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Polarized Light-induced Anisotropy Depending on Polymer Matrices Studied by Polarized FTIR Spectroscopy

Keiko Tawa*[1, 2], Kenji Kamada[2], Toru Sakaguchi[2], and Koji Ohta[2]

[1] Fields and Reactions, PRESTO, JST
[2] Osaka National Research Institute, Ikeda, Osaka 563-8577, JAPAN

SUMMARY: Polarized-light induced anisotropy of Disperse Orange 3 (DO3) depending on the polymer matrices was investigated by polarized FTIR spectroscopy. The dynamic behavior of the azo dyes doped in a series of methacrylate polymers was analyzed in terms of the orientation factors. Two factors, the free volume and the local polarity of matrices, are found to govern the dynamic behavior of DO3. It was found that induced anisotropy for trans and cis isomers varies depending on Tg of polymer matrix. Further, the thermal isomerization rate depend on the isomerization mode which is governed by the matrix polarity. The branched-alkyl chains are considered to block the interaction between ester groups and DO3 and introduce the DO3 molecules into the less polar environment.

Introduction

Azo dyes have been attractive materials for studying the various kinds of optical properties such as the second-order nonlinear optical effect and polarized light-induced anisotropy. A polarized light-induced anisotropy[1,2] has been observed in polymer films doped with photosensitive molecules. Todorov et al.[3,4] studied photoinduced anisotropy in polymer films doped with azo dyes for transient polarization holography utilized as a real-time recording. However, the physical mechanisms of the photoinduced anisotropy have not been clarified yet.

In this study, the polymer matrix dependent photoinduced anisotropy was investigated by polarized FTIR spectroscopy in order to clarify the physical mechanisms of the anisotropy. The dynamic behavior of azo molecules will be discussed in terms of the orientation factors[5] obtained from analysis of several vibrational bands in polarized FTIR spectra.

Experimental

Materials. Disperse Orange 3 (DO3, Aldrich), a push-pull azo dye, was used as a photosensitive molecule (Figure 1). A series of methacrylate polymers, poly(methyl methacrylate) (PMMA, Aldrich, M_w=120,000, Tg~114℃), poly(ethyl methacrylate) (PEMA, Aldrich, M_w=515,000, Tg~63℃), poly(propyl methacrylate) (PPMA, Scientific Polymer Products, Inc., M_w=250,000, Tg~35℃), poly(isopropyl methacrylate) (PiPMA, Aldrich, M_w=100,000, Tg~85℃), and poly(isobutyl methacrylate) (PiBMA, Aldrich, M_w=300,000, Tg ~60℃) were used as matrices. The cast films were prepared from chloroform solution.

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The thickness of the films were less than 20 μm. The dye concentration was about 1 wt %.

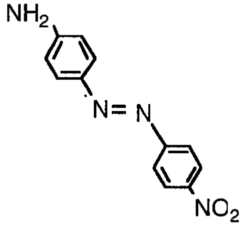

Figure 1. DO3 (trans form)

Measurements. The polarized FTIR spectra of the DO3/polymer films were measured at room temperature using a Bio-Rad FTS-175C IR spectrometer before irradiation and during irradiation of linearly polarized light. A cw Ar ion laser (488 nm) was used as the radiation source for inducing the photoinduced anisotropy. The optical power of the laser was 2 mW/cm^2 at the sample position. The IR spectra of all polymers without DO3 were also measured as references in order to observe quantitatively (by spectral subtraction) the infrared absorption bands of DO3. All spectra were measured at a wavenumber resolution of 4 cm^{-1}. Polarized FTIR spectra were observed using the polarizer (KRS-5) in the parallel (Z) and perpendicular (Y) directions to the polarization direction of an Ar ion laser.

A Shimadzu UV-2500PC spectrometer was used to measure the polarized UV-visible absorption spectra, $E_Z(\lambda)$ and $E_Y(\lambda)$, of the DO3/polymer films during irradiation, so that the mole fraction of trans isomer, α, is determined. UV-visible absorption spectra and infrared spectra were obtained under the same optical arrangement.

Analysis

The molecular orientation in the laboratory-fixed coordinates (X, Y, Z) can be represented by the matrix of orientation factors, K, which indicates the statistically averaged alignment of molecules within the molecular-fixed coordinates (x, y, z). (The detail was described in ref 6.)

