# On the Existence and Hydrolytic Stability of Titanosiloxane Bonds in the System: Glycidoxypropyltrimethoxysilane-Water-Titaniumtetraethoxide

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**Abstract.** Heterometal materials based on glycidoxypropyltrialkoxysilane and titaniumalkoxide are used for optical applications and require a high homogeneity on the molecular level. The presence of heterometal titanosiloxanes, their distribution and hydrolytic stability should influence the homogeneity of these materials. $^{29}$Si and $^{17}$O NMR spectroscopy has been used to investigate sols with molar ratios Si : Ti = 1 and $H_2O$ : OR (H) = 0.5−2.0 and their gels after heat treatment at 130°C. The presence of Si─O─Ti bonds in sols with a low water content (H < 0.2) and in the corresponding gels was identified by the high-field shift of the $^{29}$Si NMR signals of $T^1$ and $T^2$ units of up to 2–3 ppm compared to corresponding signals of homo-condensed Si─O─Si bonds. The existence of Si─O─Ti bonds in the sols is supported by $^{17}$O NMR spectra which show a characteristic signal around 340 ppm. A cleavage of the Si─O─Ti bonds occurs with increasing water/OR ratio in the sols. The cleavage of the heterometal bonds and the building up of homo-condensed species leads to a separation into areas with predominantly Ti─O─Ti and Si─O─Si bonds resulting in a decreased molecular homogeneity of the materials.

**Keywords:** heterometal bond, hydrolysis, condensation, $^{17}$O and $^{29}$Si NMR, titanosiloxane

## 1. Introduction

3-Glycidoxypropyltrimethoxysilane (GPTS) and titanium alkoxides are frequently employed for the preparation of heterometal hybrid polymers which are used for example as hard coatings on organic polymers and contact lens materials in the optical industry [1, 2]. A homogeneous distribution of structural units at the molecular level is a prerequisite for materials for optical applications and thus phase separations or inhomogeneities in composition should be kept at a level as low as possible [3, 4]. In this respect heterometal Si─O─Ti bonds, their distribution and their hydrolytic stability during sol-gel processing, play an important role in the preparation of highly homogeneous materials on a molecular scale. To date a detailed knowledge of the homo- and hetero-condensation reactions of GPTS and Ti-alkoxides during sol-gel processing is not available. The objective of this work is to attain a better insight into the reactions and interactions of the components of the system GPTS-$H_2O$-Ti$(OC_2H_5)_4$ in sol and gel states, mainly by means of $^{29}$Si and $^{17}$O NMR spectroscopy.

## 2. Experimental

Solutions of the system GPTS-$H_2O$-Ti$(OC_2H_5)_4$ were prepared at molar ratios Si : Ti = 1 and $H_2O$ : alkoxide group = 0.5 to 2 (Table 1). 0.1 M HCl was used for all steps of hydrolysis. The time interval used was 0.5 h. The water content of the sols was determined by Karl-Fischer-titration [5] 0.5 h after their preparation. The gel samples were prepared from corresponding sols, after storage at room temperature for 24 h followed by heating to 130°C for 5 h. The solid products were then crushed and heated again for 2 h at 130°C.

The $^{29}$Si and $^{17}$O NMR spectra were obtained using a Bruker AC 200 spectrometer (4.7 T). $^{29}$Si NMR: external reference: tetramethylsilane, internal standard: phenyltrimethylsilane, repetition time (r.t.): 40 s, pulse angle (p.a.): 63°, number of scans (n.s.): 45–1500. $^{17}$O

*Table 1.* Flow chart of the preparation of solutions in the system GPTS-$H_2O$-$Ti(OC_2H_5)_4$ at room temperature. Water is always added as 0.1 M HCl.

