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Side Chain Effect on Thermochromism and Solvatochromism of End-Grafted Polysilane $[Si(CH_3)_2SiR_2]_n$ ($R = C_2H_5$, n-C_4H_9, n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$)

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ABSTRACT: We synthesized a series of polysilanes $-[Si(CH_3)_2SiR_2]_n-$ [$R = C_2H_5$, n-C_4H_9, n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$] end-grafted on a quartz surface by utilizing the anionic polymerization of the corresponding source materials. We first confirmed that these symmetrically alkyl-substituted polysilanes exhibited reversible thermochromism in isooctane solution. When the polysilanes were end-grafted on the quartz surface, they also exhibited reversible thermochromism in a vacuum and reversible solvatochromism as the ratio of the isooctane/ethanol cosolvent was varied. In all of these experiments, we observed the transition between two clearly distinguishable phases. No side chain effect was observed for the peak wavelengths of the absorption band. However, the side chain effect appeared at a critical temperature and a critical cosolvent ratio for the transitions. The packing force between the alkyl chains in the highly ordered structure of the polysilane plays a dominant role in these transitions. We also discuss the difference in the transition behavior in solution, in the solid state, and in the end-grafted state.

Introduction

Polysilane is a one-dimensional silicon-catenated polymer that possesses alkyl and/or aryl groups as side chains. It exhibits a unique set of semiconducting properties that are based on the delocalization of σ-electrons along the one-dimensional silicon backbone, known as σ-conjugation.[1] In fact, photoconductivity,[2] hole drift mobility,[3] and electroluminescence[4] have been observed by using solid thin films of polysilane. The optical properties of polysilane have also already been extensively studied. Polysilane usually possesses an intense and sharp absorption band in the UV region, which is attributed to the $\sigma-\sigma^*$ transition of the one-dimensional silicon backbone.

Polysilane often exhibits reversible thermochromism, namely, a change in the UV absorption spectrum that is dependent on temperature. Typically, the response to temperature has been classified into three types.[5] Some polysilanes show clear thermochromism between two independent absorption bands, both of which are in the ultraviolet region, accompanied by an isosbestic point. Other polysilanes show a gradual shift in absorption peak wavelength, and some show no shift in absorption peak wavelength over a wide temperature range. The thermochromic behavior depends on not only the state of the polysilanes (for example, in dilute solution or in a solid state) but also, and this is often more important, the side chains.

Thermochromism is clearly observed especially from symmetrically alkyl-substituted polysilanes such as poly(dialkylsilane)s[6] and poly(di-*n*-hexyldimethyldisilene).[7] The two clearly distinguishable absorption bands observed in these polysilanes are assigned to different backbone conformations that lead to different degrees of σ-conjugation. This appears as a difference in the absorption peak wavelength because the absorption bands result from the electronic structure of the silicon backbone. Changing the backbone conformation by a stimulus other than temperature can also induce chromism.[8] For instance, solvatochromism,[9] ionochromism,[10] electrochromism,[11] and piezochromism[12] have been reported by using specifically designed polysilanes.

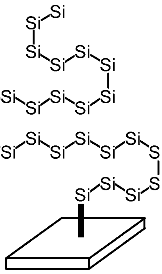

Figure 1. Schematic drawing of an end-grafted polysilane. A terminus of the polysilane is chemically bonded to a solid surface through an anchor molecule (shown as a bold line). Two side chains on each silicon atom are omitted for clarity.

Recently, we successfully synthesized end-grafted (EG) polysilane, namely a polysilane molecule whose terminus was tethered to a quartz substrate by a chemical bond (Figure 1).[13] This was achieved by means of a one-to-one chemical reaction between a reactive anchor built on a quartz surface and end-lithiated polysilane obtained by the anionic polymerization of masked disilene.[14] EG polysilane was well characterized by UV absorption spectroscopy[13] and atomic force microscopy (AFM).[15] The individual EG polysilane molecules were observed as collapsed or ropelike images depending on the chain rigidity determined by the substituents.[16] The grafting density was readily controlled by the reactive anchor density, which could be

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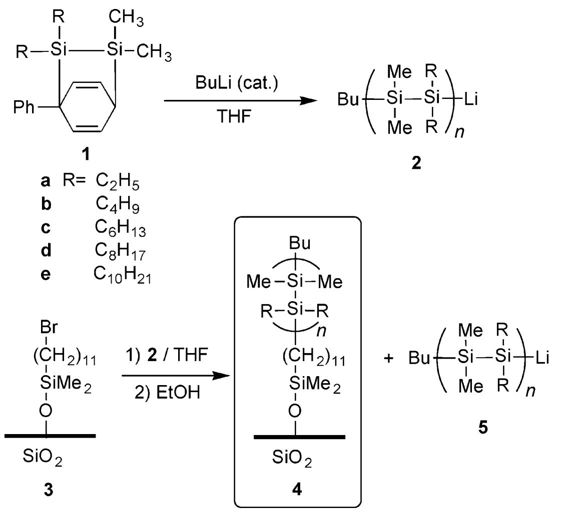
Scheme 1. Synthetic Route for End-Grafted Polysilanes; Notations 3 and 4 Indicate Organic Materials with a Quartz Substrate Included



diluted by nonreactive anchors.[13a] This enables us to observe unprecedented supramolecular structures formed by several polysilane chains.[15b]

