

FORMATION AND HYDROLYTIC STABILITY OF OXYGEN BRIDGED HETEROMETAL BONDS (Si-O-Ti, Si-O-Zr, Si-O-Ta) IN SOL - GEL MATERIALS

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ABSTRACT

Glycidoxypropyltrimethoxysilane (GPTS) and metal alkoxides are frequently used in preparation of heterometal hybrid polymers and find application e. g. as contact lens materials and hard coatings on polymers. Such materials require a high homogeneity of the structural unit at the molecular level, which is supported by the formation of oxygen bridged heterometal bonds and their hydrolytic stability. By means of ^{29}Si and ^{17}O NMR the formation of heterometal bonds like Si-O-Ti, Si-O-Zr, Si-O-Ta was evidenced in GPTS-hydrolysates with $\text{Ti}(\text{OEt})_4$, $\text{Ti}(\text{OEt})_3\text{AcAc}$, $\text{Zr}(\text{OBu}^n)_4$, $\text{Zr}(\text{OBu}^n)_3\text{AcAc}$, $\text{Ta}(\text{OEt})_5$ or $\text{Ta}(\text{OEt})_4\text{AcAc}$ (AcAc = acetylacetonate ligand) as additives. Signals of heterometal bonds can be detected in ^{17}O NMR spectra in the range of 170 to 350 ppm and are characterized in ^{29}Si NMR spectra by defined chemical shifts to low (Si-O-Ta) and high magnetic fields (Si-O-Ti, Si-O-Zr) in comparison with signals of Si-O-Si bonds. The use of AcAc modified metal alkoxides leads to well resolved ^{29}Si NMR spectra, which make the distinction between homo- and heterocondensed species easier. The addition of water to the sols (2 H_2O / alkoxy group) leads to a degradation of heterometal bonds in favour of more homocondensed species, which reduces the homogeneity of such hybrid materials at the molecular level.

INTRODUCTION

Inorganic-organic hybrid materials containing glycidoxypropyltrimethoxysilane (GPTS) and metal alkoxides like $\text{Ti}(\text{OR})_4$ and $\text{Zr}(\text{OR})_4$ have attracted much attention because of their use as contact lens materials [1] and transparent hard coatings on plastics [2]. Trialkoxysilane and tantalum alkoxide based hybrid materials are applied as waveguides [3]. There is a high demand for homogeneity at the molecular level of such materials, which is supported by the formation of heterometal Si-O-M bonds (M = Ti, Zr, Ta) between the silane and metal alkoxide. A careful control of the formation of heterometal bonds and of the hydrolytic stability is necessary to reveal, which degree of homogeneity is reached in the materials. In only few hybrid systems the formation of Si-O-Ti, Si-O-Zr bonds and their hydrolytic stability, respectively, was examined in detail by means of ^{17}O and ^{29}Si NMR [4-9]. Furthermore, the formation of Si-O-Ta bonds in sol-gel systems has only been detected by FTIR measurements until now [10, 11]. In this work ^{29}Si and ^{17}O NMR examinations on the formation and hydrolytic stability of Si-O-Ti, Si-O-Zr, Si-O-Ta bonds in the frequently used GPTS-metal alkoxide system with and without acetylacetonate (AcAc) as complex ligand are presented as contribution to a better knowledge of the structural homogeneity of sol-gel materials.

EXPERIMENTAL

First, a GPTS hydrolysate (0.5 $\text{H}_2\text{O}/\text{OR}$, $c(\text{Si}) = 2.66 \text{ M}$) was prepared in ethanol using 0.1 N HCl [Sol(Si)]. The GPTS-metal alkoxide sols [Sol(SiM), M = Ti, Zr and Ta] were prepared after addition of an ethanolic solution of $\text{Ti}(\text{OEt})_4$, $\text{Zr}(\text{OBu}^n)_4$ or $\text{Ta}(\text{OEt})_5$ to the 0.5 h aged GPTS hydrolysate [Sol(Si)] at molar ratio M : Si = 1 : 1. For the preparation of the metal alkoxide

