A NMR Study on the Hydrolysis, Condensation and Epoxide Ring-Opening Reaction in Sols and Gels of the System Glycidoxypropyltrimethoxysilane-Water-Titaniumtetraethoxide

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Abstract. The examination of hydrolysis, homo- and hetero-condensation reactions, of the condensation degree and the extent of epoxide ring opening in the course of sol-gel process was carried out by means of liquid- and solid-state ^{29}Si and ^{13}C NMR in the system 3-glycidoxypropyltrimethoxysilane (GPTS)-titaniumtetraethoxide-water (molar ratio $1:1:1.5\text{--}14$) which is frequently used for the synthesis of heterometal hybrid polymers. The monomeric silanol groups in the GPTS-prehydrolysate immediately co-condense with the Ti-tetraethoxide to Si—O—Ti bonds to an extent of about 50–60% which remain stable in sols and also in the corresponding gels at low amounts of free water ($0.02\,H_2O/OR$) in the sol. An increasing amount of free water in the sol ($\geq 0.12\,H_2O/OR$) leads to an increased hydrolytic cleavage of the heterometal bonds and to the formation of homo-condensed polysiloxanes. The condensation degree of $RSiO_{1.5}$ units in the Ti-containing sols is with 30–60% relatively high in comparison to Ti-free GPTS sols (ca. 5%) whereas the condensation degree of GPTS derived gels (81%) was found to be similar to that of the Ti-containing gels (60–80%). Ti-tetraethoxide accelerates the ring opening reaction of the epoxide group in the sols in dependence on the water content. Up to 78% of the epoxide rings are opened after 24 h in the sol with the highest water content ($2\,H_2O/OR$). No epoxide rings can be detected in Ti-containing gels which derive from sols with an amount of free water of $\geq 0.12\,H_2O/OR$. The results give a first insight into the different parallel reactions in this system and can contribute to more structure controlled syntheses of heterometal hybrid polymers.

Keywords: ^{29}Si and ^{13}C NMR, hetero-condensation, condensation degree, titanosiloxane bonds, epoxide ring opening

1. Introduction

3-Glycidoxypropyltrimethoxysilane (GPTS) and titanium alkoxides are frequently employed for the preparation of dense heterometal hybrid polymers which are used, e.g., for hard coatings of organic polymers [1, 2] and contact lens materials [3, 4] in the optical industry. Up to now only little knowledge exists about the manifold reactions which lead to hybrid materials with desirable properties. However, the continuously increasing demands on hightech materials on the basis of heterometal hybrid polymers require a better knowledge on the relationships between the structure of the materials and their properties.

Figure 1 gives an overview of different reactions in the system GPTS-water-titaniumtetraethoxide which include hydrolysis, homo- and hetero-condensation of the metal alkoxides and ring-opening reactions of the epoxide group which can lead to diols or poly(ethylene oxide) chains. The inorganic polycondensation and organic polymerisation and their interactions are responsible for the unique properties of tailor-made hybrid materials. Investigations have been made on separate reactions in liquid and solid GPTS systems of
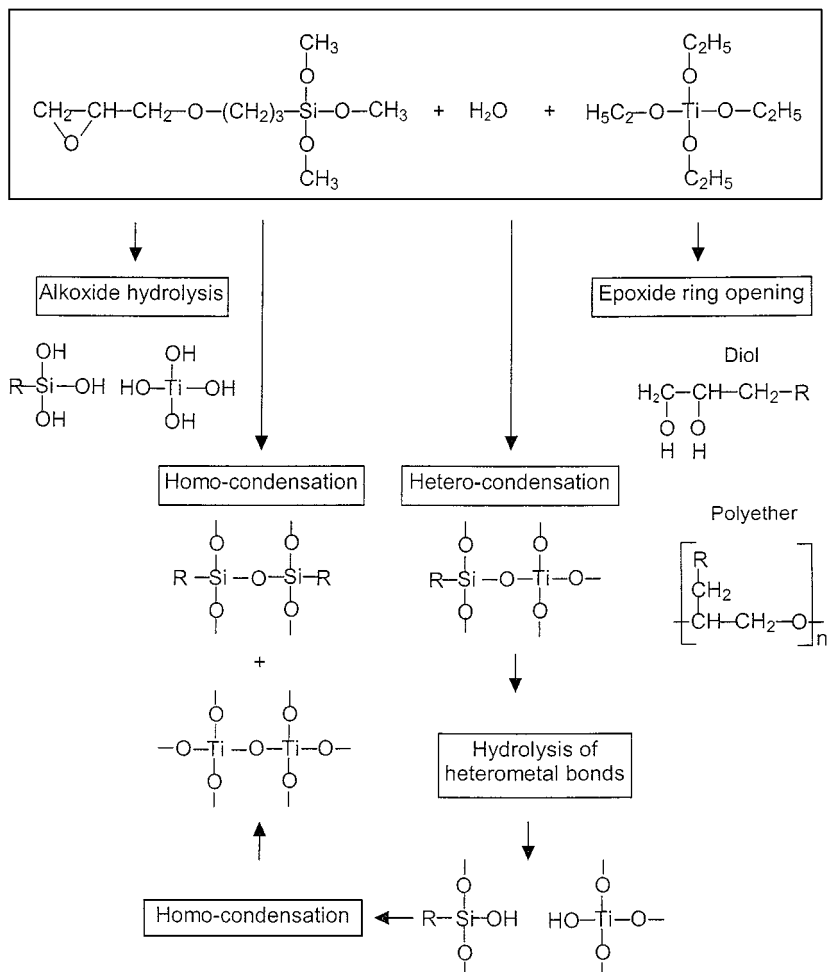
Figure 1.   Scheme of reactions in the system 3-glycidoxypropyltrimethoxysilane (GPTS)-H_2O-titaniumtetraethoxide.

