

²⁹Si and ¹⁷O NMR Investigations on Si—O—Ti Bonds in Solutions of Diphenylsilanediol and Titanium-Tetra-Isopropoxide

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Abstract. The structural units in diphenylsilanediol/titanium-isopropoxide solutions with molar ratio Si:Ti between 1:0.1 and 1:5 were examined by means of ²⁹Si and ¹⁷O NMR. The main component in solutions with molar ratio Si/Ti = 1:0.1 is the chain-like octaphenyltetrasiloxanediol. With increasing Ti-isopropoxide content (1:0.25–1:0.5) Si—O—Ti units of the spirocyclic titanasiloxane Ti[O₅Si₄(C₆H₅)₈]₂ prevail in the solutions accompanied by the chain-like tetrasiloxanediol. The ²⁹Si NMR spectra of 1:1 solutions indicate a lot of different Si containing building units with chemical shifts mainly between –40 and –46 ppm. The signals with a chemical shift between –40 and –46 ppm are probably caused by Si atoms which are connected via oxygen bridges directly (Si—O—Ti) or indirectly (Si—O—Si—O—Ti) with titanium. Contrary to the 1:1 solutions only one or two different species with Si—O—Ti units are present in high Ti-alkoxide containing solutions (1:5). ²⁹Si and ¹⁷O NMR results reveal a quick hydrolysis of the Ti—O—Si bonds to titanium-oxo-hydroxo-polymers and phenylsiloxanediols or their isopropyl esters after the addition of water to the solutions. This separation into species only containing either Ti—O—Ti or Si—O—Si bonds can entail a decreased homogeneity of the reaction products on a molecular level.

Keywords: titanasiloxanes, siloxanes, hydrolysis, condensation, structural units, NMR

1. Introduction

Oxygen bridged heterometallic Me—O—Me* bonds, i.e., between Si, Al, Ti, and Zr, play an important role in materials like ceramics, glasses, catalysts and hybrid polymers [1–7]. A reason for the synthesis of materials with heterometallic bonds is to combine material properties of the different metal oxides in one and the same product. The control of the distribution of the mixed oxides is demanded by the necessity to tailor material properties for example for electronic applications. It is frequently cited that multicomponent oxides materials derived from the sol-gel process show a far better homogeneity in the distribution of heterometal oxide bonds than those materials derived from common ceramic processing techniques [8–10]. Up to now, however, it has not been sufficiently proved whether or not an optimal homogeneous distribution of the heterometal bonds at molecular level exists in the

sol-gel derived products [10–15]. Recent NMR investigations [16, 17] on the reactions of dimethyldiethoxysilane with titanium isopropoxide have indicated that a homogeneous distribution of the heterometallic bonds does not necessarily occur in the primary stages of the sol-gel process. A remarkable separation of oxygen bridged homo-metallic bonds can rather occur during hydrolysis/condensation reactions. Because of these reactions there exist areas in which one type of metal oxide bonds prevail. This separation of metal oxides in the first stage of the sol-gel process should decrease the homogeneity of the produced materials significantly. To prevent the separation a better knowledge on the hydrolytic stability of oxygen bridged heterometal bonds is required.

The objective of this work is to contribute to the detection and identification of heterometallic Si—O—Ti bonds and to the characterisation of their hydrolytic stability by means of ²⁹Si and ¹⁷O NMR spectroscopy.

Diphenylsilanediol (DPSD) has been chosen as model compound for this basic research because of the high stability of diphenylsilanediol towards condensation reactions and its difunctionality, which only allows chain-like or cyclic structures of the homocondensation products and more simple structures in the heterocondensation products with metal alkoxides as compared to those of multifunctional alkoxy silanes. The synthesis and properties of such titanophenylsiloxanes were extensively studied in the sixties because of their remarkable thermal stability [18].

2. Experimental

Synthesis of the DPSD/Ti-Isopropoxide Solutions.

The procedure for the preparation of DPSD/Ti-isopropoxide/dioxane solutions has been kept the same, differing only in molar ratio Si:Ti from 1:0:1 to 1:5. Solutions were mostly synthesised with 1 molar concentration in DPSD except for the 1:5 solutions with a high Ti-alkoxide content (0.45 mole/l in DPSD). The following example describes the synthesis of a solution with a molar ratio Si:Ti = 1.

2 g (9.24 mmole) diphenylsiloxanediol (Fluka, >97%) were dissolved in 4.72 ml dioxane (water content <0.005%) at 25°C followed by an addition of 2.72 ml (9.24 mmole) Ti-isopropoxide (ABCR) to the stirred DPSD solution. After stirring for 3 min the solution was stored at 25°C in a tightly closed glass vessel. In general, the ^{29}Si NMR measurements of the solutions were started after 10 min, 5 h and 24 h after mixing of the components.

The DPSD/Ti-isopropoxide solutions were hydrolysed with a water-dioxane solution in a molar ratio $\text{Ti}:\text{H}_2\text{O} = 1:2$. The resulting siloxane concentration in the hydrolysed solutions was 0.7 mole/l.

