic components at the nanometric scale in virtually any ratio, have strongly contributed to the development of the so-called hybrid organic-inorganic nanocomposites in the last ten years[3-5]. These hybrids are extremely versatile in their composition, processing and optical and mechanical properties[5]. Many interesting new materials have been prepared with mechanical properties tunable between those of glasses and those of polymers, with improved optical properties (efficiency, stability, new sensors...), or with improved catalytic or membrane based properties[4]. Some examples of organic components that have been incorporated in sol-gel derived hybrid matrices are shown in figure 1.

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* email: clems@ccr.jussieu.fr

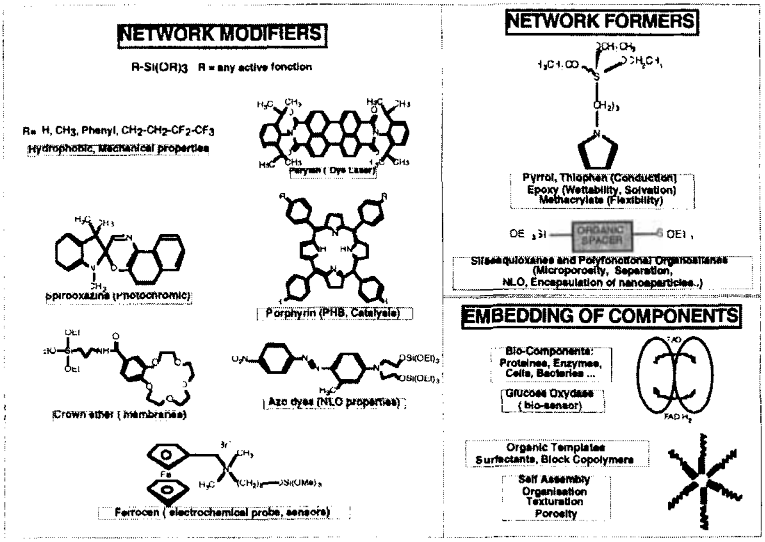

FIGURE 1. Some examples of organic molecules, bio-molecules or functions that can be embedded or grafted in hybrid sol-gel derived materials.

The chemical strategy followed for making hybrid networks ofcourse depends on the relative hydrolytic stability of the chemical links that associate the metallic centers and the organic functions.

Siloxane based hybrids[4,5] can be easily synthesized because Si-C_{sp3} bonds are rather covalent and are, therefore, not broken upon hydrolysis. This is no longer valid with transition metals (Ti, Zr, ...) for which the more ionic M-C bond is easily cleaved by water. Complexing organic ligands have then to be used. Such groups can be functionalized for any kind of organic reactions, such as organic polymerization, and lead to hybrid organic-inorganic copolymers[6-8]. For tin, the situation is somehow intermediate between silicon and transition metals. Like the latter, tin can be organically functionalized through complexation. However, as for silicon, the Sn-C_{sp3} bond is stable, especially towards nucleophilic agents such as water and consequently a chemistry similar to the one of alkoxysilanes can be developed from tin organo-alkoxides. This article reviews some of the work performed in our group on the design, synthesis and properties of hybrid organic-inorganic nanocomposites.

SILOXANE BASED HYBRIDS

Hybrid Elastomers

It is a practical goal in the area of polymers to provide an easy adjustment of the mechanical properties. For elastomers, an internal mechanical reinforcement is usually obtained by incorporating interactive inorganic fillers. Conventional filler blending, occurring under high viscosity conditions, usually leads to particle agglomeration that diminishes polymer-filler interactions. For many years metallo-organic precursors such as metal alkoxides have been used to produce via hydrolysis-condensation reactions, oxo-metallic species that act as cross linking reagents for many polymers and polydimethylsiloxane (PDMS) in particular[9,10]. Hydrolysis-condensation of diethoxydimethylsilane (DEDMS) and various metallic alkoxides, $M(OR)_n$ with M = Si, Ti, Zr, Al ,V, ... yields hybrid polydimethylsiloxane-metal oxide materials[11,12]. Depending on the nature of the metal alkoxide (compatibility of coordinence between Si and M, covalency of the Si-O-M bond), M/Si ratio, proton concentration, sequence of mixing, aging time, hydrolysis ratio a whole range of nanostructures can be obtained[4h]. The hybrid matrices obtained from DEDMS and $VO(OR)_3$ (DV) and from DEDMS and $Zr(OPr^n)_4$ (DZr) can be described as follow on the basis of multinuclear NMR studies (^{17}O, ^{29}Si, ^{51}V, ^{13}C...) and SAXS experiments[13,14].