GPTS 4.52 mM

| Sol no. | $C_{Si}$ (mole/l) | $C_{HCl}$ (mmole/l) | $H_2O$/OR molar ratio | | |
|---|---|---|---|---|---|
| 1 | 2.87 | — | — | ← | Ethanol 8.58 mM |
| | | | | 0.5 h | |
| 2 | 2.66 | 7.2 | 0.5 | ← | $H_2O$ 6.78 mM |
| | | | | 0.5 h | |
| 3 | 1.26 | 3.4 | 0.21 | ← | $Ti(OC_2H_5)_4$/Ethanol 4.52 mM 16.12 mM |
| | | | | 0.5 h | |
| 4 | 1.16 | 7.3 | 0.5 | ← | $H_2O$/Ethanol 9.0 mM 2.78 mM |
| | | | | 0.5 h | |
| 5 | 1.01 | 12.7 | 1.0 | ← | $H_2O$/Ethanol 15.78 mM 4.88 mM |
| | | | | 0.5 h | |
| 6 | 0.81 | 20.3 | 2.0 | ← | $H_2O$/Ethanol 31.56 mM 9.74 mM |

NMR: single pulse, r.t.: 300 ms, p.a.: 90°, reference $H_2O$ (1% $^{17}O$), n.s.: 8000–20,000. The $^{17}O$ NMR measurements start from $^{17}O$ labelled GPTS-hydrolysate (sol 2) using 0.1 M HCl derived from $^{17}O$ (10%) enriched water. The subsequent hydrolysis steps (sol 4–6) were carried out with non-labelled 0.1 M HCl. The NMR measurements of solutions 2–6 were started 15 min after their preparation. The $^{29}Si$ NMR spectra were accumulated for 0.5 h (solution 2) or 15 h (solutions 3–6). The $^{29}Si\{^1H\}$ inverse gated sequence was used for solid state $^{29}Si$ NMR spectra. External standard: $Q_8M_8$, MAS: 3 kHz, p.a.: 63°, r.t.: 60 s, n.s.: 200–1000.

## 3. Results and Discussion

The data in Table 2 show that the amount of water in sol 2 decreases strongly from 0.5 to 0.13 $H_2O$/OR within 0.5 h of starting hydrolysis. The remaining water in sol 2 is small enough to prevent rapid homocondensation reactions of the Ti-ethoxide and precipitations [6]. Practically, the water in sol 2 is completely consumed by the added Ti-ethoxide for partial hydrolysis of its alkoxide groups (sol 3). The amount of free water in the sols 4–6 is increased by the stepwise addition of water. A nearly constant consumption of 0.46 $H_2O$/OR is obtained in the sols 5 and 6.

*Table 2.* Content of water in the standard sols 2–6 after 0.5 h reaction time.

| Sol no. (Table 1) | Addition of water | Remaining water (0.5 h after addition) |
|---|---|---|
| 2 | 0.50 $H_2O$/OR | 0.13 $H_2O$/OR |
| 3 | (0.21 $H_2O$/OR) | 0.02 $H_2O$/OR |
| 4 | 0.50 $H_2O$/OR | 0.12 $H_2O$/OR |
| 5 | 1.0 $H_2O$/OR | 0.54 $H_2O$/OR |
| 6 | 2.0 $H_2O$/OR | 1.53 $H_2O$/OR |

### *$^{29}Si$ and $^{17}O$ NMR Examination on Heterometal Bonds*

The $^{29}Si$ NMR spectrum of the GPTS-prehydrolysate (sol 2) shows a variety of signals in the region of chemical shifts $\delta = -40$ to $-44$ ppm. This region is characteristic for monomeric silanes whose assignment