For the ^{17}O NMR examinations a ^{17}O enriched DPSD has been synthesised by hydrolysis of diphenyldiethoxysilane (ABCR, 97%) with ^{17}O labelled water as follows: 3.3 g diphenyldiethoxysilane were dissolved in 3.5 ml ethanol. Then 0.75 ml ^{17}O enriched water (Isotec, 10%) and 0.15 ml 0.1 M hydrochloric acid were added drop by drop to the stirred solution. A transparent solution was obtained after stirring for 15 min and stored at 5°C for two days. The formed crystals were isolated with a yield of 1.4 g (53%). Characterisation of the crystals: ^{29}Si NMR (in dioxane) one signal at $\delta = -32.95$ ppm, ^{17}O NMR (in dioxane) one signal at $\delta = 25.5$ ppm with 240 Hz half-line width.

The spirocyclic titanasiloxane $\text{Ti}[\text{O}_5\text{Si}_4(\text{C}_6\text{H}_5)_8]_2$ was synthesised from DPSD and Ti-*n*-butoxide according to the Zeitler method [19]. The reaction product was recrystallised from toluene. The ^{17}O labelled DPSD was used for the synthesis of the ^{17}O enriched spirocyclic titanasiloxane.

NMR Spectroscopy. The ^{29}Si and ^{17}O NMR spectra were obtained using liquid state (Bruker AC 200) and solid state (Bruker MSL 200) spectrometers operating at a field of 4.7 T. Teflon-tubes eight mm in diameter were used with a four mm tube containing tetramethylsilane (TMS) as external reference and actone- d_6 or benzene- d_6 as lock. The ^{29}Si spin-lattice relaxation times (T_1) for silicon were determined by the inversion-recovery pulse method with $\{^1\text{H}\}$ inverse-gated decoupling at 298 K. T_1 values were determined for the Si atoms in DPSD (D^0 unit) and in end groups of octaphenyltetrasiloxanediol (D^1 units) of about 26 s and for those in middle groups of the tetrasiloxanediol (D^2 units) of 72 s at 298 K. A repetition time of 40 s and a pulse angle of 63° were used as compromise for spectra with sufficiently low noise to signal ratio, a short time of recording and the different relaxation times [20]. Under these conditions the signal intensity of the D^2 unit appears about 30% too low with regard to the signals in D^0 and D^1 units. The percent values in the text always refer to the relative signal intensity of the spectra. One hour of accumulation time was used for the first sample of a series starting 10 min after the synthesis. The samples with the ageing of 5 h and 24 h were recorded over two hours. The reaction time of the solution which is specified in the text results from the averaged time between start and end of the NMR measurement.

A single pulse NMR experiment was used to record spectra of the quadrupolar nuclei ^{17}O at 298 K. Repetition time: 200 ms, pulse angle: 90°, reference: H_2O (1% ^{17}O), number of scans: 1000–10000.

3. Results and Discussion

3.1. Influence of the DPSD/Ti-Isopropoxide Ratio on the Si Building Units

In a forthcoming work [21] the catalytic activity of metal alkoxides on the condensation reactions of diphenylsilanediol (DPSD) has been investigated. The results indicated an important role of heterometallic Si—O—Me bonds as intermediate stage in the DPSD

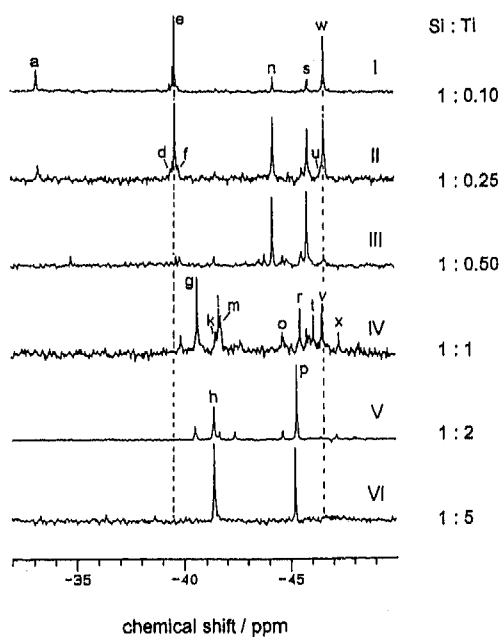


Figure 1. ^{29}Si NMR spectra of DPSD/ $\text{Ti}(\text{OPr}^i)_4$ /dioxane solutions with different Si/Ti molar ratios after 6 h reaction time.

condensation process. A ^{29}Si NMR spectroscopic evidence of the existence of such heterometallic bonds failed due to the low metal (Ti-) alkoxide concentration (molar ratio Si:Ti = 1:0.001–0.01) in the DPSD solutions.

Signals to be attributed to heterometallic Si—O—Ti bonds firstly were found in the ^{29}Si NMR spectra of DPSD solutions with a molar ratio Si:Ti = 1:0.1 (Fig. 1, signal *n*, *s*). The intensity of the new signals *n* and *s* increases and evolves to a main component in the NMR spectra of DPSD solutions with increasing Ti contents (Si/Ti = 1:0.25 and 1:0.5, Fig. 1II and 1III).

