Polysilane Bearing "Sulfide Tripod" Terminus: Preparation and Selective Chemisorption on Gold Surface

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Research on surface-grafted polymer has been drawing much attention both experimentally and theoretically for a couple of decades.¹ The grafted polymer in a high grafting density regime is often called polymer brush and well studied for the purpose of, for instance, surface modification. On the other hand, the grafted polymer in a low density regime is useful for observing structures and properties of the polymers at the single molecule level. We have proposed the end-graft technique for fixing single polymer chains individually on a solid surface and have demonstrated the usefulness of this technique using polysilanes.² We successfully visualized a variety of single molecular and supramolecular structures of polysilane molecules by using our endgrafted polysilane samples.³ Polysilanes have a semiconducting nature based on the σ -conjugation⁴ and exhibit such features as hole mobility⁵ and electroluminescence.⁶ Thus, the observation of those physical properties by using the single polysilane molecule would be also of great interest.

We have achieved the syntheses of end-grafted polysilanes on solid surfaces with the hydroxyl (-OH) and hydrosilyl (Si-H) groups. Our aim in this paper is to synthesize end-grafted polysilane on metal surface. Increasing the variety of surfaces is important for research on grafted polymer. It would be also important for studying electronic interactions between such functional polymers of polysilane and the conductive metal surface. We chose gold as the metal, because chemisorption between gold and thiol has been extensively studied and is useful for bonding molecules to the gold surface. A self-assembled monolayer (SAM) on a gold surface is one of the most important systems.⁸ The chemisorption is also quite selective⁹ so that the onepot synthesis of a gold-thiol bond and a carboxyl acidindium tin oxide bond has been proposed and demonstrated.9a

In this paper, we synthesize polysilane with a "sulfide tripod" terminus and demonstrate the selective chemisorption of the polysilane on a gold surface. As for a similar class of linker molecule, a thiol tripod linker with an amino functional group has been prepared and used for an initiator of polypeptide synthesis on a gold surface.¹⁰ The linker we designed here has a halogenated alkyl functional group. This enables us to introduce the sulfide tripod terminus to a semiconducting polymer of polysilane. We show that the chemisorption on a gold surface occurs at the sulfide tripod terminus by means of UV absorption spectroscopy. The chemi-

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Chart 1. Synthesis Route of Polysilane Bearing Sulfide Tripod Terminus



sorbed polysilanes are also confirmed by atomic force microscopy (AFM) that clearly visualizes single molecular structures of the polysilane on a gold surface.

$$\begin{array}{c} \begin{array}{c} R^{1} \\ -Si \\ R^{2} \end{array} \\ \begin{array}{c} R^{2} \end{array} \\ n \end{array}$$
 1: $R^{1} = CH_{3}, R^{2} = n - C_{3}H_{7} \\ 2: R^{1} = n - C_{18}H_{37}, R^{2} = i - C_{4}H_{8} \end{array}$

We used two polysilanes, poly(methyl-*n*-propylsilane) (1) and poly(isobutyl-*n*-octadecylsilane) (2). Both are alkyl-substituted polysilanes, but their backbone rigidities are significantly different from each other.¹¹ The strategy for synthesizing **1b** and **2b** is to modify the reaction that we have proposed (Chart 1). We use the reaction between polysilane with a silyl anion in its terminus, **1a** and **2a**, and primary alkyl bromide with a sulfide tripod, **3**. We synthesized **1a** by the living anionic polymerization of the corresponding masked disilene^{2a,12} and **2a** by the scission reaction of **2** with lithium 4,4'-di-*tert*-butylbiphenylide.^{3b}

We examined the chemisorption of **1b** and **2b** on a gold surface and confirmed it by means of UV absorption spectroscopy. The UV absorption band, which is assigned to the σ - σ * transition of the silicon backbone of **1**,^{4a} was observed only from the combination of **1b** with a gold surface as shown in Figure 1a. We did not see any absorption band from the other two samples. This indicates that the interaction, including physisorption and chemisorption, between 1b and an SiO₂ surface and between **1** and a gold surface or an SiO₂ surface is weak and cannot withstand the washing processes we employed. The results clearly show that chemisorption occurred only between the sulfide terminus of **1b** and the gold surface. Identical results were also obtained from **2** and **2b** as shown in Figure 1b, which further confirms the selective chemisorption of the sulfide tripod on a gold surface.

