Optically Induced Anisotropy in Photoresponsive Sol-Gel Matrix Bearing a Silylated Disperse red 1

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Received July 6, 2000

We synthesized the simple triethoxysilanes (SGDR1) bearing a disperse red 1 for thin film fabrication. The thin films were prepared using the solution of SGDR1 after hydrolysis and condensation. The films were annealed at two different temperatures such as 150 °C and 200 °C. *Trans-to-cis* photoisomerization was observed under the exposure of 532 nm light with UV-Vis absorption spectroscopy. The kinetic study of photoisomerization was performed in the film. Reorientation of the polar azobenzene molecules induced optical anisotropy under a linearly polarized light at 532 nm. The effect of aggregation of the chromophores and annealing of the silicon oxide in the matrix were studied on the dynamic properties of isomerization and induced birefringence.

Introduction

The materials containing an azobenzene moiety were found to possess unique optical properties.[1-5] There is constantly increasing attention in the field of optical data storage and holographic applications.[6-9] Optically induced anisotropy is a very promising property to be employed for optical information storage and erasing. The mechanism of writing information involves photo-induced excitation of the azobenzene group that undergoes *trans-cistrans* isomerization and molecular reorientation.

The photo-induced *trans-to-cis* isomerization of azobenzene moiety has been studied in amorphous and liquid crystalline polymers.[10,11] The type of optically induced isomerization is also of particular interest because the induced changes in molecular orientation of polar azobenzene moiety can affect the surrounding molecules. In addition, the induced birefringence and molecular dichroism that result from molecular reorientation could potentially be used to investigate the chain motion of polymer and environment in the vicinity of the azobenzene molecules.

If the film is subjected to a linearly polarized light with an appropriate wavelength, the azobenzene molecules that have a transition dipole ($\Delta\mu$) component in the polarization direction of the pump beam can be readily photoisomerized to the *cis* form. Through thermal effect or exposure to light, some molecules in the *cis* form can revert back to the *trans* form, although a given molecule may not be necessarily converted to the initial molecular orientation. After several repetitive photoexcitation and isomerization cycles, the azobenzene molecules with transition dipole moments perpendicular to the polarization direction of the excitation light can be stabilized to new molecular direction. The azobenzene molecules placed in the perpendicular direction of polarization of pump light cannot interact with the excitation light and therefore become inert to the pump beam. The anisotropic molecular distribution gives rise to birefringence and dichroism in the film. The photo-induced birefringence is related to the structure of azo chromophore, the type of the polymer backbone, and the interaction between azobenzene dipoles.[12-16]

In a linear polymer structure, dye aggregation can be observed when the concentration of the dye increased in the matrix. Particularly, polar chromophores were observed to be arranged in an antiparallel way.[16] When the dipoles are aligned antiparallel, the resulting local electric field will be in the opposite direction as the dipoles and hence the cosine of the angle between dipoles will be negative, increasing the absorption energy. Therefore, the absorption maximum of the film appeared at the lower wavelength compared to that in the solution state. Usually, the aggregation of the chromophores in the film could be destroyed under thermal annealing.

In this study, we synthesized functionalized triethoxysilane bearing a photosensitive chromophore. Homogeneous solution was prepared to fabricate the thin films. We also investigated the changing behavior of dye aggregation in the network structure contrary to that in a linear polymer. Photoisomerization and photo-induced birefringence were studied by using the two different samples annealed at 150 °C and 200 °C for 3 h.

Experimental Section

Materials. 3-isocyanatopropyl triethoxysilane and dibutyltin dilaurate (DBTDL) were purchased from Aldrich Chem. Co. and used without further purification. Disperse red 1 (DR1) was recrystallized from ethanol. Tetrahydrofuran was distilled over calcium hydride

Synthesis of SGDR1.[17] 3-isocyanatopropyl triethoxysilane (2.0 g, 8.08 mmole) and disperse red 1 (DR1, 1.27 g, 4.04 mmole) were stirred with freshly dried tetrahydrofuran (THF, 30 mL) at room temperature for 10 min. The mixture was refluxed for 4 h with a catalytic amount of dibutyltin dilaurate (DBTDL). The solution was poured into hexane and the red solid was filtered. The THF solution of crude product was reprecipitated into hexane. The product (SGDR1)

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*Corresponding Author. e-mail: dhchoi@khu.ac.kr was dried under vacuum at 60 °C for 24 h and stored in a dessicator. m.p. 98 °C Yield: 80%.

