Reviews

Hybrid Inorganic–Organic Materials by Sol–Gel Processing of Organofunctional Metal Alkoxides

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Metal alkoxides of the type $(R'O)_nE-X-A$, where A represents a functional organic group, and X is a hydrolytically stable spacer linking A and the metal alkoxide moiety $E(OR')_n$, are interesting precursors for the preparation of novel materials composed of both inorganic and organic entities. The basic chemistry behind the preparation and the sol–gel processing of these compounds is reviewed. The manifold options for chemical modification of both the inorganic and the organic groups allow the deliberate preparation of materials with special properties. Selected materials syntheses are discussed to demonstrate the scope of possible applications.

Introduction

A better understanding of the parameters governing sol–gel chemistry, and the development of suitable processing methods has led to the design of new materials with interesting properties in the past decade.[1] Oxide materials of a variety of compositions are now accessible as ceramic powders and fibers, glasses, thin films, or coatings. Their development was possible only by learning how to deal with such key issues as the control of the microstructure or the handling of multicomponent systems. While the early developments of the sol–gel process were mainly based on simple, readily available precursors, the hugh potential of new precursors chemically tailored for special applications is more and more realized.

Sol–gel chemistry not only offers an access to ceramics and glasses with improved or new properties. The very mild reaction conditions, particularly the low reaction temperatures, also allow to incorporate organic moieties in inorganic materials. This led to a conceptually novel class of materials composed of both inorganic and organic groupings.

The classical approach to combine the properties of different materials led to the development of composite materials or blends, where two different phases with complementary physical properties are combined. The concept of composites originated in the idea of producing materials having better properties than either of the two components. The chemical equivalent to composite materials is the combination of chemical groupings with different properties on a nanoscopic level. Although such materials are macroscopically homogeneous, their properties reflect the nature of the chemical building blocks from which they are composed. The blending of organic and inorganic components and the synergism of their properties in one material is particularly useful and allows the development of materials with totally new properties.

Organic groups in sol–gel materials can serve different purposes:

(i) During the preparation of purely inorganic materials, they can control the reaction rates of the reactants, the rheology of the sols, or the homogeneity and microstructure of the derived gels. They are degraded during calcination to get purely inorganic materials.

(ii) The organic groups can be retained to modify or functionalize the oxidic material. The final material therefore is composed of inorganic (oxidic) structures cross-linked or substituted by organic groups. In this article we will use the term "hybrid inorganic–organic materials" for such materials,[2] independent of the function and structure of the organic groups.

Hybrid inorganic–organic sol–gel materials can be prepared by two approaches. Organic molecules can be just embedded into an inorganic material, or vice versa. Alternatively, the organic and inorganic groupings can be linked by stable chemical bonds. The latter approach requires precursors in which the organic group (R) is bonded to the oxide-forming element (E) in a hydrolytically stable way. The general process is outlined in eq 1 for metal alkoxides, the most commonly used type of precursors in sol–gel processes. Although the following

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[®] Abstract published in *Advance ACS Abstracts,* November 1, 1995.

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[2] Review articles: (a) Sanchez, C.; Ribot, F. *New J. Chem.* **1994**, *18*, 1007. (b) Novak, B. M. *Adv. Mater.* **1993**, *5*, 422. (c) Schottner, G.; Rose, K.; Schubert, U. *Adv. in Science and Technology, 10. Intelligent Materials and Systems*; Vincenzini, P., Ed.; Techna Srl.: 1995; p 251. Cerveau, G.; Chorro, C.; Corriu, R.; Lepeytre, C.; Lère-Porte, J. P.; Moreau, J.; Thepot, P.; Wong Chi Man, M. In *Hybrid Organic–Inorganic Composites*; Mark, J. E., Lee, C. Y.-C., Bianconi, P. A., Eds.; *ACS Symp. Ser. 585*: Washington, 1995; p 210.

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discussion concentrates on alkoxide derivatives the same reasoning is valid for other hydrolyzable compounds.

$$x\text{RE(OR}')_n + y\text{E(OR}')_m + z\text{H}_2\text{O} \rightarrow \text{R}_q\text{EO}_p + w\text{R}'\text{OH} \quad (1)$$

There is a huge variety of possibilities for the modification of organic–inorganic hybrid materials:

(1) Variation of the Element E. In principle, any element E (or combinations of different elements in multicomponent systems) for which compounds suitable for sol–gel processing are available can be used for the formation of the inorganic structures. For the reasons discussed below, silicon is currently the most often used element.

(2) Variation of the Organic Group R. The choice of the organic group R is nearly unlimited. The only condition is that the group is hydrolytically stable or reacts with water in a controlled way. The crucial question is, of course, the hydrolytic stability of the E–R link (vide infra). More than one organic group R can be bonded to the same atom E, although such precursors are only rarely used in sol–gel chemistry.

(3) Variation of *x*:*y* (Eq 1), the Ratio between the Substituted and Unsubstituted Precursor. With decreasing *x*, the hybrid materials become "more inorganic", and vice versa. The case $y = 0$ corresponds to a one-component system with $\text{RE(OR}')_n$ as the only precursor. For example, the silsesquioxanes $\text{RSiO}_{1.5}$ are formed upon sol–gel processing of $\text{RSi(OR}')_3$, while processing of a 1:4 mixture of $\text{RSi(OR}')_3$ and $\text{Si(OR}')_4$ gives a material with the "more inorganic" composition $\text{R}_{0.2}\text{SiO}_{1.9}$. Mixtures of more than two precursors of course can also be employed.

The organic group R can have different functions; the most general is that of a network modifier. If an alkoxy group in $\text{E(OR}')_m$ is replaced by one or more hydrolytically stable groups R, the degree of cross-linking of the oxide network, formed during sol–gel processing, decreases. The physical consequences of such a substitution are very well-known from silicones. If the compounds $\text{RE(OR}')_n$ are used as network modifiers, only simple organic groups are necessary, such as alkyl or aryl groups.

A more challenging possibility is the use of precursors in which the organic group R bears some functionality. The relevant precursors are of the type $(\text{R}'\text{O})_n\text{E}-\text{X}-\text{A}$ (**1**), where A represents the functional organic group, and X is a chemically inert spacer linking A and the metal alkoxide moiety. Precursors with a direct chemical bond between A and $\text{E(OR}')_m$ (without a spacer) usually cannot be employed for chemical reasons.

This review article is limited to materials made from precursors of the type **1**. Therefore, materials in which functional compounds (dye molecules, catalysts, enzymes, etc.) are just *embedded* in sol–gel matrixes will not be considered. We restrict ourselves to materials in which the chemically bonded functional organic moieties are retained in the final material. We also exclude the sol–gel synthesis of organic–inorganic hybrid polymers from $\text{E(OR}')_n$-terminated organic macromolecules because this was recently reviewed elsewhere.[2a,b]

The term "functional group" is difficult to delimit, and the choice of our examples is therefore somewhat arbitrary. For instance, simple alkyl or aryl groups, usually not being considered "functional groups", may have an important "function" in some materials, besides being a network modifier. The following example may illustrate this point. Silica aerogels made of only $\text{Si(OR}')_4$ are very hydrophilic, due to residual Si–OR′ and Si–OH groups. However, the use of $\text{RSi(OMe}_3)$/Si(OMe)_4 mixtures (R = alkyl or aryl) resulted in hydrophobic silica aerogels, being insensitive toward moisture. This hydrophobizing effect of the organic groups is caused by the suppression and replacement of the Si–OMe and Si–OH groups.[3]

Precursors

Alkoxysilane Derivatives. Organically substituted alkoxysilanes of the type $(\text{R}'\text{O})_3\text{Si}-\text{X}-\text{A}$ (**2**), with a great variety of groups A are commercially available or easily prepared. Si–C bonds are not hydrolyzed, due to the specific properties of silicon (low Lewis acidity, rather unpolar Si–C bond). Therefore, the functional group A can be linked to the silicon atom via a Si–C bond. In the most common alkoxysilanes of the type **2**, the spacer X is a $(\text{CH}_2)_p$ (p = 2, 3) chain. They have found widespread industrial applications, for instance, in silicones, as adhesion promotors, for derivatizing surfaces, or for the immobilization of substrates.

The preparation of such compounds has been reviewed elsewhere.[4] The more general routes are summarized in Eqs 2–5.

The hydrosilylation of alkenes or alkynes, i.e., the addition of Si–H bonds to double or triple bonds, is one of the few general methods for the formation of Si–C bonds. HSiCl_3 is preferentially used for the industrial preparation of alkoxysilanes **2**. The trichlorosilyl derivatives $\text{Cl}_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{X}'-\text{A}$ are then converted to the corresponding trialkoxysilyl derivatives (eq 2).

$$\begin{aligned}&\text{Cl}_3\text{Si}-\text{H} + \text{CH}_2{=}\text{CH}-\text{X}'-\text{A} \rightarrow \\ &\qquad \text{Cl}_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{X}'-\text{A} \xrightarrow{+\text{R}'\text{OH}/-\text{HCl}} \\ &\qquad\qquad (\text{R}'\text{O})_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{X}'-\text{A} \quad (2)\end{aligned}$$

For instance, the technically very important silanes $(\text{R}'\text{O})_3\text{Si(CH}_2)_3\text{Cl}$ or $(\text{R}'\text{O})_3\text{Si(CH}_2)_2\text{CN}$ are prepared that way, starting from allyl chloride or acrylonitrile, respectively. The hydrosilylation of allyl or vinyl compounds directly with $(\text{R}'\text{O})_3\text{SiH}$ instead of Cl_3SiH requires more extensive safety efforts. It is technically mainly used for the preparation of $(\text{R}'\text{O})_3\text{Si(CH}_2)_3\text{OCH}_2\overline{\text{CH}-\text{CH}_2\text{O}}$ (GLYMO) and $(\text{R}'\text{O})_3\text{Si(CH}_2)_3\text{OC(O)C(CH}_3){=}\text{CH}_2$ (MEMO) from allyl glycidyl ether or allyl methacrylate.

Only few alkenyl compounds with functional groups are accessible by the direct route shown in eq 2. Therefore, substitution of a group A by another group

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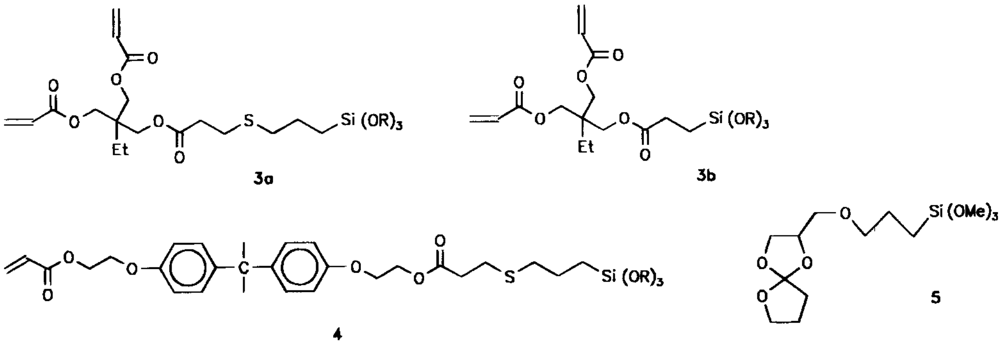

Figure 1. Selection of compounds of the type $(R'O)_3Si-X-A$ (**2**) in which A is a polymerizable group.

A′ (eq 3) or chemical modification of a functional group (eq 4) often is the easier way to anchor more complex functional groups to silicon. Many silanes of the type **2** are industrially prepared by substitution of the chloride in $(R'O)_3Si(CH_2)_3Cl$.[4] For example, the technically important thio-substituted compound $[(EtO)_3Si(CH_2)_3]_2S_4$ (used as adhesion promoter between rubber and silica fillers) is prepared by reaction of $(EtO)_3Si(CH_2)_3Cl$ (A = Cl) with Na_2S_4 (A′ = S_4).[4,5] Examples for the modification by addition reactions to functional groups A (eq 4), such as (meth)acrylate, isocyanate or epoxide groups, are given below.

$$(R'O)_3Si-(CH_2)_p-A + A' \rightarrow (R'O)_3Si-(CH_2)_p-A' + A \quad (3)$$

$$(R'O)_3Si-(CH_2)_p-A + Y-X'-A' \rightarrow (R'O)_3Si-(CH_2)_p-A(Y)-X'-A' \quad (4)$$

More recently, substitution of $(R'O)_3SiCl$ by Grignard or organolithium reagents was used to prepare, for instance, phenylene- or thiophenylene-bridged alkoxysilanes (eq 5).

$$(R'O)_3SiCl + MR \rightarrow (R'O)_3Si-R + MX \quad (5)$$

The exhaustive coverage of all known organofunctional alkoxysilanes of the type **2** would exceed the scope of this article. We therefore restrict ourselves to a few typical and topical examples. A selection is given in Figures 1–4. We want to illustrate the point that nearly any organic (or organometallic) group can be anchored to an alkoxysilyl moiety by one of these methods.

