Dynamics of Photo-Optical Effect of Azo Dyes Measured with Michelson Interferometer

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Controlling refractive index of materials is important for optical processing systems. Especially, photochromic reactions are one of the potential techniques which induce irreversible refractive index change in materials. The photochromic reactions are usually performed in the solid state because of the applications to devices. However, the kinetic and the reactivity of the photochromism are basically different from those in solution. We measured the dynamics of refractive index change of photochromic dyes by a Michelson interferometer.

Keywords: refractive index change, photo-optical effect, photoisomerization, azobenzene, 4-dimethylamino-azobenzene, 4-dimethylamino-4'-nitroazobenzene, Michelson interferometer

1. Introduction

Improvement in the information processing and large scale information storage is needed in recent years. Nonlinear optical effect, acoustic optical effect, photorefractive effects are proposed for the optical switching up to now which is the basic unit of optical integrated circuits.

We have proposed a novel method using photochemical reactions, which induce refractive index change permanently. We named the methods as Photo-Optical effects, and we have clarified that the azo compounds and norbornadiene polymers can induce refractive index change in the magnitude as large as 1×10⁻². Irie reported refractive index control using photoisomerization of diarylethene as 4×10⁻² [1]. Morino clarified relationship between the amount of dopants and refractive index, and relation between refractive index and the conversion of the doped azo derivatives in PMMA [2, 3]. However, these researches measured only refractive indices before and after the reaction.

These materials are usually used in the solid state, in which dynamics of the reaction is different from those in solution. Therefore, observing the dynamic process during refractive index change is very important. Thus, in this research, the dynamics of the refractive index change in the photoisomerization reaction of a photochromic molecule was observed by using Michelson interferometer with high sensitivity, high-speed measurement. In this paper, the feature of a Photo-Optical effect was clarified by comparing and evaluating the refractive index change of azo dyes and the parameter of each azo dyes in both ethanol solution and PMMA solid.

2. Experimental

2.1. Sample preparation

Azobenzene (AZB), 4-Dimethylaminoazobenzene (DAAB), 4-Dimethylamino-4'-nitroazobenzene (DANAB) were purchased from Tokyo Kasei Kogyo Co., and were purified by recrystallization from ethanol. Methyl methacrylate (MMA, Tokyo Kasei Kogyo Co.) was distilled under vacuum before use.

0.15 mM 2,2'-azobisisobutyronitrile (Tokyo Kasei Kogyo Co.) and AZB (3.6×10⁻² g, 2.0×10⁻⁸ mol) or DAAB (4.5×10⁻² g, 2.0×10⁻⁴ mol) or DANAB (5.3×10⁻² g, 2.0×10⁻⁴ mol) were dissolved in MMA (19 g, 0.19 mol), which were heated at 50°C for 17 hours to polymerize. The azo concentrations were about 1.0×10⁻² mol/l and the film thicknesses were about 1 mm.

2.2. Photoirradiation

The experimental setup of the Michelson interferometer is shown in Fig.1. The probe beam of a CW He-Ne laser (ORIEL Instruments 79241, λ =
632.8 nm, output power = 1 mW) was divided into two branches. Sample is placed on the pass of one branch, and the combined beam from the both branches was monitored with a fiber-coupled multi-channel spectrometer (Ocean Optics, Inc USB2000) after passing through a lens. Photoirradiation was performed at an angle of 90 degrees to the probe beam passing through the sample by the beam of a Q-Switched Nd:YAG laser (HOYA Continuum MiniLite I, λ = 355 nm, energy = 4 mJ, pulse duration = 4-6 ns) or a Xe lamp (USHIO UB3H00). The PMMA film sample containingazo dyes was placed at an angle of 45 degrees in the similar way.

AZB samples were photoirradiated with 355 nm light of a Nd:YAG laser. Actinometry was carried out with a laser power meter (OPHIR OPTRONICS, AN/2). The intensity of the light was 5.73 mw/cm². DAAB samples were photoirradiated with 512 nm light of a Xenon lamp through a monochromator (Edmund Optics Japan Co. CJ37597) and a thermocut filter (Edmund Optics Japan Co. CJ45649). Actinometry was carried out with a digital powermeter (ADVANCE TEST TQ8210). The intensity of the light was 98.12 μW/cm². DANAB samples were photoirradiated with 574 nm light in the similar way, but the intensity of the light was 87.3 μW/cm².

Absorption spectra and absorption change of the samples were measured with a UV photometer (Jasco V-550).

Hence, thermal retroisomerization of DAAB and DANAB was investigated. Fig.2 and Fig.3 shows the absorption change of DAAB and DANAB in ethanol solution at room temperature after photoirradiation. Each absorption changed exponentially. The rate constant for the thermal backward reaction of DAAB or DANAB in ethanol was determined as 0.38 s⁻¹, 0.67 s⁻¹, respectively. The thermal isomerization of DANAB is faster than that of DAAB. The dark process from cis to trans isomerization is known to proceed via inversion mechanism [4], and those azobenzene derivatives with donor and acceptor groups are known to react via a zwitter ionic intermediate of quinonoid structure [5, 6]. Unstabilization of this intermediate by those substituents is thought as the reason for their fast backward thermal isomerization.