a variety of compositions. The hydrolysis and homo-condensation reactions of GPTS were examined in [5, 6]. Likewise, the accelerating effect of titanium-alkoxides on silanol condensation [7, 8] and on the epoxide ring opening [9, 10] is described. The presence of heterometal bonds in hybrid materials is important for a high homogeneity of materials on a molecular scale which is required for, e.g., optical applications [3, 11]. Details concerning the existence and stability of heterometal Si—O—M bonds (M = Al, Ti, Zr) in different sol-gel systems were obtained during the last years [12–17]. For example, Si—O—Ti bonds were detected and characterised mainly by ^{17}O and ^{29}Si NMR in the systems dimethyldiethoxysilane-Ti(OPr^i)$_4$ [12], diphenylsilanediol-Ti(OPr^i)$_4$ [13] and

tetraethoxysilane-Ti(OPr^n)$_4$ [15, 16]. Not enough details and evidences exist concerning the formation of oxygen bridged heterometal Si—O—Ti bonds in GPTS derived hybrid polymers and their hydrolytic stability in the course of the sol-gel process, although such heterometal bonds are frequently mentioned in the literature [18–21]. Recently [22], we reported on the ^{17}O and ^{29}Si NMR spectroscopic identification of heterometal bonds in the GPTS-H_2O-Ti(OC$_2H_5$)$_4$ system which is further used in the present work. The objective of the present article is to give an overview of the main reactions and their mutual interactions in sols and gels by example of a well-defined GPTS-water-titaniumtetraethoxide system by means of ^{29}Si and ^{13}C NMR spectroscopy. Topics of the work are

the homo- and hetero-condensation reactions of the Si-component, the condensation degree of the siloxanes and titanosiloxanes and the extent of the epoxide ring-opening reaction in Ti-free and Ti-containing sols and in their corresponding gels.

2. Experimental

Solutions of the systems GPTS-H_2O-Ti(OC$_2$H$_5$)$_4$ were prepared at molar ratios Si : Ti = 1 and H_2O : OR (alkoxide group) = 0.21 to 2 in six defined steps according to the flow chart in Fig. 2. For all steps of the hydrolysis 0.1 M HCl was used and a time interval of 0.5 h was chosen between the single steps. The water content of the sols was determined by Karl-Fischer-titration [23] and the epoxide content was examined according to [24]. In each case the examination of the samples occured 0.5 h after their preparation. The gel samples were prepared from corresponding sols after their storage at room temperature for 24 h followed by their heating at 130°C for 5 h. The solid products were then crushed and heated again for 2 h at 130°C. The gelation of sol 2 required a heating at 130°C for 24 h.

The liquid-state ^{29}Si and ^{13}C NMR spectra were obtained using a Bruker AC 200 spectrometer operating at a field of 4.7 T. ^{29}Si NMR: inverse gated sequence, external reference: tetramethylsilane, internal standard: phenyltrimethylsilane, repetition time (r.t.): 40 s, pulse angle (p.a.): 63°, number of scans (n.s.): 45–1500. ^{13}C NMR: single pulse experiment, r.t.: 10 s, p.a.: 60°, n.s.: 180. Generally, the ^{13}C NMR measurements of the solutions 2–6 were started 15 min after their preparation. The ^{29}Si NMR spectra were accumulated for 0.5 h (sol 2) or 14 h (sol 3–6). The average recording time was used for characterisation of the reaction time of the samples. The solid-state ^{29}Si and ^{13}C NMR spectra were recorded using a Bruker MSL 200 spectrometer at 4.7 T. ^{29}SiNMR: ^{29}Si{^{1}H} sequence, external standard Q$_8$M$_8$, MAS 3 kHz, p.a.: 63°, r.t.: 60 s, n.s.: 200–1000 scans. ^{13}C NMR: single pulse ^{13}C{^{1}H} high power decoupling, external standard adamantane, p.a.: 50°, r.t.: 4 s, n.s.: 5000 scans. The quantitative evaluation of the liquid state NMR spectra which were recorded at identical acquisition parameters 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 regarding to the ring-opening reaction was made by comparison of the intensity of the epoxide signal around $\delta = 44$ ppm with that of the methylene group signal at $\delta = 23$ ppm which is used as reference. The T_1 values of the

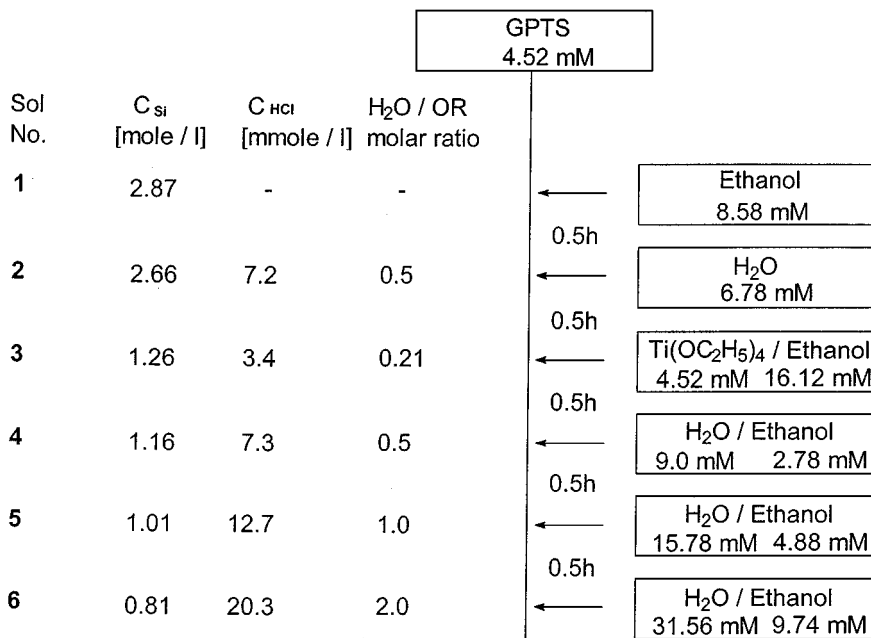| Sol No.	C$_{Si}$ [mole / l]	C$_{HCl}$ [mmole / l]	H$_2$O / OR molar ratio		
					GPTS 4.52 mM
1	2.87	-	-	← (0.5h)	Ethanol 8.58 mM
2	2.66	7.2	0.5	← (0.5h)	H$_2$O 6.78 mM
3	1.26	3.4	0.21	← (0.5h)	Ti(OC$_2$H$_5$)$_4$ / Ethanol 4.52 mM 16.12 mM
4	1.16	7.3	0.5	← (0.5h)	H$_2$O / Ethanol 9.0 mM 2.78 mM
5	1.01	12.7	1.0	← (0.5h)	H$_2$O / Ethanol 15.78 mM 4.88 mM
6	0.81	20.3	2.0	←	H$_2$O / Ethanol 31.56 mM 9.74 mM

