

Preparation and single molecule structure of electroactive polysilane end-grafted on a crystalline silicon surface

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Electrically active polysilanes of poly(methylphenylsilane) (PMPS) and poly[bis(*p*-*n*-butylphenyl)silane] (PBPS), which are, respectively, known as a good hole transporting material and a near-ultraviolet electroluminescent material, are end-grafted directly on a crystalline silicon surface. The single polysilane molecules are clearly distinguished one from the other on the surface by means of atomic force microscopy observations. End-grafted single molecules of PMPS are observed as dots while end-grafted PBPS appear as worms extending for more than 100 nm on the crystalline silicon surface. © 2000 American Institute of Physics. [S0003-6951(00)03052-7]

The microlithographic technology used for fabricating large-scale integrated circuits is approaching its scale limit. This makes it increasingly important to develop molecular scale devices. Work in this field includes the development of molecular wire, namely a nanoscale lead for connecting functional molecules and macroscale electrodes, as well as the design and synthesis of signal-processing molecules. The investigation of the carrier transport properties of a single conducting/semiconducting polymer chain is of great interest because of its potential application to this molecular wire. Polysilane, a silicon-catenated polymer with semiconducting properties based on the σ conjugation,¹ has attracted attention in this regard.

Of the various polysilanes, those with phenyl substituents exhibit the best levels of performance. Such polysilanes include poly(methylphenylsilane) (PMPS), a polysilane substituted with a phenyl group on each silicon atom, and poly[bis(*p*-*n*-butylphenyl)silane] (PBPS), a polysilane fully substituted with phenyl derivatives (Fig. 1). For instance, photoconductivity^{2,3} and hole drift mobility^{4,5} have been measured, in many cases, by using PMPS thin films. PBPS thin film exhibits monochromatic electroluminescence peaking at 405 nm at room temperature with much greater external quantum efficiency than those of any other polysilanes.⁶ We have also shown that there is electron as well as hole transport in PBPS thin film whereas only hole drift mobility has been observed in other polysilane films.⁷ Therefore, we should first investigate PMPS and PBPS, if we wish to study the optoelectronic properties of single polysilane molecules.

In order to study single molecule properties, it is necessary to extract a single molecule from a mole amount of the material. This is *not* such an easy task. We demonstrated that the “end-graft” technique is an effective way of fixing single polysilane molecules on a substrate surface in isolation.⁸ We also reported atomic force microscopy (AFM) observations of single alkyl-substituted polysilane molecules on an SiO₂ substrate.⁹ A transparent SiO₂ substrate is convenient for characterizing end-grafted polysilanes by means of

electronic absorption spectroscopy because polysilanes usually show an intense σ – σ^* transition in the ultraviolet region.¹⁰ If we aim at measuring the optoelectronic properties of a single polysilane chain, however, it may be convenient to end-graft directly on conductive bulk surfaces that can be used as an electrode. Our choice is crystalline silicon, for which surface modification and/or conductivity control techniques have been well established.

In this letter, we report on the preparation and AFM characterization of end-grafted single molecules of the electroactive polymers PMPS and PBPS on Si(111). End-grafted single molecules of PMPS are observed as dots while those of end-grafted PBPS appear as worms. We discuss these AFM images in relation to the molecular structures of both polysilanes.

We applied the slightly modified “cut and graft” technique that we have already employed with certain alkyl-substituted polysilanes.¹¹ The key to this technique is to utilize a one-to-one chemical reaction between a reactive anchor built on a substrate surface and an end-lithiated polysilane prepared by the scission reaction of an Si–Si bond in polysilanes using methylolithium in a polar organic solvent.

We dipped the Si(111) substrates in an NH₄F aqueous solution for 5 min to remove the surface oxide layer and to obtain an atomically flat surface with Si–H bonds.¹² The substrates were then immersed in a (1-*r*):*r* mixture of 11-bromo-1-undecene, Br(CH₂)₉CH=CH₂, and 1-dodecene, CH₃(CH₂)₉CH=CH₂, under photoirradiation ($\lambda > 300$ nm) for 16 h to induce an insertion reaction of a C=C double

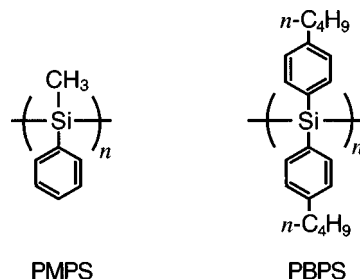


FIG. 1. The chemical formulas of PMPS and PBPS. *n*-Butyl groups in PBPS are introduced to make the polysilane soluble in organic solvents.

