Water-soluble poly(4,7,10,13-tetraoxatetradecylmethylsilane): enhanced yield and improved purity *via* polymerization using graphite-potassium (C$_8$K) as reducing agent

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Application of graphite-potassium (C$_8$K, THF, 0 °C), instead of convential Wurtz-type coupling conditions (Na, toluene, 110 °C), as reducing agent for the preparation of non-ionic, watersoluble poly(4,7,10,13-tetraoxatetradecyl-methylsilane) 1 gives a markedly enhanced yield as well as a high molecular weight polymer of high purity.

Polysilanes, *viz.* polysilylenes, exhibit (photo)physical and electronic properties of interest for application in materials science.[1] Although with the conventional Wurtz-type coupling conditions (Na, toluene, 110 °C) a number of polysilanes with alkyl and/or aryl substituents have been prepared, a drawback is that the severe polymerization conditions impair the use of monomers with functionalized side chains.[2] Hence, introduction of, for example, ionic groups has to be achieved by side chain functionalization after polymerization.[2–4] Notwithstanding using the conventional Wurtz-type coupling procedure, polysilanes containing ether linkages in their side chains[5] and, more recently, the first non-ionic water-soluble polysilanes possessing oligo(oxyethylene) side chains have become available,[6,7] albeit in low yields. Moreover, especially in the case of the non-ionic water-soluble polysilanes, their remarkable solubility in common organic solvents as well as water hampered their purification by simple (repeated) precipitation. High molecular weight material had to be separated from low molecular weight impurities (*vide infra*) by laborious preparative size exclusion chromatography (SEC). Hence as shown for poly(4,7,10,13-tetraoxatetradecylmethylsilane) 1,[6,7] isolated yields varied considerably (1; ≪ 1.0[7] up to 11%[6]). This is unfortunate, since polar polysilanes in general attract attention due to their propensity to Langmuir film formation at the air–water interface[2,3] and their potential application in (self)-assembly.[8]

Here we report that with graphite-potassium (C$_8$K),[9] instead of Na, as reducing agent, non-ionic, water-soluble **1** is accessible in a markedly enhanced yield. Furthermore, the high molecular weight fraction isolated by preparative SEC is shown to possess considerably improved purity (Scheme 1). The choice of C$_8$K was based on reported results for poly-(methylphenylsilane)[10] and poly(phenylsilyne).[11] C$_8$K was shown to be applicable at subambient temperature and to be compatible with a wide range of solvents.‡ Hence in contrast to the conventional Wurtz-type coupling procedure (Na, toluene, 110 °C), polymerization *via* the C$_8$K route requires considerably less severe conditions.

To establish the suitability of C$_8$K for the preparation of **1**, the monomer 4,7,10,13-tetraoxatetradecylmethyldichlorosilane **2**[6]

was polymerized under various conditions.§ Initial experiments revealed that both the formation of **1** as well as its final yield are strongly dependent on the ratio C$_8$K:**2**, reaction temperature and duration of polymerization, respectively. In THF, the high molecular weight polymer **1** was only obtained with a ratio C$_8$K:**2** of 2 and a reaction temperature of 0 °C. No **1** could be identified if either excess C$_8$K (ratio C$_8$K:**2** > 2) was used or in polymerizations executed with *ca.* 2 equiv. C$_8$K at $T > 0$ °C. To determine optimal polymerization conditions the effect of reaction time was studied in more detail (Table 1). The data show that for optimal formation of **1** a reaction time of 2–2.5 h is required (Table 1, entry 3). Longer reaction times lead to degradation of **1** (Table 1, entries 4 and 5, SEC). Under optimized conditions similar molecular weight distributions were found as those reported previously for **1** (Wurtz-type coupling reaction; Table 1, entry 6; M_w *ca.* 1.5×10^4).[6] In contrast to results reported for poly(methylphenylsilane) prepared *via* the C$_8$K route,[10] no polymer **1** could be extracted from the graphite phase after filtration.

After preparative SEC, polymer **1** was isolated in yields ranging from 20 to 35%. This is a considerable enhancement with respect to the yields obtained using conventional Wurtz-type coupling conditions (**1**; ≪ 1.0[7] up to 11%[6]). ^{29}Si NMR analysis only gave the characteristic silicon backbone resonance at δ −31.4 (Table 1, entry 3 and Fig. 1). The absence of resonances attributable to end-groups and/or siloxane moieties indicates that **1** prepared using C$_8$K after purification by preparative SEC is completely free from low-molecular weight material (*vide infra*). This is supported by ^{1}H and ^{13}C NMR

Table 1 Salient features of **1** obtained *via* the C$_8$K route (C$_8$K:**2** = 2.0, THF, 0 °C) with different reaction times after purification by preparative SEC.§¶

Entry	t/h	Yield (%)	$M_w \times 10^{-3\,a}$	$M_w/M_n{}^b$	λ_{max}/nm^c	ε(Si–Si)/ 10^3 dm^3 mol^{-1} cm$^{-1\,c}$
1	1.0	30	6.9	1.3	300	1.6
2	1.5	34	10.7	1.5	301	2.1
3	2.0	22	14.0	1.9	304	4.8
4	2.5	33	14.4	2.0	304	2.4
5	3.0	18	8.8	1.6	301	3.2
6^d	2.0	11	15.1	1.4	299	1.8

