8696 *Macromolecules* **1995,** *28,* 8696−8698

Poly(4,7,10-trioxaundecylmethylsilylene) and Poly(4,7,10,13-tetraoxatetradecylmethylsilylene): Nonionic Water-Soluble Polysilylenes

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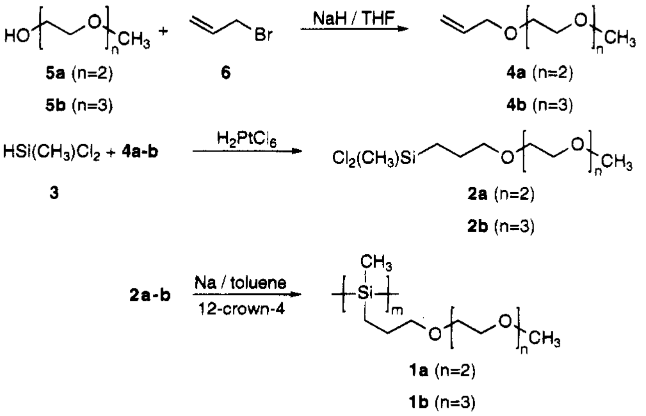
Received July 14, 1995
Revised Manuscript Received October 9, 1995

Polysilylenes, $-[SiRR']_n-$, possess promising properties for application in photonics and electronics.[1] Initially, attention was mainly focused on the study of polysilylenes containing alkyl and/or aryl substituents. Unfortunately, these representatives are only soluble in a limited number of apolar organic solvents. Therefore, there is a growing interest in novel polysilylenes with improved solubility properties.[2] Although this can be achieved by functionalization of their substituents, a drawback is the prerequisite that the monomers should withstand the generally applied severe Wurtz-type coupling polymerization conditions *i.e.*, side chain functionalization is usually done after polymerization. For example, polysilylenes containing trimethylsilylated hydroxyphenyl groups have been prepared, which after deprotection are soluble in basic aqueous solutions.[2] Chloromethylation of poly[(β-phenylethyl)methylsilylene] followed by quaternization with trimethylamine gave access to ionic polysilylenes which are moderately water soluble.[3] In poly[(phenylmethyl)silylene] the phenyl groups can be converted into triflate functionalities, which can be exchanged by other substituents.[4] Recently, alcohol-soluble polysilylenes containing methoxypropyl, ethoxypropyl, and ethoxypentyl side chains, respectively, have been synthesized.[5]

Here we report on the synthesis and characterization of two nonionic *water-soluble* polysilylenes, *i.e.*, poly(4,7,10-trioxaundecylmethylsilylene) (**1a**) and poly(4,7,10,13-tetraoxatetradecylmethylsilylene) (**1b**). The monomers 4,7,10-trioxaundecylmethyldichlorosilane (**2a**) and 4,7,10,13-tetraoxatetradecylmethyldichlorosilane (**2b**) were obtained in two steps from the monomethyl ether of oligo(ethylene) glycols **5a** and **5b**, respectively, *via* a modified literature procedure (Scheme 1).[6] Treatment of the sodium salt of **5a** and **5b** with allyl bromide (**6**) gave allylmethyl diethylene glycol (**4a**, 87%) and allylmethyl triethylene glycol (**4b**, 95%) in excellent yields. Hydrosilylation of **4a** and **4b** using methyldichlorosilane (**3**) and Speiers catalyst (H_2PtCl_6) gave compounds **2a** and **2b** in reasonable yield after purification by fractional distillation under reduced pressure (**2a**, 52%; **2b**, 57%). Their spectral data (^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR) were in line with those previously reported.[6] Monomers **2a** and **2b** were polymerized using Wurtz-type coupling conditions (2 equiv of sodium dispersed in toluene and 12-crown-4 as catalyst).[7] Size exclusion chromatography (SEC) of the crude reaction mixture showed that, besides polymer, a substantial amount of low molecular weight material was formed (Figure 1). As evidenced by ^{29}Si NMR (δ −39 ppm)[8] and FAB-MS ($[M + Na]^+$ ions), the latter primarily contains, besides linear oligomers, five- and six-membered cyclic silanes.[9] These observations are in line with those previously reported[5c,10] for polysilylenes containing polar side groups.

Scheme 1



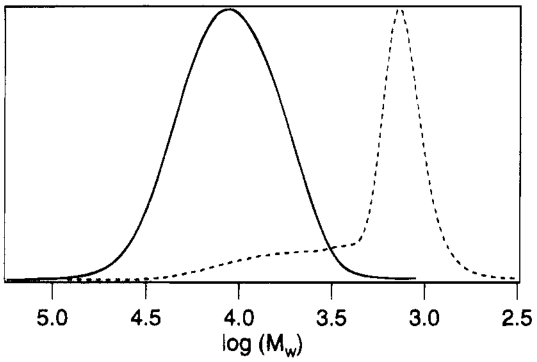


Figure 1. Size exclusion chromatogram of **1b** before (− − −) and after (−) preparative SEC. For **1a**, similar chromatograms were found.

