On the Influence of Metal Alkoxides on the Epoxide Ring-Opening and Condensation Reactions of 3-Glycidoxypropyltrimethoxysilane

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Abstract. The extent of the epoxide ring-opening, the formation of ethyl ether groups as one reaction product of the ring-opening and the condensation degree of $RSi(O_{0.5})_3$ units in sols and gels of the system 3-glycidoxypropyltrimethoxysilane (GPTS)-$1.5H_2O$-$0.01/0.1/1.0$ metal alkoxide [$Si(OEt)_4$, $Sn(OBu^t)_4$, $Al(OBu^s)_3$, $Al(OEtOBu)_3$, $Ta(OEt)_5$, $Ti(OEt)_4$, $Zr(OBu^n)_4$] in ethanol has been examined by means of liquid- and solid-state ^{13}C and ^{29}Si NMR spectroscopies. The results reveal a strong epoxide ring-opening effect of Al-alkoxides in hybrid sols after 24 h reaction time and of Zr-, Ta-, Al- and Sn-alkoxides in corresponding hybrid gels already at low concentration (1 mole%). The ring-opening rate increases in sols with higher metal alkoxide concentration (10 mole%) but decreases at 50 mole% concentration of Al-, Ti- and Zr-alkoxides. The ring-opening activity of metal alkoxides in 10 mole% hybrid sols increases after 24 h reaction time in the order $Si(OEt)_4 < Ti(OEt)_4 < Zr(OBu^n)_4 < Ta(OEt)_5$, $Sn(OBu^t)_4$, $Al(OBu^s)_3$, $Al(OEtOBu)_3$. The 24 h hybrid sols and gels contain considerable amounts (up to 90%) of ethyl ether groups as reaction product of the ring-opening reaction which lowers the formation of polyether bonds. The condensation degree (c.d.) of $RSi(O_{0.5})_3$ units of GPTS-$1.5H_2O$ sols with 10 mole% of metal alkoxides increases up to 80% after 7 h reaction time in the order: $Si(OEt)_4 \ll Sn(OBu^t)_4 < Zr(OBu^n)_4 < Al(OBu^s)_3 < Al(OEtOBu)_3 < Ta(OEt)_5 < Ti(OEt)_4$. An additional increase in c.d. up to 90% follows after the thermal sol-gel transformation. Generally, maximum activity of metal alkoxides in ring-opening and condensation reactions was found in sols and gels with 10 mole% additives. The effect of water on the epoxide ring-opening and on c.d. is discussed. Furthermore, the activity of metal alkoxides is compared with corresponding nanoscaled metal oxides.

Keywords: alkoxysilane, metal alkoxides, epoxide, ring-opening, ^{13}C and ^{29}Si NMR, condensation degree, ethyl ether groups

1. Introduction

Inorganic-organic hybrid materials prepared from 3-glycidoxypropyltrimethoxysilane (GPTS) and metal alkoxides and/or nanoscaled metal oxides via the sol-gel process find manifold interest e.g. for scratch and abrasion resistant coatings on organic polymers [1–5], for contact lenses [6], antifogging [7], pho-tochromic [8], antireflective [9], coloured layers [10] on glass, corrosion preventing coatings [11], structured layers for microelectronics [12, 13], for photographic films and ink-receiving layers [14], for membranes [15], crack-free transparent inorganic-organic mono-liths [16], SiO_2 based chromatographic phases [17–20], and solid electrolytes [21]. During the last decade numerous works have been carried out to explain the GPTS based sol-gel reactions and to search for corre-lations between structure and properties of the hybrid

materials for more controlled syntheses of materials with tailor-made properties [3, 5, 14, 22–26]. The previous investigations on differently composed GPTS derived hybrid materials have shown a great variety of reactions of alkoxy groups of GPTS and those of metal alkoxides (hydrolysis, alcohol interchange, homo- and heterocondensation) [13, 27–30]. Likewise, the works have shown several reactions of epoxide rings leading to monomeric, oligomeric and polymeric ether structures, diols, metal esters and even to double bonds, aldehydes and ketones [19, 22, 24, 26, 31–35]. Another work reports on the breaking up of Si—C bonds of trifunctional silanes by octahedral complexed Al-alkoxides, accompanied by the transfer of the Si-atoms from T-units to Q-units [36]. The catalytic effect of metal (Al-, Ti-, Zr-) alkoxides on epoxide ring-opening and on hydrolysis/condensation reactions of the $RSi(O_{0.5})_3$ groups of GPTS has already been qualitatively described for differently composed liquid or solid systems at different reaction conditions [37, 38].

So far, an extensive examination and explanation of the GPTS reactions in presence of catalytical or molar quantities of metal alkoxides in sols and gels, their quantitative evaluation and correlation with the material properties is lacking due to the great variety of reactions, their mostly parallel course and the lack of qualified methods. Furthermore, the great variety of reaction conditions which can be used in the course of the sol-gel process (type, concentration and molar ratio of components, solvent, catalyst, temperature, reaction time) at present impedes a generalization of GPTS reactions in presence of metal alkoxides.

Therefore, the aim of this work as a part of a series on GPTS based hybrid materials [39–42] is to contribute by means of liquid- and solid-state ^{29}Si and ^{13}C NMR spectroscopies to a more general knowledge on selected reactions of GPTS (condensation degree, extent of epoxide ring-opening, formation of monoethyl ether groups) in presence of Si-, Sn-, Al-, Ta-, Ti- and Zr-alkoxides. The examination has been carried out under—if possible—identical reaction conditions for a better comparison of the effect of different metal alkoxides on structural changes of GPTS. Furthermore, the investigations comprise both the sol and the gel state in the course of the hybrid material synthesis. The results shall contribute to a more detailed knowledge of the effect of metal alkoxides on GPTS reactions, to a more controlled synthesis of hybrid materials and to an experimental basis for future investigations.

2. Experimental

Chemicals. Aluminium-*sec*-butoxide $Al(OBu^s)_3$, titanium-tetraethoxide $Ti(OEt)_4$, tantalum-pentaethoxide $Ta(OEt)_5$ and tetraethoxysilane $Si(OEt)_4$ were purchased from Fluka; zirconium-tetra-*n*-butoxide $Zr(OBu^n)_4$ (79% in butanol) and 3-glycidoxypropyltrimethoxysilane from ABCR and tin-tetra-*t*-butoxide $Sn(OBu^t)_4$ from Chempur. The chemicals were used without further purification. Aluminium-*n*-butoxyethoxide $Al(OEtOBu)_3$ was prepared from $Al(OBu^s)_3$ and 2-butoxyethanol according to the procedure described in [43].

