

# End-Grafted Polysilane—An Approach to Single Polymer Science

KAZUAKI FURUKAWA\*

NTT Basic Research Laboratories, NTT Corporation,  
3-1 Morinosato Wakamiya, Atsugi,  
Kanagawa 243-0198, Japan

Received August 12, 2002

## ABSTRACT

This Account describes our approach to single polymer science in which we use end-grafted polysilane. Single polymer science, by our definition, involves isolating and observing a single polymer chain and extracting its physical properties at the single molecule level. For this purpose, we developed the end-graft technique, which is a method for fixing a polymer terminus on a solid surface by forming a chemical bond between them. We applied this technique to polysilane, a semiconducting polymer with a one-dimensional silicon-catenated backbone. Our recent experimental achievements are reviewed, which include direct observations of polysilane single-molecular structures by atomic force microscopy, the formation of unique supramolecular structures, and the observation of temperature- and solvent-dependent UV absorption spectra that are characteristic of isolated polysilane chains end-grafted on a solid surface.

## Introduction

Single polymer science, which is our field of interest, can be summarized as follows. We isolate a single polymer chain in ambient conditions, fix it on a substrate surface, observe its structure, and test its physical properties at the single molecule level. What is the significance of studying a single polymer? The author thinks it is that we can ignore such statistical factors as molecular weight distribution, diverse morphologies, and interchain interactions when we focus our attention on just one polymer chain. This will enable us to reveal more of the intrinsic properties of the polymer.

The observation of single polymer chains is a first step toward undertaking further single polymer science research.<sup>1</sup> Although there have already been several reports of observations of single organic polymer chains, they were for a limited number of polymers under limited conditions.<sup>2,3</sup> A technique for isolating a single polymer chain is a prerequisite. Unfortunately, there is no effective and simple technique for isolating single polymer chains

Kazuaki Furukawa was born in Tokyo in 1963. He received B.S. (1986) and M.S. (1988) degrees in physics from Waseda University for his work on oxide ferromagnetic materials. He joined NTT Basic Research Laboratories in 1988, where he began his research on organic silicon polymers and related organo-silicon compounds including silicon network polymers and octasilacubane. He is also interested in the device applications of these materials and has undertaken hole transport measurements and electroluminescence measurements of polysilane thin-film devices. He received Dr.Sci. (2000) from Waseda University for his work on these topics. His current research focuses on single-molecular and single polymer science including organic and biopolymers, and ranges from synthesis to measurement.

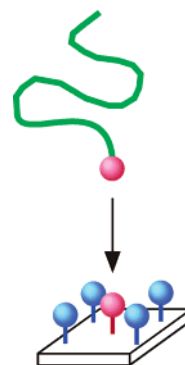
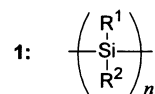


FIGURE 1. Schematic drawing of the idea behind the end-graft technique. The red and blue spheres represent reactive and nonreactive species, respectively.

that is generally applicable to common organic polymers. The main difficulty is that the polymer molecules are condensed under poor solvent conditions. We proposed a method for pinning the polymer terminus to a solid surface with a chemical bond to overcome this difficulty.<sup>4</sup> Our method, which we call the end-graft technique, is shown schematically in Figure 1. The key idea is to use a one-to-one chemical reaction between a reactive anchor built on a solid surface and an end-functionalized polymer. If the density of the end-grafted polymer is sufficiently low (this also related to the polymer chain length), then polymer chains cannot be condensed, even under poor solvent conditions. This is because the polymer chains are pinned by a strong covalent bond. Thus, an end-grafted polymer always exists alone without condensation in the vicinity of the surface. This allows us to realize a new class of polymer state that is free from the interchain interaction that cannot be avoided with bulk or thin-film polymers. This state is also different from that of polymers in a diluted solution, which is also considered to be a system free from interchain interactions, because such isolated polymers in a dilute solution move very quickly and we can measure only averaged physical values.



$R^1, R^2 = \text{organic group}$

We have been applying the end-graft technique to polysilane.<sup>4,5</sup> Polysilane is known to act as a semiconducting polymer, and this may motivate the study of the optical and electronic properties of polysilane single chains. In the following sections, the characteristics of polysilane are briefly described, and our recent experimental achievements in single polymer science based on end-grafted polysilanes are then reviewed. These consist of direct observations of polysilane single-molecular structures by atomic force microscopy (AFM), the forma-

\* Phone: +81-46-240-3551. Fax: +81-46-270-2364. E-mail: furukawa@will.brl.ntt.co.jp. URL: <http://www.brl.ntt.co.jp/people/furukawa/top.html>.

tion of unique supramolecular structures, and the observation of temperature- and solvent-dependent UV absorption spectra that are characteristic of isolated polysilane chains end-grafted on a solid surface.

## Polysilane: Optoelectronic Properties of Silicon Backbone

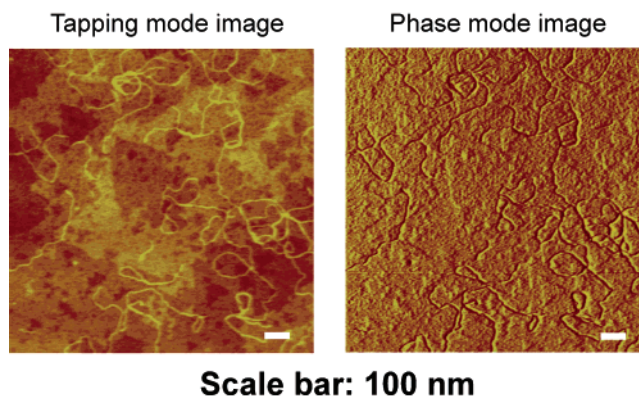
Polysilane **1** has a linear silicon-catenated backbone and two organic groups on each silicon atom.<sup>6</sup> The number of silicon atoms per polymer is usually from several hundred to several thousand and can reach over 100 000 in a polysilane with a very high molecular weight. Polysilane is a colorless solid and is soluble in common organic solvents such as hexane, toluene, and tetrahydrofuran. Although the term “colorless” makes us think of insulating material, solid thin films of polysilane exhibit such semiconducting characteristics as photoconductivity, a hole transport property, and electroluminescence. These characteristics are due to the delocalization of Si–Si  $\sigma$ -electrons along the polysilane backbone, known as  $\sigma$ -conjugation.<sup>7</sup>