Alkoxysilanes, in which A is a reactive double bond (Figure 1), are extremely interesting for the synthesis of inorganic–organic polymers by polymerization of the organic groups. In this approach, an organic network is formed in the matrix of the primarily formed inorganic network. The methacrylate substituted silane $(R'O)_3Si(CH_2)_3OC(O)C(CH_3){=}CH_2$ or vinyltrialkoxysilane are very often used for this purpose (vide infra). Recently, a class of compounds was developed that allows easy variations in the organic chain of the hybrid polymer, particularly to achieve a higher degree of crosslinking. The general idea is to use one double bond of an organic monomer with more than one acrylate function to anchor the $Si(OR')_3$ group and still have the other double bond(s) available for a later polymerization. For instance, trimethylol–propanetriacrylate, $EtC[CH_2OC(O)CH{=}CH_2]_3$, was reacted with one equivalent of $(R'O)_3Si(CH_2)_3SH$ or $(R'O)_3SiH$, respectively, to give the compounds **3a,b**.[6] The acrylate substituted silane **4** (with a very long spacer between the double bond and the $(R'O)_3Si$ group) was similarly synthesized by the thiol addition to the ethoxylated bisphenol-A diacrylate $Me_2C[C_6H_4OCH_2CH_2OC(O)CH{=}CH_2]_2$.[7] Coupling of $(EtO)_3Si(CH_2)_3NCO$ with OH-terminated bis(acrylates) is another efficient way to prepare precursors of this type.[8]

Other reactive groups suitable for organic crosslinking by polymerization reactions can, of course, be linked to the hydrolyzable $(R'O)_3Si$ group by the same methods. One example is the silane **5** (Figure 1). Ring-opening polymerization of its spiro orthoester moiety proceeds with only a very low shrinkage. The precursor silane was prepared by addition of butyrolactone to the epoxy group of GLYMO.[9]

Another subset of compounds of the type **2**, which recently has gained much interest in sol–gel chemistry are those in which the functional group A is a chromophore. The examples in Figure 2 were also selected to represent the different preparative methods by which $(R'O)_3Si$-terminated groups can be introduced into more complex organic moieties, such as dye molecules.

The alkoxysilane terminated azobenzenes **6a** and **6b** contain the same nonlinear optic (NLO) chromophore. However, different functionalities were used anchoring a $(R'O)_3Si$-containing moiety according to eq 4. For the preparation of **6a** (and related compounds), the $N(R)CH_2CH_2OH$ group of the dye (disperse red) was added to the isocyanate group of $(R'O)_3Si(CH_2)_3NCO$,[10–14] while compound **6b** was obtained by coupling of the NH_2-substituted dye with the epoxy group of GLYMO.[15] Multiple substitution is also feasible, as exemplified by

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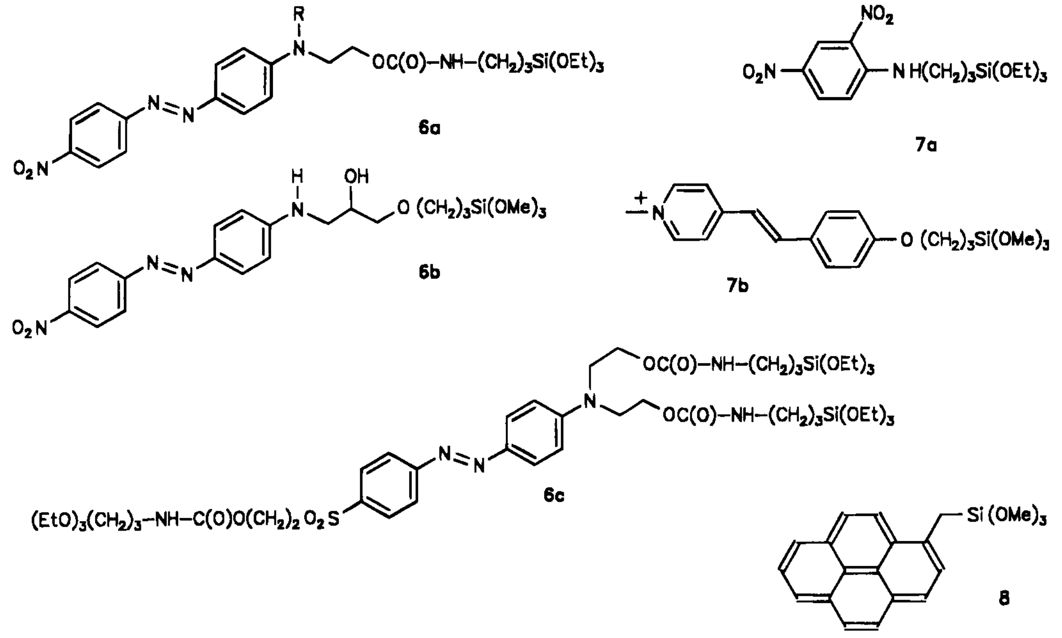

Figure 2. Selection of compounds of the type $(R'O)_3Si-X-A$ (**2**) in which A is a chromophore.

6c and related compounds.[12-14] The alkoxysilyl-substituted NLO dyes **7a**[16] and **7b**[17] were prepared by substitution reactions according to eq 3 starting from $(R'O)_3Si(CH_2)_3Cl$, and the pyrene derivative **8**, a fluorescent dye, according to eq 5.[18] Phenoxazinium and phenazinium dyes with (aminopropyl)triethoxysilyl substituents, used for the coloration of glass, were simply obtained by reaction of the corresponding parent dye with (aminopropyl)triethoxysilane.[19]

Metal complex fragments are other "functional groups" in compounds of the type **2** with a very promising potential for materials synthesis. The most common method to prepare alkoxysilyl derivatives of metal complexes is by ligand exchange (eq 6). In these reactions, one or more ligands L are replaced by functional alkoxysilanes **2**, in which the group A is capable of coordinating metal complex fragments (ML_n) or metal ions. The chemistry of such complexes was mainly developed with regard to the heterogenization of catalytically active metal complexes by anchoring them on silica as a solid support.[20] The use of the complexes $[(R'O)_3Si-X-A]_mML_{n-m}$ in sol-gel chemistry to prepare catalysts has recently been reviewed.[21] The examples (**9**,[22] **10**,[23] **11**,[26] **12**,[24] **13**[25]) in Figure 3 illustrate some of the possibilities to connect trialkoxysilyl groups and transition metals.

$$m(R'O)_3Si-X-A + ML_n \rightarrow [(R'O)_3Si-X-A]_mML_{n-m} + mL \quad (6)$$

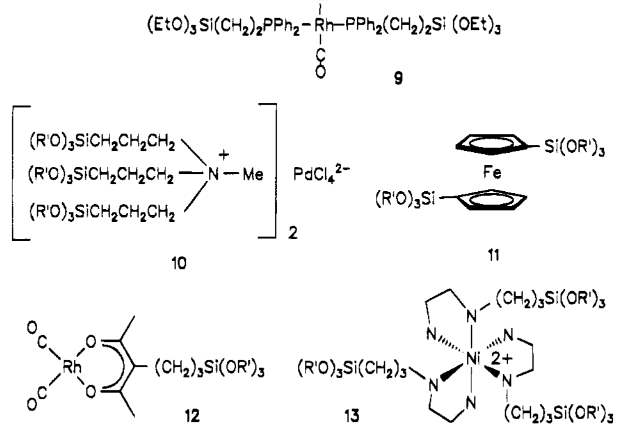

Figure 3. Selection of compounds **2** in which A is a metal complex fragment.

In principle, $(R'O)_3Si$ containing groups can be anchored to nearly any organic entity by one of the discussed methods. Figure 4 shows some additional examples of organofunctional alkoxysilanes tailored for some special use. For instance, the ethoxysilyl-substituted diamine **14** was used for the preparation of a $(EtO)_3Si$-substituted polyimide (eventually leading to polyimide-silica hybrid materials),[27] the substituted crown ether **15** for facilitated transport membranes,[28] and the silane **16** (and related single- and triple-chain compounds) for immobilized amphiphilic monolayers on glass plates.[29] For the preparation of **16** a coupling

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(16) Commercially available from ABCR Comp.

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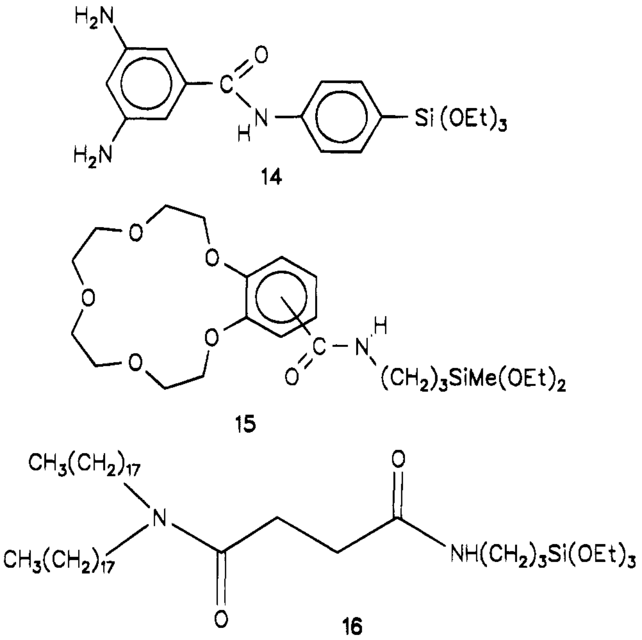


14

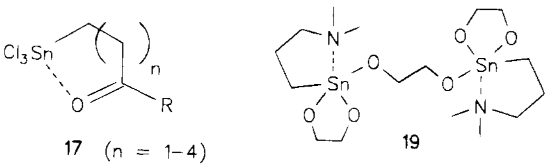
15

16

Figure 4. Selection of compounds **2** with other functional groups A than those in Figures 1–3.

strategy was developed slightly different from those previously discussed. To derivatize *N,N*-dioctadecylamine, the amine was first reacted with succinic anhydride. *N,N*-Dioctadecylsuccinamic acid was obtained by this reaction which provided a new coupling site for the later reaction with aminopropyltriethoxysilane.

Alkoxystannane Derivatives. The chemistry of alkoxystannanes is intermediate between that of alkoxysilanes and alkoxides of typical metals, such as aluminum, the transition metals, or the lanthanides. A catalyst is needed to accelerate the reaction of alkoxysilanes with water. Tin alkoxides and metal alkoxides react much faster, and their hydrolysis and condensation reactions often must be slowed down by chemical additives. On the other hand, silicon and tin have in common that Si–C or Sn–C bonds, respectively, are not easily hydrolyzed. Therefore, compounds of the type $(R'O)_3SnR$ can in principle be employed for the preparation of organically substituted stannates by sol–gel processing. This was mainly demonstrated by Reuter et al.[30] and Ribot et al.[31] Nevertheless, compounds of this type were only rarely used for sol–gel processing. This may be due to their low availability, which is particularly true for functionalized compounds of the type $(R'O)_3Sn{-}X{-}A$. The trichlorostannyl compounds **17**[32,33] (Figure 5) or $HO(CH_2)_pSnCl_3$ ($p = 3{-}6$[33]) are interesting candidates, but the corresponding alkoxides are not yet known. The alkenyl compounds $(^tAmO)_3Sn{-}X{-}CH{=}CH_2$ (Am = amyl; $X = (CH_2)_p$, $p = 2, 3$; C_6H_4) (**18**) were prepared in a multistep procedure: Reaction of Cy_3SnCl (obtained by metathesis from Cy_4Sn and $SnCl_4$; Cy = cyclohexyl) with the corresponding Grignard reagents gave $Cy_3Sn(CH_2)_pCH{=}CH_2$. This compound was then metathesized with $SnCl_4$ to give $Cl_3Sn(CH_2)_pCH{=}CH_2$. Reaction of the Cl_3Sn derivative with *tert*-amyl alcohol in the presence of a base finally resulted in the formation of **18**.[33] The only other derivative of the general type $(R'O)_3Sn{-}X{-}A$ is **19** (with chelating ethyleneglycolate substituents instead of monodendate OR′), internally coordinated by the γ-amino group (Figure 5).[34] This compound was obtained by treating $Me_2N(CH_2)_3SnPh_3$ with glycol.



17 (n = 1–4)

19

Figure 5. Compounds of the type $(R'O)_3Sn{-}X{-}A$.