^{1}H-NMR (DMSO-d^6): δ (ppm) 8.25 (d, 2H), 7.83 (d, 2H), 7.75 (d, 2H), 6.72 (d, 2H), 5.07 (t, 1H), 4.22 (t, 2H), 3.78 (q, 6H), 3.65 (t, 2H), 3.51 (q, 2H), 3.08 (m, 2H), 1.60 (m, 2H), 1.22 (m, 12H), 0.58 (t, 2H)

FT-IR: NH stretching 3329 cm^{-1} (hydrogen bonded), 3420 cm^{-1} (isolated)

C=O stretching 1698 cm^{-1} (hydrogen bonded), 1725 cm^{-1} (isolated)

NO_2 symmetric stretching 1338 cm^{-1}, asymmetric stretching 1516 cm^{-1}

Material processing. The red solid (SGDR1, 1 mole) was dissolved in THF. 4 mole of water and 0.02-0.04 mole of hydrochloric acid (HCl) were added to the solution. The solution was hydrolyzed and aged at room temperature for 48 h. For studying the photo-induced birefringence and the photoisomerization behavior, thin films were fabricated on ordinary normal microslide glasses using a filtered solution. We measured the thickness of the film using a Tencor P10 (Alpha step).

NMR spectroscopy. Proton NMR spectra were recorded on Varian 200 NMR spectrometer using tetramethylsilane as an internal standard and DMSO-d$_6$ as a solvent.

UV/VIS spectroscopy. Hewlett Packard (model 8453) spectrophotometer was utilized to record the UV/VIS absorption spectrum. The samples were irradiated with a diode pumped laser (λ = 532 nm) for investigating photoisomerization.

Photo-induced Birefringence. The change in transmittance of the He-Ne laser through the film between crossed polarizers is recorded as a function of time after irradiation of diode pumped laser (λ = 532 nm, intensity 10 mW/cm^2). He-Ne laser (~10 mW) at 632.8 nm was used as a probe light to measure the power that is transmitted. Optical anisotropy was induced in the film using a polarized UV light at a polarization angle of 45° with respect to the polarizer direction. The wavelength of the pump beam is in the absorption range of disperse red 1. The transmission was detected with a photodiode detector (New Port 818-SL). The transmitted signal I(t) due to birefringence can be shown to be proportional to $\sin^2(\pi\delta\,\Delta n/\lambda)$ where d and Δn are thickness and birefringence of the film, respectively. λ is the wavelength of the probe beam (He-Ne laser radiation at 632 nm). We measured the thickness of the films using a Tencor P10 to convert from transmittance to birefringence using the following equation (1).

$$\Delta n = [\lambda_o/\pi d] \arcsin [(I(t) / I_o)^{0.5}] \qquad (1)$$

Results and Discussion

We prepared the photosensitive triethoxy silane by simple carbamate forming reaction between alcohol and isocyanate. Synthetic scheme is simply illustrated in Figure 1. The product (SGDR1) is well soluble in THF, acetone, dimethylformamide, pyridine etc. In this study, we selected THF as a solvent for making sol.

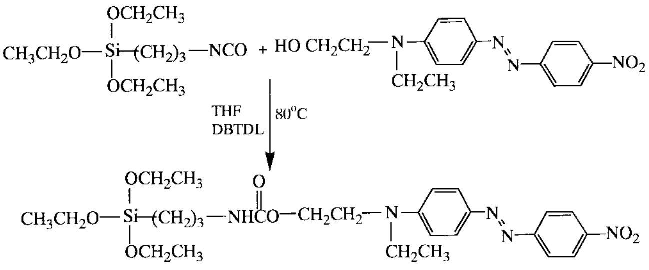

Figure 1. Synthesis of triethoxysilane (SGDR1) bearing a disperse red 1.