Polysilane possesses an intense sharp absorption band in the ultraviolet region, which is assigned to the  $\sigma$ – $\sigma^*$  transition of the silicon backbone. In physical terms, polysilane possesses a direct-type band structure with a band gap energy of more than 5.0 eV.<sup>8</sup> Since a low-dimensional semiconductor such as polysilane has a large exciton binding energy of about 1.0–1.5 eV,<sup>9</sup> the exciton level is usually observed as a sharp absorption band in the UV region between 300 and 400 nm. The degree of  $\sigma$ -conjugation depends sensitively on the main chain conformation. Polysilanes generally have various global conformations because of the small energy barriers for rotation around an Si–Si single bond. Thus, the peak wavelength of an absorption band often varies with the temperature associated with a change in the silicon backbone conformation; for example, from a random coil to a trans-planar conformation. This in turn means that we can discuss the polysilane main chain conformation by measuring UV absorption spectra. This will be discussed again later.

## Polysilane: Conformational Control by Side Chains

Another important characteristic of polysilane is that the choice of side chain affects the main chain rigidity over a wide range.<sup>10</sup> It has been reported that the logarithmic molar absorption coefficient per Si–Si bond of polysilanes is proportional to the polysilane’s viscosity index,  $\alpha$ , which is a scale for evaluating chain rigidity. The experimentally determined  $\alpha$  values for polysilanes range from 0.51 to 1.35, which includes flexible and semiflexible chains.

The structure of semiflexible polysilanes can be visualized by using AFM under ambient conditions. Figure 2 shows an example of our observations using a sample prepared by casting a very dilute hexane solution of poly-[(*S*)-2-methylbutyl]-*n*-octadecylsilane] on a piece of NH<sub>4</sub>F-treated hydrophobic Si(111). In some parts of the Si(111)



**FIGURE 2.** AFM images of poly[(*S*)-2-methylbutyl]octadecylsilane] on a NH<sub>4</sub>F-treated hydrophobic Si(111) surface. (Left) Tapping mode AFM topography. (Right) Phase mode AFM image of the same area.

surface, we can observe ropelike structures. Otherwise, we observed nothing or ugly bundles of many polysilane molecules. The ropes in the left image in Figure 2 are about 1 nm high, which is reasonable for the single chain height of polysilane. Reflecting the difference in the elasticity of Si(111) and polysilane, a phase mode observation of the same area also provides a clear image of the ropes, as shown on the right in Figure 2. These images strongly support the idea that the ropes are polysilane single chains. Some may think this evidence is sufficient to trigger further studies in single polymer science. However, Figure 2 is probably a special case that happens to satisfy several parameters at the same time, such as polymer rigidity, solution concentration, and casting conditions, and, in addition, is probably the result of some luck in finding an appropriate place for single polymer observations. Therefore, we cannot expect the sample in Figure 2 to contribute much further to single polymer science.

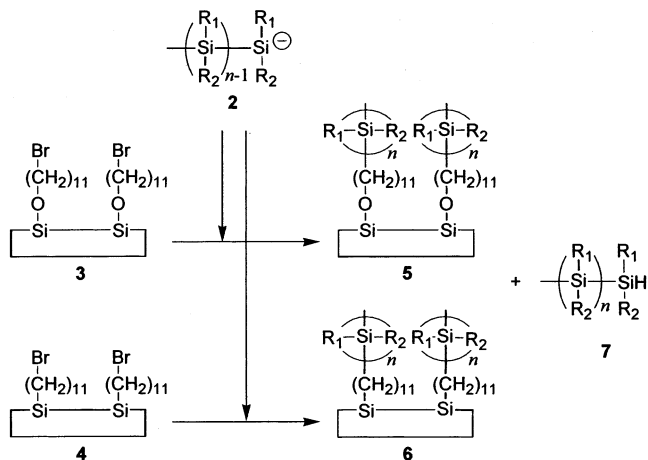
The polysilanes reviewed in this Account are summarized in Figure 3. We chose polysilanes with different types of side chains and main chain rigidity. The persistence lengths of some of these polysilanes have been determined by means of the conventional technique of light-scattering measurement using dilute polysilane solutions. We had to develop chemistry for synthesizing end-functionalized polysilane with a silyl anion at the terminus depending on the side chains of the polysilane. The main chain is, however, always identical and is a very simple silicon catenation.

## Synthesis of End-Grafted Polysilane

The synthesis route of end-grafted polysilane is summarized in Figure 4. End-grafted polysilanes **5** and **6** can be synthesized by the reaction between end-functionalized polysilane **2** and substrates **3** or **4** with reactive anchors. Note that **5** and **6** indicate the grafted state of polysilane on a quartz surface (**5**) and a silicon surface (**6**), respectively. The combination of the numbers **2**, **5**, and **6** and the suffixes **a–e** in Figure 3 identifies the individual samples described in this Account. We use polysilane with a silyl anion at the terminus as an end-

Entry	1a	1b	1c	1d	1e
Chemical structure					
Side chain type	alkyl/ alkyl	dialkyl	alkyl/ phenyl	alkyl/ alkyl	diphenyl
Chain rigidity	Flexible	Flexible	Flexible	Semiflexible	Semiflexible
Synthesis of 2	Living anionic polymerization	Scission reaction	Scission reaction	Scission reaction	Scission reaction

**FIGURE 3.** Chemical structures of polysilanes appearing in this Account. Suffixes **a–e** indicate the difference in the side chains: **a**, poly(*n*-propyltrimethyldisilene); **b**, poly(di-*n*-hexylsilane); **c**, poly(methylphenylsilane); **d**, poly[*[(S)*-2-methylbutyl]-*n*-decylsilane]; **e**, poly[bis(*p*-butylphenyl)silane].