Figure 2.   Flow chart of the preparation of sols in the system GPTS-H$_2$O-Ti(OC$_2$H$_5$)$_4$.

C-atoms in the GPTS-gel were determined to be 225 ms (44 ppm) and 156 ms (23 ppm), so that the used repetition time should be sufficient for a quantitative comparison of the signal intensities.

3.   Results and Discussion

The consumption of water in the course of the hydrolysis/condensation reactions of GPTS with titaniumtetraethoxide gives useful information on the state of the primary hydrolysis reactions. The results of the water determination in the sols 2–6 are summarised in Fig. 3. The diagram shows that the added amount of water in sol 2 (expressed as H_2O/OR ratio), strongly decreases from 0.5 to 0.13 within 0.5 h hydrolysis time. This means that about 40% of the OR groups of the GPTS should be hydrolysed to SiOH groups assuming no condensation reactions. The rest of the water in sol 2 is small enough according to [18–20] to prevent quick homo-condensation reactions of the Ti-alkoxide and precipitation. Practically, the rest of the water in sol 2 is completely consumed by the added Ti-tetraethoxide for partial hydrolysis of its alkoxide groups (sol 3). The amount of free water in the sols 4–6 is again increased by the stepwise addition of more water. A nearly constant consumption of 0.46 H_2O/OR is obtained in the sols 5 and 6. It follows from this that the amount of

water consumed for a complete hydrolysis and condensation of the reaction partners is only a little lower than the theoretically calculated one (0.5 H_2O/OR).

3.1.   Heterometal Si—O—Ti Bonds in Sols and Gels

The determination of the condensation degree of the $RSiO_{1.5}$ units and the examination of Si—O—Ti bonds in sols and gels were carried out by ^{29}Si NMR. Preliminary results [22] showed that in sol 2 (see Fig. 2) practically only monomeric silanes with OH, methoxy and ethoxy groups exist and thus condensed species can be neglected. The ethoxy group at the epoxysilane appears due to the re-esterification of silanols by ethanol which is used as solvent. The evaluation of the ^{29}Si NMR spectrum showed that about 50% of the alkoxide groups of the GPTS in sol 2 are hydrolysed to OH groups after 0.5 h. The difference in the quantity of SiOH groups as determined by the titration (ca. 40%) and the NMR (ca. 50%) could be caused by the fact that the NMR spectra have been recorded over prolonged period of time (e.g., 30 min) where as titration is done at a fixed point of time.

The ^{29}Si NMR spectrum of sol 3 after the addition of titaniumtetraethoxide (Fig. 4, II) shows three sharp signals at $\delta = -42.44$, -43.58 and -44.74 ppm which were identified as unreacted GPTS (about 4% of the signal intensity) and as the monomeric silanes
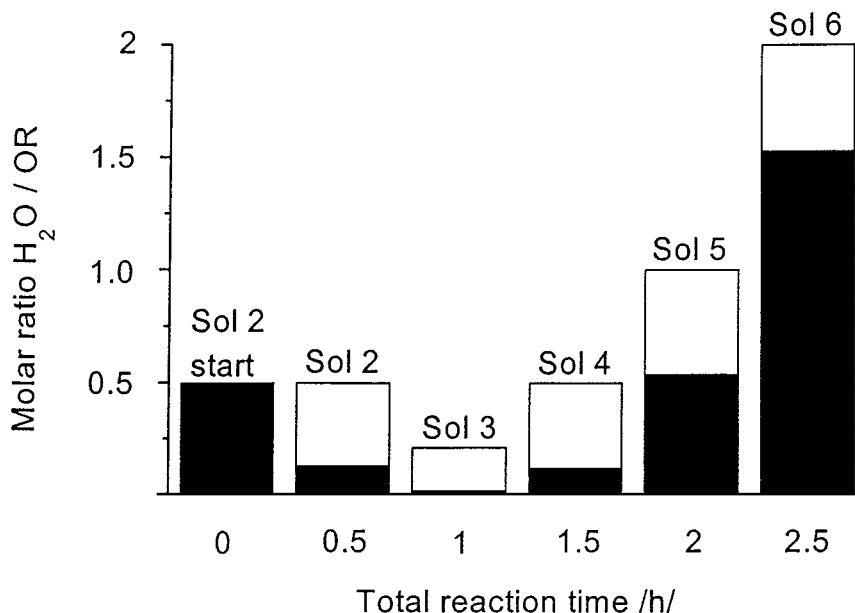