Although the sulfide group is known to chemisorb on a gold surface,¹³ the process seems to be slower and less effective than with the thiol group.¹⁴ Our present results indicate that the bond remains stable during our solvent washing processes at room temperature. Three sulfides on a terminus might help the stabilization of chemisorbed bonds.¹⁵

Figure 2 shows AFM topographic images of a gold surface with **1b** and **2b** chemisorbed on a gold surface formed on an Si(111) wafer. With the **1b** sample, we



Figure 1. UV absorption spectra of sample substrates: (a) poly(methyl-*n*-propylsilane), (b) poly(isobutyl-*n*-octadecylsilane). Au/SiO₂ indicates a quartz substrate with a gold surface on one side.



Figure 2. AFM topographic images (1000 nm \times 1000 nm) of a gold surface (deposited on a flat NH₄F-treated Si(111) surface) with **1b** (left) and **2b** (right) chemisorbed. The images were recorded in air at room temperature, using the tapping mode.

observed dots about 5 nm high and several tens of nanometers in diameter that covered the surface densely and homogeneously. This AFM image is clearly distinguished from those of a bare gold surface and a gold surface dipped in a solution of 1 (without the chemisorbed polysilane), both of which were observed as much flatter surfaces. Each dot corresponds to the collapsed structure of a **1b** single molecule chemisorbed on the surface at the terminus. The collapsed structure is a common structure for an end-grafted flexible polymer under poor solvent conditions including the air condition.^{1,3a} By contrast, **2b** was observed as ropes on the gold surface. Polysilane **2** is a semiflexible polysilane, whose main chain is very rigid.^{3b,11} The rope images therefore represent the rigidity of 2. The nature of 2, namely that it is stretched over the substrate, would

be convenient for further study of conductivity at a single molecular level.

In summary, we synthesized polysilane with a sulfide tripod terminus. We demonstrated the selective chemisorption of this terminus on a gold surface, which was confirmed by UV absorption spectroscopy and, more obviously, by AFM. This method enables us to connect a semiconducting polymer terminus selectively to a gold surface. A combination of this technique with submicrometer-scale gold electrodes would contribute to the understanding of electronic properties at the single polymer level. Furthermore, the strategy of terminating an organic polymer chain with a sulfide tripod is general and could be utilized in other systems.

Experimental Section. a. General. UV absorption spectra were recorded using a Hitachi U3500 spectro-photometer. AFM topographies were recorded on a Seiko Instruments SPI 3800N atomic force microscope. The molecular weights of the polysilanes were determined with a Shimadzu LC-10 size exclusion chromatography (SEC) system using THF eluent at 30 °C, calibrated by using polystyrene standard. NMR spectra were recorded on a Varian Unity 300 NMR spectrometer. The semi-transparent gold film was fabricated on one side of a quartz substrate by the conventional sputter deposition technique. Titanium was at first deposited on the quartz substrate, and gold was deposited on top of it. For the AFM observations, we used NH₄F-treated Si(111) pieces, on which gold was deposited in the same manner.

b. Synthesis. 1, 1a, 1b. The condensation of 1,2dichloro-1,2-dimethyl-1,2-di-n-propyldisilane (12 g, 0.05 mol) with lithium biphenylide, prepared by the reaction between biphenyl (16 g, 0.10 mol) and Li (0.68 g, 0.10 mol) in THF (200 mL) at -78 °C, yielded the monomer for 1, 1-phenyl-7,8-dimethyl-7,8-di-n-propyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (colorless oil, 12.5 g, 78% yield, bp 120 °C/0.06 Torr). ²⁹Si NMR (CDCl₃, δ): -18.424, -18.806 ppm. Polymer 1a was prepared by the living anionic polymerization of the monomer (2.0 g, 6.1 mmol) by using a drop of *n*-BuLi as an initiator in THF (15 mL). Adding a drop of **3** to the **1a** solution yielded **1b** (colorless solid, 620 mg, yield 58%, $M_{\rm w} = 6.8$ \times 10⁴, $M_{\rm n} = 5.5 \times 10^4$, $M_{\rm w}/M_{\rm n} = 1.2$).¹⁶ Adding ethanol instead of 3 quenched 1a to give 1 (colorless solid, 670 mg, yield 63%, $M_{\rm w} = 2.5 \times 10^4$, $M_{\rm n} = 2.2 \times 10^4$, $M_{\rm w}/M_{\rm n}$ = 1.2).

