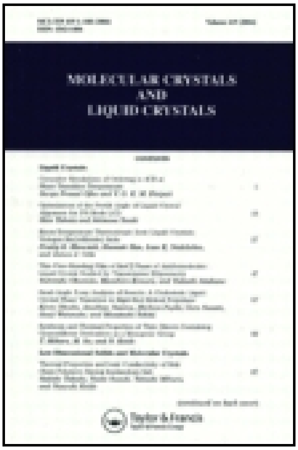

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Nanoscale Structures of Sol-Gel Materials

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Nanoscale Structures of Sol-Gel Materials

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With the development of more sophisticated, mostly multi-precursor sol-gel materials, the structure of the building blocks and their mutual arrangement on a nanoscopic scale is getting more and more important. The question how the structure of oxometallate clusters as primary hydrolysis products is influenced by bidentate organic ligands is discussed for a series of methacrylate-substituted oxozirconium clusters with different metal : methacrylate ratio. On a larger scale, assembly of the molcular building blocks to form a gel network was investigated for gels prepared by base-catalyzed reaction of $Si(OR)_4$ / $R'Si(OMe)_3$ mixtures. When the functional organic group R' has no strongly basic properties, the gel network is formed in two stages. The $R'Si\equiv$ units condense to a gel network formed by the faster reaction of $Si(OR)_4$. When R' contains a strongly basic substituent such as amino groups, both $R'Si(OMe)_3$ and $Si(OR)_4$ are involved in the built-up of the gel network, possibly by extensive hydrogen bonding between the amino groups and silanol groups.

Keywords: sol-gel processing; inorganic-organic hybrid materials; oxometallate clusters; aerogels

INTRODUCTION

While the basic chemistry of sol-gel processes was developed by investigating the hydrolysis and condensation reactions of one-component precursor systems such as $Si(OR)_4$, $Ti(OR)_4$, $Zr(OR)_4$, $Al(OR)_3$, etc. [1], technically applied sol-gel materials are mostly based on two or more precursors. Examples include the preparation of ternary oxides from the alkoxides of two different elements (for example, mullite from $Si(OR)_4$ / $Al(OR)_3$), or inorganic-organic hybrid materials prepared from an organically substituted alkoxide and the corresponding parent alkoxide (for example, $R'Si(OR)_3$ / $Si(OR)_4$) [2]. The development of multicomponent systems is often based on the „building block" approach, which implies that the properties of the resulting material are, at least to some extent, a blend of the properties of the one-component systems.

However, it is obvious that not only the chemical nature of the different building blocks, but also their mutual arrangement will have a decisive influence on many materials properties. With the development of more sophisticated sol-gel materials, questions concerning the structural arrangement of the building blocks on a nanoscopic scale in sol-gel materials are getting more and more important. Their understanding is necessary for a deliberate tailoring of the microstructure of the materials.

There are structural questions on several length scales:

(i) *Atomic (molecular) scale*:

- Kind of the primary units (coordination polyhedra).
- Linkage of the primary units (corner-, edge-, face-sharing).
- Number of links per polyhedron (which determines the crosslinking density).

In silicate-based materials, the answers to these questions are well known: there are only corner-sharing tetrahedral units, and the number of Si-O-Si links per tetrahedron is determined by the degree of organic substitution, i.e. $SiO_{4/2}$ (Q units), $RSiO_{3/2}$ (T units), $R_2SiO_{2/2}$ (D units), or $R_3SiO_{1/2}$ (M units). In contrast, the structural chemistry of other elements is more complex and answers to these questions are only available in a few cases. There is a particular lack of structural information for organically substituted metal alkoxide precursors.

(ii) *Structure and size of the primary particles (clusters)*

On this length scale, mostly one-component silicate systems have been investigated. For example, it is known that there is a strong tendency to form polyhedral silsesquioxanes $(RSiO_{3/2})_n$, when $RSi(OR)_3$ is hydrolyzed. In contrast, little is known on the structure of the primary hydrolysis products of organically modified transition metal alkoxides or of multicomponent systems.

(iii) *Network and pore structure*

- Polymeric aggregation or particulate growth of the primary particles.
- Mutual arrangement of the different building blocks in multicomponent systems.

In this article, we will discuss two issues related to these structural questions. In the first part, the structures of several primary hydrolysis products of (meth)acrylate-substituted zirconium alkoxides are reported which allow to elaborate some general structural trends with important implications on the use of bidentate anionic ligands for the modification of metal alkoxides. In the second part we turn to the question how the structural building blocks in two-component silicate systems are arranged.

METHACRYLATE-SUBSTITUTED OXOZIRCONATE CLUSTERS

Anionic bidentate ligands (BL), such as carboxylates, ß-diketonates, or sulfonates are used in sol-gel processing of metal alkoxides $E(OR)_n$ to moderate their reactivity, to introduce organic functionalities or to control the primary particle size. BL-substituted derivatives are obtained by replacing OR substituents by the bidentate ligands. The overall charge is not changed by this substitution because both types of ligands are mono-anionic. However, the number of occupied coordination sites at the central atom is increased, since alkoxides are mostly monodentate ligands, while the bidentate (chelating or bridging) ligands occupy two coordination sites.