Figure 3.   Amount of added water and content of remaining water (black bars) in the sols 2–6 each after 0.5 h reaction time.
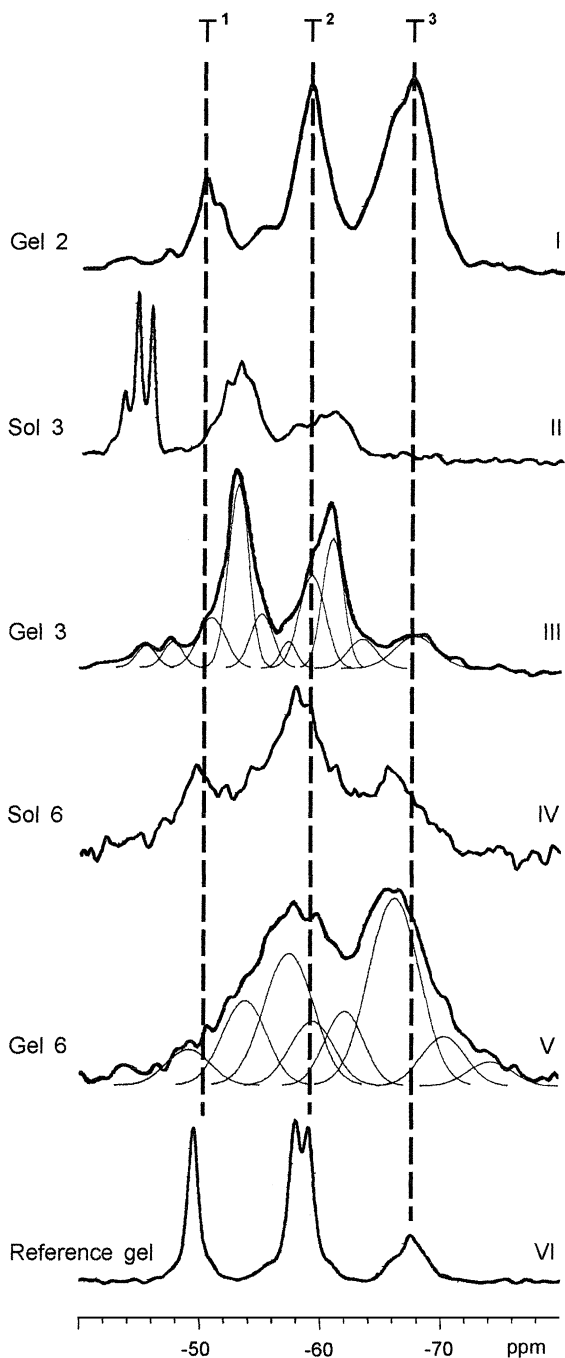
of about 65% of the expected total intensity. The addition of further water to sol 3 up to 2.0 H_2O/OR leads to sol 6. The ^{29}Si NMR spectrum of sol 6 (Fig. 4, IV) shows no more monomeric silane species but three broad signals with chemical shifts around $\delta = -50$, -58 and -66 ppm. The position of these three signals is in accordance with those of a homo-condensed GPTS hydrolysate (2 H_2O/OR). Therefore, the signals of sol 6 are mainly attributed to homo-condensed Si—O—Si sites in T^1, T^2 and T^3 building groups [22].

Comparing the spectra of sols 3 and 6 in Fig. 4 II, IV a significant difference can be seen in the chemical shift of the signals. The two signals at $\delta = -53$ and -61 ppm in the spectrum of sol 3 are shifted about 3 ppm to higher field in comparison to the T^1 and T^2 units in a homo-condensed GPTS solution (-50, -58 ppm) and a GPTS gel (Fig. 4, I). Probably, the signals at -53 and -61 ppm in the spectrum of sol 3 present Si-atoms in heterometal Si—O—Ti bonds whereas those in the spectrum of the strongly hydrolysed sol 6 are mainly caused by homo-condensed siloxane species. The presence of Si—O—Ti bonds in sol 3 and their hydrolytic instability in the course to sol 6 was confirmed by ^{17}O NMR investigations [22].

From the results it is concluded that after addition of water to sol 3 a degradation of the titanosiloxane bonds occurs in favour of homo-condensed siloxane bonds. A quantitative evaluation of the liquid-state ^{29}Si NMR spectra concerning homo- and hetero-condensed species is not precise due to the broad overlapping signals. For rough estimates by means of spectrum deconvolution signals in the region $\delta = -49.2$ to -51.4, -58.0 to 60.8 and -65.5 to 69.4 ppm were used as basis for the determination of the amount of Si sites in homo-condensed T^1, T^2 and T^3 units, and signals in the region -51.4 to -55.0 ppm, -60.8 to -64.0 ppm and -69.4 to -72.0 ppm for T_{Ti}^1, T_{Ti}^2 and T_{Ti}^3 units in hetero-condensed species. The results suggest that more than 50% of the total silicon are constituents of Si—O—Ti bonds in sol 3 before hydrolysis and only approx. 20% are left as heterometal bonds in the strongly hydrolysed sol 6 after a hydrolysis time of 7 h and 24 h (Fig. 5).

In this context it was of interest to examine the hydrolytic stability of Si—O—Ti bonds at the transition from the sol to gel state by solid-state ^{29}Si NMR. The spectrum of the Ti-free gel 2 (Fig. 4, I) which derives from sol 2 shows three signals centered at $\delta = -51$ (10%), -59 (35%) and -68 ppm (55%) which are
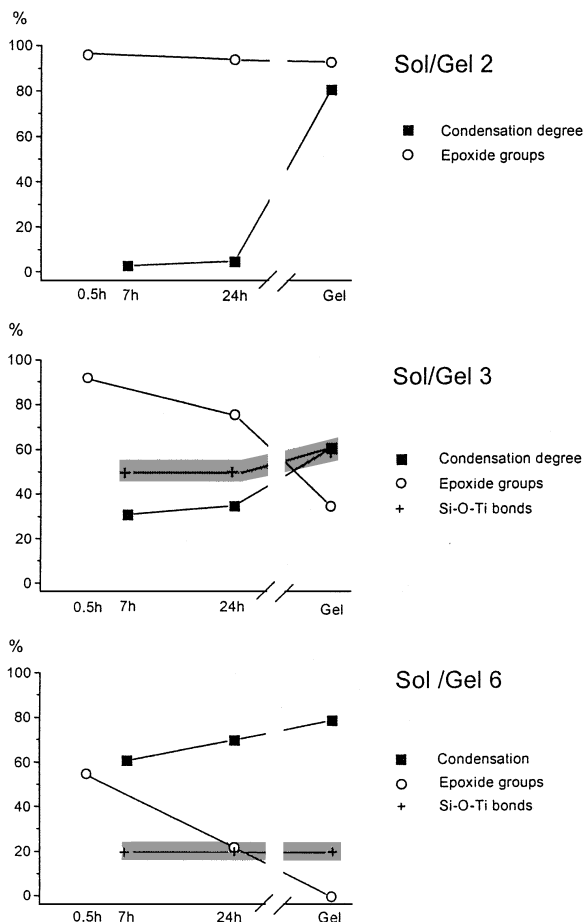

