

## <sup>29</sup>Si NMR Investigation of Condensation Reactions of Diphenylsilanediol in Presence of Ti-, Zr-, Al-, Sn- and Si-Alkoxides

DAGOBERT HOEBBEL, THOMAS REINERT AND HELMUT SCHMIDT  
*Institut für Neue Materialien, Im Stadtwald, D-66123 Saarbrücken, Germany*

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**Abstract.** The investigation of the effects of small amounts of Ti-, Zr-, Al-, Sn- and Si-alkoxides and those of triethylamine and hydrochloric acid on the condensation reaction of diphenylsiloxanediol (DPSD) in molar ratio Si : additive = 1 : 0.01 and 1 : 0.04 by <sup>29</sup>Si NMR shows a decrease in their activity in the order Ti ≈ HCl > Al > Sn ≈ N(Et)<sub>3</sub> ≈ Zr > Si after 6 h reaction time. The influence of the type of alkoxide ligands attached to the metal on the condensation rate of DPSD was found relatively low compared to the different metals. In presence of Ti-alkoxide the condensation reaction of DPSD leads to di-, tri- and tetrasiloxanediols, the latter of which dominates and crystallizes from the solution as octaphenyltetrasiloxanediol. The catalysis of DPSD solutions by Al-alkoxide and HCl results preferably in tetraphenyldisiloxanediol species even after a few days. The complexity of metal alkoxides and the hydrolytic stability of heterometallic Si—O—M bonds have been discussed as possible reasons for the differences in the catalytic activity of the metal alkoxide.

**Keywords:** metal alkoxides, catalysis, phenylsiloxanes, structural units, <sup>29</sup>Si NMR

### 1. Introduction

The reactions of alkoxysilanes or siloxanols with metal alkoxides like Al-, Ti- and Zr-alkoxides are a common route in the preparation of heterometal oxide materials such as glasses, ceramics, optical and micro-electronic materials via the sol-gel process [1-8]. The metal alkoxides, preferably Ti-alkoxides, are not only used for synthesis of heterometal oxide compounds but also for activation of condensation reactions of alkyl or arylalkoxysilanes and silanols leading to silicones or organic-inorganic polymers [1, 6, 7, 9-14]. Up to now a detailed knowledge about the effects of different metal alkoxides on silanol condensation, on the structure of the condensed species and on the advantages of metal alkoxides compared to a common base or acid catalysis is missing.

The objective of this work is to examine the influence of small amounts of Ti-, Zr-, Al-, Sn- and Si-alkoxides on the condensation rate of silanol groups and the structure of their condensation products by means of

<sup>29</sup>Si NMR spectroscopy. Diphenylsilanediol (DPSD) has been chosen as model compound due to its high stability towards condensation reactions and its difunctionality, which only allows chain-like or cyclic structures of the condensation products. These facts facilitate the identification and characterisation of the condensation products by NMR and consequently the investigation of the effects of the metal alkoxides.

### 2. Experimental

The used diphenylsilanediol (DPSD, Fluka, >97%) was characterised by <sup>29</sup>Si NMR in 1 molar dioxane solution. The <sup>29</sup>Si NMR signal with a chemical shift ( $\delta = -32.81$  ppm (95% signal intensity) was attributed to DPSD [15]. Signals with low intensity appear at ( $\delta = -39$  ppm (3%) and  $-46$  ppm (2%)) caused by minor condensation products. Dioxane (Fluka, p.a. >99.5%) with a water content lower than 0.005% was used in all cases as solvent for DPSD.

The following metal alkoxides were used as additives for the diphenylsilanediol/dioxane solution: Titanium-tetraethoxide ( $\text{Ti}(\text{OEt})_4$ ; Fluka, 97%), Titanium-tetraisopropoxide ( $\text{Ti}(\text{OPr}')_4$ ; ABCR), Titanium-tetra-*n*-butoxide ( $\text{Ti}(\text{OBU}^n)_4$ ; Fluka), Titanium-tetraisobutoxide ( $\text{Ti}(\text{OBU}^i)_4$ ; ABCR), Zirconium-tetraisopropoxide ( $\text{Zr}(\text{OPr}')_4$ ; Gelest, 80.5% in heptane), Zirconium-tetra-*n*-butoxide ( $\text{Zr}(\text{OBU}^n)_4$ ; ABCR, 84.0% in butanol), Aluminium-tetra-secbutoxide ( $\text{Al}(\text{OBU}^s)_3$ ; Fluka), Tin-tetra-*n*-butoxide ( $\text{Sn}(\text{OBU}^n)_4$ ; Inorgtech), and Silicon-tetraethoxide ( $\text{Si}(\text{OEt})_4$ ; Fluka). The additives triethylamine (Fluka, >99.5%,  $\text{H}_2\text{O} < 0.1\%$ ) and 5M hydrochloric acid were used for comparative investigations.