complexes $M(OR)_{x-1}AcAc$ ($M = Ti, Zr, Ta$) in ethanol a molar ratio of $M : AcAc = 1 : 1$ was chosen. After stirring for 1h the complexed alkoxides were added to the 0.5h aged sol (Si) to obtain the GPTS-metal alkoxide complex sols [Sol(SiM_{Ac})]. The hydrolysis of these sols ($c(Si) = 1$ M) after stirring for 0.5 h was performed by stepwise addition of 0.1 N HCl in ethanol to the molar ratio $H_2O/OR = 2$, where OR is the total molar amount of alkoxide groups in the sols (SiM) and (SiM_{Ac}), respectively. Three hydrolysis steps were performed at molar ratios $H_2O/OR = 0.5, 1$ and 2 , followed by stirring for 0.5 h after each step. The sols obtained after the last hydrolysis step ($H_2O/OR = 2, c(Si) = 0.7$ M) are denoted Sol(SiM₂) and Sol(SiM_{Ac}2). The corresponding gels were prepared after 24h storage of the sols, followed by heating at 130°C for 5h, crushing of the obtained products and following heating at 130°C for 2h. ²⁹Si and ¹⁷O NMR spectra of the sols were recorded on a Bruker AC 200 spectrometer (4.7 T). ²⁹Si NMR: inverse gated decoupling, reference: tetramethylsilane, internal standard: phenyltrimethylsilane, repetition time (r.t.): 40s, pulse angle (p.a.): 63°, number of scans (n.s.): 1100-1400. ¹⁷O NMR: single pulse, r.t.: 300 ms, p.a.: 90°, reference H₂O (1% ¹⁷O), n.s.: 5000-10000. The ¹⁷O NMR measurements start from ¹⁷O labelled GPTS hydrolysate [Sol(Si)] using 0.1 N HCl derived from ¹⁷O (10%) enriched H₂O. The preparation of the sols (SiM₂) and (SiM_{Ac}2) was performed using non labelled water in the three hydrolysis steps. For the preparation of a reference sample Ta(OEt)₅ was hydrolyzed with 0.18 H₂¹⁷O/OR and the obtained slightly cloudy hydrolysate was filtered. ²⁹Si MAS NMR spectra of the gels were recorded on a Bruker MSL 200 spectrometer (4.7 T): inverse gated decoupling, external standard: Q₈M₈, MAS: 3 kHz, r.t.: 60 s, p.a.: 63°, n.s.: 500-1000.

RESULTS

Fig. 1, I represents the ¹⁷O NMR spectrum of the GPTS hydrolysate [Sol(Si)] after 30 min. This spectrum shows two strong signals at $\delta = 26$ and -8 ppm which are assigned to Si¹⁷OH groups and H₂¹⁷O [7]. This result corresponds with the water content determined by Karl-Fischer titration and with the results of the ²⁹Si NMR measurement [12].

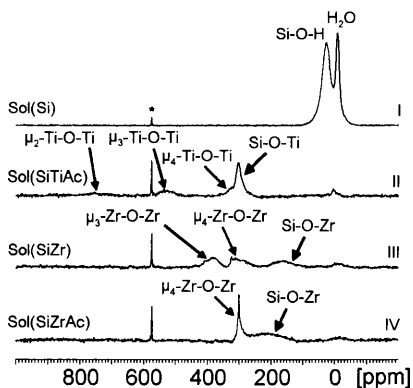


Figure 1. ¹⁷O NMR spectra of the ¹⁷O labelled GPTS-hydrolysate [Sol(Si)] after 30 min (I), after addition of Ti(OEt)₃AcAc (II), Zr(OBuⁿ)₄ (III) and Zr(OBuⁿ)₃AcAc (IV) (after 45 min)

* acetone-d₆ lock

Fig. 1, II shows the ¹⁷O NMR spectrum of the GPTS hydrolysate after addition of Ti(OEt)₃AcAc [Sol(SiTlAc)]. The strong decrease of the signal intensity of SiOH groups and H₂O in spectrum II

compared to spectrum I and the detection of a signal around 300 ppm with the main part of ^{17}O signal intensity is explained with the formation of Si-O-Ti bonds [12]. Additional signals around 540 and 750 ppm reveal the presence of homocondensed μ_3 -Ti-O-Ti- and μ_2 -Ti-O-Ti oxo species [13]. Compared to the ^{17}O NMR spectrum of the GPTS hydrolysate after addition of $\text{Ti}(\text{OEt})_4$ [Sol(SiTi)] [12], in the spectrum of the sol (SiTiAc) a higher signal intensity is found for Si-O-Ti bonds around 300 ppm and minor intensity for μ_3 -Ti-O-Ti- and μ_2 -Ti-O-Ti oxo-bridges.