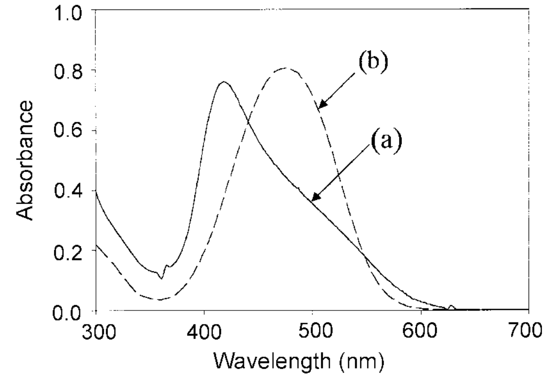

Figure 2. UV-Vis absorption spectra of SGDR1. (a) film; (b) solution (THF).

UV-VIS absorption spectroscopy. The absorption spectrum of SGDR1 film was taken after spin coating and drying at room temperature for 24 h. Compared to the absorption spectrum of the solution (solvent THF), the λ_{max} was fairly blue-shifted to 415 nm by 50-70 nm (see Figure 2). This is attributed to the antiparallel arrangement of dye molecules in the solid film.[16,18] Therefore, two absorption maxima were expected to appear arising from π-π* electronic transitions

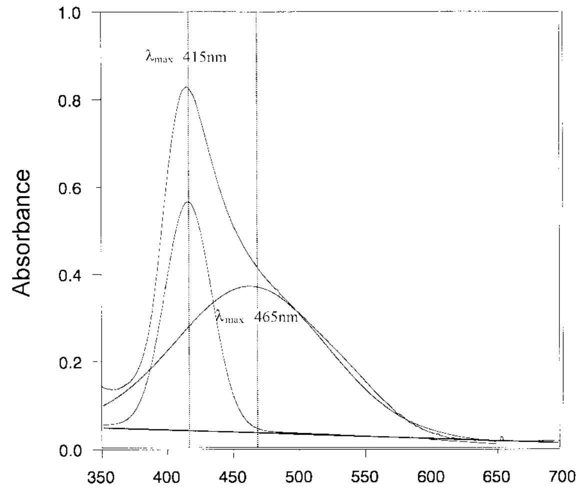

Figure 3. Curve analysis of the absorption spectrum of SGDR1 film.

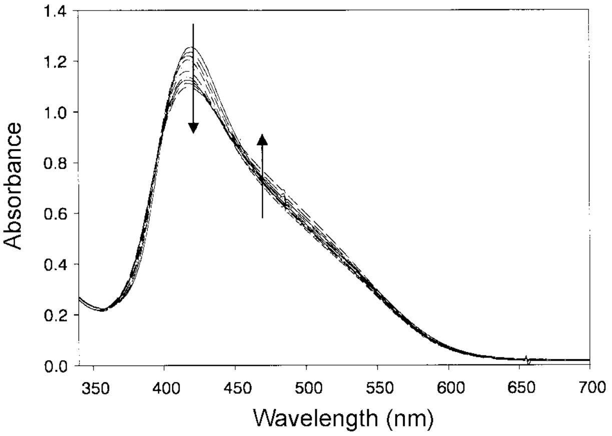

Figure 4. Change of the absorption spectrum during heating: *Sample: SGDR1 film.

in the aggregated dye molecules and the free azobenzene molecules. We resolved the absorption spectrum using PC-software (LabCalc). In Figure 3, two wavelengths at which π-π^* transition occurs were determined by using the curve fitting method. We assigned the absorbance at 415 nm to be a transition in the aggregated molecules and that at 465 nm to be a transition in the free azobenzene molecules.

As we described previously, in the case of a linear polymer with a high concentration of the polar dye molecules, the aggregation can be observed and disrupted under thermal treatment. In order to investigate the disrupting behavior of dye aggregation, we heated the sample and recorded the absorption spectra simultaneously (Figure 4). As the sample (SG200) annealed at 200 °C for 3 h was heated to 200 °C again, we could observe the decrease of the absorbance at 415 nm and slight increase of absorbance at 465 nm. This, however, is significantly different from the phenomena observed in a linear polymer such as polymethacrylate. We explained that the aggregated molecules in the annealed matrix were restricted to be mobile. It did not show the significant change of the absorption spectrum. Consequently, the dye molecules were bound by high density of silicon oxide and caged inside the network.