In order to explain the physical meaning of matrix elements, K_{Zf} (f :x, y, z), the absorption probability of the a-band along the Z-axis is represented by the dot product of the Z-polarized light, $\boldsymbol{e}_Z$(unit vector), and an electric dipole transition moment, $\boldsymbol{M}(a)$, as shown in Figure 2.

$$< (\boldsymbol{e}_Z \cdot \boldsymbol{M}(a))^2 >= M_x{}^2(a) < cos^2\theta_x > + M_y{}^2(a) < cos^2\theta_y > + M_z{}^2(a) < cos^2\theta_z > \qquad (1)$$

where the off-diagonal terms like $M_xM_y<cos\theta_x cos\theta_y>$ may vanish by selecting the appropriate system of molecular-fixed coordinates which coincide with the molecular orientation axes.

The terms of $M_f^2(a)<cos^2\theta_f>$ corresponds to the square of the projection of the f-component of the transition moment, $\boldsymbol{M}(a)$, onto the Z axis. The statistical average of the square of the cosines is defined as the orientation factors, K_{Zf}.

$$K_{Zf} = <\cos^2\theta_f> \ . \tag{2}$$

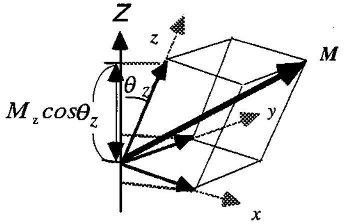

Figure 2. The projection of the molecular fixed z-component of an electric dipole transition moment, $\boldsymbol{M}$, onto the laboratory-fixed Z axis.

The observed absorbance vector in the laboratory-fixed axes, $\boldsymbol{E}(a)$ can be represented as equation (3) by the multiplication of the matrix of orientation factors, K, and the absorbance vector, $\boldsymbol{A}(a)$, in a molecular framework, x,y,z.

$$\boldsymbol{E}(a) = \mathsf{K}\cdot\boldsymbol{A}(a). \tag{3}$$

In this study, the sample is considered to have a uniaxial orientation, $E_X(a)=E_Y(a)$, since the sample was irradiated by linearly polarized light along the Z axis. Therefore, K can be described as

$$\mathsf{K} = \begin{pmatrix} \frac{1-K_{Zx}}{2} & \frac{1-K_{Zy}}{2} & \frac{1-K_{Zz}}{2} \\ \frac{1-K_{Zx}}{2} & \frac{1-K_{Zy}}{2} & \frac{1-K_{Zz}}{2} \\ K_{Zx} & K_{Zy} & K_{Zz} \end{pmatrix}. \tag{4}$$

Azo compounds can take two isomers: trans and cis. The absorbance of an a-vibrational band, $\boldsymbol{E}(a)$, can be expressed as the sum of the absorbance of the trans and cis isomers using the mole fraction of the trans isomer, α,

$$E(a) = \alpha\, K^{(t)} A(a)^{(t)} + (1-\alpha)\, K^{(c)} A(a)^{(c)} \; . \qquad (5)$$

We can estimate the orientation factors for each isomer by solving the simultaneous equations described by equation (5) for different bands.

Results

Polarized UV-visible spectra. As shown in Figure 3, the UV-visible absorption peaks are observed with λ_{max} around 430 nm. In push-pull azo dyes, it has been known that their peaks correspond to the $\pi\pi^*$ transition for the trans isomer. The blue-shift of λ_{max} was found in methacrylate polymers with branched-alkyl chains such as PiPMA and PiBMA.

The direction of the $\pi\pi^*$ transition moment of the trans isomer aligns with the long axis. All DO3 molecules were considered to take the trans form in the initial state. The mole fractions of the trans isomer, α, during irradiation (in the photostationary state) were obtained using $\{E_Z(\lambda_{max})+2E_Y(\lambda_{max})\}/3$ by normalizing the absorbances to the initial absorbances. The α values were found to be 0.80(PMMA), 0.79(PEMA), 0.78(PPMA), 0.78(PiPMA), and 0.84(PiBMA). It is known that the cis isomer has the absorption peak in the wavelength longer than 500 nm, and has little absorption at 488 nm. Therefore, it is valid to consider that the light at 488 nm excites only trans isomers.

Polarized FTIR spectra. Figure 4 shows the polarized spectra of DO3 in PMMA before irradiation and during irradiation. Three vibrational bands assigned[7,8] to symmetric (NO_2^s, 1341cm^{-1}) and antisymmetric (NO_2^{as}, 1523cm^{-1}) stretching modes of NO_2, and the C-N stretching mode of C-NH_2 (C-N, 1303cm^{-1}) are found to be useful for determining the orientation factors[6]. Table I shows the absorbances of the three bands in the photostationary state, which are normalized to their initial absorbances.