Upon hydrolysis of the BL-substituted alkoxides under carefully controlled conditions (for example, in situ generation of water), molecular oxo or oxo/alkoxide clusters can be obtained. They are the building blocks of organically modified sol-gel materials and reasonably good models for oxo particles.

A series of methacrylate-substituted oxo/hydroxo zirconate clusters was obtained from the reaction of zirconium alkoxides with (meth)acrylic acid. $Zr_6(OH)_4O_4(OMc)_{12}$ (OMc = methacrylate) (Figure 1) was quantitatively obtained by reacting $Zr(OPr)_4$ with a 4-fold amount of methacrylic acid [3]. Each of the Zr atoms is square-antiprismatically coordinated by eight oxygen atoms. The faces of the Zr_6 octahedron are alternatively capped by μ^3-O and μ^3-OH groups. Thus, each $[ZrO_8]$ square antiprism shares an edge with four neighboring antiprisms. Three methacrylate ligands are chelating, and nine bridge Zr-Zr edges. The same cluster core was found in $Ce_6(OH)_4O_4(\text{acetylacetonate})_{12}$ [4] or $U_8(O/OH)_8[O_2P(OPh)_2]_{12}$ [5], for example.

The Zr_6O_8 core of $Zr_6(OH)_4O_4(OMc)_{12}$ closely resembles the basic structural motif in tetragonal ZrO_2, which has a distorted CaF_2 structure.

Therefore, the cluster can be considered to be an embryonic, nano-sized piece of ZrO_2, wrapped by the carboxylate ligands.

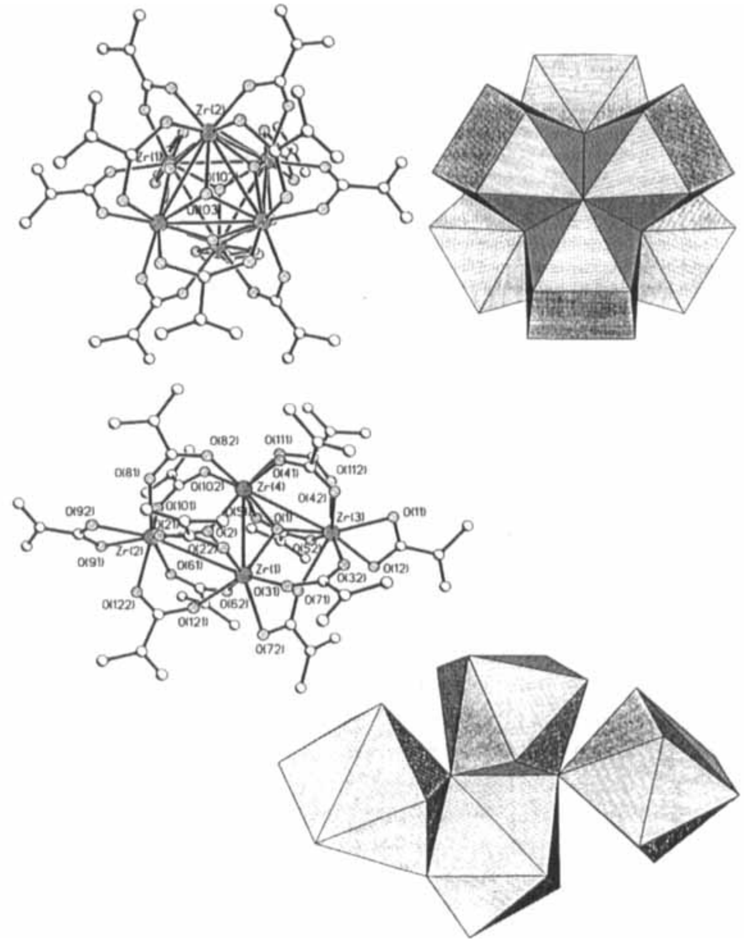

FIGURE 1 Structures of $Zr_6(OH)_4O_4(OMc)_{12}$ and $Zr_4O_2(OMc)_{12}$ and the linkage of the coordination polyhedra (reproduced by permission from Ref. 3)

The $Zr_6O_4(OH)_4$ cluster core appears to be rather robust. In $[Zr_6(OH)_4O_4(OAcr)_{12}]_2$ (OAcr = acrylate) and $Zr_6(OH)_4O_4(OMc)_{12}(PrOH)$ this structural motif is repeated, and only the arrangement of the carboxylic groups is varied [6]. In $[Zr_6(OH)_4O_4(OAcr)_{12}]_2$, two of the formerly edge-bridging methacrylate ligands now link two cluster units. In $Zr_6(OH)_4O_4(OMc)_{12}(PrOH)$, one edge-bridging methacrylate ligand of $Zr_6(OH)_4O_4(OMc)_{12}$ is converted in a monodentate ligand, and the emptied coordination site is occupied by a propanol molecule. The basic structural features of the $Zr_6(OH)_4O_4(OMc)_{12}$ cluster core are retained in both clusters.