Figure 4. ^{29}Si NMR spectra of the sols 3 and 6 (see Fig. 2), of the gels 2, 3, 6 and of the reference gel (GPTS + 2 H_2O/OR).

T^0 (2 OCH_3, 1 OC_2H_5) (18%) and T^0 (1 OCH_3, 2 OC_2H_5) (13%). The two broad signals at $\delta = -53$ and -61 ppm aside the region of Si atoms in homo-condensed T^1 and T^2 units present a signal intensity

Figure 5. Correlation between the condensation degree of $RSiO_{1.5}$ units, the amount of Si in Si—O—Ti bonds and the content of unreacted epoxide rings in the sols and gels 2, 3 and 6 (see Fig. 2).

attributed to homo-condensed Si—O—Si species in T^1, T^2 and T^3 units. The spectrum of the Ti-containing gel 3 (Fig. 4, III) likewise shows three broad signals but with a significant high field shift of the first two signals which was also found in the spectrum of the corresponding sol 3. This shift reveals that species with Si—O—Ti bonds are preserved after the sol-gel transformation at 130°C. The spectrum of gel 6 (Fig. 4, V) shows two broad overlapping signals. The maxima of the signals fall together with those of the signals of gel 2 and of the reference gel which are attributed to homo-condensed Si—O—Si species in T^2 and T^3 units. A rough approximation of the content of heterometal bonds in gel 3 by deconvolution of the spectrum leads to a somewhat higher amount ($\geq 60\%$) in comparison to sol 3 ($\geq 50\%$) (Fig. 5). Possibly, this higher amount appears due to additional reaction of the monomeric

silanes with Ti-tetraethoxide in sol 3 to titanosiloxanes during the gelation in air at higher temperatures. The amount of Si—O—Ti bonds in the strongly hydrolysed gel 6 was approximately estimated to be 20% of the total Si content. The results reveal that no detectable decrease in the content of Si—O—Ti bonds occur during the sol-gel transformation at 130°C.

3.2. Condensation Degree of the $RSiO_{1.5}$ Units

The condensation degree (c.d.) of the $RSiO_{1.5}$ units (R = glycidoxypropyl-) given in percent of condensed OH groups was calculated from the signal intensity of the deconvoluted ^{29}Si NMR spectra according to the formula c.d. (%) = $100 - [T^0 + 0.67(T^1 + T_{Ti}^1) + 0.33(T^2 + T_{Ti}^2)]$. The changes in the condensation degree of $RSiO_{1.5}$ units in Ti-free and Ti-containing samples during the transition from sol to gel state are depicted in Fig. 5. The c.d. of the Ti-free GPTS hydrolysate with a small amount of water (sol 2) is significantly lower after 7 h (c.d. = 3%) and 24 h reaction time (5%) than the c.d. of the corresponding Ti-containing sols. As expected an increased c.d. with increasing water/proton concentration of the Ti-containing sols follows from the comparison of the sols 3 (c.d. = 31/35%) and 6 (61/70%) in Fig. 5. A strong increase in the condensation degree of the Ti-free sample 2 from 5% to 81% is observed in the course of sol-gel transformation. The differences of the c.d. in sols and gels of the Ti-containing samples 3 and 6 only amount to 20–30% due to the relatively high starting c.d. in the sols. The high starting c.d. in Ti-containing sols is caused by the addition of the Ti-tetraethoxide as second condensable component and the fast heterocondensation reaction of the SiOH groups with the Ti-tetraethoxide [22]. Practically, the c.d. of the Ti-free gel 2 and of the Ti-containing gel 6 are similar, but the Ti-containing gel 3 shows a 20% lower c.d. than the corresponding Ti-free gel 2. The reason for this could be the incomplete hydrolysis of the SiOR and TiOR groups for lack of free water (Fig. 3).

3.3. Epoxide Ring Opening in Sols and Gels

The nucleophilic and electrophilic attack at the epoxide group can lead to the opening of the ring and the formation of diol groups or poly(ethylenoxide) chains [25]. ^{13}C NMR [17, 26–28], Near Infrared spectroscopy [10, 19, 29] and epoxide/diol group titration [5, 10, 26, 30]

were used in previous works for examination of the ring-opening reaction in GPTS hydrolysates and gels. Preliminary experiments showed that the presence of a large amount of Ti-tetraethoxide causes considerable defects in the determination of epoxide and diol groups which give too high values by the titration methods. Furthermore, the diol band at 4800 cm^{-1} in the NIR spectrum of the sols is overlapped by HOC-bands of the alcohols which hinder a reliable evaluation of this reaction product. These difficulties lead to significant analytical uncertainties in the determination of the type of the reaction products of the epoxide ring opening and require further detailed investigations [17].

The effect of the Ti-tetraethoxide on the epoxid ring opening of the GPTS component in sols and gels was examined in this work mainly by means of liquid and solid state ^{13}C NMR spectroscopy. This method allows a satisfactory determination of the content of unreacted epoxide rings in sols and gels by evaluation of the characteristic signal of the terminal C-atom of the epoxide ring around $\delta = 44$ ppm, but difficulties arise with the detection of the reaction products of epoxide opening. Additional reactions of the diol groups are possible in presence of excess alcohol and metal alkoxides which can lead to their etherification or esterification like $-CH_2-CH(OH)-CH_2OR$ in which R represents, e.g., $-CH_3$, $-C_2H_5$, $-TiO_{1.5}$, and $-SiR^\star(O_{0.5})_2$ units. Furthermore, the complexation of the Ti-atom by the diol group is also possible.