The examination of the effect of Ti-, Zr-, Al-, Sn- and Si-alkoxides on the DPSD condensation was generally carried out in molar ratio of diphenylsilanediol to additive 1 : 0.01 and 1 molar DPSD concentration in dioxane solution. Additional experiments were carried out at a slightly higher concentration of Al-alkoxide (1 : 0.013) and at a four-fold concentration (1 : 0.04) of triethylamine and hydrochloric acid to compensate differences in the valency or functionality. With the example of Ti-isopropoxide the effect of higher amounts (molar ratio 1 : 0.1) and lower ones (1 : 0.001) of the metal alkoxide on the DPSD condensation were examined.

The procedure for preparation of metal alkoxide doped DPSD solution has always been the same, differing only in type and amount of the additives. The following example describes the synthesis of a one molar DPSD solution doped with Ti-isopropoxide in a molar ratio Si : Ti = 1 : 0.01.

3g (13.89 mmole) DPSD were dissolved in 11.12 ml dioxane. After 1 min 0.041 ml (0.139 mmole) Ti-isopropoxide were added to the stirred DPSD solution. After 3 min stirring the solution was stored at 25°C in a tightly closed glass vessel. In general the  $^{29}\text{Si}$  NMR measurements of the solutions started 10 min, 5 h and 24 h after addition of the metal alkoxide.

**NMR Spectroscopy.** The  $^{29}\text{Si}$  spectra were obtained using liquid state (Bruker AC 200) and solid state (Bruker MSL 200) spectrometers operating at a field of 4.7 Tesla. For liquid state NMR Teflon-tubes, 8 mm in diameter were used with an inner 4 mm tube containing tetramethylsilane (TMS) as external reference and acetone- $d_6$  as lock. The  $^{29}\text{Si}$  spin-lattice relaxation times ( $T_1$ ) for silicon were determined by the inversion-recovery pulse method with  $\{^1\text{H}\}$  inverse-gated

decoupling.  $T_1$  values were determined for the Si atoms in diphenylsiloxanediol and octaphenyltetrasiloxanediol. A  $T_1$  value of about 26 s were found for the Si-atoms of DPSD ( $D^0$ ) and the Si-atoms in end-groups ( $D^1$ ) of the tetrasiloxanediol and 72 s for those Si-atoms in middle-groups ( $D^2$ ) of the tetrasiloxanediol at 298 K. A repetition time of 40 s and a pulse angle of 63° were used as a compromise for the spectra with sufficiently low noise to signal ratio, a short time of recording and the different relaxations times [16]. Under these conditions the signal intensity of  $D^2$  units appears about 30% lower as compared 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 accumulation time was used for the first sample of a series starting 10 min after the synthesis. The 5 h and 24 h samples were recorded over two hours. The reaction time of the solution, specified in the text results from the averaged time between start and end of the NMR measurement.

Solid state  $^{29}\text{Si}$  NMR spectra were recorded using the  $^{29}\text{Si}\{^1\text{H}\}$  inverse-gated sequence with a pulse angle of 63° and a repetition time of 60 s. MAS: 3 kHz, transients: 200–1000, external standard:  $Q_8M_8$ .

### 3. Results

Different metal alkoxides with various alkoxy groups were used to know the influence of the metal as well as of alkoxide groups on the silanol condensation. To compare the reactivity of metal alkoxides with common base and acid catalysis, triethylamine and hydrochloric acid were included in the experiments.

#### 3.1. The Effect of the Ti-Alkoxide Concentration on the DPSD Condensation

The  $^{29}\text{Si}$  NMR spectra of the series of Ti-isopropoxide doped DPSD solutions with molar ratio Si : Ti = 1 : 0.001, 1 : 0.01 and 1 : 0.1 after 6 h reaction time are shown in Fig. 1. The spectrum of DPSD solution with a very low concentration of  $\text{Ti}(\text{OPr}')_4$  (molar ratio Si : Ti = 1 : 0.001) shows one signal with the chemical shift  $\delta = -32.87$  ppm caused by unreacted DPSD (Fig. 1 (I)). There is hardly any condensation reaction even after a reaction time of 24 h.