The most distinctive feature of EG polysilanes is that the polysilane molecules are isolated from each other on the substrate surface. The state of the EG polysilanes would be different from those of an isolated polysilane in a dilute solution and a polysilane in the solid state. In fact, UV absorption spectra observations have revealed some unique EG polysilane behavior.[13a,17] Symmetrically alkyl-substituted polysilanes often exhibit clear thermochromism, and thus it is of interest to compare the thermochromic behavior under different conditions, namely, in dilute solution, in the solid state, and in the end-grafted state. It is also our concern to compare the solvatochromic behavior of the EG polysilanes with their thermochromic behavior.

In this paper, we report our synthesis of a series of EG polysilanes and corresponding free-standing (that is, not end-grafted) polysilanes with symmetrical alkyl side chains, $-[Si(CH_3)_2SiR_2]_n-$ ($R = C_2H_5$, n-C_4H_9, n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$). We describe the thermochromism of the EG polysilanes and discuss the effects of the side chain by comparing the thermochromism of the end-grafted state with that of the corresponding free-standing polysilanes in dilute solution and the solid thin films. We also report the solvatochromism of the EG polysilanes and discuss the effect of solvents.

Synthesis and Characterization

Synthesis of EG Polysilanes. We synthesized EG polysilanes according to our previously reported method, as shown in Scheme 1.[13a] The anionic polymerization of masked disilene **1** using *n*-BuLi as an initiator yields end-lithiated polysilane **2**. The typical polymerization time is several minutes, after which the backbiting reaction becomes superior and decomposes **2** into cyclosilane compounds. The reaction between **2** and a reactive anchor $-OSi(CH_3)_2C_{11}H_{22}Br$ built on a solid surface **3** is quick and provides EG polysilane **4** within a minute. The excess **2** is then terminated with a drop of ethanol to yield a hydrogen-terminated polysilane **5** that is not grafted on the substrate. We prepared a series of symmetrically alkyl-substituted masked disilenes **1a**–**1e** in this study to extract the side chain effect.

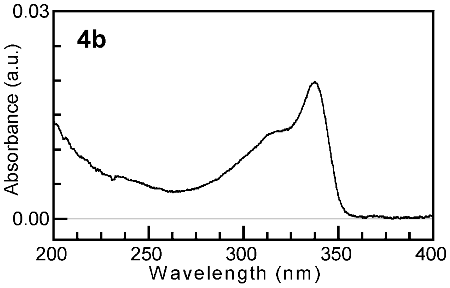


Figure 2. UV absorption spectrum of end-grafted poly(di-*n*-butyldimethyldisilene) **4b** under ambient conditions.

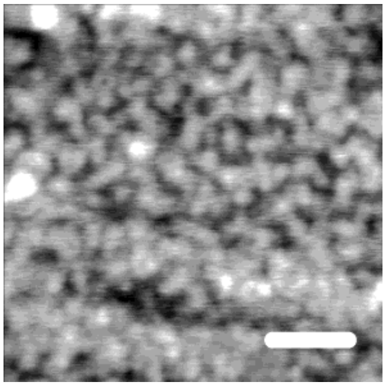


Figure 3. A topographic image of end-grafted poly(di-*n*-butyldimethyldisilene) **4b** under ambient conditions measured by atomic force microscopy using the tapping mode. Scale bar: 100 nm.

Table 1. Basic Characteristics of Polysilanes 5

entry	ϵ (cm^{-1} mol^{-1} dm^3)[a]	λ_{max} (nm)[a]	$M_w \times 10^{-3}$ [b]	M_w/M_n[b]
5a	3600	302	5.2	1.3
5b	3400	311	16	1.3
5c	5300	312	97	1.8
5d	5100	313	29	1.3
5e	3500	313	19	1.3

[a] Determined by UV absorption spectrum in hexane. [b] Determined by gel permeation chromatography using polystyrene standard.

Characterization of EG Polysilane 4. We characterize a typical EG polysilane by using **4b** as an example. Figure 2 shows the UV absorption spectrum of **4b** under ambient conditions at room temperature. It shows a sharp absorption band peaking at 337 nm. The absorption band is identical to that of a solid thin film of the corresponding polysilane **5b**, which can be attributed to the $\sigma-\sigma^*$ transition of the polysilane. The absorbance of **4b** is very small because it contains as much EG polysilane as a submonolayer film. For example, the absorbance of an LB monolayer of poly(di-*n*-hexylsilane) has been reported to be ~0.02.[18]

Figure 3 shows the AFM topography of **4b**. We observed dot images distributed homogeneously on the substrate surface. The dot corresponds to a typical structure formed by a single flexible polymer end-grafted on a solid surface under poor solvent conditions,[19] as we have discussed previously in relation to AFM images of poly(trimethyl-*n*-propyldisilene) end-grafted on a quartz substrate.[15a]