Procedure. 1 mole GPTS was diluted with ethanol to a 2.87 M solution, hydrolyzed with 1.5 mole water (as 0.1 M HCl) and stored for 0.5 h at 25°C. The metal alkoxide was added to the hydrolysate at molar ratios GPTS : metal alkoxide = 1 : 1 (50 mole% additive), 0.9 : 0.1 (10 mole%) and 0.99 : 0.01 (1 mole%). The defined amount of metal alkoxide was diluted with such an amount of ethanol that the GPTS concentration in the hybrid sols is 1.26 M (Si-, Al-, Ti-, Zr-alkoxide) and 1.0 M (Ta-, Sn-alkoxide), respectively. These hybrid sols were stored at 25°C and examined by ^{13}C NMR 0.5 h and 24 h after the addition of metal alkoxide (in the following refered to 0.5 h and 24 h hybrid sols). The ^{29}Si NMR spectra from 0.5 h hybrid sols were recorded over a period of 14 h. In a second series, additional amounts of water (0.1 M HCl) up to $2H_2O$ per OR group were added stepwise within 1.5 h to the hybrid sols for examination of the water effect. The final GPTS concentration in these strongly hydrolyzed hybrid sols amounts to 0.80 M. The 24 h hybrid sols were evaporated to dryness at 130°C for 5 h. The solid products (hybrid gels) were then crushed and heated again for 2 h at 130°C.

Measurements. The ^{29}Si and ^{13}C NMR spectra were obtained using a Bruker AC 200 spectrometer (liquid-state) and a Bruker MSL 200 (solid-state) operating at fields of 4.7 T. ^{29}Si NMR: inverse gated sequence, external reference: tetramethylsilane (TMS), internal standard for quantitative evaluation: phenyltrimethylsilane, pulse repetition time (r.t.): 40 s, pulse angle (p.a.): 63°, number of scans (n.s.): 1260. ^{13}C NMR: single pulse experiment, r.t.: 10 s, p.a.: 60°, n.s.: 180. Generally, the ^{13}C and ^{29}Si NMR measurements of hybrid sols were started 15 min after their preparation. The average recording time was used for the characterization of the reaction time of these samples. Solid-state ^{29}Si NMR: ^{29}Si{^{1}H} sequence, external standard Q_8M_8

(M signal $= 11.58$ ppm related to TMS), MAS 3 kHz, p.a.: 63°, r.t.: 60 s, n.s.: 1200 scans. The condensation degree of $RSi(O_{0.5})_3$ units was calculated according to formula: c.d. (%) $= 100 - (T^0 + 0.67\,T^1 + 0.33\,T^2)$ on basis of the signal areas of the differently condensed structural units which are indicated by the conventional T^n notation where $n = 0$, 1, 2, 3 stands for the amount of bridging oxygen atoms in $RSi(O_{0.5})_3$ groups. Solid-state ^{13}C NMR: single pulse ^{13}C{^{1}H} high power decoupling, external standard adamantane, p.a.: 50° r.t.: 4s, n.s.: 7000–9000 scans. The quantitative evaluation of the ^{29}Si and ^{13}C liquid-state NMR spectra was carried out by comparison of the integrated signal intensity with that of the internal phenyltrimethylsilane standard. The evaluation of the solid-state ^{13}C NMR spectra with regard to the epoxide ring-opening was made by comparison of the intensity of the signal of the terminal C-atom from epoxide group around $\delta = 44$ ppm with that of the methylene group signal at $\delta = 23$ ppm, used as internal reference. The ^{13}C NMR chemical shift of the signals is assigned according to literature [17]. The error of NMR data is estimated to be about $\pm 3\%$ in case of sols, about $\pm 5\%$ for c.d. in gels and $\pm 10\%$ for epoxide and ethyl ether group in gels. Additional experimental details see [39].

3.   Results and Discussion

3.1.   Effect of Si-, Sn-, Al-, Ta-, Ti- and Zr-Alkoxides on the Epoxide Ring-Opening

The catalytic effect of Al-, Ti- and Zr-alkoxides on the epoxide ring-opening has already been known for a longer time [37 and therein cited literature]. Previous ^{13}C NMR experiments on solid GPTS-derived hybrid polymers reveal the thermal stability of epoxide rings in absence of Al-alkoxide [22]. However, the epoxide signals in ^{13}C NMR spectra already disappear in presence of 1 mole% Al-alkoxide. Likewise, Zr-alkoxide causes a rapid epoxide ring-opening in a concentration of 1 mole% [22, 25, 38, 44]. Furthermore, it was found that Zr-alkoxide shows a higher ring-opening activity than Ti-alkoxide and favours the formation of polyethylene bonds even at room temperature [25]. Boron trifluoride diethyl etherate shows a similar high activity on epoxide ring-opening like Zr-alkoxides. The boron compound opens the epoxide ring already at room temperature and also leads to formation of polyether groups [44]. Regardless of the formation of polyethers, which is desired for preparation of hybrid polymers, mani-

fold additional structural groups corresponding to the formula:

$$\equiv Si-CH_2-CH_2-CH_2-O-CH_2-CH(OR^1)-CH_2OR^2$$
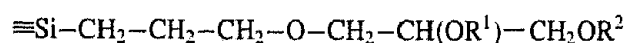
with R^1, R^2 = H, alkyl, $M(O, OR)_x$ [M = e.g. Ti, Zr, Al], $-SiR^*(O_{0.5})_2$ [R^* = glycidoxypropyl-] can appear in presence of water, alcohols and metal alkoxides [18, 22, 26, 33, 34, 42, 45–48]. Especially, the formation of $C-O-M(O, OR)_x$ and $C-O-Si(R^*)(O_{0.5})_2$ bonds in the course of the epoxide ring-opening can contribute to an extended inorganic-organic network. According to literature [32] the monoalkyl ether bond is favourably formed by reaction of alcohol with the terminal (α) C-atom of the epoxide ring due to its lower sterical hindrance in comparison with the β-C-atom. The detection of considerable amounts of monoalkyl ethers as reaction product [22, 26, 42, 47] reveals that the frequently accepted assumption of a nearly complete formation of polyethers from epoxide rings should be regarded more critically in presence of water, alcohols and metal alkoxides.

The present work examines the effect of different amounts (1–50 mole%) of Si-, Sn- Al-, Ta- Ti- and Zr-alkoxides, respectively, and the influence of water on the epoxide ring-opening and on the formation of monoethyl ether groups in GPTS derived ethanolic hybrid sols and gels at comparable reaction conditions. The ring-opening and the formation of monoethyl ether groups can be examined reliably by discrete ^{13}C NMR signals. The C-atoms of the epoxide ring are characterized by signals at $\delta = 44.2$ and 51.2 ppm and the C-atoms of the terminal ethyl ether group [$\equiv Si-(CH_2)_3-O-CH_2-CH(OH)-CH_2-O-CH_2-CH_3$] show signals at $\delta = 15.3$ and 67.1 ppm [42]. A reliable determination of methyl ether groups in presence of methanol deriving from GPTS hydrolysis failed in most cases due to the overlapping of the ^{13}C NMR signal at 58–59 ppm with those of ethanol and $C_2H_5O-Si\equiv$ groups. Characteristic liquid- and solid-state ^{13}C NMR spectra of the GPTS derived hybrid sols and gels have already been presented in previous articles [39, 42].