The other possibility to functionalize tin alkoxides would be via functionalized chelating ligands, as discussed in the next section for metal alkoxides. Although this appears to have the same potential as, for instance, for the modification of $Ti(OR')_4$ (vide infra), no compounds of this type are currently known.

Metal Alkoxide Derivatives. There are interesting potential applications for compounds **1** with $E \neq Si$. However, only very few derivatives of this type are known, i.e., the underlying basic chemistry is not yet developed. One of the reasons is that the functional group A cannot be linked to the alkoxide moiety by a hydrocarbon spacer as with silicon or tin, due to the hydrolytic cleavage of the more polar E–C bonds.

Complexing ligands (CL) have often been reported in the sol–gel literature as chemical additives to moderate the reactivity of non-silicate metal alkoxides. Acetic acid or acetylacetone were mainly used for this purpose. When non-silicon alkoxides are reacted with carboxylic acids, β-diketones, β-ketoesters, or related compounds (CL–H), part of the alkoxide groups is substituted by carboxylate or β-diketonate groups, etc. (eq 7). A new molecular precursor $E(OR')_y(CL)_x$ is obtained which exhibits a different molecular structure and reactivity. Upon addition of water, the alkoxy groups and not the complexing ligands are primarily hydrolyzed.[35]

$$E(OR')_{y+x} + x\mathrm{CL{-}H} \rightarrow E(OR')_y(\mathrm{CL})_x + x\mathrm{ROH} \qquad (7)$$

However, complexing ligands can also be used for organic functionalization. The most obvious choice are functionalized carboxylic acids. Their reaction with metal alkoxides provides the carboxylate derivatives $(R'O)_yE[OOC{-}X{-}A]_x$ where the functional group A is linked via the carboxylate group and some spacer X to the metal alkoxide moiety. [Since the degree of association was not determined for most derivatives, monomeric formulas are given in this article. However, in most cases dimerization or oligomerization is highly probable.] For instance, $Ti(OEt)_4$ reacted with methacrylic acid up to a maximum of 1.33 mol equiv. Although the substitution products themselves were not isolated, their primary hydrolysis products, discussed in the next section, showed the products to have the

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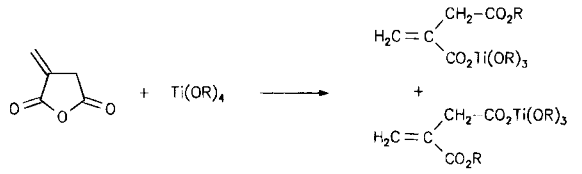

(8)

Figure 6. Reaction of $Ti(OR')_4$ with itaconic anhydride.

same constitution as those obtained in the reaction with acetic acid. From the reaction of $Zr(OPr^n)_4$ with methacrylic acid both $Zr(OPr^n)_3(OMc)$ and $Zr(OPr^n)_2(OMc)_2$ (OMc = methacrylate) were isolated.[36] Other $Zr(OR')_3$(carboxylate) derivatives were similarly obtained by reacting $Zr(OPr)_4$ or $Zr(OBu^t)_4$ with cinnamic acid or sorbic acid.[37]

The reactive double bonds in the (meth)acrylate derivatives are fully accessible for later polymerization reactions.[36] The same is true, for instance, for the chloro substituent, when chloroacetic acid is reacted with metal alkoxides. The following examples show that, in principle, the same strategies can be used to modify the carboxylate derivatives $(R'O)_yE[OOC-X-A]_x$, as for the previously discussed organofunctional alkoxysilanes $(R'O)_3Si-X-A$ (**2**, eqs 3 and 4).

Phosphanyl-substituted metal alkoxides $(R'O)_3E(OOC-X-PPh_2)$ (E = Ti, Zr) were not obtained by direct reaction of the corresponding carboxylic acids with $Ti(OR')_4$. However, addition of $HPPh_2$ to the acrylic double bond of $(PrO)_3E(OOC-CH{=}CH_2)$ (E = Ti, Zr) gave the phosphinopropionate derivatives $(PrO)_3E(OOC-CH_2CH_2PPh_2)$. The phosphinoacetate derivative $(PrO)_3Zr(OOC-CH_2PPh_2)$ was prepared by the reaction of $(PrO)_3Zr(OOC-CH_2Cl)$ with $LiPPh_2$ similar to eq 3.[38] Another phosphanyl-substituted titanium alkoxide, $(BuO)_3Ti[\pi\text{-}C_5H_4(CH_2)_2PPh_2]$, was obtained from $Li[C_5H_4(CH_2)_2PPh_2]$ and $(BuO)_3TiCl$.[38]

If the reaction of metal alkoxides with carboxylic acids is slow, esterification of the carboxylic acid by the liberated alcohol may become a competing reaction (vide infra). The same is true if the carboxylate ligand is not tightly bound and an alcohol is used as the solvent. The water produced by esterification partially hydrolyses the remaining alkoxide groups. To overcome this potential problem, $Ti(OPr^i)_4$ was reacted with itaconic anhydride (eq 8).[39] Due to the unsymmetric substitution of the five-membered ring, two isomers were formed. Both contain a polymerizable double bond, although in a different position relative to the $Ti(OPr^i)_3$ group. The reaction proceeds *without* the formation of an alcohol (Figure 6).

The formation of a five- or six-membered metallacycle results in considerable stabilization of the metal–ligand bond. For instance, compound **20** was prepared by reaction of $Ti(OPr^i)_4$ with isoeugenol. Bonding of the isoeugenolate ligand to the metal is much stronger than that of a simple alkoxy or aryloxy ligand. This is due to chelation by the α-methoxy group. The OPr groups of **20** were cleaved during base-catalyzed hydrolysis, while one isoeugenolate ligand per two titanium atoms was retained.[39]

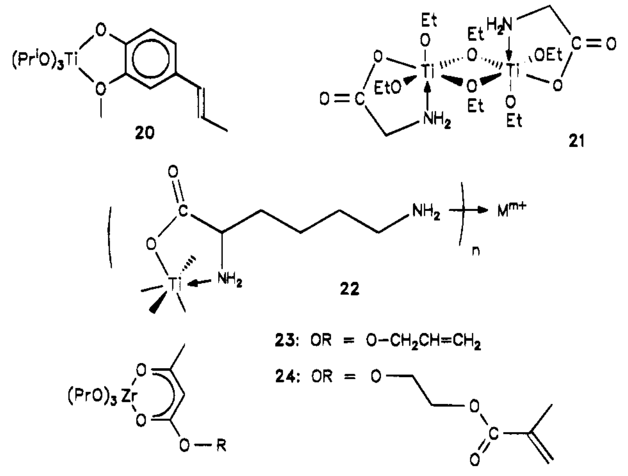

Figure 7. Compounds of the type $(R'O)_3E-X-A$ (E = Ti, Zr). The formulas of **20**, **23**, and **24** represent only the chemical composition and the mode of linking the organic group but not the structures of the compounds.

Strengthening of a metal–ligand bond by its incorporation into a five-membered chelate system is also a good strategy for carboxylic acids. For this reason α-hydroxy acids were used for the modification of metal alkoxides.[40] α-Hydroxy acids having a second functional group at a carbon atom more distant from the COOH group are therefore very well suited for the preparation of organofunctional metal alkoxide derivatives of the type **1**. Both methacrylamidosalicylicate modified $Zr(OPr)_4$[41] and 2,4-dihydroxybenzoate-modified $Ti(OPr^i)_4$[42] were used as sol–gel precursors. The former compound contains a reactive double bond as the functional group A, suitable for polymerization reactions, while in the latter compound the second OH group is available for coupling reactions, etc.

A recent study proved α-amino acids to be equally suited. The X-ray structure analysis of $[Ti(OEt)_3(glycinate)]_2$ (**21**) showed that the α-amino group participates in binding the carboxylate ligand to the metal and improves stability of the carboxylate derivative by formation of a five-membered chelate ring.[43] Amino acids with a second functional group at one of the more distant carbon atoms therefore can also be used for the preparation of type **1** compounds. This was shown for $Ti(OEt)_3(lysinate)$.[43] The uncoordinated amino group reacted with nickel salts as primary amines to give the complex $\{Ni[NH_2(CH_2)_4CH(NH_2)COOTi(OEt)_3]_4\}^{2+}$ (the precursor of **22**).

The chemical bond between β-diketonates and metal alkoxide moieties is inherently stronger than that of carboxylates. However, β-diketonates with functional substituents are less readily available. Two examples containing polymerizable double bonds as functional organic groups are shown in Figure 7 (**23**,[44] **24**[45]). These

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compounds were in situ prepared by reaction of allyl or methacryloxyethyl acetoacetate with an excess of $Zr(OPr)_4$ (i.e., the reaction mixture probably consisted of **23** or **24** and unreacted $Zr(OPr)_4$). Allyl acetoacetate derivatives were similarly obtained with $Ti(OBu)_4$[35] or $Al(OBu^s)_3$.[46] Spectroscopic and structural data of the hydrolysis products of these mixtures (see next section) showed the β-diketonate to be coordinated as indicated in Figure 7.

Reaction of benzoylacetone (bzac-H) with $Al(OBu^t)_3$, $Zr(OR')_4$, or $Ti(OBu^t)_4$ gave the β-diketonate derivatives $Al(OBu^t)_{3-p}(bzac)_p$, $Zr(OR')_{4-p}(bzac)_p$ ($p = 1, 2$), and $Ti(OBu^t)_2(bzac)_2$, respectively. Thermal reaction of some derivatives with $Cr(CO)_6$ gave metal complexes having a $Cr(CO)_3$ moiety π-bonded to the phenyl group of the benzoylacetonate ligand; i.e., the phenyl substituent was used as a "functional" group to coordinate metal complex fragments.[47]

Primary Hydrolysis and Condensation Processes

When water is added to metal alkoxides $E(OR')_m$, hydrolysis and condensation reactions are initiated, eventually leading to E−O−E groups and formation of metal oxide structures. The parameters that influence the sol−gel process have been thoroughly studied mainly for $Si(OR)_4$ but also for some non-silicon alkoxides.[1] The water:alkoxide ratio, pH, temperature, concentration of the reactants, and the kind of steric and electronic properties of the OR′ groups, to name only some of the relevant parameters, influence not only the kinetics of the hydrolysis and condensation reactions but also the nano- and microstructure of the obtained oxide.

When (organically) modified alkoxides $(R'O)_{m-n}ER_n$ are reacted instead of the parent alkoxides $E(OR')_m$, the sol−gel process is of course influenced by the nonalkoxide ligands. The hydrolytically stable groups R change the reactivity of the element E to which they are directly bonded, due to electronic and steric effects. Since they reduce the number of alkoxide ligands, the degree of inorganic cross-linking in the gels formed by the polycondensation reactions (i.e., the number of E−O−E links per atom E) is necessarily reduced. A key issue is the position and orientation of the organic groups in the primary hydrolysis products, which constitute the inorganic building blocks. Their structure predetermines the microstructure of the final materials.

When compounds of the type **1** with functional organic groups are employed, additional questions arise:

(i) How stable are the organic functions A and the E−X−A link during sol−gel processing?

(ii) Do the organic functionalities interfere with the sol−gel chemistry of the precursors?

(iii) How does the incorporation of organic functionalities, many of them being quite bulky, influence the build-up and the properties of the gel network?

(iv) How is the function of the organic groups (their optical properties or their catalytic activity, for instance) influenced by the oxide matrix in which they are incorporated?

There are only few applications where compounds of the type **1** are processed alone. In most cases mixtures of two or more different precursors are used. The control of the homogeneity (or deliberate heterogeneity) of the chemical subunits is then another key issue.

In this section we will focus on the questions arising from the presence of organic functionalities. A comprehensive treatise on the hydrolysis and condensation reactions of organically modified alkoxides is not intended.

Alkoxysilane Derivatives. *Single Precursors.* The influence of the steric and electronic properties of the group R on the hydrolysis and condensation kinetics of organically substituted alkoxysilanes $RSi(OR')_3$ was recently discussed in a review article.[48] It can be implied that functional and nonfunctional groups R of comparable size and electronic properties have the same influence, if the organic function A in **2** does not interact with the silicon atom[49] or does not catalyze the reaction. This can be expected if the group A has either basic or acidic properties.