**FIGURE 4.** Synthesis route of end-grafted polysilanes.

functionalized polymer and a bromoalkyl group as a reactive anchor on a solid surface.<sup>4</sup> This is based on the known coupling reaction of the silyl anion with primary alkyl bromide.<sup>11</sup>

End-functionalized polysilane **2** is very reactive, and we must synthesize it in a water- and oxygen-free organic solvent. One way to synthesize **2** is to use the living anionic polymerization of “masked disilene” with alkyl-lithium as an initiator.<sup>12</sup> For instance, we demonstrated that the poly(*n*-propyltrimethyldisilene) **2a** can be synthesized from the corresponding masked disilene. The advantage of this method is that we can always obtain

polysilanes with only one reactive terminus and with small molecular weight distribution factors. However, we can use this method for only a limited number of alkyl-substituted polysilanes, partly containing small alkyl groups such as methyl groups.

We have to employ a different method for synthesizing **2** with polysilanes that have longer and bulkier alkyl groups and phenyl groups.<sup>5</sup> This alternative approach utilizes the simple scission reaction of an Si–Si bond in polysilanes employing an appropriate lithium reagent. We use methyl lithium for phenyl-substituted polysilanes<sup>13</sup> and the more electron-donating reagent of lithium 4,4'-di-*tert*-butylbiphenylide for alkyl-substituted polysilanes.<sup>14</sup> This method requires a polysilane with a very high molecular weight as an initial polysilane **1b–e**, which is synthesized by the dehalogenative condensation of the corresponding dichlorosilane monomer by using sodium metal. The resulting **2b–e** contains a silyl anion at one or possibly both terminals.

By contrast, we use surface chemical reactions to build the reactive anchor on the solid surface. Typically, we use two kinds of solid surface: a transparent quartz substrate for UV studies and an atomically flat Si(111) substrate for AFM observations. On a quartz surface with a hydroxyl group, the well-known silane coupling reaction is available. We use a dimethylchlorosilane, Br(CH<sub>2</sub>)<sub>11</sub>Si(CH<sub>3</sub>)<sub>2</sub>Cl, to prepare –OSi(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>11</sub>Br on the surface.<sup>15</sup> We use monochlorosilane instead of trichlorosilane to avoid the formation of island structures by several or more tri-

chlorosilane molecules on the surface. An atomically flat Si(111) surface is available by dissolving a surface-oxidized layer on the Si(111) wafer using  $\text{NH}_4\text{F}$  aqueous solution.<sup>16</sup> The resulting surface is terminated by hydrogen, Si–H, in which a C=C double bond can be inserted by a photoinduced reaction.<sup>17</sup> We can use 11-bromo-1-undecene to prepare the reactive anchor  $-(\text{CH}_2)_{11}\text{Br}$  on the surface.

We perform the end-graft reaction under water- and oxygen-free conditions by using laboratory-made glassware.<sup>18</sup> Tetrahydrofuran is usually used as the solvent. The initial solution of either masked disilene or polysilane is colorless. When **2** is generated by addition of lithium reagent, the solution becomes colored (**2a**, dark red; **2b–e**, pale yellow). The coupling reaction is completed within several minutes by dipping **3** or **4** into the colored solution of **2**. We always prepare an excess amount of **2** in relation to the number of reactive anchors on **3** or **4**. Therefore, a drop of ethanol is added to quench **2**, to yield the corresponding polysilane **7**, the molecular weight of which is assumed to be similar to that of the end-grafted polysilane. The average number of Si atoms per chain, calculated from the weight-averaged molecular weight of **7**, is in the 500–10 000 range for our end-grafted polysilanes. Substrates **5** and **6** were repeatedly washed with good polysilane solvents such as tetrahydrofuran and toluene, and with ethanol and water to remove any substances remaining on their surfaces. The end-grafted polysilanes are not dissolved during this washing process because they form a chemical bond with the substrate surface.

We vary the reactive anchor density to control the density of the end-grafted polysilane. This is achieved, for instance, by using a  $(1-r):r$  mixture of  $\text{Br}(\text{CH}_2)_{11}\text{Si}(\text{CH}_3)_2\text{Cl}$  and  $\text{CH}_3(\text{CH}_2)_{11}\text{Si}(\text{CH}_3)_2\text{Cl}$  to prepare **3**. The latter monochlorosilane forms a normal alkyl group,  $-\text{OSi}(\text{CH}_3)_2(\text{CH}_2)_{11}\text{CH}_3$ , on the surface, which acts as a nonreactive anchor. We can dilute the reactive anchor with a nonreactive anchor when we use an  $r \neq 0$  mixture. Although  $r$  is not identical to the real reactive anchor ratio built on the surface, this provides us with control of the end-grafted polysilane density over a wide range, as we will see in the next section.

## Characterization of End-Grafted Polysilane

The end-grafted polysilane **5** is readily characterized by means of UV absorption spectroscopy. A characteristic sharp absorption band ascribable to the  $\sigma-\sigma^*$  transition of the one-dimensional silicon backbone appears in the 300–400 nm wavelength region.<sup>6</sup> One example is provided in Figure 5, which shows the electronic absorption spectra of **5c** and **5e**. Both spectra exhibit absorption bands peaking at 341 (**5c**) and 395 nm (**5e**) that are identical to those observed when we use a dilute solution of **1c** and **1e**. We therefore conclude that the polysilanes were certainly end-grafted on the substrate surface. They survived the above-mentioned washing process because

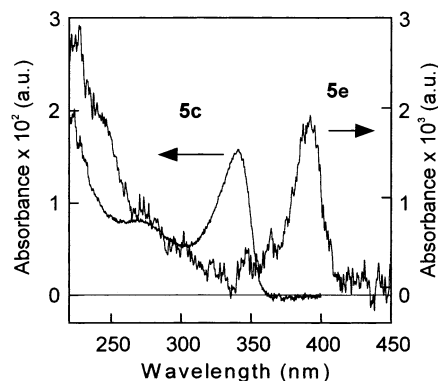


FIGURE 5. UV absorption spectra of **5c** and **5e**.