Characterization of Polysilanes 5. Table 1 summarizes the basic characteristics of the polysilanes **5a**–**5e**. Most of these polysilanes have a weight-averaged molecular weight of 10 000 or more, which corresponds to an average of ~100 or more silicon units per

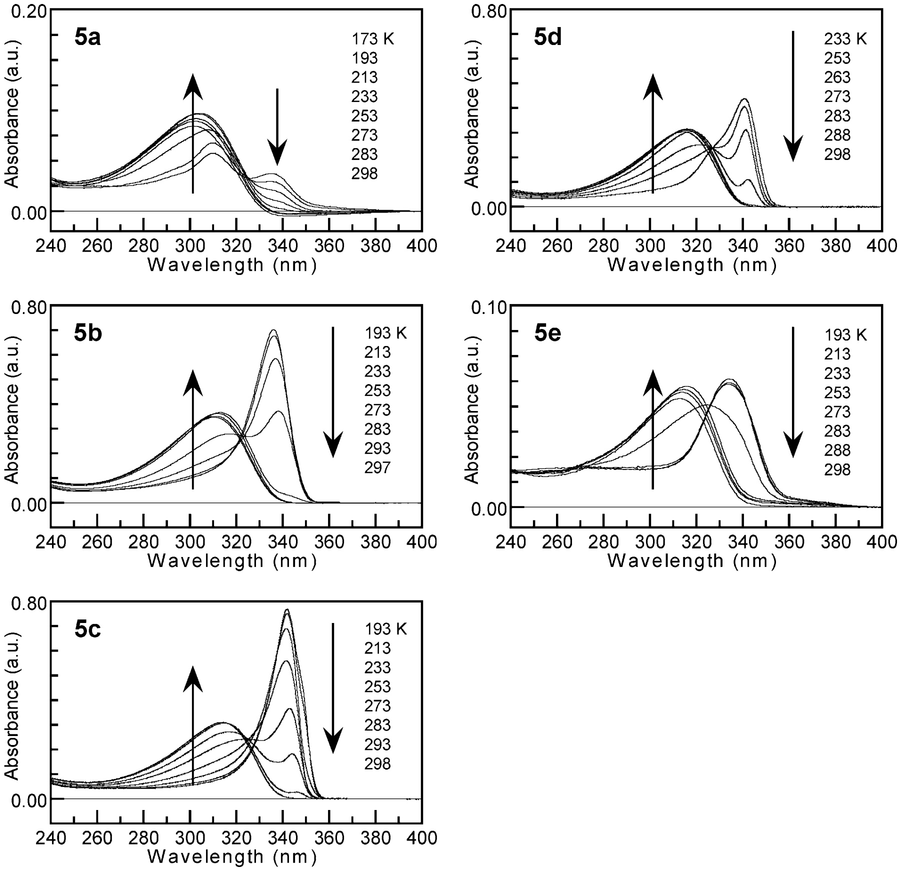


Figure 4. Temperature-dependent UV absorption spectra of polysilanes **5a**–**5e** in an isooctane solution.

chain. We reasonably assume that the molecular weight distributions of polysilanes end-grafted on a quartz surface are similar to those of **5a**–**5e**. Thus, the polysilanes end-grafted on the substrate surface possess a certain chain length, and they are unlike a short oligomer.

We observed a sharp absorption band with a peak wavelength at around 310 nm in a hexane solution of **5a**–**5e** at room temperature. The bands can be assigned to the σ–σ^* transition of the silicon backbone. The relatively short absorption peak wavelength suggests that the local conformation of the polysilanes is a disordered helical structure in solution at room temperature.

The molar absorption coefficients for **5a**–**5e** are in a range of several thousand per silicon unit. Thus, according to the empirical rule,[16] we estimate that **5a**–**5e** are all flexible polymers, namely, identical to our previously reported polysilane, poly(trimethyl-*n*-propyldisilene), which we obtained by the same scheme.[13] This estimation also corresponds to the AFM topography in Figure 3, which showed the collapsed structure that is the characteristic single molecule structure of a flexible polysilane end-grafted on a solid surface.

Results

Thermochromism of Polysilane 5 in Dilute Solution. To obtain a basic understanding of the polysilanes used in this work, we first measured the optical properties of polysilanes **5a**–**5e** in a dilute solution. This was also because most of these polysilanes are new, although **5c** is already known.[7] Figure 4 shows the temperature-dependent UV absorption spectra of polysilanes **5a**–**5e** in an isooctane solution. They all exhibited reversible thermochromism. The absorption band observed in the low-temperature regime appears in a longer wavelength region than that in the high-temperature regime. This behavior can be assigned to the thermochromic transition between two clearly distinguishable phases: one with a transoid conformation and the other with a disordered or helical conformation.[20] Although this type of clear thermochromism between two independent phases has been observed for symmetrically substituted dialkylpolysilanes, there are few examples. Here we show that polysilanes **5a**–**5e** also belong to this order.

