Nonionic Water-Soluble Polysilynes. Synthesis and Properties of a Novel Class of Functionalized Materials

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ABSTRACT: The nonionic water-soluble polysilynes poly(4,7,10-trioxaundecylsilyne) (**1**) and poly(4,7,-10,13-tetraoxatetradecylsilyne) (**2**), which are inaccessible using the conventional Wurtz-type coupling with Na in refluxing toluene, have been prepared in reasonable yields using graphite potassium C_8K as the reducing agent in THF at 0 °C. A water-insoluble analogue of **1**, viz. poly(4,7,10-trioxahexadecylsilyne) (**3**), is obtained in nearly quantitative yield under similar conditions. Despite the fact that **1** and **2** possess all the characteristic polysilyne-like (photo)physical properties, aqueous solutions of **1** and **2** unexpectedly exhibit thermoresponsive behavior; i.e., at 49 °C a lower critical solution temperature (LCST) is found. The presence of an LCST, which has to originate from folding/unfolding processes of the polysilyne backbone, suggests that polysilynes have a hybrid structure with a predominantly one-dimensional overall appearance consisting of linear fragments with small branches and/or incorporated (branched) cyclics, instead of the previously proposed extended sheetlike and/or hyperbranched/dendritic structures. Additional support for a hybrid structure was given by semiempirical PM3 calculations on a variety of oligomeric model compounds. The PM3 results suggest that Si−Cl moieties incorporated in oligomers will be more reactive than monomeric Si−Cl groups. The calculations further indicate that linear chain extension is preferred over branching. Cyclic voltammetry in combination with absorption/excitation spectroscopy reveals that in going from the related polysilane to the polysilyne the valence band edge shifts ca. −0.7 V, while the conduction band edge remains virtually unchanged. Furthermore, it is demonstrated that polysilynes **1** and **2** are effective photoinitiators for radical polymerizations upon excitation at λ 400 nm. This is exemplified for the conversion of methylacrylate into poly(methylacrylate).

Introduction

In comparison with linear polysilanes ($-(SiR_1R_2)_n-$), viz. polysilylenes, branched silicon-based polymers, polysilynes ($-(SiR)_n-$), have markedly different photophysical properties.[1,2,3] Whereas polysilanes exhibit a characteristic UV $\sigma \rightarrow \sigma^*$ absorption band, polysilynes exhibit a semiconductor-like broad tailing band that extends into the visible region of the spectrum. Polysilynes are assumed to possess a silicon backbone skeleton, which is intermediate between one-dimensional polysilanes and three-dimensional amorphous silicon, making them of potential interest for applications in optoelectronics and ceramics.[3,4,5]

Although the first successful preparation of polysilynes was accomplished in the late 1980s,[1] their structure−property relationships are still not fully resolved. Hitherto, only a small number of alkyl- and aryl-substituted varieties have become available. This is a consequence of the severe reaction conditions, which hamper the preparation of functionalized polysilynes. Notwithstanding, polysilynes containing functionalized side groups have been prepared by chemical modification, i.e., by substitution of aryl side chain moieties. For example, dephenylation of poly(phenylsilyne) with triflic acid has been accomplished. However, the experimental procedures are complicated and phenyl substitution at only part of the silicon atoms occurs.[6] These findings instigated the development of novel synthetic strategies to obtain access to novel functionalized polysilynes. Recently, promising results were obtained with electrochemical reductive coupling[7] and especially the use of graphite potassium (C_8K).[8]

An intriguing aspect that remains to be addressed is the elucidation of the silicon backbone structure of polysilynes. Initially, polysilynes were described in terms of a two-dimensional structure consisting of a large number of interconnected rings giving an extended sheetlike structure.[9] More recently, hyperbranched/dendritic structures have also been proposed for polysilynes.[10] Both proposals are in line with the general polysilyne composition and can account for their (photo)-physical properties.

In this article we present the synthesis of a novel class of nonionic water-soluble polysilynes, viz. poly(4,7,10-trioxaundecylsilyne) (**1**) and poly(4,7,10,13-tetraoxatetradecylsilyne) (**2**), employing C_8K as the reducing agent. In addition, a water-insoluble analogue of **1**, viz. poly-(4,7,10-trioxahexadecylsilyne) (**3**), has been prepared. The water-solubility of **1** and **2** prompted an investigation for the occurrence of possible thermoresponsive behavior, i.e. the presence of a lower critical solution temperature (LCST). Recently, for aqueous solutions of the related nonionic water-soluble polysilanes, thermoresponsive behavior was serendipitously found.[11] The observation of an LCST for aqueous solutions of **1** and **2** provides evidence that these polysilynes possess neither an extended sheetlike nor a hyperbranched/dendritic structure. Instead a hybrid structure is proposed with a predominantly one-dimensional overall appearrance, which consists of linear fragments with small branches and/or incorporated (branched) cyclics. This is substantiated by semiempirical PM3[12] calculations on a variety of model compounds. Cyclic voltammetry in combination with absorption/excitation spec-

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troscopy reveals that in going from the related polysilane to the polysilyne the valence band edge shifts ca. −0.7 V, whereas the conduction band edge remains virtually unchanged. Furthermore, the use of the polar polysilynes **1** and **2** as photoinitiators in the radical polymerization of methyacrylate into poly(methylacrylate) is reported.

Experimental Section

General Data. NMR spectra were recorded with a Bruker AC 300 spectrometer (^{1}H NMR 300 MHz, ^{13}C 75 MHz and ^{29}Si NMR 60 MHz). Analytical size exclusion chromatography (SEC) was performed with a Shodex KF-804 column equipped with a Thermo Separation Products Series 200 pump and a UV-detector (λ 300 nm) using THF as the solvent at a flow rate of 1 mL/min. Molecular weight distributions are given relative to polystyrene standards. The isolation of the high molecular weight polymer fraction was achieved using preparative SEC (Biobeads SX-1 gel, eluent CH_2Cl_2). GC−MS spectra are recorded on an ATI Unicam Automass System 2 quadropole mass-spectrometer (EI 70 eV). UV/vis spectra were obtained with a Varian Cary 1 UV/vis spectrophotometer. Fluorescence spectra were collected on a Spex Fluorolog apparatus. Cyclic voltammetry measurements were performed with a Princeton Applied Research (PAR) model 263 potentiostat, using THF as the solvent and $LiClO_4$ (0.2 M) as the electrolyte. The onset of oxidation, V_i, was determined according to a literature procedure,[13,14] and referenced to SCE employing a standard (ferrocene/ferrocinium couple); V_i is given in volts vs SCE. DSC measurements were performed on a TA Instruments 2920 DSC (temperature program −125 to +25 °C; heating/cooling rate 10 °C/min). TGA was performed under an N_2 atmosphere with a Perkin-Elmer TGS-2 equipped with an AR-2 autobalance; the sample was heated to 850 °C (heating rate 10 °C/min). The handling of air/moisture sensitive compounds as well as all syntheses were done under an Ar atmosphere using Schlenk techniques. Solvents were dried and distilled prior to use.

Monomer Synthesis. Trichloro(4,7,10-trioxaundecylsilane) (4). A mixture of a catalytic amount of H_2PtCl_6 (ca. 50 mg, 0.1 mmol) and $HSiCl_3$ (10 mL, 0.099 mol) was stirred for 10 min, after which it was cooled with an ice−water bath (0 °C). Subsequently, allylmethyl diethylene glycol (6.66 g, 0.042 mol)[15] was slowly added. The reaction mixture was stirred for 48 h. at room temperature after which the excess of $HSiCl_3$ was removed under reduced pressure. The crude reaction product, which contained residual catalyst and impurities, was purified by Kugelrohr distillation. Compound **4** was obtained as a clear liquid (10.32 g, 84%). ^{1}H NMR ($CDCl_3$): δ 3.65−3.49 (m, 10H, $OC\mathit{H}_2$), 3.36 (s, 3H, $OC\mathit{H}_3$), 1.84 (m, 2H, $SiCH_2C\mathit{H}_2$), 1.50 (m, 2H, $SiC\mathit{H}_2$) ppm. ^{13}C NMR: δ 71.96, 71.45, 70.59, 70.12 ($O\mathit{C}H_2$), 58.90 ($O\mathit{C}H_3$), 22.69 ($SiCH_2\mathit{C}H_2$), 21.01 $Si\mathit{C}H_2$ ppm. ^{29}Si NMR: δ 13.33 ppm. GC−MS: selected *m/e* (relative intensity) 296 (<0.01), 263 (0.02), 250 (0.03), 219 (0.35), 205 (0.21), 177 (1.00), 135 (1.00), 89 (0.97), 58 (0.98).