Significant changes appear in the spectrum of DPSD solution with a higher concentration of  $\text{Ti}(\text{OPr}')_4$  (Si : Ti = 1 : 0.01). New signals appear in the region

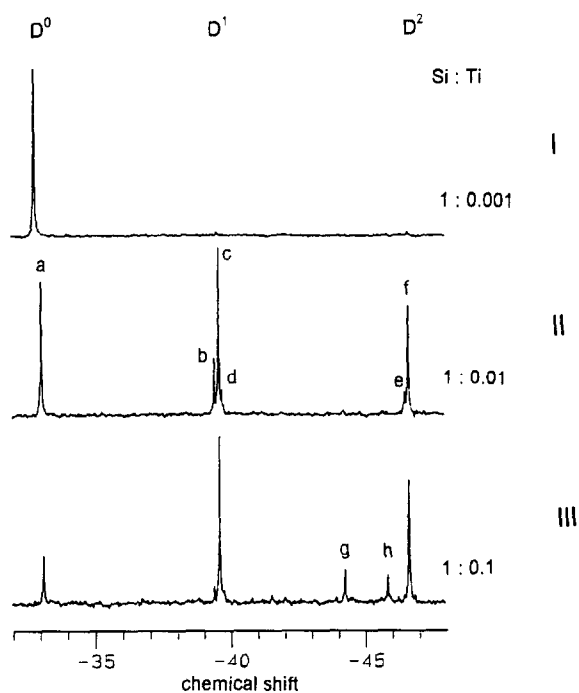


Figure 1. <sup>29</sup>Si NMR spectra of DPSD solutions doped with Ti(OPr<sup>t</sup>)<sub>4</sub> in different molar ratio Si/Ti after 6 h reaction time.

around  $\delta = -39$  and  $-46$  ppm in addition to the signal a of unreacted DPSD (Fig. 1(II)). According to literature [17, 18] the signal group at  $\delta = -39$  ppm is assigned to silanol end groups in phenylsiloxandiols ( $D^1$  units) and the signals around  $\delta = -46$  ppm are attributed to Si atoms in middle groups ( $D^2$  units) of chain-like or cyclic phenylsiloxanes. The appearance of  $D^1$  and  $D^2$  units is an evidence for condensation reactions of DPSD.

From the spectrum of DPSD solution doped with Ti(OPr<sup>t</sup>)<sub>4</sub> in molar ratio Si : Ti = 1 : 0.1 follows a more extensive condensation reaction (Fig. 1(III)). After 6 h reaction time about 90% (NMR signal intensity) of the DPSD reacted to condensed phenylsiloxanes.

The appearance of two additional signals (g and h) in the spectrum III at  $\delta = -44.27$  (7%) and  $-45.87$  ppm (9%) which are located in a region between  $D^1$  and  $D^2$  structural units of phenylsiloxanes is remarkable. These two additional signals are assigned to Si atoms in heterometallic Si—O—Ti bonds. The identification and hydrolytic stability of these Si—O—Ti bonds was the subject of a previous work [19].

A precipitation takes place in all examined solutions doped with Ti-alkoxide depending on the concentration of diphenylsilanediol, the Si/Ti ratio and stirring of the solution. For example one molar DPSD solutions

with molar ratios Si/Ti = 1 : 0.001, 1 : 0.01 and 1 : 0.1 precipitate in the same order after 10 d, 6-18 h and 4 h without stirring.

### 3.2. Identification of the Signals in the NMR Spectra

For a more detailed discussion of the condensation reaction of DPSD the identification of the signals in the NMR spectra is required. The signals in the region of  $D^1$  and  $D^2$  units (Fig. 1(II)) are very close to each other, so that the data of chemical shifts present in the literature are not sufficient for a reliable identification of the single signals mainly due to the use of a different solvent and different concentration conditions. Therefore, the identification was carried out by evaluating the changes in signal intensities in dependence on reaction time and by the structure of the above mentioned precipitate resulting from Ti-alkoxide doped DPSD solutions.

The precipitate is a crystalline sample with a good solubility in toluene, acetone and chloroform, but less soluble in dioxane. The results of the elemental analysis and the physical-chemical characterisation of the crystalline compound derived from a DPSD solution doped with Ti(OPr<sup>t</sup>)<sub>4</sub> in a molar ratio Si : Ti = 1 : 0.01 are summarised in Table 1.

It follows from the analytical data that the compound is nearly free of titanium, so that a condensed phenylsiloxane is probable. The two signals in the <sup>29</sup>Si NMR spectra of the crystals dissolved in dioxane as well as in the solid state spectra of the crystals in the region of Si atoms in  $D^1$  and  $D^2$  units and their intensity ratio near 1 : 1 are in accordance with a chain-like siloxane structure with the same number of end and middle groups. The two signals at  $\delta = 28.6$  and  $52.4$  ppm in the <sup>17</sup>O NMR spectra of the <sup>17</sup>O labelled crystals dissolved in chloroform confirm the existence of terminal silanol and bridging oxygen atoms in the structure [20]. Considering the molecular weight in conjunction with the results of the <sup>29</sup>Si and <sup>17</sup>O NMR spectroscopy the results give strong evidence for a chain-like octaphenyltetrasiloxanediol structure of the formula (C<sub>6</sub>H<sub>5</sub>)<sub>8</sub>Si<sub>4</sub>O<sub>3</sub>(OH)<sub>2</sub>.