i) for DV, copolymers of D species ($-O-Si(CH_3)_2-O-$, i.e polydimethylsiloxane (PDMS)) and tetrahedral vanadate species ($O=VO_3$) dispersed at the molecular level and acting as cross linking agents (figure 2 right),

ii) for DZr, nano-composites made of zirconium oxo-species linked to PDMS chains through a composite interface made of Zr-O-Si bonds and hydrogen bonds resulting from residual metal hydroxy groups (figure 2 left).

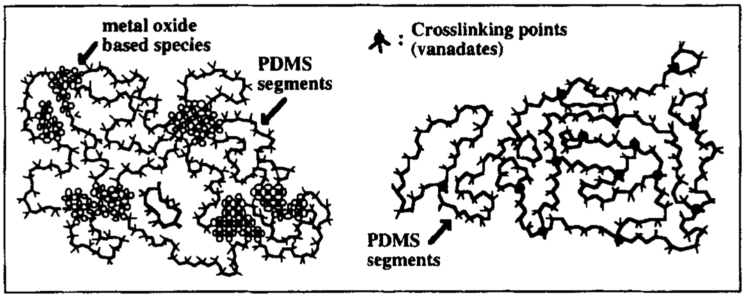

FIGURE 2. Schematic representation of DV (right) and DZr (left) hybrid matrices.

It is obvious that properties of these materials are not only the sum of the individual contributions of both phases, but also that the role of the inner interfaces could be predominant. The important role of microstructure and of the interface can be illustrated through the difference observed in the mechanical properties of DV and DZr hybrids elastomers. DSC and Dynamical Mechanical Analysis (DMA) measurements were performed on DZr and DV hybrid xerogels from 77K up to room temperature[13,14]. The glass transition temperatures measured by DSC are of about -93°C and -115°C for DV and DZr, respectively, while the corresponding variations of heat capacity are 0.41 $J°C^{-1}g^{-1}$ and 0.28 $J°C^{-1}g^{-1}$. The highest reported value of heat capacity change, ΔCp, per gram of pure PDMS[10] is of 0.42 $J°C^{-1}g^{-1}$, a value very close to the one measured for DV hybrids but different from the value reported for DZr. The decrease observed in the ΔCp of DZr hybrids can be probaly associated with the sequestering of some PDMS fragments.

The DMA spectrum of the DV hybrid (Figure 3) exhibits a unique sharp intense glass transition at about -93°C (half height linewidth of about 10°C, loss factor $\tan\delta = 6.8$) while for DZr the DMA spectrum exhibits a composite broader transition with two extrema located at -110°C and -86°C. After these transitions, the modulus for both hybrids reach a second plateau which expands over 150°C. The storage modulus measured at the rubbery plateau is of about 5 MPa for DV hybrids and range between 10 and 100 MPa for DZr hybrids. These values show that DZr are stiffer elastomers than DV hybrids. It seems also from these results that a dispersion of the trifunctionnal crosslinking points at the atomic level, as it is observed in DV hybrids, shift the glass transition to lower temperature without decreasing the value of ΔCp. In the DV systems, crosslinking, while introducing some constraints, fails to reduce the overall mobility of the system by an appreciable degree, and all the segments participate to the glass transition. The increase in the Tg of the DV hybrids, because of crosslinking, was assigned to a copolymer effect[13].

