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Investigations on the mobility of novel sol–gel processed inorganic–organic hybrid materials†

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Novel co-condensing agents of the type R′Si(OMe)$_2$(CH$_2$)$_3$R$_2$Si(CH$_2$)$_3$Si(OMe)$_2$R′ {**3[Me$_2$Si(C$_3$D^0)$_2$]** (**3a**), R = Me, R′ = Me; **3[Me$_2$Si(C$_3$T^0)$_2$]** (**3b**), R = Me, R′ = OMe; **4[Et$_2$Si(C$_3$D^0)$_2$]** (**4a**), R = Et, R′ = Me; **4[Et$_2$Si(C$_3$T^0)$_2$]** (**4b**), R = Et, R′ = OMe} were synthesised by hydrosilylation of the corresponding diallyldialkylsilanes **1**, **2** with dichloro(methyl)silane and trichlorosilane, respectively, followed by treatment with trimethyl orthoformate. These precursors were sol–gel processed with or without PhSi(OMe)$_3$ [**Ph(T^0)**] to give the xerogels **X3a**–**d**, **X4a**–**d**. The polysiloxane matrices, the degree of condensation and the integrity of the hydrocarbon backbone were investigated by means of solid state NMR spectroscopy (^{13}C, ^{29}Si). To study the polymer dynamics in the dry state ^{29}Si CP/MAS NMR measurements of relaxation times ($T_{1\rho H}$) and cross-polarisation parameters (T_{SiH}) were carried out. ^{1}H HR/MAS NMR experiments and $T_{1\rho H}$ measurements in different solvents were undertaken to get information on the mobility of the polymers in suspension. Scanning electron microscopy (SEM) images show the morphology of the polymers and energy dispersive X-ray spectroscopy (EDX) suggests that the distribution of the elements agrees with the applied stoichiometry.

Introduction

In recent years polymer-supported catalysts have evolved into an area of intensive research with the goal of combining the advantages of homogeneous and heterogeneous catalysis.[2–4] But the anchoring of reactive centres in inorganic or organic polymers entails several important disadvantages, such as high metal loss ('leaching') or inhomogeneity of the reactive centres.[5] As an efficient alternative for the reduction or even elimination of these handicaps 'Chemistry in Interphases' was recently introduced.[3] Interphases are systems in which a stationary phase and a mobile component penetrate each other on a molecular scale. An ideal interphase, which is provided with a swellable polymer, affords a solution-like state. Therefore, interphases are able to imitate homogeneous conditions, because the active centres become highly mobile, simulating the properties of a solution, and accessible to substrates.[6–9]

For the generation of stationary phases several T-functionalised silanes of the type Fn–Si(OR)$_3$ were sol–gel processed with or without co-condensation agents.[10–15] The functional group Fn generally represents either a ligand or a metal complex. These reactive centres are distributed across the entire carrier matrix. The co-condensing agents play an important role in controlling the density and the distance of the reactive centres.[4,11,16,17] Frequently applied co-condensing agents are alkoxysilanes such as Si(OEt)$_4$ (**Q^0**), MeSi(OMe)$_3$ (**T^0**) and Me$_2$Si(OMe)$_2$ (**D^0**).[18–20] D-groups show high mobility in interphases but they have the disadvantage of being washed out during the sol–gel process. By way of contrast, Q-groups cannot be washed out, but they lack the necessary mobility. By the development of D-bifunctionlised organosilanes **D^0-C$_z$-D^0** [MeSi(OMe)$_2$(CH$_2$)$_z$(MeO)$_2$SiMe, $z = 6$, 8, 14][21] and **Ph(1,4-C$_z$D^0)$_2$** (MeSi(OMe)$_2$(CH$_2$)$_z$(C$_6$H$_4$)(CH$_2$)$_z$(MeO)$_2$SiMe, $z = 3$, 4)[22] the advantages of Q- and D-groups could be successfully combined. They are not washed out during the sol–gel process and the reactive centres show a high mobility. If **D^0-C$_z$-D^0** materials are used as co-condensing agents, the mobility of the carrier matrix and the reactive centres is induced by the high flexibility of the alkyl chain. Due to the steric demand of the phenyl ring the degree of condensation in the case of **Ph(1,4-C$_z$D^0)$_2$** is somewhat lower (~80%), which means a higher mobility of the materials.[23]

In this work it was our objective to investigate novel D- and T-functionalised co-condensing agents. Through the sol–gel process they combine a highly mobile alkyl chain with a low degree of condensation induced by the steric demand of the silicon-attached substituents. In this way, enhancement of the mobility of these materials was achieved.

Results and discussion

Preparation of the monomeric precursors

The precursors for the sol–gel process, the bis{[dimethoxy(methyl)silyl]propyl}dialkylsilanes **3a** and **4a** and the bis[(trimethoxysilyl)propyl]dialkylsilanes **3b** and **4b** were prepared by hydrosilylation of the corresponding diallyldialkylsilanes **1** and **2** with dichloro(methyl)silane and trichlorosilane respectively, followed by the replacement of the chlorine atoms by methoxy groups with trimethyl orthoformate[24] (Scheme 1). After distillation under vacuum **3a**, **b** and **4a**, **b** were obtained as colourless, analytically pure liquids, which are sensitive to moisture and soluble in common organic solvents. All of the monomers were characterised by ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectroscopy and by mass spectrometry.

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†Supported organometallic complexes, Part 24. Part 23: ref. 1.

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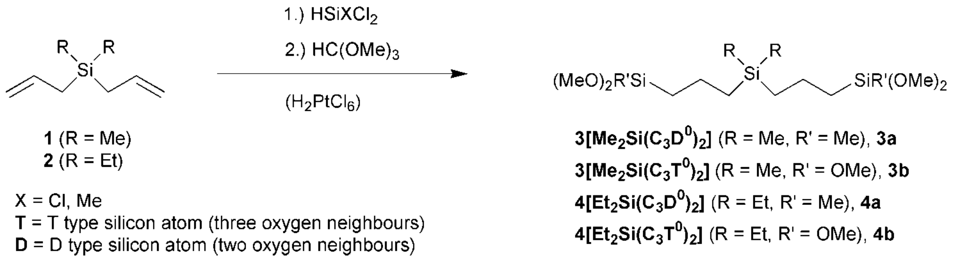


Scheme 1 Synthesis of the monomeric precursors.

Sol–gel processing of 3a, b and 4a, b

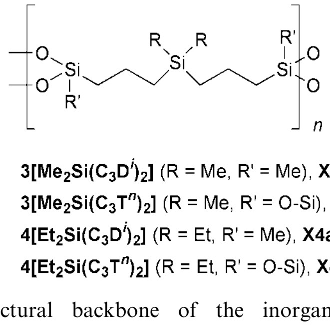
The properties of sol–gel processed materials strongly depend on the reaction conditions, such as concentration of the monomers, type of solvent and kind of catalyst.[11] To ensure comparable results, uniform reaction conditions throughout hydrolysis and the sol–gel transition must be maintained. To be able to compare the results with previous investigations $(n\text{-Bu})_2Sn(OAc)_2$[21,22] and a mixture of THF and methanol were employed as catalyst and solvent, respectively. According to these boundary conditions, two types of polysiloxanes were obtained (Scheme 2). The xerogels **X3a**, **b**, **X4a**, **b** and **X3c**, **d**, **X4c**, **d** were prepared without and with the co-condensation agent phenyl(trimethoxy)silane [**Ph(T^0)**], which was condensed into the matrix (Table 1). In this way it can be investigated whether domains are formed during the sol–gel process or whether one component of the co-polycondensates is washed out in the solvent processing (Scheme 3).

Solid state NMR spectroscopic investigations

Due to the amorphous nature of these inorganic–organic hybrid materials, solid state NMR spectroscopy is the most useful method to investigate the structure and the dynamic behaviour of such copolymers.[25–27] ^{29}Si NMR spectroscopy enables characterisation of the polymeric matrix, the degree of condensation and the stoichiometric composition of the copolymers.