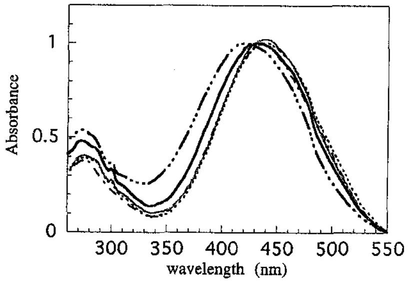

Figure 3. The UV-visible spectra of DO3 in ····PMMA, –·–PEMA, ——PPMA, ━━PiPMA, and···━PiBMA.

We defined the molecular-fixed coordinates for the trans and cis isomers, respectively, as shown in Figures 5 (a) and (b). The molecular axes for the trans isomer were chosen so that the molecule takes a planar structure in the y_t-z_t plane, where the vibrational transition moments of NO_2^s and C-N bands are parallel to the z_t axis. The relationship $K_{Z_x}^{(t)}=K_{Z_y}^{(t)}$ can be assumed in this study since the $\pi\pi^*$ transition moment is taken as parallel to the z_t axis. The cis molecule is assumed to take the structure with two phenyl ring planes perpendicular to each other. It is also assumed that the C-NO_2 bond is oriented in the direction of z_c axis and the C-NH_2 bond is oriented in the direction of y_c axis.

The determined values of $K_{Zz}^{(t)}$ and $K_{Zf}^{(c)}$ are shown in Table 2. In the trans isomer, the $K_{Zz}^{(t)}$ value in the photostationary state is smaller than 1/3 independent of polymers. The $K_{Zz}^{(t)}$ value in PMMA is found to be the smallest in the $K_{Zz}^{(t)}$ values for all polymers. In the cis isomer, the $K_{Zf}^{(c)}$ values are found to be larger than $K_{Zx}^{(c)}$ and $K_{Zy}^{(c)}$ values in every polymer. The $K_{Zz}^{(c)}$ value in PMMA is the largest in the $K_{Zz}^{(c)}$ values for all polymer matrices. In other polymers, PEMA, PPMA, PiPMA and PiBMA, the $K_{Zy}^{(c)}$ values are a little larger than the $K_{Zz}^{(c)}$ values.

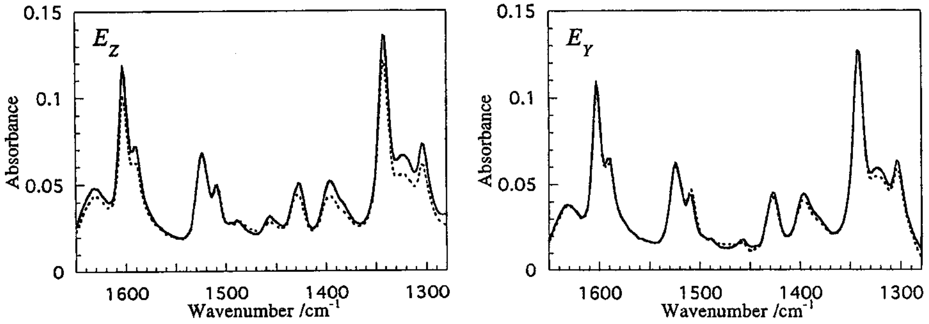

Figure 4. The polarized FTIR spectra of DO3 in the Z and Y directions obtained by subtracting PMMA spectra. —— before irradiation, ······ in the photostationary state.

Table 1. Normalized absorbance of three vibrational bands in polymer matrices in Z (parallel) and Y (perpendicular) directions measured by polarized FTIR method in the photostationary state

	$E_Z(NO_2^s)$	$E_Y(NO_2^s)$	$E_Z(NO_2^{as})$	$E_Y(NO_2^{as})$	E_Z(C-N)	E_Y(C-N)
PMMA	0.87	1.00	1.01	0.96	0.71	0.91
PEMA	0.89	0.98	0.99	0.96	0.76	0.85
PPMA	0.90	0.97	0.98	0.96	0.76	0.85
PiPMA	0.87	0.97	0.97	0.96	0.75	0.87
PiBMA	0.90	1.00	0.98	0.95	0.81	0.91

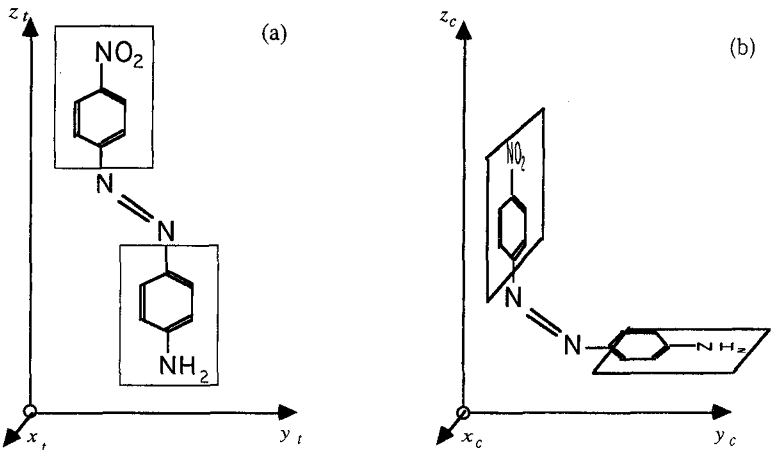

Figure 5. Molecular axes: (a) for trans isomer and (b) for cis isomer

Table 2. The orientation factors for trans and cis isomers in the photostationary state.

