



Fig. 1 ^{13}C and ^{29}Si NMR spectra of **1** prepared using either C_8K [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 \parallel and low molecular weight oligomers (for X see Scheme 1).

spectroscopy (Fig. 1, ^{13}C NMR). \parallel While for **1** prepared *via* the conventional Wurtz-type coupling reaction broad and split ^1H NMR signals were observed for the SiCH_3 , SiCH_2 and SiCH_2CH_2 moieties, 6 discrete resonances, similar to those reported for poly(γ -methoxypropylmethylsilane), 5 were found for **1** prepared using C_8K . \parallel

Additional evidence for the improved purity of **1** prepared *via* the C_8K method was obtained from its UV spectrum. The λ_{max} value at ca. 300 nm ($\sigma \rightarrow \sigma^*$ 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. \parallel 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]. $^{6\parallel}$

Footnotes

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\ddagger It is noteworthy that it was recently reported that the yield of poly(methylphenylsilane) prepared using C_8K (THF, -78 to 25°C) appears to be sensitive to the addition of a co-solvent such as 1,2-dimethoxyethane. 13

\S All polymerizations were carried out in dried glassware under an Ar atmosphere. In a typical experiment, 4,7,10,13-tetraoxatetradecylmethylchlorosilane (**2**, 1.66 g, 5.2 mmol) was slowly added *via* a syringe to a suspension of THF (10 ml) and C_8K [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 KHCO_3 (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 CH_2Cl_2 (30 ml) and the precipitated KHCO_3 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 CH_2Cl_2). Polysilane **1** was characterized with analytical SEC, DSC, TGA, UV, ^1H , ^{13}C and ^{29}Si NMR spectroscopy. \parallel

\parallel Polysilane **1** prepared using C_8K possesses improved purity compared to **1** obtained with the conventional Wurtz-type coupling procedure (Fig. 1). 6 ^1H NMR (300.13 MHz, CDCl_3) 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, CDCl_3) 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, CDCl_3) δ_{Si} -31.4 .

\parallel Cyclosiloxanes D_n $\{[-\text{Si}(\text{R}^1\text{R}^2)-\text{O}-]_n\}$ with $\text{R}^1=\text{R}^2=\text{Me}$ 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 D_3 , D_4 and D_5 species, respectively, were found. 12 This assignment is corroborated by FAB-MS.

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