Comparing the <sup>29</sup>Si NMR chemical shift of the two signals of the octaphenyltetrasiloxanediol ( $-39.55$ ,  $-46.59$  ppm) with the main signals c ( $-39.61$ ) and f ( $-46.67$ ) in the Ti-alkoxide doped DPSD solution (Figs. 1(II), (III)) practically the same chemical shift and signal intensity have been observed. It follows from this that octaphenyltetrasiloxanediol is a main

Table 1. Analytical data of octaphenyltetrasiloxanediol.

Elemental analysis of $C_{48}H_{42}O_5Si_4$	
calculated:	C 71.1%; H 5.2%; Si 13.8%
found:	C 69.6%; H 5.7%; Si 13.1%; Ti 0.01%
Molecular weight	
calculated:	810 $g \cdot mol^{-1}$
found:	$796 \pm 3\%$ $g \cdot mol^{-1}$ (vapor pressure osmometry)
	810 $g \cdot mol^{-1}$ (time of flight spectrometry)
$^{29}Si$ NMR	
dioxane solution:	2 signals at $\delta = -39.55$ ( $D^1$ ) and $-46.59$ ppm ( $D^2$ )
solid state:	2 signals at $\delta = -41.44$ and $-48.61$ ppm, ratio of intensities about 1 : 1
$^{17}O$ NMR	
chloroform solution:	2 signals at $\delta = 28.6$ and $52.4$ ppm

component in this solution which crystallises from it at sufficient concentration. The signal d at  $\delta = -39.72$  ppm (Fig. 1(II)) is attributed to the tetraphenyl-disiloxanediol according to the results described later in the text.

The signals b ( $-39.44$  ppm) and e ( $-46.54$  ppm) in Fig. 1(II) always appear together in nearly constant ratio of signal intensities at different reaction times, so that both signals seem to be constituents of one and the same compound. Obviously, on the basis of their chemical shifts the  $D^1$  signal b and the  $D^2$  signal e with lower intensity are attributed to the chain-like hexaphenyltrisiloxanediol.

From this assignment of the signals follows an order of the chemical shifts in the  $D^1$  region: at the lowest magnetic field the end groups of trimeric compound appear followed by the tetrameric ones and finally the dimeric siloxanediol. In the  $D^2$  region an expected order of the middle group signals from trimeric and tetrameric siloxanes is observed. From the assignment of the signals it follows that the addition of Ti-isopropoxide to DSPD solution in molar ratio Si : Ti = 1 : 0.01 leads within 6 h to condensation reactions resulting in mainly tetrameric siloxanediol besides dimeric and trimeric species.

The results of the  $^{29}Si$  NMR investigations on DSPD condensation reaction with regard to distribution of Si atoms in  $D^0$ ,  $D^1$  and  $D^2$  building units as a function of Ti-isopropoxide concentration and the reaction time are summarised in Fig. 2(I), (II).

### 3.3. The Influence of Alkoxy Ligands on Condensation Reaction

Ti-alkoxides with the ligands *n*-butoxide, isobutoxide, isopropoxide and ethoxide were chosen as examples

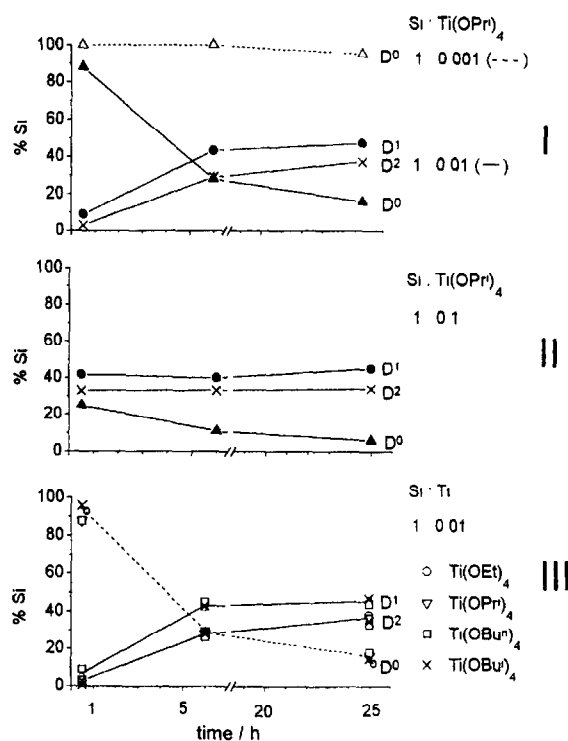


Figure 2. Distribution of Si building units in DSPD solutions doped with  $Ti(OPr)_4$  in different molar ratios Si/Ti and with different Ti-alkoxides.

for the examination of the effect of size and structure of alkoxy ligands on the rate of DSPD condensation. The molar ratio of DSPD : Ti-alkoxides was 0.01, the DSPD concentration in dioxane 1 molar. The results of the  $^{29}Si$  NMR examination are summarized in Fig. 2(III).