The crosslinking of the main siloxane polymers system modifies it into a copolymer made of difunctional units (the polymer) and isolated multifunctional units (the crosslinking agent), thus changing its inherent Tg. However because the crosslink structure of the tetrahedral vanadium oxo species appears to be quite compatible with the structure of the main dimethylsiloxane chains, the crosslinking vanadates units appear as mobile as dimethylsiloxane oligomers, and the whole hybrid polymeric network contributes to the glass transition. Thus, despite the high surface/volume ratio provided by the crosslinking at the molecular level occuring in DV hybrids, such a crosslinking appears less efficient for improving the stiffness of the elastomers than the one developed in DZr hybrids.

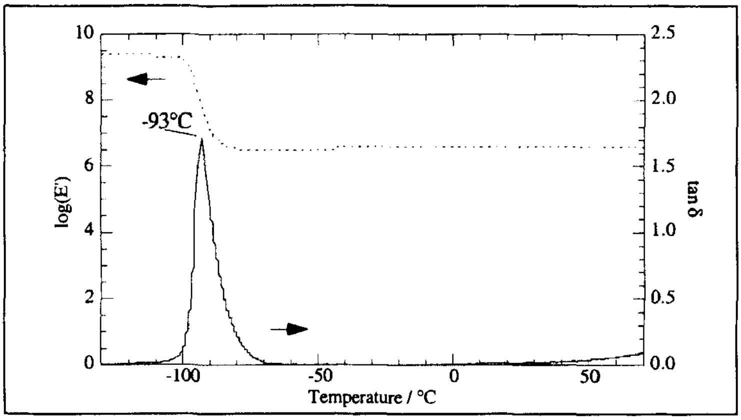

FIGURE 3. Dynamic Mechanical properties of DV hybrids (evolution of the modulus and tanδ versus temperature).

The broad and composite DMA spectrum observed for DZr hybrids result from phase segregation of a continuum of species ranging from PDMS rich phases (low transitions temperatures -110°C) with a composite crosslinking interface and better dispersed PDMS oligomers (high transition temperatures -86°C) stuck in the midst of nanometric zirconium-oxo regions resulting from the hydrolysis and condensation of $Zr(OR)_4$. The presence of crosslinking nanodomains presenting some polydispersity, together with a composite interface associating covalent and hydrogen bonds, probably induced a better sequestering of PDMS moities favorable to the improvement of the storage modulus of these hybrid elastomers.

Hybrid materials for optics

Optical properties of hybrids have been extensively investigated[4n,5]. In our group we have more specifically focused our research on the following areas of the so called "sol-gel optics" field[4n, 5d-g].

- Hydrid siloxane-oxide matrices doped with luminescent[11] or photochromic dyes[15].
- Transition metal oxide based gels doped with luminescent chromophores[16].

- Rare earth (Nd^{3+} ions and many others) doped luminescent hybrid matrices[17,18]. Recently, Eu(II) and Ce(III) oxydation states have been produced in situ within hybrid matrices by Cordoncillo *et al.*[19].
- Hybrid organic-inorganic nanocomposites synthesized trough hydrolysis and co-condensation between 4-(amino-N,N-diethoxydiurethano-propyltriethoxysilane)-2-methyl-4'-nitro-azobenzene and tetramethoxysilane. These systems exhibit the highest reported non resonant SHG response (d_{33}=150-200 pm/V) and a good stability at 80°C[20-23].

Among these different research activities which have been recently reviewed[4n], photochromic properties can be taken as an example to emphasize how a good tuning between the nature of the hybrid matrix and the dye can optimize the optical response[15]. Spiropyrans and spirooxazines are two of the fascinating families of molecules exhibiting photochromic properties. Upon irradiation, the colorless spiropyran or spirooxazine undergo an heterolytic C-O ring cleavage, producing colored forms of merocyanines. These latter species may interact with their environment (i.e. solvent, matrix) leading to different photochromic responses. Levy and Avnir[24] have first demonstrated the important role played by the dye-matrix interactions on the photochromic response of spiropyrans. This response can be strongly modified by the presence of polar groups (i.e. Si-OH), complexation, protonation, matrix rigidity and steric hindrance. As far as photochromic lenses are concerned the tuning between a strong and fast photochromic coloration (high ΔOD) and a very fast thermal fading is needed. Usually spiropyran or spirooxazine doped sol-gel matrices or even spirooxazine doped polymeric matrices exhibit slow thermal fading[25].