According to the results of our work [21] the signal *a* in the spectra I and II (Fig. 1) with a chemical shift $\delta = -33.12$ ppm is caused by the unreacted DPSD, the signal *f* at $\delta = -39.76$ ppm is attributed to the tetraphenyldisiloxanediol, the two signals *d* and *u* at -39.44 and -46.52 ppm are assigned to the Si atoms in D^1 and D^2 building units of the hexaphenyltrisiloxanediol and the two signals *e* and *w* at $\delta = -39.64$ and -46.67 ppm relate to the D^1 and D^2 units of the octaphenyltetrasiloxanediol. The signals *n* and *s* at $\delta = -44.27$ and -45.87 ppm, which do not appear in condensed DPSD solutions without additives of Ti-alkoxides are assigned to molecules with heterometallic Si—O—Ti bonds. An even more complex ^{29}Si NMR spectrum was received from a solution

with a molar ratio Si:Ti = 1:1 (Fig. 1IV). New signals appear in the region between Si atoms in D^1 (-39 ppm) and D^2 (-46 – -47 ppm) units of diphenylsiloxanediols. The signal *a* of the starting DPSD and those of the oligomeric diphenylsiloxanediols cannot be found in Si:Ti = 1:1 solutions. A further increase of the Ti-alkoxide concentration in the DPSD solution (Si:Ti = 1:2) leads to a spectrum mainly consisting of 6 signals with a chemical shift between -40 and -46 ppm (Fig. 1V). No signals are detected for D^1 and D^2 Si atoms in titanium free siloxanes. Finally, the spectrum of a solution with a molar ratio Si:Ti = 1:5 shows only two signals (*h*, *p*) at $\delta = -41.45$ and -45.31 ppm after 6 h reaction time (Fig. 1VI). It follows from the spectrum that one or two different species probably with Si—O—Ti bonds prevail in such DPSD solutions rich in titanium alkoxide. The chemical shifts of the main ^{29}Si NMR signals in the spectra of DPSD/Ti-alkoxide solutions are summarised in Table 1. As mentioned above, it is likely that the signals in the region -40 to -46 ppm whose intensity rises with an increasing Ti-alkoxide content are caused by different types of Si atoms bonded via oxygen directly or indirectly to Ti atoms. The identification and assignment of these signals to defined species is difficult due to the lack of suitable titanophenylsiloxanes with known structures.

3.2. Characterisation of Si—O—Ti Bonds

Two crystalline titanophenylsiloxanes with Si—O—Ti bonds are known in literature [19, 22]. For both samples a spirocyclic structure was suggested [19, 23] (Fig. 2). In the present work the spirocyclic titanophiloxane $\text{Ti}[\text{O}_5\text{Si}_4(\text{C}_6\text{H}_5)_8]_2$ (B) was synthesised from DPSD and $\text{Ti}(\text{O}i\text{Bu})_4$ according to Zeidler method [19] as standard sample for the determination of the chemical shift of the silicon and oxygen atoms in the heterometallic structure.

The ^{29}Si NMR spectrum of the spirocyclic compound B dissolved in dioxane shows two signals at $\delta = -44.26$ and -45.86 ppm. The solid state ^{29}Si NMR spectrum of the spirocyclic compound shows 6 signals with the following chemical shift and relative signal intensities (in brackets): -41.6 (12%), -43.3 – -43.6 (52%), -45.4 (14%), -48.1 (14%) and -49.2 ppm (8%). The assignment of the NMR signals to the Si atoms on the basis of the crystal structure was described by Rutherford [24]. The comparison of our solid state spectrum with those in literature shows an identical number of signals but differences in the

Table 1. ^{29}Si NMR chemical shift of main signals in the spectra of DPSD/Ti-isopropoxide solutions and their assignment. The structural element $-\text{Ti}-\text{O}\cdots\text{Si}-$ symbolizes building units in titanasiloxanes in which the Si atom is bonded via oxygen directly or indirectly to titanium.

Signal	Chemical shift/ppm	Assignment to building units
a	-33.12	$\text{HO}-\text{Si}-\text{OH}$
b	-34.84	$\text{HO}-\text{Si}-\text{OPr}^i$
c	-36.40	$\text{Pr}^i\text{O}-\text{Si}-\text{OPr}^i$
d	-39.44	$\text{HO}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{OH}$
e	-39.64	$\text{HO}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{OH}$
f	-39.76	$\text{HO}-\text{Si}-\text{O}-\text{Si}-\text{OH}$
g	-40.68	$-\text{Ti}-\text{O}\cdots\text{Si}-$
h	-41.45	$-\text{Ti}-\text{O}-\text{Si}-\text{O}-\text{Ti}-$
k	-41.52	$-\text{Ti}-\text{O}\cdots\text{Si}-$
l	-41.67	$\text{HO}-\text{Si}-\left(\text{O}-\text{Si}\right)_{1-3}-\text{OPr}^i$ or $-\text{Ti}-\text{O}\cdots\text{Si}-$
m	-41.77	$-\text{Ti}-\text{O}\cdots\text{Si}-$
n	-44.26	$-\text{Ti}-\text{O}-\text{Si}-\text{O}-\text{Si}-$ (spirocyclic structure B)
o	-44.67	$-\text{Ti}-\text{O}\cdots\text{Si}-$
p	-45.31	$-\text{Ti}-\text{O}-\text{Si}-\text{O}-\text{Ti}-$
r	-45.51	$-\text{Ti}-\text{O}\cdots\text{Si}-$
s	-45.86	$-\text{Ti}-\text{O}-\text{Si}-\text{O}-\text{Si}-$ (spirocyclic structure B)
t	-46.15	$-\text{Ti}-\text{O}\cdots\text{Si}-$
u	-46.52	$\text{HO}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{OH}$
v	-46.57	$-\text{Ti}-\text{O}\cdots\text{Si}-$
w	-46.67	$\text{HO}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{OH}$
x	-47.32	?