Trichloro(4,7,10,13-tetraoxatetradecylsilane) (5) was prepared following the procedure described for **4** from allylmethyl triethylene glycol (8.28 g, 0.041 mol)[15] and $HSiCl_3$ (10 mL, 0.099 mol). After Kugelrohr distillation, pure **5** was obtained as a clear liquid. Yield: 89%. ^{1}H NMR ($CDCl_3$): δ 3.65−3.50 (m, 14H, $OC\mathit{H}_2$), 3.36 (s, 3H, $OC\mathit{H}_3$), 1.85 (m, 2H, $SiCH_2C\mathit{H}_2$), 1.50 (m, 2H, $SiC\mathit{H}_2$) ppm. ^{13}C NMR: δ 72.02, 71.46, 70.69, 70.62, 70.56, 70.23 ($O\mathit{C}H_2$), 58.86 ($O\mathit{C}H_3$), 22.76 ($SiCH_2\mathit{C}H_2$), 21.07 $Si\mathit{C}H_2$ ppm. ^{29}Si NMR: δ 13.33 ppm. GC−MS: selected *m/e* (relative intensity) 340 (<0.01), 308 (<0.01), 263 (0.01), 219 (0.14), 205 (0.08), 177 (0.96), 135 (0.98), 103 (1.00), 57 (0.97).

Trichloro(4,7,10-trioxahexadecylsilane) (6) was prepared following the procedure described for **4** from allylhexyl diethylene glycol (9.97 g, 0.043 mol) and $HSiCl_3$ (10 mL, 0.099 mol). Allylhexyl diethylene glycol was prepared from allylbromide (8.65 mL, 0.10 mol) and commercially available monohexyl ether of diethylene glycol (20.35 mL, 0.10 mol) by a literature procedure.[15] Yield: 82%. ^{1}H NMR ($CDCl_3$): δ 5.87 (m, 1H, $OCH_2{-}C\mathit{H}{=}CH_2$), 5.24, 5.14 (2 × dd, 2H, $OCH_2{-}CH{=}C\mathit{H}_2$), 4.00 (d, 2H, $OC\mathit{H}_2{-}CH{=}CH_2$), 3.63−3.52 (m, 8H, $OC\mathit{H}_2$), 3.43 (t, 2H, $OC\mathit{H}_2$), 1.52 (m, 2H, $C\mathit{H}_2$), 1.26 (m, 6H, $C\mathit{H}_2$), 0.86 (t, 3H, $C\mathit{H}_3$) ppm. ^{13}C NMR: δ 134.78 ($OCH_2{-}\mathit{C}H{=}CH_2$), 116.99 ($OCH_2{-}CH{=}\mathit{C}H_2$), 71.51, 70.67, 70.63, 70.06, 69.43 ($O\mathit{C}H_2$), 31.67, 29.58, 25.74, 22.59 ($\mathit{C}H_2$), 14.00 ($\mathit{C}H_3$) ppm. After Kugelrohr distillation, pure **6** was obtained as a clear liquid. Yield: 80%. ^{1}H NMR ($CDCl_3$): δ 3.66−3.42 (m, 12H, $OC\mathit{H}_2$), 1.85 (m, 2H, $SiCH_2C\mathit{H}_2$), 1.54 (m, 2H, $C\mathit{H}_2$), 1.47 (m, 2H, $SiC\mathit{H}_2$), 1.35−1.25 (m, 6H, $C\mathit{H}_2$), 0.88 (t, 3H, $C\mathit{H}_3$) ppm. ^{13}C NMR: δ 71.58, 70.68, 70.60, 70.18, 70.00 ($O\mathit{C}H_2$), 31.68, 29.59, 25.76 ($\mathit{C}H_2$), 22.64 ($SiCH_2\mathit{C}H_2$), 22.60 ($\mathit{C}H_2$), 21.01 ($Si\mathit{C}H_2$), 14.01 ($\mathit{C}H_3$) ppm. ^{29}Si NMR δ 13.19 ppm. GC−MS: selected *m/e* (relative intensity) 366 (<0.01), 282 (<0.01), 263 (0.01), 250 (0.01), 219 (0.09), 205 (0.08), 177 (0.82), 135 (0.87), 113 (0.49), 101 (0.29), 85 (1.00), 75 (0.90), 59 (0.99).

Due to the reactivity of the monomers **4**−**6**, which turned yellow even upon storing (−20 °C) under an Ar atmosphere, they were distilled directly before use.

Polymer Synthesis. Poly(4,7,10-trioxaundecylsilyne) (**1**) In a typical C_8K[16] mediated polymerization, a mixture of potassium (0.59 g, 15.1 mmol) and graphite (1.45 g, 0.121 mol) was heated under vigorous stirring with a magnetic stirring bar at 150−200 °C (oil bath). After ca. 1 h, a gold colored powder (C_8K) was obtained. After this was cooled with an ice bath (0 °C), THF (9 mL) was added; a homogeneous suspension was obtained. Subsequently, trichloro(4,7,10-trioxaundecylsilane) (**4**, 2.00 g, 6.8 mmol) was slowly added via a syringe under rapid stirring. The reaction was allowed to proceed for 2 h. after which the mixture was quenched by the cautious addition of CH_3OH (2 mL) followed by filtering off the graphite and precipitated KCl. To the filtrate was added a solution of $KHCO_3$ (0.5 g) in water (30 mL) 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). Subsequently precipitated $KHCO_3$ and KCl were removed by filtration. The filtrate was concentrated under reduced pressure and the high molecular weight polymer fraction was isolated using preparative SEC; 0.16 g of a viscous yellow polymer was obtained. Yield: 12%. $M_w = 1.6 \times 10^4$ ($D = M_w/M_n = 1.9$). ^{1}H NMR ($CDCl_3$): δ 3.8−3.3 (br, 13H, $OC\mathit{H}_2/OC\mathit{H}_3$), 1.9−1.5 (br, 2H, $SiCH_2C\mathit{H}_2$), 1.1−0.6 (br, 2H, $SiC\mathit{H}_2$) ppm. ^{13}C NMR δ 74.02, 72.00, 70.53, 70.05 ($O\mathit{C}H_2$), 58.96 ($O\mathit{C}H_3$), 30.0−20.0 ($SiCH_2\mathit{C}H_2$), $Si\mathit{C}H_2$ broad and unresolved ppm. ^{29}Si NMR δ −45 to −70 (br) ppm.

Poly(4,7,10,13-tetraoxatetradecylsilyne) (2) was prepared by following the procedure described for **1**. Starting from trichloro-4,7,10,13-tetraoxatetradecylsilane (**5**, 2.26 g, 6.7 mmol) and C_8K [prepared from potassium (0.78 g, 20 mmol) and graphite (1.93 g, 0.16 mol)], 0.52 g of high molecular weight **2** was obtained after preparative SEC. Yield: 33%. $M_w = 1.3 \times 10^4$ ($D = M_w/M_n = 2.2$). ^{1}H NMR ($CDCl_3$): δ 3.7−3.2 (br, 17H, $OC\mathit{H}_2/OC\mathit{H}_3$), 1.8−1.4 (br, 2H, $SiCH_2C\mathit{H}_2$), 1.2−0.5 (br, 2H, $SiC\mathit{H}_2$) ppm. ^{13}C NMR δ 73.79, 71.84, 70.46, 70.40, 69.88 ($O\mathit{C}H_2$), 58.87 ($O\mathit{C}H_3$), 32.0−22.0 ($SiCH_2\mathit{C}H_2$), $Si\mathit{C}H_2$ broad and unresolved ppm. ^{29}Si NMR δ −45 to −70 (br) ppm.