In the ^{17}O NMR spectrum of the sol GPTS-Zr(OBu n) $_4$ (SiZr) (Fig. 1, III) two strong broad signals around 380 and 300 ppm are assigned to μ_3 -Zr-O-Zr- and μ_4 -Zr-O-Zr oxo bridges [14]. The broad signal centered around 170 ppm is assigned to Si-O-Zr bonds according to the results of the systems dimethyldiethoxysilane-Zr(OPr n) $_4$ [7] and methacryloxypropyltrialkoxysilane-Zr(OPr n) $_4$ [8]. Si-O-Zr bonds can be formed through reaction between Si- ^{17}OH and ZrOR groups or between SiOR groups (R = Alkyl, H) and Zr ^{17}OH groups, formed after hydrolysis of Zr(OBu n) $_4$.

In contrast, in the ^{17}O NMR spectra of the sol GPTS-Zr(OBu n) $_3$ AcAc (Fig. 1, IV) no μ_3 -Zr-O-Zr oxo bridges are evidenced besides the μ_4 -Zr-O-Zr oxo bridges detected at 300 ppm. The main part of the total ^{17}O signal intensity is detected around 200 ppm due to Si-O-Zr bonds. This shows, that by use of Zr(OBu n) $_3$ AcAc as additive in GPTS hydrolysates more Si-O-Zr- and less Zr-O-Zr bonds are formed than by use of unmodified Zr(OBu n) $_4$. Similar results were observed in the comparison of Sol(SiTiAc) with Sol(SiTi). The preferred formation of Si-O-Zr bonds in Sol(SiZrAc) is possibly due to the preferred heterocondensation reaction because of a slightly higher positive partial charge of Zr in Zr(OBu n) $_3$ AcAc compared to Zr(OBu n) $_4$ [15].

The ^{17}O NMR spectrum of the sol GPTS-Ta(OEt) $_5$ [Sol(SiTa)] shows signals around 458, 430, 260 and 190 ppm besides a small signal at 3 ppm due to remaining water (Fig. 2, I).

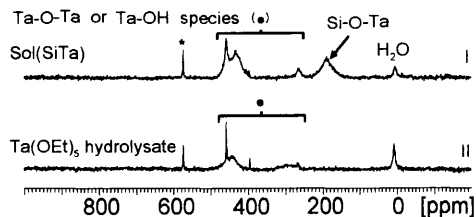


Figure 2. ^{17}O NMR spectra of the ^{17}O labelled GPTS hydrolysate 45 min after addition of $\text{Ta}(\text{OEt})_5$ (I) and of the ^{17}O labelled $\text{Ta}(\text{OEt})_5$ -hydrolysate after 30 min

* acetone-d $_6$ lock

For the identification of the signals of heterocondensed and homocondensed species in spectrum I, an ^{17}O NMR spectrum of a $\text{Ta}(\text{OEt})_5$ hydrolysate (0.18 $\text{H}_2^{17}\text{O}/\text{OR}$) was recorded (Fig. 2, II). TaOH or homocondensed Ta-O-Ta species were found in the shift range between 250-320 and 390-470 ppm. It can be followed from this, that the signals around 458, 430 and 260 ppm in spectrum I are caused by these species. The signal around 190 ppm does not appear in spectrum II, so that this signal is assigned to Si-O-Ta bonds. The intensity of the signal around 3 ppm in spectrum I shows, that a higher amount of H_2^{17}O remains in Sol(SiTa) compared to that in Sol(SiTi) [12]. This is due to the lower reactivity of $\text{Ta}(\text{OEt})_5$ towards hydrolysis and condensation reactions, because of the less positive partial charge of Ta in $\text{Ta}(\text{OEt})_5$ ($\delta \text{Ta} = +0.49$) compared to that of Ti in $\text{Ti}(\text{OEt})_4$ ($\delta \text{Ti} = +0.63$) [16].

^{29}Si NMR investigations were carried out to provide additional information about heterocondensation reactions in the GPTS-metal alkoxide sols. Fig. 3, I represents the ^{29}Si NMR spectrum of the GPTS hydrolysate [Sol(Si)] after 7h.

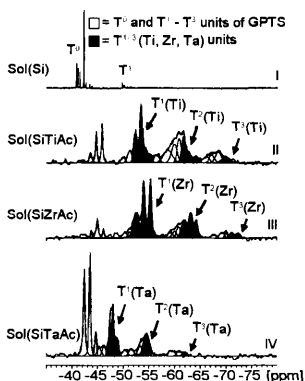


Figure 3. ^{29}Si NMR spectra of the GPTS hydrolysate (I) and after addition of $\text{Ti}(\text{OEt})_3\text{AcAc}$ (II), $\text{Zr}(\text{OBu}^n)_3\text{AcAc}$ (III) and $\text{Ta}(\text{OEt})_4\text{AcAc}$ (IV) after 7h reaction time