![Graph](image)

**Fig. 2. OD change of DAAB in ethanol at 404 nm during thermal isomerization from cis to trans form**

![Graph](image)

**Fig. 3. OD change of DANAB in ethanol at 471 nm during thermal isomerization from cis to trans form**

3. Results and Discussion

3.1. Thermal isomerization of azo dyes in solution

Thermal backward reaction of AZB is so slow that it can be neglected. But cis-Form of some substituted azobenzenes is so unstable that their thermal backward reaction cannot be neglected during photoisomerization.

3.2. Photoisomerization of azo dyes in solution

Photoisomerization rates of photochromic reactions of azobenzene derivatives are given as the difference in the rates between trans to cis and cis to trans
photoisomerizations, in addition to that of thermal isomerization. Therefore, the rate equation for the photochromic reaction can be expressed in Eq.1,

\[
\frac{d(10^3C_{\text{trans}}(t))}{dt} = I_0 S \frac{e_{\text{trans}}(\text{irr})C_{\text{trans}}(t)}{e_{\text{trans}}(\text{irr})C_{\text{trans}}(t) + e_{\text{cis}}(\text{irr})C_{\text{cis}}(t)} (1 - 10^{-6C_{\text{cis}}(t)}) \phi_{\text{trans-cis}} \]

\[-I_0 S \frac{e_{\text{cis}}(\text{irr})C_{\text{cis}}(t)}{e_{\text{trans}}(\text{irr})C_{\text{trans}}(t) + e_{\text{cis}}(\text{irr})C_{\text{cis}}(t)} (1 - 10^{-6C_{\text{cis}}(t)}) \phi_{\text{cis-trans}} \]

\[-10^{-3}k C_{\text{cis}}(t) S I \]  

(1)

where, \(C_{\text{trans}}(t)\) and \(C_{\text{cis}}(t)\) [mol L\(^{-1}\)] are the concentration of trans- and cis-isomers, \(e_{\text{trans}}(\text{irr})\) and \(e_{\text{cis}}(\text{irr})\) [mol\(^{-1}\)cm\(^{-1}\)] are their molar extinction coefficients at the photoirradiating wavelength \(\text{irr}\), \(k\) [s\(^{-1}\)] is the rate constant for the thermal reaction of azo dyes, \(I_0\) [W/cm\(^2\)] is the intensity of the irradiation light, \(S\) [cm\(^2\)] is the irradiation cross section, \(I\) [cm] is the sample thickness, \(\phi_{\text{trans-cis}}\) and \(\phi_{\text{cis-trans}}\) are the quantum yields of the photoreaction, respectively.

\(OD_{\text{obs}}(t)\) is the optical density of the sample at the wavelength of \(\text{obs}\) at time \(t\) during photoirradiation at the wavelength of \(\text{irr}\). Therefore, the \(OD_{\text{obs}}(t)\) stands for the optical density of the sample at the photoirradiating wavelength. The left hand term of the equation expresses the decrease in the quantity of \text{trans} isomer per unit time, and each term of the right hand expresses the product of quantum yield of photoisomerization and quantity of absorbed light by the \text{trans-} or \text{cis-} isomer, respectively.

Fig.4 shows the OD changes of DAAB in ethanol solution at room temperature during 404 nm light irradiation. Fitting of the observed OD change to Eq.1 gives the values of quantum yield for photoreaction of DAAB, \(\phi_{\text{trans-cis}}\) as 0.18.

Fig.5 shows the OD changes of DANAB in ethanol solution at room temperature during 471nm light irradiation. Fitting of the observed OD change to Eq.1 gives the values of quantum yield for photoreaction of DANAB in the similar way, but \(\phi_{\text{trans-cis}}\) as 0.19.

3.3. Interference study of azo dyes

Fig.6 shows the probe beam intensity change of AZB in ethanol during photoirradiation.

When a sample which is placed in one arm of the Michelson interferometer is photoirradiated by pump beam, refractive index of the sample changes, which in turn changes the interference intensity of the probe beam, because the combined beams interfere constructively to give maximum intensity, while minimum intensity is observed when the beams arrive out of phase. Therefore, the refractive index change of solution samples or film samples can be expressed as Eq.2, or Eq.3, for solution samples, film samples respectively.

\[
\Delta n = \frac{\delta \lambda}{4 \pi d} = \frac{\lambda}{4 \pi d} \cos^{-1} \left( \frac{A - A_0}{A_1} \right) \]

(2)

\[
\Delta n = \frac{\delta \lambda}{4 \sqrt{2} \pi d} = \frac{\lambda}{4 \sqrt{2} \pi d} \cos \left( \frac{A - A_0}{A_1} \right) \]

(3)

where, \(\Delta n\) is the refractive index change induced by photoisomerization, \(\delta\) is the phase change, \(\lambda\) is the wavelength of probe beam (632.8 nm), \(d\) is the sample thickness, \(A\) is the detected probe beam
intensity, and $A_0$ is the middle of amplitude in Fig. 6. $A_1$ is the width in Fig. 6. The $\sqrt{2}$ is requested because film sample is placed on the sample holder at 45 degrees to the incident light. The refractive index change of other samples was also calculated in the similar way.