The synthesis of polysilynes **1** and **2** was also attempted using the conventional Wurtz-type coupling procedure with Na as the reducing agent.[3] To this end a mixture of molten Na (1.31 g, 57 mmol) and the appropriate monomer (**4** or **5**, 20 mmol) in toluene (60 mL) was refluxed for 2.5 h. After workup of the reaction mixture as described for the C_8K-mediated polymerizations, preparative SEC as well as ^{1}H, ^{13}C, and ^{29}Si NMR revealed only the presence of branched oligo- or polysiloxanes; no polysilyne-like material could be identified.

Poly(4,7,10-trioxahexadecylsilyne) (3) was prepared following the procedure described for **1**. Starting from trichloro-4,7,10-trioxahexadecylsilane (**6**, 2.00 g, 6.8 mmol) and C_8K [prepared from potassium (0.79 g, 20 mmol) and graphite (1.94 g, 0.16 mol)], 1.28 g of high molecular weight **3** was isolated. Yield: ca. 100%. Analytical SEC revealed that in the case of **3** no purification by preparative size exclusion chromatography was necessary. $M_w = 7.8 \times 10^3$ ($D = M_w/M_n = 1.5$). ^{1}H NMR

($CDCl_3$): δ 3.73−3.43 (m, 12H, OC*H*$_2$), 1.9−1.5 (m, 2H, SiCH$_2$C*H*$_2$), 1.58 (m, 2H, C*H*$_2$), 1.40−1.20 (m, 6H, C*H*$_2$), 0.89 (t, 3H, C*H*$_3$), 1.2−0.5 (br, 2H, SiC*H*$_2$) ppm. ^{13}C NMR δ 73.81, 71.57, 70.62, 70.09 (O*C*H$_2$), 31.74, 29.66 (*C*H$_2$), 32.0−28.0 (SiCH$_2$*C*H$_2$), 25.81, 22.65 (*C*H$_2$), 14.06 (*C*H$_3$), Si*C*H$_2$ broad and unresolved ppm. ^{29}Si NMR δ −50 to −80 (br) ppm.

Radical Polymerization of Methylacrylate Using 2 as Photoinitiator. For the photoinitiated radical polymerization of methylacrylate into poly(methylacrylate), polysilyne **2** (1.5 wt %) was dissolved in pure methylacrylate (10 g) from which the inhibitor was removed by passing it over neutral alumina prior to use. Sampling of the polymerization mixture during irradiation (λ 400 nm) was done under a N_2 flow to prevent the undesired influence on the polymerization kinetics by introduction of contaminants such as O_2. For photoinitiation the 150 W xenon lamp in combination with a double excitation monochromator of a SPEX Fluorolog apparatus at λ 400 nm was used (fwhm of the light source was adjusted to about 12 nm). The extent of monomer conversion as a function of time was determined by weighing of small samples, before and after careful vacuum treatment in order to remove the remainder of the volatile monomer methylacrylate.

Semiempirical PM3 Calculations. Semiempirical calculations were performed with the MOPAC 7.0 package,[17] which was compiled under IRIX6.2. All calculations were performed with the RHF PM3 Hamiltonian; for the radicals the half-electron approach RHF PM3 method was used.[12] All structures were optimized using the Eigenvector Following routine (keyword EF) until a GNORM $\leq$ 0.05 (see Supporting Information). All minima were characterized by a Hessian calculation (keywords Force, Large); no imaginary vibrations were found.

Results and Discussion

Polysilyne Synthesis. Successful syntheses of polysilynes, bearing alkyl or aryl substituents, has been accomplished using either Na or Na/K alloy as the reducing agent.[1,2,3,10] Although the use of ultrasound was found to be of great help,[9] it is not a prerequisite, and a conventional Wurtz-type coupling with Na in refluxing toluene has given satisfactory results as well.[3,10] Therefore, the synthesis of **1** and **2** was initially attempted using the conventional Wurtz-type coupling conditions. However, after work up analytical SEC as well as ^1H, ^{13}C, and ^{29}Si NMR revealed that no material possessing polysilyne-like characteristics was present. Especially diagnostic was ^{29}Si NMR; distinct peaks at δ −65.65, −66.60, −68.42 ppm, which were also obtained after direct hydrolysis of monomers **4**−**6**, were found. This suggests that polymerization has not occurred to a substantial extent and that after workup the remaining quenched functionalities, i.e. Si−OCH_3 moieties, were hydrolyzed, thus giving ultimately oligo- or polysilsesquioxanes (branched oligo- or polysiloxanes).

For the syntheses of nonionic water-soluble polysilanes, C_8K has proven to be a considerably more effective reducing agent than Na. With C_8K the polymerization can be performed at low temperatures (0 °C) enabling the use of more polar solvents such as THF. Indeed both improved yields and polymers of higher purity were obtained.[16] In this context, it is noteworthy that in the case of poly(phenylsilyne) the use of either C_8K (THF, 0 °C),[8] Na/toluene at reflux temperature[4] or Na/K alloy (THF)[1,9] gave nearly identical materials. These results prompted us to employ C_8K, instead of Na, for the synthesis of **1** and **2**. Using C_8K satisfactory results were obtained. Polysilynes **1** and **2** could be isolated in 10−40% yield after preparative SEC (see Experimental Section and vide infra). Interestingly, an analogue of **1**, i.e. **3**, in which the oligo(oxyethylene) substituent is terminated with a hexoxy instead of a methoxy unit, was obtained in near quantitative yield using these conditions. All C_8K-mediated polymerizations were allowed to proceed for 2.5 h. After this period in neither the molecular weight distributions (SEC) nor the optical spectra (UV/vis) of the crude polysilynes was a significant change noticeable. In contrast to the behavior of the related polysilanes of **1**−**3** no degradation occurred even after prolonged reaction times.[16] The molecular weight distributions of pure polysilynes **1**−**3** range from M_w 7.8 × 10^3 to 1.6 × 10^4 ($D = M_w/M_n$ = 1.5−2.2) and support their polymeric nature. It should be stipulated, however, that the poly(styrene) standards are not entirely comparable with the polysilynes. Hence, the actual molecular weight distributions will probably deviate.[9]

Properties of Polysilynes 1-3. As demonstrated by ^1H, ^{13}C, and ^{29}Si NMR, polysilynes **1**, **2**, and **3** exhibit both broad and narrow resonances. The NMR resonances of the silicon backbone as well as those corresponding to carbon and hydrogen atoms in close proximity of the backbone are all broadened in comparison to related resonances in polysilanes and polysiloxanes. This indicates that the atoms positioned either in or near the polymer backbone possess restricted mobility, whereas those present in the side chains and thus further removed from the backbone remain mobile. Especially the characteristic ^{29}Si resonance of the backbone around δ −60 ppm is very broad (range δ −45 to −80 ppm), and is therefore difficult to detect. The presence of only a single broad ^{29}Si resonance is characteristic for all known polysilynes.[2,3,8,9]

