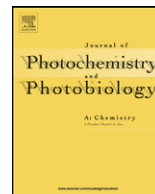




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## Conformational change of poly(methylphenylsilane) induced by the photoisomerization of pendant azobenzene moiety in the film state

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### ABSTRACT

Conformational change of the main chain of poly(methylphenylsilane) functionalized with pendant azobenzene has been studied in the solution and in the film state. The conformation of the main chain was found to depend on the molar ratio of the Si units with and without the pendant azobenzene moiety. The inflection region for the conformational change was 0.3–0.5 of the molar ratio. The conformation of the main chain changed by the photoisomerization of the pendant azobenzene moiety in the film state. The efficiency of the conformational change of the main chain increased with the decrease of the molar ratio, accompanied by the highest final value of degree of the conformational change at the molar ratio of 0.5. The reverse conformational change was induced by heating.

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### 1. Introduction

Polysilanes have attracted much attention because of their unique electronic and optical properties such as conductivity, thermochromism, and non-linear optical effect [1–4]. These unique properties originated from the  $\sigma$ -conjugation system along the main chain, and thus their electronic and optical properties strongly depend on the conformation and orientation of the main chain [1,5]. Therefore the control of the conformation and orientation of polysilanes is one of the important subjects not only in understanding their fundamental properties but also in utilizing the electronic and optical properties. Many studies have been devoted to control their conformation and/or orientation.

To control the orientation of polysilanes, various techniques such as the stretching method [6], Langmuir–Blodgett (LB) method [7], and friction transfer method [8] were studied. We have also studied the orientation mechanism of poly(di-*n*-hexylsilane) induced upon the stretching and have clarified that poly(di-*n*-hexylsilane) molecules in transoid conformation are formed on the surface of the poly(vinyl alcohol) substrate in the stretching process to induce the whole orientation of the poly(di-*n*-hexylsilane)

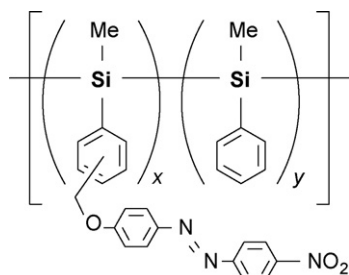
thin film [9]. Thermal processes were mainly studied to control the conformation of polysilanes, because remarkable changes in their optical and electronic properties are induced by the conformational change depending on the temperature [6,10]. We have also studied the thermochromism of the oriented poly(di-*n*-hexylsilane) thin film [9]. On the other hand, little report has been published on the study of the control of the polysilane conformation by light irradiation [11]. Seki et al. studied the film of poly(di-*n*-hexylsilane) spin-cast on azobenzene LB film and reported that the conformation of polysilane can be controlled by making use of both the thermochromism of polysilanes and photochromism of azobenzenes [11]. In their system, at first, the conformational change of the polysilane from the all-*trans* to disordered conformation was induced by raising temperature. Then UV or visible light irradiation and cooling of the sample specimen induce the photoisomerization of the azobenzene LB film and conformational change of polysilanes from the disordered to all-*trans* conformation, respectively. The cooling with simultaneous light irradiation changes the equilibrium state between polysilanes in all-*trans* and that in disordered conformation. Although this process used light irradiation to control the conformation of polysilanes, the fundamental process of this system is considered to be the thermochromic process.

Recently, much attention has been paid for the introduction of functional units to polysilanes as pendants [7,12]. Azobenzene derivatives are one of functional pendants and the introduction of azobenzene derivative enhances the photostability of polysilane [13]. We have synthesized poly(methylphenylsilane)

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Scheme 1. Molecular structure of PMPS-azo derivatives.

functionalized with pendant 4-nitroazobenzene (**PMPS-azo**) and have studied photophysical and photochemical processes of the main chain [14]. Photoisomerization of the pendant azobenzene is known to influence the polymer structure. Yu et al. reported that the photoisomerization of pendant azobenzene induces the bending of the polymer gel film [15]. Zhao et al. reported that the photoisomerization of pendant azobenzene induces the change in the  $\pi$ -conjugation system of polythiophene in solution [16]. Based on this result, they suggested that the conformational change of polythiophene is induced by the photoisomerization of the pendant azobenzene. Harbron et al. reported that the conformation of azobenzene-substituted fluorescent  $\pi$ -conjugated polymer poly(*p*-phenylenevinylene) can be controlled by the photoisomerization of azobenzene moiety in solution [17–20] and in film state [21].

We have reported preliminary results on the photo-control of polysilane conformation induced by the photoisomerization of the pendant azobenzene in the film state [22]. In this paper, the relationship between the photoisomerization of azobenzene and conformational change of the main chain of **PMPS-azo** has been studied. We have also studied the effect of molar ratio of azobenzene on the photo-control of the conformation of the main chain in the film state.