After 0.5 h reaction time 88 to 96% of DSPD remains unchanged in the four examined solutions. With increasing time the DSPD content decreases to about

28% (6 h) and finally to about 15% (25 h). With the decrease of DPSD concentration an increase of *D*<sup>1</sup> end groups and *D*<sup>2</sup> middle groups appears which can mainly be attributed to the octaphenyltetrasiloxanediol. From Fig. 2(III) a nearly identical distribution of the Si-building units and a comparable condensation rate follows for the different alkoxide ligands of titanium. From the results, it can be concluded that the alkoxide type does not influence the condensation reaction significantly.

### 3.4. The Effect of Al-, Zr-, Sn- and Si-Alkoxides

A selection of <sup>29</sup>Si NMR spectra of DPSD solutions doped with Ti-, Al-, Zr- and Sn-alkoxides after 25 h reaction time is shown in Fig. 3.

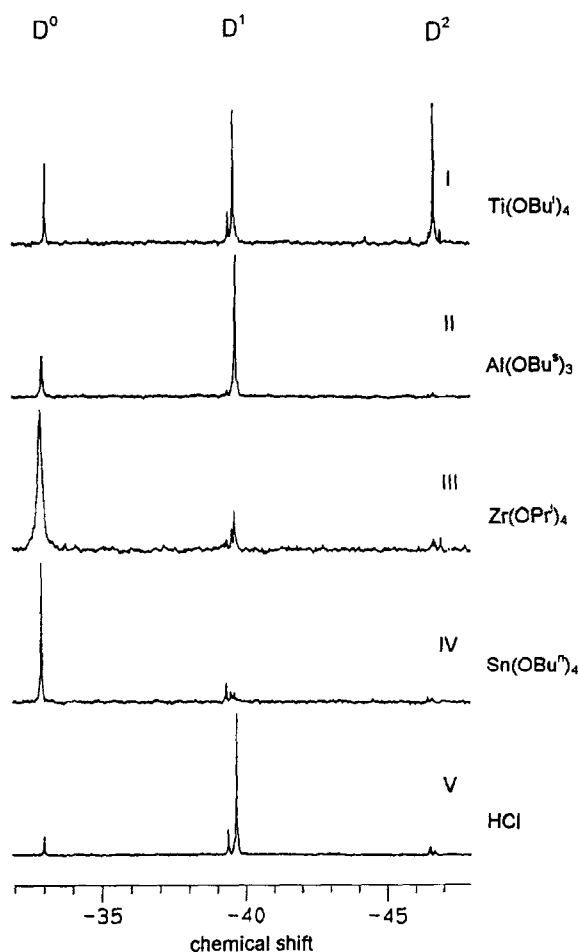


Figure 3. <sup>29</sup>Si NMR spectra of DPSD solutions doped with Ti(OBu)<sup>4</sup>, Al(OBu)<sup>3</sup>, Zr(OPr)<sup>4</sup> and Sn(OBu)<sup>4</sup> in molar ratio Si : M = 1 : 0.01 and Si : HCl = 1 : 0.04 after 25 h reaction time.

As already mentioned, the NMR spectrum of the reaction product of DPSD with Ti-alkoxides shows as main components signals of unreacted DPSD and of tetrasiloxanediol among signals of minor products of trisiloxanediol.

The NMR spectrum of the Al(OBu)<sup>3</sup> doped DPSD solution shows a strong single signal at  $\delta = -39.76$  ppm and a DPSD signal of lower intensity. The strong signal in the region of *D*<sup>1</sup> units can only be attributed to the two identical Si atoms in a tetraphenyl-disiloxanediol. A low-field shifted single signal of *D*<sup>2</sup> units of hexaphenylcyclotrisiloxane [17] at  $\delta = -34.11$  ppm or the signal of an octaphenylcyclotetrasiloxane at  $\delta = -43.27$  ppm can be excluded because of their different chemical shifts. A crystalline compound was isolated from the Al-alkoxide doped DPSD solution after 14 d. This compound dissolved in dioxane shows only a single signal at  $\delta = -39.77$  ppm in the <sup>29</sup>Si NMR which corresponds with the main signal in spectrum II (Fig. 3). The <sup>17</sup>O NMR spectrum of the crystals doped with the <sup>17</sup>O isotope indicates two overlapped signals with chemical shifts at  $\delta = 30$  and 53 ppm. The latter signal is attributed to the bridging oxygen atom and the first one to the oxygen atoms in the two terminal silanol groups of the tetraphenyl-disiloxanediol [20]. The molecular weight of the crystalline compound was determined to 414 g · mole<sup>-1</sup> by means of time of flight spectrometry. The result is in agreement with calculated molecular weight and supports the structure of a tetraphenyl-disiloxanediol.