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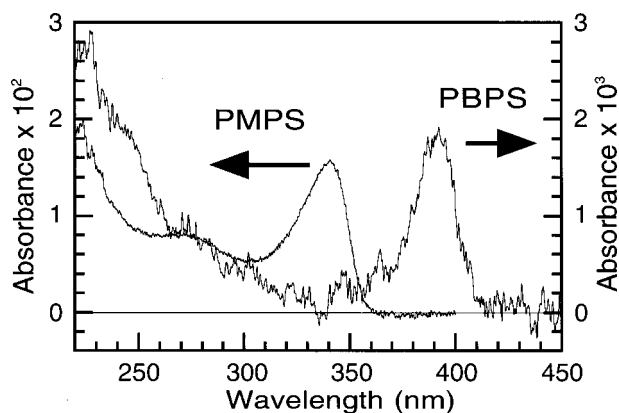


FIG. 2. The electronic absorption spectra of PMPS and PBPS end-grafted on SiO_2 .

bond into a surface Si–H bond.¹³ The resulting substrates have alkylbromide $-(\text{CH}_2)_{11}\text{Br}$ as reactive anchors, which are diluted by $-(\text{CH}_2)_{11}\text{CH}_3$ when we use an $r \neq 0$ mixture. We also prepared the SiO_2 substrate with $-\text{OSi}(\text{CH}_3)_2(\text{CH}_2)_{11}\text{Br}$ as a reactive anchor by a silane coupling reaction using a corresponding dimethylchlorosilane, $\text{Br}(\text{CH}_2)_{11}\text{Si}(\text{CH}_3)_2\text{Cl}$, to characterize the end-grafted polysilanes by UV spectroscopy.⁸

We synthesized the polysilanes, PMPS and PBPS, using a previously reported method.^{10,14} These polysilanes are colorless powders and highly soluble in organic solvents such as tetrahydrofuran and toluene. The end-graft reaction was conducted at room temperature in dried and oxygen-free conditions by using hand-made glassware.⁹ In a dried and oxygen-free tetrahydrofuran solution (10 mL) of PMPS (100 mg), or in a dried and oxygen-free toluene/tetrahydrofuran (2 mL/8 mL) solution of PBPS (40 mg), a few drops of methyllithium (1 mol/L) was added. Preparation of the end-lithiated polysilanes was completed in a few minutes, and the solution turned yellow. The solution was then poured on the substrates with reactive anchors. The grafting reaction was completed within a minute, and the excess end-lithiated polysilane was then inactivated by the addition of a drop of ethanol. The obtained substrates were repeatedly rinsed with tetrahydrofuran and toluene, and then immersed in toluene overnight to remove any polysilane physically adsorbed on the surface. The substrates were further rinsed with ethanol and water, and dried in a nitrogen gas flow for AFM observations (Digital Instruments Nanoscope III, tapping mode, air atmosphere). The weight-average molecular weights (M_w) of the initial polysilanes were 2.8×10^5 and 3.1×10^5 , respectively, for PMPS and PBPS, measured by gel permeation chromatography (Shimadzu LC-10) using polystyrene standard. The M_w of PMPS and PBPS after the scission reaction were 5.1×10^4 and 1.5×10^5 .

Figure 2 shows the electronic absorption spectra of end-grafted PMPS and PBPS on an SiO_2 substrate. Both spectra exhibit sharp absorption bands peaking at 341 nm (PMPS) and 395 nm (PBPS), that are identical to those observed when we use a dilute solution of the corresponding polysilanes. We therefore conclude that the polysilanes were certainly end-grafted on the substrate surface: they did survive after the earlier-mentioned washing process because the end-grafted polysilanes form covalent bond with the surface.

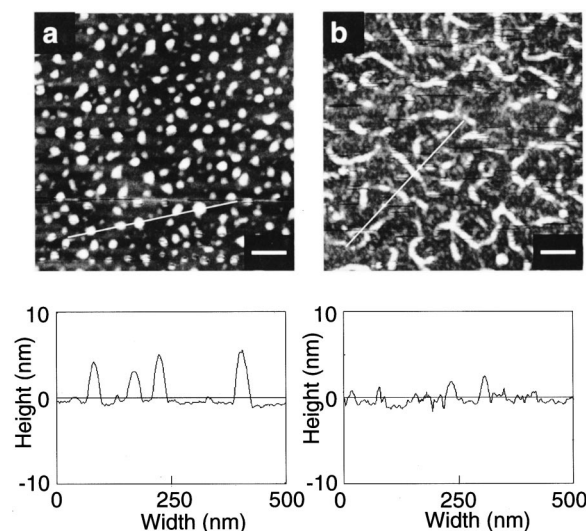


FIG. 3. The tapping mode AFM topographies (top) and the cross sections (bottom) of (a) PMPS and (b) PBPS end-grafted on Si(111). Scale bar, 100 nm.