Aminoalkyl-substituted alkoxysilanes are an example to illustrate this point. Both internal coordination of the amino group to the weakly Lewis acidic silicon atom and strong hydrogen bonds between the silanol groups of hydrolyzed (aminopropyl)trialkoxysilanes and the NH_2 group were debated.[50] Due to these interactions, the rates of the uncatalyzed hydrolysis and condensation reactions of (aminopropyl)trialkoxysilanes are similar to those of alkyltrialkoxysilanes in the presence of a base catalyst.[51−53] According to gel permeation chromatographic (GPC) studies, the octameric species $[Et_2N(CH_2)_3SiO_{3/2}]_8$ were predominantly formed in the methanolic solution upon addition of water to $Et_2N(CH_2)_3Si(OEt)_3$. Dimerization of these species occurred to an appreciable amount without methanol, but no higher oligomers were observed. A higher silane:water ratio resulted in a faster reaction but did not significantly influence the oligomer distribution.[53]

The development of the molar mass distribution by GPC was also investigated for vinyltrimethoxysilane (VTMS),[54] GLYMO,[55,56] and MEMO.[55,57] GPC and ^{29}Si NMR investigations[54,58] of the HCl-catalyzed hydrolytic polycondensation of VTMS in ethanol showed that increasing the H_2O:VTMS ratio increased the average degree of oligomerization (n, maximum of $n = 18$ for H_2O:VTMS = 1.6) and the molecular weight distribution. With an increasing H_2O:VTMS ratio the percent-

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age of $Vi(MeO)_2SiO-$ units decreased, while the percentage of $ViSi(O-)_3$ units increased. The spinnability of the sols was related to the ratio of the different structural units.[54]

The uncatalyzed hydrolysis of both GLYMO and MEMO resulted in the slow formation of rather small oligomers.[55,59] The degree of oligomerization was also influenced by the silane:water ratio. 1-Methylimidazol as the catalyst accelerated the formation of oligomers (with $n = 8$ and 16) from GLYMO.[55] Acid-catalyzed reaction resulted in the formation of a mixture of oligomers, a significant portion being the cyclic tetramers.[56]

According to the GPC investigations, the growth of oligomers from MEMO strongly depends on the used catalyst. With 1-methylimidazol, methacrylic acid, or $Zr(OPr^n)_2(OMc)_2$ as catalysts condensation essentially stopped at the stage of medium-sized oligomers ($M_p < 10^4$). Only with the strongly basic (dimethylamino)ethanol or with HF as the catalysts larger polymers were formed. In the (dimethylamino)ethanol-catalyzed reaction the polymer growth was not finished after 3 months.[55,60] According to another GPC and FTIR study, both the configuration and the molecular weight distribution of the polymers obtained from MEMO are dependent on the solution pH. Below pH 4, a beaded chain structure of cubical octamers or polycyclic caged blocks was obtained, while in neutral or basic environments a double ladder structure was formed.[57] A ^1H and ^{29}Si NMR spectroscopic analysis of the hydrolysis and condensation process of MEMO at pH = 2 with a stoichiometric amount of water showed that hydrolysis of the SiOMe groups is fast, but not complete.[61] The composition of the sol reached a stationary state after 4 days. The larger percentage of $R(MeO)Si(O-)_2$ units (60%) in this state is consistent with mainly linear or cyclic species in the aged sols. The number of $RSi(O)_3$ (20%) units allowed an estimate of the upper limit of 10 for the chain length. The difficulty of three-dimensional polycondensation was attributed to the size of the organic groups. Similar ^{29}Si NMR spectroscopic results were also reported by another group.[62]

The results on the molecular mass distribution in hydrolyzed alkoxysilanes **2** can be summarized as follows. The growth mechanism of the siloxane oligomers is probably the same as proposed by Brown for the condensation of cyclohexyl- or phenylsilanetriol.[63] Condensation of the functionalized silanes stops at the stage of rather small oligomers unless very active catalysts are used. This is probably due to steric effects of the rather bulky organic groups.

A major concern is the fate of the functional organic group A during sol–gel processing, particularly if they are not totally inert toward water. Although this is a very critical issue, there are only few systematic investigations, most of them for GLYMO. The epoxy group in GLYMO is capable of forming either diol units by hydrolytic ring opening or polyethylene oxide chains by polymerization.[64] Since a catalyst has to be used for sol–gel processing, its influence on the epoxy group is crucial. Complete hydrolytic opening of the epoxide ring within 17 h was observed at low pH with $HClO_4$, H_2SO_4, or H_3PO_4 as the catalyst. At pH 5.5 (H_2CO_3), ring opening was negligible even if an excess of water was employed.[65] In the presence of 0.1 equiv of 1-methylimidazol, i.e., under basic conditions, and an excess of water the epoxide concentration decreased slowly. Glycol and epoxide analyses after one day showed about 15% of the epoxide groups converted to the glycol, and about 50% after 7 days at 25 °C. However, the rate of the epoxide hydrolysis reaction was slow compared with the siloxane polycondensation reaction. The different reaction rates allow the preparation of hybrid materials by a two-step process, in which formation of the Si–O–Si network is carried out first and later the epoxy polymerization is induced.[59,66]

Precursor Mixtures. One of the basic ideas behind the development of inorganic–organic hybrid materials by sol–gel processing is the blending of materials properties by using mixtures of different precursors. In the early days of this chemistry it was more or less implicitly assumed that in multicomponent precursor systems there is a statistical distribution of the molecular building blocks in the final materials. However, considering the steric and electronic influence of different organic groups R on the hydrolysis and condensation rates of $RSi(OR')_3$, it is obvious that this will rather be the exception than the rule. This is not necessarily a disadvantage. In the contrary, the deliberate engineering of some nanoheterogeneity provides additional possibilities for materials developments. However, this requires the thorough investigation of the chemical behavior and mutual influence of the precursors in multicomponent sol–gel systems.

A recent example to illustrate this point is the development of inorganic-organic hybrid aerogels from $RSi(OMe)_3/Si(OMe)_4$ mixtures (R = terminal alkyl and aryl or functional organic groups, such as 3-methacryloxypropyl or 3-glycidoxypropyl).[3] It was shown that under basic conditions the built up of the gel network is a two-step process. In the first stage, $SiO_x(OH)_y(OMe)_z$ clusters are formed by hydrolysis and condensation of $Si(OMe)_4$, while $RSi(OMe)_3$ basically is a cosolvent. In the later stage of the reaction the $RSi\equiv$ units condense at the surface of the primary clusters. The fate of the individual alkoxides was conveniently monitored by micro-Raman spectroscopy, which provided clear evidence for the two-step mechanism.[67]

A structure in which organofunctional groups are located at the outside of the polysiloxane building blocks, was also postulated from a ^{29}Si and ^{31}P solid-state NMR study of a gel obtained from $(MeO)_3Si(CH_2)_6P(Ph)(CH_2)_2OMe$ and $Si(OEt)_4$ (1:2).[68]

In a mixture of two alkoxide precursors a mutual influence on the hydrolysis and condensation processes

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can be expected. For the MEMO/$Si(OEt)_4$ system this was studied by measuring the gel times (t_G).[69] The addition of MEMO to an acidic mixture of $Si(OEt)_4$, ethanol and water resulted in a considerable increase of t_G. Under basic conditions the increase of t_G was less dramatic. The influence of MEMO cannot only be attributed to the effective decrease of the water concentration because of the faster hydrolysis of MEMO in acidic environment compared to $Si(OEt)_4$. It is rather due to the incorporation of the methacryloxypropylsilyl units in the gel network, which strongly influence the cross-linking by polycondensation due to steric hindrance of the methacrylate group (vide supra) and the smaller number of hydrolyzable OR′ groups.

Micro-Raman spectroscopy shed light on the fundamental chemical processes in another system composed of two precursor silanes. There are three competing reactions in the GLYMO/3-(aminopropyl)triethoxysilane/H_2O system: ring opening of the epoxy group to give a diol, formation of polyethylene units by polymerization, and reaction of both silanes to give β-amino alcohol links. Raman spectroscopy showed that the latter reaction is dominating.[70]

The pH, the concentration of F^- (as the catalyst) and the silane ratio was optimized by light scattering to improve the clarity and structural homogeneity of gels from $Si(OEt)_4/(MeO)_3Si(CH_2)_3NHCH_2CH_2NH_2$ or $(EtO)_3Si(CH_2)_3NH_2$ mixtures.[52]

Analysis of the chemical processes in systems with two different alkoxide precursors and their relation to the nanoscopic structure of the derived materials is already very difficult. With more precursors this task becomes even more complicated. In the present time, an optimization of such multicomponent sol–gel processes is only empirically possible because the fundamentals for a more rational proceeding are still lacking. An example for such an optimization procedure in a ternary system is the preparation of spheres of 0.2–1.5 mm in diameter from the three-component system $Si(OEt)_4/(MeO)_3SiMe/(MeO)_3Si(CH_2)_3NH(CH_2)_2NH_2$ or $(MeO)_3Si(CH_2)_3NH_2$.[71]

Alkoxystannane Derivatives. The sol–gel chemistry of tin alkoxides is only little developed, compared with silicon alkoxides. Structural information on the hydrolysis products of tin alkoxide derivatives $(Am^tO)_3SnR$ with R = *n*-butyl, *n*-butenyl, or *p*-styryl[31] was obtained by ^{119}Sn NMR. In each case tin expands its coordination from 4 in the monomeric precursors to 5 and 6 in the hydrolysis products. Incomplete hydrolysis yielded tin oxo hydroxo clusters. The cluster $[(BuSn)_{12}O_{14}(OH)_6]^{2+}$ was identified by X-ray structure analysis (Figure 8). According to the ^{119}Sn NMR spectrum, the butenyl derivative has the same structure. The cagelike cluster is surrounded by the organic groups, and none of the organic groups R was cleaved during hydrolysis. The covalent bond between tin and carbon allows the formation of inorganic–organic hybrid materials, with the oxo cluster as a nanosized building block. One should bear in mind (also in the following section on metal alkoxide derivatives) that the crystalline compounds are only models for the structural units in (amorphous!) gels.

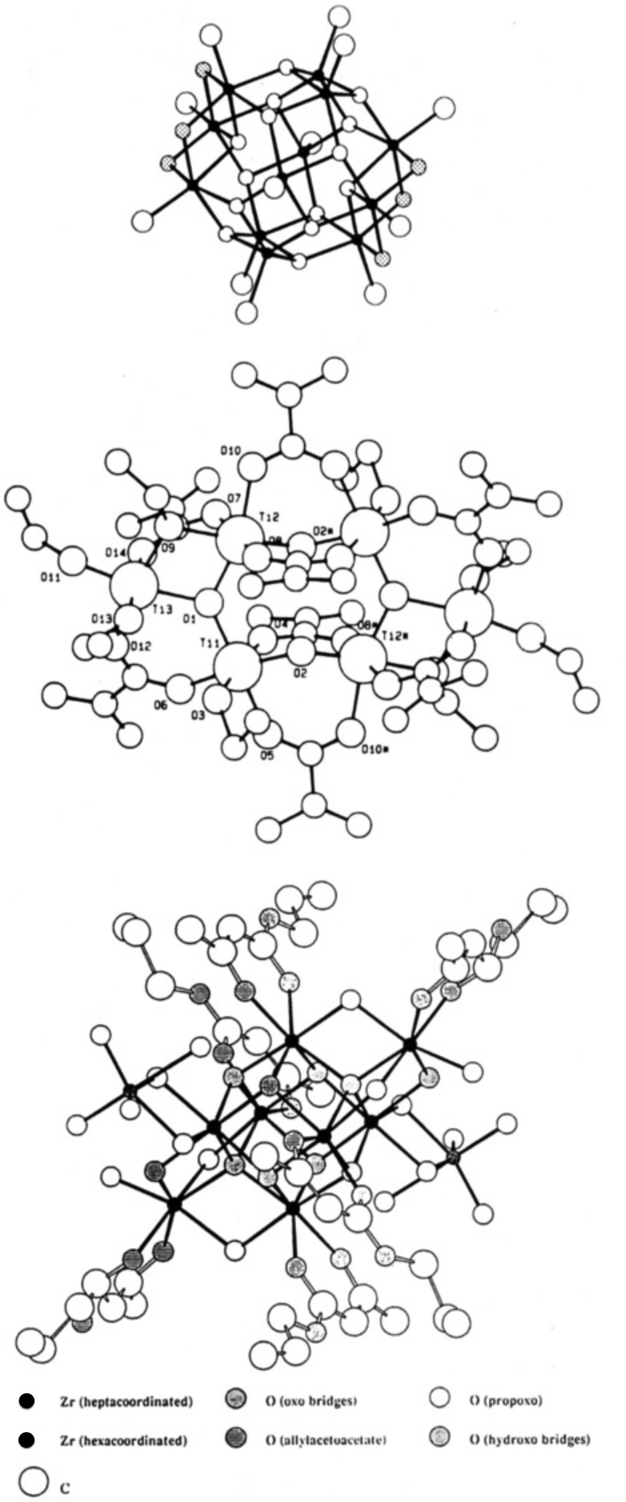

Figure 8. Structures of the primary hydrolysis products $[(BuSn)_{12}O_{14}(OH)_6]^{2+}$ [31] (top) (only the first carbon of the butyl group is drawn), $Ti_6O_4(OR')_8(OMc)_8$,[36] (middle) and $Zr_{10}O_6(OH)_4(OPr)_{18}(allylacetoacetate)_6$[44] (bottom). Reprinted by permission of the Materials Research Society and Kluwer Academic.