Only minor condensations products are detectable in the spectra of Zr- and Sn-alkoxide doped solutions (Fig. 3(III), (IV)) and in Si-ethoxide containing solutions. It is noticeable, that the DPSD signal in the spectra of Zr- and Al-alkoxide doped solutions shows a considerable line broadening (linewidth 10–12 Hz) with respect to Ti- and Si-alkoxide doped solutions (1 Hz), possibly, showing a restricted mobility of the DPSD molecule.

The distribution of Si-building units depending on the type of metal alkoxide and reaction time is summarized in Fig. 4. After 25 h reaction time the distribution of Si building units in Zr(OPr)<sup>4</sup> and Zr(OBu)<sup>4</sup> doped samples are similar showing mainly the *D*<sup>0</sup> signal of unreacted DPSD (86–96%). The similar effects of the two Zr-alkoxides confirm the low influence of alkoxide groups on condensation rate as shown by Ti-alkoxides also.

For comparative examinations the DPSD solution was doped with the common catalysts triethylamine

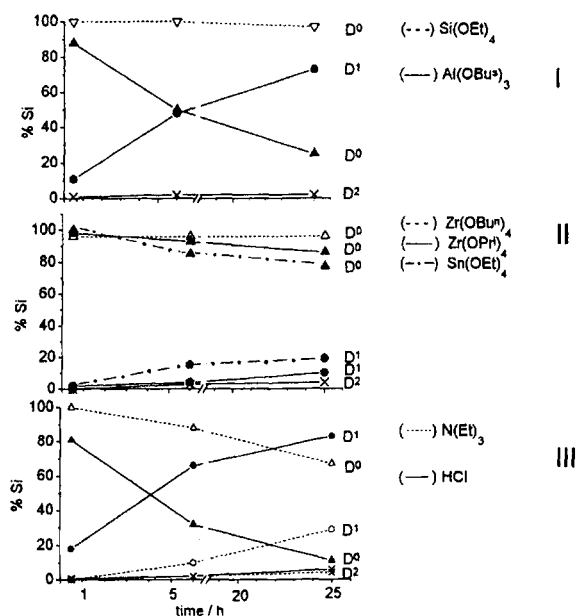


Figure 4. Distribution of Si building units in DPSD solutions doped with Al-, Zr-, Sn- and Si-alkoxides in molar ratio Si : M = 1 : 0.01 and Si : HCl and Si : N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> = 1 : 0.04.

and HCl. In respect to the tetra-valent Ti- and Zr-alkoxides a four-fold concentration of the acidic and basic catalysts was used to compensate the differences in valency. From the <sup>29</sup>Si NMR spectra of the DPSD solution, catalyzed by hydrochloric acid follows a strong condensation reaction leading preferably to the D<sup>1</sup> signal of the tetraphenyldisiloxanediol (65%) after 25 h reaction time (Fig. 3(V)). Additional signals at -39.47 (20%) and -46.57/-46.72 ppm (6%) are attributed to trisiloxanediol and traces of tetrasiloxanediol. The unreacted DPSD amounts to 9% (Fig. 4(III)).

Triethylamine catalyzed DPSD solutions in contrast to acid catalysis condense very slowly leading only to 33% of condensation products consisting of D<sup>1</sup> and D<sup>2</sup> building units after 25 h (Fig. 4(III)). A low amount (3–5%) of cyclic tri- (-34.1 ppm) and cyclic tetrameric diphenylsiloxanes (-43.3 ppm) has been detected in the amine catalyzed solution after 9 d. These cyclic species were not found in acid or Ti-alkoxide catalyzed solutions. The higher activity of hydrochloric acid in comparison with the amine can rather be caused by a better protonation of the oxygen in the DPSD than by a nucleophilic attack of the amine to the phenyl groups shielded Si atom. The different activities of the additives relating to DPSD condensation

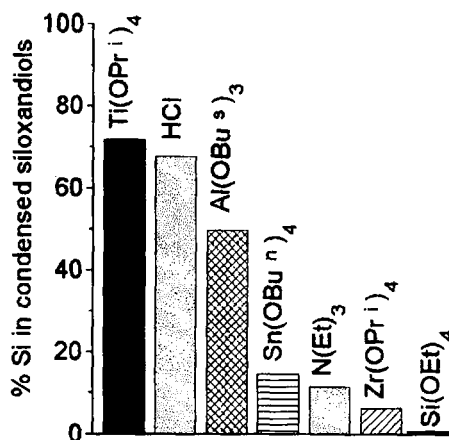


Figure 5. Amount of condensed phenylsiloxanediols in DPSD solutions doped with different metal alkoxides (Si : M = 1 : 0.01), HCl (1 : 0.04) and N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (1 : 0.04) after 25 h reaction time.

after a reaction time of 25 h are summarised in Fig. 5.