Due to their solubility in both polar and apolar organic solvents, the high molecular weight fraction of **1a** and **1b** could not be isolated and purified by (repeated) precipitation. Hence, **1a** and **1b** were isolated using preparative SEC (isolated yield for **1a** and **1b**, 20%);[11] a degree of polymerization (DP = *m*) of 78 (**1a**) and 61 (**1b**) is estimated (Scheme 1). As an illustration, the SEC chromatogram of **1b** before and after preparative SEC is shown in Figure 1. The ^{1}H NMR and ^{13}C NMR spectra of **1a** and **1b** are in full agreement with the proposed structures and corroborate their polymeric character. Multiple signals (^{1}H NMR) are found for the Si−CH_2 and Si−CH_3 resonances which can be attributed to tacticity.[5c] The ^{29}Si NMR spectra of **1a** and **1b** contain one major resonance at δ −31.5 ppm, in agreement with the ^{29}Si chemical shift observed for the related poly[(methoxypropyl)methylsilylene].[5,12]

Unlike typical poly(dialkylsilylene)s, **1a** and **1b** are sparingly soluble in *n*-hexane (<0.05 mg/mL) but possess reasonable to excellent solubility in solvents such as toluene, tetrahydrofuran, chloroform, methanol, acetonitrile (>100 mg/mL), and water (*ca.* 10 mg/mL).

DSC (heating/cooling rate 10 °C min^{-1}, N_2) revealed that **1a** and **1b** are amorphous polymers; only a glass transition (T_g) centered at −82 (**1a**) and −80 °C (**1b**), respectively, is found. No crystallization phenomena (first-order phase transition) of the methoxy(oxyethylene)propyl chains are discernible in the temperature range −100 to 200 °C. This is corroborated by polarization microscopy, which showed no optical birefringence. Polymers **1a** and **1b** decompose above 250 °C, furnishing a residue of *ca.* 15% w/w at 850 °C (TGA (N_2)).

0024-9297/95/2228-8696$09.00/0

Table 1. Solution Absorption and Emission Characteristics of Polymers 1a and 1b

polymer	solvent	λ_{max} (UV) (nm)	ϵ/Si–Si × 10^{-3} (L mol^{-1} cm^{-1})	λ_{exc} (nm)	λ_{em} (nm)
1a	C_6H_{14}	*a*	*a*	306	332
	$(C_2H_5)_2O$	299	1.8	311	334
	THF	304	3.0	313	336
	CH_3CN	300	3.3	323	337
	C_2H_5OH	299	2.3	311	334
	H_2O	288	2.2	310	333
1b	C_6H_{14}	*a*	*a*	304	331
	$(C_2H_5)_2O$	296	1.2	310	331
	THF	305	2.1	316	338
	CH_3CN	299	1.8	320	335
	C_2H_5OH	296	1.1	310	334
	H_2O	287	2.0	310	334

[a] Due to the low solubility of **1a** and **1b** in *n*-hexane (<0.05 mg/mL), no $\sigma \rightarrow \sigma^*$ transition is discernible in their UV absorption spectra.

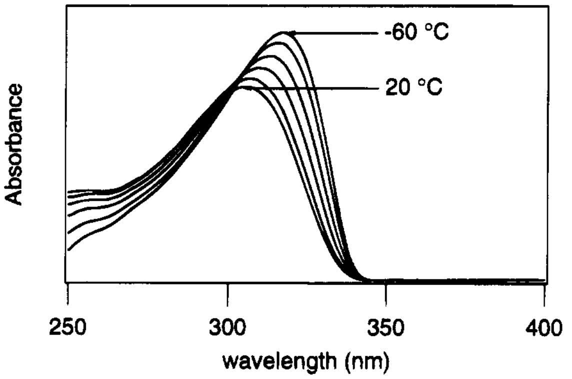


Figure 2. UV thermochromism (solvent THF) of **1b**. For **1a**, a similar behavior was found.

Solution UV absorption spectra of **1a** and **1b** possess the characteristic near-UV $\sigma \rightarrow \sigma^*$ transition with λ_{max} 300 nm, in line with λ_{max} values of methyl/alkyl-substituted polysilylenes (Table 1).[1] With increasing solvent polarity, a hypsochromic shift of *ca.* 10 nm is observed, indicating that conformational changes due to solute–solvent interactions affect the position of λ_{max}. Upon cooling from room temperature to −60 °C, the $\sigma \rightarrow \sigma^*$ transition of **1a** and **1b** (solvent THF) undergoes a continuous bathochromic shift of 12 nm (Figure 2). The absence of an abrupt thermochromic change of the transition, as observed for poly(di-*n*-hexylsilylene),[1] is rationalized using the Schweizer theory of conformation-dependent solute (polymer)–solvent interactions by invoking a slow single-chain order–disorder transition.[13] According to this model, unsymmetrically substituted polysilylenes with high free energies (ϵ) of defect formation, *i.e.*, the energy required to create a *non-trans* defect in a *trans* silicon backbone, will have low coupling constants v_D/ϵ, with v_D describing the solute (polymer)–solvent interaction. Hence, their thermochromism has to be electronically driven.

