*J. Am. Chem. Soc.* **1998,** *120,* 7367−7368 7367

# Synthesis and Characterization of End-Grafted Polysilane on a Substrate Surface

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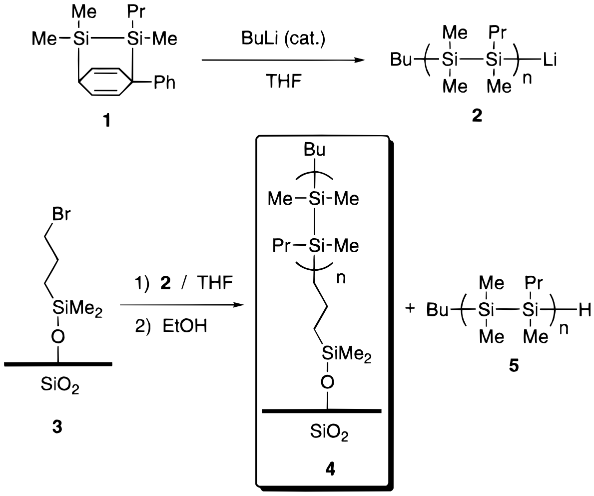
*Received March 10, 1998*

Polysilanes, which are linear Si-catenated polymers, exhibit unique electronic, photochemical, and optical properties resulting from the delocalization of Si−Si $\sigma$-electrons along the polymer backbone.[1] The direct observation and electronic measurement of individual polysilane molecules are currently of great interest both for a basic understanding of the physical properties of one-dimensional semiconductors and for the development of novel devices with unusual electronic and optical properties on a molecular scale.[2] For such investigations, it is important to fix the target polysilane molecules on suitable substrates homogeneously and extensively with the required molecular density. There are basically two recognized methods of accomplishing this. One is adsorption by means of the attractive interaction between the side chains and the substrate surface.[3] The other is to attach one end of the polymer main chain to the surface. This type of polymer, known as a "tethered polymer", has been well studied.[4] Tethered polymers have various morphologies, and an end-grafted polymer, which is covalently bonded to a substrate surface, can be prepared by the one-to-one reaction of end-functionalized polymers with a density-controlled reactive site on the surface. However, this type of polysilane has not been reported until now. The end-grafted polysilane not only has a new morphology but also represents a new class of tethered polymer which has a variety of electronic properties based on the backbone. The corresponding end-grafted polysilane will be well characterized by UV spectroscopy since polysilanes exhibit an intense $\sigma-\sigma^*$ transition strongly related to the conformation of their backbone. Herein, we report the density-controllable synthesis and UV spectroscopic characterization of end-grafted polysilane molecules on quartz substrates. We describe their conformational features without a solvent and in poor and good solvents, as well as their noticeable solvatochromism. To our knowledge, this is the first characterization of a tethered polymer by UV spectroscopy.

We prepared the end-grafted polysilane **4** by the reaction between the end-functionalized polysilane and the substrate surface with homogeneous and extensively distributed reactive anchors. In this study, polysilanyllithium **2** formed by the anionic polymerization[5] of masked disilene **1** and (3-bromopropyl)dimethylsilylated quartz surface **3** were employed, respectively.[6] We chose one propyl and three methyl groups on silicon atoms of **1** that were as small as possible but which maintained the solubility of the resulting polymer because longer side chains have a greater effect on the conformational behavior of polysilanes.[7] Substrates **3** with reactive anchor ratios of 100, 75, 50, 25, and 0% were prepared.[8] All the substrates were dipped for 1 min in a THF solution of polysilanyllithium **2** obtained by the anionic polymerization of **1** under inert atmosphere at room temperature.[9] The large excess of **2** was quenched with ethanol, which affords hydrogen-terminated free polysilane **5**.[10] The resulting substrates were then washed with THF, ethanol, and finally toluene.



UV spectra of the resulting substrates are shown in Figure 1 together with that of a spin-coated film of **5**. Each substrate has an absorption band peaking at 330 nm except for the one without the reactive anchors. Because this absorption corresponds to that of **5**, polysilane molecules equivalent to **5** with $M_n = 17\,000$ must be present on each substrate. This absorbance did not decrease after leaving the substrate in toluene in the dark overnight. The absorbance of each substrate is directly proportional to the ratio of the reactive anchor. These results clearly confirm that these polysilane molecules are covalently bonded to the substrate through propyldimethylsilyl groups. We also show that the

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[1] For reviews of polysilane polymers, see: (a) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359−1410.