The results of the ^{13}C NMR examination of hybrid sols and gels in presence of small amounts (1 mole%) of metal alkoxides are summarized in Fig. 1. The results of $Si(OEt)_4$ and $Ti(OEt)_4$ addition [39] are also included in the diagram for comparison. The three bars for one single metal alkoxide each characterize the epoxide content and the amount of ethyl ether groups in hybrid sols 0.5 h and 24 h after addition of metal
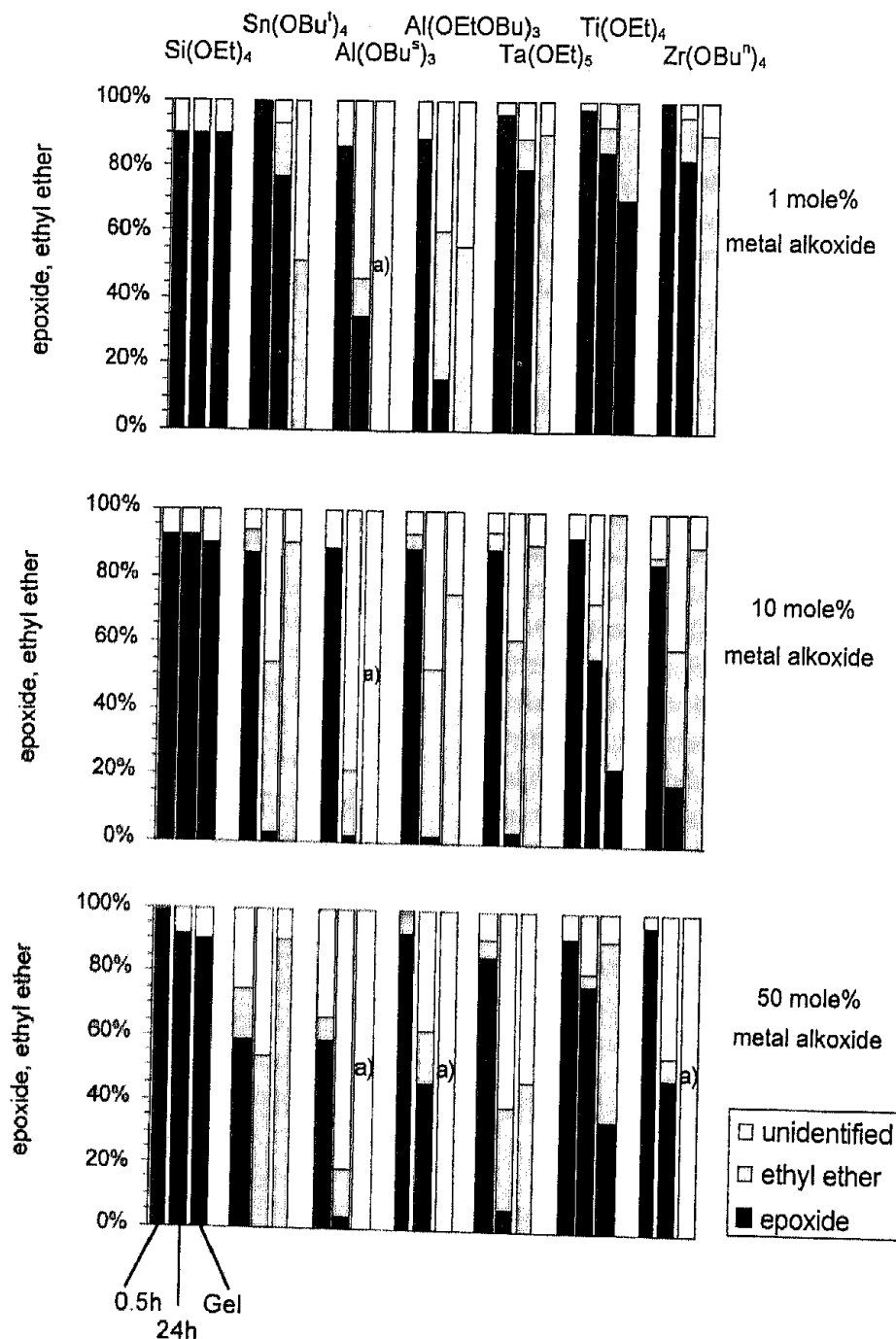
Figure 1. Amount of epoxide rings and ethyl ether groups in hybrid sols after 0.5 h and 24 h reaction time and in corresponding gels of the system $1.0GPTS-1.5H_2O-0.01/0.1/1.0$ metal alkoxide (1/10/50 mole%). [a] determination of ethyl ether groups failed.

alkoxide and in the corresponding hybrid gels. The graph shows that the addition of 1 mole% metal alkoxide causes only a low epoxide ring-opening in sols (max. 15%) after a short reaction time (0.5 h). The amount of opened rings in these hybrid sols has increased to 10–25% after a reaction time of 24 h with the exception of Al(OBu^s)_3 and Al(OEtOBu)_3 which lead to 65% and 84% ring-opening. This high ring-opening activity of the Al-alkoxides corresponds with results in literature [22]. The examination of the corresponding

hybrid gels reveals a practically complete ring-opening in presence of 1 mole% Sn-, Al-, Ta- and Zr-alkoxides after the thermal sol-gel transformation. $Si(OEt)_4$ show no significant ring-opening activity and $Ti(OEt)_4$ only to a relatively low extent (ca. 30%). Simultaneously with the ring-opening considerable amounts of ethyl ether groups, up to 90% with respect to the starting epoxide ring concentration, can be detected in sols and gels. Because of the high content of ethyl ether groups in hybrid gels it can be concluded that only a small

amount of polyether bonds should be present in the hybrid polymers after the complete epoxide ring-opening.

At higher concentrations of metal alkoxides (10 mole%, Fig. 1) only a slightly stronger ring-opening (10–20%) is observed in hybrid sols after 0.5 h reaction time in comparison with 1 mole% sols. A considerably increased ring-opening activity, however, is visible in 24 h sols. Al-, Ta-, and Sn-alkoxides cause a ring-opening already higher than 90% followed by Zr-alkoxide (80%) and Ti-alkoxide (44%). The results of Si-alkoxide confirm again its very low ring-opening activity. A complete ring-opening is detected in the hybrid gels with the exception of the Ti- and Si-alkoxides as additives similar to the 1 mole% system. Apart from the low-active $Si(OEt)_4$ high amounts (>50%) of ethyl ether groups were detected in the hybrid gels.
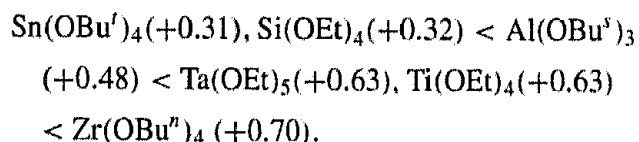
The hybrid sols and gels with the highest concentration of metal alkoxides (50 mole%, Fig. 1) reveal some significant differences in comparison to the 10 mole% system. The 24 h hybrid sols with 50 mole% $Al(OEtOBu)_3$, $Ti(OEt)_4$ or $Zr(OBu^n)_4$ show a remarkably lower epoxide ring-opening rate than the corresponding 10 mole% sols. A complete ring-opening is detected again in the Sn-, Al-, Ta- and Zr-alkoxide derived hybrid gels. Apart from low-active Si-alkoxide the Ti-alkoxide derived gel still contains considerable amounts of unopened epoxide rings.