In the (meth)acrylate-substituted oxozirconium clusters discussed so far, the carboxylate / metal ratio (x) is 2. The structure of $Zr_4O_2(OMc)_{12}$ (Figure 1), with $x = 3$, [3] allows to study the effect of increasing x beyond the value required for stabilizing an „embryonic" piece of ZrO_2. The four zirconium atoms in $Zr_4O_2(OMc)_{12}$ have a distorted butterfly arrangement. Three of the four Zr atoms are square-antiprismatically coordinated by eight oxygen atoms, but with different coordination environments. The fourth Zr atom is only seven-coordinate (distorted capped octahedron). There are three different coordination modes of the OMc ligands: two are chelating, nine are symmetrically bridging, and one has the rare η^2,μ^2-coordination in which one of the oxygen atoms of a chelating carboxylate group additionally coordinates to a second metal atom. The main structural difference between $Zr_6(OH)_4O_4(OMc)_{12}$ and $Zr_4O_2(OMc)_{12}$ is the linkage of the coordination polyhedra (Figure 1). The less condensed structure of $Zr_4O_2(OMc)_{12}$ (partial corner-sharing linkage instead of edge-sharing) is a consequence of the higher degree of substitution by OMc groups.

An even less condensed structure was found in $[Zr(OPr)(O_3SMe)_3]_n$ (Figure 2) [7]. Although $x = 3$ as in $Zr_4O_2(OMc)_{12}$, this compound is truly polymeric with both chelating and bridging sulfonate ligands. The zirconium atoms are only seven-coordinate (pentagonal bipyramidal), with the propoxy group and one bridging sulfonate oxygen atom in the axial positions. The lower coordination number of the zirconium atoms is the reason why $Zr(OPr)(O_3SMe)_3$ is polymeric, while $Zr_4O_2(OMc)_{12}$ (= „$ZrO_{0.5}(OMc)_3$") is more condensed.

The general conclusion for sol-gel processing of BL-modified metal alkoxides drawn from this series of structures is that the BL / metal ratio should not be forced to too high values if sufficiently condensed oxo structures are desired. The limit for oxozirconium clusters (with eight-coordinate Zr) appears to be $x = 2$. Higher values of x result in polymeric rather than condensed structures. Thus, it is possible to deliberately prepare polymeric or particulate metal oxide gels by varying the BL / metal ratio.

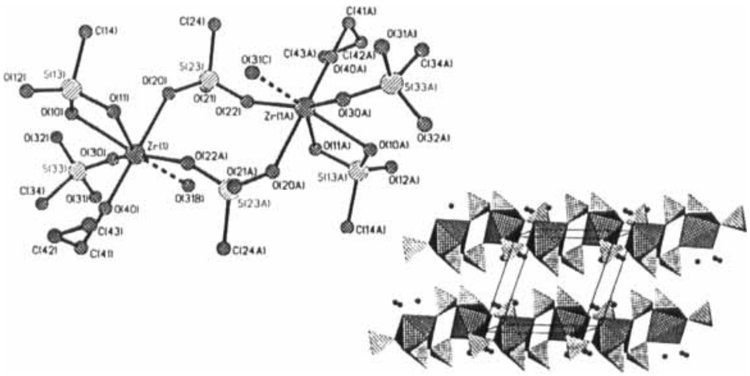

FIGURE 2 Structure of $Zr(OPr)(O_3SMe)_3$ (reproduced by permission from Ref. 7)

The same general results were obtained by studying the primary hydrolysis products of methacrylate-substituted titanium alkoxides. The cluster core of $Ti_6O_4(OR)_8(OMc)_8$ [8] is weakly related to the basic structural motif in rutile. Thus, as $Zr_6(OH)_4O_4(OMc)_{12}$ can be considered the smallest possible section of the structure of tetragonal zirconia, $Ti_6O_4(OR)_8(OMc)_8$ can be considered a piece of rutile in an embryonic state. The limiting BL / metal ratio (x) to stabilize a rutile-like cluster core is 1.33, because titanium is only 6-coordinate. Again, increasing x results in more open or polymeric structures. The structure of $Ti_9O_8(OPr)_4(OMc)_{16}$ consists of a ring of Ti octahedra. Only one pair of octahedra is edge-sharing, while the others share corners [9]. Thus, this structure is close to a polymeric chain of Ti octahedra.

In studying the structural chemistry of oxo clusters derived from carboxylate-substituted zirconium and titanium alkoxides, we chose (meth)acrylic acid, because the reactive double bond should allow the clusters to be incorporated into organic polymers. The olefinic units are fully accessible for chemical reactions, because they are located at the surface of the clusters. In silicon chemistry, much work was already done to reinforce organic polymers by covalently bonded polyhedral oligomeric silsesquioxanes (POSS), mainly the cubic $R_8Si_8O_{12}$ clusters, with reactive organofunctional substituents R (Figure 3). The doped polymers were shown to have very interesting properties [10]. We used the methacrylate-substituted zirconium cluster $Zr_6(OH)_4O_4(OMc)_{12}$ in the same way. Copolymerization with ethylmethacrylate gave polymers crosslinked by the structurally well defined oxometallate units [11]. SAXS measurements indicate that the clusters are retained in the polymer.