All silicon atoms in the polysiloxane matrix are in direct proximity of protons, thus all silyl species are detectable *via* cross-polarisation techniques.[26,28] The ^{29}Si CP/MAS spectra of selected polymers are depicted in Fig. 1. The ^{29}Si signals of these copolymers are in the typical range for R_2Si (R = Me, Et), D-, T- and T_{Ph}-silyl functions and their substructures D^0–D^2, T^0–T^3 and $T^1{}_{Ph}$–$T^3{}_{Ph}$, which indicates an incomplete condensation. Average chemical shifts are Et_2Si, 4.8; Me_2Si, 1.4; D^0, −2.4; D^1, −12.4; D^2, −22.2; T^0, −42.4; T^1, −50.6; T^2, −59.3; T^3, −68.3; $T^1{}_{Ph}$, −62.8; $T^2{}_{Ph}$, −71.4; $T^3{}_{Ph}$, −79.8. D^0- and T^0-species, which are attached to the polymeric matrix *via* the second silyl function, cannot be removed during solvent processing.

The degree of condensation of the D-, T- and T_{Ph}-species and the real ratios of $T_{Ph} : D$ and $T_{Ph} : T$ (Table 2) were determined by generally known methods.[21,29,30] The degrees of condensation range between 70 and 96% for the D-functions and 52 and 70% for the T-groups. The T_{Ph}-species show a degree of condensation between 68 and 93%. These values are lower than the degrees of condensation that were determined in the case of the bifunctionalised silanes $(MeO)_2MeSi(CH_2)_zSiMe(OMe)_2$ (**D^0-C_z-D^0**, $z = 6$, 8, 14; >92%),[21] $(MeO)_2MeSi(CH_2)_z(C_6H_4)(CH_2)_zSiMe(OMe)_2$ (**Ph(1,4-C_zD^0)$_2$**, $z = 3$, 4; >77%) and $(MeO)_3Si(CH_2)_3(C_6H_4)(CH_2)_3Si(OMe)_3$ (**Ph(1,4-C_3T^0)$_2$**, >67%).[22] The steric demand of the internal organosilicon function influences the kinetics and seems to be responsible for the rather low degree of condensation. The experimentally determined composition of the T_{Ph}/D- and T_{Ph}/T-polymers do not differ significantly from the applied compositions. None of the D-, T- or T_{Ph}-functions were washed out during the solvent processing. Thus, the monomeric co-condensing agents **3a**, **b** and **4a**, **b** are useful precursors to generate carrier matrices for 'Chemistry in Interphases'.



Scheme 2 Structural backbone of the inorganic–organic hybrid materials.

The ^{13}C CP/MAS NMR spectra of the pure D-polymers show a small peak at 49.6 ppm for the non-hydrolysed Si–OMe functions and for the pure T-polymers a relative high intense peak, indicating a high and a rather low degree of hydrolysis, respectively.

Studies on the dynamic behaviour of the polysiloxanes by solid state and suspension state NMR spectroscopy

To optimise the stationary component for use in interphase chemistry, it is necessary to get detailed information on the dynamic properties of the materials.

The values of the spin–lattice relaxation time of the protons in the rotating frame ($T_{1\rho H}$) were determined *via* a ^{29}Si direct spin lock–τ–CP experiment.[31] The observed decays of the magnetisation were monoexponential in each of the samples. Thus, the relaxation mechanism is spin-diffusion controlled and the occurrence of domains within 1–2 nm is excluded. Therefore, the materials are considered as homogeneous. In the solid state none of the polymers differ significantly in their relaxation time $T_{1\rho H}$ and cross-polarisation parameter T_{SiH} (Table 3). An unambiguous discussion of the dynamic properties of materials based on relaxation parameters ($T_{1\rho H}$) is only possible if the corresponding correlation time τ_c is known. The dependence of $T_{1\rho H}$ on the correlation time τ_c is given by the correlation time curve.[25] For measurements of temperature dependent relaxation times two cases have to be distinguished. In the slow-motion regime the increasing temperature correlates with decreasing relaxation times (shorter τ_c), whereas in the fast-motion regime $T_{1\rho H}$ values increase with increasing temperature. With rising temperature for all samples, except for **X3a**, **X4a** and **X4c**, the increasing $T_{1\rho H}$ values indicate that the polymers are in the fast-motion regime of the correlation time curve. This high mobility is due to the rather low degree of condensation (Table 2). The polymers **X3a**, **X4a** and **X4c** do not show a constant trend of the $T_{1\rho H}$ values with an increase of temperature. This fact indicates that these materials are in a broad minimum of the correlation time curve, and therefore no precise prediction on the mobility can be made (Table 4).[25]

For 'Chemistry in Interphases' it is necessary to study the mobility and dynamics of the materials in the suspension state. Therefore ^{1}H high resolution magic angle spinning (^{1}H HR/

Table 1 Sol–gel processes and labeling of the xerogels.

Monomeric silanes	Co-condensation agent	Polysiloxanes	Xerogels
$3[Me_2Si(C_3D^0)_2]$, **3a**		$3[Me_2Si(C_3D^i)_2]$	**X3a**
$3[Me_2Si(C_3T^0)_2]$, **3b**		$3[Me_2Si(C_3T^n)_2]$	**X3b**
$4[Et_2Si(C_3D^0)_2]$, **4a**		$4[Et_2Si(C_3D^i)_2]$	**X4a**
$4[Et_2Si(C_3T^0)_2]$, **4b**		$4[Et_2Si(C_3T^n)_2]$	**X4b**
$3[Me_2Si(C_3D^0)_2]$, **3a**	$Ph(T^0)$[a]	$3[Me_2Si(C_3D^i)_2]_x[Ph(T^n)]_y$	**X3c**
$3[Me_2Si(C_3T^0)_2]$, **3b**	$Ph(T^0)$	$3[Me_2Si(C_3T^n)_2]_x[Ph(T^n)]_y$	**X3d**
$4[Et_2Si(C_3D^0)_2]$, **4a**	$Ph(T^0)$	$4[Et_2Si(C_3D^i)_2]_x[Ph(T^n)]_y$	**X4c**
$4[Et_2Si(C_3T^0)_2]$, **4b**	$Ph(T^0)$	$4[Et_2Si(C_3T^n)_2]_x[Ph(T^n)]_y$	**X4d**

[a] $T^0 = Si(OMe)_3$.

MAS) experiments and $T_{1\rho H}$ measurements of suspensions of all polymers in different solvents (methanol, tetrahydrofuran and chloroform) were carried out (Tables 5 and 6). Representative ^1H HR/MAS NMR spectra of **X3c** are depicted in Fig. 2 and compared with a ^1H MAS spectrum without any solvent. If solvents of medium polarity ($CDCl_3$ and THF-d_8) are used, nearly all the signals of the aliphatic and aromatic protons are resolved, in contrast to those of the spectra obtained in methanol. In the ^1H MAS spectrum of the dry xerogel only one sharp signal is visible, which is assigned to the

Idealised polycondensation of the D-polymers:

$$R_2Si[(CH_2)_3(MeO)_2SiMe]_2 \xrightarrow[-\ 4\ MeOH]{+\ 2\ H_2O} R_2Si[(CH_2)_3O_{2/2}SiMe]_2$$

$\mathbf{3,4[R_2Si(C_3D^0)_2]}$ (**3a**, **4a**) $\qquad$ $\mathbf{3,4[R_2Si(C_3D^2)_2]}$

Realistic composition of the D-polymers: $R_2Si[(CH_2)_3(OX)_{2\text{-}i}O_{i/2}SiMe]_2$

$\mathbf{3,4[R_2Si(C_3D^i)_2]}$ (**X3a**, **X4a**)

Idealised polycondensation of T-polymers:

$$R_2Si[(CH_2)_3Si(MeO)_3]_2 \xrightarrow[-\ 6\ MeOH]{+\ 3\ H_2O} R_2Si[(CH_2)_3SiO_{3/2}]_2$$