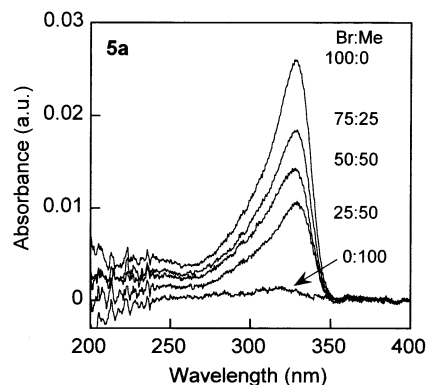


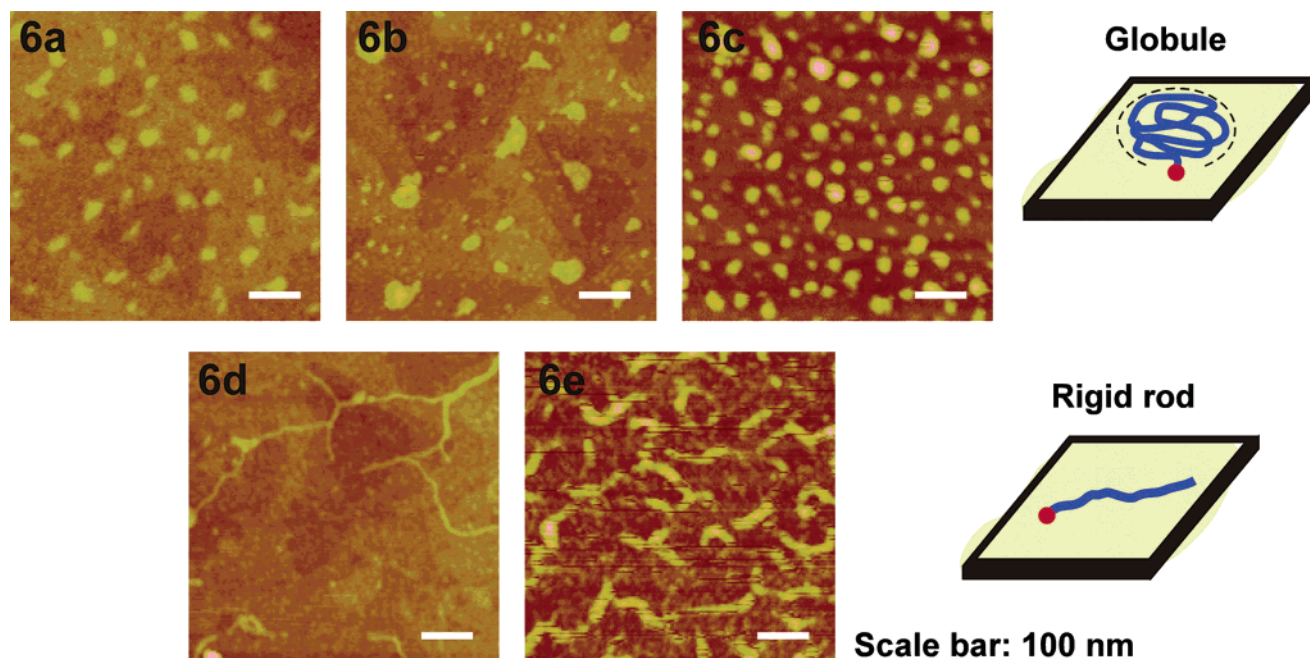
FIGURE 6. UV absorption spectra of **5a** with a controlled surface density.

the end-grafted polysilanes form a covalent bond with the surface.

The absorbance we observe from **5** is always very small, and it is possible to think that this absorbance is due to a small amount of polysilane remaining on the surface after the washing process. This suspicion can be discounted by observing the UV spectra of samples with different grafting densities.<sup>4</sup> Figure 6 shows the UV absorption spectra of **5a** synthesized on **3** with different reactive anchor ratios  $r$  of 0.00, 0.25, 0.50, 0.75, and 1.00. To make the other parameters identical, the prepared substrates are simultaneously dipped into the same solution of **2a** to complete the end-graft reaction. As  $r$  is increased, the reactive anchor density is decreased, and the peak absorbance becomes smaller. This indicates that the surface density of end-grafted polysilane can be controlled by the reactive anchor density. When  $r = 1$ , which builds only a nonreactive anchor on the surface, we cannot recognize the absorption band of **1a**. This shows that a normal alkyl group certainly acts as a nonreactive anchor and that our washing process is good enough to remove polysilanes that are not end-grafted on the surface.

## Single-Molecular Structure

We use AFM observations to confirm that single polysilane molecules are distributed homogeneously and individually on the substrate surface with controllable densities. These AFM observations are indispensable for the current purpose, which is to determine whether the end-grafted



**FIGURE 7.** Tapping-mode AFM topographies of **6a–e** with low surface grafting density. Scale bar: 100 nm. The equilateral triangle patterns seen in the topographies are of the Si(111) surface. The dots in the top three images are of single chains of **1a–c**, and the ropes in the bottom two images are of single chains of **1d** and **1e**. The sketches are schematic drawings of a collapsed structure and a ropelike structure under poor solvent conditions. Polymers are grafted at the points indicated by filled red circles.

polysilanes are isolated from each other. The observations are also beneficial for polymer chemists, who can determine the polysilane chain rigidity by means of direct observations of individual polymer chains.