A strong improvment of the kinetics of thermal fading can be achieved with spirooxazine (SO :1,3,3-trimethylspiro-{indoline 2,3'(3H)naph(2,1-b)(1,4)oxazine}) doped hybrid matrices[15]. SO doped matrix prepared from the hydrolysis and cocondensation of $(CH_3)HSi(OC_2H_5)_2$ (D^H) and $HSi(OC_2H_5)_3$ (T^H) precursors can be described as strongly interpenetrated nanocomposites where D and T units are cross-linked close to the molecular level. The environment experienced by the SO dye within the matrix D^H/T^H is cartooned in figure 4.

The SO doped D^H70/T^H30 matrices exhibit a normal photochromism (all the samples are colorless before irradiation). For this photochromic dye, the thermal fading can be fitted with an excellent agreement with a monoexponential equation. This can be related to the quasi-liquid mobility observed by NMR for this matrix[26]. The photochromic behavior is reversible, extremely fast ($k = 0.2\ s^{-1}$) and corresponds to a very high absorption jump (ΔOD = 1.2). The photochromic kinetics of these SO doped hybrid materials are to the best of our knowledge much faster than those reported for SO in any other matrix (sol-gel matrices, organic polymers, alcohols, ...). The very high reactivity of the D^H/T^H precursors towards hydrolysis condensation reactions (all Si-OH groups are efficiently consumed) and the flexibility (low Tg) of the resulting matrix are both responsible for the direct and very fast photochromic behavior observed.

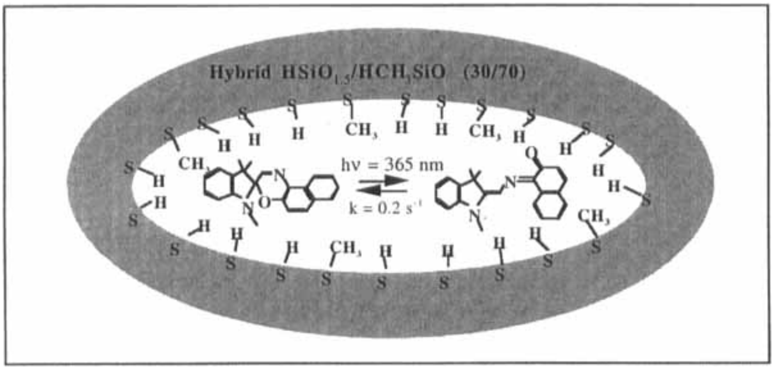

FIGURE 4. Schematic representation of the environment experienced by the SO dye within the matrix D^H70/T^H30

MOLECULAR DESIGN OF TRANSITION METAL ALKOXIDES FOR THE SYNTHESIS OF HYBRID ORGANIC-INORGANIC COPOLYMERS

The chemical tailoring performed with systems containing a Si-C bond cannot be directly extended to transition metals because the more ionic M-C bond is broken upon hydrolysis. Organic modification can however be performed by means of strong complexing ligands such as ß-diketones and allied derivatives, polyols, and α- or ß-hydroxyacids. These ligands (HL) react readily with transition metal alkoxides $M(OR)_4$ ($M = Ce, Ti, Zr, \ldots$) to yield new precursors $M(OR)_{3-x}L_x$[27,28]. Upon hydrolysing these new precursors, most of the alkoxy groups are quickly removed while all strong complexing ligands cannot be completely removed. Complexing ligands appear to be quite stable towards hydrolysis because of chelation and steric hindrance effects. Thus, they allow to anchor polymerizable organic groups to transition metal oxo-polymeric species and synthesize new hybrid organic-inorganic materials.