$\mathbf{3,4[R_2Si(C_3T^0)_2]}$ (**3b**, **4b**) $\qquad$ $\mathbf{3,4[R_2Si(C_3T^3)_2]}$

Realistic composition of the T-polymers: $R_2Si[(CH_2)_3(OX)_{3\text{-}n}SiO_{n/2}]_2$

$\mathbf{3,4[R_2Si(C_3T^n)_2]}$ (**X3b**, **X4b**)

Idealised polycondensation of the D/T-polymers:

$$x\ R_2Si[(CH_2)_3(MeO)_2SiMe]_2 + y\ PhSi(OMe)_3 \xrightarrow[-\ (4x\ +\ 3y)\ MeOH]{+\ (2x\ +\ 3/2y)\ H_2O} \{R_2Si[(CH_2)_3O_{2/2}SiMe]_2\}_x[PhSiO_{3/2}]_y$$

$\mathbf{3,4[R_2Si(C_3D^0)_2]}$ (**3a**, **4a**) $\quad$ $\mathbf{Ph(T^0)}$ $\qquad$ $\mathbf{3,4[R_2Si(C_3D^2)_2]_x[Ph(T^3)]_y}$

Realistic composition of the D/T-polymers: $\{R_2Si[(CH_2)_3(OX)_{2\text{-}i}O_{i/2}SiMe]_2\}_x[PhSiO_{n/2}(OX)_{n\text{-}3}]_y$

$\mathbf{3,4[R_2Si(C_3D^i)_2]_x[Ph(T^n)]_y}$ (**X3c**, **X4c**)

Idealised polycondensation of T/T-polymers:

$$x\ R_2Si[(CH_2)_3Si(MeO)_3]_2 + y\ PhSi(OMe)_3 \xrightarrow[-\ (6x\ +\ 3y)\ MeOH]{+\ (3x\ +\ 3/2y)\ H_2O} \{R_2Si[(CH_2)_3SiO_{3/2}]_2\}_x[PhSiO_{3/2}]_y$$

$\mathbf{3,4[R_2Si(C_3T^0)_2]}$ (**3b**, **4b**) $\quad$ $\mathbf{Ph(T^0)}$ $\qquad$ $\mathbf{3,4[R_2Si(C_3T^3)_2]_x[Ph(T^3)]_y}$

Realistic composition of the T/T-polymers: $\{R_2Si[(CH_2)_3(OX)_{3\text{-}n}SiO_{n/2}]_2\}_x[PhSiO_{n/2}(OX)_{n\text{-}3}]_y$

$\mathbf{3,4[R_2Si(C_3T^n)_2]_x[Ph(T^n)]_y}$ (**X3d**, **X4d**)

R = Me, Et
T = T type of silicon atom (three oxygen neighbours)
D = D type of silicon atom (two oxygen neighbours)
i, *n* = numbers of Si-O-Si bonds (*i* = 0-2; *n* = 0-3)
X = H, Me

Scheme 3 Idealised and realistic compositions of the sol–gel materials.

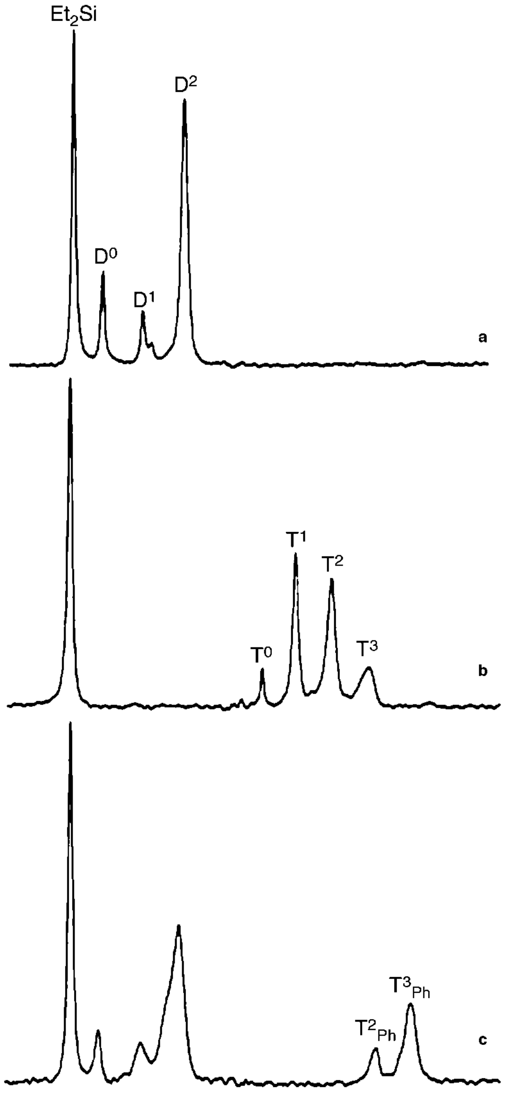


Fig. 1 ^{29}Si CP/MAS NMR spectra of selected xerogels: (a) **X4a**, (b) **X4b**, (c) **X4c**.

protons of the mobile $SiCH_3$ groups. All other peaks cannot be resolved.

$T_{1\rho H}$ values determined *via* a ^{1}H spin lock–SPE experiment in suspension[22] increase by an order of magnitude unless MeOH is used as a solvent. In solvents of medium polarity all of the investigated xerogels form highly mobile interphases and their relaxation times $T_{1\rho H}$ are located on the fast-motion regime of the correlation time curve.[22] In suspension spin diffusion no longer plays the dominant role in the relaxation processes. The different proton sites relax at varying rates. By these measurements it can be corroborated that the non-hydrolysed methoxy protons (3.5 ppm) are the most mobile followed by the protons of the methyl (0.0 ppm) or ethyl groups (0.9 and 0.4 ppm) adjacent to the internal silicon atom. Due to the low swelling capability, determination of the $T_{1\rho H}$ values of the mentioned polymers swollen in MeOH is rather difficult.

With the exception of **X4d**, pure D-polymers show the lowest $T_{1\rho H}$ values and therefore the lowest mobility in suspension, which can be explained by the rather high degree of condensation.

Surface area measurements, SEM images and EDX measurements

Due to the high proportions of organic content in these inorganic–organic hybrid materials the surface area measurements according to the BET method reveal very low values ($<10\ m^2\ g^{-1}$), which is in agreement with former results.[21,22]

SEM images of the polymers **X3a** and **X3b** are depicted in Fig. 3. In contrast to **X3b**, which consists of smaller particles due to the higher brittleness of T-polymers, **X3a** as a pure D-polymer is rubber-like with mainly large particles.

Fig. 4 illustrates typical EDX spectra of **X3a** and **X4b** including peak assignment. A qualitative analysis confirms the presence of carbon, oxygen and silicon. For purposes of quantification, however, the measured composition has to be compared with theoretical values calculated by excluding hydrogen, since hydrogen is a single electron atom and thus does not emit characteristic X-rays. Due to uncertainties in the fundamental parameters at low X-ray energies and in the spectrometer calibration correct quantification of light elements is a principal problem of EDX. Although errors of up to 5% have to be taken into account, oxygen and silicon can be detected and quantified directly, which is not possible with chemical elemental analysis. In Table 7 the quantification results of the EDX measurements are summarised and compared to reference data from NMR measurements.

