Control of Polysilane Conformation by Photoisomerization of Pendant Azobenzene Groups

Hiroaki Horiuchi,* Toru Fukushima, Changli Zhao, Tetsuo Okutsu, and Hiroshi Hiratsuka*
Department of Chemistry, Gunma University, Kiryu, Gunma 376-8515

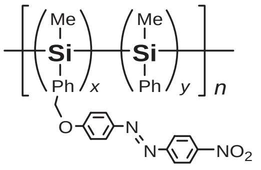
(Received June 30, 2005; CL-050843)

Conformational study of silicon backbone of poly(methylphenylsilane) functionalized with pendant azobenzene groups has been carried out. The conformation of the silicon backbone depends on the molar ratio of the Si units with and without the pendant azobenzene group, and the inflection point for the conformational change from the slowly winding helix to random coil has been found to be ca. 0.5 of the molar ratio. The conformational change has been induced by the photoisomerization of pendant azobenzene groups in the film state.

Polysilanes exhibit unique properties as one-dimensional semiconductors (i.e. quantum wires) due to the delocalized σ-electrons along the silicon backbone.[1] Because of the σ-conjugation, their electronic and optical properties strongly depend on the conformation and orientation of the silicon backbone.[1,2] Therefore the control of the conformation and orientation is one of important subjects not only in understanding the fundamental properties of polysilanes but also in utilizing the electronic and optical properties.[3] Control of conformation of polysilanes has been studied by changing temperature, i.e. thermochromism.[3–5] On the other hand, little report has been published on the study on the control of the conformation by light irradiation.[6] Seki et al. studied the spin cast film of poly(di-*n*-hexylsilane) on azobenzene monolayer and found out that the ratio of all-trans to disordered conformation can be controlled by the photoisomerization of the monolayer azobenzene.[6]

Recently, much attention has been paid for the introduction of functional groups to polysilanes as pendant groups.[7–11] It has been reported that the photostability of polysilane is enhanced by the introduction of azobenzene derivative as a pendant group.[11] For non-conjugated polymers, the conformation of backbone can be controlled by the photoisomerization of the pendant azobenzene group.[12,13] Therefore in the case of polysilane, the photoisomerization of pendant azobenzene groups is expected to induce the conformational change, i.e. pendant azobenzene gives multifunctions. We have synthesized poly(methylphenylsilane) functionalized with pendant 4-nitroazobenzene and have studied photophysical and photochemical processes of silicon backbone.[7] In this paper, we report the effect of the photoisomerization of pendant groups on the conformation of the silicon backbone in the film state.

As a pendant group, 4-nitroazobenzene (abbreviated to azo group) was introduced at the phenyl group of poly(methylphenylsilane) (**PMPS**) with various molar ratio (x/y) of the Si units with and without the pendant azo group.[7] The molecular structure and molar ratio of the azo group of functionalized polysilanes (**PMPS-azo** x/y) are shown in Scheme 1. Number averaged molecular weight M_n and polydispersity of the synthesized polysilane were 5000–16,000 and 1.7–2.3, respectively. Figure 1 shows UV–vis absorption spectra of **PMPS** (thin solid line), 4-nitro-4′-methoxyazobenzene (**azo**: broken line), and **PMPS-azo0.5** (bold solid line) and **PMPS-azo0.9** (dotted line) in tetrahydrofuran (THF) at room temperature. The molar absorption coefficients of **PMPS** and **PMPS-azo** x/y were estimated for a silicon unit. The 340-nm band observed in the absorption spectrum of **PMPS** (thin solid line) is due to the slowly winding helical conformation with the dihedral angle of ca. 160°,[14] and the 380-nm band observed for **azo** (broken line) is due to its trans form.[15] In the absorption spectrum of **PMPS-azo0.5** (bold solid line), there are two absorption bands due to the silicon backbone in the helical conformation (340 nm) and trans form of the azo group (380 nm). This spectrum can be reproduced by the sum of the absorption spectra of **PMPS** and **azo** multiplied by $x/(x+y)$, indicating that the electronic interaction between the silicon backbone and azo group in the ground state is negligibly small[7] and thus the absorption spectrum is considered to give information on conformational changes in both the silicon backbone and azo group, independently. However, the absorption band due to the silicon backbone in the helical conformation (340 nm) was not observed in the absorption spectrum of **PMPS-azo0.9** (dotted line). This indicates that the increase of the molar ratio (x/y) induces the increase of the steric hindrance between pendant azo groups to give conformational changes of the silicon backbone from the helix to random coil. The inset of Figure 1 shows the population of the silicon backbone in



