Distribution and Anisotropy of Free-Volume in Solid State Polymers with Photo-Induced Orientation Reaction

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Reactions in solid state polymers are different from those in solutions because the mobility of the polymer molecules is so restricted that reactivities vary with the local environment of site by site. One of the influencing factors on their reactivity is the free volume in polymers. In this paper, free volume effect on the photo-induced molecular orientation reaction of azobenzene derivatives in polymethyl methacrylate (PMMA) was described and the distribution of the kinetic parameters is discussed in terms of the free volume distribution in PMMA.

Keywords: free volume distribution, kinetic constant, photoisomerization, 4-dimethylaminoazobenzene, 4-dimethylamino-4'-nitroazobenzene, photo-induced orientation.

1. Introduction
Many organic photofunctional materials, such as optical memories, photomeric molecules and photoresists use the reactions in polymer solid. Developing such polymer materials requires the study on their microstructure or nanostructure because the reactions in solid state polymers are different from those in solutions, often affected by their solid state structure and their homogeneity. And hence the solid state reactions in polymers are composed of the distribution of various kinetics due to the inhomogeneity of the matrix. Photochemical and photochromic reactions are often utilized as a key step of the reactions in a variety of functional materials. They are also used as probes to investigate microstructure of various polymers.

We have reported on free volume of polymers with photocromatic probe technique [1], fluorescent probe technique [2], photochemical hole burning [3], where the free volume of polymers are estimated by non-homogenous decay of the optical behavior of probes during photoirradiation, and where critical free volume is qualitatively discussed based on the final degree of photoreaction. Positronium annihilation technique is one of the tools estimating free volume distribution recently developed. However interpretation of the positronium annihilation data is not established [4-6]. Recently we have analytically solved the differential equation of photochromic reactions to enable analysis of photochemical reactions quantitatively [7]. We have also reported quantum yield distribution of photoisomerization of azobenzene in PMMA solids to give a quantitative explanation of the free volume effect and the distribution on the photoisomerization of azobenzene [8]. In this paper, we describe the distribution of the kinetics of photoinduced orientation reaction of azo compounds in terms of free volume distribution in the polymer matrix.

2. Experimental
2.1. Sample preparation
4-Dimethylaminoazobenzene (DAAB) was purchased from Tokyo Kasei Kogyo Co., and was purified by recrystallization from ethanol. 4-Dimethylamino-4'-nitroazobenzene (DANAB) was purchased from Tokyo Kasei Kogyo Co., and was purified by recrystallization from benzene. Methyl methacrylate (MMA, Tokyo Kasei Kogyo Co.) was distilled under vacuum before use.
1.5 mM 2,2'-azobisisobutyronitrile (Tokyo Kasei Kogyo Co.) and DAAB (5.2×10⁴ g, 2.3×10⁻⁷ mol) or DANAB (6.2×10⁴ g, 2.3×10⁻⁷ mol) were dissolved in MMA (30 g, 0.30 mol), then the mixture was heated at 50°C for 15 hours to polymerize. The azo concent-

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rations were about 7.0×10^5 mol/l and the thicknesses were about 4 mm.

2.2. Photoirradiation
DAAB in methylcyclohexane was photoirradiated with 404 nm light of a Xenon lamp (USHIO UBH300) through a monochromator (Edmund Optics Japan Co. C1737597) and thermo-cut filter (Edmund Optics Japan Co. C145649). Absorption spectra of the samples were measured with a UV photometer (Jasco V-550) in a cryostat (Unisoku Co. USP-203). Actinometry was carried out with a digital powermeter (ADVANCE TEST TQ820). The intensity of the light was 6.079×10^{10} einstein cm^{-2} s^{-1}. DANAB solution was photo-irradiated with 444 nm light in the similar way, but the intensity of the light was 8.166×10^{10} einstein cm^{-2} s^{-1}.