These new approach was performed with different ligands, such as acetoacetoxyethylmethacrylate (AAEM) and methacrylamidosalicylic acid (MASA), which both present a strong chelating part and a highly reactive methacrylate group[6]. Zirconium-oxo-PAAEM copolymers were synthesized from zirconium propoxide modified at the molecular level with AAEM[6]. These hybrid organic-inorganic copolymers are made of zirconium oxo-polymers and polymethacrylate chains. The zirconium oxo species, in which zirconium is coordinated by seven oxygen atoms, are chemically bonded to methacrylate chains through the ß-ketoester complexing function. The complexation ratio (AAEM/ Zr) is the key parameter that controls the structure and the texture of these hybrid materials (figure 5).

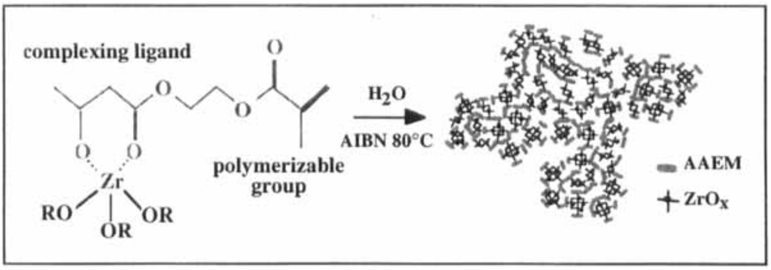

FIGURE 5. Schematic structures of class II hybrid materials made from zirconium n-propoxide complexed by the acetoacetoxyethylmethacrylate (AAEM).

A careful adjustment of this parameter leads to the tailoring of the ratio between organic and inorganic components and also to zirconium oxo species with more or less open structures. The ratio inorganic/organic increases when the complexation ratio decreases. For a high complexation ratio both networks interpenetrate intimately at the nanometer scale, while for a low ratio the size of the inorganic domains increases to the sub-micron range. Organic and inorganic growths are not independent and such systems exhibit probably similar behavior to the so-called interpenetrating polymer networks. Moreover, by adding acetylacetone to the hybrid Zirconium-oxo-PAAEM based sol, inorganic and organic components can be separated into surface capped zirconium oxo nanoparticules and insoluble PAAEM polymers. Acetylacetone beeing a better complexing ligand than acetoacetoxyethylmethacrylate, it displaces the previous ligand leading to the cleavage of hybrid. This process allows the recuperation of both components which can be analyzed separately[6b].

HYBRIDS MADE THROUGH THE ASSEMBLY OF NANO-BUILDING BLOCKS

One way to achieve some control over the growth and morphology of inorganic materials, obtained from molecular precursors, is the use of organic templates which self-organized into complex structures. The use of perfectly calibrated preformed objects, that keep their integrity in the final material, is also a method to reach a better definition of the inorganic component[4m]. The use of nanobuilding blocks as starting units to obtain hybrid organic-inorganic structures is an approach followed by organometallic chemists for various systems such as oligosilsesquioxanes and derivatives[29], organically fonctionnalized polyoxometalates (POM)[30], transition metal oxo clusters complexed with polymerizable ligands[31] or organo tin oxo clusters[32].

The most studied nanobuilding blocks are well defined silicon oxo-clusters of general formula $[XSiO_{1.5}]_n$ (n = 6 to 12) which belong to the families of polyhedral oligohydridosilsesquioxanes (X=H), polyhedral oligosilsesquioxanes (X=R) or spherosilicates ($X=OSiR_1R_2R_3$). These functionalized silicon oxo cages can be coupled to form hybrid network through hydrosilylation, polymerization or polycondensation reactions[29].

POM form a peculiar class of clusters which are very interesting for their structure, their electronic properties and their use in different domains[33]. POM entities can be easily organically functionnalized through M-O-Si-C links. The lacunar polyoxotungstate $[SiW_{11}O_{39}]^{8-}$, which formally derives from Keggin's structure by the removing of a "WO" fragment, reacts with trichloro or trialkoxysilanes to yield the modified polyoxotungstates, $[SiW_{11}O_{40}(SiR)_2]^{4-}$, which can be isolated by crystallization. $[SiW_{11}O_{40}(SiR)_2]^{4-}$ units carrying two reactive organic groups (R=vinyl, allyl, methacryl, styryl) can be further polymerized in the presence of a radical initiator and yields hybrid polymers in which POM are linked by polymethacrylate or polystyrene chains[30a-b]. A similar strategy to the one pionered by P. Judeinstein[30a] have been recently developped with trivacant polyoxotungstate α-A-$[SiW_9O_{34}]^{10-}$ which yields, upon reaction with $RSiCl_3$ (R = H, $CH=CH_2$ or any functional group), tetrafunctionalized polyoxotungstates, $[SiW_9O_{37}(SiR)_4]^{4-}$ [30c-d].