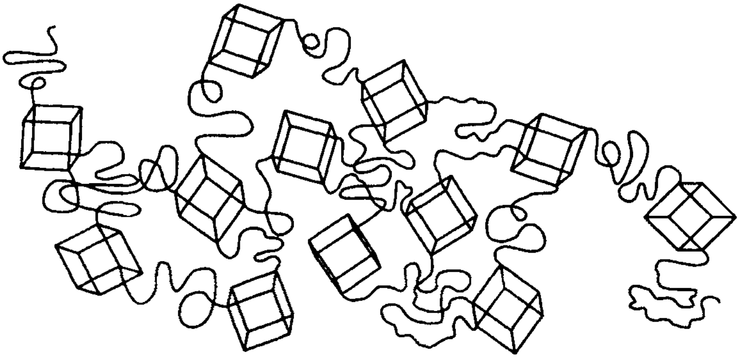

FIGURE 3 Schematic representation of POSS-reinforced polymers

MICROSTRUCTURE OF GELS OBTAINED FROM TWO-COMPONENT ALKOXYSILANE MIXTURES

A great number of hybrid inorganic-organic materials has been prepared by sol-gel processing of R'Si(OMe)$_3$ / Si(OR)$_4$ mixtures, with a variety of functional and non-functional organotrialkoxysilanes. However, surprisingly little attention was paid to how the microstructure and particularly the mutual arrangement of the molecular building blocks in such materials is related to the chemical processing parameters. Aerogels [12] are materials in which the structure of the wet gel can be largely preserved if supercritical drying is performed with liquid carbon dioxide as a fluid. Thus, CO$_2$-dried aerogels are well suited to correlate the chemistry during sol-gel processing with the structural characteristics of the gel network [13].

The influence of the kind and portion of the organically substituted silane R'Si(OMe)$_3$ on the structure of the gel network was studied for two groups of silanes:

- Silanes with non-basic or weakly basic substituents [= $R_{nb}Si(OMe)_3$]:

$(MeO)_3Si(CH_2)_3SH$	(MTMO)
$(MeO)_3Si(CH_2)_3OC(O)CH(Me){=}CH_2$	(MEMO)
$(MeO)_3Si(CH_2)_3Cl$	(CHLO)
$(MeO)_3Si(CH_2)_3OCH_2CHCH_2O$	(GLYMO)
$(MeO)_3Si(CH_2)_3NHC(O)OMe$	(CARBA, ISO)
$(MeO)_3Si(CH_2)_2PPh_2$	(PHOS)

- Silanes with basic substituents [= $R_bSi(OMe)_3$]:

$(MeO)_3Si(CH_2)_3NH_2$	(AMMO)
$(MeO)_3Si(CH_2)_3NHCH_2CH_2NH_2$	(AEAPS)

The aerogels were prepared as follows. $Si(OMe)_4$ (TMOS, for mixtures with $R_{nb}Si(OMe)_3$) or $Si(OEt)_4$ (TEOS, for mixtures with $R_bSi(OMe)_3$), the silane $R'Si(OMe)_3$ and methanol were mixed, the $Si(OR)_4$: $R'Si(OMe)_3$ ratio ranging from 9:1 to 6:4. Methanol was added to adjust the theoretical density (d_{theor}) of the final aerogel according to the formula $d_{theor} = [m_{SiO_2} + m_{R'SiO_{3/2}}] / (V_{Si(OR)_4} + V_{R'Si(OMe)_3} + V_{H_2O} + V_{ROH}$ (V = volume, m = mass). The sol-gel reactions were started by adding 0.01 N aqueous NH_4OH solution (for $R_{nb}Si(OMe)_3$ / TMOS mixtures) or water (for $R_bSi(OMe)_3$ / TEOS mixtures), corresponding to a water / OR ratio (r_w) of 1.0. Thus, for a mixture of x parts of $R'Si(OMe)_3$ and (1-x) parts of $Si(OMe)_4$, (4-x) molar equivalents [= 3x + 4(1-x)] of water were added. The sol was stirred for 5 min and then transferred to cylindrical polyethylene vessels with 1.5 cm in diameter and 4.5 cm in height. The obtained wet gels were aged without solvent exchange at 30 °C for 7 d and then dried with supercritical CO_2.

All aerogel samples were obtained as cylindrical monoliths with low densities and high porosities. Although the theoretical density was adjusted to 0.20 gcm^{-3} (for the samples prepared from $R_{nb}Si(OMe)_3$) or 0.10 gcm^{-3} (for the samples prepared from $R_bSi(OMe)_3$), the experimentally determined bulk densities of the final material were 0.18 - 0.29 gcm^{-3} and 0.07 - 0.26 gcm^{-3}, respectively.

