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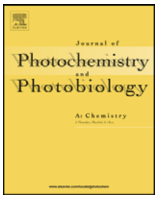

Conformational change of poly(methylphenylsilane) induced by the photoisomerization of pendant azobenzene moiety in the film state

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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.

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 σ-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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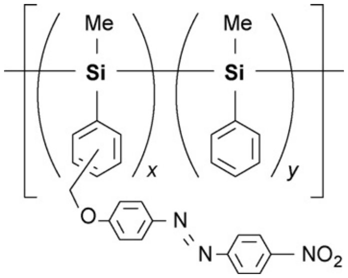


Scheme 1. Molecular structure of **PMPS-azo** derivatives.

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 π-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 π-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 CH_2O linkage ($\delta = 4.88$) and CH_3 of the main chain ($\delta = -1.2$ to 0.4) in the ^1H 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 μL) was spin-coated on a quartz plate (25 mm × 25 mm × 1.2 mm).

UV–vis absorption spectra were recorded on a Hitachi U3310 spectrophotometer. A 300-W Xe short arc lamp (Ushio UXL-300DO) 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_{HR}-M). The column was calibrated using polystyrene standards. Glass transition temperature T_g was determined by thermogravimetry/differential thermal analysis (Rigaku, Thermo Plus TG8120).

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[a]	T_g (°C)
0.0	**PMPS-azo0.0**	11,300 ± 1500	2.4	94 ± 12	230 ± 10
0.1	**PMPS-azo0.1**	16,300 ± 1300	1.8	118 ± 9	230 ± 10
0.5	**PMPS-azo0.5**	15,700 ± 1100	1.7	77 ± 5	190 ± 10
0.6	**PMPS-azo0.6**	5,200 ± 500	2.9	24 ± 2	100 ± 20
0.9	**PMPS-azo0.9**	2,300 ± 200	1.4	10 ± 1	130 ± 10

[a] Number of Si units was calculated from M_n.

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 ε 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 π–π* and n–π* transitions of the *trans*-form, respectively [23]. The absorption band of **PMPS-azo0.0** observed at 340 nm is due to the σ–σ* 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

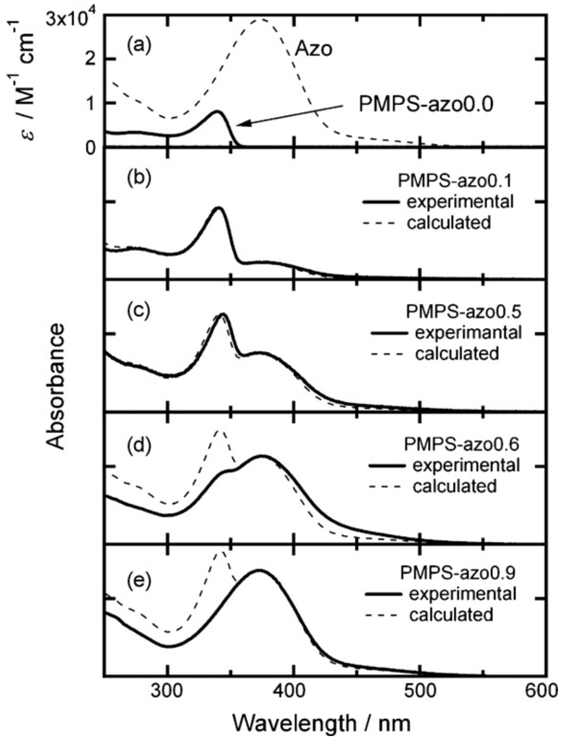
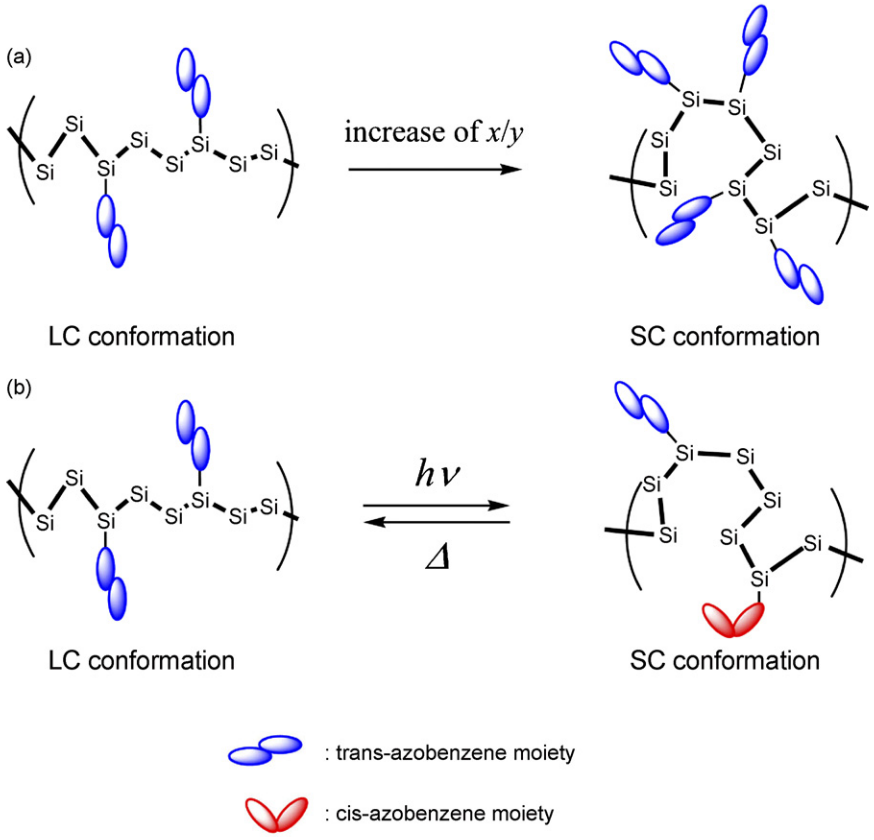


Fig. 1. Absorption spectra of **PMPS-azo0.0** and **Azo** (a) and **PMPS-azo0.1–0.9** (b) in THF.