Photo-induced orientation of the azo compounds in PMMA was monitored by photoirradiating at their isosbestic points and measuring the OD change at the isosbestic points, which were 372 nm for DAAB and 407 nm for DANAB, respectively. The intensity of the light was 1.338×10^{10} einstein cm^{-2} s^{-1}. Fig.1 shows the experimental setup. The light of a Xe lamp was divided with a beam splitter (Edmund Optics Japan Co. C 43359), one of which was measured with a photo-diode (Hamamatsu Co. S1337-1010BQ) as reference, and the other was measured with a photo multiplier (Hamamatsu Co. H6780-04) through a polarizer (Sigma koki Co. SPF-30C-32) and the sample. These data were collected on an A/D converter (National Instruments Co. DAQPad-6020E) to a PC.

![Figure 1](image1.png)

Figure 1. The experimental setup for the measurement of photo-induced orientation reaction

3. Results and Discussion
3.1. Thermal isomerization of DAAB and DANAB in solution

Absorption spectrum of trans-DAAB is shown as the solid line in Fig.2. The absorption of trans-DAAB decreases upon photoirradiation at the peak wavelength due to photosomerization of the DAAB. cis-Form of some substituted azobenzenes are not so stable that thermal backward reaction cannot be neglected during the photosomerization. Hence, thermal retroisomerization of DAAB is investigated. Fig.3 shows the absorption change of DAAB in methylcyclohexane solution at 303, 273 and 243K after photoirradiation of 404 nm light. The absorption spectra changed exponentially at all temperatures. Thermal isomerization at 243K may be ignored during the photosomerization. The activation energy for thermal isomerization of DAAB was determined as 33.1 kJ mol^{-1} from Arrhenius Plots shown in Fig.4.

![Figure 2](image2.png)

Figure 2. The UV absorption spectra of trans- and cis-DAAB in methylcyclohexane solution

![Figure 3](image3.png)

Figure 3. OD change of DAAB during thermal isomerization from cis to trans form in methylcyclohexane solution at 243, 273 and 303K

![Figure 4](image4.png)

Figure 4. Arrhenius plots of thermal back reaction of DAAB in methylcyclohexane solution
The UV absorption spectra of trans- and cis-DANAB in methylcyclohexane solution shows two peaks at different wavelengths. The thermal reaction of DANAB was determined to have an activation energy of 23.2 kJ mol\(^{-1}\) from Arrhenius plots shown in Fig. 7. The dark process of cis to trans isomerization is known to proceed via inversion mechanism [9], and those azobenzene derivatives with donor and acceptor groups are known to react via a zwitter ionic intermediate of quinonoid structure [10, 11]. Unstabilization of this intermediate by those substituents is thought to be the reason for their low activation energy for the thermal isomerization.

3.2. Absorption spectra of cis-isomers

The absorption rates of photochromic reactions of azobenzene derivatives are given as a difference between trans to cis and cis to trans isomerizations. Therefore, the rate equation for the photochromic reaction can be expressed as Eq. 1.

\[
\frac{d(t)}{dt} = k \left[ \epsilon_{\text{trans}} \frac{C_{\text{trans}}(t)}{C_{\text{trans}}(t) + C_{\text{cis}}(t)} - \epsilon_{\text{cis}} \frac{C_{\text{cis}}(t)}{C_{\text{trans}}(t) + C_{\text{cis}}(t)} \right]
\]

where, \(C_{\text{trans}}(t)\) and \(C_{\text{cis}}(t)\) [mol l\(^{-1}\)] are the concentration of trans- and cis-isomers, \(\epsilon_{\text{trans}}(irr)\) and \(\epsilon_{\text{cis}}(irr)\) [1 mol\(^{-1}\) cm\(^{-1}\)] are their molar extinction coefficients at the photomiradiating wavelength \(irr\), \(\phi_{\text{trans} \rightarrow \text{cis}}\) and \(\phi_{\text{cis} \rightarrow \text{trans}}\) are the quantum yields of the photoreaction, respectively.

The Arrhenius plots of thermal back reaction of DANAB in methylcyclohexane solution shows a linear relationship between \(\log K\) and \(T^{-1}/10^{-3} \text{K}^{-1}\).