Thermochromism of EG Polysilane 4 under Solventless Conditions. Figure 5 shows the temperature-dependent UV absorption spectra of **4a**–**4e** measured in a vacuum. They all show clear thermochromism with an isosbestic point. All the spectra exhibit low-energy (longer wavelength) shifts as the temperature decreases. They also exhibit a thermochromic transition between two clearly distinguishable phases, which are identical to those in Figure 4.

Solvatochromism of EG Polysilane 4. Figure 6 shows the UV absorption spectra of **4a**–**4e** immersed in ethanol/isooctane cosolvent with various volume ratios. Ethanol and isooctane are a poor and a good solvent, respectively, for **5a**–**5e**. The absorption band under poor solvent conditions is in a longer wavelength region than that under good solvent conditions. The absorption spectrum between these two bands varied with changes in the volume ratio of the ethanol/isooctane cosolvent. The results indicate that **4** exhibits clear solvatochromism between two independent phases.

It is usually impossible to observe UV absorption spectra under poor solvent conditions because we cannot dissolve the polymer in a poor solvent. The EG

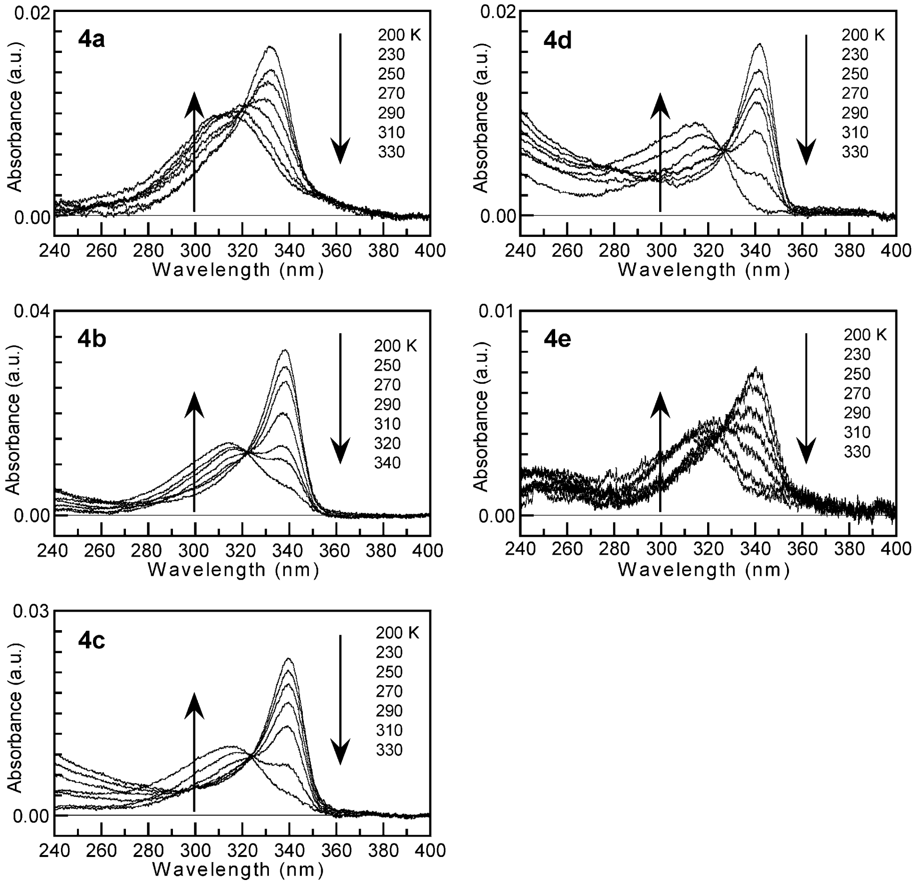


Figure 5. Temperature-dependent UV absorption spectra of end-grafted polysilanes **4a**−**4e** measured in a vacuum.