Scheme 2. Conformational changes of **PMPS-azo** derivatives in the film state.

of **PMPS-azo0.0** prepared by the friction transfer technique and reported that the main chain of **PMPS-azo0.0** responsible for the 340-nm absorption band was oriented along the friction transfer direction [24]. We also observed the similar orientation of the **PMPS-azo0.0** thin film by the stretching technique. These facts indicate that average orientation of local segments is uniaxial and the conformation of the local segment is in certain order. Toyoda and Fujiki reported that **PMPS-azo0.0** has helicity in solution and the slowly winding helical feature was proposed [25]. Fig. 1b–e shows absorption spectra of **PMPS-azo0.1–0.9** in THF. Except for **PMPS-azo0.9**, the absorption bands due to the main chain and the pendant azobenzene moiety in the *trans*-form were observed at 340 nm and around 380 nm, respectively. In the case of **PMPS-azo0.9**, only the absorption band due to the pendant azobenzene moiety in the *trans*-form was observed around 380 nm. To discuss the absorption spectrum of the local segment of the main chain, sum of absorption spectra of **PMPS-azo0.0** and **Azo** were estimated by $A_{\mathbf{PMPS\text{-}azo0.00}} + A_{\mathbf{Azo}}\ x/(x+y)$, where $A_{\mathbf{PMPS\text{-}azo0.00}}$ is the absorption of **PMPS-azo0.0** and $A_{\mathbf{Azo}}$ is that of **Azo**. These resultant spectra are shown by the broken line in Fig. 1b–e. In the cases of **PMPS-azo0.1** and **PMPS-azo0.5**, the estimated absorption spectra agree with the observed one, indicating that the electronic interaction between the σ-conjugation system in the main chain and pendant azobenzene moiety in the ground state is negligibly small. Thus information on conformational changes in both the main chain and pendant azobenzene moiety can be obtained from the absorption spectrum. On the other hand, the intensity of the absorption band due to the main chain is weaker than that of the estimated spectra in the cases of **PMPS-azo0.6** and **PMPS-azo0.9**. This indicates that sizes of the σ-conjugation system of **PMPS-azo0.6** and **0.9** are smaller than those of **PMPS-azo0.0–0.5**. Although the molecular weights of **PMPS-azo0.6** and **0.9** are smaller than those of **PMPS-azo0.0–0.5**, the average number of Si unit in a polymer is over 10 (Table 1), which is considered to be large enough to show a sharp and intense absorption band due to the σ–σ* transition of the main chain [26,27]. Therefore the small size of σ-conjugation for **PMPS-azo0.6** and **0.9** is due to the conformational change of the main chain. In this paper, we designate the conformations of the local segment with larger and smaller σ-conjugation size "LC conformation" and "SC conformation", respectively. For some polysilanes such as poly(di-*n*-hexylsilane), the conformational change can be induced by raising temperature, i.e. thermochromism [6,10]. Thus we studied the thermochromism of **PMPS-azo0.0** thin film

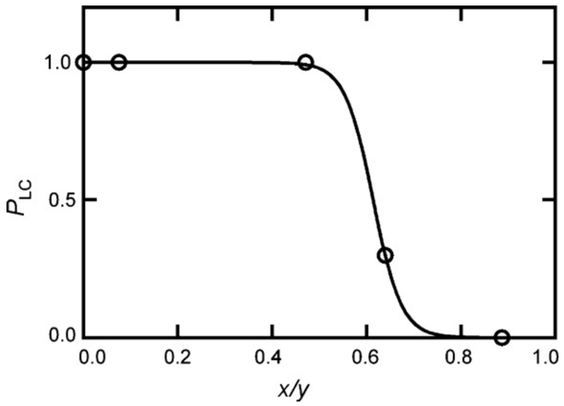


Fig. 2. Plots of the proportion of the Si unit in the LC conformation P_{LC} against the molar ratio of the Si units with and without the pendant azobenzene moiety x/y.

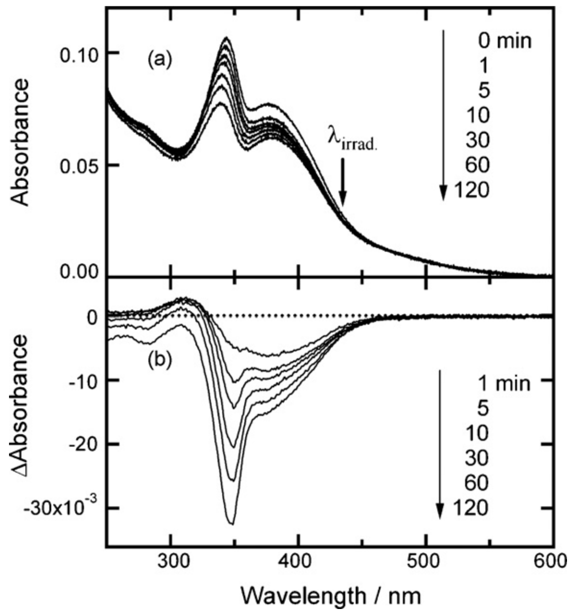


Fig. 3. Absorption spectral change of **PMPS-azo0.5** thin film observed upon irradiation with 435 nm light (a) and difference absorption spectra before and after the irradiation (b).