Summarizing the results it can be stated that apart from the practically non-active Si-alkoxide and the low-active Ti-alkoxide a small amount (1 mole%) of Zr-, Al-, Ta- and Sn-alkoxides already activates the ring-opening in 24 h hybrid sols and leads to a complete ring-opening in hybrid gels after thermal treatment. A higher concentration of metal alkoxides (10 mole%) results in an increasing ring-opening rate in 24 h sols whereas the maximum concentration of 50 mole% Ti-, Zr- or Al-alkoxide can diminish this rate. The decreased ring-opening rate at a high metal alkoxide concentration can be attributed to the low amount of unreacted water in this system [39] which reduces the hydrolysis reactions of metal alkoxides and the formation of reactive MOH groups. The presence of significant amounts of ethyl ether groups in the hybrid gels independent of the metal alkoxide concentration means that a considerable part of the epoxide did not polymerize to polyether chains. This result should have a significant influence on the properties of resulting hybrid materials.
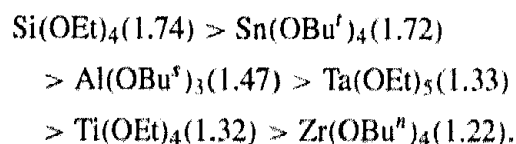
Reasons for the remarkable differences in the ring-opening activity of the metal alkoxides should be first searched for in the electronegativity [49] or partial charge [50] of the metal atoms. A metal atom with a high positive partial charge and high electrophilicity is able to carry out a stronger attack on the oxygen atom of the epoxide ring than a metal atom with a lower one.
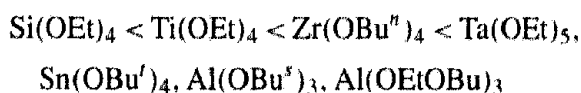
The calculated positive partial charge of the metal atoms according to literature [50] on basis of Allred-Rochow electronegativities increases in dependence on the type of alkoxide groups in the following order:

$$Sn(OBu^t)_4(+0.31), Si(OEt)_4(+0.32) < Al(OBu^s)_3$$
$$(+0.48) < Ta(OEt)_5(+0.63), Ti(OEt)_4(+0.63)$$
$$< Zr(OBu^n)_4 (+0.70).$$

Practically, the order of partial charge corresponds with the electronegativity of the metal atoms with exception of the Sn- and Si-atoms which are replaced by one another:

$$Si(OEt)_4(1.74) > Sn(OBu^t)_4(1.72)$$
$$> Al(OBu^s)_3(1.47) > Ta(OEt)_5(1.33)$$
$$> Ti(OEt)_4(1.32) > Zr(OBu^n)_4(1.22).$$

The epoxide ring-opening activity in e.g. 24 h sols with 10 mole% metal alkoxide follows the order:

$$Si(OEt)_4 < Ti(OEt)_4 < Zr(OBu^n)_4 < Ta(OEt)_5,$$
$$Sn(OBu^t)_4, Al(OBu^s)_3, Al(OEtOBu)_3$$

No satisfied correlation can be formulated comparing the order of electronegativity or positive partial charge of metal atoms with those of the metal alkoxide activity in epoxide ring-opening. For example, Sn-alkoxide with a low positive partial charge and high electronegativity, respectively, which occurs similarly to low-reactive $Si(OEt)_4$ shows a significant higher ring-opening activity than Ti-alkoxide with a high positive Ti-atom. This result reveals that the positive partial charge or electronegativity of the metal atoms alone is not sufficient for the explanation of the different metal alkoxide activities. It is known from literature [48, 51] that the structure and complexity of used metal alkoxides are very different due to the different size of alkoxide groups, the coordination state of the metal atom and the metal alkoxide concentration. Moreover, the hydrolysis and condensation reactions of metal alkoxides are different depending on the polarity of M—O—R bonds, the bulkiness of the alkoxide groups, the coordination of metal atoms and the amount of present water [52]. Additionally, the reactivity of metal alkoxides can

be changed by alcohol interchange in presence of other types of alcohols (here ethanol as solvent) [48]. Also, the extent and condensation degree of homo- and heterocondensation products of metal alkoxides and the sterical hindrance of the condensation products can influence the epoxide ring-opening reaction. Considering these facts a satisfactory explanation of the different activities of metal alkoxides cannot be made at present due to the lack of detailed knowledge.

3.2.   Effect of Water on Epoxide Ring-Opening

The original molar ratio $H_2O/OR = 0.5$ of GPTS hydrolyzates is reduced within 0.5 h reaction time to 0.13 due to hydrolysis reactions [39]. This remaining amount of water in the GPTS-hydrolyzate before the addition of metal alkoxides is to small for a complete hydrolysis of the metal alkoxides. The following experiments were carried out in presence of larger amounts of water ($2H_2O$ per total alkoxide groups) to examine the effect of more hydrolyzed/condensed metal alkoxide species on epoxide ring-opening reaction. The results of the 10 mole% metal alkoxide series are summarized as one example in Fig. 2. The lines in the figure are depicted for better clarity. Comparing the results of ring-opening in low-water containing systems with those of a high-water content, a primary increase in the ring-opening rate is likely to occure in sols with high-water content after short reaction time. The some what longer preparation time (2 h) of the sols with high water content is expected to increase the ring-opening

rate minimally but cannot be denied. However, the rate of ring-opening is partially retarded in water-rich hybrid sols (Al, Zr, Sn) after 24 h reaction time compared with 24 h sols with low-water content. Possibly, the higher water content leads primarily to more extended hydrolysis and to the formation of active MOH groups. However, the number of the MOR/OH rich species decreases with progressive condensation reactions leading to larger molecules or particles with a reduced number of active groups after 24 h reaction time. This reduced number and additional sterical effects caused by the size of the molecules could be a reason for the slow-down of the attack on epoxide rings after a longer reaction time. A complete ring-opening is found in hybrid gels which derive from water-rich 10 mole% sols. Please note that the complete ring-opening occurs also in Ti-containing hybrid gels which have shown a significant part of unopened epoxide rings in the low-water series (Fig. 1). A comparable effect of additional water on ring-opening in hybrid sols and gels was detected in water-rich systems with 50 mole% metal alkoxides as additive. Generally, high proportions of ethyl ether groups (>50%) were detected also in gels deriving from water-rich systems.