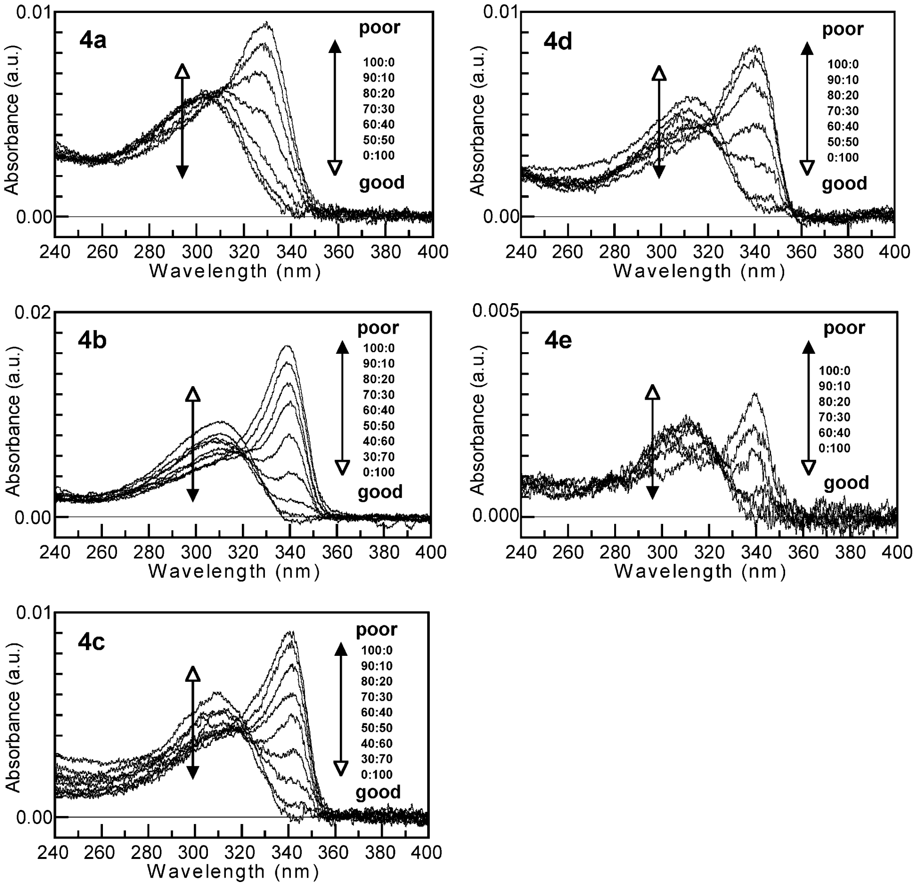


Figure 6. UV absorption spectra of end-grafted polysilanes **4a**−**4e** under isooctane/ethanol cosolvent conditions.

Table 2. Thermochromic and Solvatochromic Parameters for 4 and 5.

	thermochromism of **5**			thermochromism of **4**			solvatochromism of **4**		
R	λ_1 (nm)	λ_2 (nm)	T_c (K)	λ_1^{EG} (nm)	λ_2^{EG} (nm)	T_c^{EG} (K)	λ_1^{poor} (nm)	λ_2^{good} (nm)	R_c (EtOH:isooctane)
C_2H_5	335	302	173	331	311	290	329	303	40:60
n-C_4H_9	336	310	253	338	314	300	339	310	40:60
n-C_6H_{13}	342	313	283	340	314	310	341	309	40:60
n-C_8H_{17}	341	313	273	342	315	330	340	312	60:40
n-$C_{10}H_{21}$	335	313	273	340	310	330	339	310	70:30

polysilane, however, gives us a unique opportunity to observe the UV absorption spectra of single polysilane chains under any solvent conditions. The EG polysilane is neither dissolved under good solvent conditions nor precipitated under poor solvent conditions because the EG polysilanes are covalently bonded to the quartz surface and isolated from each other. To date, the solvatochromism of polysilane has been observed only from ether-substituted polysilanes.[9]

Discussion

Table 2 summarizes some important data obtained from the results shown in Figures 4−6. They are the absorption peak wavelengths for the thermochromism of **5** in an isooctane solution in low- and high-temperature regimes (λ_1 and λ_2) and the transition temperatures (T_c), those for the thermochromism of **4** in a vacuum (λ_1^{EG}, λ_2^{EG}, and T_c^{EG}), the peak wavelengths of **4** in ethanol and isooctane (λ_1^{poor} and λ_2^{good}), and the critical condition R_c for solvatochromism. Here R_c is defined as the ethanol:isooctane ratio at the transition from one phase to the other.

In the following, we discuss the effect of a side chain on the chromism. This corresponds to a comparison of each column in Table 2. We also discuss the difference between the thermochromism of **4** and **5** depending on the state of the polysilane as well as the relation between the thermochromism and solvatochromism of **4**. This corresponds to a comparison of each row in Table 2.

Side Chain Effect on Thermochromism of 5 in Dilute Solution. The values λ_1 (about 340 nm) and λ_2 (about 310 nm) are independent of the side chain. This means that the conformations in low- and high-temperature regimes are similar irrespective of the length of the alkyl chains.

According to a previous report, polysilanes synthesized by the dehalogenative coupling of dichlorodisilane $Cl(CH_3)_2Si-Si(C_6H_{13})_2Cl$ or of a mixture of two dichlorosilanes $(CH_3)_2SiCl_2$ and $(C_6H_{13})_2SiCl_2$ never exhibit thermochromism in the same way as **5c**.[7] This shows that the highly ordered structure, which is the result of the head-to-tail polymerization mechanism proposed for synthesis using masked disilene, is essential for clear thermochromism. Thus, the fact that **5a**−**5e** in the present work all show clear thermochromism means that the polysilanes have highly ordered alternating structures, as schematically shown in Figure 7.

By contrast, a side chain effect appeared in T_c. As the alkyl chain becomes longer, T_c tends to increase. This can be explained by the interaction between the alkyl side chains at every other silicon atom (Figure 7). Longer alkyl chains should have greater packing force and therefore make the conformation more stable. Thus, a higher temperature is needed to induce a conformational change in polysilanes with longer alkyl side chains.

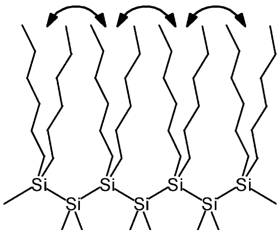


Figure 7. A schematic illustration of the side chain packing effect in poly(dialkyldimethyldisilene).