Conclusion

A new type of polysiloxanes with tunable T : T- and T : D-ratios were synthesised by sol–gel processing of the novel monomeric precursors $R'Si(OMe)_2(CH_2)_3R_2Si(CH)_3Si(OMe)_2R'$ (R = Me, Et; R′ = Me, OMe) (**3a**, **b**; **4a**, **b**). Since they combine the advantages of a mobile alkyl chain with a lower degree of condensation, which is induced by the steric demand of the internal organosilicon function, the mentioned precursors are suitable to form highly mobile carrier matrices for ‘Chemistry in Interphases’. As a result of the $T_{1\rho H}$ measurements in the solid state the formation of domains is excluded, which means that the materials are homogeneous. ^{1}H HR/MAS NMR spectroscopy and $T_{1\rho H}$ measurements in suspension furnish

Table 2 Relative I_0 data, degree of condensation, degree of hydrolysis of the silyl species in the copolymers

	Relative I_0 data of D-, T- and T_{Ph}-species[a]										Degree of condensation (%)				
Xerogel	D^0	D^1	D^2	T^0	T^1	T^2	T^3	T^1_{Ph}	T^2_{Ph}	T^3_{Ph}	D	T	T_{Ph}	Real T_{Ph} : D- and T_{Ph} : T-moiety	Degree of hydrolysis (%)[b]
X3a	[c]	7.7	100								96				97
X3b				13.4	100	95.9	24.5					52			80
X4a	22.5	18.2	100								78				89
X4b				13.9	90.3	100	43.8					57			70
X3c	9.6	100	88.2					3.5	40.7	43.6	70		82	1 : 2.2	92
X3d				7.0	77.2	100	51.3	24.5	46.4	28.6		61	68	1 : 2.4	72
X4c	14.6	26.6	100					[c]	14.3	56.3	80		93	1 : 2.0	92
X4d				2.8	48.5	100	81.1	23.7	40.0	61.9		70	77	1 : 1.9	83

[a] Determination *via* ^{29}Si SPE/MAS experiment. [b] For the determination of the degree of hydrolysis, see ref. 22. [c] Species not detectable.

Table 3 T_{SiH} and $T_{1\rho H}$ data of the silyl species in the copolymers

Xerogel	T_{SiH}/ms^{a} R$_2$Si^{d}	D^0	D^1	D^2	T^0	T^1	T^2	T^3	T$^1_{Ph}$	T$^2_{Ph}$	T$^3_{Ph}$	$T_{1\rho H}$/ms^{b}	$T_{1\rho H}$/ms^{c}
X3a	0.9	^{e}	^{f}	2.0								5.1	2.5
X3b	0.9				^{f}	2.0	1.0	1.0				44.9	2.4
X4a	0.8	2.0	1.1	0.7								9.1	2.1
X4b	1.4				^{f}	2.1	1.8	1.5				4.8	1.6
X3c	1.4	^{e}	1.9	0.8					^{f}	0.8	1.0	29.3	1.9
X3d	0.9				^{f}	1.3	1.0	1.0	0.6	0.9	^{e}	38.8	2.1
X4c	1.2	1.8	1.0	1.1					^{e}	2.3	1.7	4.2	2.5
X4d	0.9				1.0	1.4	1.2	1.3	1.1	1.5	2.5	8.0	2.3

[a] Determination at 300 K *via* contact time variation. [b] Determination *via* contact time variation (values are significantly too high, since the relaxation of the protons takes place during the contact time). [c] Determination at 300 K *via* ^{29}Si according to ref. 31. [d] R = Me, Et. [e] Species not detectable. [f] Intensity too low for precise determination.

Table 4 Temperature dependence of the $T_{1\rho H}$

Xerogel	$T_{1\rho H}$/ms^{a} 300 K	310 K	320 K	330 K
X3a	2.5	2.0	2.5	1.0
X3b	2.4	3.3	6.2	6.8
X4a	2.1	1.2	2.6	1.0
X4b	1.6	3.5	6.4	^{b}
X3c	1.9	4.4	5.6	^{b}
X3d	2.1	1.2	4.1	4.3
X4c	2.5	3.3	1.5	2.7
X4d	2.3	4.1	6.0	6.7

[a] Determination *via* ^{29}Si according to ref. 31. [b] Not determined.

evidence that the xerogels form highly mobile interphases if solvents of medium polarity like chloroform or tetrahydrofuran are used. Due to a lower degree of condensation the polymers with T-silyl functions seem to be more mobile in the solid and in suspension than the pure D-polymers. Despite low degrees of condensation the cross-linking in these novel inorganic–organic hybrid materials is sufficient to resist even a partial decomposition during sol–gel processing. These properties afford the precondition that the leaching of catalytically active transition metal complexes is reduced in 'Chemistry in Interphases'.

Experimental

Materials and instrumentation

Elemental analyses were carried out on a Vario EL (Elementar Analytische Systeme Hanau) Model 1106. IR data were obtained on a Bruker IFS 48 FT-IR spectrometer. Solution nuclear magnetic resonance spectra were recorded on a Bruker DRX 250 spectrometer (field strength 5.87 T) at 296 K. Frequencies are as follows: ^{1}H NMR: 250.13 MHz; ^{13}C{^{1}H} NMR: 62.90 MHz; ^{29}Si{^{1}H} NMR: 49.69 MHz. Chemical shifts in the ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra were measured relative to partially deuterated solvent peaks, which are reported relative to TMS. Mass spectra (EI) were acquired on a TSQ Finnigan (70 eV, 473 K) and reported as mass/charge (*m*/*z*).

CP/MAS solid state NMR spectra were recorded on a Bruker DSX 200 multinuclear spectrometer equipped with a wide bore magnet (field strengths of 4.7 T). Magic angle spinning was applied up to 10 kHz (4 mm ZrO$_2$ rotors) and 3–4 kHz (7 mm ZrO$_2$ rotors). Frequencies, standards and acquisition parameters: ^{13}C, 50.288 MHz (4.7 T), [TMS, carbonyl resonance of glycine ($\delta = 176.0$) as secondary standard], 90° proton pulse length 3.8 µs (B_1 field 65 kHz), contact time T_c 1 ms, recycle delay 2 s, spectral width 15 kHz, 2 K data points in the time domain; ^{29}Si, 39.73 MHz (4.7 T), (Q$_8$M$_8$, secondary reference), 90° proton pulse length 3.8 µs (B_1 field 65 kHz), contact time T_c 1 ms, recycle delay 2 s, spectral width 8 kHz, 2 K data points in the time domain. The cross-polarisation parameters T_{SiH} were determined by variations of the contact time T_c (14–16 experiments). The proton relaxation times in the rotating frame were measured by direct proton spin lock–τ–CP experiments[31] *via* ^{29}Si [90° proton pulse length 3.8 µs (B_1 field 65 kHz), contact time T_c 1 ms, recycle delay 2 s, spectral width 8 kHz, 2 K data points in the time domain]. The relaxation parameters were obtained using the Bruker software SIMFIT and WINFIT following the procedure given in ref. 21. In this reference the quantification of the ^{13}C and ^{29}Si species is also described. The ^{1}H HR/MAS suspension state NMR spectra were recorded at 300 K on a Bruker ASX 300 spectrometer equipped with a wide bore magnet (field strength 7.05 T, proton resonance frequency 300.13 MHz). Acquisition parameters: 90° proton pulse length 3.5 µs (B_1 field 70 kHz), recycle delay 3 s, spectral width 50 kHz, 16 K data points in the time domain. The chemical shifts were referenced with respect to TMS. The $T_{1\rho H}$ values in suspension were determined by a spin lock–SPE experiment by ^{1}H[22] [90° proton pulse length 3.5 µs (B_1 field 70 kHz), recycle delay 3 s, spectral width 50 kHz, 16 K data points in the time domain]. The polysiloxanes were allowed to swell in solvents at least for one hour in 4 mm rotors with inserts. In all cases the rotation frequency was 4 kHz. Samples were employed in amounts of 20 mg.

