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Spectroscopic Evidence of Si−H End Groups in Dialkylpolysilanes Synthesized via Wurtz Coupling

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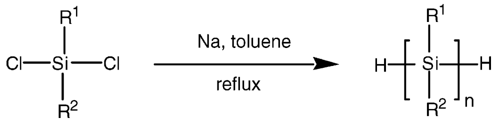
ABSTRACT: We demonstrate unambiguously the presence of Si−H end groups in σ-conjugated polysilanes **1**−**5**, with alkyl groups as side chains synthesized via Wurtz coupling by means of IR, ^{1}H, ^{29}Si, and {^{1}H−^{29}Si} heteronuclear correlation NMR spectroscopy. However, there were no detectable Si−Cl, Si−OH, and Si−OR groups that would be associated with end groups of polysilanes. This implies that either such groups are not present or are too small to be detectable by IR and NMR spectra. The presence of Si−H end groups in low as well as high molecular weight polysilanes suggests the sequential existence of silyl radicals and anions in Wurtz coupling reactions and termination reaction involving a radical coupling in the solvent phase as previously described.

Introduction

One-dimensional silicon catenated polysilanes are promising candidates for constructing building blocks for molecular electronics and optoelectronics due to their remarkable semiconducting properties.[1,2] One of the fundamental goals in designing of molecular electronic devices based on polymer chains is the immobilization of isolated single chains to a solid surface and the control of their structures. Only a few reports are appeared recently on immobilization of polysilanes on solid surfaces.[3] The tethered polymers were achieved by the reaction of polysilanes with a silyl anion at the terminus with lithium as a countercation and reactive sites on solid substrate surface. Such polysilanes were synthesized either by anionic polymerization of masked disilenes or by Si−Si main-chain scission reaction with alkyllithium. However, to obtain end-grafted polysilanes with desired molecular weight, polydispersity, and main-chain rigidity, several tedious synthetic steps and extremely dry conditions are required.

The main-chain rigidity and conformation of polysilanes strongly depend on the proper choice of side chains and branching at β or γ positions.[4,5] Wurtz coupling reaction is known to be the most widely used method for the synthesis of high molecular weight rodlike, flexible, and semiflexible polysilanes in appreciable yields. The identification of end groups of polysilanes obtained by this synthetic approach, however, is still not very clear. The chlorine end functionalization of α,ω-dichloropolymethylphenylsilane was reported on the basis of elemental analysis of chlorine and ^{29}Si NMR spectroscopy while the presence of Si−H end groups of poly(3,3,3-trifluoropropylmethylsilane), synthesized via Wurtz coupling, was postulated on the basis of the IR spectrum.[6,7] Here we demonstrate the presence of Si−H as the end groups unambiguously in some of the earlier reported alkyl-substituted polysilanes,[1,7,8] $-(R^1R^2Si)_n-$ [where $R^1 = CF_3(CH_2)_2$, $R^2 =$ Me (**1**); $R^1 = n$-$C_{10}H_{21}$, $R^2 = -(CH_2)_3CH(CH_3)_2$ (**2**); $R^1,R^2 = n$-Hex (**3**); $R^1 = n$-Pr, $R^2 =$ Me (**4**); $R^1 = n$-$C_{10}H_{21}$, $R^2 =$ (S)-$CH_2CH(CH_3)CH_2CH_3$ (**5**)], synthesized via Wurtz coupling, by IR, ^{1}H, ^{29}Si, and {^{1}H−^{29}Si} heteronuclear correlation NMR spectroscopy (Scheme 1). The presence of Si−H end groups in the rigid and flexible polysilanes may offer a simple and convenient way to immobilize single polymer chains on various semiconducting and conducting solid surfaces, as compared to the existing methods for end-grafted polysilanes.[3]

Scheme 1. Synthetic Scheme of Polysilanes 1−5



$$Cl-SiR^1R^2-Cl \xrightarrow[\text{reflux}]{\text{Na, toluene}} H-[SiR^1R^2]_n-H$$

Experimental Section

Sample Preparation. All the reactions were carried out in dried glassware under a dry nitrogen atmosphere using Schlenk techniques. The polysilanes reported in this paper were synthesized via Wurtz coupling from their corresponding dichlorosilanes with sodium as reported earlier.[1,7,8] After the polymerization, the reaction mixture was filtered through a 2 μm Teflon filter under nitrogen gas. The obtained polysilanes were repeatedly fractionated in toluene solution by careful successive addition of 2-propanol, ethanol, and methanol. The white precipitates were collected by centrifugation and dried overnight at 60 °C in a vacuum.