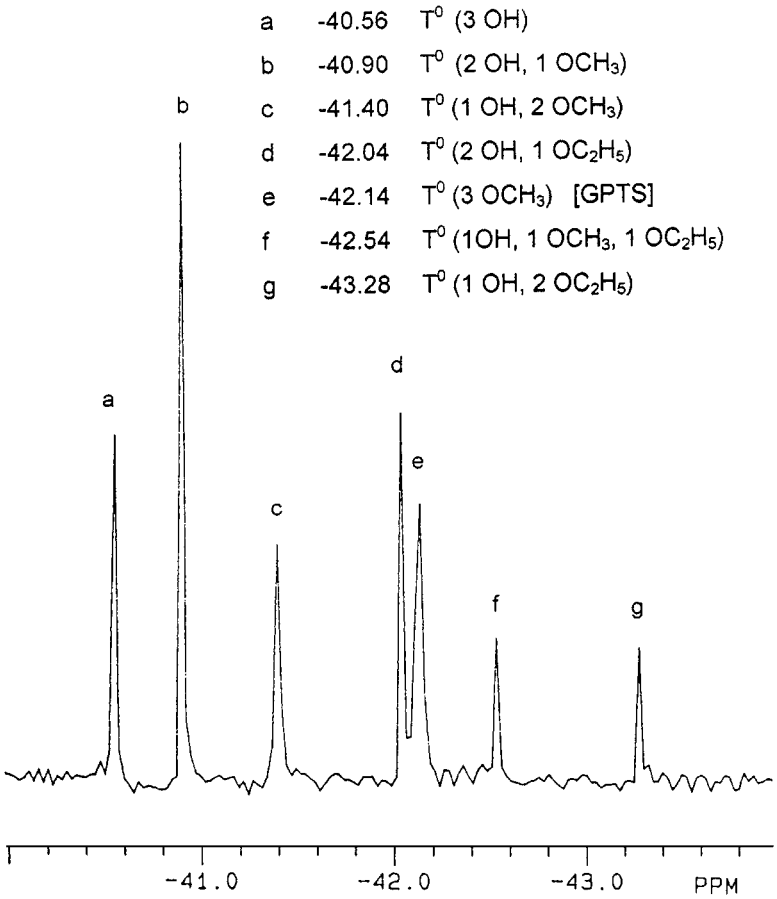


*Figure 1.* $^{29}$Si NMR spectrum of the GPTS-hydrolysate (0.5 $H_2O$/OR, sol 2) and assignment of the signals.

follows from Fig. 1. Practically, the intensity of the seven visible signals represents the total content of Si-atoms so that condensed species can be neglected. From the spectrum it follows that about 50% of the alkoxy-groups are hydrolyzed. The dominant amount of monomeric silanols and the absence of condensed siloxanes gives a good basis to examine the reaction of these Si-species with the Ti-tetraethoxide.

The $^{29}$Si NMR spectrum of solution 3 after addition of Ti-ethoxide shows three sharp signals at $\delta = -42.44$, $-43.58$, and $-44.74$ ppm which were identified as unreacted GPTS (4% of the total signal intensity) and the monomeric silanes $T^0$ (2 $OCH_3$, 1 $OC_2H_5$) (18%) and $T^0$ (1 $OCH_3$, 2 $OC_2H_5$) (13%) (Fig. 2, I). Furthermore, two broad signals at $\delta = -53.2$ (40%) and $-61.1$ ppm (25%) are visible in the region of $T^1$ and $T^2$ units implying that the predominant amount of Si in sol 3 is present as a condensed species. The stepwise addition of further water to sol 3 leads to the spectra of sols 4 and 6 shown in Fig. 2, II and III; no further signals of monomeric species are detected. The position of the three signals in the spectrum of sol 6 ($\delta = -49.7$ (14%), $-58.0$ (64%) and $-65.6$ ppm (22%)) is in accordance with homo-condensed Si-sites in $T^1$, $T^2$ and $T^3$ building groups of a long-term condensed GPTS hydrolysate (Fig. 2, IV). Comparing spectrum I with III a significant high-field shift of the $T^1$ and $T^2$ signals of up to 2–3 ppm can be seen. This shift cannot be caused by the influence of the Ti-atom on the chemical shift of the Si-atoms alone; this latter shift contributes 0.3 ppm at the most. It is very likely that the two signals in the spectrum of sol 3 reflect Si-atoms in heterometal Si─O─Ti bonds. Such a high field shift has been found for Si-atoms in Ti─O─Si─O─Ti bonds in previous works on titanodiphenylsiloxanes [7]. From the result it is concluded that after addition of water to sol 3 a degradation of the titanosiloxane bonds occurs in favor of homo-condensed siloxane bonds.