The solid line of Fig. 5 shows absorption spectrum of trans-DANAB in methylcyclohexane solution. The absorption changes at 303, 273 and 243K after photomiradiation of 444 nm light are shown Fig. 6. The thermal isomerization of DANAB is so faster than that of DAAB that the absorbance of DANAB in the photostationary state at 303K is larger than those at other temperatures because of non-negligible contribution of the thermal reaction. The activation energy for the thermal reaction of DANAB was determined as 23.2 kJ mol\(^{-1}\) from Arrhenius plots shown in Fig. 7. The dark process of cis to trans isomerization is known to proceed via inversion mechanism [9], and those azobenzene derivatives with donor and acceptor groups are known to react via a zwitter ionic intermediate of quinonoid structure [10, 11]. Unstabilization of the intermediate by those substituents is thought to be the reason for their low activation energy for the thermal isomerization.
photoirradiation at the wavelength of $\lambda$, where the ratio $C_{\text{cis}}/C_{\text{trans}}$ is determined only by the irradiating wavelength.

$$OD_{\text{cis}}^\text{obs}(t) = e_{\text{obs}}(\text{obs})C_{\text{trans}}(t)l + e_{\text{cis}}(\text{obs})C_{\text{cis}}(t)l$$  \hspace{1cm} (2)

$C_{\text{trans}}(t)$ and $C_{\text{cis}}(t)$ [mol/l] are the concentration of the photochromic molecules, $l$ [cm] is the sample thickness, respectively. Combining two experiments irradiating the samples at the wavelengths of the absorption peak, $\lambda$ of the isosbestic point, $\lambda$, gives molar extinction coefficient spectrum of cis isomer, expressed by Eq.3,

$$\epsilon_{\text{cis}}(\lambda) = \left( \frac{OD_{\text{cis}}^\text{obs}(\lambda)}{OD_{\text{cis}}^\text{obs}(0)} - 1 \right) \epsilon_{\text{obs}}(\lambda) \hspace{1cm} (3)$$

$$r_{\text{trans}}^\text{obs}(\lambda) = \left( \frac{OD_{\text{peak}}^\text{obs}(\lambda)}{OD_{\text{peak}}^\text{obs}(0)} \right)^2 - \left( \frac{OD_{\text{peak}}^\text{obs}(\lambda)}{OD_{\text{peak}}^\text{obs}(0)} \right) + 1$$  \hspace{1cm} (4)

where, $\lambda$ is the wavelength observing the spectrum. The concentration ratio of cis to trans isomers in the photosationary state after photoirradiation at the peak wavelength, $r_{\text{trans}}^\text{obs}(\lambda)$ is given in Eq.4. The molar extinction coefficient spectrum of cis-isomer, $\epsilon_{\text{cis}}(\lambda)$ [l mol$^{-1}$ cm$^{-1}$] can be calculated from Eqs.3 and 4.

Two samples of DAAB in methycyclohexane were photoirradiated either at 406 nm as peak or 362 nm as isosbestic point at 213K. The values of $OD_{\text{peak}}^\text{obs}(0)$, $OD_{\text{peak}}^\text{obs}(0)$, $OD_{\text{peak}}^\text{obs}(0)$, $OD_{\text{peak}}^\text{obs}(0)$, $r_{\text{trans}}^\text{obs}(\lambda)$ were 0.82945, 0.17282, 0.81471, 0.52107 and 0.87461, respectively. Two samples of DANAB in methycyclohexane were photoirradiated either at 455 nm of peak or 394 nm of isosbestic point at 223K. The values of $OD_{\text{peak}}^\text{obs}(0)$, $OD_{\text{peak}}^\text{obs}(0)$, $OD_{\text{peak}}^\text{obs}(0)$, $OD_{\text{peak}}^\text{obs}(0)$, $r_{\text{trans}}^\text{obs}(\lambda)$ were 0.75491, 0.36309, 0.75952, 0.52388 and 0.72846, respectively. From the data, absorption spectra of cis-DAAB, and cis-DANAB was obtained which are shown as dotted lines in Fig.2 and Fig.5, respectively. From Fig.2 and Fig.5, the isosbestic points were determined to be 305 nm, 362 nm and 450 nm for DAAB, 394 nm and 515 nm for DANAB respectively.