As mentioned before, tin alkoxide carboxylates derived from functional carboxylic acids are a still unexplored possibility to anchor functional groups to a stannoxane network. Succinic acid reacts with Sn-

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$(OBu^t)_4$ in a 1:1 ratio by substitution of two equivalents of butanol and formation of a tin alkoxide derivative with a chelating succinate ligand. Upon hydrolysis of $(Bu^tO)_2Sn(OOCCH_2CH_2COO)$ at neutral pH with an excess of water the succinate ligand was retained. Its cleavage was achieved only when 70% nitric acid was added to a suspension of the hydrolysis product $SnO(OOCCH_2CH_2COO)$.[72] Although this behavior may not be typical for simple carboxylic acids, it at least shows that the tin–carboxylate bond can be stabilized by chelation, as previously discussed for metal alkoxide carboxylates.

Metal Alkoxide Derivatives. There are a few X-ray structure analyses of oxo clusters modified by organofunctional chelating ligands. They show that the nature and the structure of the primary hydrolysis products, as in silicon chemistry, is the same with functional or the corresponding nonfunctional organic ligands. Although these results were obtained from crystalline materials, it can be assumed that they also apply to the amorphous state.

The primary hydrolysis products $Ti_6O_4(OR')_8(OAc)_8$ were obtained by partial hydrolysis of acetic acid modified $Ti(OR')_4$ (R′ = Et, Bu^n, Pr^i).[73] The structurally same type of compound was isolated from the reaction of $Ti(OEt)_4$ with methacrylic acid (Figure 8).[36] The carboxylate groups in each compound are exclusively in a bridging mode. This places the methacrylate units at the outside of the cluster and makes them fully accessible for later chemical reactions. Hydrolysis of the bismethacrylate compound $Zr(OPr^n)_2(OMc)_2$ gave $ZrO(OMc)_2$, a polymeric compound already known with other carboxylate ligands. The monomethacrylate $Zr(OPr^n)_3(OMc)$ only reacted with 1.33 equiv of water to yield a compound of the composition $Zr_3O_3(OH)(OPr^n)_2(OMc)_3$ with an unknown structure.[36]

In these examples, the metal:methacrylate ratio was retained during hydrolysis. However, simple carboxylates are rather weak ligands and are largely removed upon *extended* hydrolysis.[74] A large amount of organic groups is then lost. This situation is considerably improved by using α-hydroxy or α-amino acids.[42,43] If a *permanent* organic modification of metal oxides is intended, i.e., if the carboxylates are not just used to control the reactivity of the alkoxides or the morphology of the derived oxides, the use of such acids is strongly adviced (see precursors sections).

Localization of the (functional) organic groups at the periphery of oxo clusters is also a common feature of the hydrolysis products of β-diketonate-modified metal alkoxides. Structurally characterized examples are $Ti_{18}O_{22}(OBu)_{26}(acac)_2$ (acac = acetylacetonate), formed by partial hydrolysis of a solution of $Ti(OBu^n)_4$ in the presence of 0.1 mol equiv of acetylacetone,[75] $Ce_6O_4(OH)_4(acac)_{12}$, the hydrolysis product of $[Ce(OPr^i)_2(acac)_2]_2$,[76] or $Zr_4O(OPr)_{10}(acac)_4$, the primary hydrolysis product of $[Zr(OPr)_3(acac)]_2$.[77] A smaller metal:β-diketone ratio results in the formation of larger clusters. The decameric cluster $Zr_{10}O_6(OH)_4(OPr)_{18}(allylacetoacetate)_6$ (Figure 8) carrying functional organic ligands, was obtained from hydrolysis of a solution of $Zr(OPr)_4$ and 0.6 equiv of allyl acetoacetone.[44]

Hydrolysis experiments of methacryloxyethyl acetoacetate modified $Zr(OPr)_4$ (**24**) (Figure 7) with different Zr:β-diketonate ratios showed that this is the key parameter that controls the structure and texture of the derived organic–inorganic hybrid materials. A careful adjustment of this ratio led to zirconium oxo species with more or less open structures.[45]

These and related examples can be generalized as follows:[44]

(i) In all examples where the primary hydrolysis products were identified, the β-diketonate ligands were completely retained during hydrolysis, i.e., the metal–diketonate bond is rather hydrolytically stable. However, there is one report that part of the allyl acetoacetate ligands was lost during hydrolysis of Zr– and Al–alkoxide derivatives.[46]

(ii) The β-diketonate ligands cover the oxo clusters formed during hydrolysis. They are terminating ligands preventing further condensation. The size of the oxo clusters can therefore be tailored by the metal:β-diketone ratio.

(iii) The β-diketone ligands can additionally be used to carry an organic functionality.

Another approach for the preparation of organofunctional capped metal oxide clusters is the organic modification of preformed oxo clusters or colloids. The principle was very impressively demonstrated by Judeinstein, who prepared organically modified polyoxotungstates of the composition $[W_{11}SiO_{35}(Si_2O_5R'_2)]^{4-}$ by reaction of organofunctional alkoxy- or chlorosilanes $R'SiX_3$ (R′ = vinyl, allyl, 3-methacryloxypropyl or styryl) with $K_4[W_{11}SiO_{39}]$.[78]

Materials Syntheses

In this section representative materials will be discussed, which have been developed by sol–gel processing of organofunctional metal alkoxides as precursors. There are already so many examples in the scientific and patent literature that it is impossible to discuss or even mention all of them. We rather focus on some general aspects of preparation and the scope of currently feasible applications.

1. Inorganic–Organic Hybrid Polymers. Inorganic–organic hybrid polymers, mostly used as coatings for different purposes but recently also as bulk materials, constitute the technically most advanced type of applications in this field. They consist of a dual polymer network, in which cluster- or polymer-type inorganic structures are linked by organic groups or polymer fragments. Such materials combine to some extent the properties of organic polymers with those of metal oxides.

Excluding materials in which the organic and inorganic polymer units are not covalently bonded together

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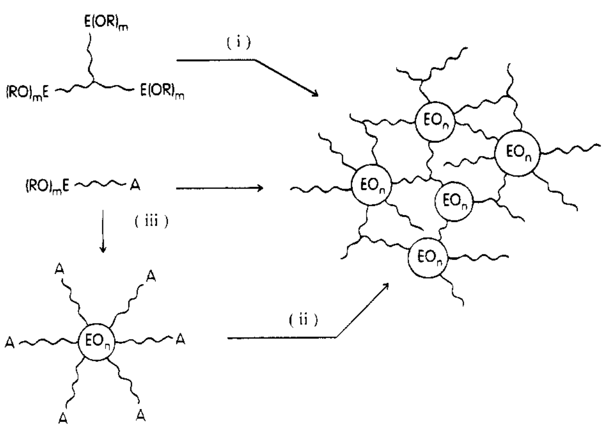
Scheme 1. Sketch of the Different Possibilities of Preparing Organic–Inorganic Hybrid Polymers from Organofunctional Alkoxides[a]



[a] The circles represent the inorganic substructure (which can be cluster- or polymer-like), the sinuous lines the organic substructure. The connectivity is arbitraryly drawn.

(see Introduction), there are three principal approaches and several options to prepare inorganic–organic hybrid polymers from organofunctional alkoxide precursors and related compounds (Scheme 1).

(i) Formation of the hybrid polymers from compounds of the type $[(R'O)_nE]_xY$, in which Y is an organic group or a macromolecule linking two ($x = 2$) or more ($x > 2$) $E(OR')_n$ units. The structure of the preformed organic building blocks Y is retained in the final material. The organic substructures are cross-linked by hydrolysis and condensation of the $E(OR')_n$ units and, optionally, added $E(OR')_m$, i.e., by formation of the inorganic network.

(ii) Formation of the hybrid polymers from functionalized inorganic building blocks (oxo clusters or colloidal particles). The inorganic structures are cross-linked by reactions of the organic functions.

(iii) Formation of the hybrid polymers from the bifunctional molecular precursors $(R'O)_nE{-}X{-}A$ (**1**) bearing an inorganic ($(R'O)_nE$) and an organic functionality (A). The latter must be capable of undergoing polymerization reactions (see Figure 1 for some examples). In the vast majority of examples these precursors are first reacted with water, and after sol–gel processing, the organic groups A attached to the inorganic building blocks are polymerized or cross-linked to form the organic network. Although the order of forming both networks is the same as in the second approach, there is a procedural difference, as the inorganic building blocks are formed only in situ.

There are several options for all approaches by which the composition, structure and properties of the materials can be varied:

(i) Cocondensation of several alkoxides (either binary alkoxides, $E(OR)_m$, or different organically or organofunctionally substituted alkoxides); alkoxides of different elements can be combined.

(ii) Organic copolymerization with organic monomers, macromolecules, or a reactive substituent originating from another organofunctional alkoxide.

(iii) Choice of thermal or photochemical polymerization.

With these options, there are many possibilities to chemically modify organic–inorganic hybrid polymers and thus to tailor their macroscopic properties. Not only the kind and connectivity of both the organic and inorganic building blocks can be varied (including combinations of different groupings in both parts), but also their ratio.

The following selected examples shall illustrate the potential of the different approaches and options for the sol–gel synthesis of hybrid polymers.

$(R'O)_nE$-terminated organic (macro)molecules $[(R'O)_nE]_xY$ as Precursors. The nature and dimensionality of the organic groupings Y linking the $(R'O)_nE$ groups can be quite different. It can range from short links (for example, very interesting microporous, high-surface-area materials were made from alkenyl-, alkinyl-, arylene-, or oligo(arylene)-bridged alkoxysilanes with different structural features of the group Y[79,80]) to shorter or longer organic macromolecules. Hybrid polymers with highly branched organic cores were recently prepared by sol–gel processing of dendritic organo(alkoxy)silanes.[81] Non-silicate hybrid polymers have rarely been prepared by this route. As mentioned in the Introduction, this approach to the synthesis of organic–inorganic hybrid polymers was recently reviewed[2a,b] and will therefore not be further discussed here.

Organofunctional Inorganic Clusters as Precursors. Molecular oxo clusters of various sizes are available for many elements. However, their modification by organofunctional groups is not trivial. Therefore, only few materials have been prepared by this route. Although metal alkoxides are not necessarily involved, some aspects will nevertheless be discussed because of their relevance to sol–gel chemistry. Since the inorganic building blocks formed during sol–gel processing of metal alkoxides often (depending on the reaction conditions) are like oxide clusters or colloidal oxide particles, the chemistry of defined clusters with organofunctional groups models the situation during sol–gel processing of the bifunctional molecular precursors **1** (Scheme 1).

One of the best defined type of clusters in *silicon* chemistry is that of the octameric spherosilicates $(ROSiO_{3/2})_8$ or silsesquioxanes $(RSiO_{3/2})_8$. They have a ("double four ring") structure with the silicon atoms being located at the corners of a cube and the groups OR or R sticking out of the cluster. Clusters with various groups OR or R have been synthesized[82,83] and allow the deliberate preparation of hybrid polymers with very defined structures.[83] The cubic silsesquioxanes are structurally related to the oligomeric intermediates formed during sol–gel processing of the alkoxysilanes **2** (see Hydrolysis and Condensation section). The organic cross-linking of the octameric species models, in some way, the synthesis of hybrid polymers starting from $(R'O)_3Si{-}X{-}A$ (**2**).