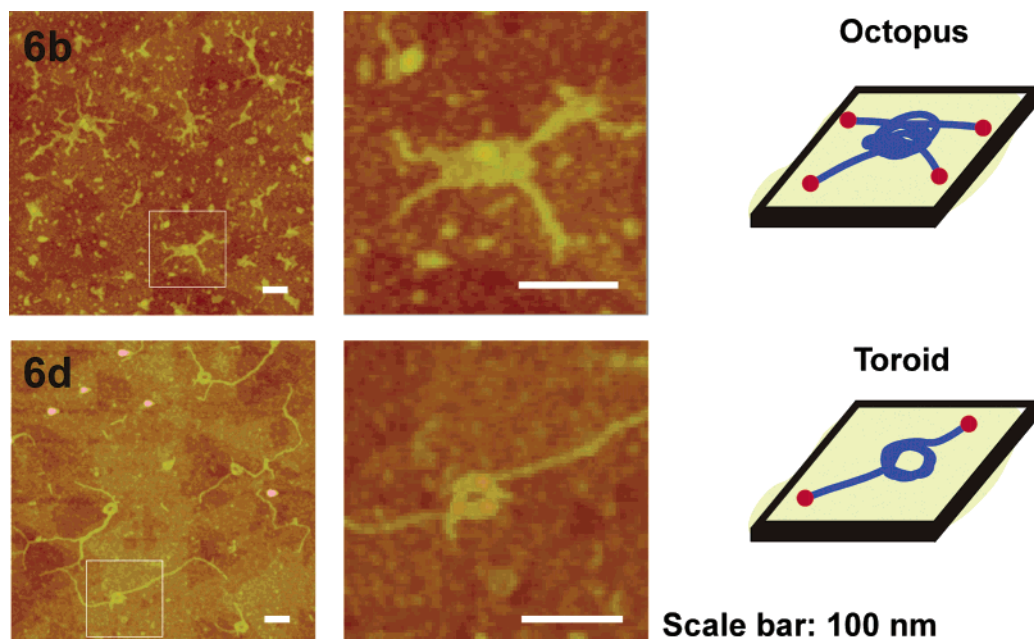
The AFM images were taken in air by using the tapping mode (tip radius 5–10 nm) of a Digital Instruments Nanoscope III. We controlled the grafting densities of the samples so that they were low enough for us to observe single end-grafted polysilane molecules on the surface. A quartz substrate is sufficient for observing such simple structures as dots, but more complicated and therefore more interesting structures require an atomically flat Si(111) surface.

Figure 7 summarizes our AFM observations of **6a–e**. We observed dot and pancake structures from **6a–c**. Here, the word “pancake” indicates a dot with a relatively low height compared with its diameter. We reasonably concluded that each dot is one polysilane molecule. The structure formed by an end-grafted polymer chain has been considered in the statistical physics of polymers.<sup>19,20</sup> The dot and pancake images are due to the collapsed structure, which is often found with isolated flexible polymers grafted on a surface. This is because, as far as possible, flexible polysilanes avoid contact with poor solvents, namely the air. The slight difference in structures was caused by the packing force for self-aggregation or by a repulsive force against the substrate.

By contrast, we observed rope structures from **6d** and **6e**. The rope images of these polysilanes are reasonable, because the persistence lengths of these polymers are relatively long; they were determined as 100 and 10 nm, respectively. The rigidity is mainly due to the packing effect of side chains: **1d** has bulky branched alkyl groups,

which lock together strongly against any conformational change, and **1e** is fully substituted by bulky phenyl groups.

The AFM images clearly reflect the differences in the main chain rigidity, which depends on the side chains of the polysilanes. This leads us to the conclusion that the AFM images of the end-grafted polysilane single molecules represent the main chain rigidity of the corresponding polysilanes in a dilute solution. In particular, no observations of a single chain of a flexible polymer other than end-grafted polystyrene<sup>21,22</sup> have yet been reported. In addition to the above discussion, we also conducted several experiments and obtained data supporting our conclusion that the observed images, especially the dots, are of single polysilane molecules.<sup>18</sup> For instance, we can judge from the image size whether the observed image is of a single molecule. Assuming that the specific gravity of an organic material such as polysilane is 1 g/cm<sup>3</sup>, the average volume that a polysilane molecule on **6c** should occupy can be estimated to be 85 nm<sup>3</sup> by using the molecular weight of **7c**. This corresponds to the volume of a sphere 6 nm in diameter. The height of the observed dots (about 5 nm) is in good agreement with this value. It should be noted that 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). On the other hand, we also tested the relationship between the dot density and the peak intensity of the UV absorption spectra by using **5a**. We found no change in the shape of the UV absorption spectra but observed an increase in the peak intensity as the dot density increased. This result also supports the belief that the dot is a single polysilane molecule.



**FIGURE 8.** Tapping-mode AFM topographies of **6b** and **6d** in relatively high density regime, which show supramolecular structures formed by flexible polysilane **1b** (top) and semiflexible polysilane **1d** (bottom). Enlargements of the white squares are also shown. Scale bar: 100 nm. The sketches are schematic drawings of the octopus structure formed by flexible end-grafted polymers and the toroid structure formed by semiflexible end-grafted polymers under poor solvent conditions. Polymers are grafted at the points indicated by filled red circles.

As briefly summarized above, our end-graft technique for polysilane provides unprecedented samples in that the main chain rigidity and surface grafting density are rigorously controlled. This gives us opportunities to take the first steps in the field of single polymer science. The formation of supramolecular structures described in the next section also supports our conclusion that the end-graft technique enables us to realize an isolated polymer chain on a solid surface.