Measurements. Infrared spectra were routinely obtained as thin films on a Horiba FT-730 infrared spectrometer. ^{1}H and ^{29}Si NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-LA 400 NMR spectrometer at frequencies of 400 and 79.6 MHz, respectively. The {^{1}H−^{29}Si} heteronuclear correlation NMR spectra were recorded using a standard pulse sequence with a relaxation delay of 5 s for each of the 512 t_1 experiments. Chemical shifts were referenced to internal tetramethylsilane. Molecular weight, polydispersity, and on-line absorption spectra of polysilanes were recorded on a Shimadzu A 10 series HPLC apparatus with photodiode array detector. The average molecular weights of polysilanes were measured relative to polystyrene standards in tetrahydrofuran solution. The degree of polymerization was calculated on the basis of number-average molecular weight (M_n).

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Table 1. IR, ^{1}H, ^{29}Si NMR, and GPC Data of Polysilanes 1−5

polysilanes	IR[a] (cm^{-1})	^{1}H NMR[b] (ppm)	^{29}Si NMR (ppm)	M_n (DP)[c]	PDI
1	2098	3.45−3.82	−31.4 (Si-backbone); −38.6 (end group)	3010 (21)	1.35
2	2086	3.44−3.72	−27.7 (Si-backbone); −28.2 (end group)	3640 (14)	1.21
3	2079	3.42−3.75	−24.5 (Si-backbone); −26.2 (end group)	13200 (67)	2.06
4	2084	3.32−3.68	−32.4 (Si-backbone)[d]	29200 (340)	2.12
5	2086	3.52−3.71	−22.5 (Si-backbone)[d]	7100 (30)	1.12
				11500 (48)	1.11
				12300 (51)	1.21
				16700 (70)	1.19
				50200 (209)	1.18
				61800 (257)	1.24

[a] ν_{Si-H}. [b] Chemical shift values of Si−H protons. [c] Molecular weights determined by gel permeation chromatography (GPC) and relative to polystyrene standards: eluent, tetrahydrofuran; 30 °C, and degree of polymerization (DP) were calculated on the basis of M_n. [d] End groups were not detected due to main-chain rigidity of rodlike nature along with broad line widths and high molecular weight.

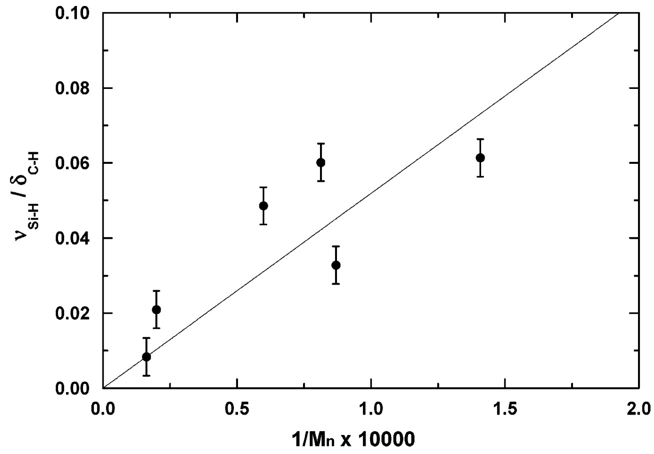
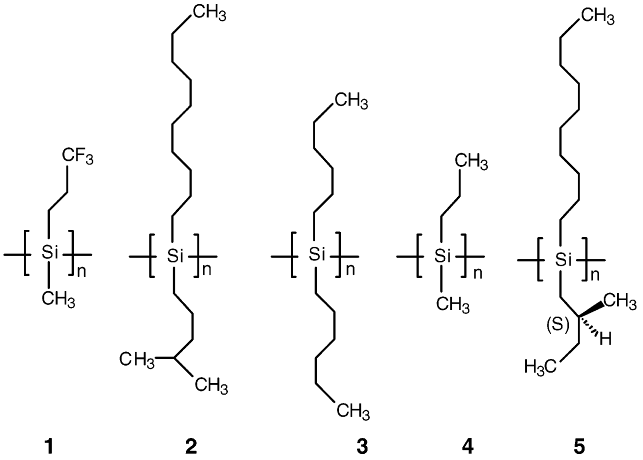


Figure 1. Molecular weight dependency of normalized intensities of ν_{Si-H} at 2086 cm^{-1} by δ_{C-H} at 1457 cm^{-1} of **5** with different molecular weights.

Scheme 2. Structures of Polysilanes 1−5



Results and Discussion

The fractionated samples were used for the characterization of polysilanes **1**−**5** (Scheme 2). IR spectra of **1**−**5** show a weak absorption band due to Si−H stretching in the region 2079−2098 cm^{-1} along with other characteristic bands due to aliphatic side chains.[7] We were not able to detect bands arising from other possible end groups of polysilane, e.g., ν_{Si-OH} and ν_{Si-OR} (R = alkyl groups), as these bands are normally expected to be very strong due to the ionic character of the Si−O bond. The presence of terminal Si−H groups in alkyl-substituted polysilane synthesized via Wurtz coupling is expected to arise due to silyl radical abstraction of hydrogen from solvent.