Change of the absorption spectrum under an excitation light. SGDR1 film (SG200) annealed at 200 °C for 3 h was irradiated under a circularly polarized light (λ=532 nm) and the absorption spectra were recorded during light exposure. Absorption spectra (a), (b), and (c) were taken during irradiation of the excitation light. Spectrum (d) was recorded after irradiating the excitation light for 600 sec and turning off the light (Figure 5). We focused on the change of absorbances at 415 and 465 nm that were assigned to be π-π^* electronic transition peaks. Although the molar extinction coefficient, ε of the aggregated chromophores at 532 nm is quite small, we could figure out that the extent of aggregated chromophores became smaller than that before exposure. Previously, we observed the slight change of absorption spectrum during heating to 200 °C in Figure 4. Compared to the thermal effect on disruption of the chromophores, photo-irradiation is much more effective on it.

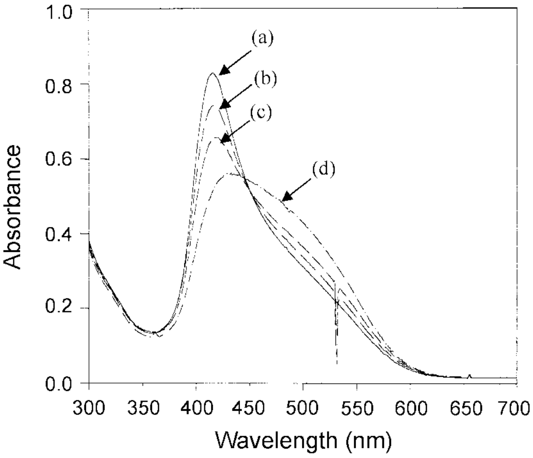

Figure 5. Absorption spectra of the SGDR1 film during photo-irradiation: (a) Exposure time, 10 sec; (b) 30 sec; (c) 200 sec; (d) 600 sec.

Photoisomerization behavior. In order to observe the *trans-to-cis* isomerization and compare the rate constants, we irradiated the excitation light to the film sample. We prepared two different samples after annealing at 150 °C (SG150) and 200 °C (SG200) for 3 h in this study.

Photoisomerization can take place under irradiation of excitation light whose wavelength is in the middle of the wavelength range of π-π^* electronic transition of the azobenzene chromophore. The prepared two films showed a typical aggregation behavior in the chromophores. When the pump beam (λ=532 nm) was turned on, the absorbance at 415 nm decreased slowly due to the photoisomerization in the aggregated chromophores. Simultaneously, we could observe the change of absorbance at 465 nm during exposure. The absorbance at 465 nm was assigned to be π-π^* electronic transition of the free azobenzene molecules. Therefore, the molecules also are subject to undergo *trans-to-cis* isomerization under photo-irradiation too. So the absorbance decreased quickly as soon as the pump beam was turned on. As the exposure time elapsed, the absorbance at 465 nm increased gradually. Although the absorbance continued to decrease at 415 nm during irradiation, the absorbance at 465 nm increased continuously after initial drop resulting from the disruption of aggregation in the chromophores. As the proportion of the free molecules increased, the absorbance at 465 nm became larger relatively. However, at the same time, we can expect the superposing effects of increasing the absorbance due to increase of extent of the free chromophores and decrease of absorbance at 465 nm due to *trans-to-cis* isomerization. As the pump beam was turned off, the absorbance at 465 nm jumped instantly and was reaching to the asymptotical value resulting from *cis-trans* thermal back reaction.

We showed the change of absorbance at 415 nm and 465 nm in two different samples that were annealed at 150 °C and 200 °C for 3 h. In Figure 6(A) and 7(A), the changing behavior of absorbance at 415nm is quite similar and relatively slower due to low molar extinction coefficient, ε at 532 nm. However, the rates of decay and growth in both