## Supramolecular Structure

When the surface density is appropriately high and an end-grafted polymer can reach its neighbors, these end-grafted polymers are expected to affect each other and form structures other than single-molecular structures. Figure 8 shows such supramolecular structures formed by flexible polysilane **1b** (top) and semiflexible polysilane **1d** (bottom).<sup>14</sup>

We found the complicated patterns shown in Figure 8 when we increased the grafting density of **6b** above that used to obtain the results shown Figure 7. One such structure, shown in the enlargement in Figure 8, is 1.5 nm high and 50–100 nm wide. It appears that the patterns were formed by several polysilane chains, because they occupy an area larger than those occupied by the single end-grafted polysilane molecules of **1b** seen in Figure 7. When we used the semiflexible polysilane **1d**, a ringlike structure appeared, as seen at the bottom of Figure 8. These ring structures are 30–40 nm in diameter, about 100 nm in circumference, and about 2 nm high. The height of the ropelike image is about 1 nm, which is reasonable for the height of a single molecule. These ringlike structures have never been observed when using

the casting method to obtain samples, such as the one in Figure 2. We concluded that these interesting structures are supramolecular structures that are demanded by the weak noncovalent interchain interactions of end-grafted polysilanes.

Very recently, several end-grafted polymers with supramolecular structures that depend on the chain rigidity under poor solvent conditions were theoretically predicted.<sup>23,24</sup> The idea is also shown schematically in Figure 8. A possible supramolecular structure for flexible chains was named the “octopus” structure.<sup>23</sup> In such a structure, the total energy is stabilized because the surface area in contact with the air is reduced, but chain extension can be the penalty for energy minimization. The octopus structure is the result of a balance between these effects. Although the formation of octopus structures has been reported,<sup>21</sup> the present image is striking in that the “tentacles” of the octopus are clearly visualized. Thus, we can even count the number of polymers agglomerating to form the structure. For instance, the octopus structure in Figure 8 is formed by four end-grafted polysilanes. By contrast, a possible supramolecular structure for semiflexible chains was named the “toroid” structure.<sup>24</sup> The increased rigidity of **1d** leads to an elastic penalty for bending deformation. We can clearly see that two end-grafted polysilanes **1d** agglomerate to form the toroid structure. The circumference of the toroid agrees with the persistence length of **1d** of about 100 nm. It should be noted that these structures can be observed only under optimized chain length and grafting density conditions.

These nanoscale supramolecular structures can be compared with the shapes in which wool and metal wire are commonly sold in stores. Wool is sold in a ball,

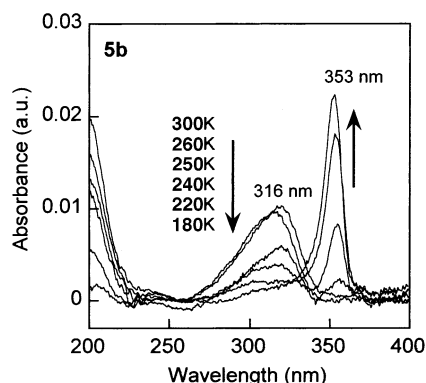


FIGURE 9. Temperature-dependent UV absorption spectra of **5b**.

whereas metal wire is sold in a toroidal ring shape. Store owners probably use these shapes because they are the most compact way of displaying the item while maintaining the intrinsic nature of the material. The solution for wool is fine: it is flexible enough to form into a ball. But this is not true for the metal wire, which is formed into a ring because otherwise it would lose its mechanical property. The circumference of the ring corresponds to the “persistence length” of the metal wire. If the metal wire were wound with a smaller curvature, it would lose its usefulness.

### Thermochromism: Test of Intermolecular Interaction-Free Behavior

This section describes the physical properties, mainly the optical properties, characteristic of our end-grafted polysilane system. As was mentioned above, polysilane chains are isolated from each other on a solid surface under both good and poor solvent conditions. This makes it different from polymers both in the solid thin-film form and in dilute solution. Measurements of thermochromism, namely the reversible spectral change that depends on temperature, of **5b** revealed that end-grafted **1b** under poor solvent conditions behaves similarly to **1b** in dilute solution but not to the solid thin film of **1b**.<sup>25</sup>

Figure 9 shows the temperature-dependent electronic absorption spectra of **5b** in a vacuum. There is an absorption band peaking at 316 nm at 300 K, which is characteristic of the  $\sigma\text{--}\sigma^*$  transition of **1b**. The absorption spectrum was reversibly changed, depending on the temperature. The absorption band peaked at 316 nm in the high-temperature region (>250 K) and at 353 nm in the low-temperature region (<220 K). During the transition between 220 and 250 K, we observed a clear isosbestic point (at 332 nm). The change in the spectra can be assigned to the conformational transition known for **1b**.

Typically, **1b** in dilute solution shows abrupt thermochromism at a transition temperature ( $T_c$ ) of 242 K between two phases: one peaking at 317 nm and the other at 353 nm.<sup>26</sup> Although thermochromism is also observed for a solid thin film of **1b**, its  $T_c$  is relatively higher (315 K), and one of the phases has a different absorption peak at 374 nm.<sup>27</sup> The result in Figure 9 is very interesting in that the end-grafted polysilane chains behave like the

polysilane in dilute solution but unlike the solid thin film of the same polysilane, even under solventless conditions:  $T_c$  is comparable to that of the polysilane in dilute solution and, more obviously, the longer wavelength absorption band appears at the same wavelength as that of **1b** in dilute solution (353 nm) but not for its solid thin film (374 nm). This result shows that the interchain interaction between the end-grafted **1b** chains is as low as it is in solution. This is simple to understand because the end-grafted **1b** chains are isolated from each other, even under solventless conditions, and are thus free from the complex interchain interactions that occur in bulk.