polymer	$K_{Zz}^{(t)}$	$K_{Zz}^{(c)}$	$K_{Zy}^{(c)}$	$K_{Zx}^{c)}$
PMMA	0.285	0.42	0.29	0.29
PEMA	0.305	0.35	0.33	0.32
PPMA	0.308	0.36	0.34	0.30
PiPMA	0.300	0.36	0.35	0.29
PiBMA	0.308	0.35	0.36	0.29

Discussion

In the trans isomers, the $K_{Zz}^{(t)}$ values in the photostationary state are smaller than 1/3. This means that the trans isomers with a small angle between the Z and z_t axis were excited selectively by linearly Z-polarized light. The smallest $K_{Zz}^{(t)}$ value in PMMA indicates the movement of trans isomers is restricted into a small free volume as shown by a high glass transition temperature (Tg). In the cis isomers, the $K_{Zz}^{(c)}$ values are larger than $K_{Zy}^{(c)}$ and $K_{Zx}^{(c)}$ in every polymer. The larger $K_{Zz}^{(c)}$ values indicate that there are a lot of cis molecules with a small angle between the Z and the z_c axis. It represents that p-NH_2-C_6H_4 apparently moves easily, probably because the relative volume of p-NH_2-C_6H_4 is smaller than that of p-NO_2-C_6H_4. PMMA gives the largest $K_{Zz}^{(c)}$ value of all polymers for the same reason as the trans isomers. From the orientation factors determined by polarized FTIR spectra in the photostationary state, we found that the free volume is one of the factors which govern the mobility of DO3 molecules, and we can classify the mobility into two types with Tg.

Furthermore, we can classify the mobility of DO3 into two types with the structure of the alkyl chains as the other matrix effect. Blue-shifts of λ_{max} are observed for branched-alkyl methacrylates such as PiPMA and PiBMA as shown in Figure 3. The blue-shift indicates that the microscopic environment surrounding DO3 is less polar[9]. In push-pull azo dyes, cis molecules in the polar solvents generally isomerize not only via slow inversion processes, but also by rapid rotation processes promoted by charge separation[10,11]. In addition to this blue-shift, we also have the experimental results that cis forms in branched-alkyl methacrylates isomerized slowly to trans forms compared with in *n*-alkyl methacrylates such as PMMA, PEMA, and PPMA. Such a different thermal isomerization rate is considered to reflect the different isomerization mechanisms depending on the local polarity in matrix. Our results in UV-visible spectra show that the branched-alkyl chain blocks the interaction between ester groups and DO3 molecules.

If the NH_2 group of DO3 interacts with ester group of the polar matrix, the movement of p-NH_2-C_6H_4 group may be restricted and p-NO_2-C_6H_4 group can move more easily in the thermal isomerization processes. In that case, the $K_{Z_y}^{(c)}$ value should be expected to be larger than $K_{Z_z}^{(c)}$. However, in the photostationary state, our results for the orientation factors indicate that the orientation of cis molecules appears independent of the polarity. The isomerization by the rotation mode promoted in the polar matrices is much faster than that by the inversion mode. Therefore, we interpret that it is difficult to observe the orientation of cis molecules in the polar environment in the photostationary state.

Conclusion

Polarized IR spectroscopy was used to clarify the dynamic behavior of DO3 molecules in polymer matrices induced by the polarized light. It was found that more DO3 molecules isomerize by the movement of p-NH_2-C_6H_4 group than that by p-NO_2-C_6H_4 group due probably to its relatively small volume. In the photostationary state, we classified the behavior of DO3 into three types by local environments surrounding DO3. In PMMA with a high Tg, the movement of both trans and cis molecules is restricted in small free volume. However, in PEMA, PPMA, PiPMA, and PiBMA with lower Tg, both trans and cis molecules move easily and show small anisotropy. The polarized UV-visible spectra indicate that the local polarity of the matrix also governs the dynamics of DO3 molecules. The thermal isomerization rate depends on the isomerization mode determined by local polarity. The branched-alkyl chains block the interaction between ester groups and DO3, and introduce the DO3 molecules to less polar fields.

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