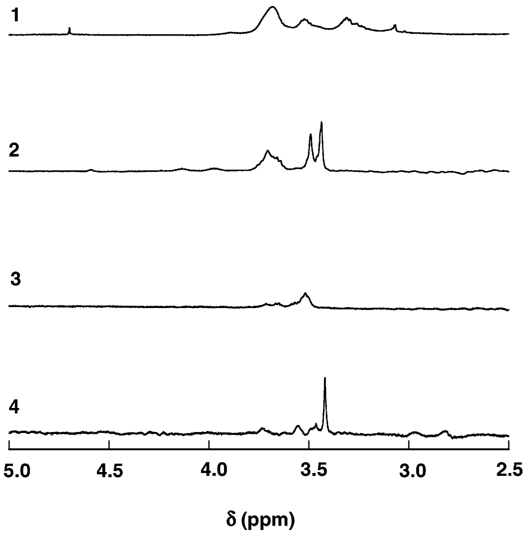


Figure 2. ^{1}H NMR spectra (400 MHz) of **1**−**4** in Si−H region (in $CDCl_3$ at room temperature).

Figure 1 shows the molecular weight dependency of the normalized intensity of the ν_{Si-H} band (2086 cm^{-1}) of **5** by the C−H bending vibration (δ_{C-H}) at 1457 cm^{-1}. The normalized intensity tends to increase with the inverse of the number-average molecular weight of the polysilane, suggesting the presence of Si−H groups at the end of the polymer chain. The IR, ^{1}H, and ^{29}Si NMR spectral data along with GPC data of **1**−**5** are summarized in Table 1.

Additional evidence in favor of the presence of SiH end groups comes from the ^{1}H and ^{29}Si NMR spectra of polysilanes. The ^{1}H NMR spectra of **1**−**5** reveal two distinct resonances in the region δ 0.2−2.1 and 3.3−3.8, which are attributed to alkyl protons associated with the side chain and Si−H end groups of the polysilanes, respectively. The chemical shift values of Si−H protons are consistent with earlier reported alkyl-substituted poly(hydrosilanes).[9]

Figure 2 shows the ^{1}H NMR spectra of **1**−**4** in the Si−H region. Polysilane **1** was used for calculating the degree of polymerization, as the number of protons in the side chain is minimum among other polysilanes used for study. The integrated ratios of Si−H and other aliphatic protons in **1** indicate the presence of two Si−H groups, suggesting the degree of polymerization to be nearly 17, which is slightly lower than that calculated on the basis of $M_n = 3010$, obtained from GPC. Although the ^{1}H NMR spectra reveal the presence of Si−H signals for low as well as high molecular weight polysilanes (M_n = 30 000), the integration ratio was found to be incon-

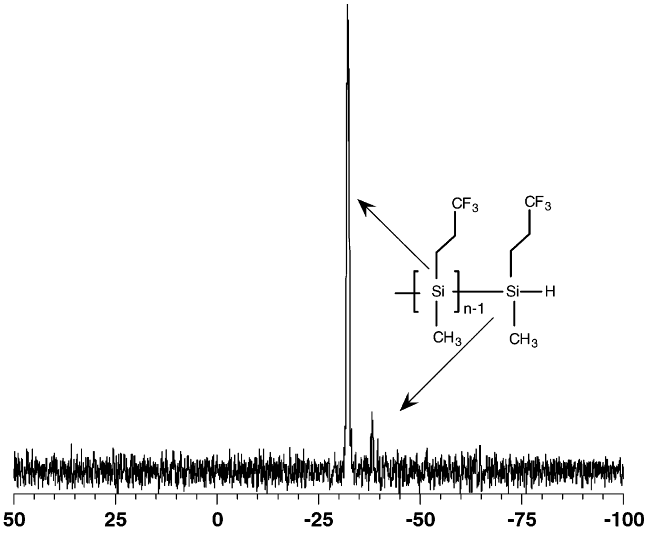


Figure 3. $^{29}Si\{^1H\}$ NMR spectrum of **1** in THF-d_8 at 25 °C.