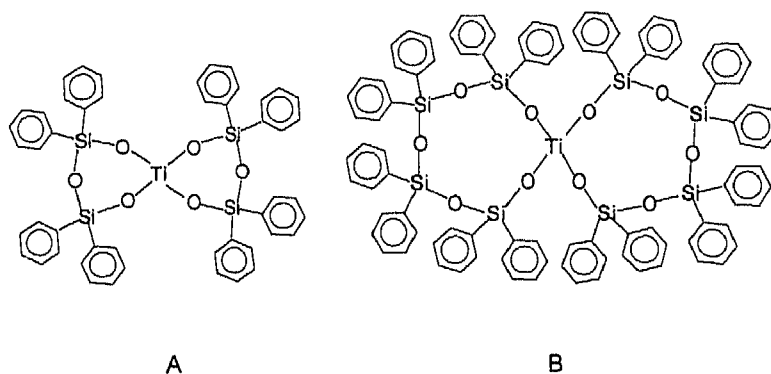


Figure 2. Structural scheme of spirocyclic titanophenylsiloxanes.

chemical shift of the signals. Probably, two different crystalline modifications of the sample as described by Zeitler [19] were used for the NMR examinations.

Assuming that the chemical shift of Si atoms which are directly bonded via oxygen with Ti shows a low field shift compared to corresponding Si—O—Si bonds [15, 24] in the liquid state NMR spectrum, the signal at $\delta = -44.26$ ppm can be attributed to Si atoms in the Si—O—Ti bonds [$D^2(1\text{Ti})$ unit] and the signal at -45.86 ppm to those in Ti—O—Si—O—Si—O—Si bonds (D^2) of the spirocyclic compound. As expected [25] the signal of this D^2 unit shows due to its cyclic structure a down field shift compared with the D^2 signals of the chain-like trimeric and tetrameric diphenylsiloxanediols ($-46.52/-46.67$ ppm), but a high field shift compared to D^2 units in a cyclic tetrameric diphenylsiloxane (-43.3 ppm). This is probably due to the bigger ring size (pentameric ring) in the spirocyclic structure. The chemical shift of the Si atoms in the spirocyclic compound *B* supports the assumption that Si atoms which are connected via oxygen bridges directly or indirectly with Ti atoms appear in the region at $\delta = -40$ to -46 ppm.

The ^{17}O NMR spectrum of the ^{17}O enriched spirocyclic compound *B* dissolved in chloroform at 313 K shows one signal at 297 ppm and two overlapped broad signals at 116 and 69 ppm. The first signal is assigned to the oxygen atoms in Ti—O—Si bonds, the second one to the oxygen in Ti—O—Si—O—Si and the signal at 69 ppm to Ti—O—Si—O—Si—O—Si—O—Si—O—Si—O—Ti bonds [16, 17].

Comparing the two signals of the spirocyclic compound *B* in the liquid state ^{29}Si NMR spectrum with the two signals *n* (-44.26 ppm) and *s* (-45.87 ppm) in the DPSD/Ti(OPr^{*t*})₄ solution 1:0.25 and 1:0.5 (Fig. 1I–III)

it was found that the chemical shifts and signal intensities were identical. Therefore, the spirocyclic molecule should be a main component in this solution. The result explains the synthesis conditions described by Zeitler in 1957 for the spirocyclic compound consisting of a molar ratio Si:Ti = 1:0.13 from a solution with a ratio 1:0.5. According to the NMR spectra the 1:0.5 solution contains more than 60% (signal intensity) of the spirocyclic molecule but a 1:0.1 solution only 15%.

Furthermore, the NMR result explains the preferred forming of the unique spirocyclic structure *B* in 1:0.1 to 1:0.5 solutions. In these solutions the chain-like octaphenyltetrasiloxanediol molecules exists as building unit of this spirocyclic structure [21]. It is likely that two molecules of the tetrasiloxanediol react directly with one molecule of Ti-alkoxide forming the spirocyclic molecule *B* (Fig. 2). This direct way is supported by the synthesis route of the second spirocyclic compound (Fig. 2A). Andrianov [22] prepared this compound starting from the dimeric tetraphenyl-disiloxanediol and TiCl₄.

3.3. Time Dependent Changes in the Distribution of Si Building Units

The ^{29}Si NMR examination of the distribution of structural units in the DPSD/Ti-isopropoxide solutions showed remarkable differences in their time dependence. These changes are demonstrated for example by solutions with a molar ratio Si:Ti = 1:0.25 and 1:5. Figure 3 shows the ^{29}Si NMR spectra of these solutions after a reaction time of 1 h, 7 d and 21 d. In the spectra of the 1:0.25 solution, changes appear mostly in the signal intensities during 7 d reaction time (Fig. 3I, II). The signal intensity of the spirocyclic species decreases from