[2] There have been two reports on monomolecular images of polysilanes obtained using STM and AFM: (a) Gröppel, M.; Roth, W.; Elbel, N.; von Seggern, H. *Surf. Sci.* **1995**, *323*, 304−310. (b) Ebihara, K.; Koshihara, S.; Yoshimoto, M.; Maeda, T.; Ohnishi, T.; Koinuma, H.; Fujiki, M. *Jpn. J. Appl. Phys.* **1997**, *36*, L1211−L1213.

[3] For this class of polysilanes, Langmuir−Blodgett monolayers of polysilanes with polar functionalized side chains have been reported: (a) Yoshida, M.; Seki, T.; Nakanishi, F.; Sakamoto, K.; Sakurai, H. *Chem. Commun.* **1996**, 1381−1382. (b) Yoshida, M.; Nakanishi, F.; Seki, T.; Sakamoto, K.; Sakurai, H. *Macromolecules* **1997**, *30*, 1860−1862. (c) Seki, T.; Tohnai, A.; Tanigaki, N.; Yase, K.; Tamaki, T.; Kaito, A. *Macromolecules* **1997**, *30*, 1768−1775.

[4] For reviews of tethered polymers, see: (a) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31−71. (b) Szleifer, I.; Carignano, M. A. *Adv. Chem. Phys.* **1996**, *94*, 165−260.

[5] (a) Sakamoto, K.; Obata, K.; Hirata, H.; Nakajima, M.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 7641−7643. (b) Sakamoto, K.; Yoshida, M.; Sakurai, H. *Macromolecules* **1990**, *23*, 4494−4496. (c) Sakamoto, K.; Yoshida, M.; Sakurai, H. *Macromolecules* **1994**, *27*, 881−882. (d) Sakamoto, K.; Yoshida, M.; Sakurai, H. *Polymer* **1994**, *35*, 4990−4997.

[6] It is well-known that silyl anions are readily alkylated by the coupling reactions with primary alkylhalides. (a) Corriu, R. J. P.; Guerin, C. *J. Chem. Soc., Chem. Commun.* **1980**, 168−169. (b) Allred, A. L.; Smart, R. T.; Van Beek, D. A., Jr. *Organometallics* **1992**, *11*, 4225−4230. See also references therein.

[7] Fujiki, M. *J. Am. Chem. Soc.* **1996**, *118*, 7424−7425.

[8] The surface derivatization is as follows. Prior to silylation, 1.8 cm × 2.5 cm quartz substrates were dipped in a 1:1 mixture of 30% $H_2O_2$ and concentrated $H_2SO_4$ overnight followed by repeated rinsing with distilled water and drying at 80 °C for several hours. Each substrate was heated under reflux in 0.2 mol/L solutions of (3-bromopropyl)dimethylchlorosilane and/or butyldimethylchlorosilane in dry toluene overnight. The substrates were removed from the solution, rinsed throughly with toluene and acetone, and dried in air at room temperature.

[9] Monomer **1** was prepared by the reaction of 1,2-dichloro-1-propyl-1,2,2-trimethyldisilane and lithium biphenylide in THF in 77% yield as a 6:4 mixture of two regio isomers (bp 110 °C/0.1 Torr, mp 43−57 °C). A 100-mL three-necked flask, equipped with a magnetic stirrer, a glass stopper (24 mm $\phi$), a rubber septum, and a three-way stopcock, was dried and filled with argon. A solution of **1** (2.0 g, 6.7 mmol) in dry THF (25 mL) was placed in the flask. A hexane solution of *n*-BuLi (0.23 mmol) was added to the solution at room temperature. A dark red solution of **2** was obtained within 1 min. The five silane coupled substrates were put into the solution at room temperature all together. After 1 min, a few drops of ethanol was added to quench the large excess of **2**.