DSC analysis of polysilynes **1**−**3** only gave a glass transition (T_g), i.e. **1**−**3** are amorphous polymers. The T_g of **1** and **2** is −80.7 °C (T_{onset} −84.8 °C and T_{offset} −76.6 °C) and −79.5 °C (T_{onset} −86.7 °C and T_{offset} −72.5 °C), respectively. These T_g values are nearly identical to those found for the linear polysilane representatives possessing identical side chain substituents.[15] Hence, T_g appears to be primarily controlled by the type of side chain and not by the silicon backbone. Further support for this contention is provided by the T_g of **3,** viz. −91.3 °C (T_{onset} −98.0 °C and T_{offset} −84.7 °C), which is ca. 10 °C lower than that of **1** and **2**. The hexoxy moieties terminating the oligo(oxyethylene) substituents of **3** act as an "internal plasticizer". A similar effect of terminal alkyl chain length in combination with the position of the ether units, on T_g was also found for the corresponding polysilanes of **1**−**3**, viz. poly[(4,7,10-trioxaundecyl)methylsilane], poly[(4,7,10,13-tetraoxatetradecyl)-methylsilane], and poly[(4,7,10-trioxahexadecyl)methylsilane], respectively.[15,18] Whereas polysilanes containing an identical oligo(oxyethylene) substituents as **1** and **2** have a T_g of ca. −81 °C,[15] the polysilane analogue of **3** has a T_g of −85.2 °C.[18] Similar observations were previously reported for other polysilanes containing at least one ether linkage in one of their side chains.[19] As shown by thermogravimetry [TGA(N_2)], thermal decomposition of **1**, **2**, and **3** starts above 150 °C; at 800 °C a residue of 20−40 wt % remains.

The solubility of polysilynes **1**−**3** in a variety of regular solvents is excellent. However, whereas **1** and **2** do not dissolve in *n*-hexane, they are water-soluble (solubility > 5 mg/mL). Hence, they are representatives of a novel class of nonionic water-soluble polysilynes! In contrast, **3** does not dissolve in water, but readily

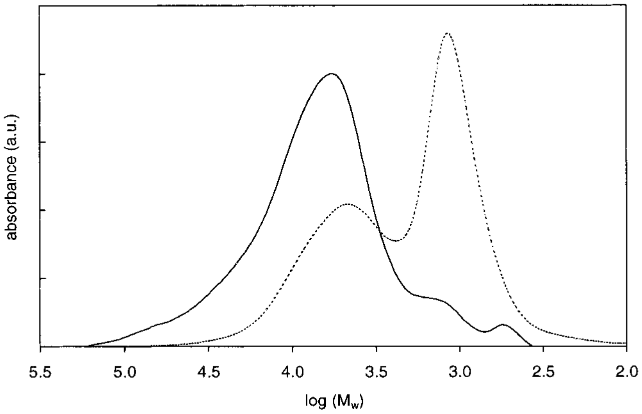


Figure 1. SEC curves of polysilyne **2** before and after preparative SEC. (UV detection: λ 300 nm).

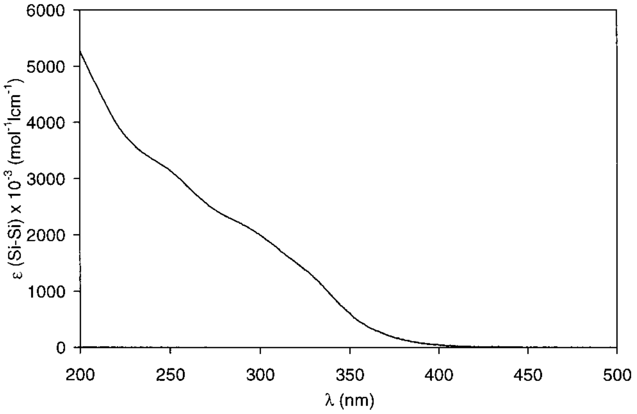


Figure 2. UV absorption spectrum of polysilyne **1** (solvent CH_3CN). Polysilynes **2** and **3** (solvent THF) exhibit nearly identical spectra.

dissolves in *n*-hexane. Since **3** resembles **1** with the exception of the type of terminal alkoxy moiety of the oligo(oxyethylene) substituent, a dominant effect of the oligo(oxyethylene) side chains in controlling their solubility properties must be present. This is corroborated by the strikingly similar solubility properties of polysilynes **1**−**3** with those of their related polysilane counterparts.[15,18] Unfortunately, the solubility of **1** and **2** in a wide variety of solvents is also disadvantageous. Whereas polysilanes and polysilynes containing alkyl and aryl substituents are readily purified by (re)-precipitation, this is impossible for **1** and **2**. Their high molecular weight fraction has to be isolated and purified from oligomeric material by preparative SEC (Figure 1).

Optical Properties of Polysilynes 1−3. Polymers **1**−**3** exhibit the typical optical characteristics of polysilynes. Their UV/vis absorption spectrum consists of a broad semiconductor-like band, which tails into the visible range of the optical spectrum (Figure 2). The extinction coefficients (ϵ) are low in the near UV range of the spectrum (λ 300 nm, ϵ 1.0 × 10^3 to 1.8•10^3 mol^{-1} L cm^{-1}) and increase in going into the UV region (λ 200 nm, ϵ 5.4 × 10^3 mol^{-1} L cm^{-1}). It is noteworthy that these ϵ values are lower than those found for poly(hexylsilyne) (range ϵ (2.8−3.5) × 10^4 mol^{-1} L cm^{-1}).[9] Apparently both in the case of polysilanes and polysilynes, the type of substituent markedly affects the conformation of the silicon backbone, the distribution of available chromophores, and consequently their electronic properties.[20]

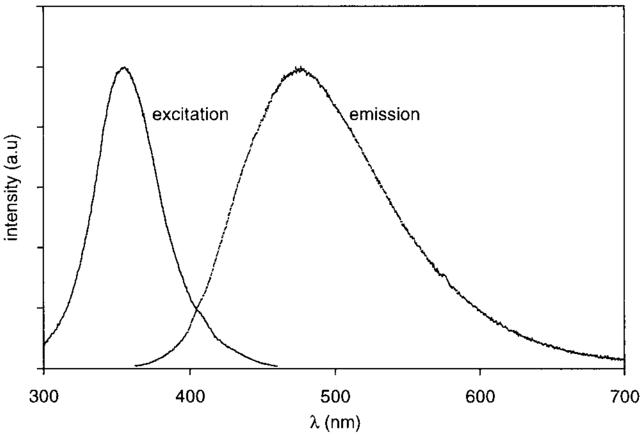


Figure 3. Fluorescence excitation (λ_{em} 480 nm) and emission spectra (λ_{exc} 362 nm) of polysilyne **1** (solvent CH_3CN). Polysilynes **2** and **3** (solvent THF) exhibit nearly identical spectra (Table 1).

Table 1. Fluorescence Excitation and Emission Maxima of 1−3

	1		**2**		**3**	
solvent	λ_{exc} (nm)[a]	λ_{em} (nm)[b]	λ_{exc} (nm)[a]	λ_{em} (nm)[b]	λ_{exc} (nm)[a]	λ_{em} (nm)[b]
n-hexane	*c*	*c*	*c*	*c*	340	435
CCl_4	366	466	357	460	312	468
THF	370	475	361	476	347	480
ethanol	361	466	365	475	322	434
CH_3CN	356	471	360	475	*c*	*c*
water	361	467	355	476	*c*	*c*

[a] Excitation maximum for emission at emission maximum. [b] Emission maximum for excitation at the excitation maximum. [c] Insoluble.

The fluorescence spectra of **1**−**3** also resemble those of known polysilynes.[2] The emission spectrum consists of a broad band centered around λ 470 nm with a fwhm of ca. 100 nm; a large Stokes-shift of ca. 100 nm is found (Figure 3). This suggests that the increase in dimensionality leads to a number of different chromophores, which exhibit various degrees of exciton trapping/scattering at the branching points. This is in marked contrast to polysilanes, which possess narrow emission bands with a small Stokes-shift.[21] The position of the excitation and absorption maximum does not show a significant solvent dependence (Table 1). Hence, polymer−solvent interactions do not substantially influence the conformation of the lowest energy chromophores in the silicon backbone.