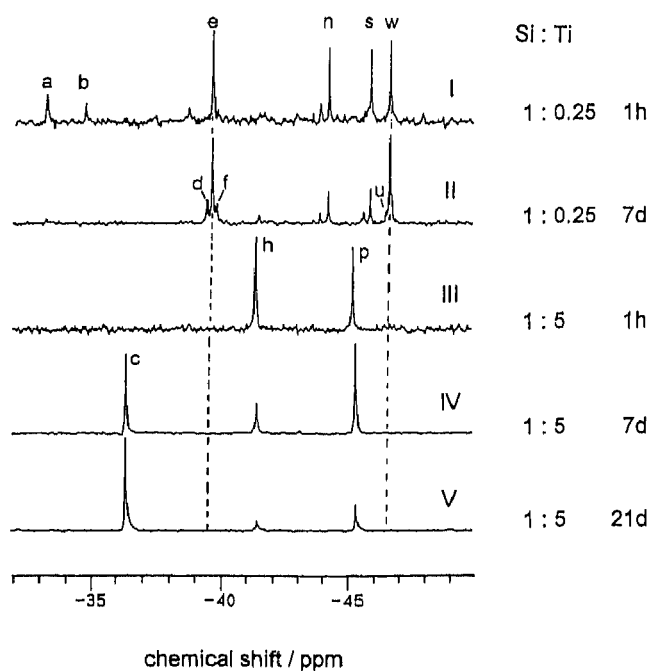


Figure 3. ^{29}Si NMR spectra of DPSD/ $\text{Ti}(\text{OPr}^t)_4$ /dioxane solutions with molar ratio $\text{Si}/\text{Ti} = 1:0.25$ and $1:5$ after 1 h, 7 d and 21 d reaction time.

about 24% to 15% and those of the phenylsiloxanediols increase from 50% to 70%. The DPSD concentration is reduced to 1% and the signal *b* at $\delta = -34.8$ ppm which is attributed to the diphenylisopropoxysilanol cannot be detected after 7 d. Crystals of the octaphenyltetrasiloxanediol are formed in the solution after 1 d which additionally increase the actual amount of the phenylsiloxanediols. It follows from the NMR spectra, that with increasing reaction time, a gradual cleavage of titanasiloxane bonds to phenylsiloxanediols appears accompanied by condensation of DPSD to chain-like siloxanes.

In the spectrum of the 1:5 solution, at first the above mentioned two signals at $\delta = -41.45$ and -45.31 ppm appear (Fig. 3III). An additional signal *c* is detected at $\delta = -36.40$ ppm after 6 h reaction time whose intensity increases continuously and achieves a relative intensity of 70% after 21 d (Fig. 3V). The intensity of the signals *h* and *p* does not decrease equally in favour of the new signal *c*. It can be concluded that the two signals are caused by two different molecules which finally are transformed to an identical reaction product. The single signal *c* at -36.40 ppm is attributed to the diphenyldisopropoxysilane which is formed by the cleavage of the titanasiloxane species in presence of isopropanol.

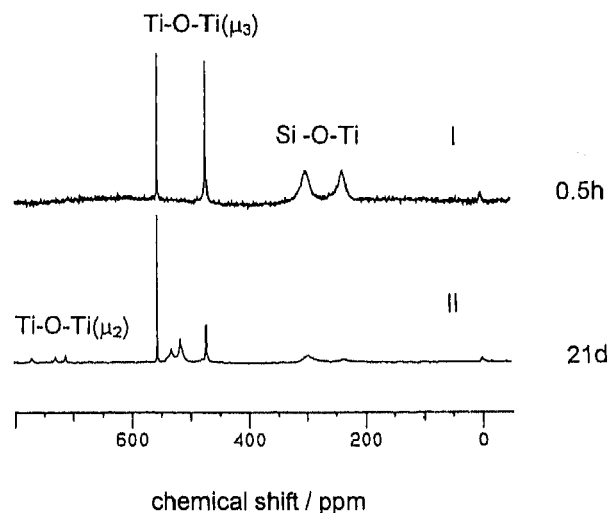


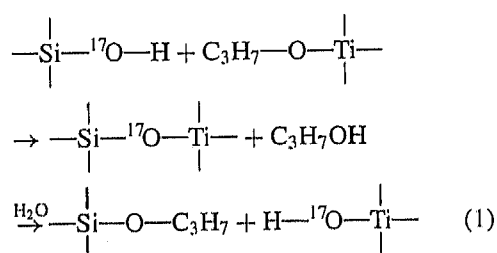
Figure 4. ^{17}O NMR spectra of a DPSD/ $\text{Ti}(\text{OPr}^t)_4$ /dioxane solution with molar ratio $\text{Si}/\text{Ti} = 1:5$ after 0.5 h and 21 d reaction time.

The ^{17}O NMR spectrum of the ^{17}O enriched 1:5 solution shows two broad signals at 237 and 300 ppm in the region of $\text{Si}-\text{O}-\text{Ti}$ bonds and $\text{Ti}-\text{OR}$ bonds in Ti -isopropoxide [26] after 0.5 h reaction time (Fig. 4I). It is likely that both signals are caused by $\text{Si}-\text{O}-\text{Ti}$ bonds due to their high intensity assuming that no significant

exchange of the ¹⁷O isotope appears between the ¹⁷O labelled DPSD and Ti-isopropoxide. Furthermore, two sharp signals appear at 470 and 554 ppm caused by Ti—O—Ti (μ_3) bonds of condensed Ti-oxo-alkoxo clusters probably with a defined structure because of the small signal width [27].