The β-C-atom of the diol group gives a signal at 71 ppm [31] and the poly(ethylene oxide) chains cause signals in the region at 71–74 ppm [17]. Additionally, the signal of the Ti$-$O$-\underline{C}H_2-CH_3$ group appears at around 70 ppm [32]. These signals in the region 70 to 74 ppm tend to overlap with those of the C-atoms in the ether bridge of the glycidoxypropyl group (73.5, 72.1 ppm) due to the similar chemical shift and the broadening of the signals in presence of Ti-alkoxides, especially in the solid-state spectra. Therefore, the signal of the terminal α-C-atom in diol groups at $\delta = 64.1$ ppm and of the C-atoms in the methylether (59.0 ppm) and ethylether group (15.3/67.1 ppm) could only be used for reliable identification of the reaction products in the ^{13}C NMR spectrum. Unfortunately, these signals can also be overlapped in the solid-state NMR spectra. Because of these uncertainties in the ^{13}C NMR identification and quantitative determination of the reaction products of epoxide ring opening, only the extent of the ring opening in presence of titaniumtetraethoxide will be considered here.

Table 1. Assignment of signals in the ^{13}C NMR spectra of sols 2, 3 and 6.

Abbre-viation	Structural group	Chemical shift (ppm)
a	$\underline{C}H_3-CH_2OH$	18.1
b	$CH_3-\underline{C}H_2OH$	57.7
c	CH_3OH	49.5
d	CH_3-O-Si	50.4
e	$\underline{C}H_3-CH_2-O-Si$	18.5
f	$CH_3-\underline{C}H_2-O-Si$	58.4
g	$\underline{C}H_2(OH)-CH(OH)-CH_2-$	64.1
h	$CH_2(O\underline{C}H_2-CH_3)-CH(OH)-CH_2-$	67.1
i	$CH_2(OCH_2-\underline{C}H_3)-CH(OH)-CH_2-$	15.3
k	$CH_2(OH)-\underline{C}H(OH)-CH_2-$	71.3

Figure 6 shows the ^{13}C NMR spectra of the Ti-free sol 2 and the Ti-containing sol 3 after 0.5 h hydrolysis time and of sol 6 after 0.5 and 24 h hydrolysis. The assignment of the signals in the spectra follows from Fig. 6 and Table 1 and is based on the measurements of standard samples and on the values of chemical shift taken from the literature [17, 25, 31, 32]. The splitting of signals in the spectra is caused by the hydrolysis and condensation reactions of the alkoxysilane groups which influence the chemical shift of the neighbouring C-atoms to a different extent.

For the evaluation of the ring-opening reaction in the different sols the signal intensity of the terminal α-C-atom (6) of the epoxide ring at $\delta = 43.49$ ppm was compared to that of the internal phenyltrimethylsilane standard ($\delta = -1.30$ ppm) by using identical accumulation times for the spectra. The deviation of the integrated signal intensities amounts to 5%. It is seen from the ^{13}C NMR spectra in Fig. 6 that the intensity of signal 6 decreases in the order from sol 2 to sol 6 when the intensity of the standard signal is kept constant. The results of the evaluation of the ^{13}C NMR spectra of the sols 2–6 and of the reference sol (GPTS + 2 H$_2$O/OR) after 0.5 and 24 h hydrolysis time are summarised in Fig. 7. The diagram exhibits nearly 92–96% unchanged epoxide groups in the Ti-free GPTS hydrolysates (sol 2 and reference sol) after 0.5 and 24 h hydrolysis time. The high amount of unreacted epoxide rings in GPTS hydrolysates is in agreement with the results in [5] found by epoxide titration. About 15% of the epoxide ring is only cleaved in the Ti-containing sol 3 after 24 h. A stronger ring opening of about 35% occurs
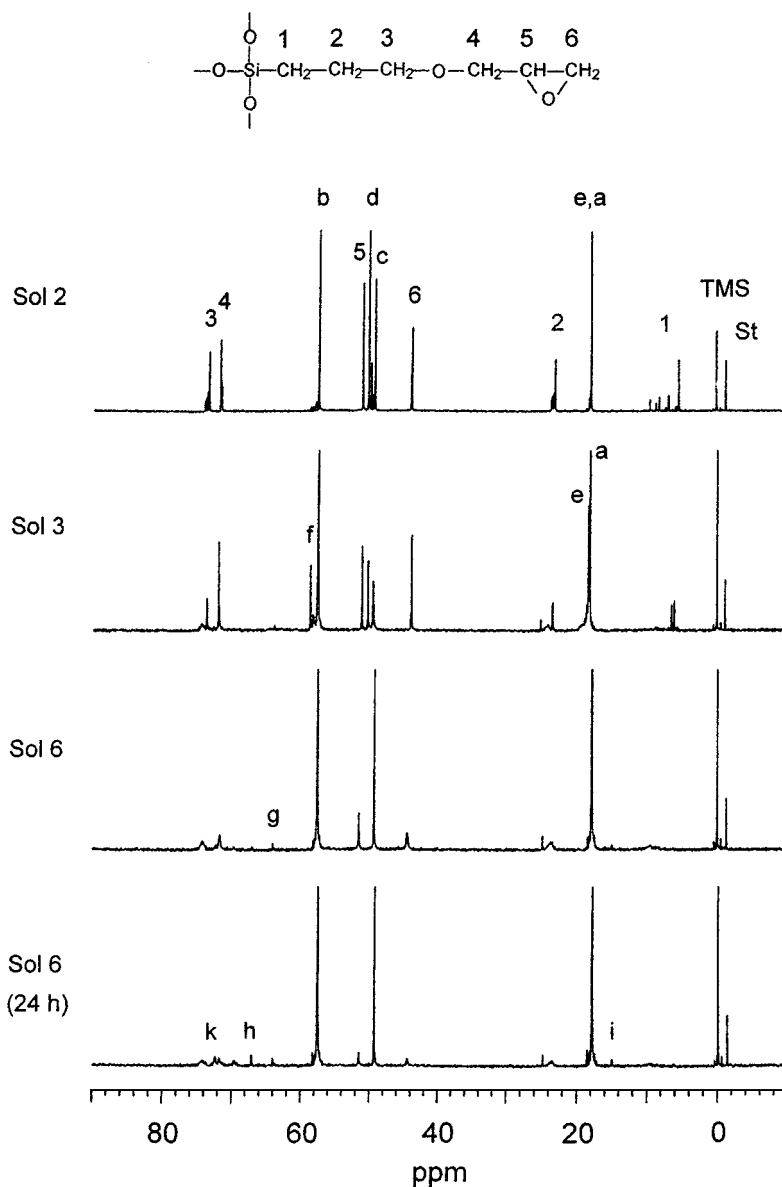
Figure 6. ^{13}C NMR spectra of the sols 2, 3, and 6 after 0.5 h and sol 6 after 24 h reaction time.