in the temperature range between 25 and 170 °C to observe the absorption spectrum of the main chain in the SC conformation. No significant spectral change was observed, indicating that the main chain in the SC conformation could not be obtained by the heating even at 170 °C. This may due to high glass transition temperature of **PMPS-azo0.0** (230 °C, Table 1). Unfortunately 230 °C is not available for our apparatus. In general, the absorption band blue-shifts with decreasing molar absorption coefficient upon changing to the smaller conjugation system. However, the absorption band ascribable to the main chain in the SC conformation was not observed in the wavelength region below 340 nm, indicating that molar absorption coefficient of the main chain in the SC conformation is much smaller than that in the LC conformation (8100 M^{-1} cm^{-1} at 340 nm). Because molar absorption coefficient of trimethylphenylsilane was reported to be much smaller (300 M^{-1} cm^{-1} at 260 nm [28]) than that of the main chain in the LC conformation, the electronic structure of the main chain in the SC conformation is considered to be similar to that of monomer (methylphenylsilane). Based on these results, the main chain is considered to be changed to extremely disordered conformation by the strong steric hindrance between pendant moieties as shown in Scheme 2a. To discuss the conformation, the proportion of Si unit in the LC conformation (P_{LC}) was estimated by the following equation:

$$P_{LC} = \frac{\varepsilon_{LC}^{340\,nm}}{\varepsilon_{\mathbf{PMPS\text{-}azo0.0}}^{340\,nm}} \tag{1}$$

$$\varepsilon_{LC}^{340\,nm} = \varepsilon_{\mathbf{PMPS\text{-}azo}}^{340\,nm} - \varepsilon_{\mathbf{Azo}}^{340\,nm} \times \frac{x}{x+y} \tag{2}$$

where $\varepsilon_{\mathbf{PMPS\text{-}azo}}^{340\,nm}$, $\varepsilon_{\mathbf{Azo}}^{340\,nm}$, $\varepsilon_{\mathbf{PMPS\text{-}azo0.0}}^{340\,nm}$ are the molar absorption coefficients at 340 nm of **PMPS-azo** derivatives, **Azo**, and **PMPS-azo0.0**, respectively. Fig. 2 shows the proportion of Si unit in the LC conformation (P_{LC}) as a function of the molar ratio x/y. It is found out that the inflection region for the conformational change of the main chain is in between 0.5 and 0.9 of x/y.

3.2. Conformational change of the main chain induced by light irradiation

Trans → *cis* photoisomerization of the pendant azobenzene moiety is expected to increase the intramolecular steric hindrance between the pendant moieties to induce the conformational change of the main chain. We at first studied the effect of the photoisomerization of the pendant azobenzene moiety on the conformation of the main chain for **PMPS-azo** derivatives in THF. As shown in Fig. 2, x/y of **PMPS-azo0.5** is very close to the inflection region of the conformational change of the main chain. Thus **PMPS-azo0.5** is expected to easily take place the conformational change of the main chain by the photoisomerization of the pendant azobenzene. The 410-nm light was selected for the irradiation light to avoid the direct excitation of the main chain. By the light irradiation to the THF solution of **PMPS-azo0.5**, the absorption at 380 nm due to the π–π* transition of the azobenzene moiety in *trans*-form decreased with the slight increase of the absorption around 470 nm due to the n–π* transition of the *cis*-form. However no change was observed for the absorption band due to the main chain, indicating that only *trans* → *cis* photoisomerization of the azobenzene moiety took place. Thus the conformational change of the main chain was not induced by the photoisomerization of the azobenzene moiety, indicating that the increase of the steric hindrance between the pendant moieties was cancelled by the rotation of the –CH_2–O– linkage between the main chain and pendant azobenzene moiety in solution. It is expected that the rotation of the –CH_2–O– linkage is suppressed in the film state because of the intermolecular steric hindrance. Thus we carried out the photoisomerization experiment in the film state. Thin film of **PMPS-azo0.5** was prepared by the spin-coating of the **PMPS-azo0.5** solution on a quartz plate and the resulting absorption spectrum is shown in Fig. 3a. The absorption spectrum in the film state is similar to that in THF except for a little band-broadening. This indicates that the initial conformation of the local segments of the main chain is the LC conformation even in the film state. In the case of the film state, 435-nm light was selected for the irradiation light to avoid direct photolysis of the main chain. By the irradiation, the absorption in the region of 250–500 nm decreased. Fig. 3b shows the difference absorption spectra between before and after the irradiation. At the irradiation time of 1 min, a negative peak around 380 nm and a positive peak around 310 nm were observed. This spectral change is similar to that observed for the *trans* → *cis* photoisomerization of **Azo** in solution except for no increase of the absorption band around 470 nm due to n–π* transition of the *cis*-form. To clarify this spectral change, we have tried to study the photoisomerization of **Azo** in **PMPS-azo0.0** film. To prepare thin film of **PMPS-azo0.0** containing **Azo**, the solution of **PMPS-azo0.0** with various concentration of **Azo** was spin-coated on a quartz plate. But the concentrations of **Azo** in each **PMPS-azo0.0** films were too low to study the photoisomerization because of low affinity between **Azo** and **PMPS-azo0.0**. Even in solution, the increase of the absorption band around 370 nm due to n–π* transition of the *cis*-form is slight (4%) in comparison with the decrease at 380 nm due to the π–π* transition of the *trans*-form. Furthermore, the absorption spectrum in the film state is broader compared with that in solution and the absorption band of the π–π* transition is considered to overlap with that of the n–π* transition. Therefore the slight increase of the absorption band due to n–π* transition of the *cis*-form is considered to be cancelled by the large decrease of the broad absorption band due to π–π* transition of the *trans*-form in the film state. Based on these considerations, *trans* → *cis* photoisomerization of the pendant azobenzene moiety took place at this irradiation time. With the increase of the irradiation time, the 380-nm absorption band due to the *trans*-azobenzene moiety decreases accompanied by the