Transition metal oxo clusters capped with polymerizable complexing ligands, i.e. allylacetoacetate (AAA) or methacrylate (OMc), could also be linked together when an organic polymerization is initiated, leading to an assembly of nano-building blocks. With these ligands, $Ti_6O_4(OEt)_8(OMc)_8$, $Zr_{10}O_6(OH)_4(OPr^i)_{18}(AAA)_6$, $Nb_4O_4(OPr^i)_8(OMc)_4$, $Zr_6(OH)_4O_4(OMc)_{12}$, and

$Zr_4O_2(OMc)_{12}$ have been prepared and characterized by single crystal X-ray diffraction[31]. However, because of their small size and of the presence of several alkoxy groups on their surface, these functionalized nanobuilding blocks likely exhibit a poor stability in presence of water or nucleophiles.

Such a stability problem can be overcome by using tin-oxo clusters. As for silicon, the $Sn\text{-}C_{sp3}$ bond is stable, especially towards nucleophilic agents such as water. This last characteristic allows to chemically link organic moieties to the tin oxo polymers/oligomers, but it also reduces the inorganic functionality of tin and therefore favors the formation of oxo-clusters which can be used as nano building block to design new hybrid materials[4e,32,34,35].

The nanobuilding block $\{(RSn)_{12}(\mu_3\text{-}O)_{14}(\mu_2\text{-}OH)_6\}^{2+}$, "Tin-12", (figure 6) can be obtained through several chemical pathways: hydrolysis of $RSn(OR')_3$, $RSnCl_3$ or $RSn\text{-}C{\equiv}C\text{-}R'$ [36,38,39], or by refluxing in toluene butyltin hydroxide oxide (BuSnO(OH)) in the presence of sulfonic acids ($R'SO_3H$)[34b]. This tin oxo-hydroxo cluster contains an equal amount of six- and five-coordinate tin atoms. The twelve organic chains surround the oxo core and prevent from further condensation. Depending of the synthesis conditions the positive charge 2+ is balanced by different anions (OH^-, Cl^-, $R'SO_3^-$, $R'CO_2^-$, ...). These charge compensating anions are located at both cage poles, close to the hydroxy groups which bridge the six-coordinate tin atoms (figure 6).

This cluster is easily evidenced in solution and in the solid state by ^{119}Sn NMR[36]. Thus, its integrity can be easily verify after the polymerization or crosslinking reactions needed to tranform these discrete clusters into an hybrid material. As a consequence "Tin-12" clusters are good nanobuilding blocks for the synthesis of well defined tin-oxo based hybrid materials that can be used as models[32,34,35]. Moreover, these clusters exhibit a high versality to design hybrids (figure 6). "Tin-12" clusters can be assembled through organic networks by using the covalent interface provided by the Sn-C bond or by using the ionic interface associated to the charge compensating anions X^-, or even by using both. In the first case, the organic moiety bound to tin should be polymerizable (i.e. R: butenyl, propylmethacrylate, propylcrotonate, 4-styryl, ...). In the second case charge compensating organic dianions can be used to bridge the clusters. This was achieved by reacting $\{(BuSn)_{12}O_{14}OH_6\}(OH)_2$ with carboxymethyl terminated PEG macromonomers[34].