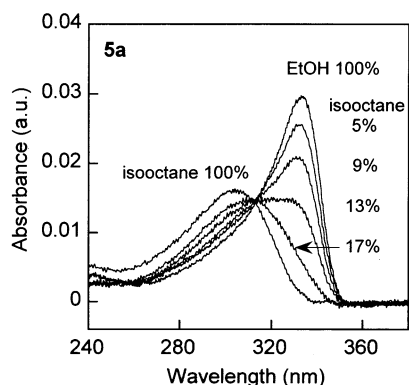
In addition to the example of **1b** above, the UV absorption spectra of **5** often exhibit interesting behavior. We found that the thermochromism of **5a** is different from that of **1a** in dilute solution and in solid thin-film form. This behavior is again attributed to the small intermolecular interaction and, in addition, to the reduced degree of freedom of intramolecular motion caused by pinning the terminus to a solid surface.<sup>5</sup> In Figure 5, the absorption spectrum of **5e** was identical to that in solution but unlike that of the solid thin films of **1e**. Namely, the absorption peak at 315 nm observed for the solid thin film of **1e** is not found in the spectrum of **5e**.<sup>13</sup> This means the spectrum is characteristic of an isolated polysilane system that is unaffected by intermolecular interaction.

### Solvatochromism: Chain Conformations in Various Environments

A particular advantage of end-grafted polysilane is that it can be measured in any solvent without elution. This gives us unique opportunities to measure solvatochromism,<sup>28</sup> namely the reversible spectral change that depends on the solvent. Few polymers exhibit solvatochromism, because of the difficulty involved in designing polymers that are soluble in, for example, both hydrophilic and hydrophobic solvents. It is impossible to measure the UV absorption spectra of a single polymer chain in poor solvents, because polymers are always precipitated. However, if we end-graft the target polymer, we can observe the electronic absorption spectra under any conditions.

Figure 10 shows one such example, namely the measurement of the UV spectra of **5a** in ethanol/isooctane cosolvent. The spectrum of **5a** in pure ethanol, which is a poor solvent for **1a**, is almost the same as that obtained without a solvent, but an abrupt broadening and blue shift are caused by increasing the ratio of isooctane, a good solvent for **1a**. This chromism, which was reversibly observed, can be clearly seen to result from the fact that the ordered conformation is gradually being disordered and becoming random with the increasing isooctane solvation. This conformational disordering was very sensitive to the amount of isooctane, and a full transformation was almost achieved by the addition of 20% isooctane.

In the solvatochromism observations described here, grafting the polymer terminus means no more than pinning the polymer chains. This is because the substrate



**FIGURE 10.** UV absorption spectra of **5a** under isooctane/ethanol cosolvent conditions. Isooctane is a good solvent for polysilane **1a**, while ethanol is a poor one.

is an insulator and has no electronic effect on the polysilane. Under this condition, the band in the absorption spectra is determined solely by the main chain conformation of the polysilanes. Therefore, we can discuss the main chain conformation in terms of the UV absorption spectra if the polymer backbone is a chromophore. Polysilane is one example, but most  $\pi$ -conjugated polymers also fall into this group. The universally applicable end-graft technique may take the place of the conventional procedures employed for determining the conformations of single polymer chains that use light-scattering, small-angle X-ray, or neutron-scattering measurements.

## Summary and Perspectives

End-grafted polysilanes have been synthesized by a reaction between an end-functionalized polysilane, which was prepared by either the anionic polymerization of masked disilene or the scission reaction of a high polymer, and a reactive anchor of primary alkyl bromide built on a substrate surface. Our end-graft technique for polysilanes provided unprecedented samples in that the main chain rigidity and surface grafting density were rigorously controlled. This gives us the opportunity to take our first steps into the field of single polymer science. In fact, we succeeded in the direct AFM observation of single-molecular structures and supramolecular structures. One of the most interesting features is that all the polymers we used have a silicon catenation backbone; i.e., the polymer main chain is always identical.

In addition, it is interesting to measure the physical properties of isolated polysilane chains. Some interesting optical properties, such as thermochromism and solvatochromism, both of which exhibit characteristic features with respect to isolated polysilane chains, have been observed. However, it would attract even more interest were we to measure optical and electronic properties using only a single polysilane. The present end-graft technique provides a substrate with isolated single polysilane molecules over almost the whole of the surface. These samples would be suitable for the further study of the optoelectronic properties of single polysilane mol-

ecules by means of scanning probe microscopy. We can also expect to realize two terminal electric measurements, which we can probably extend to three or more terminals, for some of the polysilanes with elongated structures on a surface under air conditions. Furthermore, the end-graft technique is surface selective. We started to apply the technique to surfaces of different materials with fine structures fabricated by state-of-the-art nanolithography.

End-grafted polymers in the high grafting density regime have thus far been attracting more interest than those in the low density regime. However, the latter regime is now very important to research in single polymer science. We have demonstrated this idea throughout our study using end-grafted polysilanes. The end-graft technique is not limited to polysilane. It is also applicable to other polymers, some of which possess optical and electrical functions, if we use appropriate chemistry for synthesizing end-functionalized polymers and building reactive anchors for them. This must lead to the observation of optical and electrical properties of other functional polymers at the single polymer level.