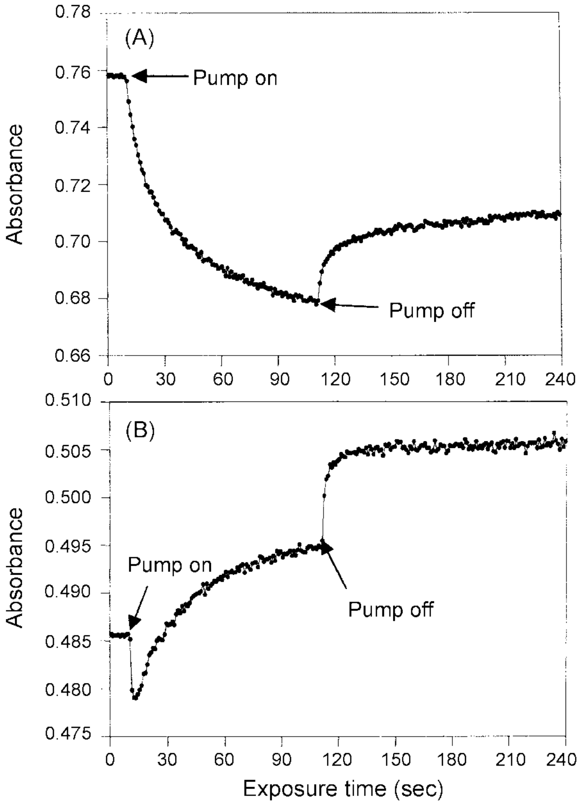

Figure 6. Change of the absorbance at 415 nm(A) and 465 nm(B) under light excitation: *The sample (SG150) was annealed at 150 °C for 3 h.

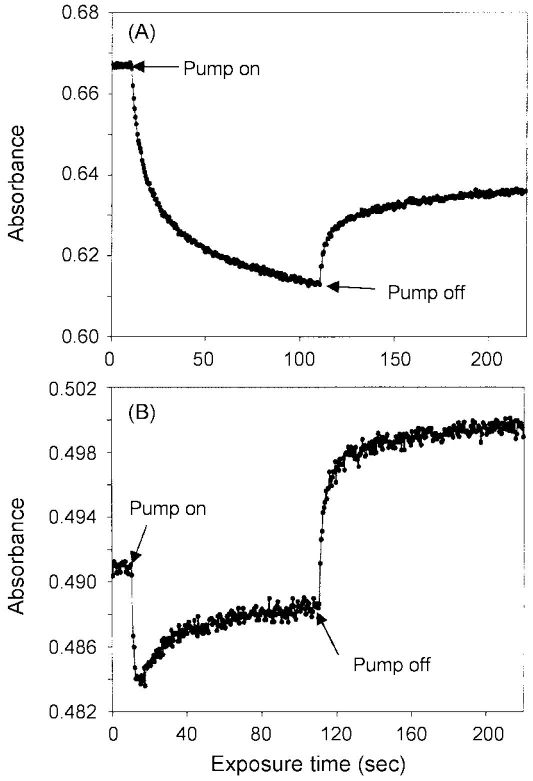

Figure 7. Change of the absorbance at 415 nm(A) and 465 nm(B) under light exciation: *The sample (SG200) was annealed at 200 °C for 3 h.

samples are different. The sample (SG200) showed relatively smaller rates in both cycles. After 30 sec exposure, SG150 and SG200 showed 11% and 7% decrease of the initial absorbance, respectively. In order to fit these data to the theoretical exponential function, too much error will be expected. Besides the effect of low molar extinction coefficient, ε at 532 nm, the density of silicon oxide in the sample (SG200) can be expected to be higher than that in the sample (SG150) annealed at 150 °C. Therefore, the azobenzene chromophores were expected to be surrounded or caged in the network structure. The *trans-to-cis* photoisomerization was found to be affected by the structural environment. In Figure 6(B) and 7(B), we could observe the change of absorbance at 465 nm. After the initial drop of absorbance, the extent and rate of increase in absorbance were different in both samples too. Within the identical exposure time, increment of absorbance and the rate are all smaller in SG200. This is also attributed that the disruption of chromophores in the matrix is more difficult to occur compared to the other sample (SG150). Then, when the pump beam was turned off, the rate of *cis-trans* thermal back reaction is larger and continuously increased. Above phenomena were thought to be affected by a higher density of matrix due to annealing at higher temperature for the same period.