## 2. Experimental

Poly(methylphenylsilane) functionalized with 4-nitroazobenzene (**PMPS-azo**, Scheme 1) was synthesized according to the procedure reported [14]. The molar ratio of the Si units with and without the pendant azobenzene moiety was defined as  $x/y$ , where  $x$  and  $y$  are the number of unit with and without pendant. The molar ratio ( $x/y$ ) of pendant 4-nitroazobenzene moieties in **PMPS-azo** derivatives was determined by using the integrated values of signals of  $\text{CH}_2\text{O}$  linkage ( $\delta=4.88$ ) and  $\text{CH}_3$  of the main chain ( $\delta=-1.2$  to  $0.4$ ) in the  $^1\text{H}$  NMR spectra [14]. Pendant 4-nitroazobenzene moiety was considered to bond at the para-position of the phenyl rings of poly(methylphenylsilane) [14]. The samples with various molar ratios from 0.0 to 0.9 were studied to clarify the effects of molar ratio ( $x/y$ ) on the initial conformation of the main chain and its photo-control. The molar ratio, number averaged molecular weight  $M_n$ , polydispersity  $M_w/M_n$ , average number of Si units, and glass transition temperature  $T_g$  are summarized in Table 1. As a reference compound, 4-methoxy-4'-nitroazobenzene (**Azo**) was synthesized according to the procedure reported [23]. Tetrahydrofuran (THF) without stabilizer was purchased from Wako Pure Chemical Industries Ltd. and used as-received to measure the UV-vis absorption spectra in solution. To prepare thin films, **PMPS-azo** derivatives were dissolved into the mixed solution of toluene and THF (5:4, vol/vol) with the concentration of 0.2 wt%. This solution (40  $\mu\text{L}$ ) was spin-coated on a quartz plate (25 mm  $\times$  25 mm  $\times$  1.2 mm).

UV-vis absorption spectra were recorded on a Hitachi U3310 spectrophotometer. A 300-W Xe short arc lamp (Ushio UXL-300DO)

Table 1  
Molecular weight and glass transition temperature of **PMPS-azo** derivatives

$x/y$	Abbreviation	$M_n$	$M_w/M_n$	No. of Si units <sup>a</sup>	$T_g$ ( $^\circ\text{C}$ )
0.0	<b>PMPS-azo0.0</b>	11,300 $\pm$ 1500	2.4	94 $\pm$ 12	230 $\pm$ 10
0.1	<b>PMPS-azo0.1</b>	16,300 $\pm$ 1300	1.8	118 $\pm$ 9	230 $\pm$ 10
0.5	<b>PMPS-azo0.5</b>	15,700 $\pm$ 1100	1.7	77 $\pm$ 5	190 $\pm$ 10
0.6	<b>PMPS-azo0.6</b>	5,200 $\pm$ 500	2.9	24 $\pm$ 2	100 $\pm$ 20
0.9	<b>PMPS-azo0.9</b>	2,300 $\pm$ 200	1.4	10 $\pm$ 1	130 $\pm$ 10

<sup>a</sup> Number of Si units was calculated from  $M_n$ .

was used as a light source and 435-nm light was selected by dispersion with a monochromator (JASCO, CT-10; slit: 1 mm).  $M_n$  and  $M_w/M_n$  were determined by the gel permeation chromatography (Tosoh HLC-8120GPC) using a column (Tosoh TSK GMH<sub>HR</sub>-M). The column was calibrated using polystyrene standards. Glass transition temperature  $T_g$  was determined by thermogravimetry/differential thermal analysis (Rigaku, Thermo Plus TG8120).

## 3. Results and discussion

### 3.1. Initial conformation of PMPS-azo derivatives in solution

To study whether the conformational change of the main chain is induced by the steric hindrance between the pendant moieties or not, the effect of the molar ratio  $x/y$  on the conformation of the main chain was studied. Fig. 1a shows absorption spectra of 4-methoxy-4'-nitroazobenzene (**Azo**) and **PMPS-azo0.0** in THF. Molar absorption coefficient  $\epsilon$  for **PMPS-azo0.0** was estimated for a silicon unit. The absorption bands of **Azo** observed at 380 nm and around 450 nm are due to the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transitions of the *trans*-form, respectively [23]. The absorption band of **PMPS-azo0.0** observed at 340 nm is due to the  $\sigma$ - $\sigma^*$  transition of the main chain. The conformation of local segments of **PMPS-azo0.0** has not been clarified. Tanigaki et al. studied the thin film

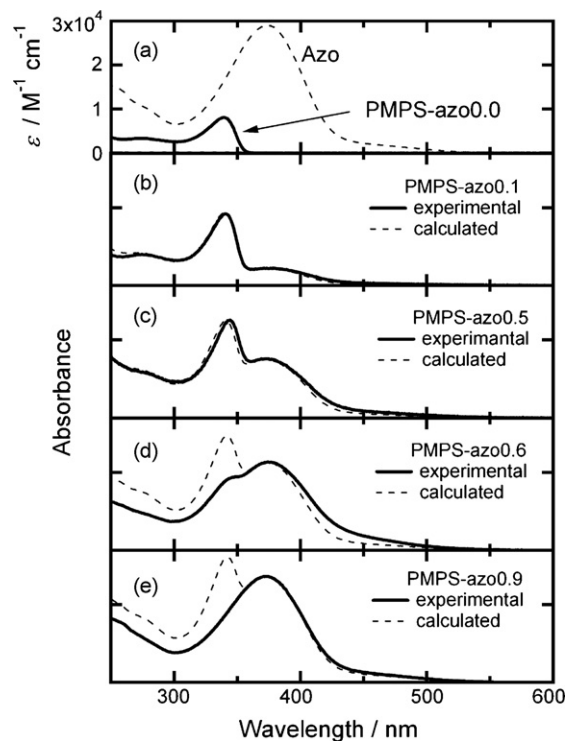


Fig. 1. Absorption spectra of **PMPS-azo0.0** and **Azo** (a) and **PMPS-azo0.1–0.9** (b) in THF.

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