The shrinkage was 5 - 10% for all samples prepared with a 10% portion of $R'Si(OMe)_3$ and rather independent of the kind of functional group. Increasing the portion of $R'Si(OMe)_3$ in the starting mixture to 40% lead to a large increase of the shrinkage. Larger portions than 40 mol% do not result in stable gel networks, probably because the portion of Q^4 units is then insufficient. Shrinkage during aging and supercritical drying is qualitatively connected with the stability of the gel network. Therefore, increasing the portion of $R'Si(OMe)_3$ causes a larger shrinkage due to the lower $c_{Si(OR)4}$, which is equivalent to decreasing the bulk density of an unmodified silica aerogel from $Si(OR)_4$. Shrinkage of the gel body during supercritical drying should result in a proportional increase of the bulk density relative to the theoretical density. In the aerogels prepared in this work, this is partially compensated by the loss of mass during supercritical drying.

The hystereses of the adsorption /desorption isotherms had about the same shape as that of unmodified silica aerogels. Therefore, the organically modified samples also have open, cylindrical pores. The specific surface areas (σ) of the functionalized aerogels were significantly lower than those of unmodified silica aerogels. For the aerogels obtained from $R_bSi(OMe)_3$, σ was distinctly lower than for the aerogels obtained from $R_{nb}Si(OMe)_3$. The determination of the porosity or pore radii of the aerogels by nitrogen sorption was not possible, because the samples are compressed during measurement. This results in an underestimation of the specific pore volumina [14].

Non-basic or weakly basic organotrialkoxysilanes

Gelling is increasingly retarded relative to a pure TMOS system (t_g = 28 min) when the portion of non-basic silanes $R_{nb}Si(OMe)_4$ in the starting solution is increased. For example, t_g is 50 min for a 9:1 mixture of TMOS and GLYMO, 65 min for a 8:2 mixture, and 410 min for a 6:4 mixture. Corresponding to this observation, the rate of water consumption (determined by Karl-Fischer titrations) is retarded. Only negligible hydrolysis was observed during several hours for the pure trialkoxysilanes $R_{nb}Si(OMe)_3$.

The decelerated gelling of $R_{nb}Si(OMe)_3$ / TMOS solutions relative to one-component TMOS solutions can be explained by what we will call the „two-stage" model. This model is based on the known effect that under base-catalysis organotrialkoxysilanes react slower with water than the tetraalkoxysilane with the same OR substituents. This is due to the inductive effect of the organic group which increases the electron density at silicon.

Raman spectroscopic investigations showed that in base-catalyzed reactions of $R_{nb}Si(OMe)_3$ / TMOS mixtures the tetraalkoxysilane reacts first. The organotrialkoxysilane acts as a kind of co-solvent while the silica backbone is built (Figure 5). Raman spectroscopy also showed that the hydrolysis reactions of $R_{nb}Si(OMe)_3$ start only hours after mixing the precursors and, in most cases, after gelation has already occurred [15]. The R'Si≡ units condense on the then existing silica network in a later stage of the reaction, when enough acidic surface silanol groups are available.

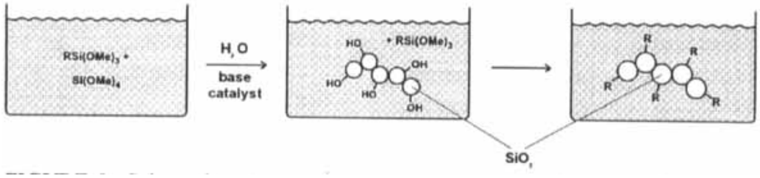

FIGURE 5 Schematic representation of two-stage hydrolysis and condensation of $R_{nb}Si(OMe)_3$ / $Si(OR)_4$ mixtures

The structure of aerogels prepared from only TMOS under alkaline conditions is described as a network of interconnected chains of spherical primary particles [16]. Since $R_{nb}Si(OMe)_3$ is not involved in the formation of the basic network, there is no principal structural difference when $R_{nb}Si(OMe)_3$ / $Si(OMe)_4$ mixtures are processed. Particularly, there is no influence of the *kind* of the functional group R_{nb}. The existence of spherical primary particles in the aerogels described in this work is, *inter alia*, supported by the good correlation between the particle radii (calculated from the SAXS data with the assumption of spherical particles) and the experimental BET surface areas (Figure 7b).

There is other experimental evidence for the two-stage process:

- The C parameter is an indicator for the polarity of the surface. A C parameter of 110 was found for an unmodified silica aerogel with a polar surface. With the incorporation of 10 mol% of $R_{nb}Si(OMe)_3$, the C parameter drops drastically to about 60, i.e. the polarity of the surface decreases relative to an unmodified silica aerogel. For gels with a portion of 40 mol% of the organic units, the C parameter levels at about 40. This is exemplarily shown in Figure 6 for aerogels prepared from MTMO, GLYMO and MEMO. The kind of organic group R_{nb} only plays an insignificant role. When TEOS is reacted in the presence of $R_{nb}Si(OMe)_3$, the C parameter drops because the inner surface is successively covered by the organic groups and therefore becomes less polar. Once the inner surface is covered with $R_{nb}Si\equiv$ groups, a limiting value for the C parameter is reached.