Photo-induced anisotropy. Two annealed samples (SG150, SG200) were used to investigate the photo-induced birefringence.[17] Employing the same light intensity of a linearly polarized pump beam (λ=532 nm, I=200 mW/cm^2), we obtained the rising and decaying curves in the two samples. When the light is on, the birefringence starts to increase fast. Then when the excitation light is off, the birefringence quickly decreases at the initial stage (Figure 8).

Rising and decaying curves were analyzed by curve fitting the data to double exponential function which is shown in equation 2 and 3. The determined dynamic parameters were tabulated in Table 1.

$$\text{Growth: } \Delta n(t) = \text{A}\,[1-\exp(-k_1\,t)] + \text{B}\,[1-\exp(-k_2\,t)] \quad (2)$$

$$\text{Decay: } \Delta n(t) = \text{C}\exp(-k_3\,t) + \text{D}\exp(-k_4\,t) + \text{R} \quad (3)$$

As was expected, the rate of rising and decaying are all smaller in the sample, SG200 due to the higher density of network matrix. However, the difference of the rising rates is not significant in both samples. Additionally, the value of the induced birefringence was smaller than that of SG150. In the case of SG150, the rate of *trans-to-cis* isomerization is slightly larger and the extent of the free molecules became much larger for the same exposure time. The angular selective optical pumping induced *trans-to-cis* isomerization at a similar rate ("angular hole burning") and extent in both samples because of the small required free volume for *trans-to-cis* isomerization. However, the molecular reorientation from *cis-to-trans* isomerization is much more difficult in the SG200 because it requires much larger free volume. Therefore, as the sol-gel processed sample is annealed at the higher tempertaure, the photoisomerization and molecular reorientation are all retarded.

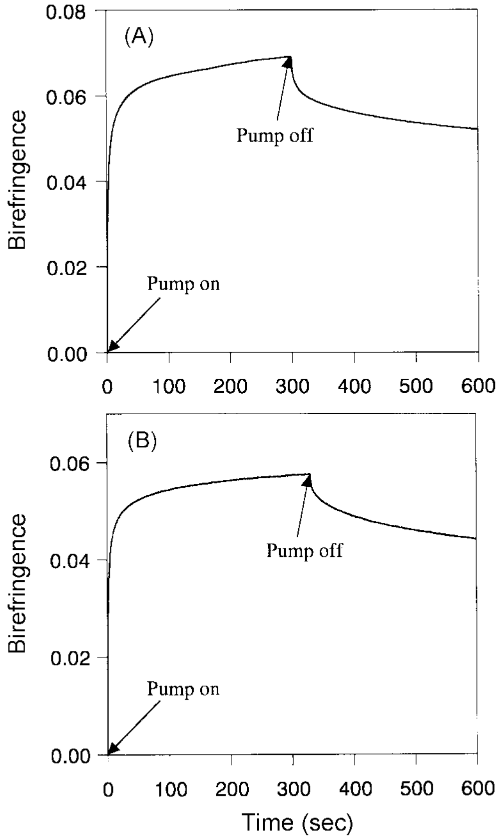

Figure 8. Growth and decay of birefringence on SGDR1 film. (A) SG150; (B) SG200: *Pump beam intensity 200 mW/cm^2.

Table 1. Parameters obtained by fitting the birefringence data to equation (2) and (3) *Experiments were performed at room temperature

	k_1	k_2	k_3	k_4	Δn^a
SG150	0.5930	0.0243	0.2707	0.0102	0.065
SG200	0.4390	0.0225	0.1860	0.0089	0.054

*Unit of k: /sec. ^{a}The value of birefringence after 180 sec exposure.

Conclusion

We synthesized the triethoxysilane bearing an azobenzene moiety. The thin films were fabricated using the sol after hydrolysis and condensation. We observed the effect of aggregation on the photoisomerization and the photo-induced birefringence in the SGDR1 film. Disrupting behavior of the dye aggregation in the network structure was also observed under thermal treatment. Additionally, photo-induced effect on disruption of dye aggregation was also observed compared to the thermal effect. Thermal annealing at higher temperature induced the increase of the matrix density so that the degree of freedom in the mobility of the azobenzene chromophore was limited in the network structure. It affects the dynamic behaviors on the disruption of the dye aggregation, photoisomerization, and photo-induced anisotropy.

Acknowledgment. This work was supported by Kyung Hee University (Jayugongmo, 2000)

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