### 3.5. Examination of the Water Content

The condensation of the diphenylsilanediol is connected with the release of water, which can be partially consumed by the hydrolysis of the added metal alkoxides. The amount of water present in the metal alkoxide doped solutions should give additional information on the degree of DPSD condensation. The release of water in the course of the condensation process in Ti- and Al-alkoxide doped solutions (DPSD : M = 1 : 0.01) was followed by the Karl-Fischer-titration. An amount of 0.10% water was recorded after 0.5 h in a DPSD solution doped with Ti(OPr<sup>i</sup>)<sub>4</sub>. The water content increases to 0.83 and 1.04% after 6 and 25 h, respectively. In the Al(OBu<sup>s</sup>)<sub>3</sub> doped solution water contents of 0.21, 0.47 and 0.67% were analyzed after 0.5, 6 and 25 h reaction time. Assuming a complete condensation of all silanol groups of DPSD a total water amount of 1.76% should be present in the solution. With respect to a complete alkoxide hydrolysis of the added metal alkoxides this value could be reduced to 1.69% for Ti-alkoxide and 1.71% for the Al-alkoxide doped solution. From the measured water content and the theoretical value an averaged condensation degree was calculated to 6%, 49% and 62% in the Ti-alkoxide doped solution and of 12, 27 and 39% in the Al-alkoxide doped solution after 0.5, 6 and 25 h reaction time, respectively. Except for the short time value this result confirms the difference

in the condensation degree of Ti- (mainly tetrameric siloxanes) and Al-alkoxide (mainly dimeric siloxanes) doped solution as proven by <sup>29</sup>Si NMR.

Finally, the results of the water determination in condensed DPSD solutions shall be compared to the structure of the solution with the example of the DPSD/Ti(OPr<sup>i</sup>)<sub>4</sub> = 1 : 0.01 system. The released water in the solution determined by Karl-Fischer-titration amounts to 0.83% after 6 h reaction time. Calculating the released water on the basis of the condensation products identified by NMR (28% DPSD, 4% disiloxanediol, 15% trisiloxanediol and 53% tetrasiloxanediol, related to the total amount of Si) the water amounts to 0.84% which is in good agreement with the measured value by Karl-Fischer titration. Thus, the result of direct water determination supports the quantitative result of NMR spectroscopy.

#### 4. Discussion

From the results in Figs. 1 and 2 follows an increasing reaction rate of DPSD condensation with increasing Ti(OPr<sup>i</sup>)<sub>4</sub> concentration. The examination of the influence of Ti- and Zr-alkoxides with different types of alkoxide ligands on the condensation of DPSD showed no significant effect of the alkoxide ligands on the structure of the formed siloxane species and on the rate of condensation reaction (Figs. 2 and 4). From this it is concluded that the size differences of the ligands, the stability differences of the ligands towards hydrolysis and the complexity of titanium alkoxides do not on the whole effect their catalytic activity. This is surprising since smaller sized species, e.g., Ti(OPr<sup>i</sup>)<sub>4</sub> with a complexity of 1.4 [13], could lead to an easier nucleophilic attack on the Si atom surrounded by bulky phenyl groups from sterical reasons as compared to Ti(OEt)<sub>4</sub> and Ti(OBu<sup>n</sup>)<sub>4</sub> with complexities of 2.4 and 3.0 [13, 21]. Therefore, it is probable that only non-associated monomeric species are present in the solution due to the low concentration of the metal alkoxides. A possible effect of the different alkoxide groups attached on monomeric titanium species could be lost in the course of the reaction because of their hydrolysis by water derived from DPSD condensation.

The NMR results show a remarkable dependence of the condensation reaction of DPSD on the type of metal in the alkoxide (Figs. 3 and 4). All DPSD solutions doped with different Ti-alkoxides in identical molar ratio Si/M = 1 : 0.01 show a higher rate of condensation than solutions with Al-, Zr-, Sn- and Si-alkoxide

additives (Figs. 2 and 4). The acid catalysed DPSD solutions show a condensation rate comparable with corresponding Ti-alkoxide doped solutions (Fig. 5).