As regards the same class of polysilanes synthesized from masked disilene, asymmetrically substituted polysilanes $[Si(CH_3)_2SiRCH_3]_n$ with R = n-butyl and isobutyl are known.[14] These polysilanes also exhibit thermochromism in a dilute solution, and it is worth comparing their T_c with those seen in Figure 4. The T_c values observed for the polysilanes with asymmetrical side chains are 200 (R = isobutyl) and 230 K (R = n-butyl). They are about 50 K lower than the T_c values for **5a**−**5e**. This effect is also understandable in terms of the packing force between side chains. It is greater in symmetrically substituted polysilanes with highly ordered structures.

Side Chain Effect on Thermochromism of End-Grafted Polysilane 4. The side chain effect cannot be recognized in λ_1^{EG} and λ_2^{EG}. The wavelength λ_1^{EG} is about 340 nm, and λ_2^{EG} is 310 nm, irrespective of the side chains. These values are also very similar to λ_1 and λ_2. By contrast, we can recognize the side chain effect on T_c^{EG}. As the alkyl chain becomes longer, T_c tends to become higher. This is related to the motion of the side chains. The packing force of longer side chains is stronger than that of shorter side chains, and this makes the conformation more stable. If we compare T_c^{EG} with T_c, T_c^{EG} is higher than the T_c, which is 30−50 K. This temperature difference is also related to the motion of the polysilane. Polysilanes in solution have a greater degree of freedom of motion than their end-grafted form.

Characteristics of Individual Polysilane Chains End-Grafted on Solid Surface. Next we compare the thermochromism in different states and discuss the characteristic features of EG polysilanes. For this purpose, we prepared a solid thin film of **5c** on a quartz substrate and measured its thermochromism, as shown in Figure 8. Thermochromic behavior was not observed in the solid thin film of **5c** within a similar temperature range,[21] although clear thermochromism was observed with **4c** in a vacuum (Figure 5) and **5c** in a dilute solution (Figure 4).

The difference between the phenomena can be understood in terms of the degree of freedom of the motion of the polysilane chains in each environment. An isolated polysilane chain in a dilute solution, which is free from any interchain interaction, is most flexible as regards motion. Thus, its conformation can be changed with a small stimulus. This leads to clear and abrupt thermochromism. In complete contrast, polymer chains

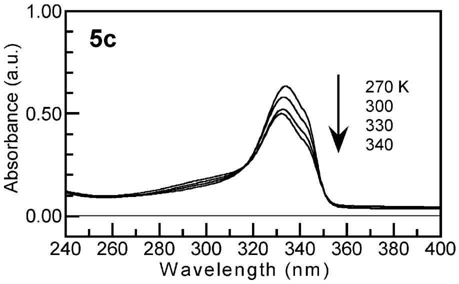


Figure 8. Temperature-dependent UV absorption spectra of a thin solid film of polysilane **5c** in a vacuum.

in a solid film suffer from unavoidable interchain interactions with many other surrounding polymer chains. This prohibits change in the conformation of the polymers and provides no thermochromism under this condition.

The EG polysilanes show clear thermochromism despite being placed in a vacuum, namely, a condition under which the polymers cannot move very freely. The EG polysilanes are neither in solution nor in the solid state. The characteristic feature of the EG polysilanes is that they are isolated from each other under any conditions. Thus, the results here can be explained by the idea that there is little or no interchain interaction in an end-grafted system in which the polymer chains are independently fixed to the surface. This conclusion may provide a clue that will help us to answer the long-standing question as to whether the thermochromic behavior of polysilane in solution is a single molecular event or the result of an aggregation of polysilane molecules.[5b] Our present results showed it to be a single molecular event because polysilane molecules are not readily aggregated in our system where they are tethered on the solid surface and placed in a vacuum.

Poly(di-*n*-hexylsilane) (PDHS) is an example of a polysilane whose thermochromism has been observed in solution, in the solid state, and in the end-grafted state. Our previous study revealed that PDHS end-grafted on a quartz surface exhibits thermochromism in a vacuum, which is similar to that in dilute solution but different from that in a solid state.[17] In this regard, the current observations agree with this earlier finding. There is approximately a 50 K difference between the T_c of **5** in solution and that of **4** in a vacuum. The difference in T_c seems to be reasonable because polysilane in solution is much more mobile than that in a vacuum. However, the T_c values of PDHS in a hexane solution and EG PDHS in a vacuum are in the same temperature range. PDHS is fully substituted by long alkyl chains. Thus, in PDHS the packing force may be greater than the solvent effect.

Side Chain Effect on Solvatochromism of End-Grafted Polysilane 4. The absorption band appeared in the longer wavelength region under poor solvent conditions, whereas it appeared in the shorter wavelength region under good solvent conditions. Again, as found with the thermochromic behavior of **4** and **5**, the peak wavelengths of the solvatochromism are all similar irrespective of the side chains. Furthermore, the values λ_1^{poor} and λ_2^{good} are identical to λ_1 and λ_2, as well as λ_1^{EG} and λ_2^{EG}. Thus, the conformations induced by the temperature and solvent conditions are identical.