Two signal groups are detected, which are marked by T^0 and T^1 according to the conventional T^n -nomenclature, where $n = 0, 1, 2, 3$ denotes the number of bridging oxygen atoms in $\text{RSi}(\text{O}_{0.5})_3$ units. The content of condensed species amounts to only 9 % of the total Si-signal intensity in $\text{Sol}(\text{Si})$. The ^{29}Si NMR spectra of the GPTS hydrolysates after addition of $\text{Ti}(\text{OEt})_3\text{AcAc}$ (Fig. 3, II), $\text{Zr}(\text{OBu}^n)_3\text{AcAc}$ (III) and $\text{Ta}(\text{OEt})_4\text{AcAc}$ (IV) show additional signals in the shift ranges of T^1 , T^2 and T^3 units indicating strong condensation reactions. A deconvolution of these ^{29}Si NMR spectra was performed to determine the condensation degree of the $\text{RSi}(\text{O}_{0.5})_3$ units and to approximate the content of heterometal bonds after addition of metal alkoxide. The known shift ranges of the T^0 - T^3 units in GPTS hydrolysates and condensates, given in Fig. 4, are used as a basis for the deconvolution of spectra.

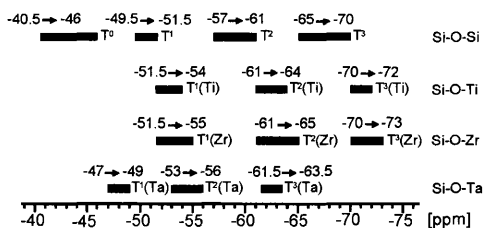


Figure 4. Range of the chemical shifts $\delta^{29}\text{Si}$ for T^{0-3} and T^{1-3} (Ti, Zr and Ta) units of GPTS

The comparison of the chemical shift of homocondensed Si-O-Si building units (T^1 - T^3) with the signal positions in the spectra II-IV (Fig. 3) shows, that additional signals are detected after addition of metal alkoxide. As the addition of metal alkoxides has practically no influence on the chemical shift of Si-O-Si units, these signals are assigned to the heterometal bonds Si-O-Ti, Si-O-Zr and Si-O-Ta, already evidenced by means of ^{17}O NMR. The measured shift ranges for signals of heterometal bonds are presented in Fig. 4. Signals for Si-O-Ti and Si-O-Zr bonds in T^1 - T^3 units, that are denoted $\text{T}^1(\text{Ti})$ - $\text{T}^3(\text{Ti})$ and $\text{T}^1(\text{Zr})$ - $\text{T}^3(\text{Zr})$, show a high field shift of about 2-4 ppm compared to corresponding signals for Si-O-Si bonds in T^1 - T^3 units. In contrast to this, signals for Si-O-Ta bonds in T^1 - T^3 units [$\text{T}^1(\text{Ta})$ - $\text{T}^3(\text{Ta})$] are shifted by about 2-4 ppm to lower magnetic field compared to corresponding signals for Si-O-Si bonds. By means of the shift differences a

rough separation between homocondensed (T^{1-3}) and heterocondensed building units ($T^{1-3}(M)$) is possible. The content of heterometal bonds (in % of total signal intensity of Si) can be roughly approximated by summation of the integrated values of signals in $T^{1-3}(M)$ building units after deconvolution of spectra. In addition, the condensation degree (c.d.) of the GPTS-metal alkoxide sols can be calculated according to the formula [17]: $c. d. (\%) = 100 - (T^0 + 0.67 (T^1 + T^1(M)) + 0.33 (T^2 + T^2(M)))$. The c.d. and contents of heterometal bonds resulting from the deconvoluted ^{29}Si NMR spectra of the sols (SiM) and (SiMAc) are summarized in Fig. 5.

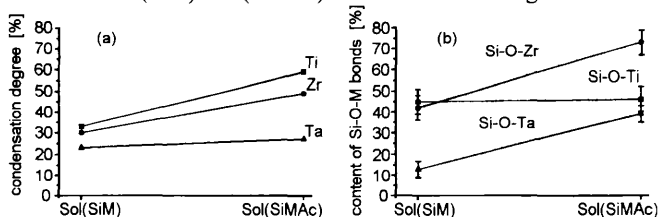


Figure 5. Condensation degree (c.d.) of the $\text{RSi}(\text{O}_{0.5})_3$ units [%] (a) and content of heterometal Si-O-M bonds [%] (b) in the sols (SiM) and (SiMAc) (M = Ti, Zr, Ta)