3.3.   Ring-Opening Activity of Metal Alkoxides in Comparison to Nanoscaled Metal Oxides

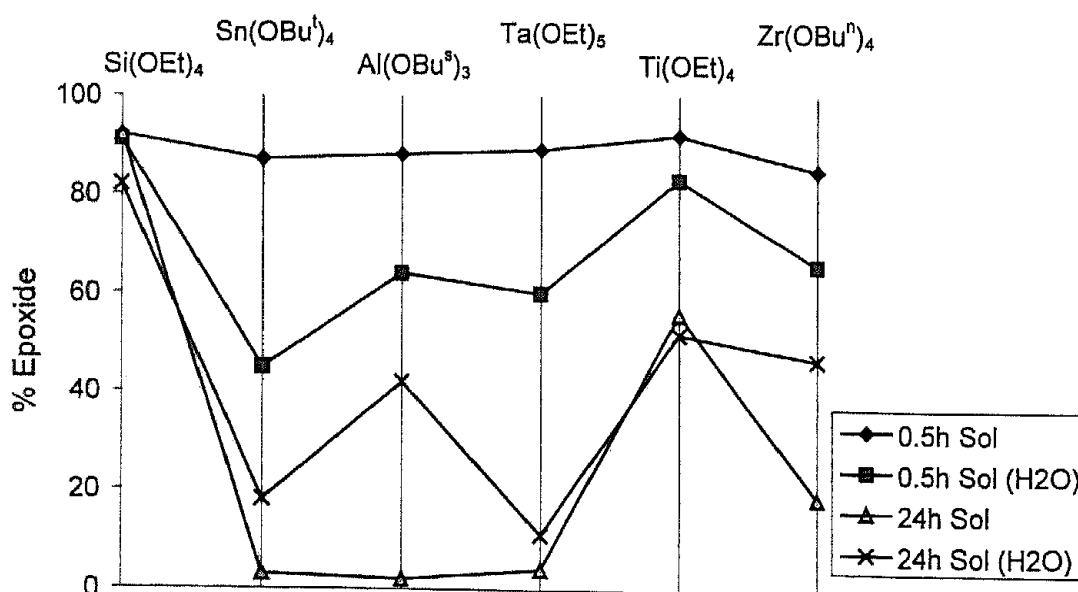Previous works [42] on the effect of nanoscaled $AlO(OH)$- (boehmite), SiO_2-, ZrO_2-, and CeO_2-sols on

Figure 2.   Amount of epoxide rings in hybrid sols of the system $1.0GPTS-1.5H_2O-0.1$ metal alkoxide (10 mole%) and with additional water up to $2H_2O/OR$ after 0.5 h and 24 h reaction time.

epoxide ring-opening in GPTS hydrolyzates have revealed significant differences in the activity of nanoparticles. In the following, the results on the activity of metal oxide nanoparticles shall be compared with those of the corresponding metal alkoxides at identical molar concentration and comparable reaction conditions.

The highest ring-opening activity in GPTS hydrolyzates with 10 mole% metal oxide sol was found for boehmite [AlO(OH)] and for acidic stabilized silica sols [42]. The surprisingly high activity of the acidic silica sol in comparison with the low-active Si(OEt)$_4$ is explained by the presence of catalytically active Al-oxo-hydroxo-species in the acidic silica sol. These Al-species are used as positively charged stabilisators of the SiO$_2$ particle surface. Comparing the ring-opening activity of Si(OEt)$_4$ with a basically (ammonia, alkali hydroxides) stabilized silica sol which contains only a very small amount of AlO/OH-groups (natural abundance of impurities) a similar low ring-opening activity (about 10%) can be detected in both GPTS derived 24 h hybrid sols and gels. The result confirms that metal oxide free ≡SiOH-species do not significantly activate the epoxide ring-opening reaction.

The comparison of 10 mole% Al- and Zr-alkoxide containing 24 h hybrid sols with corresponding nanoscaled Al- and Zr-oxides containing sols shows for the latter a lower ring-opening (ca. 15%) than for the alkoxides (>80%). The reason is the lesser content of reactive OR/OH groups per metal-oxo-bond on the nanoscaled particle surface in comparison with low-molecular metal alkoxy/hydroxy species. For example the boehmite particles consist of a layer structure with active AlOH groups only at their surface [53]. The Al-alkoxides [54] and their primarily low-molecular hydrolysis and condensation products in presence of a low water content show a high number of OR/OH groups per M—O bond and a more flexible structure so that the AlOR/OH groups are well accessible for catalytic epoxide ring-opening reactions.

Regardless of the strong differences in ring-opening activities of 10 mole% nanoscaled metal oxides or metal alkoxides containing 24 h hybrid sols, the corresponding hybrid gels of both systems show a ring-opening to a great extent (80—100%). From this it follows that the heat treatment of the 24 h sols significantly increases the activity of nanoscaled oxides with regard to a stronger epoxide ring-opening.

Additional ^{13}C NMR experiments were carried out on GPTS-1.5H$_2$O hydrolyzates with different amounts of boehmite sol and Al(OBu^s)$_3$ for more quantitative

data. The results show that the concentration of the high-reactive Al-alkoxide can be decreased to a molar ratio GPTS : Al $= 1 : 4 \times 10^{-4}$ to get a comparable ring-opening activity in hybrid sols and gels with the system containing 10 mole% boehmite (GPTS : Al $= 0.9 : 1 \times 10^{-1}$). This example reveals that only about a two hundredth part of the Al-content of boehmite is required for the Al-alkoxide to result in comparable epoxide ring-opening activities. The result stresses the structural aspect of additives with the same metal atom on the epoxide ring-opening activity.