Figure 3 shows AFM topographies of end-grafted PMPS and PBPS on an Si(111) surface. The end-grafted PMPS was observed as dot images, while the end-grafted PBPS appeared as worm images. The dots and worms were observed over the whole substrate area. We also confirmed that the number of dots and worms on the surface depended on the reactive anchor density, which we controlled by varying the r values while building the reactive anchor on the surface, as reported in our recent letter.⁹ This supports the idea that the observed dot and worm images correspond to single molecules of PMPS and PBPS.

We can also judge from the image size whether or not the observed image is of a single molecule. Here we assume that the observed height is a good measure, although the lateral resolution of the AFM is limited due to the finite cantilever tip radius (usually 5–10 nm). The PMPS polymer chain itself attempts to shrink to make a surface in contact with the air (a poor solvent for polysilanes) as small as possible. This is commonly observed for a flexible polymer chain placed in a poor solvent.¹⁵ This parallels the situation in our latest report on the single molecule observation of end-grafted flexible polysilane, poly(propyltrimethylsilyl)silane.⁹ The average volume that a single PMPS molecule should occupy can be estimated to be 85 nm^3 by using the M_w value of PMPS, that corresponds to the volume of a sphere 6 nm in diameter. The height, about 5 nm, of the observed dots is in good agreement with this value.

Next we discuss the worm images observed for end-grafted PBPS molecules in relation to the PBPS molecular structure. We approach this issue in terms of both spectroscopy and molecular structure. First, we must return to the absorption spectrum of the end-grafted PBPS shown in Fig. 2. The extraordinarily long peak wavelength (395 nm) among the absorption spectra of polysilanes¹⁴ leads us to believe that the PBPS conformation is very close to a *trans*-planar conformation, which is advantageous for the σ conjugation in the silicon backbone.^{14,16} The present absorption spectrum is identical to that in solution but unlike that of the

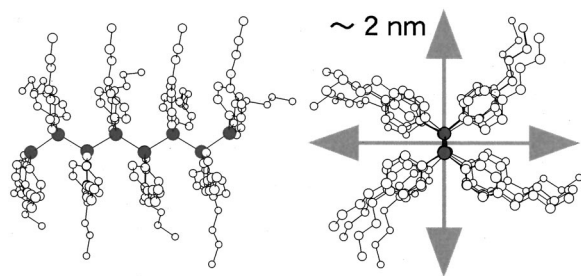


FIG. 4. The molecular structure of $H(R_2Si)_8H$ ($R=n$ -butylphenyl) optimized by MM2 calculations. The sideview (left) and the axial view (right). The shaded and open circles indicate silicon and carbon. Hydrogen atoms are omitted for clarity.

solid thin films.¹⁷ Namely, the absorption peak at 315 nm observed for the solid thin film of PBPS is not found in the present spectrum. The peak at 315 nm is ascribable to a rather disordered conformation induced by the entangling of neighboring polymer chains.¹⁷ This means the current spectrum is characteristic of an *isolated* polysilane system that is unaffected by intermolecular interaction.

The observed worm images are about 2 nm high, which is somewhat greater than the height of the single polysilane molecules reported thus far.^{18,19} We now evaluate the polymer size by assuming that PBPS possesses a *trans*-planar conformation. Figure 4 shows the molecular structure of $H(R_2Si)_8H$ ($R=n$ -butylphenyl) optimized by MM2 calculations (CS Chem3D Pro, CambridgeSoft Corporation). The sectional view in Fig. 4 indicates that the height of PBPS can reach 2 nm if the molecule lies on the surface as shown in Fig. 4. Therefore, our conclusion that the worm images correspond to single PBPS molecules is reasonable. The chain extension, even under the poor solvent conditions, is due to the rigidity of the PBPS resulting from the intramolecular stacking force between the phenyl rings. The structure is also favorable for the σ conjugation of the silicon backbone. For the end-grafted PBPS single chains extending more than 100 nm, it may also be possible to execute transport measurements along the one-dimensional silicon backbone.

In summary, we described the preparation and single molecule structure of electroactive polysilane single molecules end-grafted directly on an Si(111) surface. AFM observations revealed that end-grafted single molecules of PMPS appear as dots while those of PBPS appear as worms. Its excellent electronic performance and extended single molecule structure on the surface make end-grafted PBPS a

good candidate for molecular wire. The present samples would also be suitable for the further study of the optoelectronic properties of single polysilane molecules by means of scanning probe microscopy. For instance, we recently succeeded in the local-area detection of electroluminescence from PBPS thin film²⁰ by using a transparent and conductive scanning tunneling microscopy tip probe designed both for tunneling current excitation and near-field photon detection.^{21,22} By applying this technique to the present sample of end-grafted PBPS, we expect to achieve the two-dimensional mapping of electroluminescence from PBPS single molecules.

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