Furthermore, it follows from the spectra in Fig. 3 that the distribution of the condensed species in Ti- and Al-doped solutions is very much different. The ratio of condensed dimeric and tetrameric siloxanediols in the Ti-alkoxide doped solution after 6 h is nearly 1:8 but in the Al-alkoxide doped ones the dimeric species is the only condensation product. Such preferred formation of tetraphenyldisiloxanediol was also found in HCl catalyzed DPSD solutions (Fig. 3). The results show that the different metal alkoxides not only influence the rate of condensation but also the structure of condensation products and their distribution. The catalysis by Ti-alkoxides is the only one which leads under the used conditions to condensation products with the highest condensation degree (tetrameric species). The abrupt ending of condensation reactions in Ti-alkoxide catalyzed DPSD solutions at tetrameric species could be explained by the low solubility of the octaphenyltetrasiloxanediol in dioxane which results in its precipitation connected with a steady shift of the equilibrium in favour of new tetrameric species. In solution with Al-alkoxide, disiloxanediol appears as main component. Up to now no satisfactory explanation can be given for the break in condensation reaction of DPSD at disiloxanediol in the presence of catalytic amounts of Al-alkoxides. The preferred forming of tetraphenyldisiloxanediol in Al-alkoxide doped DPSD solutions can be used for the synthesis of the pure dimeric compound (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>Si<sub>2</sub>O<sub>3</sub>H<sub>2</sub>.

The reasons for the significant differences in the catalytic activity of the metal alkoxides should be looked for in the electronegativities of the metals leading to different polar Si—O—M bonds as intermediates, the hydrolytic stability of heterometal bonds, the coordination of the metal atoms by oxygen and the size and complexity of metal alkoxides.

Differences in the complexity of metal alkoxides, the coordination of the metal and the effect of solvents are known [5, 13]. According to the literature [13] the used metal alkoxides have the following complexities: Ti(OPr<sup>i</sup>)<sub>4</sub> = 1.4, Al(OBu<sup>n</sup>)<sub>3</sub> = 2.4 and Zr(OBu<sup>n</sup>)<sub>4</sub> = 3.4. Assuming that the complexity remains unchanged against degradation in the strongly diluted solutions there could be seen a relation between the size and complexity of the metal alkoxides and the rate of the condensation reaction. Following this assumption the Zr(OBu<sup>n</sup>)<sub>4</sub> complex as largest molecule

is not able to come into sufficient contact with the DPSD within 25 h probably due to the steric hindrance of the phenyl groups. The smaller  $\text{Al}(\text{O}i\text{Bu})_3$  complex should have a better contact to the DPSD molecule than the Zr-alkoxide, but a worse one than the Ti-alkoxide. However, there could arise objections to this hypothesis due to the above discussed degradation of Ti-alkoxide complexes and the insufficient knowledge of the complexity and structure of metal alkoxides in diluted polar solution [21–23].

A further point of discussion is the hydrolytic stability of the heterometallic Si—O—M bonds as intermediate of the DPSD condensation reaction. In general, the heterometallic Si—O—M bond is more polar than the Si—O—Si bond with respect to the different electronegativities of the metals. A higher polarity of the bonds induces an easier nucleophilic attack of water or silanol groups of DPSD. From this point of view the absence of a catalytic effect of  $\text{Si}(\text{OEt})_4$  doped solutions can be explained due to the relatively low polarity of the Si—O—Si bonds and their high hydrolytic stability.

From NMR experiments [20] in the system dimethyldimethoxysilane- $\text{Ti}(\text{OR})_4/\text{Zr}(\text{OR})_4$  a lower hydrolytic stability of Si—O—Ti bonds results compared to Si—O—Zr bonds. Therefore, the Zr—O group should be a weaker leaving group from the siloxane than the Ti—O group. The easier hydrolytic cleavage of Si—O—Ti bonds should lead to a faster reaction of Ti-species with new DPSD molecules forming condensed siloxanes releasing Ti-species for further catalytic activity. Accordingly, in the case of the Zr-alkoxides the stronger Zr—O—Si bond leads to a lower rate of DPSD condensation as proved by the experiments.

## 5. Conclusion

The results show that the rate of silanol condensation is more influenced by the type of metal alkoxide and less by the type of alkoxide ligands. Different types of metal alkoxides influence not only the rate of DPSD condensation but also the structure of condensation products. Ti-alkoxide catalysis only leads to the highest condensation rate and to the highest condensed (tetrameric) species. The condensation reaction of Al-alkoxide doped DPSD solution is restricted to dimeric species which can be used for the synthesis of tetraphenyl-disiloxanediol. The different condensation degree of siloxane species induced by Ti- and Al-alkoxide catalysis, and also HCl, influences the structure and consequently the properties of the reaction products

and should have a significance also for condensation reaction of multifunctional alkoxy silanes.

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