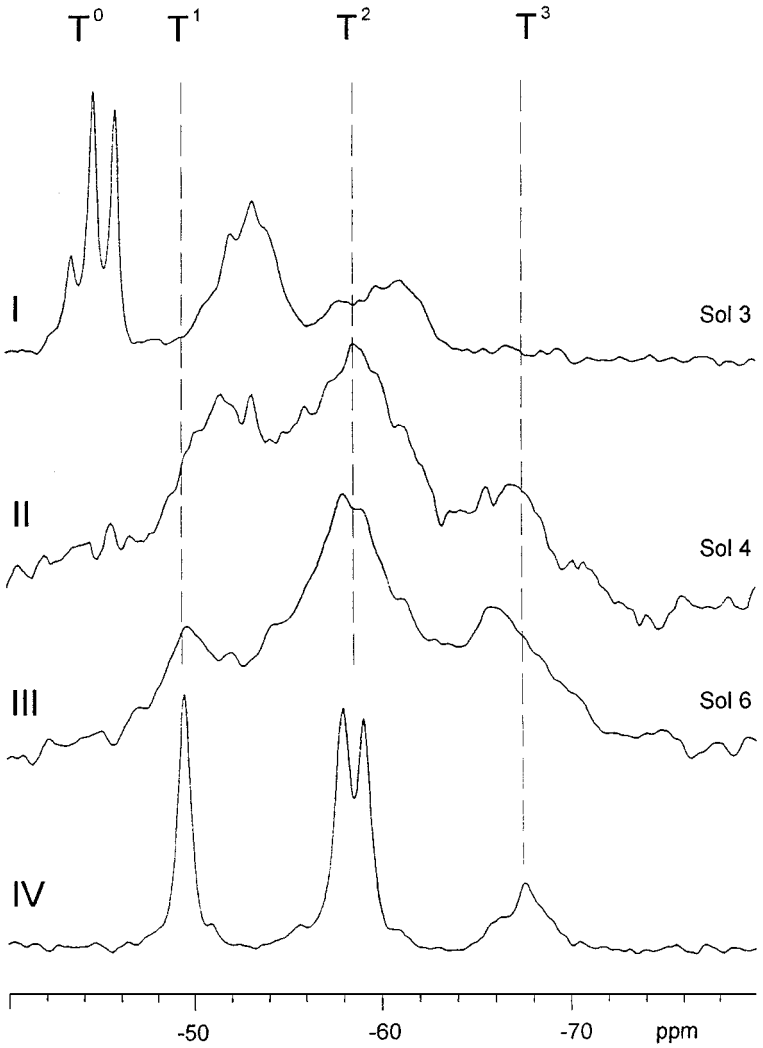


*Figure 2.* $^{29}$Si NMR spectra of the sols 3, 4 and 6 (see Table 1) and of the GPTS-hydrolysate (2 $H_2O$/OR) after 15d.

The solid state $^{29}$Si NMR spectrum of the Ti-containing gel 3 (Fig. 3, II) shows three broad signals with similar high-field shifts (−53.3 (32%), −60.3 (47%), −68.9 ppm (16%)) as those seen in the spectrum of the corresponding sol 3. This signal shift shows that species with Si─O─Ti bonds remain after the sol-gel transformation. The spectrum of gel 6 has two overlapped signals around $\delta = -58$ (56%) and −66 ppm (44%) whose maxima are in good agreement with those of the signals for homo-condensed Si─O─Si bonds of the reference gel (Fig. 3, IV).

$^{17}$O NMR was used to prove the existence of Si─O─Ti bonds. The $^{17}$O NMR spectrum of the $^{17}$O labelled GPTS hydrolysate (sol 2) shows strong signals at $\delta = 26$ and −8 ppm (Fig. 4, I) which are caused by the Si $^{17}$OH groups of the prehydrolyzed GPTS and by $^{17}$O labelled water [8]. The signal at $\delta = 575$ ppm derives from deutero-acetone used as external lock and standard. A dramatic decrease in intensity of the SiOH and $H_2O$ signal appears after the addition of Ti-ethoxide to sol 2. Meanwhile a broad asymmetrical signal centered around $\delta = 340$ ppm and signals at 540 and around 750 ppm develop (Fig. 4, II). The resonance at 340 ppm is attributed to O-atoms in Si─O─Ti bonds [7, 8], the signal at 540 ppm to $\mu_3$- and those around 750 ppm to $\mu_2$-Ti─O─Ti bonds according to [9]. It can be concluded from the $^{17}$O NMR spectrum that the SiOH species in GPTS-hydrolysate are consumed