Thermoresponsive behavior of 1 and 2. Recently, we reported that aqueous solutions of the linear polysilane analogues of **1** and **2** possess thermoresponsive behavior; at 46 °C a lower critical solution temperature (LCST) was discernible. At the LCST the aqueous solution becomes turbid, and upon prolonged standing (60 h), ultimately full phase separation occurs.[11] The water solubility of **1** and **2** instigated the investigation of similar thermoresponsive behavior. Indeed, upon heating of aqueous solutions of **1** and **2** an LCST of 49 °C was found (Figure 4). The observed phase separation/aggregation process appeared to be reversible; no significant hysteresis was discernible. Unexpectedly, the LCST of **1** and **2** is close to that found for the related linear polysilanes (LCST 46 °C[11]).

Upon addition of $LiClO_4$ the LCST of **1** and **2** shifts to higher temperatures (concentrated 1.4 M $LiClO_4$, LCST 72 °C, Figure 5). This indicates that the alkali-

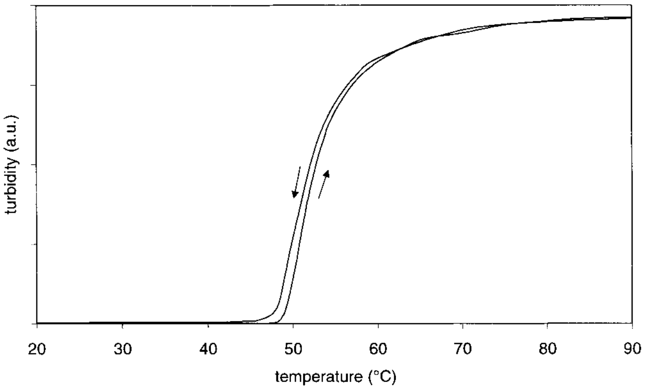


Figure 4. Turbidity vs temperature of an aqueous solution of **1** (monitoring at wavelength λ 750 nm to avoid absorption by **1**). For **2** a nearly identical curve was observed.

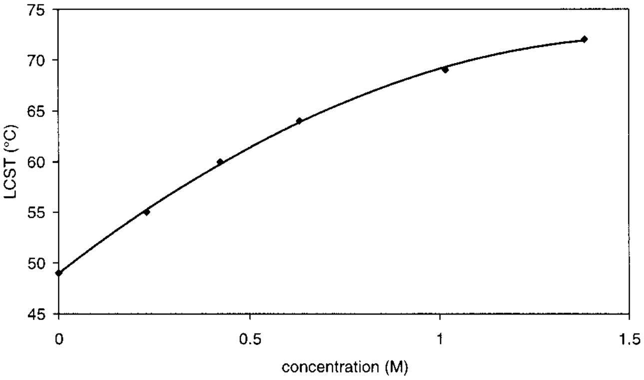
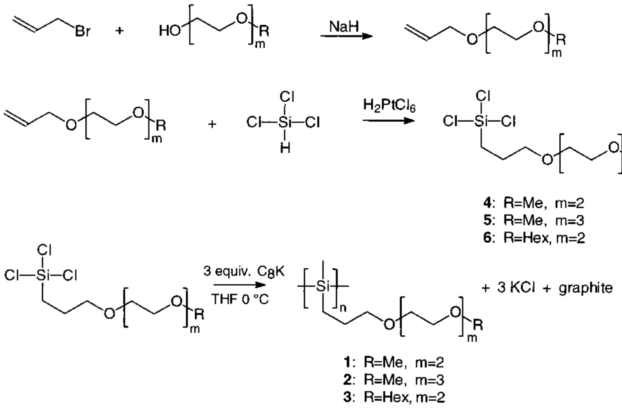


Figure 5. Change of the LCST of an aqueous solution of **1** vs the concentration of added $LiClO_4$.

metal cations stabilize the polysilyne perimeter presumably by complexation with the oxyethylene moieties. These results are in good agreement with the behavior of the nonionic water-soluble polysilanes, which also exhibit a dramatic increase of the LCST upon addition of $LiClO_4$ (concentrated 1.4 M $LiClO_4$, LCST 75 °C[11]). However, upon addition of alkali-metal hydroxide salts, such as LiOH and NaOH, instead of a decrease of the LCST, as was observed for the related polysilanes,[11] degradation of **1** and **2** occurs. The susceptibility of **1** and **2** toward degradation in the presence of hydroxide ions was corroborated by independent ^{29}Si NMR (solvent D_2O) experiments. Upon addition of NaOH to a D_2O solution of **1** or **2** the broad ^{29}Si resonance centered around δ −60 ppm gradually disappeared and was replaced by a narrow resonance at δ −41 ppm. The latter is assigned to a partially oxygen-substituted silicon atom.[22] The detailed mechanism of this degradation process is subject of further investigations.

Structure of Polysilynes. Recently, we have shown using UV/vis spectroscopy, turbidity measurements, and static as well as dynamic light scattering, that in aqueous solutions of nonionic water-soluble polysilanes the occurrence of an LCST corresponds to a folding/unfolding process of the catenated silicon backbone.[11] The thermoresponsive behavior of aqueous solutions of polysilynes **1** and **2**, in combination with the observation that their LCST is nearly identical to that found for their linear counterparts, suggests that the polysilyne and polysilane structures have to be correlated. This is an unexpected finding, since polysilynes obtained by reductive coupling of organotrichlorosilanes with either Na or C_8K were proposed to possess a two-dimensional extended sheetlike structure consisting of a large number of interconnected rings.[2,9] To rationalize their remarkable solubility, it was assumed that the side chains play an important role; viz., they are responsible for separating the sheets. However, only limited evidence is available to support this proposal. More recently, evidence has been put forward that polysilynes may possess a hyperbranched/dendritic structure[10] instead of an extended sheetlike structure.[2,9] The preferred formation of a hyperbranched/dendritic structure was proposed on the basis of assumed differences in reactivity between Si−Cl functionalities of monomers and those incorporated in either oligomers or polymers. As a consequence, the build up of a hyperbranched/dendritic structure of the AB_2 type was suggested.[23] Notwithstanding, whereas differences in reactivity of the Si−Cl functionalities in monomers and oligomers are taken into account, it is implicitly assumed that Si−Cl functionalities in oligomers occupying either an end position or another position in the backbone have similar reactivity.

Scheme 1. Syntheses of Polysilynes 1−3

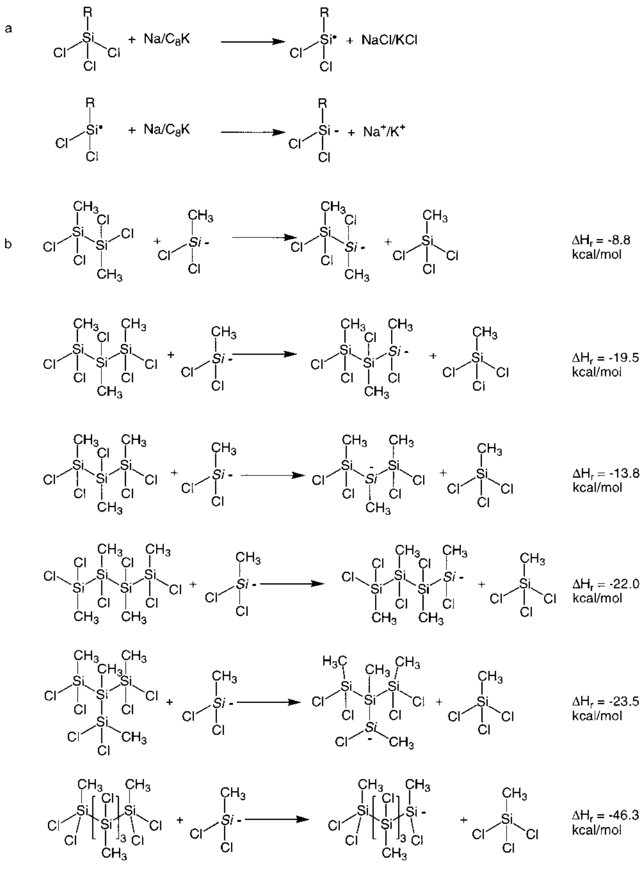


In view of the thermoresponsive behavior of aqueous solutions of **1** and **2**, both the extended sheetlike or hyperbranched/dendritic structure appears to be implausible, i.e. folding/unfolding of such structures in solution is unlikely to occur. Moreover, if such a process is still feasible a significantly different LCST (if not absent) is expected for **1** and **2** in comparison with that of their corresponding polysilane analogues.