Generally, a higher c.d. (23 - 33%) was found in GPTS sols after addition of the metal alkoxides [Fig.5 (a)] in comparison with the c. d. of the GPTS hydrolysate (5%). Furthermore, the c.d. shows differences in dependence on the type of metal alkoxide. The c.d. increase in the order $\text{Ta} < \text{Zr} < \text{Ti}$, which is distinctly observed for the sols with metal alkoxide complexes as additives. The low c.d. of the sol (SiTaAc) compared to the sol (SiTiAc) can be explained by the lower reactivity of $\text{Ta}(\text{OEt})_4\text{AcAc}$ towards hydrolysis and condensation reactions probably due to a less positive partial charge of Ta compared to Ti in the corresponding metal alkoxide complexes. The sols (SiMAc) show higher c.d. than the corresponding sols with unmodified metal alkoxides as additives [Sol(SiM)]. This could be due to a higher amount of Si-O-M bonds in case of the sols (SiZrAc) and (SiTaAc) compared to the corresponding sols (SiZr) and (SiTa). Sols with AcAc modified metal alkoxides as additives [Sol(SiZrAc), Sol(SiTaAc)] lead to a higher content of heterometal bonds compared to the corresponding sols with unmodified metal alkoxides [Fig.5 (b)]. The lower content of Si-O-Ta bonds in the sol (SiTa) compared e.g. to the sol (SiTi) results from the lower reactivity of $\text{Ta}(\text{OEt})_5$ towards hydrolysis and heterocondensation reactions compared to $\text{Ti}(\text{OEt})_4$ resulting from the partial charge model [16].

The ^{29}Si solid state NMR spectra of the gels deriving from the sols (SiM) and (SiMAc) generally show broad overlapping signals covering the shift range of Si-O-Si and Si-O-M building units, which makes a deconvolution of spectra difficult. The detected signal intensities in the shift range of $T^1(M)-T^3(M)$, however, show clearly, that Si-O-M bonds are also present in the gels.

^{17}O NMR measurements of the hydrolyzed sols (SiMAc2) show, that the ^{17}O NMR signals for Si-O-Ti, Si-O-Zr and Si-O-Ta bonds disappear in favour of the signal of H_2^{17}O . It can be concluded from this that the heterometal bonds are cleaved by hydrolysis. Deconvolutions of the ^{29}Si NMR spectra of the sols (SiTiAc2) and (SiZrAc2) show that after addition of water the content of Si-O-Ti and Si-O-Zr bonds is lowered by ca. 30% in favour of more Si-O-Si bonds. This is also supported by high signal intensities in the shift ranges of T^2-T^3 units in the corresponding ^{29}Si solid state NMR spectra. It is remarkable, that in the sol (SiTaAc2) a degradation of Si-O-Ta bonds as in case of Si-O-Ti bonds is observed according to the ^{17}O NMR results, but the content of Si-O-Ta remains almost constant after hydrolysis (ca. 35%) based on the results of the corresponding ^{29}Si NMR spectrum. Further investigations on this sol are in progress to find an explanation of the inconsistent ^{17}O and ^{29}Si NMR results.

CONCLUSIONS

- Si-O-Ti, Si-O-Zr bonds and for the first time Si-O-Ta bonds were evidenced by means of ^{17}O NMR and ^{29}Si NMR in GPTS-metal alkoxide and GPTS-metal alkoxide complex systems.
- Generally, a higher condensation degree of the $\text{R}(\text{SiO}_{0.5})_3$ units results after addition of complexed and uncomplexed metal alkoxides in comparison with the GPTS hydrolysate.
- By use of AcAc modified metal alkoxides as additives a higher condensation degree is achieved in GPTS sols compared to sols with unmodified metal alkoxides as additives.
- Reactions of acetylacetone modified metal alkoxides $\text{M}(\text{OR})_{x-1}\text{AcAc}$ with GPTS-hydrolysates ($0.5 \text{ H}_2\text{O}/\text{OR}$) lead to a higher amount of heterometal Si-O-M bonds in comparison with unmodified metal alkoxides $\text{M}(\text{OR})_x$ ($\text{M} = \text{Zr}, \text{Ta}$). Therefore, a higher structural homogeneity in GPTS based sol-gel materials could be achieved by use of complexed metal alkoxides.
- The addition of water ($2 \text{ H}_2\text{O}/\text{OR}$) to the sols (SiMAc) leads to a degradation of the heterometal bonds in favour of more homocondensed species. Therefore, the water amount used for these sol-gel systems should be minimized to avoid increasing structural inhomogeneities in the materials.

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