Coupling between the $(ROSiO_{3/2})_8$ building blocks was, for instance, done for $R = SiMe_2H$ by hydrosilylation

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with vinyl-substituted siloxanes[85] or, vice versa, for R = $SiMe_2CH{=}CH_2$ by hydrosilylation with hydrogenosiloxanes.[85,86] Microporous, hydrophobic hybrid polymers with an ordered silicate substructure were obtained by direct coupling of vinyl- and hydrogenoterminated spherosiloxane units.[86] The chain length connecting the spherosiloxane units was found to be very critical with regard to the porosity of the hybrid material. Porous materials were obtained only with O–Si–C–C–Si–O links, while shorter or longer links resulted in materials with low surface areas.[83,84] Recently, heterocoupling between the siloxane clusters with R = $SiMe_2H$ and allyl acetoacetate-modified aluminum and zirconium alkoxides was also reported.[46,83]

Hybrid polymers with *tin oxide* clusters as the inorganic building block were obtained by AIBN promoted organic polymerization of the butenyl groups of $[(\text{butenyl}-Sn)_{12}O_{14}(OH)_6]^{2+}$.[31] Quasi-elastic light scattering indicated that the hydrodynamic diameter of the particles increased from 1 to 6 nm by the polymerization. The small size of the organically cross-linked particles was attributed to the low reactivity of the butenyl groups. In another strategy $[(BuSn)_{12}O_{14}(OH)_6]^{2+}$ clusters were transformed to hybrid polymers by cross-linking with dicarboxylic acids, such as adipic, dodecanoic, or terephthalic acid.[87]

The organic functions of the organofunctional polyoxo*tungstates* $[W_{11}SiO_{35}(Si_2O_5R'_2)]^{4-}$ (R' = vinyl, allyl, 3-methacryloxypropyl, or styryl) were polymerized in the presence of a radical initiator. The optical and electrochemical properties of the polyoxotungstates were not changed by the organic cross-linking. Therefore, the transparent thin films obtained on different kind of substrates turned blue on UV irradiation or electrochemical reduction.[78]

The polymerization of oxide (colloid) particles surface-capped with functional organic groups is a very promising but virtually unexplored strategy for the preparation of organic–inorganic hybrid polymers. For instance, hybrid polymers with *titanate* building blocks were obtained by prehydrolysis of $Ti(OBu)_4$ with only 1 equiv of water (presumably forming titanate clusters or oligomers), followed by complexation with unsaturated organic acids, such as cinnamic acid. Copolymerization with styrene was then performed to give transparent brown, water-stable polymers.[88] Core-shell materials with a titania core and a polymer shell were made by grafting $Ti(OPr^i)_2(OOC-C_{17}H_{35})$(methacrylate) to the surface of submicron TiO_2 particles, followed by emulsion polymerization with methyl methacrylate.[89]

Hybrid Polymers from Single-Component Alkoxide Precursors. Inorganic–organic hybrid polymers are prepared from organofunctional alkoxides $(R'O)_yE-X-A$ (**1**, see Figure 1 for some suitable examples) in a two-step procedure. During sol–gel processing the inorganic network develops to which the functional organic groups are attached. While gelation occurs, the materials can be moulded or applied as coatings with conventional coating techniques (spray, dip, spin-on coating, etc.). Following the sol–gel step, the organic groups are thermally or photochemically polymerized or crosslinked to form the organic network. This results in a permanent hardening of the materials. Whether thermal or photochemical curing is more suitable depends on the chemical system and the kind of application. Photochemical curing is preferred for coatings of polymers with low thermal stability or for applications in which very rapid curing is essential.

For example, a highly flexible, nevertheless abrasion resistant coating for polyethyleneterephthalate or polycarbonate was obtained from GLYMO, with 1-methylimidazol as the catalyst. 1-Methylimidazol acts as a sol–gel catalyst at room temperature, and in the second step of the materials synthesis as an initiator for the epoxide polymerization at a higher temperature.[59,66] Due to the different reaction modes of the epoxide group (vide supra) sol–gel processing of GLYMO can, of course, also be run in a way to deliberately produce diol units. Antifogging coatings on glass were developed by this approach.[90]

However, only a few materials developments are based on a single precursor because precursor mixtures usually allow a better tailoring of the materials properties. To avoid the potential problems associated with precursor mixtures (see Hydrolysis and Condensation section), the acrylate-substituted alkoxysilanes **3** and **4** (Figure 1) and related compounds were developed. Although they are single precursors, the macroscopic properties of the derived hybrid materials can easily be modulated by varying the structure of the organic spacer between the (meth)acrylate group(s) and the $(R'O)_3Si$ group, as well as the number of (meth)acrylate groups available for polymerization (i.e., the degree of organic cross-linking).[6-8] The Young's modulus of the photochemical cross-linked materials was adjustable between less than 1 and 4000 MPa, and the thermal expansion coefficient between 50×10^{-6} K^{-1} and more than 250×10^{-6} K^{-1}, just by varying the organic structures.[8] Some other advantages of these hybrid polymers, such as low shrinkage, high flexural strength, and the low water adsorption, led to their application as dental filling materials (combined with some inorganic fillers).[8] The refractive index is another physical parameter that was varied by modification of the organic structures of the precursors. Lenses made from the acrylate(alkoxy)silanes as precursors had comparable optical properties and densities than those made from purely organic polymers. However, their abrasion resistance was distinctly better.[7] The materials made from these single-precursor silanes very impressively illustrate that tailoring of materials properties is possible by tailoring the organic and inorganic building blocks.

Only few non-silicate materials were synthesized from organofunctional single-component alkoxides. One example is the preparation of photochromic coatings from $(Bu^nO)_3Ti$(allyl acetoacetate).[35]

Co-Condensation of Organofunctional Alkoxides with Binary Alkoxides. The general idea behind the prepa-

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ration of inorganic–organic hybrid polymers from organofunctional alkoxides **1** is the notion of getting materials with properties between those of purely organic polymers and purely inorganic materials. A steady change of materials properties between the two extremes is possible only if the ratio between the organic and inorganic building blocks is adjustable. The inorganic portion in the final materials can be increased by co-condensation of the organofunctional alkoxides **1** with binary alkoxides $E(OR)_m$. Employing alkoxides of different elements E additionally allows some variation of the chemical nature of the inorganic building blocks and of the materials properties originating from them.

The first commercial application of inorganic–organic hybrid polymers may illustrate this point. A scratch-resistant, transparent hard coating for polycarbonate lenses was developed from mixtures of GLYMO, $Si(OMe)_4$, and $E(OR)_m$ ($E(OR)_m = Ti(OEt)_4$, $Zr(OPr)_4$, or $Al(OR)_3$, respectively).[91] The binary alkoxides have two functions: they build up the inorganic substructure of the final material, and the non-silicon alkoxides $E(OR)_m$ already at room temperature catalyze the polymerization of the epoxide groups. $Zr(OPr)_4$ is a more effective catalyst than $Ti(OEt)_4$.[64] A prepolymer of low viscosity was first obtained by very slow addition of $^1/_{16}$ to $^3/_{16}$ of the stoichiometric amount of water and HCl as the catalyst to the mixture of alkoxides. In the prepolymer the alkoxide moieties were partially hydrolyzed and condensed, and partial polymerization of the expoxide groups had taken place. After addition of the rest of water and, optionally, dilution with butanol, the mixtures were applied to the plastic lenses by the spin-on coating technique. The coatings were then thermally cured.[91] The viscosity of the prepolymers increased steadily, mainly because of progressive polymerization of the epoxide groups.[64] Coating is possible only within a certain viscosity range. Since the ratio of the alkoxides in the GLYMO/$Si(OMe)_4$/$E(OR)_m$ mixtures influences both the rate of the polymerization reaction (and thus the viscosity increase) and the macroscopic properties of the coatings,[65,91] these parameters have to be carefully balanced.

With the notion in mind that the hardness and abrasion resistance of such hybrid materials originates from the inorganic building blocks, the dimension of the inorganic phase and thus the hardness of coatings was further increased by incorporating inorganic nanoparticles, such as boehmite, zirconia, titania, or alumina.[90]

In a non-silicate system the effect of "diluting" an organofunctional alkoxide with the unsubstituted parent alkoxide was studied for methacryloxyethyl acetoacetate modified $Zr(OPr)_4$ with different complexation ratios (i.e., different ratios of, presumably, complex **24** (Figure 7) and unreacted $Zr(OPr)_4$). Hybrid polymers were obtained after simultaneous sol–gel processing and radical polymerization of the unsaturated organic groups. Spectroscopic data indicated that a high Zr:β-diketonate ratio led to large zirconate building blocks connected by short polymer chains, while with a low Zr:β-diketonate ratio small oxide clusters are connected by long polymer chains (Figure 9). The ratio between substituted and unsubstituted alkoxides thus controls the structure and texture of the derived organic–inorganic hybrid materials.[45]

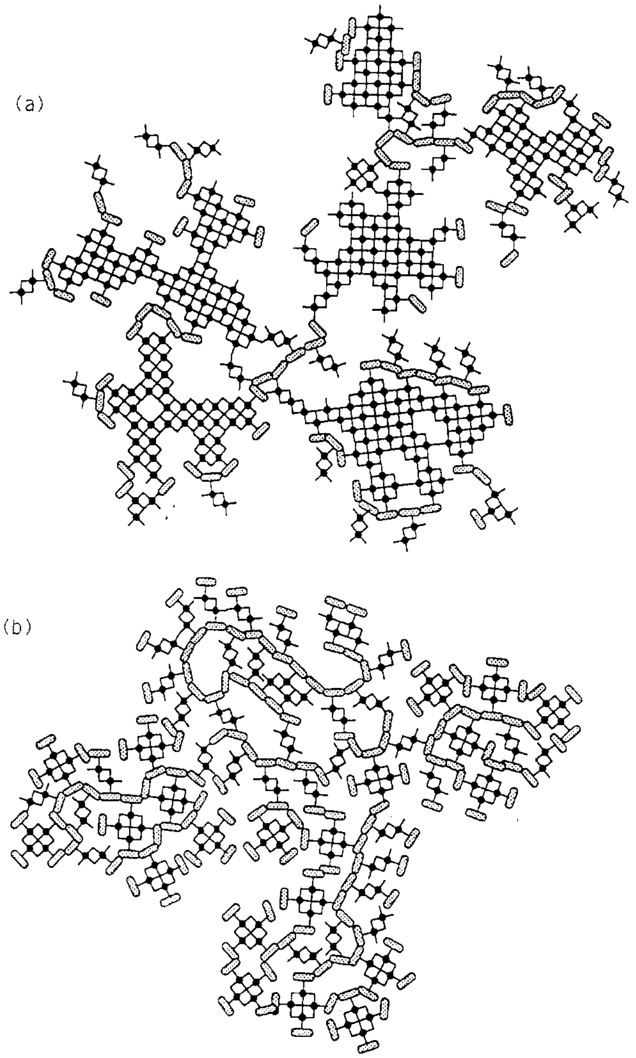

Figure 9. Cartoon of hybrid organic–inorganic polymers obtained from methacryloxyethyl acetoacetate modified $Zr(OPr)_4$ with different complexation ratios. (a) High Zr/β-diketonate ratio; (b) low Zr/β-diketonate ratio. Reproduced by permission of Elsevier Publishing, from ref 45.

Copolymerization with Organic (Macro-)Monomers. The dimension of the organic structures and the degree of organic cross-linking in inorganic–organic hybrid polymers can be increased by copolymerizing the reactive groups of the organofunctional alkoxide **1** with organic monomers or small oligomers. When hybrid polymers are prepared from organofunctional alkoxides **1**, the cross-linking of all available organic groups is often difficult, probably for sterical reasons. For example, quantitative analysis of the photochemical polymerization reaction in an aged gel, obtained from a 1:1 mixture of MEMO and $Si(OEt)_4$, revealed that about 20% of the initial double bonds remained unreacted. However, addition of 2 equiv of methyl methacrylate (MMA) led to the complete polymerization of the methacrylate groups from both sources (MEMO and MMA) upon UV irradiation.[61]

The development of the hybrid structure in the MEMO/$Si(OEt)_4$/MMA system[92] was investigated by differential scanning calorimetry and mechanical spec-

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troscopy.[93] In a related study with a hybrid polymer obtained from MEMO and propyl methacrylate, relaxation of the polymer in the range 100−400 K was attributed to the large-scale motion of the polyacrylate chains, the rotation of the ester groups, and configurational modification of the propyl groups.[94]

The general idea behind the copolymerization of MEMO with acrylate monomers can, of course, also be applied to other reactive organic groups. For example, abrasion-resistant transparent coatings were prepared by crosslinking the epoxy groups of GLYMO with cycloaliphatic diepoxide monomers. The diepoxide and a cationic initiator were added to a sol obtained by acid-catalyzed sol−gel processing of a GLYMO/$Si(OEt)_4$ mixture. After coating on glass or polyethylene terephthalate, the films were dried and then UV cured. Mechanical properties of the films were found to be dependent on type and amount of diepoxide. Films prepared without the diepoxide were brittle, while those with the diepoxide were flexible.[95] There were two noteworthy findings about the epoxide polymerization: A tighter silicate network retarded the polymerization, probably by restricting the diepoxide mobility. Second, after triggering the cationic polymerization process by UV light, it continued in the absence of light until it was limited by severe diffusion limitations.[95]

Recently, electrically conducting black hybrid polymers were prepared from *N*-(3-(trimethoxysilyl)propyl)-pyrrole which, after sol−gel processing (with or without $Si(OEt)_4$), was oxidatively copolymerized with pyrrole.[96]

Hybrid Polymers from Two Different Organofunctional Alkoxide Precursors. The use of two different organofunctional alkoxides can serve different purposes: (i) new ways for the cross-linking of the inorganic building blocks, (ii) modulation of the organic substructure, or (iii) linking chemically different inorganic building blocks, as illustrated by the following examples.