To assess if differences in reactivity of Si−Cl functionalities play a decisive role in determining the polysilyne structure, we have performed semiempirical PM3 calculations on a series of oligomeric model species with methyl substituents.[12,17] Note that Si−Si bond formation by reductive coupling involves two important steps, i.e. the formation of silyl radical and silyl anion intermediates. By a single electron-transfer process from the reducing agent (Na or C_8K) to a Si−Cl bond a silyl radical anion is formed, which rapidly decomposes into a silyl radical and a chloride ion. Subsequently, by a second single electron transfer, the silyl radical is converted into the silyl anion, which can finally attack another Si−Cl functionality furnishing a new Si−Si bond (Scheme 2a).[23]

Interestingly, the homodesmotic reactions presented in Scheme 2b using PM3 heats of formation (ΔH_f^0 and see Supporting Information) show that silyl anion formation becomes energetically favored concomitant with increasing oligomer length. Hence, Si−Cl functionalities of oligomers, instead of those present in the monomers, are predicted to be preferentially converted into silyl anions. This is in line with the proposed AB_2

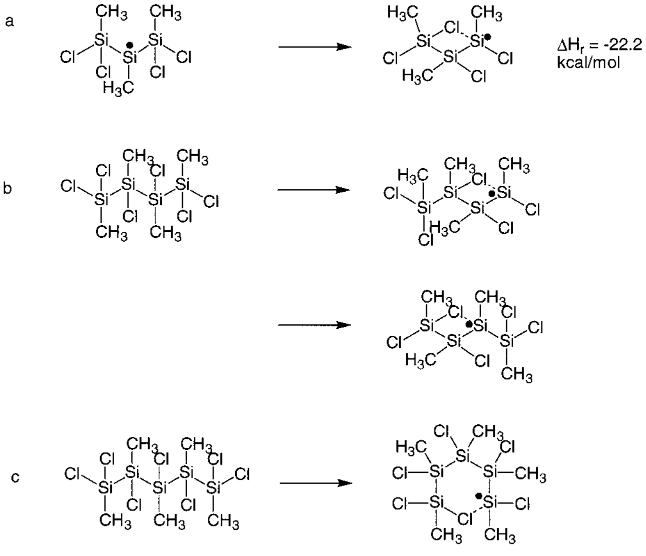
Scheme 2. Schematic Representation of Silyl Radical and Silyl Anion Formation by Two Consecutive Single Electron Transfers from the Reducing Agent Na/C$_8$K (a) and PM3 Enthalpies of Reaction (ΔH_r) for Model Reactions Involving Silyl Anions (b)



mechanism.[23] These results also indicate that there is no clearly favored position for silyl anion formation in the oligomers.

As illustrated in Scheme 2a, silyl anion formation is preceded by the formation of the related silyl radical. Therefore, additional PM3 calculations were performed on the corresponding silyl radicals. Qualitatively the results unequivocally show that in oligomers the formation of silyl radicals at the termini is energetically favored. Hence in oligomers, the substantial stabilization of silyl radicals positioned at the termini, by bending backward to the silicon backbone, will ultimately lead to the preferred formation of silyl anions at the termini, instead of other positions (Scheme 3a and see Supporting Information). In the case of a trisilane this backbiting effect results in a lowering in energy of the silyl radical by ca. 22 kcal/mol, as compared to a radical positioned at the central Si atom. This suggests that chain extension will be favored over branching. For a tetrasilane, the PM3 results indicate that independent of the position of the radical in the silicon chain, identical structures will be obtained, which will subsequently propagate toward longer linear systems (Scheme 3b). Hence, a description as an AB$_2$ system is not sufficient, and an "ABC system" seems to be more appropriate. As a consequence, the calculations also give no evidence for the preferred formation of hyperbranched/dendritic structures.

Scheme 3. Model Reactions Involving Silyl Radicals: (a) Trisilane, (b) Tetrasilane, and (c) Pentasilane.



It is noteworthy that our model calculations suggest that in pentasilanes the formation of a cyclic compound is slightly favored over the formation of a linear hexasilane derivative. Apparently, the propensity toward cyclization in these pentasilanes is a consequence of the fact that the "cyclic" pentasilane radical precursor is a stable intermediate (Scheme 3c and see Supporting Information). In addition, the enthalpy difference between linear Si$_6$Me$_6$Cl$_8$ and cyclic Si$_5$Me$_5$Cl$_5$ (+SiCl$_3$Me) is ca. 5 kcal/mol, in favor of the cyclic system. Hence, the PM3 results support the experimental observation that cyclopentasilane derivatives are major intermediates in the formation of polysilynes.[8]

Subsequently, polysilyne formation has to be achieved by coupling of cyclic silane and (branched) oligosilane intermediates as well as by ring opening reactions, similar to what was proposed for spiro silicon compounds.[23] The actual propagation path will presumably be further affected by the applied synthetic methodology and the bulkiness of the substituents involved. Hence, polysilynes are expected to possess a hybrid structure with a predominantly one-dimensional overall appearance consisting of linear fragments with small branches and/or incorporated (branched) cyclics, instead of the previously proposed sheetlike[9] and hyperbranched/dendritic[10] structures. The proposed hybrid structure will have a certain degree of rigidity (restricted mobility) and will contain many different structural elements, thus accounting for the characteristic polysilyne properties, i.e. the observed broad NMR resonances as well as the semiconductor-like absorption and fluorescence spectra (vide supra). However, in contrast to previous proposals the overall appearance of polysilynes will still be semilinear, which reconciles their excellent solubility properties as well as the observed thermoresponsive behavior in the case of **1** and **2**. It should be stipulated that no spectroscopic evidence (additional ^{29}Si resonances and UV; additional superimposed $\sigma \rightarrow \sigma^*$ transition)[3,24] for the presence of extensive polysilane-like sequences was found. This is in conjunction with the proposed predominantly one-dimensional overall appearance consisting of linear fragments with small branches and/or incorporated (branched) cyclics of polysilynes.

Further evidence that polysilyne properties can be satisfactorily explained by a hybrid structure is suggested by the study of branched model compounds.[25,26] The observation that, in particular, the optical proper-

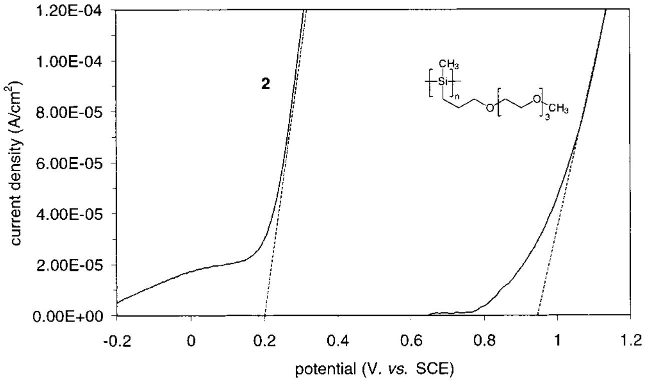


Figure 6. Onset of oxidation (V_i) of polysilyne **2** and the corresponding polysilane, poly[(4,7,10,13-tetraoxatetradecyl)-methylsilane]. For clarity the start of the first anodic scan is shown.