By contrast, R_c depends on the side chains. As the side chain becomes longer, it requires less good solvent for the transition. For instance, it needs only 30% of isooctane for **4e** with long decyl chains, whereas it needs 60% to induce the transition for **4a**. This seems to show that the change in the EG polysilane conformation is driven by the solvation of isooctane molecules into polysilane chains. This can be understood to mean that a longer alkyl chain has a stronger affinity with a good solvent and induces the transition with less good solvent.

We can compare R_c with that of the asymmetrically substituted EG polysilane, poly(trimethyl-*n*-propyldisilene). In this case, the transition was almost complete when the isooctane ratio reached 17%, which corresponds to an R_c of 83:17.[13a] The isooctane ratio for the transition is smaller than those in Table 2, although the alkyl side chains for the asymmetrically substituted polysilane are much shorter than that of **4e**. This means that side chain symmetry plays a more effective role in solvatochromism than the length of the alkyl side chains.

Comparison of Solvatochromism and Thermochromism of EG Polysilane 4. We can compare the effect of solvent with that of temperature by comparing Figures 5 and 6. The local conformation under poor and good solvent conditions corresponds to that at low and high temperature, respectively. The EG polysilane chain attempts to form a globule under poor solvent conditions so that there is as little contact as possible with the poor solvent. In this collapsed structure, the packing effect influences the form of structures with a transoid conformation. This is also true for polysilane in a low-temperature regime. By contrast, when chains become more mobile under good solvent conditions, the motion can supersede the packing force. Therefore, the conformations adopted in this regime are somewhat random and referred to as disordered structures. This has already been discussed in detail by using thermochromism data measured with polysilane in dilute solution. Our present results provide new opportunities to study the effects of a variety of stimuli on the conformation of polysilanes.

Conclusions

We synthesized EG polysilanes **4** as well as the free-standing polysilane **5** and studied their temperature- and solvent-dependent UV absorption spectra. We obtained the following results and reached a number of conclusions.

1. Polysilanes **5** in isooctane solution exhibit thermochromism between two clearly distinguishable absorption bands, showing that they have highly ordered alternating structures.
2. The EG polysilanes **4** exhibit thermochromism in a vacuum and solvatochromism in ethanol/isooctane cosolvent between two clearly distinguishable absorption bands. Both bands are identical to those in the thermochromism of polysilane **5** in solution.
3. No side chain effect appears in the peak wavelengths of the two phases.
4. Dynamic parameters for chromism behavior, such as the temperature and volume ratio of the transitions, are dependent on the length of the alkyl side chain. This can be qualitatively understood in terms of the packing force between the alkyl side chains on every other silicon atom.
5. The packing force is stronger than that of asymmetrical poly(alkyltrimethyldisilene)s and weaker than that of fully symmetrically substituted poly(dialkylsilane)s.

6. An EG polysilane chain can move and change the conformation in a vacuum. Although it is less mobile than an isolated polymer in solution, it is much more mobile than a chain in a solid thin film.

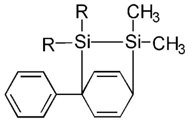
In this paper, we discussed the effects of temperature and solvent based on a comparison of independent experiments. Much greater detail regarding the relationship between the temperature and solvent effects could be revealed by measuring, for instance, temperature-dependent UV spectra in a poor/good cosolvent system at different volume ratios.

Experimental Section

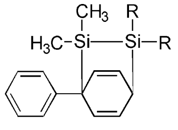
General. UV absorption spectra were recorded by using a Hitachi U3500 spectrophotometer equipped with a Daikin CRYOTEC cooling system. We used a 10 mm path length quartz cell to measure the absorption spectra of **5a**−**5e** in dilute hexane solution. We determined the temperature of the temperature-dependent UV absorption spectra measurements of **5** in a dilute isooctane solution with a thermocouple immersed in the solvent. The temperature was determined by attaching the thermocouple to a copper mount for the measurements of **4** in a vacuum. The solvent-dependent spectra were recorded by placing **4** in a 5 mm path quartz cell filled with cosolvent. The solid thin film sample was fabricated by the spin-coating technique from a toluene solution of **5** and used for measuring its thermochromism in a vacuum.

Topographic images were observed by using Seiko SII 3800 atomic force microscopy under ambient conditions in the dynamic force mode. NMR spectra were recorded with a Varian Unity 300. Molecular weight was determined by Shimadzu LC-10 size exclusion chromatography using polystyrene standards.

Synthesis of Monomers 1a−**1e.** Monomers **1a**−**1e** were prepared by the reaction of the corresponding 1,2-dichlorodisilane and lithium biphenyide in THF according to a previously reported method.[22] The major isomer was 1-phenyl-7,7-dialkyl-8,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (Ma) over 1-phenyl-7,7-dimethyl-8,8-dialkyl-7,8-disilabicyclo[2.2.2]-octa-2,5-diene (Mi). We did not separate these two isomers for the following anionic polymerization and end-graft reaction.