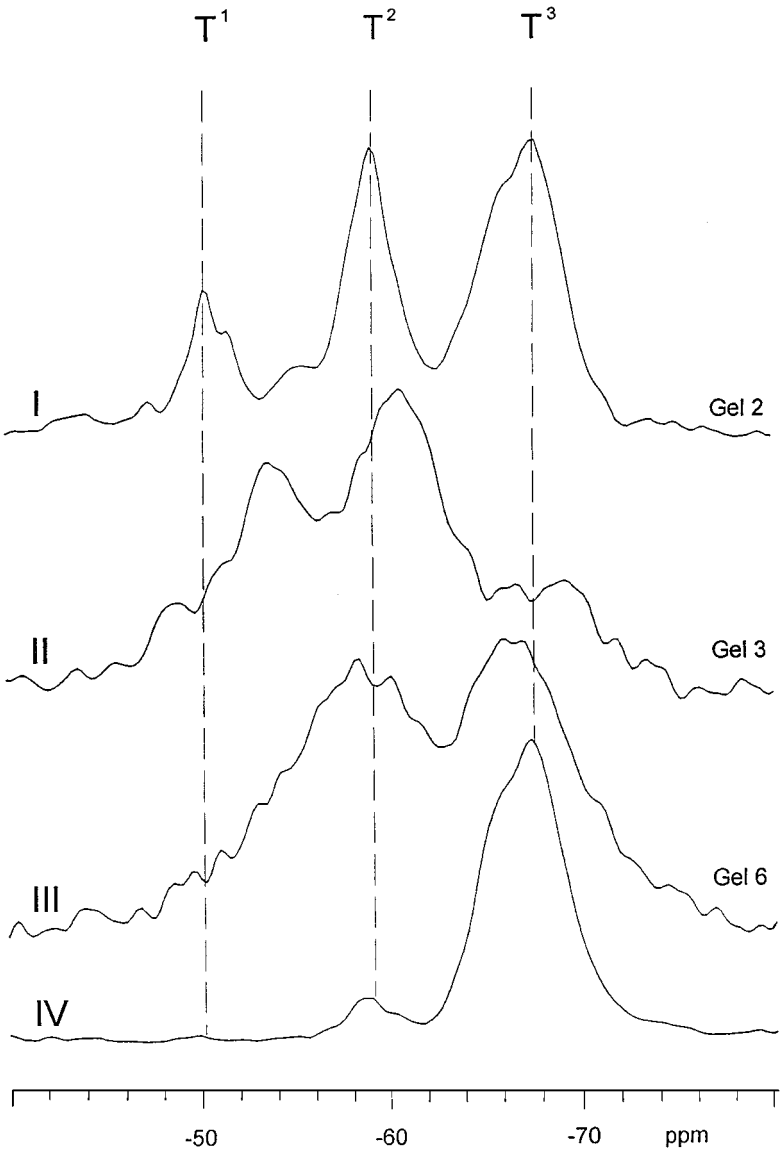


*Figure 3.* Solid state $^{29}$Si NMR spectra of the gels 2, 3, 6 and the reference gel derived from GPTS-hydrolysate (2 $H_2O$/OR) by heat treatment at 130°C.

for hetero-condensation reaction with the Ti-ethoxide leading to Si─O─Ti bonds immediately after the Ti-ethoxide addition.

After repeated addition of 0.1 M HCl the intensity of the signals at 340 and 540 ppm decreases and a signal around 0 ppm appears (Fig. 4, III–V). This signal is mainly caused by $^{17}$O labelled water and possibly some Si$^{17}$OH groups but it can hardly be caused by condensed Si─$^{17}$O─Si species which should appear in the region at $\delta = 50$–80 ppm. The $H_2{}^{17}O$ signal mainly derives from $^{17}$O-atoms in Si─$^{17}$O─Ti bonds. This means that the Si─$^{17}$O─Ti bonds undergo a quick isotope exchange during their cleavage with non-labelled water. The quick $^{17}$O isotope exchange leads eventually to mostly non-labelled Si─O─Si bonds in the condensation products which cannot be detected in the $^{17}$O NMR but they are detectable in the corresponding $^{29}$Si NMR spectra. No significant signals can be found for homo-condensed Ti─$^{17}$O─Ti species. It is probable that the signals are overlapped by the broad oscillation bands or that the $^{17}$O isotope is exchanged in favor of $^{17}$O labelled water.