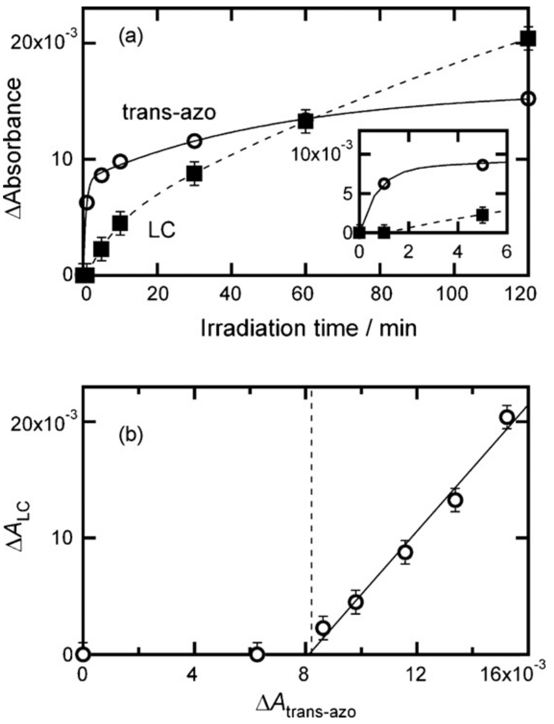


Fig. 4. Absorbance changes due to the pendant azobenzene moiety ($\Delta A_{trans\text{-azo}}$, open circles) and the main chain in the LC conformation (ΔA_{LC}, filled square) of the **PMPS-azo0.5** in the film state as a function of irradiation time (a) and plots of ΔA_{LC} against $\Delta A_{trans\text{-azo}}$ (b).

decrease of the 340-nm band due to the main chain in the LC conformation. This suggests that the photoisomerization of the pendant azobenzene moiety induces the conformational change of the main chain from the LC to SC conformation. As another possibility, the decomposition of the main chain can be also pointed out. To verify the conformational change, we examined whether the 435-nm light irradiation induces the decomposition of the main chain or not. At first we irradiated the thin film of **PMPS-azo0.0** with the 435-nm light. No spectral change was observed, indicating that the 435-nm light irradiation does not induce the photodecomposition of the main chain. The product analysis was also carried out. Two thin films of **PMPS-azo0.5** were prepared under the same condition. A thin film was dissolved into 10 mL of THF and the absorption spectrum of this solution (solution A) was measured. Another thin film was irradiated with the 435-nm light for 60 min followed by dissolving into 10 mL of THF (solution B). Absorption spectrum of the solution B was measured and compared with that of the solution A. Both spectral shape and intensity of the absorption spectra are essentially the same with each other, indicating that no decomposition took place by the irradiation. Therefore, we can conclude that the *trans* → *cis* photoisomerization of the pendant azobenzene moiety induces the conformational change of the main chain from the LC to SC conformation in the film state as shown in Scheme 2b.

3.3. Mechanism of the conformational change

To clarify the mechanism of the conformational change induced by the irradiation, the conformational changes of the pendant azobenzene and main chain were studied as a function of irradiation time. Fig. 4a shows absorbance change of the *trans*-azobenzene moiety at 380 nm ($\Delta A_{trans\text{-azo}}$, open circles) observed for **PMPS-azo0.5**. The contribution of *cis*-azobenzene to the absorbance at 380 nm was neglected in this time range because of the low absorption coefficient of the *cis*-form at this wavelength. The time profile of $\Delta A_{trans\text{-azo}}$ could not be analyzed by a first-order kinetics with one component but by first-order kinetics with two components described by the following equation:

$$\Delta A_{trans\text{-azo}} = A_f + A_s - A_f \ \exp(-k_f t) - A_s \ \exp(-k_s t) \tag{3}$$

where A_f and A_s are preexponential factors for the fast and slow components, respectively, and k_f and k_s are rate constants for the fast and slow components, respectively. This indicates that there are two different *trans* → *cis* photoisomerization processes. The photoisomerization processes of azobenzene derivatives in the polymer film were studied by Sung et al. [29,30]. They reported that there are two components in the isomerization processes of azobenzene in the polymer, reflecting the distribution of free volume size in the polymer glass. The free volume sizes for the pendant azobenzene moiety corresponding to the fast and slow components are considered to be larger and smaller than the critical size, respectively. According to their consideration, the free volume sizes in the vicinity of the pendant azobenzene moiety corresponding to the fast and slow components are attributed to those larger and smaller than critical size, respectively. We call this critical size “critical free volume size V_c” in this paper. The photoisomerization mechanism(s) of azobenzene derivatives remains obscure but the inversion and rotation mechanism were suggested [31–34]. Chang et al. reported that the mechanism of the photoisomerization is the inversion in the viscous solvent [32]. Thus the inversion mechanism may be suitable for the photoisomerization mechanism of azobenzenes in the polymer matrix. The volume required for isomerization of azobenzene was estimated to be 127 Å^3 [35]. The critical free volume size V_c is expected to be in this order.