The surface areas were determined by analysing the N$_2$ adsorption isotherms according to the BET method using a Micromeritics Gemini II. Scanning electron micrographs and energy dispersive X-ray analysis (EDX) were performed on a Philips XL 30 scanning electron microscope (SEM) equipped with a DX-4 X-ray detection system by EDAX. This consists of an energy dispersive Si(Li)-detector with an active area of 10 mm^2 and the eDX software package. The primary beam energy was set to 20 keV for all measurements. Micrographs were recorded detecting secondary electrons generated by a probe current of approximately 50 pA, whereas a 575 pA probe

Table 5 $T_{1\rho H}$ data for suspension of the polymers **X3a**, **X3b**, **X3c** and **X3d**^{a}

	$T_{1\rho H}$/ms **X3a**			**X3b**			**X3c**			**X3d**		
δ (^{1}H, ppm)	CDCl$_3$	THF	MeOH	CDCl$_3$	THF	MeOH	CDCl$_3$	THF	MeOH	CDCl$_3$	THF	MeOH
0.0	38.2	23.6	2.7	55.9	48.4	7.8	68.9	62.4	9.2	55.0	46.3	12.1
0.6	28.7	21.2		28.7	47.1	6.6	58.7	56.0	5.6	46.2	38.0	
1.5	31.9	29.2		54.0	55.7	6.2	63.3	63.4	5.5	52.6	38.0	
3.5	38.1	36.6	4.3	71.8	70.3	14.3	86.8	84.8	16.2	66.9	49.6	9.0
7.1							66.2	60.5	7.8	64.4	50.6	7.2
7.4							67.4	57.1	7.7	58.1	46.1	7.2

[a] Determination at 300 K *via* ^{1}H according to ref. 22

Table 6 $T_{1\rho H}$ data in suspension of the polymers **X4a**, **X4b**, **X4c** and **X4d**[a]

	$T_{1\rho H}$/ms											
	X4a			**X4b**			**X4c**			**X4d**		
δ (^{1}H, ppm)	$CDCl_3$	THF	MeOH	$CDCl_3$	THF	MeOH	$CDCl_3$	THF	MeOH	$CDCl_3$	THF	MeOH
0.0	28.6	22.8	7.6				37.1	33.7				
0.4				36.4	22.8					41.0	18.4	
0.7	26.1	19.6		36.4	22.9	6.0		23.6	5.5	26.0	18.4	7.1
0.9	26.1	19.7	5.7	36.4	22.8		25.5					
1.5	22.6	23.8		36.4	22.3					18.9	19.7	7.1
3.5	42.4	31.1	12.3	45.9	29.3	13.3	37.7	40.0	19.7	35.0	22.8	6.6
7.1								24.1		29.7	20.8	7.5
7.4							26.9	24.1	5.4	29.7	20.8	

[a] Determination at 300 K *via* ^{1}H according to ref. 22.

current was applied for carrying out elemental analysis by EDX. Quantification of X-ray emission spectra was achieved employing the ZAF as well as the φ(ρz) correction procedure to convert X-ray intensities to elemental contents.[32] The sample powder was placed on a specimen stub covered with a conductive adhesive tab and subsequently provided with a sputtered 20 nm gold layer to avoid specimen charging. Spectra were recorded with spot illumination of the sample for 300 seconds, yielding count rates of about 2000 s^{-1}. Spectra were acquired several times at different sample positions to ensure reproducibility. The various measurements were found to differ by about 3% which is within the limits of error, especially for light element samples with pronounced topography. For this reason, special care was taken to find specimen areas exhibiting flat surfaces to ensure the validity of the correction models. All measurements were performed at ambient temperature.

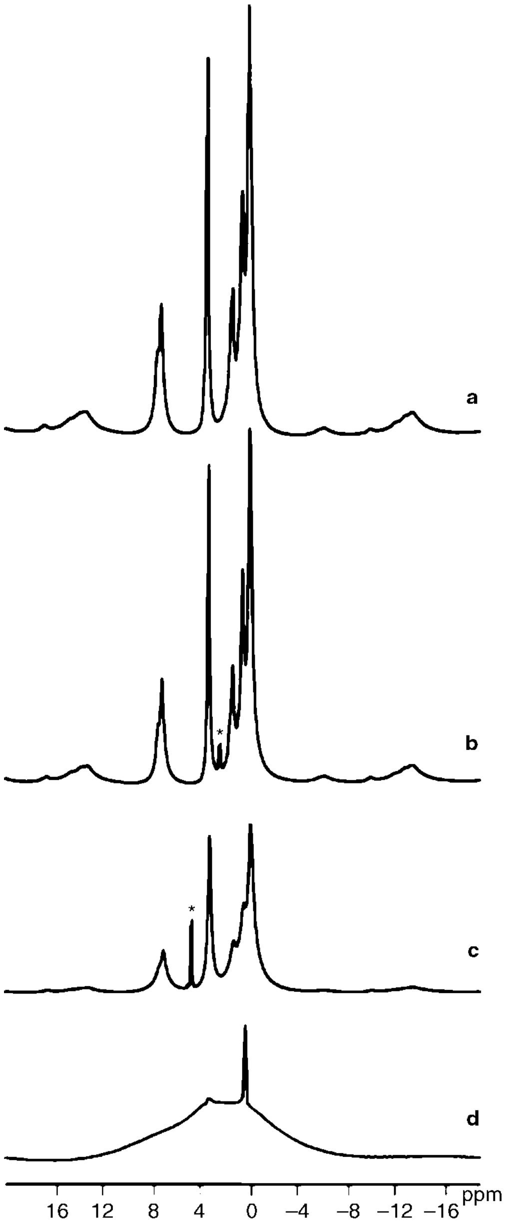


Fig. 2 ^{1}H HR/MAS NMR spectra of **X3c** (a) in $CDCl_3$, (b) in THF-d_8, (c) in MeOH-d_4, and (d) without solvent. Peak assignment: δ 7.4–7.1 (aromatic protons), δ 3.5 (MeO), δ 1.5–0.0 (aliphatic protons); peaks originating from the solvent are denoted by *.

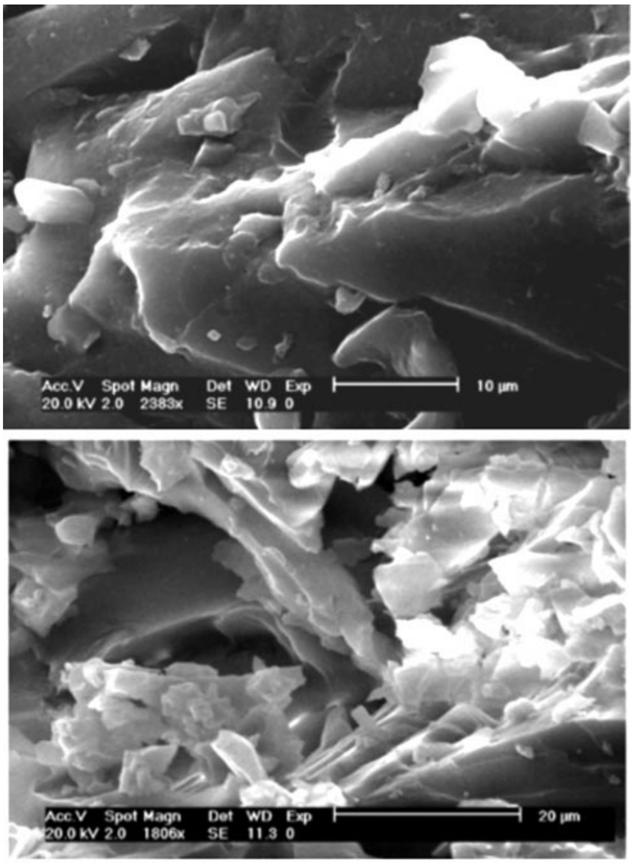


Fig. 3 SEM images of **X3a** (top) and **X3b** (bottom).

