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Photoinduced Reorientation of Azo Dyes Bonded to Polyurethane Studied by Polarized FT-IR Spectroscopy

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ABSTRACT: A large photoinduced anisotropy ratio was observed in the push−pull azo dyes bonded covalently to polyurethane by polarized UV−vis spectroscopy. During irradiation with an Ar^+ laser, the absorbance perpendicular to the polarization direction of the laser light increases gradually even when the photoisomerization rate of trans to cis forms is equal to the reisomerization rate of cis to trans forms. The trans molecules are considered to reorient during the trans−cis−trans isomerization cycles. The process of photoinduced reorientation was also observed by polarized FT-IR spectroscopy. The dynamic behavior of trans and cis isomers is discussed in terms of orientation factors evaluated using the absorbance of some IR vibrational bands. The values of orientation factors for the trans and the cis isomers vary with irradiation time due to the reorientation. The reorientation process for the cis molecules was found to be essential to the reorientation for the trans molecules. On the other hand, according to the result of no variation of absorbance for the C═O group in urethane main chain, the urethane main chain may not move together with azo moieties by polarized light irradiation.

Introduction

Azobenzene derivatives with both electron donor (D) and acceptor (A) at each para position of two phenyl groups (push−pull type) have attracted interest of a large number of researchers in the field of photonic materials and photonic devices. The push−pull type of azo dyes has important characteristics, i.e., the larger polarity than that of azobenzene without substituent, and the fast thermal reisomerization from cis to trans forms,[1] because of a large charge separation induced by D and A. These characteristics lead push−pull azo dyes to the prospect of the new optical functional materials utilizing the second-order nonlinear optical effect[2−4] or photoinduced anisotropy.[5−8]

A polarized light-induced anisotropy has been observed in polymer films including photochromic molecules. Since the 1980s, this type of anisotropy has been studied in polymers doped with azo dyes for transient polarization holography by Todorov and co-workers.[9,10] It has also been utilized as new optical switching materials in the liquid crystal systems,[11,12] because the orientation of azo dyes induced by irradiation with a polarized light can be a driving force for the alignment of the liquid crystals. As the other promising application of almost permanent photoinduced anisotropy, photofabrication of surface relief polarization gratings[13−16] has been studied in polymer thin films. While the technology for the application to various optical devices[17−19] has been advanced, studying the dynamics of azo dyes is essential to comprehension of the physical mechanisms for the photoinduced anisotropy.[20]

We have studied the physical mechanisms of photoinduced anisotropy of azo dyes doped in polymer matrices.[21] The matrix dependence and the azo structure dependence of photoinduced anisotropy have been studied in terms of orientation factors obtained from polarized UV−vis and FT-IR spectroscopies.[22,23] Push−pull azo dyes such as Disperse Orange 3 ($NO_2-C_6H_4-N{=}N-C_6H_4-NH_2$) and 4-(dimethylamino)-4′-nitroazobenzene ($NO_2-C_6H_4-N{=}N-C_6H_4-N(CH_3)_2$) were used in our previous studies.[24] In most polymer matrices such as methacrylate polymers and polystyrene which have little specific interaction with azo dyes, we found that trans forms tend to isomerize to cis forms by the motion of a phenyl side with smaller substituent compared with the other phenyl side.

In this paper, the linkage effect of azo dyes to a polymer chain on a photoinduced reorientation is reported. Photoinduced reorientation has been studied in various polymer films including azo moieties, e.g., Langmuir−Blodgett films,[25] liquid crystalline polymers,[12b,26] polyglutamate,[27] and polyimide.[28] Irradiation with the linearly polarized light can change the orientation of azo dyes from the original direction to that perpendicular to the polarization direction of irradiation light. In other words, irradiation can control the orientation of molecules. To realize the control of molecular reorientation, it is necessary to understand the photoinduced reorientation process of the azo dyes. In this study, we use a push−pull azo dyes covalently attached to polyurethane side chain (Figure 1) to investigate the dynamic behavior of both trans and cis isomers in the reorientation process. The polarized FT-IR and UV−vis spectroscopic techniques help us to comprehend how

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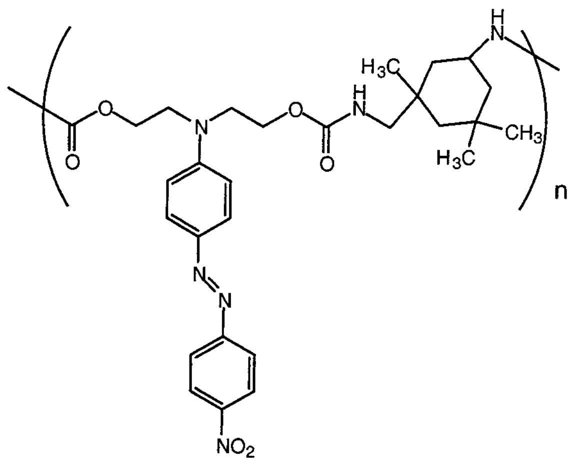

Figure 1. Chemical structure of a sample (polyurethane with azo dyes).

the chemical bonding can restrict the rotational diffusion and how it can contribute to the reorientation of azo moieties during trans–cis–trans isomerization cycles.