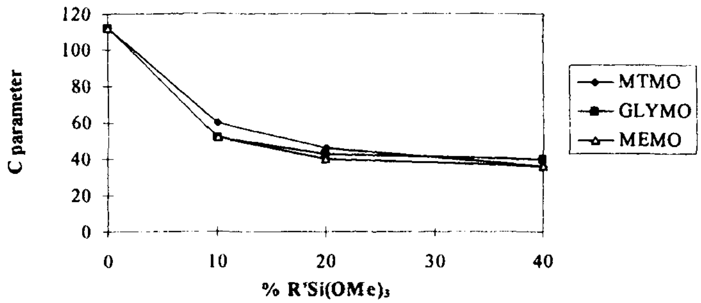

FIGURE 6 Dependence of the C parameter on the portion of $R_{nb}Si(OMe)_3$

- An increasing portion of $R_{nb}Si(OMe)_3$ in the starting mixture decreases the incorporated portion of $R_{nb}Si\equiv$ groups. For 9:1 mixtures of TMOS and $R_{nb}Si(OMe)_3$, the complete incorporation was obtained, while only about 70% were incorporated starting from 6:4 mixtures. For samples with 10 mol% of $R_{nb}Si(OMe)_3$ in the precursor mixture, the incorporation of the organic moieties appears to be almost complete. This implies that only a certain portion of $R_{nb}Si\equiv$ units can be accommodated at the inner surface. An excess could remain uncondensed or undergo self-condensation to small oligomers which are extracted during the supercritical drying process.
- *The polarity of $R'Si(OR)_3$ influences the fractal dimension* D *(surface* roughness), which is a measure for the degree of branching of the network formed by the primary particles. It typically increases with increasing specific surface area, i.e. with a decreasing portion of $R_{nb}Si(OR)_3$ for all aerogel samples. Fig. 7a shows that the aerogels fall into two classes. This is explained by $R'Si(OR)_3$ being a co-solvent in the network-forming stage. It is well known that solvents may change the rates of hydrolysis and condensation of alkoxides and thus the structure of the gel network and derived physical properties. The most important parameter is probably the ability of the solvent to reinforce or weaken the hydrogen-bond network [17]. The aerogels prepared from CARBA / ISO or PHOS have fractal dimensions in the same range as those prepared from $Si(OR)_4$ under base-catalyzed conditions. Thus, the higher polarity of the functional groups in these silanes obviously results in only little changes of the solvent properties relative to pure methanol. The dilution of methanol by the

less polar MTMO or MEMO seems to interrupt the hydrogen-bond network and thus changes the relative rates of hydrolysis and condensation.

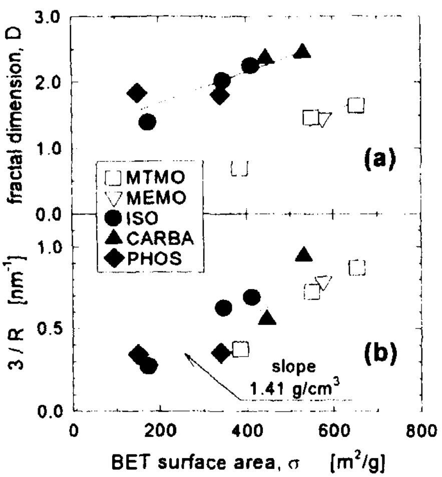

FIGURE 7 SAXS parameters as a function of the BET surface area (σ). Different specific surface areas for samples prepared from the same silanes are due to different precursor ratios. (a) Fractal dimension of the aerogel network. The full lines are separate linear regressions to the data shown by open and full symbols, respectively. (b) Inverse particle radius, 3/R. The ratio (3/R) / σ corresponds to the skeletal density of the aerogel. The dotted line corresponds to the skeletal density of pure silica (reproduced by permission from Ref. 13).

While the nature of the organic group R_{nb} hardly influences the basic structure of the gel network (except the roughness of the surface), there is an influence of the *portion* of $R_{nb}Si(OMe)_3$ on the size of the primary particles (determined by SAXS). The main changes upon increasing the $R_{nb}Si(OMe)_3$ / $Si(OMe)_4$ ratio in the starting mixture are the larger particles and smaller specific surface areas. An example is shown in Figure 9.

The explanation for the larger particles is the increased water/silane ratio (r_w) and the higher catalyst concentration (c_{cat}) acting on TMOS in the initial stage of the overall reaction.

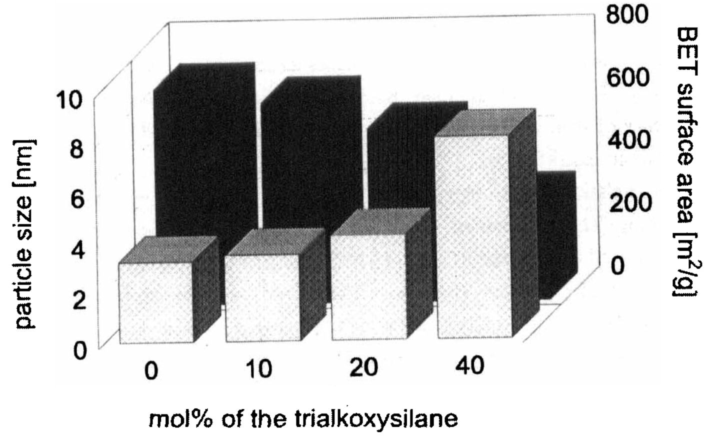

FIGURE 9 Change of the particle radii and the specific surface areas in aerogels from MTMO / $Si(OR)_4$ mixtures upon increasing the portion of MTMO.