[10] Polysilane **5** was precipitated from ethanol in 60% yield. It is highly soluble in such common solvents as THF, toluene, and hexane. The molecular weight distribution of **5** was determined by GPC, calibrated by polystyrene standards, with THF as the eluent: $M_n = 17\,000$, $M_w/M_n = 1.2$.

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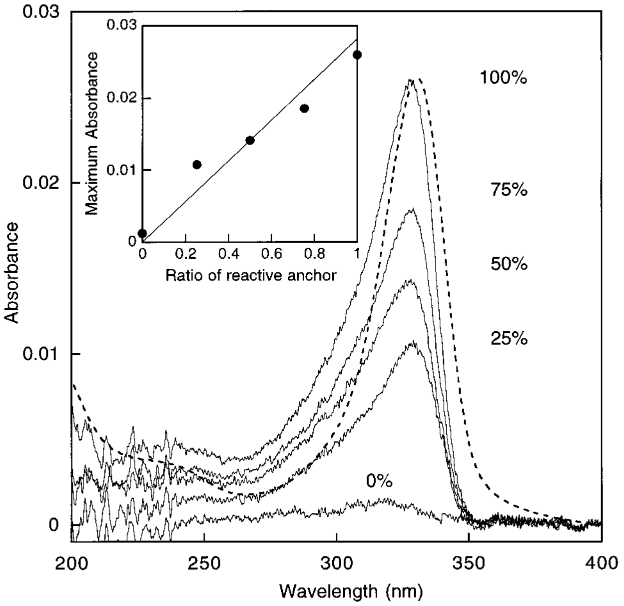

**Figure 1.** UV spectra of **4** with reactive anchor ratios of 100, 75, 50, 25, and 0% (solid lines) and UV spectrum of a spin-coated film (thickness of 260 Å) of **5** (dotted line). The absorbance of the spin-coated film of **5** is normalized. The inset shows the plot of the maximum absorbance vs the ratio of the reactive anchor.

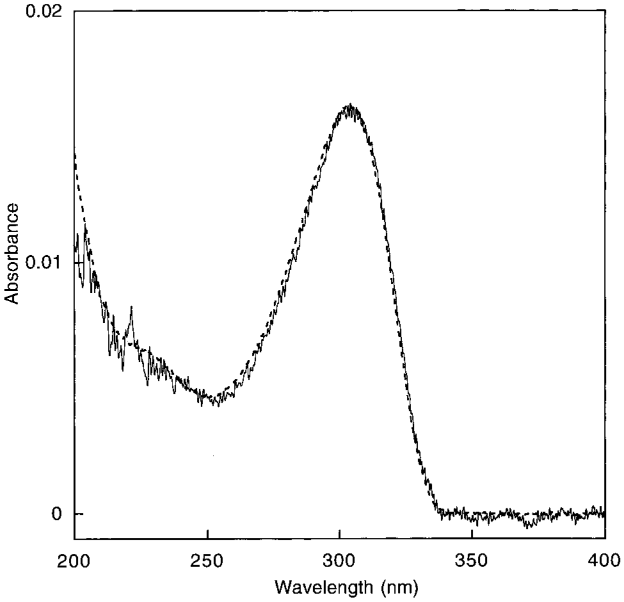

**Figure 2.** UV spectra of **4** dipped in isooctane (solid line) and polysilane **5** in isooctane solution (dotted line). Absorbance of the solution of **5** is normalized.