A remarkable fact is the absence of oxygen signals in terminal SiOH groups at about 25 ppm and in oxygen bridged Si—O—Si bonds at 50 to 60 ppm [16, 21]. The weak signal in Fig. 4 at 0 ppm is caused by the dioxane used as solvent. The absence of these types of oxygen reveals that oxygen bridged siloxane structures and terminal Si—O—Si—OH groups do not exist in the Ti rich solution in detectable amounts. Consequently, the two signals *h* and *p* in the ²⁹Si NMR spectrum (Fig. 3III) should originate from Si atoms in Ti—O—Si—O—Ti or Ti—O—Si—O—Si—O—Ti bonds.

The ¹⁷O NMR spectrum of the 1:5 solution after a reaction time of 21 d shows a decreased intensity of the oxygen signals of Si—O—Ti bonds and Ti—O—Ti bonds at 470 ppm. Additional signals in the region 515 to 530 ppm and 710 to 770 ppm appear after 21 days. These new signals are attributed to oxygen in μ_3 —Ti—O—Ti and μ_2 —Ti—O—Ti bonds in condensation products of Ti-alkoxides according to literature [28]. Corresponding to the ²⁹Si NMR results diphenyldiisopropoxysilane is formed as main constituent after 21 d which should lead to an intensive ¹⁷O signal in the region 0 to 40 ppm. The relative decrease of the signal intensity of Si—O—Ti bonds from 67% to 24% after 21 d and the lack of new Si—O—Si, Si—OH or Si—OR bonds (region 0 to 60 ppm) makes it probable that an exchange of the ¹⁷O isotope from the Si to Ti atom occurs during the structural changes. The following reaction scheme illustrates the possible reactions of DPSD with an excess of Ti-isopropoxide (1:5).



The ¹⁷O isotope of the DPSD is present in the titanasiloxane bond. The later alcoholysis/hydrolysis of the titanasiloxane bonds result in a nucleophilic attack of the non-labelled alcohol or water to the Si atom

leading to a non-labelled diphenyldiisopropoxysilane and to ¹⁷O doped Ti-oxo-hydroxo compounds. From the reaction scheme it follows that only the ¹⁷O labelled Ti-species should give intensive signals in the ¹⁷O NMR spectrum after 21 d in contrast to the silane which cannot be detected.

It is likely that the changes in the distribution of the building units with time are influenced by the water content of the solution, which derives from the condensation reaction of the DPSD silanol groups. The examination of the water content in the 1:0.25 solution by means of Karl-Fischer-Titration shows a nearly constant water content of 0.55–0.59% within 7 days. This water amount corresponds to 32% of the theoretical amount which can be released after a complete condensation of DPSD. The difference of 68% water should be bonded as silanol and preferably as Ti—OH groups. The free water can entail the hydrolysis of the Si—O—Ti bonds and the release of stable Si—O—Si fragments (phenylsiloxanes) and Ti-oxo-hydroxo clusters from the titanasiloxanes in the 1:0.25 solution.

With the following hydrolysis experiments the effect of water on the reorganisation of the molecule structures in the DPSD/Ti(OPr^{*i*})₄ solutions will be examined in detail.

3.4. Hydrolysis of Si—O—Ti Bonds

The first examinations of the hydrolysis reactions were carried out on the defined spirocyclic titanasiloxane Ti[O₃Si₄(C₆H₅)₈]₂ (Fig. 2B). Nine moles water per mole Ti were used for the hydrolysis of the 0.05 molar titanasiloxane/dioxane solution. The ²⁹Si NMR spectrum of the solution 0.75 h after addition of water shows two signals (*n*, *s*) at –44.25 and –45.84 ppm caused by the starting spirocyclic compound (Fig. 5I). Two poor additional signals (*e*, *w*) appear at –39.59 and –46.62 ppm which are attributed to the octaphenyl-tetrasiloxanediol. After three days the amount of the tetrasiloxanediol is increased to about 50% (Fig. 5II). The cleavage rate of the spirocyclic compound is significantly increased by hydrolysis with a molar ratio Ti:H₂O = 1:44. The NMR spectra account for an amount of 90% tetrasiloxanediol after only 1.5 h hydrolysis (Fig. 5III). At the same time the solution becomes cloudy. The precipitate is probably caused by Ti—O—Ti polymers and not by the octaphenyl-tetrasiloxanediol due to insolubility of the precipitate in chloroform. From the results it follows that only the Ti—O—Si bonds of the central Ti atom of the

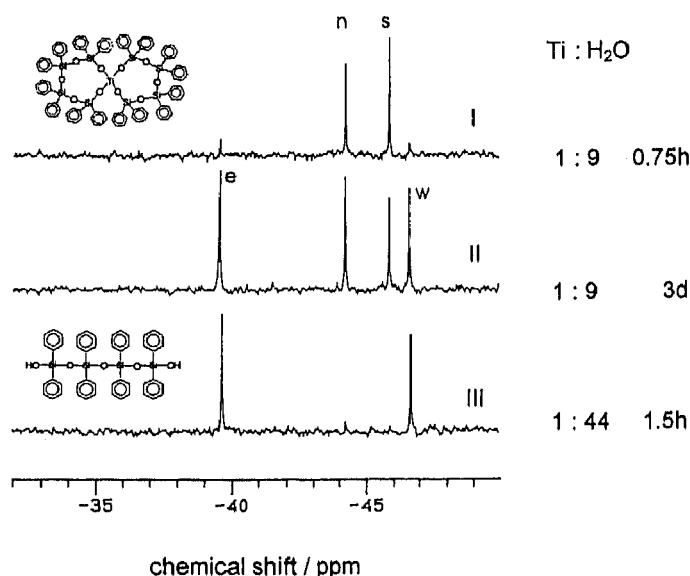


Figure 5. ^{29}Si NMR spectra of the spirocyclic titanophenylsiloxane *B* after hydrolysis.