All manipulations were performed under argon by employing the usual Schlenk techniques. Methanol was dried with magnesium and distilled. All other solvents are distilled from sodium–benzophenone ketyl or from calcium hydride. $HSiMeCl_2$ and $HSiCl_3$ were used as purchased without any purification. H_2O and $(n\text{-}Bu)_2Sn(OAc)_2$ were distilled under

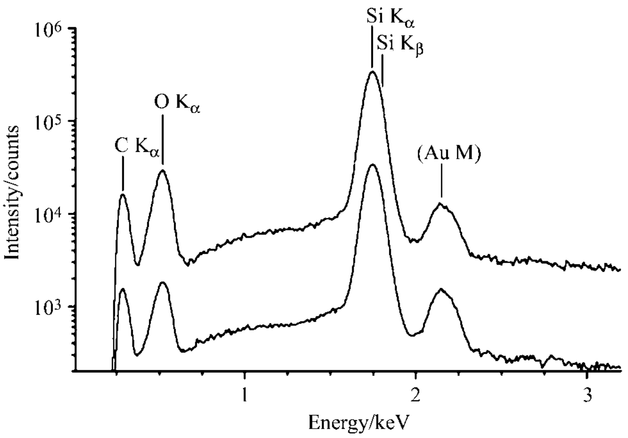


Fig. 4 EDX spectra of **X4b** (top) and **X3a** (bottom). The spectrum of **X4b** is offset by a factor of 10 for clarity. It can be seen that the oxygen content of **X4b** is significantly higher than in **X3a**.

inert gas prior to use. All solvents were stored under argon. Diallyldimethylsilane (**1**)[33] and diallyldiethylsilane (**2**)[34] were synthesised as described elsewhere. Dichloro(methyl)silane and trichlorosilane were purchased from Aldrich. Trimethyl orthoformate and phenyl(trimethoxy)silane were purchased from Fluka. All other chemicals were purchased from Merck (Germany).

Preparation of the monomeric precursors

Bis{3-[dimethoxy(methyl)silyl]propyl}dimethylsilane (3a). A mixture of diallyldimethylsilane (**1**) (6.27 g, 44.7 mmol), dichloro(methyl)silane (17.25 g, 150 mmol) and hexachloroplatinic acid (15.0 mg, 0.029 mmol) in 75 ml of THF was stirred for 2 d at room temperature. Then the solvent was removed under reduced pressure. To the remaining viscous oil trimethyl orthoformate (100 ml, 960 mmol) was added. After stirring for 4 d all volatile components were removed under reduced pressure and distillation under vacuum afforded 11.68 g (75%) of **3a**, which was obtained as a colourless, air-stable liquid sensitive to moisture, bp 110 °C (4 mbar).

^{1}H NMR (C_6D_6): δ 3.43 (s, 12H, Si-OCH$_3$), 1.49 (m, 4H, Si-CH$_2$-CH_2-CH$_2$-Si), 0.73 (t, ^3J(HH) = 7.69 Hz, 4H, (H$_3$C)$_2$Si-CH_2-CH$_2$-), 0.63 (m, 4H, H$_3$C(H$_3$CO)$_2$Si-CH_2-CH$_2$-), 0.11 (s, 6H, Si(OCH$_3$)$_2$CH_3), 0.00 (s, 6H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 49.7 (Si-OCH$_3$), 19.8 ((H$_3$C)$_2$Si-CH$_2$-), 18.1 (Si-CH$_2$-CH$_2$-CH$_2$-Si), 17.8 (H$_3$C(H$_3$CO)$_2$Si-CH$_2$-), −3.3 (Si(CH$_3$)$_2$), −5.5 (Si(OCH$_3$)$_2$CH$_3$). ^{29}Si{^{1}H} NMR (C_6D_6): δ 1.1 (Si(CH$_3$)$_2$), −2.8 (Si(OCH$_3$)$_2$CH$_3$). IR (KBr, cm^{-1}): 1258 s [ν(Si–CH$_3$)], 1190 s [ν(Si–CH$_2$–)], 1087 vs [ν(Si–OCH$_3$)]. MS (EI): m/z = 337 [M$^+$−CH$_3$], 291 [M$^+$−2CH$_3$−OCH$_3$], 205 [H$_3$C(H$_3$CO)$_2$Si(CH$_2$)$_3$Si(CH$_3$)$_2$$^+$]. Anal. calc. for $C_{14}H_{36}O_4Si_3$ (352.69): C, 47.68; H, 10.29. Found: C, 46.98; H, 10.25%.

Bis[3-(trimethoxysilyl)propyl]dimethylsilane (3b). A mixture of diallyldimethylsilane (**1**) (13.62 g, 97.0 mmol), trichlorosilane (39.5 g, 300 mmol) and hexachloroplatinic acid (15.0 mg, 0.029 mmol) in 150 ml of THF was stirred for 2 d at room temperature. Then the solvent was removed under reduced pressure. To the remaining viscous oil trimethyl orthoformate (200 ml, 1.92 mol) was added. After stirring for 4 d all the volatile components were removed under reduced pressure and distillation under vacuum afforded 9.98 g (27%) of **3b**, which was obtained as a colourless, air-stable liquid sensitive to moisture, bp 110 °C (3 mbar).

^{1}H NMR (C_6D_6): δ 3.53 (s, 18H, Si-OCH$_3$), 1.54 (m, 4H, Si-CH$_2$-CH_2-CH$_2$-Si), 0.74 (t, ^3J(HH) = 7.85 Hz, 4H, (H$_3$C)$_2$Si-CH_2-CH$_2$-), 0.64 (m, 4H, (H$_3$CO)$_3$Si-CH_2-CH$_2$-), 0.00 (s, 6H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 50.5 (Si-OCH$_3$), 20.0 ((H$_3$C)$_2$Si-CH$_2$-), 18.2 (Si-CH$_2$-CH$_2$-CH$_2$-Si), 14.6 ((H$_3$CO)$_3$Si-CH$_2$-), −3.0 (Si(CH$_3$)$_2$). ^{29}Si{^{1}H} NMR (C_6D_6): δ 1.2 (Si(CH$_3$)$_2$), −42.4 (Si(OCH$_3$)$_3$). IR (KBr, cm^{-1}): 1248 s [ν(Si–CH$_3$)], 1192 s [ν(Si–CH$_2$–)], 1077 vs [ν(Si–OCH$_3$)]. MS (EI): m/z = 369 [M$^+$−CH$_3$], 307 [M$^+$−CH$_3$−2OCH$_3$], 221 [(H$_3$CO)$_3$Si(CH$_2$)$_3$Si(CH$_3$)$_2$$^+$]. Anal. calc. for $C_{14}H_{36}O_6Si_3$ (384.69): C, 43.71; H, 9.43. Found: C, 43.63; H, 9.39%.

Bis{3-[dimethoxy(methyl)silyl]propyl}diethylsilane (4a). A mixture of diallyldiethylsilane (**2**) (7.69 g, 45.7 mmol), dichloro(methyl)silane (17.25 g, 150 mmol) and hexachloroplatinic acid (15.0 mg, 0.029 mmol) in 75 ml of THF was stirred for 2 d at room temperature. Then the solvent was removed under reduced pressure. To the remaining viscous oil trimethyl orthoformate (100 ml, 960 mmol) was added. After stirring for 4 d all the volatile components were removed under reduced pressure and distillation under vacuum afforded 5.26 g (54%) of **4a**, which was obtained as a colourless, air-stable liquid sensitive to moisture, bp 135 °C (4 mbar).