A coating system for the mechanical protection of plastics, particularly poly(methyl methacrylate), was obtained from $(MeO)_3Si{-}CH{=}CH_2$ (VTMS) and $(MeO)_3Si(CH_2)_3SH$ (MPTMS). Two cross-linking modes of the organic groups are possible upon UV irradiation: vinyl groups may react with themselves to yield polymethylene links between silicon atoms, or the −SH function may be added to a vinyl group to give $-(CH_2)_2{-}S{-}(CH_2)_3-$ links. When a 9:1 molar ratio of VTMS and MPTMS was employed, vinyl polymerization prevailed. Starting with equal amounts of the two silanes, the thiol addition reaction was dominating during the photochemical curing. In the latter case, the coatings were then cured in about half the time because this reaction is faster than vinyl polymerization. Owing to the different chain lengths of the alternative links, the flexibility of the coating can be varied by the ratio of the starting compounds.[66]

Combination of the silanes **3a** and **4** (Figure 1) allowed the development of fast-curing primary and secondary coatings with very good adhesion to optical glass fibres. UV curing is possible in less than 0.1 s, even on a technical scale. The different modulus of elasticity and scratch resistance required for primary or secondary coatings was adjusted by the ratio of the two silanes.[7]

A scratch-resistant coating material for polycarbonate (for instance, compact disks) was developed by combination of $(Pr^nO)_3Zr$(methacrylate) or $(Pr^nO)_2Zr$(methacrylate)$_2$ with MEMO. MEMO was prehydrolyzed with 1.5 mol equiv of water. Before use, 0.1−0.2 mol equiv of one of the methacrylate-substituted zirconium alkoxides were added, and then the coatings were thermally or photochemically cured.[60,66] Transparent monoliths[97] and materials for optical and microoptical applications[62] were also prepared from the $(Pr^nO)_3Zr$(methacrylate)/MEMO combination.

Materials Tailoring by Multicomponent Systems. In the previous paragraphs the different options for the preparation of sol−gel-derived organic−inorganic hybrid polymers were demonstrated. We now want to discuss a few selected materials where a combination of these options was used to tailor materials properties. Although sometimes difficult to control, multicomponent systems allow to some extent the fine-tuning of macroscopic materials properties, due to the specific functions and properties of each component.

One of the earliest developments of organic−inorganic hybrid polymers may illustrate this point. Major requirement for contact lenses are a good wettability and O_2 permeability, and sufficient scratch resistance, flexibility, and optical properties. Silicone materials do not meet these requirements because they are hydrophobic. Therefore, GLYMO was prehydrolyzed, and then hydrophilic diol units were generated by controlled hydrolytic epoxide ring opening. $Ti(OR')_4$ was added to improve the mechanical properties of the obtained materials and to decrease shrinkage. At this stage of the development the materials had sufficient hydrophilicity and O_2 permeability, but were to brittle to be machined. Therefore, MEMO and methyl methacrylate were added to generate a flexible polymethacrylate substructure by thermal polymerization. The resulting materials then exhibited all the required properties.[92,98]

A commercially available scratch- and abrasion-resistant, corrosion-preventing coating system for brass is another example for this deliberate tailoring of materials properties by combination of precursors with different functions. The three components from which it is composed have different functions: GLYMO allows the formation of flexible poly(ethylene oxide) chains during thermal curing. $Al(OBu^s)_3$ is the source for alumina building blocks providing hardness, and an alkyltrimethoxysilane modifies the inorganic network and reduces brittleness of the coating. Addition of a defined amount of water to an alcoholic solution of the three components gave a transparent lacquer, which was then electrostatically sprayed to the brass items and cured at 130 °C. Adhesion to the metal surface was very good, even after weathering, due to the covalent bonding between the metal surface and the coating.[99]

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A hybrid polymer with potential application for ultrafiltration and reverse osmosis membranes was developed from a mixture of four silanes with different functions. The first silane was prepared by reaction of (3-aminopropyl)triethoxysilane with phthalic anhydride or pyromellitic dianhydride and provided the hydrophilic function in the polymer. MEMO was added for the organic crosslinking of the hybrid polymer, and Ti(OPr^i)$_4$ to provide a higher mechanical resistance and a higher thermal stability. Finally, (MeO)$_3$SiMe was used to obtain silicone-like surface properties of the obtained material.[100]

Very versatile hybrid materials for applications in microsystem technologies were prepared from a mixture of MEMO, GLYMO, Si(OEt)$_4$, and VTMS or diphenylsilane diol.[101] They show good to very good adhesion to a variety of substrates, such as steel, copper, aluminum, silicon, glass, alumina, polyimide, or polyesters. Water vapour permeation rates are low and the electrical data very good. These materials were used, inter alia, for passivation and encapsulation of electrical components, as protective coatings for thin-film capacitors,[102] or as patternable coatings. Patterning is possible by different techniques, such as laser writing, proximity printing, contact printing, embossing, laser ablation, or replication technology. The photolithographic structuring procedure exemplarily illustrates the functions of the different precursors. During sol–gel processing the inorganic network is formed. The thus-obtained coating lacquer was applied to the substrates by standard techniques. By structuring UV irradiation (masks or laser writing) the methacrylate groups of MEMO were polymerized. The nonexposed parts of the coating was then dissolved by a developer solution. Finally, the structured coating was thermally cured by polymerization of the epoxy groups of GLYMO. Very high aspect ratios were obtained by laser writing or mask aligning in the proximity mode.[101]

The idea of incorporating complementary functions to the hybrid polymers by an additional, organofunctional precursor is demonstrated by the following examples. The properties of the above mentioned scratch-resistant coating material for polycarbonate, obtained by the combination of MEMO and methacrylate-modified Zr(OPr)$_4$, were supplemented by fluorinated alkoxysilanes of the type (R′O)$_3$Si(CH$_2$)$_n$(CF$_2$)$_m$CF$_3$. Addition of this alkoxide resulted in low-energy coatings with antisoiling properties.[90] Functional coatings on glass were varied by the same approach. Such coatings with good long-term adhesion to glass, scratch and abrasion resistance, and stability against weathering and corrosive delamination were prepared from MEMO, (EtO)$_3$SiPh, and Al(OBu^s)$_3$ for photochemical curing. Thermally curable coatings were obtained when GLYMO was used instead of MEMO. The polarity of the surface was varied by addition of tridecafluorooctyltrimethoxysilane (increased hydrophobicity) or *N*-((2-aminoethyl)(3-aminopropyl))trimethoxysilane (increased hydrophilicity), respectively.[103] These hybrid polymers are also very suitable hosts for a variety of organic dyes. They can be used for the low-temperature coloring of glass, both for decorative, optical, and optoelectronical applications.[103]

2. Solid Electrolytes. Polymeric ion conductors are prepared by dissolving Li salts or strong acids in a polymer host matrix. Conductivity of these materials is often limited by partial crystallization of the polymers. This problem was overcome by incorporating the Li$^+$-solvating polymer in sol–gel-derived amorphous hybrid polymer networks. MEMO and GLYMO were hydrolyzed, and then ethyleneglycol diglycidyl ether was added. Methylimidazole was used both as a catalyst for the sol–gel step and the copolymerization of the epoxide groups of GLYMO and the diglycidyl ether. Due to the presence of polyethylene oxide units, LiClO$_4$ is easily dissolved in the hybrid polymer, which was cured as described above. The obtained material is amorphous and can be applied as coatings or in bulk. The ion conductivity was 10^{-5} Ω^{-1} cm^{-1} at 25 °C and 10^{-3} Ω^{-1} cm^{-1} at 125 °C.[104] A modification of the above-mentioned material obtained from sulfonated MEMO or allyl(trimethoxy)silane also showed Li$^+$ conductivity.[105]

As an alternative to organic polymers, aminoalkyl-substituted siloxanes made by sol–gel processing of (MeO)$_3$Si(CH$_2$)$_n$NR$_2$ (for example, $n = 3$; NR$_2$ = NH$_2$, NH(CH$_2$)$_2$NH$_2$, NH(CH$_2$)$_2$NH(CH$_2$)$_2$NH$_2$) were investigated. The obtained transparent, amorphous films are stable in air up to 220 °C. Doping with CF$_3$SO$_3$H resulted in proton conductivities up to 3×10^{-5} Ω^{-1} cm^{-1} at 25 °C and 10^{-2} Ω^{-1} cm^{-1} at 120 °C.[106]

Only cation conductivity is desired for many applications. An improved type of protonic electrolyte was derived by grafting sulfonate anions to the phenyl groups of poly(benzyl)siloxane. This was done by treating the material with chlorosulfonic acid after sol–gel processing of benzyl(trimethoxy)silane. The plasticity of this material had to be improved for applications as membranes in low-temperature fuel cells. This was achieved by co-condensation of (EtO)$_3$SiCH$_2$Ph, (EtO)$_3$SiC$_6$H$_{13}$, and (EtO)$_3$SiH. After sol–gel processing, the polymer was sulfonated as above and organically cross-linked by hydrosilylation of the Si–H groups with divinylbenzene. Flexible membranes of about 100 μm thickness were obtained with an ac conductivity of 1.6×10^{-2} Ω^{-1} at 25 °C.[107] In a related approach, the polymeric hybrid polymer was prepared by sol–gel processing of MEMO (or allyl(trimethoxy)silane), GLYMO, and Si(OEt)$_4$. The sulfonyl groups were introduced by adding variable amounts of sulfonated MEMO or allyl(trimethoxy)silane. Curing of the polymers was done as described before.[105]

3. Materials Containing Covalently Bonded Organic Dyes. The possibility to tailor the chemical

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and physical properties of sol−gel materials, their excellent optical quality, their low preparation temperatures, and their easy deposition as coatings makes them ideally suited for optical applications. Extensive work on dyes *embedded* in sol−gel materials has been performed in the past 10 years and was reviewed elsewhere.[108] In a few cases, inorganic−organic hybrid sol−gel polymers were used as a host for dyes. The above-mentioned hybrid polymer obtained from the GLYMO and $Al(OBu^s)_3$ was recently shown to be a very interesting host for laser dyes. By doping with $YbCl_3$ and dihydroxyanthraquinone (DAQ) or oxazine 170 (9-(ethylamino)-5-(ethylimino)-10-methyl-5*H*-benzo(*a*)-phenoxazonium perchlorate) materials for optical data storage in the frequence domain were obtained. This method allows the frequency-selective addressing of dye molecules embedded in an amorphous matrix. To get high data-storage densities, line broadening caused by an interaction between the laser dye and the host has to be minimized. Doping of the sol−gel hybrid polymer was easily achieved by adding the dopants to the sol. The dyes are trapped in the hybrid network just by drying the material. Surprisingly narrow spectral holes in the absorption bands of the dyes were generated by photophysical or photochemical hole-burning at 2−50 K. For the dihydroxyanthraquinone/$YbCl_3$ complex the hole width was about one-fifth of that found in a ethanol/methanol glass matrix and almost 1 order of magnitude smaller than that obtained with DAQ or its derivatives in organic polymers or amorphous inorganic matrices.[109]

According to the scope of the present article, we will now discuss only those materials having the dye molecules chemically *bonded* to the oxide matrix. This comparatively recent approach is still in development.

The chemical bonding of dye molecules to the oxide matrix requires its modification by $E(OR')_3$ (mostly $Si(OR')_3$) containing groups (see Figure 2). This is mostly not a trivial task, since the chromophor has to remain undisturbed. Embedding organic dye molecules in sol−gel materials without a chemical link is definitely easier. Therefore, the chemical linking of the dye molecules is only worthwhile if it results in a substantially better performance of the resulting materials.

There are several potential benefits:

(i) The dye concentration in the final material can be considerably increased. For example, coloration of glass by anthraquinone or naphthoquinone doped sols is not possible, because of their low solubility. This was not a problem when $(EtO)_3Si$-substituted phenoxazinium and phenazinium dyes were used.[19] It was demonstrated for several types of $(R'O)_3Si$-functionalized NLO dyes that the chemical bonding to the oxide network allowed high dye concentrations without any crystallization occuring.[11,12,15,110−112]

(ii) Leaching of the dye is prevented by covalent bonding to the sol−gel matrix. For example, a $(MeO)_3Si$-substituted rhodamine 110 derivative was prepared by coupling the dye molecule with GLYMO. When rhodamine 110 was embedded only in a sol−gel-derived silica matrix, leaching was a severe problem. When the dye was covalently bonded to the matrix, no leaching was observed. Furthermore, a higher concentration of the dye was achieved.[113]

(iii) The incorporation of NLO dyes in various organic polymer guest systems showed that chemical bonding to the polymer provides for better stability of the nonlinearity after alignment than physical doping.[114] Glasslike sol−gel matrixes appear to be even more suitable guests than organic polymers. Therefore, most work on covalently bonded dye molecules in sol−gel matrixes was done with NLO chromophores.