spirocyclic compound *B* were cleaved by hydrolysis leading to the octaphenyltetrasiloxanediol and Ti-oxo-hydroxo-polymers. The structure of the tetrasiloxane building unit in the spirocyclic compound is preserved due to the high hydrolytic stability of the Si—O—Si bonds. Therefore, the siloxanes identified in the hydrolysates can be considered as structural elements of the primary spiro-structure of the titanosiloxane.

The ^{29}Si NMR spectra of DPSD/Ti-isopropoxide solutions with molar ratio Si:Ti = 1:1 and 1:2 hydrolysed after a storage of 2 h in a molar ratio Ti:H₂O = 1:2 show a completely different picture than those of non-hydrolysed solutions (Fig. 6). Most of the signals in the region of Si—O—Ti bonds (−40 to −46 ppm) are absent after hydrolysis and the signal intensity of the phenylsiloxanediols (*d*–*f*, *w*) is increased significantly. An additional signal *b* of high intensity appears at −34.8 ppm and is attributed to the diphenylisopropoxysilanol. The possible forming of a hexaphenylcyclotrisiloxane ($\delta = -34.1$ ppm) is to be excluded due to the significant differences in the chemical shifts. The appearance of a signal (I) at −41.64 ppm in both hydrolysates is noteworthy. This signal could originate from a titanosiloxane bond because its chemical shift does not correspond with possible phenylsiloxanediol structures. Yet, the forming of an isopropyl ester of the condensed di-, tri- or tetrameric phenylsiloxanediols is more likely. This assumption is supported by the comparison of the differences in the chemical shifts of DPSD (−33.1 ppm) and its

isopropoxide esters (monoester: −34.7 ppm, diester: −36.4 ppm) of 1.6 and 3.3 ppm. Assuming similar shift differences between the condensed phenylsiloxanediols and their esters, signals with a chemical shift at about −41.1 to −41.4 ppm should be expected. The detected signal at −41.6 ppm corresponds with the assumption of a condensed phenylsiloxane-isopropylester. The results reveal complicated reactions in the DPSD/Ti-alkoxide system in the presence of water. The considerable instability of the Si—O—Ti bonds towards hydrolysis is a characteristic property of the DPSD/Ti-alkoxide solutions.

Additional ^{17}O NMR studies were carried out to confirm the hydrolytic degradation of Si—O—Ti and the preservation of Si—O—Si bonds. The solutions with molar ratio Si:Ti = 1:1 and 1:2 synthesised from a ^{17}O enriched DPSD and Ti-isopropoxide were hydrolysed by non-labelled water in molar ratio Ti:H₂O = 1:2. The final Si concentration amounts to 0.7 mole/l. The ^{17}O NMR spectra of the solutions before and 0.5 h after hydrolysis are shown in Fig. 7. The signals of Si—O—Ti bonds which are present in both of the spectra of the non-hydrolysed solutions (Fig. 11, III) disappear after hydrolysis. New broad signals are detected in the region −2 to 60 ppm caused by oxygen atoms in H₂O, Si—OH and Si—O—Si groups. The sharp Ti—O—Ti signals at 470 and 483 ppm in the spectra of the non-hydrolysed solutions (Fig. 7I, III), indicating more defined oligomeric Ti-oxo-alkoxo structures convert abruptly to a broad signal after hydrolysis. The