x/y	abbreviation
0	**PMPS**
0.1	**PMPS-azo0.1**
0.5	**PMPS-azo0.5**
0.6	**PMPS-azo0.6**
0.9	**PMPS-azo0.9**

Scheme 1. Molecular structure of **PMPS-azo** x/y and their abbreviations.

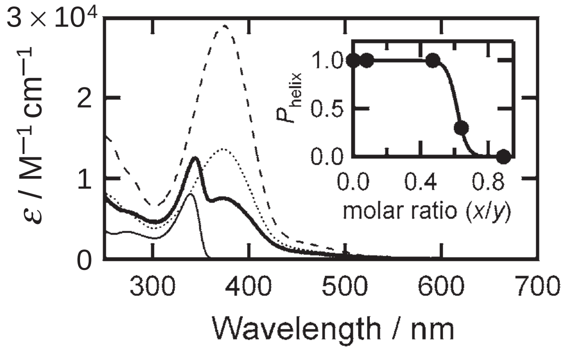


Figure 1. Absorption spectra of **PMPS** (thin solid line), **azo** (broken line), **PMPS-azo0.5** (bold solid line), and **PMPS-azo0.9** (dotted line) in THF. Inset; Plots of the population of the silicon backbone in the helical conformation (P_{helix}) against the molar ratio of the pendant azo group (x/y).

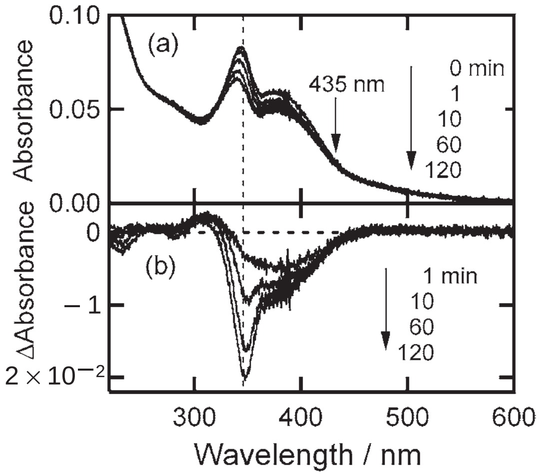
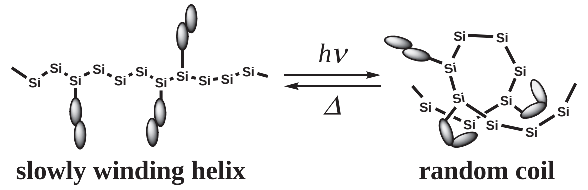


Figure 2. Absorption spectral change of **PMPS-azo0.5** thin film observed upon irradiation with 435 nm light (a) and difference absorption spectra before and after the irradiation (b).



Scheme 2. Schematic presentation of conformational change of the silicon backbone induced by photoisomerization of the pendant azo groups.

the helical conformation (P_{helix}) as a function of the molar ratio. It is found that the inflection point for the conformational change of the silicon backbone is ca. 0.5 of x/y.

Trans → cis photoisomerization of the pendant azo groups is expected to increase the intramolecular steric hindrance between pendant groups. In the solid state, the intermolecular steric hindrance between the photoisomerized azo groups and other polysilane chains (and their pendants) is expected to increase. These intra- and inter-molecular steric hindrances may induce the conformational changes of the silicon backbone from the helix to random coil. We have studied the effect of the photoisomerization of the pendant azo group on the conformation of the silicon backbone. As shown in the inset of Figure 1, the molar ratio of the azo group of **PMPS-azo0.5** is very close to the inflection point for the conformational change of the silicon backbone from the helix to random coil. Thus we selected **PMPS-azo0.5** as the sample for the photoisomerization experiment. To avoid the photodecomposition of the silicon backbone, the 435-nm light was selected to excite the azo group.