3.4.   Condensation Degree of RSi(O$_{0.5}$)$_3$ Units

Besides organic reactions of the epoxide group in GPTS derived systems the extent of homo- and heterocondensation reactions of the alkoxy groups of organofunctional alkoxysilanes and of metal alkoxides should affect the properties, e.g. homogeneity and rigidity, of hybrid materials [41, 55]. Examinations by NMR and IR spectroscopies on hydrolysis and condensation reactions of different organofunctional trialkoxysilanes in dependence on organic ligands, water content, type of alcohol, reaction time, temperature and pH are reported in literature [24, 26, 28–30, 47, 56–58]. The catalytic effect of metal alkoxides on condensation reactions is also described e.g. [43, 44, 55]. Moreover, works have been published on the formation of heterocondensed species with Si—O—M bonds in GPTS-metal alkoxide systems [16, 22, 41] and on their hydrolytic stability [40, 41]. Most of the previous examinations on condensation reactions of RSi(O$_{0.5}$)$_3$ units in GPTS-hydrolyzates and in presence of metal alkoxide have been carried out either on solutions or solids and in most cases qualitative results were reported. This work presents a more quantitative examination of the condensation degree of RSi(O$_{0.5}$)$_3$ units in GPTS derived hybrid sols and also gels in dependence on different types and concentrations of metal alkoxides and on water content by means of liquid- and solid-state ^{29}Si NMR. The condensation degree (c.d.) of the RSi(O$_{0.5}$)$_3$ unit was examined in hybrid sols of the composition GPTS-1.5H$_2$O-0.01/0.1/1.0M(OR)$_n$ after an average reaction time of 7 h and in corresponding hybrid gels. The relatively high reaction time of sols (7 h) is due to the necessarily high number of spectra accumulation for a reliable signal to noise ratio of the NMR spectra (see experimental). Homo- and heterocondensed species are considered in the c.d. on the basis of their known regions of the chemical shift of
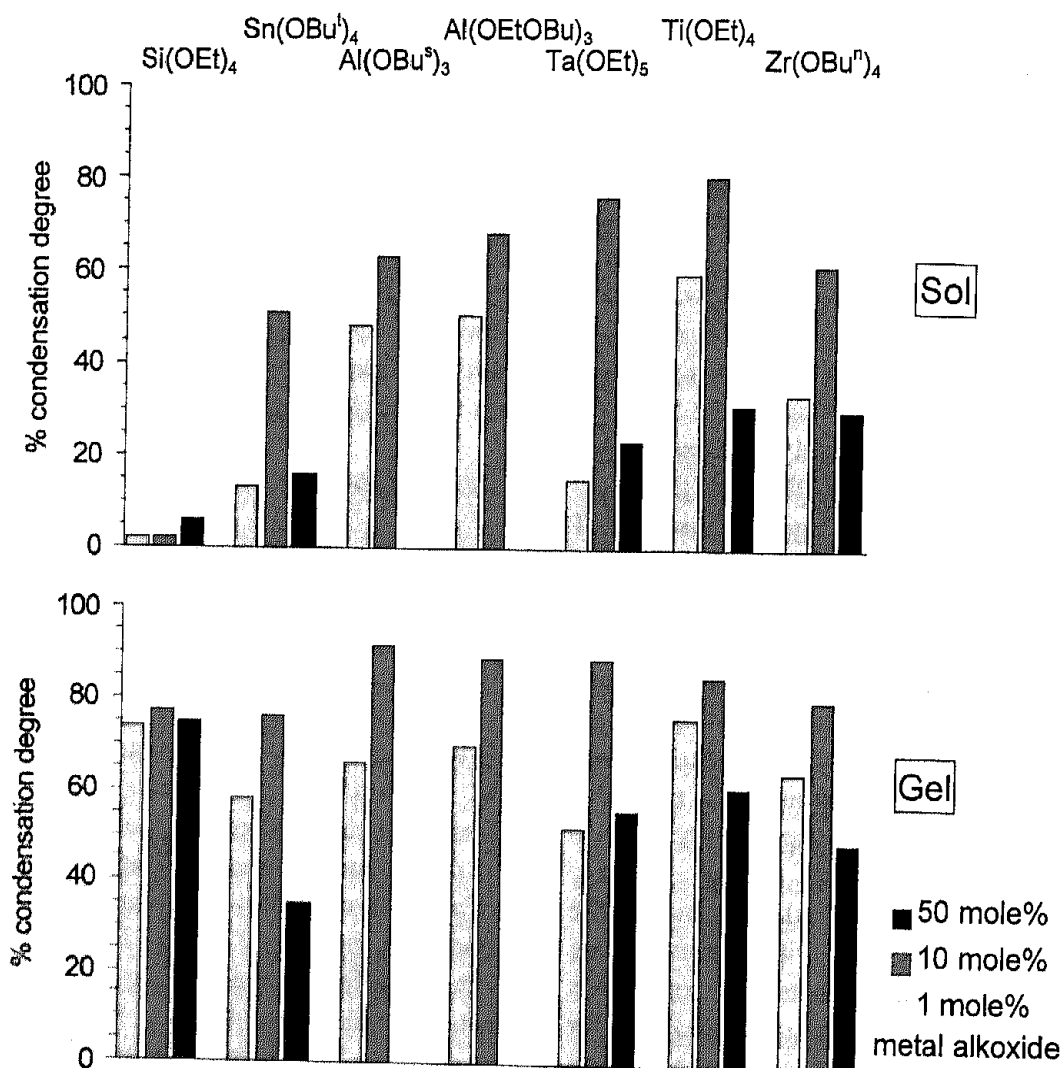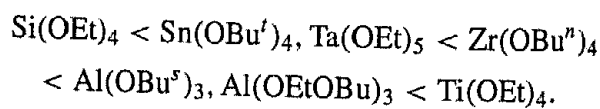
Figure 3. Condensation degree of $RSi(O_{0.5})_3$ units in hybrid sols (7 h) and gels of the system $1.0GPTS-1.5H_2O-0.01/0.1/1.0$ metal alkoxide (1/10/50 mole%).

^{29}Si NMR signals [40, 41]. However, difficulties arise in c.d. determination when signals of heterocondensed species of a defined T-type shift into a region of another T-structure. This is known in the case of ^{29}Si NMR signals of Al—O—Si bonds which show a strong low-field shift compared with corresponding homocondensed Si—O—Si bonds [22, 59]. Therefore, the c.d. of $RSi(O_{0.5})_3$ units is underestimated in presence of significant amounts of Si—O—Al bonds. For this reason no data are given here for c.d. in GPTS-Al-alkoxide systems with an Al-alkoxide content higher than 10 mole%. Characteristic ^{29}Si NMR spectra of hybrid sols and gels have already been presented in previous works of this series [39, 42].

The results of ^{29}Si NMR investigation on c.d. in hybrid sols after 7 h reaction time and in gels are summarized in Fig. 3. The GPTS sols with different additions of $Si(OEt)_4$ show only a very low c.d. of ca. 5% after 7 h reaction time. However, the addition of a small amount (1 mole%) of Ti-, Al-, Zr-, Ta- or Sn-alkoxide to a GPTS hydrolyzate results in a remarkable increase of c.d. up to 60% in case of $Ti(OEt)_4$ in hybrid sols. According to Fig. 3 the effect of 1 mole% metal alkoxides on c.d. of $RSi(O_{0.5})_3$ units increases in the following order:

$$Si(OEt)_4 < Sn(OBu^t)_4, Ta(OEt)_5 < Zr(OBu^n)_4$$
$$< Al(OBu^s)_3, Al(OEtOBu)_3 < Ti(OEt)_4.$$

A metal alkoxide concentration of 10 mole% leads to an additional increase in c.d. up to 80% [$Ti(OEt)_4$] in hybrid sols (Fig. 3). The order of c.d. in 10 mole% hybrid sols differs in the position of Ta-alkoxide and is found to:
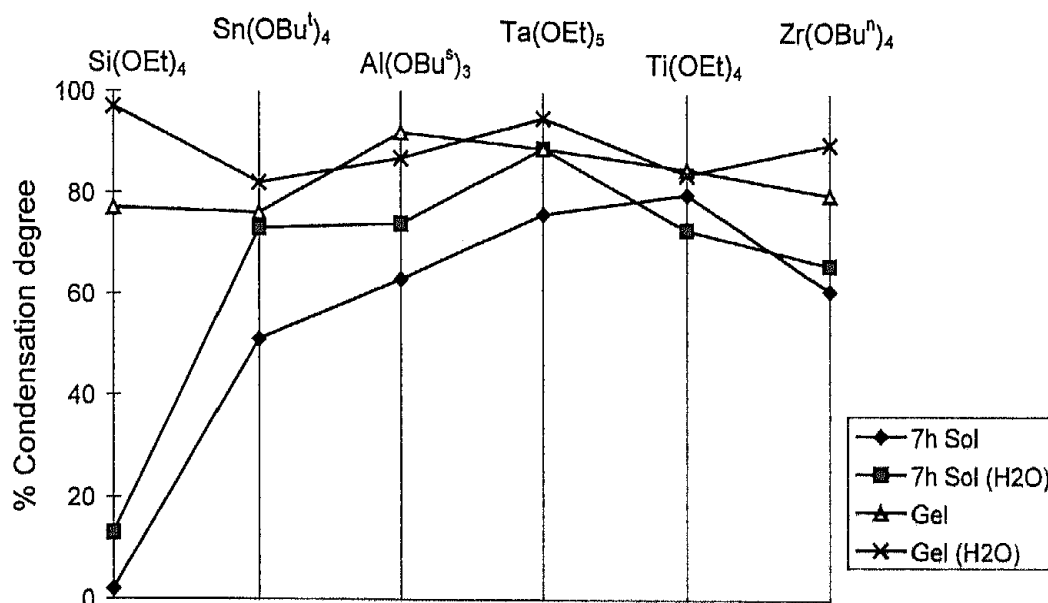
$$Si(OEt)_4 \ll Sn(OBu^t)_4 < Zr(OBu^n)_4, Al(OBu^s)_3$$
$$< Al(OEtOBu)_3 < Ta(OEt)_5 < Ti(OEt)_4.$$
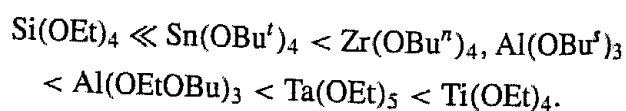
Figure 4. Condensation degree of $RSi(O_{0.5})_3$ units in hybrid sols of the system $1.0GPTS-1.5H_2O-0.1$ metal alkoxide (10 mole%) and with additional water up to $2H_2O/OR$ after 7 h reaction time and in corresponding hybrid gels.