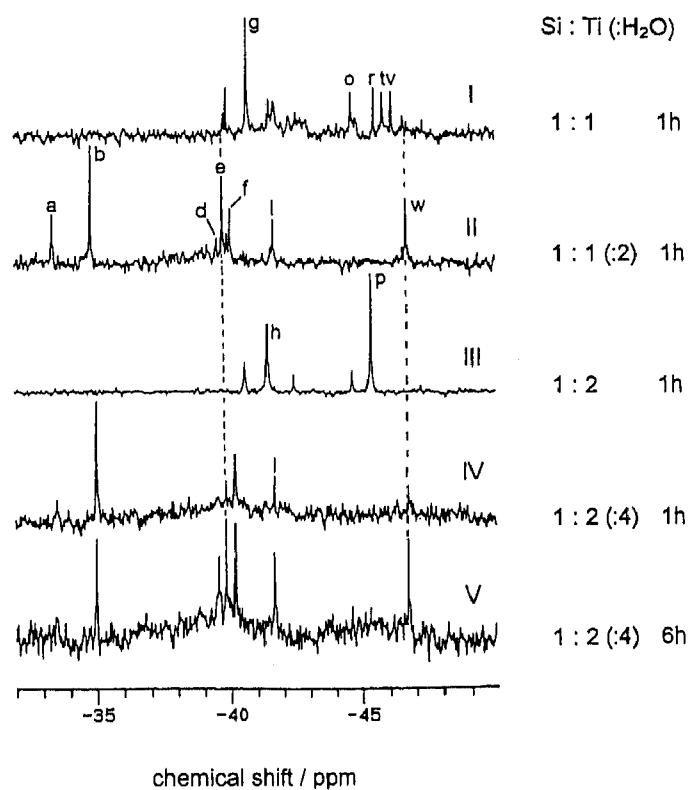


Figure 6. ^{29}Si NMR spectra of DPSD/ $\text{Ti}(\text{OPr}^i)_4$ /dioxane solutions with molar ratios $\text{Si}/\text{Ti} = 1:1$ and $1:2$ after 1 h reaction time before (I, III) and after hydrolysis in molar ratio $\text{Ti}/\text{H}_2\text{O} = 1:2$ (II, IV, V).

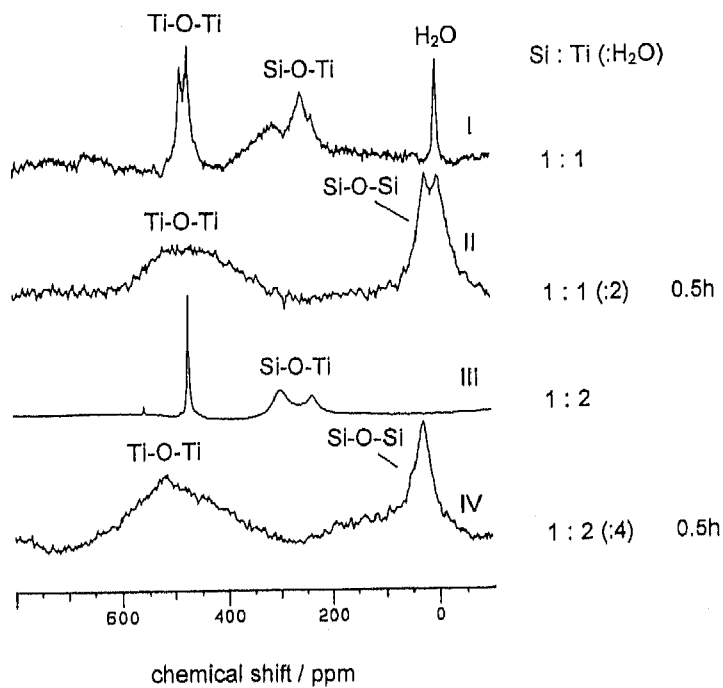


Figure 7. ^{17}O NMR spectra of DPSD/ $\text{Ti}(\text{OPr}^i)_4$ /dioxane solutions with molar ratios $\text{Si}/\text{Ti} = 1:1$ and $1:2$ before (I, III) and after 1 h hydrolysis (II, IV).

reasons are the hydrolysis of Ti—O—Si and TiOR bonds and the condensation reaction of the Ti—OH groups to a great variety of poorly ordered polymeric Ti-oxo-hydroxo-species. The relatively high signal intensity of the oxygen atoms in Ti—O—Ti bonds in the ^{17}O NMR spectra of solutions before and after hydrolysis confirms the above mentioned intensive exchange of the ^{17}O isotope from the DPSD molecule to the titanium atom.

A remarkable difference in the water content is noticed, comparing the two ^{17}O NMR spectra of the non-hydrolysed solutions (Fig. 7I, III). Water can be identified in 1:1 solution by the signal at -0.7 ppm, but it is absent in the spectrum of the 1:2 solution with a higher Ti-alkoxide content. Possibly the SiOH groups of DPSD in the later Ti-alkoxide rich solution react completely with the TiOR groups releasing isopropanol. The signal of isopropanol cannot be detected in the ^{17}O NMR spectrum III according to the reaction scheme (1).

The results of the ^{17}O NMR show a correspondence with those of the ^{29}Si NMR. Both methods confirm the high instability of most Si—O—Ti bonds towards hydrolysis.

4. Conclusion

The Si atoms bonded via oxygen bridges directly or indirectly to Ti atoms can be identified in diphenylsilanediol/Ti-isopropoxide solutions by means of ^{29}Si and ^{17}O NMR spectroscopy.

The reaction of diphenylsilanediol with Ti-isopropoxide leads, depending on the molar ratio, to mixtures of phenylsiloxanediols and titanosiloxanes, whereby the amount of titanosiloxanes dominates at a molar ratio Si/Ti lower than 2. With the ageing of the solutions the Si—O—Ti bonds are partially hydrolysed by water/isopropanol released from the condensation reaction of the DPSD. Additional water accelerates the cleavage of the Si—O—Ti bonds so that their complete destruction can occur within a short time (i.e., 1 h) leading to mainly di-, tri- and tetrameric phenylsiloxanediols and Ti-oxo-hydroxo-polymers. The results on DPSD as model compound show the excessive hydrolytic instability of the heterometallic bond and its separation in Ti-oxo-polymers and polysiloxane rich phases. This separation should considerably decrease the homogeneity of the Ti/Si distribution in the reaction products on a molecular level. Regardless of the problems still unsolved in the assignment of NMR

signals to defined species with Ti—O—Si bonds the results can contribute to a better understanding of the behaviour of heterometal bonds in the sol-gel process.

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