2. The monomer for **2**, *i*- C_4H_9-n - $C_{18}H_{37}SiCl_2$, was prepared by the condensation of *n*- $C_{18}H_{37}MgCl$ Grignard reagent with *i*- $C_4H_9SiCl_3$ (colorless liquid, 69% yield, bp 140–150 °C/0.1 Torr). ²⁹Si NMR (CDCl₃, δ): –28.941 ppm. Polysilane **2** was synthesized by the sodium-mediated (1.7 g, 0.073 mol) condensation of the monomer (10 g, 0.024 mol) in refluxing *n*-octane (30 mL) with a small piece of 18-crown-6. The synthesized polymer had a bimodal molecular weight distribution, and fractionation yielded **2** with a monomodal distribution (colorless solid, 280 mg, yield 3.4%, $M_w = 1.3 \times 10^7$, $M_n = 2.2 \times 10^6$, $M_w/M_n = 5.8$).

2a, **2b**. Lithium 4,4'-di-*tert*-butylbiphenylide was added to a hexane solution of **2** (ca. 50 mg/20 mL) until the solution became pale yellow, yielding **2a**. One drop of **3** was added to this solution to yield **2b** (colorless solid, 36 mg, yield 70%, $M_{\rm w} = 8.5 \times 10^5$, $M_{\rm n} = 1.2 \times 10^5$, $M_{\rm w}/M_{\rm n} = 7.3$).

3. Methylthiomethyllithium, CH₃SCH₂Li (ca. 0.08 mol), prepared by the previously reported reaction,¹⁷ was added to a hexane (50 mL) solution of 1-bromoun-

decyltrichlorosilane, Br(CH₂)₁₁SiCl₃ (10 g, 0.027 mol), within 40 min. This was an exothermic reaction yielding a colorless suspension, which was further stirred for 1 h. Then the solution was dehydrated with diluted aqueous HCl, extracted from ethyl ether, washed with water, neutralized with saturated NaHCO₃, dried with saturated NaCl and Na₂SO₄, and evaporated to yield **3** (pale yellow oil, 8.2 g, 68% yield). ¹H NMR (C₆D₆, δ): 0.8–1.7 (22H), 1.907 (s, 9H), 1.956 (s, 6H) ppm. ¹³C NMR (C₆D₆, δ): 12.388, 17.208, 20.266, 23.985, 28.378, 29.032, 29.613, 29.753, 29.913 (2C), 33.051, 33.639, 33.966 ppm. ²⁹Si NMR (C₆D₆, δ): -3.221 ppm.

UV Studies. The quartz substrates with gold on one side were immersed in a 5×10^{-2} wt % toluene solution of **1** and **1b** for 5 min. A quartz substrate without gold was also immersed in a solution of **1b** as a reference. The substrates were removed from the solutions, washed repeatedly, and then immersed in fresh toluene for 1 h. The same procedures were employed, using hexane solutions of **2** and **2b**. The background absorption, mainly due to the deposited gold, was between 0.7 and 1.2 and possessed a smoothly curved shape. The subtraction of the background absorption successfully extracted the absorption spectrum with such small absorbance (~0.01) of chemisorbed polysilanes on gold surfaces.

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- (14) We attempted to introduce the thiol group at the initial stage of our research. However, it was difficult to synthesize the counterpart of 3 with the thiol group. The reaction yielded a cyclic compound rather than a linear compound because of the intramolecular reaction that occurred due to the high reactivity of the primary alkyl bromide and thiol groups.
- (15) A question for the stability of the chemisorbed polysilane molecules is still open. We should prepare not only 3 but also the linkers with one or two sulfide groups for comparison. The washing conditions, especially the time and temperature, must be considered as well for further discussions of the stability.
- (16) ¹H NMR of **1b** also indicated the existence of a sulfide tripod terminus. The two ¹H NMR peaks (C_6D_6 , δ) were observed at 1.917 (s, 9H) and 1.966 (s, 6H), together with 0–0.7, 0.7–1.3, and 1.3–1.8. From the observed integral areas of these peaks, we can estimate the ratio of the sulfide tripod/monomer unit to be 1:650 on average. This corresponds to a molecular weight of 5.6 × 10⁴, which is in good agreement with the weight-average molecular weight determined by size exclusion chromatography using the polystyrene standard.
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