## References

- (1) Sheiko, S. S.; Moeller, M. Visualization of Macromolecules—a First Step to Manipulation and Controlled Response. *Chem. Rev.* **2001**, *101*, 4099–4123.
- (2) Groeppel, M.; Roth, W.; Elbel, N.; von Seggern, H. Self-Assembly of Organopolysilanes on Graphite: a Scanning Tunneling Microscopy Study. *Surf. Sci.* **1995**, *323*, 304–310.
- (3) Ebihara, K.; Koshihara, S.; Yoshimoto, M.; Maeda, T.; Ohnishi, T.; Koinuma, H.; Fujiki, M. Direct Observation of Helical Polysilane Nanostructures by Atomic Force Microscopy. *Jpn. J. Appl. Phys.* **1997**, *36*, L1211–1213.
- (4) Ebata, K.; Furukawa, K.; Matsumoto, N. Synthesis and Characterization of End-Grafted Polysilane on a Substrate Surface. *J. Am. Chem. Soc.* **1998**, *120*, 7367–7368.
- (5) Ebata, K.; Furukawa, K.; Matsumoto, N.; Fujiki, M. End-Grafted Polysilane on a Substrate Surface: Surface-Tethered  $\sigma$ -Conjugated Polymer Chain. *Polym. Prepr.* **1999**, *40* (2), 157–158.
- (6) Miller, R. D.; Michl, J. Polysilane High Polymers. *Chem. Rev.* **1989**, *89*, 1359–1410.
- (7) Matsumoto, N.; Takeda, K.; Teramae, H.; Fujino, M. Electronic Structures of Silicon-Based Polymers. In *Silicon-Based Polymer Science*; Zeigler, J. M., Gordon Fearon, F. W., Eds.; ACS Advanced in Chemistry Series 224; American Chemical Society: Washington, DC, 1990; pp 515–541.
- (8) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals and Polymers*, 2nd ed.; Oxford Press: New York and Oxford, 1999; Chapter XI.
- (9) Matsumoto, N. Overview of Silicon-Based Materials. *Jpn. J. Appl. Phys.* **1998**, *37*, 5425–5436.
- (10) Fujiki, M. A Correlation between Global Conformation of Polysilane and UV Absorption Characteristics. *J. Am. Chem. Soc.* **1996**, *118*, 7424–7425.
- (11) Corriu, R. J. P.; Guerin, C. Alkali Metal Hydrides: New Metallating Reagents at Silicon. *J. Chem. Soc., Chem. Commun.* **1980**, 168–169.
- (12) Sakamoto, K.; Obata, K.; Hirata, H.; Nakajima, M.; Sakurai, H. Novel anionic polymerization of masked disilenes to polysilylene high polymers and block copolymers. *J. Am. Chem. Soc.* **1989**, *111*, 7641–7643.
- (13) Furukawa, K.; Ebata, K. Preparation and Single Molecule Structure of Electroactive Polysilane End-Grafted on a Crystalline Silicon Surface. *Appl. Phys. Lett.* **2000**, *77*, 4289–4291.
- (14) Furukawa, K.; Ebata, K.; Fujiki, M. One-dimensional Silicon Chain Architecture: Molecular Dot, Rope, Octopus and Toroid. *Adv. Mater.* **2000**, *12*, 1033–1036.
- (15) Liang, Y.; Schmehl, R. H. Coordination Chemistry at a Surface: Polymetallic Complexes Prepared on Quartz by Alternate Deposition of Iron(II) and Ruthenium(II) Centers. *J. Chem. Soc., Chem. Commun.* **1995**, 1007–1008.



- (16) Higashi, G. S.; Chabal, Y. J.; Trucks, G. W.; Krishnan Raghavachari. Ideal Hydrogen Termination of the Si(111) Surface. *Appl. Phys. Lett.* **1990**, *56*, 656–658.
- (17) Effenberger, F.; Goetz, G.; Bidlingmaier, B.; Wezstein, M. Photoactivated Preparation and Patterning of Self-Assembled Monolayers with 1-Alkenes and Aldehydes on Silicon Hydride Surfaces. *Angew. Chem., Int. Ed.* **1998**, *37*, 2462–2464.
- (18) Furukawa, K.; Ebata, K.; Matsumoto, N. An Isolated Silicon Single Chain End-Grafted onto a Substrate Surface. *Appl. Phys. Lett.* **1999**, *75*, 781–783.
- (19) Halperin, A.; Tirrell, M.; Lodge, T. P. Tethered Chains in Polymer Microstructures. *Adv. Polym. Sci.* **1992**, *100*, 31–71.
- (20) Szleifer, I.; Carignano, M. A. Tethered Polymer Layers. *Adv. Chem. Phys.* **1996**, *94*, 165–260.
- (21) Stamouli, A.; Pelletier, E.; Koutsos, V.; van der Vegte, E.; Hadziioannou, G. An Atomic Force Microscopy Study on the Transition from Mushrooms to Octopus Surface "Micelles" by Changing the Solvent Quality. *Langmuir* **1996**, *12*, 3221–3224.
- (22) Koutsos, V.; van der Vegte, E.; Pelletier, E.; Stamouli, A.; Hadziioannou, G. Structure of Chemically End-Grafted Polymer Chains Studied by Scanning Force Microscopy in Bad-Solvent Conditions. *Macromolecules* **1997**, *30*, 4719–4726.
- (23) Williams, D. R. M. Grafted Polymers in Bad Solvents: Octopus Surface Micelles. *J. Phys. II (France)* **1993**, *3*, 1313–1318.
- (24) Bright J. N.; Williams D. R. M. Grafted Semiflexible Polymers in Poor Solvents: Toroidal and Tower Surface Micelles. *Europhys. Lett.* **1999**, *45*, 321–326.
- (25) Furukawa, K.; Ebata, K. Conformational Transition of End-Grafted Poly(di-*n*-hexylsilane) in Solventless Conditions. *Macromolecules* **2002**, *35*, 327–329.
- (26) Harrah, L. A.; Zeigler, J. M. Rod-to-Coil Transition in Solutions of Poly(di-*n*-hexylsilane). *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 209–211.
- (27) Miller, R. D.; Hofer, D.; Rabolt, J.; Fickes, G. N. An Anomalously Long-Wavelength Electronic-Transition in Conformationally Locked Organosilane High Polymers. *J. Am. Chem. Soc.* **1985**, *107*, 2172–2174.
- (28) Oka, K.; Fujiue, N.; Dohmaru, T.; Yuan, C. H.; West, R. An Abrupt Solvatochromic Transition in a Polar Polysilane. *J. Am. Chem. Soc.* **1997**, *119*, 4074–4075.

AR020072Q