To clarify the relationship between the photoisomerization of the pendant azobenzene moiety and conformational change of the main chain, absorbance change due to the main chain was also studied. To estimate the absorbance change of the main chain at 340 nm (ΔA_{LC}), the contribution of absorbance change due to the *trans* → *cis* photoisomerization of the pendant azobenzene moiety was subtracted. The conformational change of the main chain upon irradiation did not occur in the early stage and started at 1 min (the inset of Fig. 4a). Fig. 4b shows the absorbance change of the main chain in the LC conformation (ΔA_{LC}) as a function of that of the *trans*-azobenzene moiety ($\Delta A_{trans\text{-azo}}$). ΔA_{LC} did not change up to $\sim 8 \times 10^{-3}$ of $\Delta A_{trans\text{-azo}}$ but increased almost linearly above this value. This threshold value is similar to A_f (8.2×10^{-3}, shown by the vertical broken line in Fig. 4b), indicating that the conformational change of the main chain is induced by the photoisomerization of the azobenzene moiety with the free volume smaller than V_c (slow component). Based on these results, the mechanism of the conformational change of the main chain is considered as follows. The precursor state in the isomerization is considered to be easily produced upon the excitation. But structural change from the precursor to *cis*-form induces the steric repulsion toward the surrounding molecules and the increase of the steric repulsion depends on the free volume size. In the case of the azobenzene moiety with the free volume smaller than V_c, the increase of the steric repulsion is large. Because temperature was below T_g, the precursor may return to the *trans*-form. However the glass transition temperature of **PMPS-azo** decreased with increase of the molar ratio x/y as shown in Table 1, indicating that the introduction of the pendant decreases the intermolecular interaction and increases the flexibility of the polymer structure. Thus the local structure of the main chain connected with the pendant azobenzene moiety is considered to be more flexible and therefore the increase of the steric repulsion is cancelled by the structural change of the main chain connected with the pendant to form *cis*-form. As a result, the conformational change of the main chain was induced by the photoisomerization of the pendant azobenzene moiety, although the quantum yield of the photoiso-

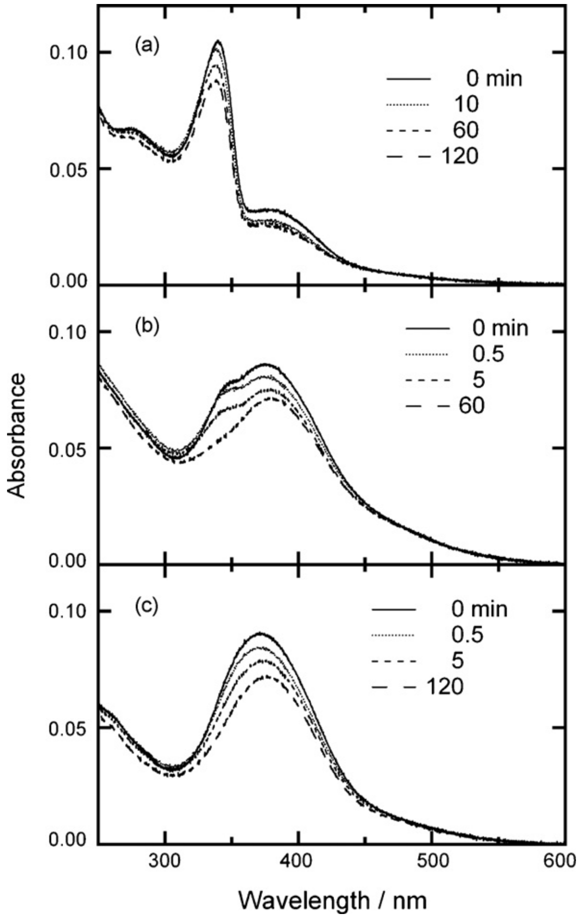


Fig. 5. Absorption spectral change of thin films of **PMPS-azo0.1** (a), **PMPS-azo0.6** (b), and **PMPS-azo0.9** (c) induced by the 435-nm light irradiation.

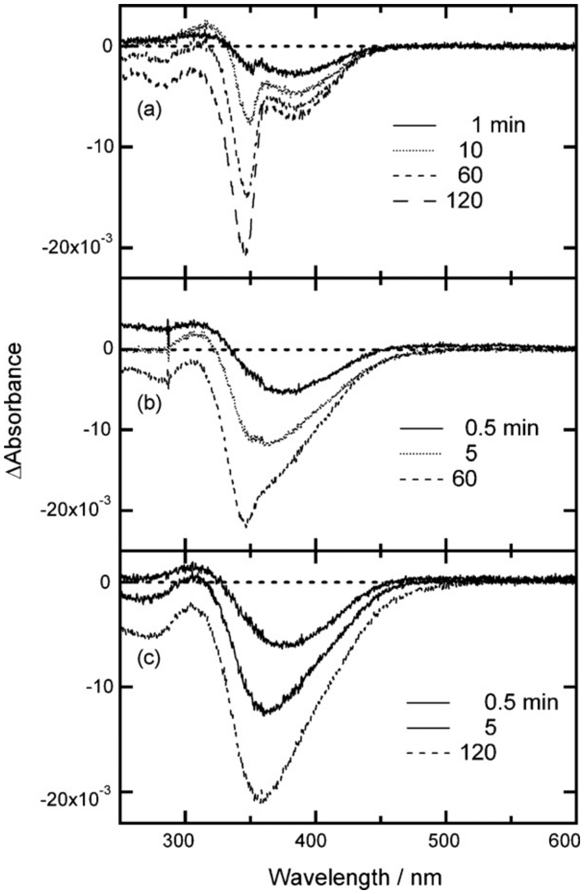


Fig. 6. Difference absorption spectra of thin films of **PMPS-azo0.1** (a), **PMPS-azo0.6** (b), and **PMPS-azo0.9** (c) before and after the 435-nm light irradiation.

merization is low. On the other hand, in the case of the azobenzene moiety with the free volume larger than V_c, the increase of the steric repulsion was cancelled by the rotation of the $-CH_2-O-$ linkage as in the case of solution. Thus photoisomerization does not induce the conformational change of the main chain.

3.4. *Effect of molar ratio x/y on the conformational change*

We have studied the effect of the molar ratio x/y on the conformational change of the pendant azobenzene moiety and polysilane main chain.