The significant decrease in c.d. of $RSi(O_{0.5})_3$ groups in hybrid sols in presence of high amounts (50 mole%) of metal alkoxides is especially remarkable (Fig. 3). Possibly, the insufficient water content for extended hydrolysis of the added metal hinders additional condensation reactions of $RSi(O_{0.5})_3$ units.

As expected the transformation of hybrid sols in gels by heat treatment shows an additional increase of c.d. in hybrid gels due to thermally induced condensation of unreacted SiOH/OR and MOH/OR groups (Fig. 3). A c.d. between 52% [$Ta(OEt)_5$] and 76% [$Ti(OEt)_4$] in hybrid gels is already found with 1 mole% additives. Noteworthy, the c.d. of the hybrid gel deriving from 1 mole% $Si(OEt)_4$ addition also shows a relatively high c.d. up to 77% in comparison to ca. 5% in hybrid sols. Obviously, the strong differences in c.d. found between hybrid sols with $Si(OEt)_4$ as additive and metal alkoxide catalyzed sols equalize after the sol-gel transformation at higher temperatures. Thus, the thermally induced condensation can compensate for a weak catalytic effect of metal alkoxides on condensation reactions. Generally, the highest c.d. is found in hybrid gels with 10 mole% additives like the corresponding 10 mole% hybrid sol series. Obviously, the retarded condensation reactions already detected in 50 mole% sols cannot be compensated for by thermal activation.

The activities of metal alkoxides concerning the c.d. of $RSi(O_{0.5})_3$ units in 10 mole% hybrid sols follow satisfactorily the decreasing electronegativity of their metal atoms (order of metal alkoxides from left to right

in Fig. 3) except for the Zr-containing hybrid sol. No correlation with electronegativity, bulkiness of alkoxide groups or size of metal atoms is found for 1 mole% hybrid sols or for hybrid gels so that a general correlation of metal alkoxide reactivity with the electronegativity/positive partial charge of the metal atoms cannot be established. Probably, the manifold—until now unknown—reactions and structures of metal alkoxide components, already discussed in the paragraph on the epoxide ring-opening, are also responsible for their different activities concerning condensation reactions.

Figure 4 shows on example of 10 mole% series that an additional amount of water ($2H_2O/OR$) leads most often to an increased c.d. of hybrid sols. The Ta-alkoxide containing hybrid sol shows a maximum c.d. of 89% in this series and the Zr-hybrid sol a minimum c.d. of 66%. The activity of 10 mole% metal alkoxides concerning condensation reactions in water-rich hybrid sols increases in the order:

$$Si(OEt)_4 \ll Zr(OBu^n)_4 < Al(OBu^s)_3, Al(OEtOBu)_3,$$
$$Sn(OBu^t)_4, Ti(OEt)_4, < Ta(OEt)_5.$$
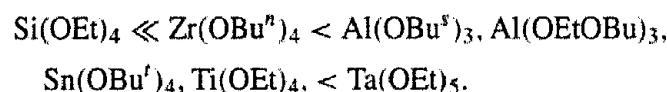
Probably, the increase in c.d. in presence of an excess of water is due to more extended hydrolysis of alkoxide groups resulting in stronger condensation reactions.

Partially, a slightly additional increase in c.d. is found in hybrid gels which derive from water-rich sols ($2H_2O/OR$). The other gels show a comparable c.d. with hybrid gels which derive from systems containing little water.

4. Conclusions

- In contrast to low reactive $Si(OEt)_4$ the metal alkoxides $Al(OBu^s)_3$, $Al(OEtOBu)_3$, $Ti(OEt)_4$, $Zr(OBu^n)_4$, $Ta(OEt)_5$ and $Sn(OBu^t)_4$ catalyse the epoxide ring-opening and condensation reaction of $RSi(O_{0.5})_3$ units, especially in hybrid sols, to a different extent. A correlation of the activity of metal alkoxides towards epoxide ring-opening and condensation reactions with electronegativity, positive partial charge and size of metal atoms or bulkiness of alkoxy groups could not be found. The results reveal that additional structural parameters of all participating components and of their reaction products are necessary for a satisfactory explanation of the different metal alkoxide activities.

- The extent of the epoxide ring-opening and of the condensation degree of $RSi(O_{0.5})_3$ units in GPTS-$1.5H_2O$ hydrolyzates strongly depends on the amount (1–50 mole%) of metal alkoxide additive. The maximum in ring-opening and in condensation degree has been found in hybrid sols and gels with 10 mole% metal alkoxides as additives each.

- Al-alkoxide already shows at lowest concentration (1 mole%) a prefered activity in ring-opening in long term (24 h) hybrid sols which results in a complete ring-opening in corresponding hybrid gels. Except for Si- and Ti-alkoxide a complete epoxide ring-opening was found in hybrid gels after the thermal sol-gel transformation.

- Ti-alkoxide shows a relatively low activity in epoxide ring-opening in hybrid sols and gels but always causes the highest condensation degree of $RSi(O_{0.5})_3$ units in hybrid sols after 7 h reaction time independent of its concentration.

- Hybrid sols with an excess of water ($2H_2O/OR$) reveal an accelerated ring-opening after short reaction times, but a sometimes retarded ring-opening in 24 h sols compared with corresponding low water containing systems (GPTS-$1.5H_2O$). Nevertheless, a complete epoxide ring-opening is mostly found in hybrid gels not dependend on the water content of the sols used for their preparation. Generally, the condensation degree of hybrid sols increases at high water content.

- In presence of ethanol as solvent remarkable amounts of ethyl ether groups (>50% with regard to epoxide) are detected in course of the epoxide ring-opening which decrease the amount of polyether bonds. Therefore, the content of alcohols should be diminished or replaced by a non-reactive polar solvent for a preferred formation of polyether bonds in hybrid polymers.