ties of such small branched silicon-based structures already resemble those of polysilynes indicates that an extensive two-dimensional structures is not a prerequisite. For example, $[(Me_3Si)_3SiSiMe_2]_3SiMe$, exhibits broad bands in its fluorescence emission spectrum with a stokes shift of ca. 50 nm.[25]

Electronic Properties. To gain further insight into the electronic properties of these polysilynes, we have obtained an estimate of the valence band edge using cyclic voltammetry.[13,14] Because the "highest occupied molecular orbital (HOMO)" in silicon-based polymers is related to the silicon backbone and **1**−**3** have a similar substitution pattern near the silicon backbone, they are expected to possess similar electrochemical behavior. Therefore, **2** was chosen as a representative example and subjected to cyclic voltammetry. In comparison with its corresponding polysilane analogue, viz. poly[(4,7,-10,13-tetraoxatetradecyl)methylsilane], the value onset of oxidation (V_i) of **2** exhibits a remarkable shift of ca. −0.7 V, for example, whereas for the polysilane V_i is 0.94 V, V_i of **2** is ca. 0.20 V (Figure 6). The shift of V_i rationalizes the increased propensity of polysilynes toward oxidation. The value of V_i of **2** is at the lower limit of V_i values reported previously for functionalized linear polysilanes.[13] Hence, branching of the silicon backbone enlarges the available potential window in which the band gap of silicon-based polymers can be tailored. This aspect is subject of further investigations.

As shown in Figure 6, V_i of **2** is less defined than that of its linear analogue. Apparently due to their hybrid structure in polysilynes, several isolated domains are discernible, which oxidize at slightly different potentials, i.e. they possess slightly different energy levels, therefore creating a less abrupt onset of oxidation. This band dispersity could reflect the proposed hybrid structure.

Since V_i gives an estimation of the band edge of the valence band of the solvated (THF) polymer, this band edge actually gives the oxidation energy of the lowest energy fragments in the σ-conjugated backbone, instead of an average value for all the different structural elements. The connection between the electrochemically determined valence band edge and data obtained from optical spectroscopy is interesting. Whereas UV/vis absorption spectroscopy provides an estimate of the optical band gap, it is known that the excitation maximum gives an estimate of the energy of the optical transition from the lowest energy fragments present in the σ-conjugated backbone.[21] The energy of this excitation maximum should give direct information about the band gap with a valence band-edge at V_i. The excitation maxima of **1** and **2** (solvent THF) are λ 370 and 361 nm, respectively, which is on average 3.39 eV (Table 1). The excitation maxima for the linear analogues of **1** and **2** under similar conditions are λ 313 and 316 nm, respectively,[15] which averages to 3.94 eV. This indicates a decrease in band gap of 0.55 eV, which nearly equals the change in V_i (ca. −0.7 V, vide supra). Hence, we conclude that upon going from a linear polysilane to the corresponding polysilyne the valence band edge shifts considerably, whereas the conduction band edge remains virtually unchanged.

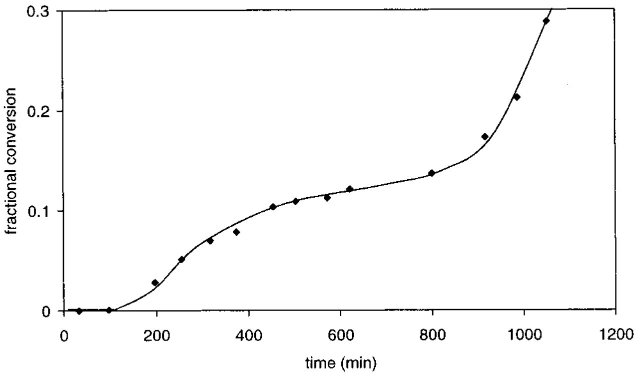


Figure 7. Fractional conversion of methylacrylate vs time. The polymerization is initiated at λ 400 nm employing **2** as photoinitiator.

Polymerization of Methylacrylate Using 1 and 2 as Photoinitiator. The excellent solubility properties of polysilynes **1** and **2** prompted us to investigate their applicability as photoinitiators for radical polymerizations. It should be stipulated that the linear polysilanes represent a unique class of radical photoinitiators.[27] However, they possess two disadvantages. Many representatives only absorb ($\sigma \rightarrow \sigma^*$ transition) at ca. λ 300 nm, which is an undesired wavelength for efficient photoinitiation in many applications. Furthermore, the majority of polysilanes possess apolar alkyl or aryl substituents and are insoluble in pure monomers, such as acrylate derivatives. Although the latter problem was solved by the availability of polar polysilanes,[15] their absorption maximum is still positioned at ca. λ 300 nm.

Photoexcitation of **2** was performed in the visible region of the absorption spectrum (λ 400 nm). Since the extinction coefficient ε is rather low at λ 400 nm, 1.5 wt % of **2** was used as photoinitiator. After an incubation period of ca. 150 min, in which presumably traces of O_2 and other radical quenchers are consumed, the bulk radical polymerization of methylacrylate starts (Figure 7). The progress of radical polymerization follows the conventional characteristics; at a fractional conversion of ca. 0.15 (after 900 min) the Trommsdorff-effect occurs, resulting in a dramatic increase in the conversion rate.[28] The obtained poly(methylacrylate), which was purified by (re)precipitation from THF/CH_3OH, possesses a T_g of 5 °C [analytical SEC; M_w 1.3 × 10^6 ($D = M_w/M_n$ = 1.7)]. This T_g value is in good agreement with that of poly(methylacrylate) [T_g 8 °C[29]] polymerized using conventional photoinitiators. This indicates that the use of polysilyne **2** as photoinitiator does not induce structural defects or cross-linking.

It is noteworthy that, in marked contrast to previously reported results using polysilanes, such as poly(methylphenylsilane), as photoinitiators,[27] no change in molecular weight distribution M_w 1.3 × 10^6 ($D = M_w/M_n$ =

1.7) during the course of the polymerization is observed. In fact the latter result, viz. the nearly constant molecular weight distribution, is characteristic for the occurrence of a proper radical polymerization reaction![28] As a result, after just a short reaction time a high molecular weight polymer is already obtained, and the molecular weight distribution does not change significantly over the course of the polymerization. The fact that, with a polysilyne as photoinitiator, M_w remains constant, whereas in the case of polysilanes M_w markedly changes, is attributed to differences in extinction coefficient ϵ at the applied wavelength. Since for polysilanes ϵ at the UV wavelength maximum ($\sigma \rightarrow \sigma^*$ transition) is in the order of several thousands mol^{-1} L cm^{-1}, polysilyne **2** only exhibits a $\epsilon \leq 10$ mol^{-1} L cm^{-1} at λ 400 nm. Hence, irradiation of a mixture of methylacrylate and **2** will give a homogeneous distribution of radicals throughout the bulk of the reaction mixture. In contrast irradiation of a polysilane leads to an inhomogeneous distribution of radicals which will be predominantly present in the outer layer of the sample, which is exposed to UV radiation.[27]

The photochemical generation of radicals from polysilanes has been studied in detail[21,30] and was shown to be decoupled from the photochemical processes responsible for formation of silylene intermediates. In polysilanes the following wavelength dependence for these two processes was found: whereas irradiation at $\lambda > 300$ nm excites the longest *all-trans* chromophores and, thus, creates only radicals by homolytic Si−Si bond cleavage, irradiation at $\lambda < 300$ nm will excite shorter fragments. Either this short wavelength excitation subsequently can induce the extrusion of a silylene fragment or the exciton can migrate by energy transfer processes to the longer *all-trans* fragments, which subsequently will give radicals.[30] Transient absorption spectra of polysilynes give evidence that a similar radical formation mechanism is present.[24] This is in line with the observation from the above presented photoinitiated polymerization of methylacrylate that, by long wavelength irradiation (λ 400 nm), substantial amounts of radicals are generated. The photochemically induced degradation of polysilynes **1** and **2** is supported by SEC analyses of the polymer solutions after prolonged irradiation; the molecular weight distribution of **1** or **2** dissolved in CH_2Cl_2 (ordinary glass tube) decreased by ca. 50% after exposure to direct sunlight for 12 h. To what extent radical formation competes with the extrusion of silylene fragments during λ 400 nm excitation of **2** is still unclear and is a topic for further investigation.