in the more hydrolysed sols 4–6 already after 0.5 h hydrolysis. No additional results are available from the sols 4 and 5 after 24 h hydrolysis time due to gelation. The sol 6 with the highest water and proton concentration (see Fig. 2) shows a ring opening of about 78% after 24 h hydrolysis.

From the results it follows that the addition of Ti-tetraethoxide to GPTS hydrolysates with a low content of free water (0.12 H$_2$O/OR) does not show a significant effect to epoxide ring opening. Only sufficient

amounts of free water (>0.5 mole H$_2$O/OR) accelerates the ring-opening reaction of the epoxide group by Ti-species in the sols. The ring opening in the series was proven by titration of the unreacted epoxide groups. The absolute epoxide content which was found by titration [24] is identical with the NMR results in case of the Ti-free GPTS-hydrolysates but it shows about 20% higher values for sols 4, 5 and 6 than determined by NMR. The reason for this difference is the consumption of additional amount of titration reagent by
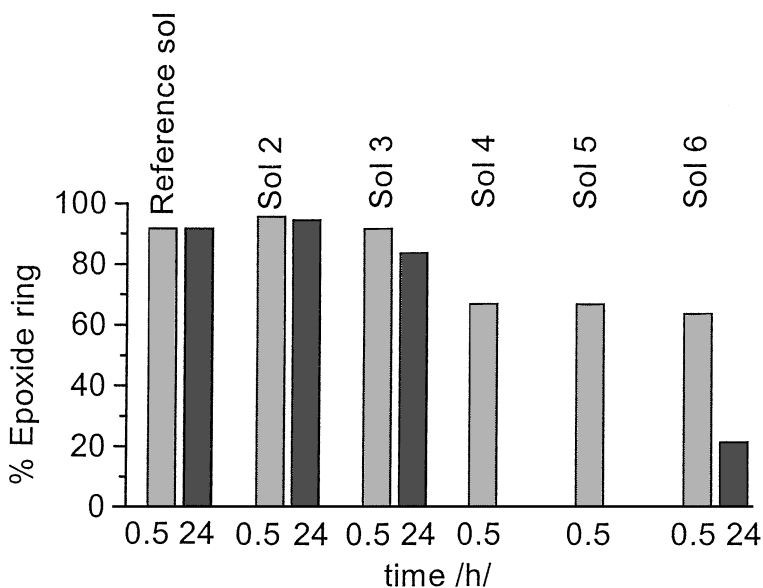
Figure 7.   Amount of epoxide rings in the Ti-free sol 2, in the reference GPTS sol (2 H$_2$O/OR) and in the Ti-containing sols 3–6 after 0.5 h and 24 h reaction time.

Ti-tetraethoxide. The ^{13}C NMR spectra of sol 6 (Fig. 6) show additional signals at $\delta = 15.3$ (i), 64.1 (g) and 67.1 ppm (h) which indicate the presence of diol groups and of their ethylether derivative (Table 1). It follows from the intensities of the signals g and i that ca. 18% diol groups and 20% ether groups should exist in sol 6 after 24 h hydrolysis. This would mean that in sol 6 at the most half of the opened rings exists as poly(ethylene oxide) chains.

The following experiments deal with the ring opening reaction during the transition of sols into gels. The Ti-tetraethoxide containing sols 3, 4 and 6 and the Ti-free GPTS hydolysates with 0.5 (sol 2) and 2 H$_2$O/OR were transformed to gels at 130°C according to the described procedure. The solid-state ^{13}C NMR spectra of the gels 2, 3 and 4 are shown in Fig. 8. The assignment of the signals follows from Fig. 6 and Table 1. For evaluation of the solid-state spectra the signal 2 at $\delta = 23.5$ ppm was chosen as "internal" standard due to the only small influence of condensation reactions of the alkoxysilyl groups and the epoxide-ring opening on the line shape and intensity of this methylene group signal. The intensity of signals 6 and 2 are nearly comparable in gels with intact epoxide rings due to the similar and short relaxation time of both C atoms and the chosen acquisition parameters. The identical intensities of the epoxide signal 6 and of the signal 2 in the solid state ^{13}C

NMR spectra of the Ti-free gel 2 reveal that the epoxide rings remain nearly unchanged during the transformation of sol 2 into gel 2 (Fig. 8). A significant decrease in the relative intensity of signal 6 to 35% occurs in the spectrum of the Ti-containing gel 3. Practically, no signals of epoxide rings can be detected in the spectra of gel 4 (Fig. 8) and of the gels 5 and 6. From the results it can be concluded that a low amount of epoxide rings (5–10%), if at all, can be opened during the gelation of Ti-free GPTS hydrolysates at 130°C, whereas a strong cleavage occurs in the Ti-containing gels. The result of gel 3 in comparison with gel 4 reveals that in spite of the high Ti-content of gel 3 (Ti : Si = 1) no complete epoxide ring opening occurs even after heating at 130°C when the water content in the starting sol (3) is too low. As mentioned above the extent of epoxide ring opening by Ti-alkoxide in sol 3 is very small (15% after 24 h). Obviously, a higher content of free water is required to make the Ti-oxo-alkoxide species more active for an electrophilic attack at the epoxide ring. It is assumed that an increased number of TiOH groups at the surface of the Ti-oxo-alkoxide species could enable an easier electrophilic attack at the epoxide due to steric reasons.