Solid-state optical absorption spectra of thin films obtained by solution casting of **1a** and **1b** on quartz substrates resemble their solution spectra (T = 26 °C: $\sigma \rightarrow \sigma^*$ transition; λ_{max} (**1a**) 296 nm and λ_{max} (**1b**) 298 nm). No thermochromism is discernible in the temperature range 20–80 °C.

Polymers **1a** and **1b** exhibit characteristic polysilylene solution emission spectra; narrow bands with high intensities and small Stokes shifts (*ca.* 35 nm) are found, and λ_{em} is almost solvent independent (Table 1).[1] Hence, solute–solvent interactions apparently do not influence the conformation of the largest (all-*trans*) segments of the silicon backbone from which fluorescence occurs.

Additional evidence for specific interactions with the 4,7,10-trioxaundecyl side chains was obtained from ^{13}C NMR experiments of **1a** to which 1 equiv of $LiClO_4$ per side chain was added.[14] Especially for the carbon atoms of the oxyethylene units, shifts of their ^{13}C resonances were found, while those of the propyl unit were less affected (cf. also ref 6). Although hitherto the oxyethylene carbon atoms could not be assigned unequivocally, it is apparent that the side chains participate in complex formation. Note that addition of $LiClO_4$ does not influence λ_{max} (300 nm) of the $\sigma \rightarrow \sigma^*$ transition.

In summary, nonionic water-soluble polysilylenes can be prepared. Their optical properties resemble those of asymmetrically alkyl/methyl-substituted polysilylenes. Further experiments to gain insight into their properties and possible application are in progress.

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(6) Wang, L.; Weber, W. P. *Macromolecules* **1993**, *26*, 969. Spectral data: **2a**, ^1H NMR (300.13 MHz, $CDCl_3$) δ 0.75 (s, 3H), 1.11 (m, 2H), 1.71 (m, 2H), 3.36 (m, 3H), 3.41–3.57 (m, 10H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 5.2, 18.3, 22.9, 58.9, 70.2, 70.5, 70.6, 72.0, 72.2; ^{29}Si NMR (59.63 MHz, $CDCl_3$) δ 33.1; **2b**, ^1H NMR (300.13 MHz, $CDCl_3$) δ 0.71 (m, 3H), 1.11 (m, 2H), 1.71 (m, 2H), 3.30 (s, 3H), 3.41–3.60 (m, 14H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 5.1, 18.1, 22.7, 58.9, 70.1, 70.5, 70.6, 70.7, 71.9, 72.3; ^{29}Si NMR (59.63 MHz, $CDCl_3$) δ 33.1.

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(11) After preparative size exclusion chromatography (SEC; Biobeads SX-1, eluent CH_2Cl_2), a monomodal molecular weight distribution was obtained for polymers **1a** and **1b** (analytical SEC; column Shodex KF-804, eluent THF, UV detection 320 nm); **1a**, $M_w = 1.59 \times 10^4$; $D = M_w/M_n = 1.54$; **1b**:, $M_w = 1.51 \times 10^4$; $D = M_w/M_n = 1.43$. Spectral data, **1a**: ^1H NMR (300.13 MHz, $CDCl_3$) δ 0.03, 0.21 (2× br, 3H, $SiCH_3$), 0.44, 0.73 (2× br, 2H, $SiCH_2$), 1.56 (br, 2H, $SiCH_2CH_2$), 3.33 (s, 3H, OCH_3), 3.50–3.60 (10H, OCH_2); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ −4.0, 10.6, 27.0, 59.2, 70.4, 70.8, 70.9, 72.2, 74.6; ^{29}Si NMR (59.63 MHz, $CDCl_3$) δ −31.5; **1b**, ^1H NMR (300.13 MHz, $CDCl_3$) δ 0.02–0.12 (br, 3H, $SiCH_3$), 0.42–0.71 (br, 2H, $SiCH_2$), 1.54 (br, 2H, $SiCH_2CH_2$), 3.33 (s, 3H, OCH_3), 3.50–3.61 (14H, OCH_2); ^{13}C NMR (75.47

MHz, $CDCl_3$) δ −4.3, 10.4, 26.7, 59.0, 69.9, 70.1, 70.5, 70.6, 71.9, 74.0, 74.3; ^{29}Si NMR (59.63 MHz, $CDCl_3$) δ −31.4.

(12) After preparative SEC, an additional very weak ^{29}Si resonance at δ −22 attributable to end groups is discernible for **1a** and **1b**.

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(14) **1a**, ^{13}C NMR (75.47 MHz, CD_3CN) δ −3.7, 11.5, 27.9, 59.0, 70.9, 71.2, 71.3, 72.7, 74.8; **1a** + 1 equiv of $LiClO_4$, ^{13}C NMR (75.47 MHz, CD_3CN) δ −3.7, 11.1, 27.2, 59.3, 69.5, 70.3, 70.6, 71.7, 74.7.

MA9510146