Ma: Major Isomer



Mi: Minor Isomer

Spectroscopic Data. 1a. Colorless solid, bp 120 °C (0.1 Torr), 68% yield, Ma:Mi = 85:15. ^{1}H NMR ($CDCl_3$, δ): 0.249 (s, 6H), 0.601 (m, 4H), 0.870 (t, 6H), 2.999 (dd, 1H), 6.025 (dd, 2H), 6.245 (d, 2H), 7.3−7.5 (m, 5H). ^{13}C NMR ($CDCl_3$, δ): −2.150 ($SiMe_2$), 3.965 ($SiCH_2$), 8.626 (CH_3-CH_2), 34.791 (CH), 47.570 (q), 124.283, 125.331, 126.900, 128.109, 128.289 (CH=, Ph), 143.144 (q). ^{29}Si NMR ($CDCl_3$, δ): −16.881, −10.119.

1b. Pale yellow oil, bp 150 °C (0.1 Torr), 63% yield, Ma:Mi = 82:18. ^{1}H NMR ($CDCl_3$, δ): 0.214 (s, 6 H), 0.555 (m, 4H), 0.836 (t, 6H), 1.1−1.3 (m, 8H), 2.976 (dd, 1H), 5.996 (dd, 2H), 6.213 (d, 2H), 7.3−7.5 (m, 5H). ^{13}C NMR ($CDCl_3$, δ): −2.090 ($SiMe_2$), 12.171 ($SiCH_2$), 13.660 (CH_3-CH_2), 26.806, 27.120, ($-CH_2-$), 34.851 (CH), 47.576 (q), 124.283, 125.432, 126.834, 128.162, 128.376 (CH= , Ph), 143.251 (q). ^{29}Si NMR ($CDCl_3$, δ): −16.652, −13.498.

1d. Pale yellow oil, bp 190 °C (0.1 Torr), 31% yield, Ma:Mi = 85:15. ^{1}H NMR ($CDCl_3$, δ): 0.232 (s, 6 H), 0.571 (m, 4H), 0.928 (t, 6H), 1.2−1.3 (m, 16H), 1.3−1.4 (m, 8H), 2.994 (dd, 1H), 6.014 (dd, 2H), 6.230 (d, 2H), 7.3−7.5 (m, 5H). ^{13}C NMR ($CDCl_3$, δ): −2.077 ($SiMe_2$), 12.551 ($SiCH_2$), 14.120 (CH_3-CH_2), 22.693, 24.910, 29.149, 29.229, 31.900, 33.930 ($-CH_2-$), 34.871 (CH), 47.590 (q), 124.297, 125.432, 126.814, 128.176, 128.396 (CH= , Ph), 143.298 (q). ^{29}Si NMR ($CDCl_3$, δ): −16.638, −13.555.

1e. Pale yellow oil, bp 180−200 °C (0.1 Torr), 31% yield, Ma:Mi = 85:15. ^{1}H NMR ($CDCl_3$, δ): 0.176 (s, 6 H), 0.511 (m, 4H), 0.877 (t, 6H), 1.1−1.4 (m, 32H), 2.941 (dd, 1H), 5.962 (dd, 2H), 6.174 (d, 2H), 7.2−7.5 (m, 5H). ^{13}C NMR ($CDCl_3$, δ): −2.064 ($SiMe_2$), 12.565 ($SiCH_2$), 14.120 (CH_3-CH_2), 22.700, 24.916, 29.189, 29.363, 29.563, 29.603, 29.683, 31.933 ($-CH_2-$), 33.930 (CH), 47.610 (q), 125.452, 126.840, 127.141, 128.189, 128.409, (CH= , Ph), 143.325 (q). ^{29}Si NMR ($CDCl_3$, δ): −16.623, −13.570.

Synthesis of 3. A quartz substrate was immersed into a 1:4 mixture of 30% H_2O_2 (30%) and concentrated H_2SO_4 for 1 h. The substrates were then rinsed in a water flow and dried in an 80 °C oven. Then the substrates were treated in a 5 wt % toluene solution of $Br(CH_2)_{11}SiMe_2Cl$ at 110 °C for 1 h, thus forming a reactive anchor on the surface by the silane coupling reaction. The substrates were rinsed thoroughly with toluene and acetone and dried in an 80 °C oven.

End-Graft Reaction. The anionic polymerization for synthesizing **2** was conducted under dry and oxygen-free conditions. Glassware consisting of two vessels connected by a rotatable neck was used for the end-graft reaction.[15a] Typically, monomer **1** (3 mmol) was dissolved in dry THF (10 mL). Approximately 100 μL of *n*-BuLi was added to the solution to initiate polymerization. After several minutes the solution turned deep red, indicating the generation of **2**. The solution was then transferred to another vessel, which held **3**. After a minute, a drop of ethanol was added to quench any excess **2**. The remaining THF solution was poured into ethanol to precipitate **5**. The obtained **4** was repeatedly rinsed with good solvents for polysilane such as THF and toluene and then immersed in toluene overnight. The substrate was further rinsed with ethanol and water. The EG polysilanes were not dissolved during this washing process because the polymer was covalently bonded to the surface, while the polysilanes left on the surface disappeared completely.

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