^{a} Molecular weight distributions determined with analytical SEC (UV detection λ 300 nm, polystyrene standards). ^{b} Polydispersity [see footnote (*a*)]. ^{c} Solvent MeCN. ^{d} Prepared using conventional Wurtz-type coupling conditions.[6]
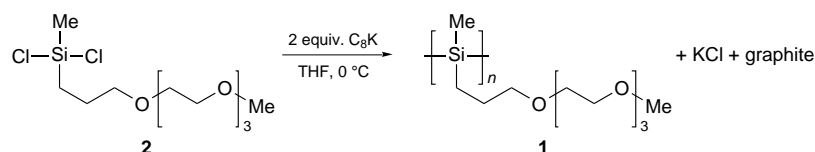
Scheme 1
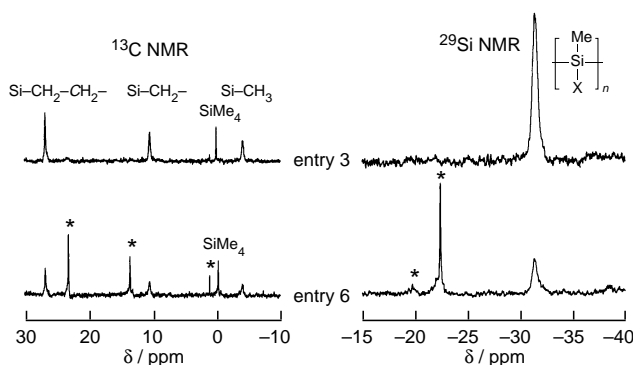
Fig. 1 ^{13}C and ^{29}Si NMR spectra of **1** prepared using either C₈K [THF, 0 °C (entry 3)] or conventional Wurtz-type coupling conditions [Na, toluene, 110 °C (entry 6)]. Peaks marked with * are due to impurities such as cyclosiloxanes‖ and low molecular weight oligomers (for X see Scheme 1).

spectroscopy (Fig. 1, ^{13}C NMR).¶ While for **1** prepared *via* the conventional Wurtz-type coupling reaction broad and split ^{1}H NMR signals were observed for the SiCH₃, SiCH₂ and SiCH₂*CH₂* moieties,[6] discrete resonances, similar to those reported for poly(γ-methoxypropylmethylsilane),[5] were found for **1** prepared using C₈K.¶

Additional evidence for the improved purity of **1** prepared *via* the C₈K method was obtained from its UV spectrum. The λ_{max} value at *ca.* 300 nm (σ → σ* transition) in combination with the increase of the extinction coefficient ε are in agreement with the presence of only a high molecular weight polymer (Table 1; entries 2–5 *vs.* entry 6).[1,6]

^{29}Si NMR and FAB-MS of the low molecular weight fractions indicate that they mainly consist of cyclosiloxanes [D$_n$ with n = 3, 4 and 5], which apparently are formed during work-up.‖ This result differs from that found for the low molecular weight fractions for **1** prepared using conventional Wurtz-type coupling conditions. In that case the low molecular weight fraction primarily consists of cyclosilanes (five- and six-membered) and cyclosiloxanes [D$_n$ with n = 4 and 5].[6]‖

Footnotes

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‡ It is noteworthy that it was recently reported that the yield of poly(methylphenylsilane) prepared using C₈K (THF, −78 to 25 °C) appears to be sensitive to the addition of a co-solvent such as 1,2-dimethoxyethane.[13]

§ All polymerizations were carried out in dried glassware under an Ar atmosphere. In a typical experiment, 4,7,10,13-tetraoxatetradecylmethyldichlorosilane (**2**, 1.66 g, 5.2 mmol) was slowly added *via* a syringe to a suspension of THF (10 ml) and C₈K [prepared by stirring graphite (1.00 g, 83.2 mmol) and potassium (0.41 g, 10.4 mmol) for 1 h at 150 °C][9] cooled at 0 °C. After the appropriate reaction time (see Table 1) the reaction mixture was quenched by adding MeOH (2 ml) followed by filtering off the graphite and precipitated KCl. To the filtrate a solution of KHCO₃ (0.5 g) in water (30 ml) was added to neutralize dissolved HCl and to prevent polymer degradation. After removal of solvents *in vacuo* the oily residue was redissolved in CH₂Cl₂ (30 ml) and the precipitated KHCO₃ as well as additional KCl were removed by filtration. The filtrate was concentrated *in vacuo* and the high molecular weight polymer fraction was subsequently isolated by preparative SEC (Biobeads SX-1, eluent CH₂Cl₂). Polysilane **1** was characterized with analytical SEC, DSC, TGA, UV, ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy.¶

¶ Polysilane **1** prepared using C₈K possesses improved purity compared to **1** obtained with the conventional Wurtz-type coupling procedure (Fig. 1).[6] ^{1}H NMR (300.13 MHz, CDCl₃) δ_H 0.26 (br, 3 H), 0.77 (br, 2 H), 1.60 (br, 2 H) and 3.38–3.66 (br, 17 H); ^{13}C NMR (75.47 MHz, CDCl₃) δ_C −4.1, 10.4, 26.8, 59.0, 70.1, 70.5, 70.6, 72.0 and 74.4; ^{29}Si NMR (59.63 MHz, CDCl₃) δ_{Si} −31.4.

‖ Cyclosiloxanes D$_n$ {−[−Si(R¹R²)−O−]$_n$ with R¹=R²=Me} possess ^{29}Si NMR chemical shifts at δ −8.93, −20.00 and −22.62 for n = 3, 4 and 5, respectively. For the low molecular weight fractions isolated from the crude reaction mixture ^{29}Si NMR chemical shifts at δ −11.94 and −12.32, −21.06 and −22.0 assigned to D₃, D₄ and D₅ species, respectively, were found.[12] This assignment is corroborated by FAB-MS.

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