![Interferogram of AZB in ethanol during photoisomerization from trans to cis form induced by 355 nm light (5.73 mW/cm²)](image)

**Fig. 6.** Interferogram of AZB in ethanol during photoisomerization from trans to cis form induced by 355 nm light (5.73 mW/cm²)

Fig. 7 shows the refractive index change of AZB in ethanol or PMMA as the function of OD change. The refractive indices were changing linearly corresponding to OD change. From Fig. 7, it is found that the refractive index change is induced by OD change during photochromic reactions. That refractive index change can be explained based on Kramers-Kronig relationship. When azobenzene derivative changes from trans-isomers to cis-isomers by photoradiation, the electronic state of the molecule changes, which causes the change of the absorption of the molecule as well as its refractive index.

Fig. 8, Fig. 9, Fig. 10 show the plots of the refractive indices of AZB, DAAB and DANAD to irradiation photon numbers. In every azo dyes, refractive index changes of the samples doped in PMMA induced photoirradiation is smaller than those in ethanol. This is considered as the effect of the free volume of PMMA. During photoisomerization of azo dyes, i.e., critical free volume is requested for the azo dyes to isomerize. While the molecules confined in the small free volume cannot isomerize. However, the content of the free volume in PMMA is relatively small compared to that in solution due to the restriction of molecular motion [7]. Therefore, the refractive index change of the sample in PMMA is smaller.

![Refractive index change of AZB samples during photoisomerization](image)

**Fig. 8.** Refractive index change of AZB samples during photoisomerization

![Refractive index change of DAAB samples during photoisomerization](image)

**Fig. 9.** Refractive index change of DAAB samples during photoisomerization

![Refractive index change of DANAB samples during photoisomerization](image)

**Fig. 10.** Refractive index change of DANAB samples during photoisomerization
In ethanol solution, the refractive index change of DANAB was induced most efficiently. The conversion of a photoisomerization reaction, $R^{irr}$ [7], have already determined as 0.90, 0.87, 0.70, for AZB, DAAB, DANAB respectively,

$$\frac{R^{irr}}{r_e^{(irr)} r_\phi + 1}$$

which shows that the photosomerization reaction of DANAB has the smallest in conversion. However, the absorption band of DANAB exists relatively in the long wavelength region tailing near 632.8 nm at which the refractive index change is observed. Thus, the refractive index change is affected both by the reactivity and specific refractive index change. The latter one is dominant in the case of DANAB.

The refractive index change per molecule of DAAB in PMMA was induced most efficiently. This is considered by both the free volume of PMMA and the critical free volume compared to other the azo dyes. Since the DANAB has dimethylamino group and nitro group bonded to azobenzene structure, its critical free volume of DANAB is the largest. Therefore, photosomerization of DANAB is restricted most strongly in PMMA. Thus, it is necessary to take into consideration not only the parameter of azo dyes but also outer environment factor called free volume of polymer chain in polymer solid.

The quantum yield, $\phi_{trans\rightarrow cis}$, the rate constant for the thermal reaction $k$, the conversion of a photoisomerization reaction $R^{irr}$, maximum absorption wavelength $\lambda_{max}$ of azo dyes are listed in Table 1. Although quantum yield of DAAB or DANAB is larger than AZB, by the substituent effects, molecular polarization together at DAAB or DANAB, the rate constant for the thermal reaction of DAAB or DANAB also becomes larger. Therefore, it is considered that the conversion of a photoisomerization reaction of AZB molecule becomes the largest. However, bonding of the substituent also causes the blue shift of absorption band, consequently absorption changes near the observation wavelength, and the refractive index change per molecule is induced more efficiently. Thus, it was found that various factors called quantum yield of photoisomerization, the rate constant for the thermal backward reaction, the conversion of a photoisomerization reaction, and absorption wavelength have contributed the refractive index change in photochromic molecule. Moreover, in polymer solid, free volume of polymer chain and critical free volume of molecule are also important factors.

<table>
<thead>
<tr>
<th>Table 1. Various factors of azo dyes</th>
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<tr>
<td>factor</td>
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<tr>
<td>$\phi_{trans\rightarrow cis}$</td>
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<tr>
<td>$k [s^{-1}]$</td>
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<tr>
<td>$R^{irr}$</td>
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<tr>
<td>$\lambda_{max}$ [nm, cis]</td>
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4. Conclusion

The dynamics of refractive index change of the azo dyes induced by the photoisomerization reaction was measured. Consequently, at photoisomerization reaction, it is found that quantum yield of photoisomerization reaction, the rate constant for the thermal backward reaction of molecules, the conversion of a photoisomerization reaction and absorption wavelength have contributed to the induced refractive index change. Moreover, in polymer solid, it is found that it is the important factor to which free volume of polymer chain and critical free volume of molecule has also contributed by the refractive index change. Therefore, if these factors are controllable, it will be thought that the molecule which can the refractive index change induced more efficient can be designed.

References