Figure 2a shows absorption spectral change of **PMPS-azo0.5** thin film observed upon the 435-nm light irradiation. Figure 2b shows difference spectra between the absorption spectra observed before and after the irradiation. At the irradiation time of 1 min, there are a negative peak around 380 nm and two positive peaks around 310 and 490 nm. This spectral change is similar to that observed for trans → cis photoisomerization of **azo** except for a weak shoulder around 340 nm, indicating that trans → cis photoisomerization of the pendant azo group predominantly took place. The weak shoulder is due to the slight decrease of the silicon backbone in the helical conformation. With the increase of the irradiation time, the decrease in the 340-nm band due to the silicon backbone in the helical conformation became remarkable. As the 435-nm irradiation did not induce the photodecomposition of PMPS, the decrease in the 340-nm band is attributable to the conformational change of the silicon backbone from the helix to random coil by the trans → cis photoisomerization of pendant azo groups as shown in Scheme 2. The reverse process was also observed upon heating to 130 °C, although the efficiency of the reverse process was not so high (25%). Above 130 °C, thermal decomposition of the pendant azo group was observed. Glass transition temperature of PMPS functionalized with azobenzene derivative was reported to be 155 °C[16] and this high glass transition temperature of the silicon backbone may be responsible for the low conversion efficiency at 130 °C.

This work was supported by a Grant-in-Aid for Scientific Research (Nos. 15350004, 16550005, and 16750110) and Scientific Research on Priority Areas (417) (No. 15033213) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japanese Government.

References

1 R. D. Miller and J. Michl, *Chem. Rev.*, **89**, 1359 (1989).
2 T. Sato, N. Nagayama, and M. Yokoyama, *J. Mater. Chem.*, **14**, 287 (2004).
3 H. Horiuchi et al., *J. Organomet. Chem.*, submitted for publication.
4 H. Kuzmany, J. F. Rabolt, B. L. Farmer, and R. D. Miller, *J. Chem. Phys.*, **85**, 7413 (1986).
5 K. Terao, Y. Terao, A. Teramoto, N. Nakamura, M. Fujiki, and T. Sato, *Macromolecules*, **34**, 4519 (2001).
6 T. Seki, K. Fukuda, and K. Ichimura, *Langmuir*, **15**, 5098 (1999).
7 C. Zhao, H. Horiuchi, T. Okutsu, S. Tobita, S. Takigami, and H. Hiratsuka, *Bull. Chem. Soc. Jpn.*, **76**, 961 (2003).
8 S. Nešpurek, F. Schauer, and A. Kadashchuk, *Monatsh. Chem.*, **132**, 159 (2001).
9 T. Seki, N. Tanigaki, K. Yase, A. Kaito, T. Tamaki, K. Ueno, and Y. Tanaka, *Macromolecules*, **28**, 5609 (1995).
10 R. Kani, Y. Nakano, Y. Majima, S. Hayase, C. H. Yuan, and R. West, *Macromolecules*, **27**, 1911 (1994).
11 S. Nešpurek, H. Kishida, and Y. Tokura, *Appl. Phys. Lett.*, **132**, 159 (2001).
12 M. Müller and R. Zentel, *Macromolecules*, **27**, 4404 (1994).
13 R. Mruk and R. Zentel, *Macromolecules*, **35**, 185 (2002).
14 S. Toyoda and M. Fujiki, *Chem. Lett.*, **1999**, 699.
15 C. Zhao, H. Horiuchi, T. Hoshi, M. Hasegawa, M. Kobayashi, and H. Hiratsuka, *Chem. Lett.*, **32**, 124 (2003).
16 C. Zhan, H. Zeng, J. Qin, D. Liu, N. Cheng, and Y. Cui, *Synth. Met.*, **84**, 397 (1997).

Published on the web (Advance View) August 20, 2005; DOI 10.1246/cl.2005.1292