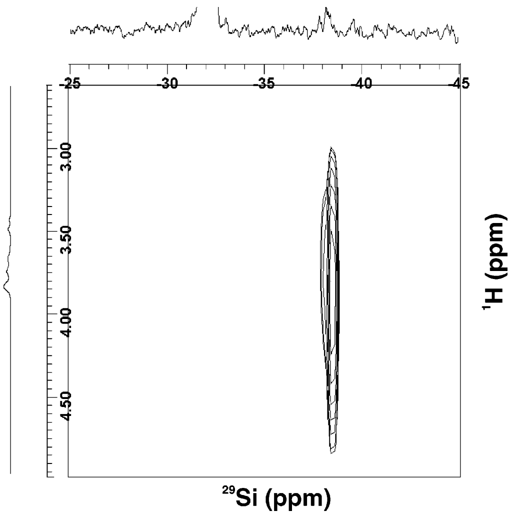


Figure 4. $\{^1H-^{29}Si\}$ heteronuclear correlation NMR spectrum of **1 (**in THF-d_8 at 25 °C). The spectrum was recorded using a standard pulse sequence with relaxation delay of 5 s for each of the 512 t_1 experiments.

sistent with increase in molecular weight as the ratio of Si−H and alkyl protons becomes very small.

Figure 3 shows the ^{29}Si NMR spectrum of **1** in THF-d_8. The spectrum reveals a broad resonance centered at δ −31.4, corresponding to the silicon backbone and one at −38.6 ppm characteristic of Si−H chain ends of polymer. However, there are no detectable resonances due to Si−OR and Si−Cl groups in the ^{29}Si NMR spectrum at around 10.0−25.0 ppm. The ^1H and ^{29}Si NMR spectral assignments have been further confirmed by two-dimensional heteronuclear correlation $\{^1H-^{29}Si\}$ NMR spectrum of **1**, which shows a dominant cross-peak at −38.6/3.8, revealing the presence of Si−H end groups, as shown in Figure 4. Similar experiments were carried out for **2** and **3**, while end groups were not detected in the ^{29}Si NMR spectra of **4** and **5** due to main-chain rigidity of rodlike nature along with broad line widths and/or high molecular weight. We could not observe the Si−Cl, Si−OH, and Si−OR end groups of **1**−**5** in IR and NMR spectra. These experiments suggest that either such groups are not present or are too small to be detectable by IR and NMR spectroscopy.

It is now understood that the polymodal molecular weight distributions that result from the Wurtz-type synthesis of polysilanes most probably do not arise from variations in molecular mechanism.[10] However, the presence of Si−H end groups in the polysilanes of the present study may throw further light on the nature of the chain carriers in this reaction. Silyl radicals, silyl anions, silyl anion-radicals, and silylenes have all been proposed as chain carriers at one time or another. Of these, the most probable intermediates are silyl anions and radicals. The effect of additives like 15-crown-5 and cryptands on the molecular weight of polysilanes reveals an importance of the silyl anion as an intermediate,[11] though Zeigler et al. previously showed the involvement of radical intermediates by their control experiments.[12] Computational studies on oligosilanes also suggested that silyl radicals at the end position of the oligomeric chain are energetically preferred.[13] It is assumed that silyl radicals and anions exist sequentially rather than simultaneously.[14] Our observation of Si−H end groups in low as well as high molecular weight polysilanes with alkyl side groups may support this presumption. The silyl radical may either abstract a hydrogen from the solvent resulting in Si−H end groups or accept an electron and be converted into a radical anion that can participate in chain extension. The Si−Cl end groups of poly(methylphenylsilane) are presumably due to the silyl anion as an intermediate stabilized with phenyl groups.[6] We assume that substituents on polysilanes play an important role in the mechanism of Wurtz coupling, and the radical species are the key intermediate for alkyl-substituted polysilanes synthesis.

The reaction chemistry of Si−H at the molecular level is very rich and well established.[15] The terminal Si−H groups are more air and moisture stable than Si−Cl and Si−OMe. This knowledge can be utilized to transformation of Si−H end groups of polysilanes to various functional groups (e.g., OR, NR, SR, or Cl) and would be of interest to expand the scope of end-group functionalization of polysilanes. Thus, the present study may be one of the milestones in the development of molecular devices based on semiconducting polysilanes. The studies on the immobilization of rodlike polysilanes on solid surface (e.g., mica, quartz, ITO, Au, etc.) by using the chemical reactivity of Si−H end groups are in progress and will be reported in a forthcoming paper.

Conclusions

We demonstrated the presence of Si−H end groups in the alkyl-substituted polysilanes **1**−**5** by means of IR and 1D and 2D NMR spectroscopy. The presence of Si−H end groups in high as well as low molecular weight polysilanes suggests the presence of a radical as one of the main intermediates in the dialkyl-substituted polysilanes.

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Supporting Information Available: IR spectrum of **1** exhibiting the Si−H end groups of polysilanes. This material is available free of charge via the Internet at http://pubs.acs.org.

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