Experimental Section

Sample. Polyurethane having push–pull azo dyes as the side chain (Figure 1) is a commercial product (Chromophore Inc.). The glass transition temperature, T_g, of this polymer is 140 °C. The films were prepared on two kinds of substrates by spin-coating method from dioxane solution. The substrates were ZnSe for FT-IR measurement and slide glass for UV–vis measurement. The thickness of the films was about 100 nm. The films were annealed at 140 °C for several hours before the measurements.

Measurements. All spectra were measured at room temperature (23 °C). Linearly polarized continuous-wave light (488 nm) from an Ar^+ laser (Spectra-Physics, model 161C) was used as the excitation light. The optical power of the Ar^+ laser was 6 mW/cm^2 at the sample position. Polarized UV–vis spectra and polarized FT-IR spectra were measured in the parallel (Z) and perpendicular (Y) directions to the polarization direction of the incident laser light.

UV–vis spectra were measured by a Shimadzu UV-2500PC spectrometer. The time (t) variaion of UV–vis absorbance was measured at $\lambda_{\max}$ along the Z and Y directions before irradiation, during irradiation, and after irradiation with polarized excitation light. Normalized absorbances to the initial absorbance before irradiation are described as $E_Z(\lambda,t)$ and $E_Y(\lambda,t)$ in the Z and Y directions, respectively. The initial absorbances measured in the Z and Y directions are equivalent to each other, and therefore, $E_Z(\lambda,0) = E_Y(\lambda,0) = 1$. On the other hand, as the averaged value of normarized absorbances ($E_Z(\lambda,t)$, $E_Y(\lambda,t)$, and $E_X(\lambda,t)$), $\alpha'(t)$ is also obtained from $\{E_Z(\lambda_{\max},t) + 2E_Y(\lambda_{\max},t)\}/3$, because the linearly polarized light can be assumed to induce the optical anisotropy in the film plane.

The FT-IR spectra were measured using a Bio-Rad FTS-175C IR spectrometer equipped with an MCT detector. The wavenumber resolution was 4 cm^{-1}. Polarized FT-IR spectra were obtained using a wire grid polarizer (KRS-5). All interferograms were collected for every 10 s.

Analysis

Orientation factors are useful to discuss statistically averaged alignment of two isomeric forms of azo dyes induced by the polarized-light irradiation.[23] We have established the method for determining the orientation factors of the two isomers as reported in our previous study.[22]

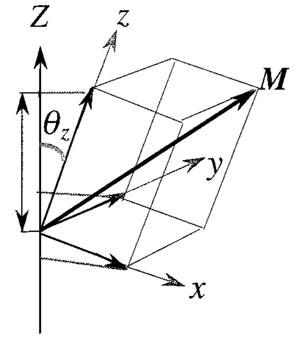

Figure 2. Projection of z-component of transition moment, $\mathbf{M}$, expressed in the molecular axes.

The absorption probability by a vibrational band of a along the Z-axis in the laboratory-fixed coordinates ($F = X, Y, Z$) can be represented by

$$\langle(\mathbf{e}_Z\cdot\mathbf{M}(a))^2\rangle = M_x^{\,2}(a)\langle\cos^2\theta_x\rangle + M_y^{\,2}(a)\langle\cos^2\theta_y\rangle + M_z^{\,2}(a)\langle\cos^2\theta_z\rangle \quad (1)$$

where $\mathbf{e}_Z$ is a unit vector of the Z-polarized light, $\mathbf{M}(a)$ is an electric dipole transition moment, and $\langle\ \rangle$ represents the statistical average. $\mathbf{M}(a)$ is composed of three components, $M_x(a)$, $M_y(a)$, and $M_z(a)$, in the molecular-fixed coordinates (x, y, z). Each term of $M_f^{\,2}(a)\langle\cos^2\theta_f\rangle$ described in eq 1 ($f = x, y, z$) corresponds to the square of the projection of the f-components of $\mathbf{M}(a)$ onto the Z axis (Figure 2). The off-diagonal terms like $M_x(a)M_y(a)\langle\cos\theta_x\cos\theta_y\rangle$ may vanish by selecting the appropriate system of molecular-fixed coordinates which coincide with the molecular orientation axes. The averaged square cosine θ_f is defined as an orientation factor, K_{Zf}

$$K_{Zf} = \langle\cos^2\theta_f\rangle \quad (2)$$

The F components of observed absorbance vector in the laboratory-fixed axes, $E_F(a)$, can be represented by the sum of each matrix element, K_{Zf}, multiplied by the f components of absorbance vector, $A_f(a)$, in a molecular framework.

$$\begin{aligned} E_F(a) &= \sum_f K_{Ff}A_f(a) \\ &= K_{Fx}A_x(a) + K_{Fy}A_y(a) + K_{Fz}A_f(a) \end{aligned} \quad (3)$$