Conclusions

Nonionic water-soluble polysilynes **1** and **2**, which cannot be prepared with a conventional Wurtz-type coupling with Na in refluxing toluene, are accessible in reasonable yields using C_8K as the reducing agent in THF at 0 °C. In addition an analogue of **1**, viz. polysilyne **3**, which contains a hexoxy instead of a methoxy group as the terminating functionality of the oligo(oxyethylene) substituent, was obtained in a near quantitative yield under similar conditions. The polymers exhibit typical optical characteristics for branched silicon based systems, i.e., a semiconductor-like band in the UV spectrum, which extends from the UV into the visible part of the spectrum, and broad fluorescence excitation and emission bands which have a large Stokes shift. The polysilynes have a markedly shifted onset of oxidation V_i compared to the V_i of the corresponding linear polysilanes.

Aqueous solution of **1** and **2** exhibit thermoresponsive behavior; viz., at the LCST the polymer conformation changes, eventually leading to phase separation. The observation of an LCST concomitant with the fact that the position of the LCST is nearly identical to that found for the corresponding polysilanes provides strong evidence that the polysilyne backbone possesses a hybrid structure with a predominantly one-dimensional overall appearance consisting of linear fragments with small branches and/or incorporated (branched) cyclics, instead of the previously proposed sheetlike[9] and/or hyperbranched/dendritic[10] structures. Additional support for a hybrid structure was given by semiempirical PM3 calculations on a variety of oligomeric model compounds. The PM3 results suggest that Si−Cl moieties incorporated in oligomers are more reactive than monomeric Si−Cl groups. The PM3 calculations also indicate that linear chain extension is preferred over branching.

Due to their excellent solubility properties polysilynes **1** and **2** readily dissolve in regular organic solvents, water and also pure monomers such as methylacrylate. Upon excitation at λ 400 nm of polysilynes **1** and **2**, radicals are generated due to photochemically induced homolytic Si−Si bond cleavage, thus creating an effective photoinitiator; poly(methylacrylate) of high molecular weight was obtained.

The results show that especially the nonionic water-soluble polysilynes **1** and **2** are an exiting class of new materials with remarkable properties that are complementary to those of other silicon-based materials. This renders them interesting candidates for further investigations.

Supporting Information Available: Printout of PM3 archive files of all model compounds presented in the homodesmotic reactions presented in Schemes 2 and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Bianconi, P. A.; Weidman, T. W. *J. Am. Chem. Soc.* **1988**, *110*, 2342.
(2) Furukawa, K.; Fujino, M.; Matsumoto, N. *Macromolecules* **1990**, *23*, 3423.
(3) Walree, C.A van; Cleij, T. J.; Jenneskens, L. W.; Vlietstra, E. J.; van der Laan, G. P.; de Haas, M. P.; Lutz, E. T. G. *Macromolecules* **1996**, *29*, 7362.
(4) Watanabe, A.; Tsutsumi, Y.; Matsuda, M. *Synth. Met.* **1995**, *74*, 191.
(5) Watanabe, A.; Nagai, Y.; Matsuda, M., Suezawa, M.; Sumino, K. *Chem. Phys. Lett.* **1993**, *207*, 132.
(6) Smith, D. A.; Freed, C. A.; Bianconi, P. A. *Chem. Mater.* **1993**, *5*, 245.
(7) Watanabe, A.; Komatsubara, T.; Matsuda, M.; Yoshida, Y.; Tagawa, S. *Macromol. Chem. Phys.* **1995**, *196*, 1229.
(8) Uhlig, W. *Z. Naturforsch.* **1995**, *50B*, 1674.
(9) Bianconi, P. A.; Schilling, F. C.; Weidman, T. W. *Macromolecules* **1989**, *22*, 1697.
(10) Sasaki, M.; Matyjaszewski, K. *J. Polym. Sci. Part A, Polym. Chem.* **1995**, *33*, 771.
(11) Cleij, T. J.; Jenneskens, L. W.; Kluijtmans, S. G. J. M. *Adv. Mater.* **1997**, *9*, 961.
(12) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.
(13) Cleij, T. J.; King, J. K.; Jenneskens, L. W.; Lubberhuizen, W. H.; van Faassen, E. *Polym. Prep.* **1998**, *39* (*1*), 94.
(14) Cleij, T. J.; King, J. K.; Jenneskens, L. W. Manuscript in preparation.
(15) Walree, C. A. van; Cleij, T. J.; Zwikker, J. W.; Jenneskens, L. W. *Macromolecules* **1995**, *28*, 8696.

(16) Cleij, T. J.; Tsang, S. K. Y.; Jenneskens, L. W. *Chem. Commun.* **1997**, 329 and references cited.

(17) Stewart, J. J. P. MOPAC: A Semiempirical Molecular Orbital Program, Version 7.0, 1993.

(18) Details of the synthesis of poly[(4, 7, 10-trioxahexadecyl)-methylsilane], will be reported elsewhere. Salient analytical data: SEC (THF): M_w 3.0 × 10^4 ($D = M_w/M_n = 2.9$). ^{1}H NMR ($CDCl_3$): δ 3.65−3.42 (m, 12H, OCH_2), 1.58 (m, 4H, $SiCH_2CH_2$ and CH_2), 1.29 (m, 6H, CH_2), 0.88 (t, 3H, CH_3), 0.79 (br, 2H, $SiCH_2$), 0.26 (br, 2H, $SiCH_3$) ppm. ^{13}C NMR: δ 74.42, 71.56, 70.68, 70.61, 70.10 (OCH_2), 31.74, 29.66 (CH_2), 26.80 ($SiCH_2CH_2$), 25.81, 22.65 (CH_2), 14.08 (CH_3), 10.42 ($SiCH_2$), −4.19 ($SiCH_3$) ppm. ^{29}Si NMR: δ −31.32 ppm. DSC: T_g −85.2 °C (T_{onset} −90.5 and T_{offset} −80.0 °C).

(19) Yuan, C.-H.; West, R. *Macromolecules* **1998**, *31*, 1087.

(20) In addition, a lower degree of polymerization of **1**, **2**, and **3**, as compared to poly(hexylsilyne), may also affect the extinction coefficients. Whereas for poly(hexylsilyne) analytical SEC suggested a degree of polymerization of ca. 200,[1] for **1**−**3** a degree of polymerization in the range 30−90 was found.

(21) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359 and references cited.

(22) Williams, E. A.; Cargioli, J. D In *Annual Reports on NMR Spectroscopy*; Webb, G. A., ed., Academic Press: London, 1979; Vol. 9, p 221.

(23) Maxka, J.; Chrusciel, J.; Sasaki, M.; Matyjaszewski, K. *Macromol. Symp.* **1994**, *77*, 79.

(24) Watanabe, A.; Miike, H.; Tsutsumi, Y.; Matsuda, M. *Macromolecules* **1993**, *26*, 2111.

(25) Suzuki, H.; Kimata, Y.; Satoh, S.; Kuriyama, A. *Chem. Lett.* **1995**, 293.

(26) Lambert, J. B.; Pflug, J. L.; Ster, C. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 98.

(27) West, R.; Wolff, A. R.; Peterson, D. J. *J. Radiat. Curing* **1986**, 35.

(28) For example see: Cowie, J. M. G. *Polymers: Chemistry & Physics of Modern Materials*, Blacky: Glasgow **1991**, p 60.

(29) Shetter, J. A. *J. Polym. Sci., Polym. Chem. Lett.* **1963**, *1*, 209.

(30) Trefonas, P., III; West, R.; Miller, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 2737.

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