References

1. T. Mogami, H. Kawashima, H.S.N. Deguchi, German Patent DE 33 35 557, 1984.
2. H. Schmidt, J. Non-Cryst. Solids **178**, 302 (1994).
3. R. Kasemann, H. Schmidt, and E. Wintrich, Mat. Res. Soc. Symp. Proc. **346**, 915 (1994).
4. W. Que, Y. Zhou, Y.L. Lam, Y.C. Chan, Z. Sun, S.D. Cheng, H.P. Li, and C.H. Kam, J. Mater. Sci. Lett. **19**, 1247 (2000).
5. H.K. Schmidt, J. Sol-Gel Technol. **8**, 557 (1997).
6. G. Philipp and H. Schmidt, J. Non-Cryst. Solids **63**, 283 (1984).
7. R. Kasemann, H. Schmidt, E. Arpac, and V. Gerhard, German Patent DE 43 38 361, 1995.
8. P. Judeinstein, P.W. Oliveira, H. Krug, and H. Schmidt, Advanced Materials for Optics and Electronics **7**, 123 (1997).
9. P.W. Oliveira, H. Krug, A. Frantzen, M. Mennig, and H. Schmidt, SPIE Proceedings **3136**, 452 (1997).
10. M. Mennig, K. Endres, M. Schmitt, and H. Schmidt, J. Non-Cryst. Solids **218**, 373 (1997).
11. U. Schubert, N. Hüsing, and A. Lorenz, Chem. Mater. **7**, 2010 (1995).
12. M. Popall, H. Meyer, H. Schmidt, and J. Schulz, Mat. Res. Soc. Symp. Proc. **180**, 995 (1990).
13. J. Livage, C. Sanchez, and F. Babonneau, in *Chemistry of Advanced Materials, An Overview*, edited by L.V. Interrante and M.J. Hampden-Smith (J. Wiley-VCH, 1998), New York.
14. M.W. Daniels and L.F. Francis, J. Colloid Interface Sci. **205**, 191 (1998).
15. M.L. Sforca, I.V.P. Yoshida, and S.P. Nunes, J. Membr. Sci. **159**, 197 (1999).
16. I. Gautier-Luneau, A. Mosset, J. Galy, and H. Schmidt, J. Mater. Sci. **25**, 3739 (1990).
17. E. Bayer, K. Albert, J. Reiners, and M. Nieder, J. Chromatogr. **264**, 197 (1983).
18. G.R. Bogart, D.E. Leyden, T.M. Wade, W. Schafer, and P.W. Carr, J. Chromatogr. **483**, 209 (1989).
19. J.J. Pesek and M.T. Matyska, J. Chromatogr. A **687**, 33 (1994).
20. A. Tuel, H. Hommel, A.P. Legrand, M.F. Gonnord, E. Mincsovics, and A.M. Siouffi, J. Chim. Phys. **89**, 477 (1992).
21. M. Popall and H. Durand, Elektrochim. Acta **37**, 1593 (1992).
22. M. Templin, U. Wiesner, and H.W. Spiess, Adv. Mater. **9**, 814 (1997).
23. A.M. Zaper, A. Cholli, and J.L. Koenig, Polymer Sci. Technol. **27**, 299 (1985).
24. K.W. Allen, J. Adhesion Sci. Technol. **6**, 23 (1992).
25. H. Schmidt and B. Seiferling, Mat. Res. Soc. Symp. Proc. **73**, 739 (1986).

26. T.J. Horr and G.D. Reynolds, J. Adhesion Sci. Technol. 11, 995 (1997).

27. G. Xue, J.L. Koenig, D.D. Wheeler, and H. Ishida, J. Appl. Polym. Sci. 28, 2633 (1983).

28. G. Tesoro and Y. Wu, J. Adhesion Sci. Technol. 5, 771 (1991).

29. M.P.J. Peeters, W.J.J. Wakelkamp, and A.P.M. Kentgens, J. Non-Cryst. Solids 189, 77 (1995).

30. L. Lan, A. Montenero, G. Gnappi, and E. Dradi, Gazz. Chim. Ital. 127, 505 (1997).

31. G. Odian, Principles of Polymerization (J. Wiley and Sons, New York, 1981), p. 512.

32. Chemistry and Technology of Epoxy Resins, edited by B. Ellis (Blackie Academic Professional, London, 1993).

33. G. Xue, Angew. Makromol. Chem. 151, 85 (1987).

34. G.A. Sigel, R.C. Domszy, and W.C. Welch, Mat. Res. Soc. Symp. Proc. 346, 135 (1994).

35. J. Comyn, D.P. Oxley, R.G. Pritchard, C.R. Werrett, and A.J. Kinloch, Int. J. Adhesion and Adhesives 9, 201 (1989).

36. M.P.J. Peeters, A.P.M. Kentgens, and I.J.M. Snijkers-Hendrickx, Mat. Res. Soc. Symp. Proc. 435, 415 (1996).

37. R. Wegler, Angew. Chem. 67, 582 (1955).

38. G. Philipp and H. Schmidt, J. Non-Cryst. Solids 82, 31 (1986).

39. D. Hoebbel, M. Nacken, and H. Schmidt, J. Sol-Gel Sci. Technol. 12, 169 (1998).

40. D. Hoebbel, M. Nacken, and H. Schmidt, J. Sol-Gel Sci. Technol. 13, 37 (1998).

41. M. Nacken, D. Hoebbel, and H. Schmidt, Mat. Res. Soc. Symp. Proc. 576, 221 (1999).

42. D. Hoebbel, M. Nacken, and H. Schmidt, J. Sol-Gel Sci. Technol. 19, 305 (2000).

43. E. Geiter, PhD Thesis, University of Saarland, Saarbrücken, Germany, 1997.

44. P. Innocenzi, G. Brusatin, M. Guglielmi, and R. Bertani, Chem. Mater. 11, 1672 (1999).

45. G. Xue, J.L. Koenig, H. Ishida, and D.D. Wheeler, Rubber Chem. Technol. 64, 162 (1991).

46. G.G. Habermehl and I. Wippermann, Z. Naturforsch. 46b, 1421 (1991).

47. K. Piana and U. Schubert, Chem. Mater. 6, 1504 (1994).

48. D.C. Bradley, R.C. Mehrotra, and D.P. Gaur, Metal Alkoxides (Academic Press, San Diego, 1978).

49. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry (J. Wiley & Sons, New York, 1966).

50. J. Livage and M. Henry, in Ultrastructure Processing of Advanced Ceramics, edited by J.D. Mackenzie and D.R. Ulrich (J. Wiley, New York, 1988), p. 183.

51. M. Guglielmi and G. Carturan, J. Non-Cryst. Solids 100, 16 (1988).

52. J. Blanchard, F. Ribot, C. Sanchez, P. Bellot, and A. Trokiner, J. Non-Cryst. Solids 265, 83 (2000).

53. G.G. Christoph, C.E. Corbato, D.A. Hofmannn, and R.T. Tettenhorst, Clays and Clay Minerals 27, 81 (1979).

54. O. Kriz, B. Casensky, A. Lycka, J. Fusek, and S. Hermanek, J. Magn. Reson. 60, 375 (1984).

55. J.D. Basil and C.C. Lin, Mat. Res. Soc. Symp. Proc. 121, 49 (1988).

56. E.R. Pohl and F.D. Osterholtz, Polymer Sci. Technol. 27, 157 (1985).

57. M.W. Daniels, J. Sefcik, L.F. Francis, and A.V. McCormick, J. Colloid Interface Sci. 219, 351 (1999).

58. C.J. Brinker, J. Non-Cryst. Solids 100, 31 (1988).

59. G. Engelhardt and D. Michel, High Resolution Solid-State NMR of Silicates and Zeolites (J. Wiley & Sons, New York, 1987).