One has to keep in mind that sol-gel processing of the two-component alkoxysilane mixtures was initiated by adding the *whole amount* of water and catalyst necessary for the hydrolysis and condensation *of both compounds* to alcoholic solution of the silanes. This is a common procedure for the preparation of sol-gel materials from mixtures of two or more different alkoxysilanes. The added amount of aqueous 0.01 N NH_4OH solution corresponded to $r_w = 1$. The delayed reaction of the $R'Si(OMe)_3$ affects the hydrolysis and condensation reaction of TMOS, because the *water / silane ratio* (r_w) and the *catalyst concentration* (c_{cat}) are indirectly changed, both being important parameters with regard to the structural properties of the gel network. Since in the first stage of the reaction $R_{nb}Si(OMe)_3$ is basically a co-solvent and does not compete for the consumption of water, the amount of water available for the hydrolysis and condensation of the *tetraalkoxysilane* ($r_{w(TMOS)}$) is higher than 1. The relative $r_{w(TMOS)}$ increases with an increasing portion of $R'Si(OMe)_3$ in the starting mixture. For the same reason, the effective catalyst concentration acting on TMOS is increased with an increasing portion of $R_{nb}Si(OMe)_3$.

The consequences of changing r_w and c_{cat} in base-catalyzed hydrolysis and condensation reactions of $Si(OR)_4$ are well known. A higher concentration of ammonia and a higher r_w result in larger particles [18], unless there is no large excess of water.

Organotrialkoxysilanes with strongly basic functional groups

The silanes with basic organic substituents ($R_bSi(OMe)_3$) show a distinctly different gelation behavior than $R_{nb}Si(OMe)_3$, and particularly a different dependence of structural parameters on the $R'Si(OMe)_3$ / $Si(OR)_4$ ratio.

In contrast to $R_{nb}Si(OMe)_3$ / TMOS mixtures

- the gelation is strongly accelerated when TMOS is co-reacted with $R_bSi(OMe)_3$. The reaction of AMMO / TMOS mixtures under the reaction conditions used for the $R_{nb}Si(OMe)_3$ / TMOS mixtures resulted in the immediate formation of precipitates. Therefore, TMOS was exchanged by the slower reacting TEOS, and no catalyst was added, because the amino groups of the R_b substituent act as an „internal catalyst". With the latter in mind, it appears surprising that under these conditions, the gel times of $R_bSi(OMe)_3$ / TEOS mixtures *increase* when the portion of $R_bSi(OMe)_3$ is increased. For example, a 1:9 mixture of AMMO and TEOS gelled after 10 min, while it took 30 min for a 4:6 mixture. An increasing portion of $R_bSi(OMe)_3$ in the reaction mixtures has obviously two contrasting effects on the gelation behavior: the higher concentration of the catalytically active amino groups which also act as hydrogen-bond acceptors (both effects should shorten gelation times), but a decreasing portion of network-forming units. The latter effect appears to dominate.
- the integrated portion of R_b groups is very high.
- no saturation behavior of the C parameter was observed when the portion of $R_bSi(OR)_3$ was increased.

The gelation behavior of TEOS / AMMO or TEOS / AEAPS mixtures thus corresponds neither to that of the $R_{nb}Si(OMe)_3$ / TMOS mixtures nor to that of TEOS under strongly basic conditions. It is known from the literature that alcoholic solutions of AMMO quickly react with water, but no gel is formed. This was explained by the formation of intramolecular hydrogen bonds in the hydrolyzed species which inhibit formation of the gel network (Figure 10, left)[19].

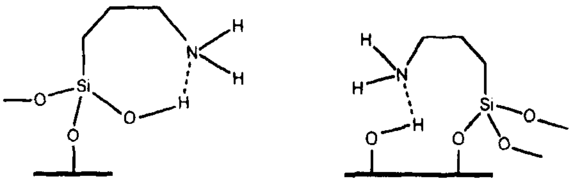

FIGURE 10 Potential involvement of aminoalkyl groups in hydrogen bonding.

When TEOS / $R_bSi(OMe)_3$ mixtures are reacted, gels are formed within a few minutes, although Karl-Fischer titrations showed that only a small amount of water was consumed. One of the reasons for the rapid formation of gels may be the catalysis of TEOS hydrolysis and condensation by the amino groups of $R_bSi(OMe)_3$. Furthermore, the *inter*molecular formation of hydrogen bridges between the amino groups of $R_bSi(OMe)_3$ and silanol groups derived from TEOS could promote gelation. The OH groups attached to Q silicon atoms are more acidic than those attached to T silicon atoms and therefore should preferentially act as hydrogen donors in hydrogen bonds (Figure 10, right).