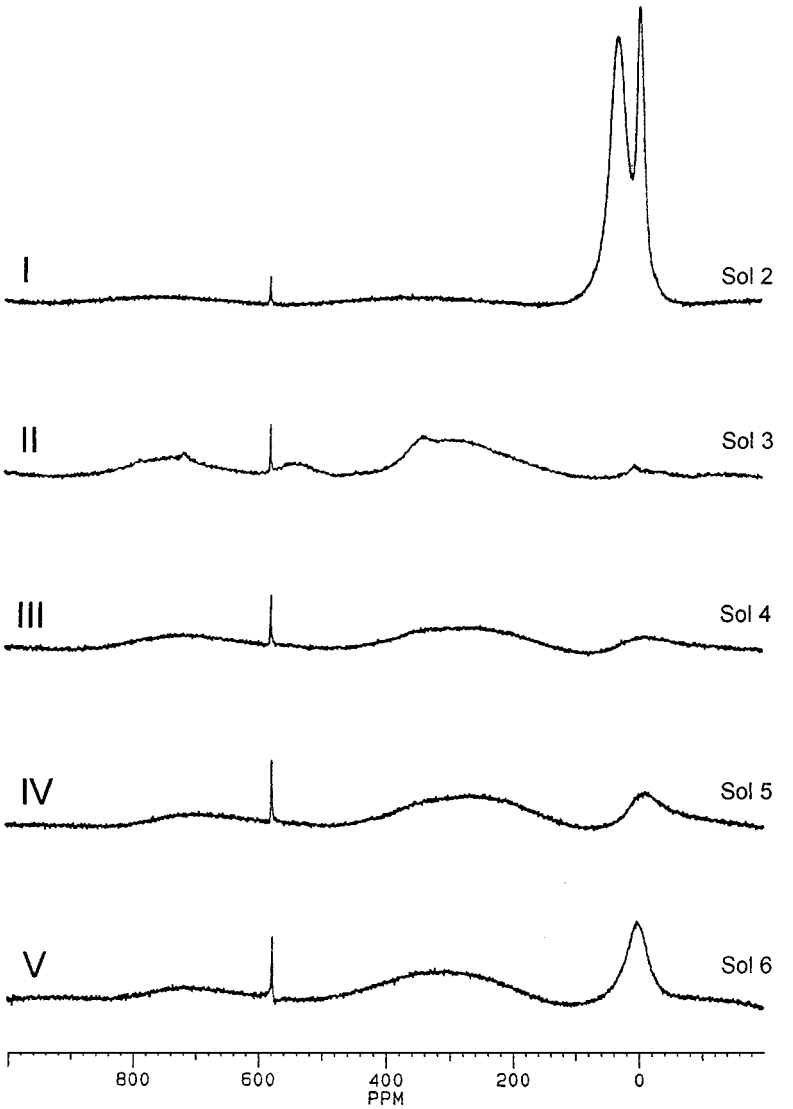


*Figure 4.* $^{17}$O NMR spectra of the sols 2–6 (see Table 1).

## 4. Conclusions

GPTS-prehydrolysates which contain monomeric silanols and a low content of free water (0.13 $H_2O$/OR) react with titanium-tetraethoxide to form sols mainly consisting of titanosiloxane species. The heterometal bonds can be identified by the high-field shift of the $T^1$ and $T^2$ signals of up to 2–3 ppm in the liquid and solid state $^{29}$Si NMR spectra of the sols and corresponding gels. The existence of titanosiloxane bonds is confirmed by the signal at $\delta = 340$ ppm in the $^{17}$O NMR spectra. Considerable hydrolytic cleavage of the heterometal bonds can be detected with increasing amounts of water. Mainly species with homo-condensed Si─O─Si bonds appear in the sols and corresponding gels after the hydrolysis at molar ratio $H_2O/OR = 2$. The drastic cleavage of the heterometal bonds and the preferential building up of homo-condensed Si─O─Si species and probably also the species with Ti─O─Ti bonds lead to a separation in $(RSiO_{1.5})_x$ and $TiO_2$ rich areas which lower the homogeneous distribution of Si and Ti on a molecular scale. This result has to be considered for more controlled syntheses of highly homogeneous heterometal materials.

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