^{1}H NMR (C_6D_6): δ 3.30 (s, 12H, Si-OCH$_3$), 1.49 (m, 4H, Si-CH$_2$-CH_2-CH$_2$-Si), 0.93 (t, ^3J(HH) = 7.85 Hz, 6H, Si-CH$_2$-CH_3), 0.70 (t, ^3J(HH) = 8.01 Hz, 4H, (H$_5$C$_2$)$_2$Si-CH_2-CH$_2$-), 0.61 (m, 4H, H$_3$C(H$_3$CO)$_2$Si-CH_2-CH$_2$-), 0.48 (q, ^3J(HH) = 7.85 Hz, 4H, Si-CH_2-CH$_3$), 0.07 (s, 6H, Si(OCH$_3$)$_2$CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 49.9 (Si-OCH$_3$), 18.5 ((H$_5$C$_2$)$_2$ Si-CH$_2$-), 18.0 (Si-CH$_2$-CH$_2$-CH$_2$-Si), 16.5 (H$_3$C(H$_3$CO)$_2$Si-CH$_2$-), 7.8 (Si-CH$_2$-CH$_3$), 4.2 (Si-CH$_2$-CH$_3$), −5.3 (Si(OCH$_3$)$_2$CH$_3$). ^{29}Si{^{1}H} NMR (C_6D_6): δ 4.5 (Si(CH$_2$-CH$_3$)$_2$), −2.6 (Si(OCH$_3$)$_2$CH$_3$). IR (KBr, cm^{-1}): 1258 s [ν(Si–CH$_3$)], 1190 s [ν(Si–CH$_2$–)], 1089 vs [ν(Si–OCH$_3$)]. MS (EI): m/z = 351 [M$^+$−C$_2$H$_5$], 305 [M$^+$−C$_2$H$_5$−CH$_3$−OCH$_3$], 233 [H$_3$C(H$_3$CO)$_2$Si(CH$_2$)$_3$Si(C$_2$H$_5$)$_2$$^+$]. Anal. calc. for $C_{16}H_{40}O_4Si_3$ (380.74): C, 50.47; H, 10.59. Found: C, 50.40; H, 10.50%.

Table 7 EDX data of **X3a–d** and **X4a–d**

	Composition (%)[a]								
	Reference data[b]			EDX [ZAF correction][c]			EDX [φ(ρz)-correction][c]		
Xerogel	C	O	Si	C	O	Si	C	O	Si
X3a	49.2	16.4	34.4	50.0	14.9	35.1	51.1	15.9	33.0
X3b[d]	40.9	27.2	31.9	—	—	—	—	—	—
X3c	51.9	17.3	30.8	54.6	19.4	26.0	54.7	20.7	24.6
X3d[d]	45.1	26.2	28.7	—	—	—	—	—	—
X4a	53.7	14.9	31.4	53.2	12.9	33.9	54.2	13.9	31.9
X4b	45.8	25.0	29.2	47.2	20.9	31.9	48.0	22.0	30.0
X4c	55.1	16.3	28.6	56.6	17.2	26.2	56.7	18.5	24.8
X4d	49.6	23.3	27.1	50.6	21.4	28.0	51.0	22.6	26.4

[a] Calculated excluding hydrogen. [b] Derived from NMR data according to ref. 21. [c] Calculated according to ref. 32. [d] Sample topography does not allow quantification.

Bis[3-(trimethoxysilyl)propyl]diethylsilane (4b). A mixture of diallyldiethylsilane (**2**) (9.68 g, 57.5 mmol), trichlorosilane (24.5 g, 190 mmol) and hexachloroplatinic acid (15.0 mg, 0.029 mmol) in 75 ml of THF was stirred for 2 d at room temperature. Then the solvent was removed under reduced pressure. To the remaining viscous oil trimethyl orthoformate (100 ml, 960 mmol) was added. After stirring for 4 d all volatile components were removed under reduced pressure and distillation under vacuum afforded 14.57 g (62%) of **4b**, which was obtained as a colourless, air-stable liquid sensitive to moisture, bp 120 °C (3 mbar).

^{1}H NMR (C_6D_6): δ 3.53 (s, 18H, Si-OCH_3), 1.49 (m, 4H, Si-CH_2-CH_2-CH_2-Si), 0.89 (t, ^3J(HH) = 8.06 Hz, 6H, Si-CH_2-CH_3), 0.68 (t, ^3J(HH) = 7.85 Hz, 4H, $(H_5C_2)_2$Si-CH_2-CH_2-), 0.57 (m, 4H, $(H_3CO)_3$Si-CH_2-CH_2-), 0.43 (q, ^3J(HH) = 8.06 Hz, 4H, Si(CH_2-$CH_3)_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 50.2 (Si-OCH_3), 17.9 ($(H_5C_2)_2$Si-CH$_2$-), 16.2 (Si-CH_2-CH$_2$-CH_2-Si), 14.5 ($(H_3CO)_3$Si-CH$_2$-), 7.6 (Si-CH_2-CH$_3$), 4.0 (Si-CH$_2$-CH_3). ^{29}Si{^{1}H} NMR (C_6D_6): δ 4.7 Si(CH_2-$CH_3)_2$), −42.3 (Si$(OCH_3)_3$). IR (KBr, cm^{-1}): 1192 s [ν(Si–CH_2–)], 1092 vs [ν(Si–OCH_3)]. MS (EI): $m/z = 383$ [$M^+ - C_2H_5$], 337 [$M^+ - C_2H_5 - CH_3 - OCH_3$], 249 [$(H_3CO)_3Si(CH_2)_3Si(C_2H_5)_2{}^+$]. Anal. calc. for $C_{16}H_{40}O_6Si_3$ (412.74): C, 46.56; H, 9.77. Found: C, 46.39; H, 9.78%.

General procedure for the sol–gel processing and preparation of the polysiloxanes

To a solution of the monomeric precursors in 4 ml of THF : MeOH (3 : 1) water and the catalyst (n-Bu)$_2$Sn(OAc)$_2$ were added. This mixture was stirred for 12 h at room temperature until a gel was formed. Then the solvent was removed under reduced pressure and the obtained gels were dried for 1 h. The crude gels were washed three times with toluene (5 ml), Et_2O (5 ml) and n-pentane (10 ml). After aging by drying for 8 h *in vacuo* the gels were obtained as rubber-like, colourless solids.

Bis[3-(polymethylsiloxanyl)propyl]dimethylsilane (X3a). A mixture of **3a** (1.51 g, 4.3 mmol), water (440 mg, 24.6 mmol) and (n-Bu)$_2$Sn(OAc)$_2$ (30 mg, 0.087 mmol) in 4 ml of THF : MeOH (3 : 1) was sol–gel processed to give a colourless swollen gel. After purification and aging 1.11 g of a colourless powder were formed.

^{13}C CP/MAS NMR: δ 49.7 (Si-OCH_3), 26.1–14.3 (Si-CH$_2$-CH$_2$-CH$_2$-Si), 0.1 ($O_{2/2}$Si-CH_3), −2.8 (Si$(CH_3)_2$). ^{29}Si CP/MAS NMR: δ 1.5 (Si$(CH_3)_2$), −11.6 (D^1), −22.0 (D^2). Anal. calc. for $C_{10}H_{24}O_2Si_3$ (idealised stoichiometry): C, 46.10; H, 9.28. Corrected stoichiometry:[21] C, 44.39; H, 9.69. Found: C, 44.46; H, 9.54%.

Bis[3-(polysiloxanyl)propyl]dimethylsilane (X3b). A mixture of **3b** (1.38 g, 3.6 mmol), water (440 mg, 24.6 mmol) and (n-Bu)$_2$Sn(OAc)$_2$ (30 mg, 0.087 mmol) in 4 ml of THF : MeOH (3 : 1) was sol–gel processed to give a colourless swollen gel. After purification and aging 0.95 g of a colourless powder were formed.

^{13}C CP/MAS NMR: δ 49.8 (Si-OCH_3), 19.4–15.5 (Si-CH$_2$-CH$_2$-CH$_2$-Si), −3.3 (Si$(CH_3)_2$). ^{29}Si CP/MAS NMR: δ 1.6 (Si$(CH_3)_2$), −42.3 (T^0), −50.5 (T^1), −59.4 (T^2), −68.8 (T^3). Anal. calc. for $C_8H_{18}O_3Si_3$ (idealised stoichiometry): C, 38.98; H, 7.36. Corrected stoichiometry:[21] C, 37.60; H, 8.06. Found: C, 37.55; H, 8.35%.