With these notions, a two-stage reaction can no longer be expected for the $R_bSi(OMe)_3$ / TEOS mixtures. Raman spectroscopic investigations showed that both compounds react very fast and that highly branched units (Q^4) are formed in a very early stage of the overall reaction. The complete incorporation of AMMO and AEAPS into the gels, even if their portion in the starting mixture is as high as 40%, is possibly also due to the fast hydrolysis reaction and the hydrogen bonding. This notion is also supported by the fact that no saturation behavior of the C parameter is observed.

The reaction of tetraalkoxysilanes with water under strongly alkaline conditions is known to lead to particulate gels with large primary particles and large pores [18]. Large particle radii are indeed found by the SAXS measurements (6.0 - 6.3 pm). The specific surface areas, which are rather low for aerogels of that density are consistent with that. However, contrary to the aerogels prepared from $R_{nb}Si(OR)_3$ / TMOS mixtures, the particle radii in the aerogels prepared from AMMO / TEOS or AEAPS / TEOS apparently do not depend on the $R_bSi(OMe)_3$ portion in the starting mixture, which again supports the notion that both silanes are involved in the formation of the gel network.

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References

[1] C. J. Brinker and G. W. Scherer, *Sol-Gel-Science* (Academic Press, New York, 1990).
[2] U. Schubert, N. Hüsing, and A. Lorenz, *Chem. Mater.*, **7,** 2010 (1995).
[3] G. Kickelbick and U. Schubert, *Chem. Ber.*, **130,** 473 (1997).
[4] P. Toledano, F. Ribot, and C. Sanchez, *Compt. Rend. Acad. Sci. Paris,*Ser. II, **311,** 1315 (1990).
[5] L. M. Mokry, N. S. Dean, and C. J. Carrano, *Angew. Chem.*, **108,** 1676. *Angew. Chem. Int. Ed. Engl.*, **35,** 1497 (1996).

[6] G. Kickelbick, P. Wiede, and U. Schubert, *Inorg. Chim. Acta,* **284,** 1 (1999).

[7] A. Lorenz, G. Kickelbick, and U. Schubert, *Chem. Mater.,* **9,** 2551 (1997).

[8] U. Schubert, E. Arpac, W. Glaubitt, A. Helmerich, and C. Chau, *Chem. Mater.,* **4,** 291 (1992).

[9] G. Kickelbick and U. Schubert, *Europ. J. Inorg. Chem.* 159 (1998).

[10] For example, J. J. Schwab, J. D. Lichtenhan, K. P. Chaffee, P. T. Mather, and A. Romo-Uribe, *Mat. Res. Soc. Symp. Proc.,* **519,** 21 (1998).

[11] G.Trimmel, *Ph.D.* Thesis, Technische Universität Wien (2000).

[12] N. Hüsing and U. Schubert, *Angew. Chem.,* **110,** 22 (1998); *Angew. Chem. Int. Ed. Engl.,* **22,**37 (1998).

[13] N. Hüsing, U. Schubert, K. Misof, and P. Fratzl, *Chem. Mater.,* **10,** 3024 (1998). N. Hüsing, U. Schubert, R. Mezei, P. Fratzl, B. Riegel, W. Kiefer, D. Kohler, and W. Mader, *Chem. Mater.,* **11,** 451 (1999).

[14] G. W. Scherer, D. M. Smith, and D. Stein, *J. Non-Cryst. Solids,* **186,** 309 (1995).

[15] N. Hüsing, U. Schubert, B. Riegel, and W. Kiefer, *Mat. Res. Soc. Symp. Proc.,* **435,** 339 (1996). B. Riegel, S. Plitterdorf, W. Kiefer, N. Hüsing, and U. Schubert, *J. Mol. Struct.,* **410&411,** 157 (1997).

[16] D. W. Schaefer, *Science,* **243,** 1023 (1989); *Mat. Res. Soc. Bull.,* **24**(4), 49 (1994). P. Wang, A. Emmerling, W. Tappert, O. Spormann, J. Fricke, and H.-G. Haubold, *J. Appl. Crystallogr.,* **24,** 777 (1991). A. Emmerling, J. Gross, R. Gerlach, R. Goswin, G. Reichenauer, J. Fricke, and H.-G. Haubold, *J. Non-Cryst. Solids,* **125,** 230 (1990). A. Emmerling, P. Wang, G. Popp, A. Beck, and J. Fricke, *J. Phys.,* **3,** 357 (1993).

[17] T. W. Zerda, and G. Hoang, *Chem. Mater.,* **2,** 372 (1990).

[18] T. Matsoukas and E. Gulari, *J. Colloid Interface Sci.,* **124,** 252 (1988). K. T. Keefer, *Mat. Res. Soc. Symp. Proc.,* **73,** 295 (1986). K. D. Keefer and D. W. Schaefer, *Phys. Rev. Lett.,* **56,** 2199, 2376 (1986).

[19] E P. Plueddemann, *Silane Coupling Agents* (Plenum Press, New York 1991) p.63. C. Rousseau, C. Poinsignon, J. Garcia, and M. Popall, *Chem. Mater.,* **7,** 828 (1995).