Another stategy is to use polymerizable anions. By a simple acid-base reaction, the oxo-hydroxo butyltin macrocation, $\{(BuSn)_{12}O_{14}OH_6\}^{2+}$, can be functionalized with 2-acrylamido-2-methyl-1-propanesulfonate, affording nanobuilding blocks with two highly polymerizable groups. For the first time[35], the direct polymerization of such functionalized oxo-hydroxo butyltin nanoclusters has been successfully performed, yielding hybrid materials in which the nano-sized inorganic component is perfectly defined. Two types of organic components are found in such materials. The butyl groups covalently bound onto tin atoms, and, more importantly, poly(2-acrylamido-2-methyl-1-propanesulfonate) chains which interact through electrostatic interactions with the oxo-hydroxo butyltin macrocations and afford the cross-linking.

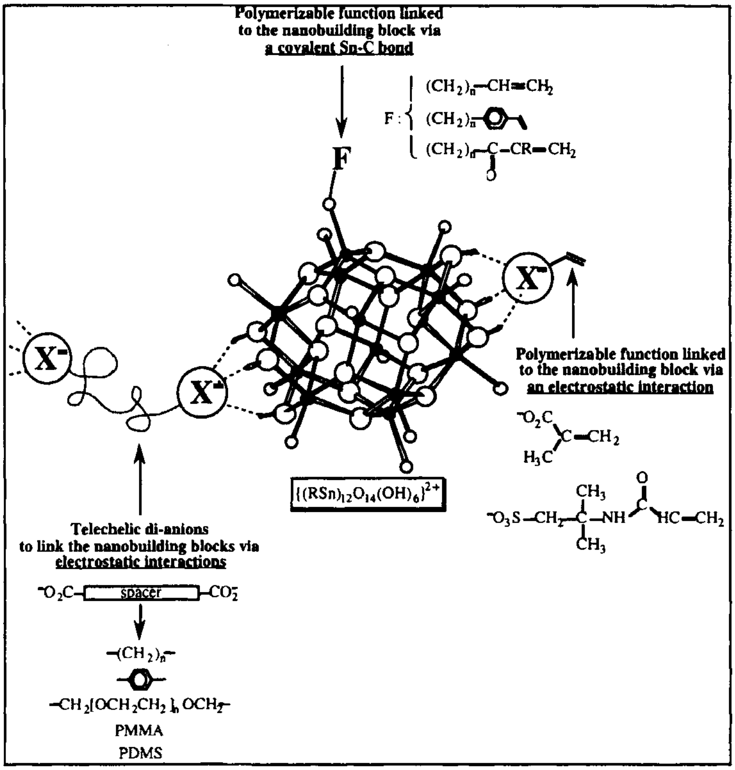

FIGURE 6. Some of the possible stategies that can be used with the hybrid nanobuilding block $\{(RSn)_{12}(\mu_3\text{-}O)_{14}(\mu_2\text{-}OH)_6\}^{2+}2X^-$.

Tin oxo-carboxylate clusters[37], such as $\{RSnO(O_2CR')\}_6$ ("Tin-6", R= methyl, phenyl, butyl and R' being any organic fonction), represent an other type of nanobuilding blocks, in which the carboxylate groups could be used to provide the assembling functions. "Tin-6" clusters can be easily prepared either by reacting oxo-hydroxo-organotin polymers (organostannonic acids) with carboxylic acids[32,37] or "Tin-12" clusters also with carboxylic acids[32,38].

The "Tin-6" molecular structure (figure 7), where all tin atoms are six-coordinate (distorted octahedra), exhibits a hexagonal prismatic or "drum" arrangement made of two interconnected "$[Sn\text{-}O]_3$" rings in which all the oxygen atoms are triply bridging. The carboxylate groups are located on the six side square faces of the "drum", each bridging two tin atoms. This results in a fairly anisotropic overall shape as the six carbons atoms of the carboxylates are almost coplanar, while the organic moieties bound to tin point outside the top or bottom hexagonal faces of the "drum".