The signal (i) at $\delta = 15.3$ ppm which already appears in the spectrum of sol 6 is visible in large intensity in the spectra of the Ti-containing gels 3 and 4 (Fig. 8). The
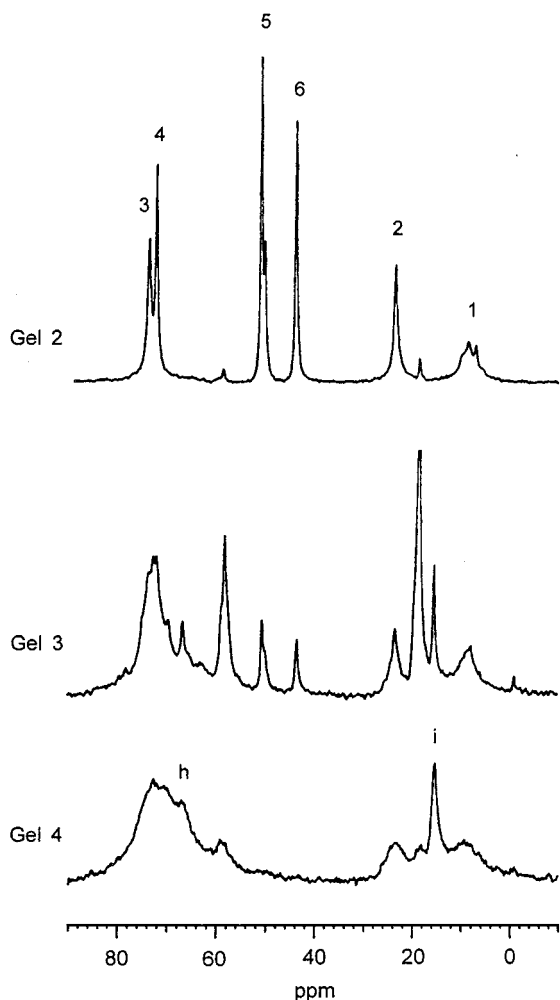
Figure 8. ^{13}C NMR MAS spectra of the gels 2, 3 and 4.

corresponding signal of the ethylether group (h) appears around 67 ppm. Possibly, a considerable amount (ca. 60%) of cleaved epoxide rings does not react to polyether chains but to low molecular ethylethers during the sol-gel transition.

The ^{13}C NMR results on the sols and gels underline the significant effect of the Ti-tetraethoxide on the epoxide ring opening and the supporting role of the water content and the heat treatment of sols. The diagrams in Fig. 5 summarise the parallel reactions (condensation, hetero-condensation and opening of epoxide rings) at the same time scale for Ti-free and Ti-containing GPTS sols and gels. The hatched area in the diagrams symbolises the mentioned uncertainties in the quantitative determination of the Si—O—Ti bonds.

4. Conclusions

The results reveal the presence of heterometal Si—O—Ti bonds in sols and gels of the system 1.0 glycidoxypropyltrimethoxysilane : 1.0 titaniumtetraethoxide : 0.2–2.0 H_2O/OR. More than 50% of the Si-atoms appear in Si—O—Ti bonds in almost water-less sols and in the corresponding gels. Higher amounts of free water in Ti-containing sols (≥ 0.12 H_2O/OR) accelerate the cleavage of the Si—O—Ti bonds in favour of homo-condensed Si—O—Si units. About 20% of Si-atoms are only left in Si—O—Ti bonds in strongly hydrolysed sols and in the corresponding gels which can lead to a lower molecular homogeneity of the heterometal hybrid materials. The results reveal that the amount of Si—O—Ti bonds in sols and the corresponding gels is not significantly influenced by the sol-gel transformation at 130°C.

On the other hand, the sol-gel transition strongly influences the condensation degree of $RSiO_{1.5}$ units in the Ti-free and Ti-containing samples. The condensation degree of the Ti-containing sols is significantly higher in comparison with Ti-free GPTS sols due to the presence of Ti-tetraethoxide as second condensable component which reacts very quickly with silanol groups to titanosiloxanes.

The extent of the ring-opening reaction of the epoxide group is very low (up to 10%) in Ti-free GPTS-hydrolysates within 24 h and also in the corresponding gels. A strong cleavage of the rings up to 78% occurs in the Ti-containing sols with a high amount of free water and no epoxide groups can be detected in the corresponding Ti-containing gels. The activity of the Ti-oxo-alkoxide species concerning the epoxide attack is low when the sols and the corresponding gels contain only a low amount of free water. The result implies that not alone a high (molar) amount of Ti-oxo-alkoxide species ensure a complete cleavage of the epoxide rings but rather a sufficient amount of TiOH groups is needed to enable an easier electrophilic attack at the epoxide ring for sterical reasons. Probably, a considerable amount of ethylether groups exists in Ti-containing gels which hinder the building up of polymeric ethylene oxide chains from epoxide rings.

This first insight into the parallel course of the manifold hydrolysis, homo- and hetero-condensation and ring-opening reactions in sols and gels from the same inorganic-organic hybrid system can contribute to a better understanding of the relations between structure and material properties and to more optimal

reaction conditions in the production of tailor-made hybrid materials.

Acknowledgment

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