Fig. 5 shows absorption spectral change of thin films of **PMPS-azo0.1** (a), **PMPS-azo0.6** (b), and **PMPS-azo0.9** (c) observed upon irradiation with 435-nm light. Difference absorption spectra before and after the irradiation are also shown in Fig. 6. In the case of **PMPS-azo0.1** the molar ratio x/y is far from the inflection region, where the conformational change of the main chain takes place from the LC to SC conformation as shown in Fig. 2. However, the conformation of the main chain changed from LC to SC conformation by the photoisomerization of the pendant azobenzene moiety (Fig. 6a) as in the case of **PMPS-azo0.5**. In the case of **PMPS-azo0.6** whose x/y is in the inflection region, the conformational change of the main chain was also induced by the photoisomerization of the pendant azobenzene moiety (Fig. 6b). It is noted that the absorption band due to the main chain in the LC conformation is no longer observed at the irradiation time of 60 min (Fig. 5b). In the case of **PMPS-azo0.9** (Figs. 5c and 6c), only the photoisomerization of the pendant azobenzene moiety was observed because the main chain is in the SC conformation from the beginning.

Fig. 7a shows the absorbance change ($\Delta A_{trans\text{-azo}}$) at 380 nm of the pendant azobenzene moiety induced by the 435-nm light irradiation. To compare the photoisomerization efficiency of the pendant azobenzene, the irradiation time was corrected by the absorption efficiency ($1-10^{-A_{435}}$), where A_{435} is the initial absorbance at the irradiation wavelength (435 nm). These irradiation time profiles can be analyzed by the following equation:

$$\Delta A_{trans\text{-azo}} = A_f + A_s - A_f \exp\{-k'_f t(1-10^{-A_{435}})\}$$

Table 2
Analytical parameters of photoisomerization of the pendant azobenzene moiety

Sample	A_f ($\times10^{-3}$)	k'_f (min)	A_s ($\times10^{-3}$)	k'_s (min)	$A^0_{trans\text{-azo}}$	$A_f/A^0_{trans\text{-azo}}$	$A_s/A^0_{trans\text{-azo}}$
PMPS-azo0.1	3.7	16.3	3.4	0.32	0.033	0.11	0.10
PMPS-azo0.5	8.2	8.5	7.8	0.12	0.077	0.11	0.10
PMPS-azo0.6	9.6	9.6	5.8	0.35	0.086	0.11	0.07
PMPS-azo0.9	11.1	6.6	8.8	0.08	0.089	0.12	0.10

errors: ±10%.

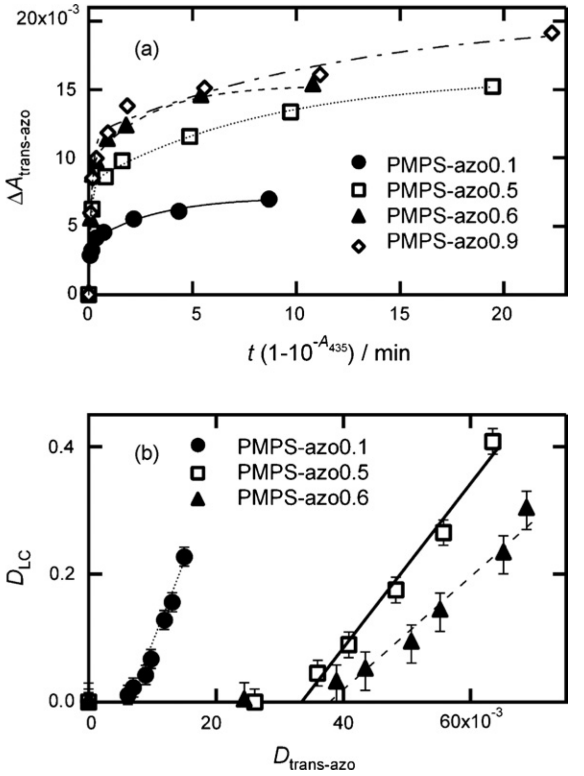


Fig. 7. Absorbance changes due to the pendant azobenzene moiety ($\Delta A_{trans\text{-azo}}$) for **PMPS-azo** derivatives as a function of irradiation time (a) and plots of the degree of the conformational change of the main chain D_{LC} against that of photoisomerization of the pendant azobenzene $D_{trans\text{-azo}}$ (b).

$$-A_{\text{s}}\ \exp\{-k'_{\text{s}}t(1-10^{-A_{435}})\} \tag{4}$$

where k'_{f} and k'_{s} are corrected rate constants for the fast and slow components, respectively, with the absorption efficiency. Analytical parameters are summarized in Table 2. The rate constants of the photoisomerization of these samples are similar to each other for both the fast and slow components. The value of $\Delta A_{trans\text{-azo}}$ at the irradiation time of 120 or 60 min was over 95% of the value of $A_{\text{f}}+A_{\text{s}}$, indicating that the photoisomerization of the pendant azobenzene almost reached the photostationary state at this irradiation time. To discuss the distribution of the free volume in the vicinity of the pendant azobenzene moiety, we estimated the ratio of the fast and slow components to total amount of the pendant azobenzene. The ratio was determined by $A_{\text{f}}/A^0_{trans\text{-azo}}$ and $A_{\text{s}}/A^0_{trans\text{-azo}}$ for the fast and slow components, respectively, where $A^0_{trans\text{-azo}}$ is the absorbance at 380 nm before irradiation. Both $A_{\text{f}}/A^0_{trans\text{-azo}}$ and $A_{\text{s}}/A^0_{trans\text{-azo}}$ are independent of the molar ratio of the pendant azobenzene as shown in Table 2, indicating that the free volume of polysilane thin film did not depend on the molar ratio x/y. To clarify the relationship between the photoisomerization of the pendant azobenzene moiety and conformational change of the main chain, the process of conformational change of the main chain was studied. Degree of the conformational change of the main chain (D_{LC}) can be defined by the following equation:

$$D_{\text{LC}}=\frac{\Delta A_{\text{LC}}}{A^0_{\text{LC}}}P_{\text{LC}} \tag{5}$$

where ΔA_{LC} is the absorbance change due to the conformational change of the main chain from the LC to SC conformation, and A^0_{LC} is the initial absorbance due to the main chain in the LC conformation. This D_{LC} value corresponds to number of silicon units changed in the LC conformation against total number of silicon unit in the thin film. Degree of photoisomerization of the pendant azobenzene ($D_{trans\text{-azo}}$) can be also defined by the following equation:

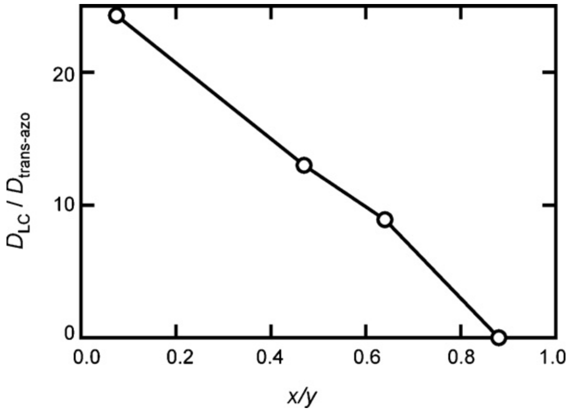
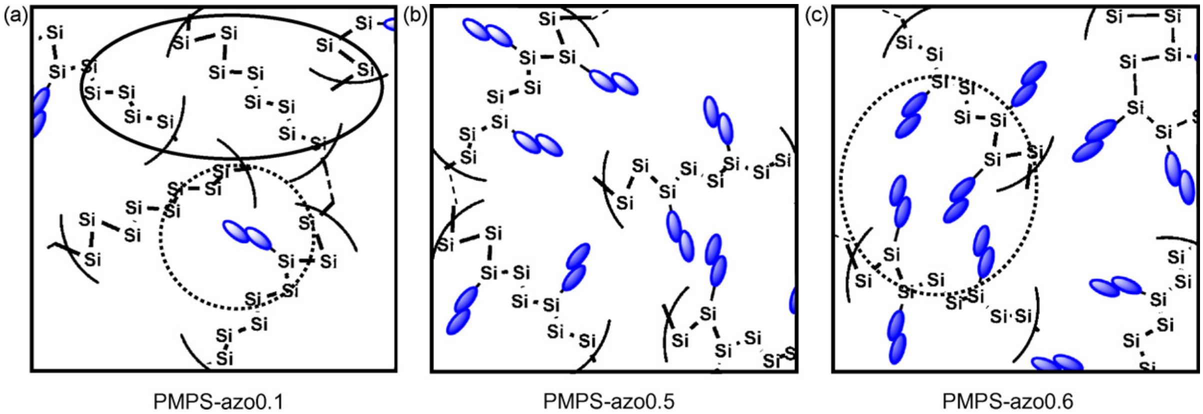


Fig. 8. Dependence of the efficiency of the conformational change of the main chain $D_{\text{LC}}/D_{trans\text{-azo}}$ on the molar ratio x/y.

$$D_{trans\text{-azo}}=\frac{\Delta A_{trans\text{-azo}}}{A^0_{trans\text{-azo}}}\frac{x}{x+y} \tag{6}$$

where $\Delta A^0_{trans\text{-azo}}$ is the initial absorbance due to the pendant azobenzene moiety at 380 nm. This $D_{trans\text{-azo}}$ value may be proportional to number of the photoisomerized azobenzene molecules per unit volume of thin film. Fig. 7b shows the degree of the conformational change of the main chain (D_{LC}) as a function of the degree of the photoisomerization of the pendant azobenzene moiety $D_{trans\text{-azo}}$. The final values of D_{LC} ($D^{\text{final}}_{\text{LC}}$) were 0.23, 0.41, and 0.30 for **PMPS-azo0.1**, **PMPS-azo0.5**, and **PMPS-azo0.6**, respectively, and maximum value was observed for **PMPS-azo0.5**. In the case of **PMPS-azo0.1**, the molar ratio x/y is low, so that most of the main chain are not located close to the azobenzene moiety as shown by the circle in Scheme 3a. The conformation of these main chains could not be changed by the photoisomerization of the pendant azobenzene moiety to induce the low $D^{\text{final}}_{\text{LC}}$. With increase of the molar ratio x/y, proportion of the main chain close to the azobenzene moiety increases to enhance the $D^{\text{final}}_{\text{LC}}$. However, the proportion of the main chain in the LC conformation decreases over the molar ratio x/y of 0.5 and thus the $D^{\text{final}}_{\text{LC}}$ is considered to decrease.

The threshold values of $D_{trans\text{-azo}}$ for the conformational changes of the main chain were 7×10^{-3} and 38×10^{-3} for **PMPS-azo0.1** and **PMPS-azo0.6**, respectively, and are close to the contribution of the fast component $A_{\text{f}}/A^0_{trans\text{-azo}}\times x/(x+y)$ of **PMPS-azo0.1** (8×10^{-3}) and **PMPS-azo0.6** (43×10^{-3}), respectively. This indicates that the conformational changes of the main chain for **PMPS-azo0.1** and **PMPS-azo0.6** were induced by the photoisomerization of the pendant azobenzene moiety with the free volume size smaller than V_{c} (the slow component) as in the case of **PMPS-azo0.5**. To determine the relative efficiency of the conformational change of the main chain, the plots of D_{LC} shown in Fig. 7b were analyzed by the linear function above the threshold value of $D_{trans\text{-azo}}$ and fitting lines are shown in Fig. 7b. The slopes ($D_{\text{LC}}/D_{trans\text{-azo}}$) obtained were 24, 13, and 9 for **PMPS-azo0.1**, **PMPS-azo0.5**, and **PMPS-azo0.6**, respectively. These values were plotted against the molar ratio x/y (Fig. 8). The efficiency of the conformational change of the main chain increases with the decrease of the molar ratio. With the decrease of the molar ratio, the density of the pendant azobenzene moiety in the thin film of **PMPS-azo** becomes low and then the surroundings of the azobenzene are considered to be the polysilane main chain as shown by the dotted circles in Scheme 3. Thus the influence of the photoisomerization of the pendant azobenzene



PMPS-azo0.1 PMPS-azo0.5 PMPS-azo0.6

Scheme 3. Illustrations of the thin film of **PMPS-azo** derivatives.

on the conformation of the main chain becomes greater to increase the efficiency of the conformational change of the main chain.