The "Tin-6" cluster $\{BuSnO(O_2CC_6H_4NH_2)\}_6$, prepared from 4-aminobenzoic acid, exhibits on its periphery 6 amino functions amenable to subsequent reactions[32]. Its functionalization or assembling (figure 7) has indeed been achieved by reaction with isocyanates (Eq. 1), resulting in the formation of urea bridges.

$$\{BuSn(O_2CC_6H_4NH_2)\}_6 + 6\ O{=}C{=}N\text{-}R \rightarrow \{BuSn(O_2CC_6H_4NHCONHR)\}_6 \qquad (1)$$

The reaction with $OCN(CH_2)_3Si(OEt)_3$ affords in quantitative yield a "Tin-6" oxo core with 18 peripheral ethoxy functions amenable to hydrolysis-condensation[32]. This functionalized nanobuilding block could then be used to prepared, by sol-gel process, silica based materials in which the pore size could be controlled by a templating effect[4d,40].

Assembling was also evidenced by the formation of insoluble systems, within a few hours, upon reacting $\{BuSnO(O_2CC_6H_4NH_2)\}_6$ with commercial diisocyanates, 1,4-$(OCN)_2C_6H_4$ or $OCN(CH_2)_6NCO$[32]. The resulting urea bridges were clearly evidenced by ^{13}C CP MAS and ^{119}Sn MAS NMR showed that the "Tin-6" oxo-cores were fully preserved in the solid[32]. The hexa functionality of the nanobuilding blocks results in an important cross-linking, likely responsible of the insolubility. The "Tin-6" oxo-cores are quite stable and obtained with good yields. They should open a land of opportunities in the design of new hybrid materials which synthesis is based on the nanobuilding blocks approach.

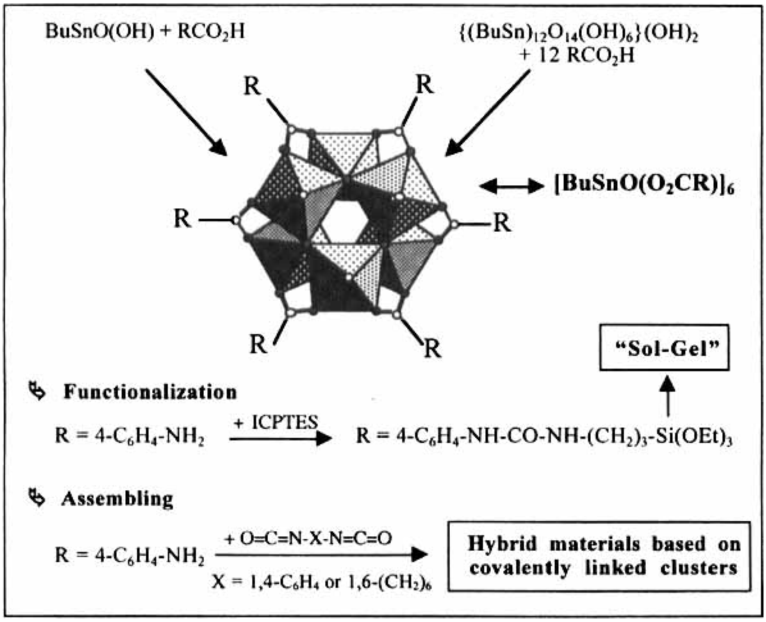

FIGURE 7 Synthesis of "Tin-6" clusters and some of the possible stategies to assemble $\{RSnO(O_2CR')\}$ nanobuilding.

CONCLUSIONS

The combination at the nanosize level of inorganic and organic or even bio-active components in a single material makes accessible an immense new area of materials science that has extraordinary implications for developing novel multi-functional materials exhibiting a wide range of properties. This fascinating new field of research bring together scientist working in many different domains. Among soft chemistry processes, sol-gel chemistry offers a versatile access to chemically designed new hybrid organic inorganic materials. Many new combinations between an inorganic component and an organic or biologic component will likely appear in the future. Yet, a better understanding and control of the local and semi-local structure of these materials is an important issue, especially if tailored properties are sought for. To achieve such a control of the materials structure, the assembling of well-defined nano-building blocks is an interesting approach.

The traditional view of inorganic solids is currently being reshaped and many research groups are strongly involved in a field named by S. Mann *"organized matter chemistry"*[41-46]. In such field, the sol-gel derived hybrids materials and more particularly those obtained through the "nanobuilding block approach"[4m] will have a paramount importance in exploring the theme of "synthesis with construction" of hierarchically organized materials.

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