Bis[3-(polymethylsiloxanyl)propyl]diethylsilane (X4a). A mixture of **4a** (1.35 g, 3.6 mmol), water (440 mg, 24.6 mmol) and (n-Bu)$_2$Sn(OAc)$_2$ (30 mg, 0.087 mmol) in 4 ml of THF : MeOH (3 : 1) was sol–gel processed to give a colourless swollen gel. After purification and aging 1.01 g of a colourless powder were formed.

^{13}C CP/MAS NMR: δ 49.6 (Si-OCH_3), 20.2–14.3 (Si-CH$_2$-CH$_2$-CH$_2$-Si), 7.6 (Si-CH_2-CH$_3$), 4.0 (Si-CH$_2$-CH_3), −0.1 ($O_{2/2}$-Si-CH_3). ^{29}Si CP/MAS NMR: δ 4.8 (Si$(C_2H_5)_2$), −2.5 (D^0), −12.6 (D^1), −23.1 (D^2). Anal. calc. for $C_{12}H_{28}O_2Si_3$ (idealised stoichiometry): C, 49.94; H, 9.78. Corrected stoichiometry:[21] C, 48.43; H, 9.82. Found: C, 48.63; H, 9.48%.

Bis[3-(polysiloxanyl)propyl]diethylsilane (X4b). A mixture of **4b** (1.42 g, 3.5 mmol), water (440 mg, 24.6 mmol) and (n-Bu)$_2$Sn(OAc)$_2$ (30 mg, 0.087 mmol) in 4 ml of THF : MeOH (3 : 1) was sol–gel processed to give a colourless swollen gel. After purification and aging 1.07 g of a colourless powder were formed.

^{13}C CP/MAS NMR: δ 49.7 (Si-OCH_3), 21.3–14.0 (Si-CH$_2$-CH$_2$-CH$_2$-Si), 7.4 (Si-CH_2-CH$_3$), 4.0 (Si-CH$_2$-CH_3). ^{29}Si CP/MAS NMR: δ 4.9 (Si$(C_2H_5)_2$), −42.4 (T^0), −50.7 (T^1), −59.6 (T^2), −68.8 (T^3). Anal. calc. for $C_{10}H_{22}O_3Si_3$ (idealised stoichiometry): C, 43.75; H, 8.08. Corrected stoichiometry:[21] C, 41.87; H, 8.62. Found: C, 43.48. H, 8.67%.

Bis[3-(polymethylsiloxanyl)propyl]dimethylsilane[Ph(T″)] (X3c). A mixture of **3a** (0.87 g, 2.5 mmol), phenyl(trimethoxy)silane (0.49 g, 2.5 mmol), water (440 mg, 24.6 mmol) and (n-Bu)$_2$Sn(OAc)$_2$ (30 mg, 0.087 mmol) in 4 ml of THF : MeOH (3 : 1) was sol–gel processed to give a colourless swollen gel. After purification and aging 0.96 g of a colourless powder were formed.

^{13}C CP/MAS NMR: δ 134.3–127.7 (C_6H_5), 49.6 (Si-OCH_3), 26.1–14.3 (Si-CH$_2$-CH$_2$-CH$_2$-Si), −0.3 ($O_{2/2}$Si-CH_3), −3.1 (Si$(CH_3)_2$). ^{29}Si CP/MAS NMR: δ 1.3 (Si$(CH_3)_2$), −2.0 (D^0), −12.5 (D^1), −21.6 (D^2), −62.8 (T$^1{}_{Ph}$), −71.4 (T$^2{}_{Ph}$), −80.3 (T$^3{}_{Ph}$). Anal. calc. for $C_{32}H_{58}O_7Si_8$ (idealised stoichiometry): C, 49.31; H, 7.50. Corrected stoichiometry:[21] C, 47.81; H, 7.93. Found: C, 48.18; H, 7.97%.

Bis[3-(polysiloxanyl)propyl]dimethylsilane[Ph(T″)] (X3d). A mixture of **3b** (0.92 g, 2.4 mmol), phenyl(trimethoxy)silane (0.47 g, 2.4 mmol), water (440 mg, 24.6 mmol) and (n-Bu)$_2$Sn(OAc)$_2$ (30 mg, 0.087 mmol) in 4 ml of THF–MeOH (3 : 1) was sol–gel-processed to give a colourless swollen gel. After purification and aging 0.91 g of a colourless powder were formed.

^{13}C CP/MAS NMR: δ 134.4–127.8 (C_6H_5), 49.8 (Si-OCH_3), 26.0–14.0 (Si-CH$_2$-CH$_2$-CH$_2$-Si), −3.4 (Si$(CH_3)_2$). ^{29}Si CP/MAS NMR: δ 1.3 (Si$(CH_3)_2$), −42.3 (T^0), −50.6 (T^1), −59.2 (T^2), −62.9 (T$^1{}_{Ph}$), −68.1 (T^3), −71.6 (T$^2{}_{Ph}$), −79.8 (T$^3{}_{Ph}$). Anal. calc. for $C_{32}H_{58}O_7Si_8$ (idealised stoichiometry): C, 44.76; H, 6.17. Corrected stoichiometry:[21] C, 42.14; H, 6.75. Found: C, 43.09; H, 7.04%.

Bis[3-(polymethylsiloxanyl)propyl]diethylsilane[Ph(T″)] (X4c). A mixture of **4a** (0.85 g, 2.2 mmol), phenyl(trimethoxy)silane (0.44 g, 2.2 mmol), water (440 mg, 24.6 mmol) and (n-Bu)$_2$Sn(OAc)$_2$ (30 mg, 0.087 mmol) in 4 ml of THF : MeOH (3 : 1) was sol–gel processed to give a colourless swollen gel. After purification and aging 0.94 g of a colourless powder were formed.

^{13}C CP/MAS NMR: δ 134.2–127.8 (C_6H_5), 49.7 (Si-OCH_3), 26.0–14.3 (Si-CH$_2$-CH$_2$-CH$_2$-Si), 7.6 (Si-CH_2-CH$_3$), 4.0 (Si-CH$_2$-CH_3), −0.3 ($O_{2/2}$Si-CH_3). ^{29}Si CP/MAS NMR: δ 4.7 (Si$(C_2H_5)_2$), −2.1 (D^0), −12.6 (D^1), −22.1 (D^2), −71.1 (T$^2{}_{Ph}$), −79.6 (T$^3{}_{Ph}$). Anal. calc. for $C_{36}H_{66}O_7Si_8$ (idealised stoichiometry): C, 51.75; H, 7.96. Corrected stoichiometry:[21] C, 50.42; H, 8.46. Found: C, 50.35; H, 8.04%.

Bis[3-(polysiloxanyl)propyl]diethylsilane[Ph(T″)] (X4d). A mixture of **4b** (0.93 g, 2.2 mmol), phenyl(trimethoxy)silane (0.47 g, 2.2 mmol), water (440 mg, 24.6 mmol) and (n-Bu)$_2$Sn-

$(OAc)_2$ (30 mg, 0.087 mmol) in 4 ml of THF : MeOH (3 : 1) was sol–gel processed to give a colourless swollen gel. After purification and aging 0.98 g of a colourless powder were formed.

^{13}C CP/MAS NMR: δ 134.3–127.7 (C_6H_5), 49.8 (Si-OCH_3), 26.2–13.3 (Si-CH_2-CH_2-CH_2-Si), 7.4 (Si-CH_2-CH_3), 3.9 (Si-CH_2-CH_3). ^{29}Si CP/MAS NMR: δ 4.8 ($Si(C_2H_5)_2$), −42.4 (T^0), −50.5 (T^1), −59.0 (T^2), −62.8 ($T^1{}_{Ph}$), −67.9 (T^3), −71.4 ($T^2{}_{Ph}$), −79.5 ($T^3{}_{Ph}$). Anal. calc. for $C_{32}H_{54}O_9Si_8$ (idealised stoichiometry): C, 47.60; H, 6.74. Corrected stoichiometry:[21] C, 46.01; H, 7.21. Found: C, 46.55; H, 7.47%.

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