3.5. Reverse processes

For the application of the thin film of **PMPS-azo** derivatives to the switching materials, the reversibility is very important. Reversible structural change takes place in azobenzene derivatives between their *trans*- and *cis*-form [36]. The *cis* → *trans* isomerization of azobenzene derivatives is known to take place photochemically or thermally. We thus expected that the main chain returns from the SC conformation to the original LC conformation by the *cis* → *trans* isomerization of the azobenzene moiety. We at first studied the photochemical processes. As described before, the n–π* transition of *cis*-azobenzene moiety is not clearly observed in the film state but it should be in a wavelength region similar to the n–π* transition of *trans*-azobenzene moiety. Thus we selected 530-nm light for the *cis* → *trans* isomerization as an irradiation light. At first, the main chain changed from the LC to SC one upon 435-nm light irradiation to the thin film of **PMPS-azo0.5** for 60 min (forward process). After the 435-nm light irradiation, the 530-nm light was irradiated for 120 min. Contrary to our expectation, the absorption band due to the main chain in the LC conformation decreased with the decrease of that due to the pendant *trans*-azobenzene moiety. This indicates that the forward processes proceed even by the 530-nm light irradiation and the product of the absorption coefficient and quantum yield of photoisomerization of the *trans*-form is larger than that of the *cis*-form even at 530 nm.

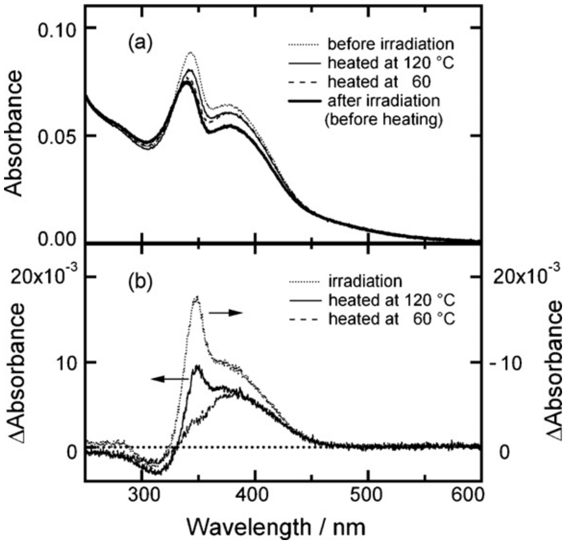


Fig. 9. Absorption spectral change of **PMPS-azo0.5** thin film induced by the 435-nm light irradiation followed by heating (a) and difference absorption spectra before and after the irradiation and heating (b).

As an alternative way, the thermal processes were studied. The absorption spectra of the **PMPS-azo0.5** thin film were measured before and after the 435-nm light irradiation and are shown by the dotted and bold solid lines in Fig. 9a, respectively. The difference absorption spectrum before and after the irradiation is shown by the dotted line in Fig. 9b. To measure the thermal change of the absorption spectra, the irradiated film was heated for 40 min followed by cooling to room temperature. The absorption spectra before and after heating are shown in Fig. 9a. By the heating at 60 °C, the absorption spectral change (the broken line in Fig. 9b) is similar to that due to the isomerization of the azobenzene moiety, indicating that only the *cis* → *trans* isomerization took place by the heating at 60 °C. By raising the heating temperature to 120 °C, the absorption band due to the main chain in the LC conformation increased, indicating that a part of the main chain in the SC conformation return to the original LC conformation. It is noted that no absorption spectral change was observed after the heating of the non-irradiated **PMPS-azo0.5** thin film to 120 °C. From these results, it is concluded that the conformational change of the main chain is reversible as shown in Scheme 2b. Absorbance around 380 nm did not change by raising the heating temperature from 60 to 120 °C, suggesting that the *cis* → *trans* thermal isomerization may not be responsible for the conformational change. The temperature (∼120 °C) in this experiment was below T_g (190 °C) of **PMPS-azo0.5**. But this T_g value is for bulk polymer and lower value is expected for the thin film [37]. Furthermore the local structure of the main chain connected with the pendant azobenzene moiety is considered to be more flexible as described before. Thus the main chain may be thermally returned to the original LC conformation. We would like to study this subject in near future.

4. Concluding remarks

We have investigated the conformation of the main chain of poly(methylphenylsilane) functionalized with the pendant azobenzene (**PMPS-azo**) in solution and demonstrated that the conformation of the local segment of the main chain changed with the increase of the molar ratio of the pendant azobenzene. The inflection region for the conformational change has been found to be 0.3–0.5 of the molar ratio. In the film state, the conformational change was induced by the photoisomerization of the pendant azobenzene moiety for **PMPS-azo** derivatives with molar ratio of 0.1–0.6. The free volume distribution of the pendant azobenzene moiety is independent of the molar ratio and the photoisomerization of the pendant azobenzene moiety with free volume smaller than the critical value induces the conformational change of the main chain. The efficiency of the conformational change induced by the photoisomerization of a pendant azobenzene moiety increased with the decrease of the molar ratio, accompanied by the highest value of degree of the conformational change at 0.5 of the molar ratio. The conformationaly changed main chain by the photoisomerization of the pendant azobenzene is found to return to the original conformation by heating.

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