Noncentrosymmetric alignment of the chromophores inside sol−gel matrixes to achieve second-order nonlinearities was possible by corona poling, despite the more ionic character of sol−gel matrixes compared with classical polymers. Transparent films with large coefficients for second harmonic generation (SHG) were obtained.

The effect of binding the dye to the oxide network was studied by preparing poled and cured films either by chemical binding of **6b** (Figure 2) to a phenylsiloxane polymer or by incorporating the NLO dye disperse red 1 in the same matrix without chemical bonding. The former system had a much better stability. This was, inter alia, attributed to restriction of the molecular motion of the segments, due to the bonding between the chromophore and the polysiloxane.[15] A similar observation was made when the stability of a sol−gel-derived TiO_2 film doped with 4-(2-(4-hydroxyphenyl)ethenyl)-*N*-methylpyridinium iodide and a film prepared by sol−gel processing of the corresponding $(MeO)_3Si$-substituted derivative **7b** and $Ti(OPr^i)_4$ was compared.[17] The effect of covalently bonding the dye molecule to the matrix was also probed by the trans−cis−trans isomerization of azo compounds, which results in the reorientation of the dipole moment of the active component. High values of birefringence were only observed when the dye was covalently bonded to the silicate matrix (sol−gel processing of **6** or related compounds and $Si(OEt)_4$). A large part of birefringence remained after the optical pump had been switched off.[11] Somewhat contradictory results were obtained when the fluorescent dye pyrene or its covalently bound derivative **8** was included in glasses or films prepared by fast sol−gel reaction of $RSi(OMe)_3$ (R = alkyl, phenyl). The fluorescence characteristics showed that the chromophores were not aggregated and well dispersed throughout the product matrix. However, covalent attachment of the chromophore did not result in any change in rotational or diffusional mobility. The emission anisotropies for glassy films containing pyrene or **8** were virtually identical.[18]

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The relaxation behavior of NLO chromophores strongly depends on the rigidity of the matrix, which is influenced by the processing conditions and their composition.[115] The optical response of films made from **7a** and $Si(OEt)_4$ was found to be strongly dependent on the poling voltage, the poling temperature, the substrate resistivity, and the extent of polymerization. The sol derived from only **7a** was mainly composed of dimeric species and linear chains with no cross-links. This resulted in poor thermal stability of the SHG signal. Films made from **7a**/$Si(OEt)_4$ mixtures had a better stability but were still not satisfactory because the degree of cross-linking was limited.[116]

One approach to solve this problem was the use of the inorganic–organic hybrid polymers discussed in the previous section as the matrix materials. They can be hardened by organic and inorganic cross-linking after poling. The azo dye 4-nitro-4′-((trimethoxysilyl)propoxy)azobenzene was added to a prehydrolyzed sol of MEMO and $(R'O)_3Zr$(methacrylate). Films from this sol were poled and then thermally or photochemically cured. However, preliminary experiments did not result in a substantially better optical response or stability, compared with organic polymers.[117] The presence of only one $Si(OR')_3$ unit per chromophore makes the formation of a highly cross-linked sol–gel network very difficult. The high mobility of the NLO dye in the free volume of the host network causes relaxation of the poling-induced order. Another approach to improve the stability of the second-order optical nonlinearity therefore was the use of multiple-substituted dyes such as **6c** (Figure 2). Although the stability of a poled and cured film made from **6c** and $Si(OEt)_4$ was enhanced, further improvement was considered necessary.[14] In a sol–gel film made from $Si(OEt)_4$ and 4-methoxy-4′-(*N*-(3-triethoxysilylpropyl)carboxymethyl)azobenzene, attachment of the chromophore to the silicate matrix had slight effect on photochemical trans–cis as well as thermal cis–trans isomerizations, whereas the photoisomerization was markedly suppressed when the azobenzene was fixed to the matrix at *both* ends of the chromophore.[13] It was later found that the isomerization kinetics of these azo dyes is different in sol–gel films and bulk materials. The larger free volume in the bulk material was attributed to larger pores.[118]

New photochromic hybrid materials were recently prepared by sol–gel processing of $Si(OEt)_4$, silanol-terminated dimethylsiloxane oligomers and (triethoxysilyl)propyl-substituted spirobenzopyranes. The transparent gels exhibited the normal photochromism.[119]

4. Metal-Containing Materials. The sol–gel method is an attractive possibility for the heterogenization of homogeneous metal complex catalysts by anchoring them on silica as a solid support. A much higher metal loading can be achieved than with other methods. Work in this area was recently reviewed in another article, where also a list of selected sol–gel heterogenized metal complexes was given.[21]

Such metal complexes have the same spectroscopic properties as the corresponding complexes with unmodified ligands in solution. In the known examples, the structures of the complexes are therefore only insignificantly altered by the modification of the ligand and by heterogenization. This means that the silicate matrix surrounding the metal complexes does not interact significantly with the metal centers. The important difference of catalysts obtained by sol-gel processing of metal complexes of the type $[(R'O)_3Si{-}X{-}A]_nML_m$ (Figure 3) is that the catalytically active metal moieties are homogeneously distributed throughout the whole material. This has very beneficial effects on the catalyst stability. Since the structure (porosity, surface area, etc.) of the support can be tailored to some extent, the catalytically active centers are still accessible to the reactants. Therefore, the catalytic activity of the sol–gel catalysts is not inhibited, provided that the matrix structure is appropriate.

In another group of materials, organofunctional alkoxides were used to immobilize metal ions. Sol–gel processing of metal alkoxides in the presence of metal ions mostly does not result in a stable incorporation of the metal ions into the resulting oxide materials. They are eluted by water or alcohols. However, the leaching was prevented when organofunctional alkoxides capable of coordinating the metal ions were added. The ethylene diamine derivative $(EtO)_3Si(CH_2)_3NHCH_2CH_2NH_2$ proved to be very effective for anchoring Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pd^{2+}, or Pt^{2+}, while Ag^+ was better coordinated by $(EtO)_3Si(CH_2)_3NH_2$ or $(EtO)_3Si(CH_2)_3CN$.[25] When one of the organofunctional silanes and a metal salt are mixed, metal complexes of the type $[(R'O)_3Si(CH_2)_3A]_mM^{n+}$ are formed in situ. Coordination of the metal ions is retained during sol–gel processing[25] and even in aerogels after supercritical drying.[52] The substituted thiourea $(EtO)_3Si(CH_2)_3NHC(S)NHPh$ was prepared by reaction of $(EtO)_3Si(CH_2)_3NH_2$ with PhNCS and was used to coordinate Pd^{2+} ions.[120]

Modification of non-silicon alkoxides with diamino carboxylates resulted in the organofunctional alkoxides $(R'O)_nE(OOC(H_2N)C{-}X{-}NH_2)$ (Figure 3), which can be analogously used to immobilize metal ions by formation of complexes of the type $[(R'O)_nE{-}X{-}A]_mM^{n-}$.[43]

In a related approach, organofunctional alkoxysilanes were used to stabilize small CdS or metal clusters in sol–gel matrixes.[121]

5. Sensors. The alternative methods used for the immobilization of dyes or catalysts can also be used for the preparation of sol–gel-derived sensors: doping, covalent bonding to the preprepared matrix, or co-condensation of modified precursors. The advantages and disadvantages of these methods for sensor applications were discussed in a recent article.[122] Following the general intention of the present article, we will again only discuss the preparation of those sensor materials in which $(R'O)_nE$-substituted precursors are involved.

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The sensitive layers of SO_2 gas sensor systems were synthesized from a 7:3 mixture of $(EtO)_3Si(CH_2)_3NR''_2$ (R'' = Me, Et) and $(EtO)_3SiPr^n$. The adsorption mechanism is presumably the formation of a weak adduct between the amino group of the silane and SO_2. The propylsilane reduced the hydrophilic character of the material.[65,123,124] A sensor system with an integrated optical device was described, based on changes of the refractive index of the sensitive layer upon gas adsorption. The sensor can only be used under special conditions, because some other gases, especially NO_2 or NH_3, cause irreversible reactions.[124] Another system consists of two different transducers for the same material. The ambiguity of a single sensor signal at higher SO_2 concentrations was avoided by integrating both a dielectric sensor and a mass sensor in the system.[123] Two gas-sensitive layers for different SO_2 concentration ranges were developed in another work: for low concentration (≈2 ppm) based on $(EtO)_3Si(CH_2)_3NMe_2$, and for concentrations up to 6000 ppm based on $(EtO)_3Si(CH_2)_3NEt_2$.[125] A slight modification, replacement of the NR''_2 group in the starting silane by NH_2, resulted in a material suitable for the detection of CO_2.[124]

A $(MeO)_3Si$-substituted derivative of methyl red [(p-$Me_2N)C_6H_4{-}N{=}N{-}(C_6H_4$-$o$-COOH)] was prepared by coupling of the COOH groups with $(MeO)_3Si(CH_2)_3NH_2$. The alkoxysilyl derivative was used to prepare a sensor with a nonleachable pH indicator.[126]

In another approach to prepare a sol–gel-derived pH sensor, fluorescein was added to sols made from either $Si(OEt)_4$ or an organically modified alkoxysilane (prepared by coupling $(EtO)_3Si(CH_2)_3NH_2$ with terephthaloyl chloride). While the purely inorganic material gave promising results in terms of stability, repeatability, and response time, the hybrid polymer proved to be less suited.[127]

Within the framework of the development of an optical immunosensor, a sol prepared from $(EtO)_3Si(CH_2)_3A$ (A = NHMe, NH_2, or SH) was coated on gold-coated glass surfaces. After activation of the organofunctional hybrid polymer films in aqueous buffers by bifunctional coupling agent, immunoglobulin was covalently anchored to the transducer surface with an optimal stability and biological activity.[128]

6. Membranes. While considerable progress has been made in the preparation of ceramic membranes by sol–gel processing, the development of membranes from hybrid polymers is in its infancy. Apart from a poorly documented early attempt,[129] only few, very recent reports are available. This is, nevertheless, a very promising area of development, because the possibility of forming mechanically stable membranes by inorganic polycondensation is implemented by the possibility to incorporate organic functions.

Hybrid polymers prepared by coupling $(EtO)_2MeSi(CH_2)_3NH_2$ or $(EtO)_3Si(CH_2)_3NH_2$ with terephthaloyl chloride and sol–gel processing of the thus-obtained precursors $[(EtO)_2R'Si(CH_2)_3NHC(O)]_2C_6H_4$ (precursor A: R' = Me, precursor B: R' = OEt) were casted on alumina supports.[28] A dense structure was obtained for the material prepared from precursor A, in which gas molecules can solubilize and diffuse under a pressure gradient. Therefore, membranes prepared from this materials have gas separation ability. Due to their more hydrophilic character, membranes prepared from precursor B were better suited for nanofiltration. Facilitated transport membranes were obtained by cocondensation of precursor A with the substituted crown ether **15** (Figure 4).[28] The transport selectivity of K^+ over Li^+ was about 4 and only due to the presence of the crown ether moieties. Since the selectivity is in good agreement with the properties of benzo-15-crown-5, the character of the carrier was not changed by incorporation into the membrane. Transport is facilitated by lipophilic counteranions, indicating that ion pairs are carried.[28]

A covalently bonded monolayer of the silane amphiphile **16** (Figure 4) was immobilized on a porous glass plate by the Langmuir–Blodgett technique. The lipid monolayer acted as a gate membrane for permeation of ions and water-soluble fluorescent probes. The corresponding single- or triple-chain silane amphiphiles (one or three $CH_3(CH_2)_{17}$ units instead of two) were not suitable for this purpose.[29]

Conclusions

Materials with a variety of potential applications can be prepared starting from organofunctional metal alkoxide precursors. Most applications are in a rather early stage, except the development of inorganic–organic hybrid polymers. The many possibilities of chemically modifying the precursor systems and the inherent advantages of the sol–gel process allow the deliberate tailoring of materials properties in a wide range. Most materials developments are presently based on alkoxysilanes. To fully exploit the wealth of this approach for materials syntheses, the underlying chemistry, particularly of non-silicon alkoxides, has to be further developed.

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