3.3. Photo-induced orientation of DAAB and DANAB

Fig.8 shows the OD changes of DAAB in PMMA during non-polarized 372 nm light irradiation. Based on the Eq.2, the OD should not change the during because the molar extinction coefficients of trans- and cis-isomers are equal and so the degree of the reaction does not change the total OD. However the decrease in the OD of DAAB is observed in Fig.8 even by photoirradiation at the isosbestic point. This can be explained by the photo-induced orientation of DAAB. Such molecules with long molecular axis like DAAB are usually dichroic, and the average of the projection of the absorption of the molecules with various molecular directions to observing plane is observed in solution. However the absorption of the molecules in polymer solid is direction dependent because molecular motion is so restricted. Photoirradiation of the molecules rotates the molecular axis during a number of trans to cis and cis to trans isomerization cycles. The decay of absorption in Fig.8 corresponds to the orientation of DAAB along to the axis parallel to the propagating direction of the light. Fig.9 shows the OD change of DAAB in PMMA during polarized 372 nm light irradiation in the similar way. The decay rate by non-polarized light irradiation was apparently smaller than that by polarized light irradiation. The OD change of DAAB by non-polarized light irradiation corresponds only to orientation of the DAAB described.

![Figure 8](image1.png)

Figure 8. OD change of DAAB in PMMA solid during orientation process induced by non-polarized 372 nm light (40\text{\mu}W/cm²)

![Figure 9](image2.png)

Figure 9. OD change of DAAB in PMMA solid during orientation process induced by polarized 372 nm light (40\text{\mu}W/cm²)
above, while that by polarized light includes the orientation of DAAB out of the polarized light plane in addition.

This orientational motion is one of the relaxation processes of self correlation of the molecules, and so the relaxation process should decay exponentially. However the OD change of DAAB in Fig.8 and Fig.9 cannot be fitted with exponentially decaying curves. We think the reason as that the OD change consists of various decaying components because there are distribution of various size of free volumes in PMMA. Fig.10 shows the distribution of the rate constants of the OD change of DAAB under polarized and non-polarized light irradiation, assuming that the decaying curves consist of a series of exponentials in Eq.5,

\[ F(t) = A_0 + A_1 \exp(-k_1 t) + A_2 \exp(-k_2 t) + \cdots \]

\[ = \sum_{i=0}^{\infty} A_i \exp(-k_i t) dt \]  

(5)

where \( k_i \) are rate constants which varies according to the free volume size of the matrix. \( A_i \)'s are pre-exponential factors which we assume obeys to Gaussian distribution.

![Figure 10. The kinetic constants distributions of DAAB induced by polarized and non-polarized light in PMMA solid](image)

Population of pre-exponential factor for the smaller \( k \) region is relatively small for the experiment with non-polarized light irradiation, which is consistent with the observation of total OD change. And the distribution of rate constants during non-polarized light irradiation is thought not to reflect only the molecules of orientational relaxation to an unobservable direction but also those which move around in the plane parallel to the electric field of light. Therefore we decided to use the kinetics by the polarized light irradiation for the comparison with DANAB. Fig.11 shows the OD change of DANAB in PMMA during polarized 407 nm light irradiation. Fig.12 shows comparison of the distribution of the \( k \) for DANAB and DAAB during polarized light irradiation. Average kinetic constants of DAAB is higher than that of DANAB, which is unexpected because the thermal isomerization rate of DANAB is larger than DAAB and so the number of trans to cis isomerization cycle of DANAB should be larger than that of DAAB. This result is explained by the activation free volume; i.e., nitrogoup on DANAB increases the size of the volume required for the isomerization and hence the efficiency of molecular orientation is thought to be decreased.

4. Conclusion

Distribution of the rate constants for the photo-induced orientation reaction of DAAB and DANAB was obtained both by polarized and non-polarized light irradiation. The apparent photo-induced orientation rate is larger for the experiment with polarized light because of selective observation of reorientating molecules. The rate constant for photo-induced orientation of DAAB is found to be larger than that of DANAB, because of the smaller activation free volume of DAAB due to the lack of nitrogoup.
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References