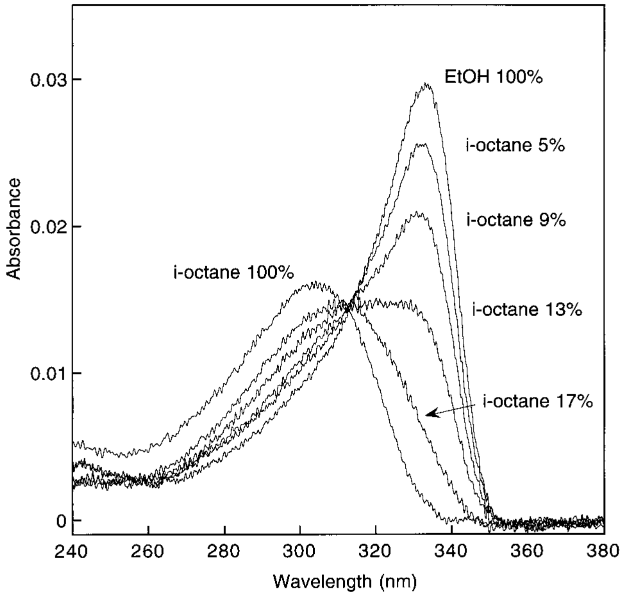

**Figure 3.** UV spectra of **4** dipped in isooctane/ethanol cosolvents with a variety of volume ratios.

molecular density can be controlled by varying the reactive anchor ratio on the substrate surface. The density is estimated to be about $10^{-11}$ mol cm$^{-2}$.[11] This value is consistent with the reported values (typically, $10^{-10}$ mol cm$^{-2}$) for transition metal complexes bonded to functional silane coupled quartz substrates in a similar manner.[12]

A particular advantage of this end-grafted polysilane is that it can be measured in any solvent without elution. The UV spectrum of **4** dipped in isooctane, which is a good solvent for **5**, is shown in Figure 2 with that of **5** in a dilute isooctane solution. The two spectra are identical, both peaking at 304 nm. This result indicates that the conformational feature of **4** is the same as that of the isolated fully solvated free molecules in solution. Furthermore, **4** exhibits noticeable and fully reversible solvatochromism in ethanol/isooctane cosolvents as shown in Figure 3.[13] The spectrum of **4** in pure ethanol, which is a poor solvent, is almost the same as that without a solvent, but an abrupt broadening and blue shift are caused by increasing the ratio of isooctane. This chromism can be well recognized as resulting from the fact that the ordered conformation, which is favorable to $\sigma$-conjugation, is gradually being disordered and becoming random with the increasing isooctane solvation. This conformational disordering is very sensitive to the amount of isooctane, and a full transformation is almost achieved by the addition of 20% of isooctane. The absorption of the ordered phase in **4** is independent of the density of the molecules on the surface, as shown in Figure 1. In addition, **4** exhibits thermochromism similar to the solvatochromism, whereas the solid film of **5** does not show it.[14] Consequently, the ordered structure in **4** results from the intramolecular collapse of the polymer main chain. These end-grafted polysilane molecules exhibit little intermolecular interaction, that is, they behave as isolated free molecules. This type of sample is thus expected to be extensively applicable to the determination of polysilane properties on a monomolecular level. We are currently undertaking the direct determination of these properties on various types of substrate made of semiconductive and conductive materials including Si and Pt. Our results will be reported in a forthcoming paper.

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(11) The density of $10^{-11}$ mol cm$^{-2}$ was estimated by using the absorbance of **4** and the average $M_n = 17\,000$ and the molar extinction coefficient $\epsilon = 5400$ per Si unit for **5**. The distances between the polysilane molecules are estimated to be 30−40 Å on average. This value is shorter than the presumed polymer length of 460 Å estimated from their average molecular weight in a trans-zigzag conformation.

(12) (a) Paulson, S.; Morris, K.; Sullivan, B. P. *J. Chem. Soc., Chem. Commun.* **1992**, 1615−1617. (b) Liang, Y.; Schmehl, R. H. *J. Chem. Soc., Chem. Commun.* **1995**, 1007−1008. (c) Zhou, M.; Laux, J. M.; Edwards, K. D.; Hemminger, J. C.; Hong, B. *Chem. Commun.* **1997**, 1977−1978.

(13) This is the first example of solvatochromism in a polysilane with no functional groups. There have been only two reports on the solvatochromism of polysilanes with ethereal functional side chains. (a) Miller, R. D.; Sooriyakumaran, R. *Macromolecules* **1988**, *21*, 3120−3122. (b) Oka, K.; Fujiue, N.; Dohmaru, T.; Yuan, C. H.; West, R. *J. Am. Chem. Soc.* **1997**, *119*, 4074−4075.

(14) Thermochromism of solventless **4** was measured in the 200−340 K region. The absorbance increased by 40% without shifts at 200 K, while it decreased by 50% with a blue shift of 13 nm at 340 K. On the other hand, the absorbance of the solid film of **5** only varied within a 10% range without shifts in the same temperature region. The crystalline packing in the solid state should be tight as a result of the small side chains. Further details will be discussed elsewhere.