In this study, the sample is considered to have a uniaxial orientation, i.e., $E_X(a) = E_Y(a)$, since the linearly Z-polarized light was used for the source of irradiation and the molecules are selectively excited by the Z-polarized light. Therefore, the matrix, $\mathbf{K}$, can be described as

$$\mathbf{K} = \begin{pmatrix} K_{Xx} & K_{\mathrm{Xy}} & K_{\mathrm{Xz}} \\ K_{\mathrm{Yx}} & K_{\mathrm{Yy}} & K_{\mathrm{Yz}} \\ K_{\mathrm{Zx}} & K_{\mathrm{Zy}} & K_{\mathrm{Zz}} \end{pmatrix} = \begin{pmatrix} \dfrac{1-K_{Zx}}{2} & \dfrac{1-K_{Zy}}{2} & \dfrac{1-K_{Zz}}{2} \\ \dfrac{1-K_{Zx}}{2} & \dfrac{1-K_{Zy}}{2} & \dfrac{1-K_{Zz}}{2} \\ K_{Zx} & K_{\mathrm{Zy}} & K_{Zz} \end{pmatrix} \quad (4)$$

Azo molecules can take two isomeric forms, trans and cis isomers. So, the F component of absorbance in a vibrational band of a, $E_F(a)$, can be expressed as the sum

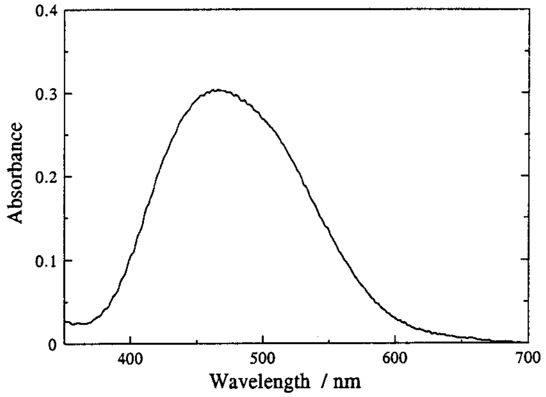

Figure 3. UV−vis absorption spectra for polyurethane sample. It was measured in the *Z* direction before irradiation.

of the absorbance for two kind of isomers using the mole fraction of the trans isomer, α

$$E_F(a) = \alpha \sum_f K_{Ff}^{(t)} A_f(a)^{(t)} + (1 - \alpha) \sum_f K_{Ff}^{(c)} A_f(a)^{(c)} \qquad (5)$$

Therefore, the orientation factors for each isomer can be estimated by solving above simultaneous equations for several different bands. In fact, the orientation factor, K_{Ff}, is also a function of time because the α and $E_F(a)$ are functions of time.

Results and Discussion

Isomerization of Azo Moiety. Before irradiation, the absorbance at $\lambda_{\max}$ corresponds to the absorption by the trans isomer, and the maximum absorption of the trans isomer in this sample is located at 466 nm as shown in Figure 3. During irradiation, the absorption peak at $\lambda_{\max}$ is composed of the absorption by both trans and cis isomers, although it is observed at the same wavelength. The mole extinction coefficient (ϵ) for the trans isomers at $\lambda_{\max}$ is about 2 times as large as that for the cis isomers.[29] Therefore, the mole fraction of the trans isomers, α(*t*), can be obtained from the relationship with α′(*t*) including the contribution of cis isomers as follows:

$$\alpha'(t) = \alpha(t) + (1 - \alpha(t))\epsilon_{\text{cis}}/\epsilon_{\text{trans}}$$
$$\alpha(t) = 2\alpha'(t) - 1 \qquad (6)$$

The result is depicted in Figure 4. The α(*t*) value began to decrease when the Ar^+ laser was turned on, and during irradiation for 140 s, it can be regarded as reaching a nearly constant value of 0.83. A stationary state essentially means that the slope of α(*t*) is equal to 0 when the photoisomerization rate of trans to cis forms is equal to the reisomerization rate of cis to trans forms. On turning the light off, the α(*t*) value quickly increased and gradually approached to 1. In this reisomerization (thermal back-isomerization) process, a half of the cis forms isomerizes to trans forms in 30 s after turning the light off.

Such an isomerization behavior is different from that of our previous result[24] in the DO3-doped PMMA, of which the absorbance is almost the same as that of a polyurethane film used in this study. Considering the molecular structure of push−pull azo dyes, the isomerization time of DO3 is expected to be longer than that of 4-(dialkylamino)-4′-nitroazobenzene used in this study because of a smaller charge separation.[24] However, according to the experimental result in DO3-doped PMMA, α(*t*) value reached a constant by the irradiation with Ar^+ laser for 30 s, which is shorter than 140 s in urethane polymer used in this study. Half of the cis forms in DO3-doped PMMA reisomerized to trans forms in 12 s after turning the light off. The reisomerization time in doped PMMA was also shorter than that in polyurethane. The result of longer reisomerization time observed in polyurethane was contrary to the expectation in the point of the molecular structure of push−pull azo dyes. Therefore, it is attributed to the restriction of the dynamics of an azo moiety by bonding covalently to a main chain.

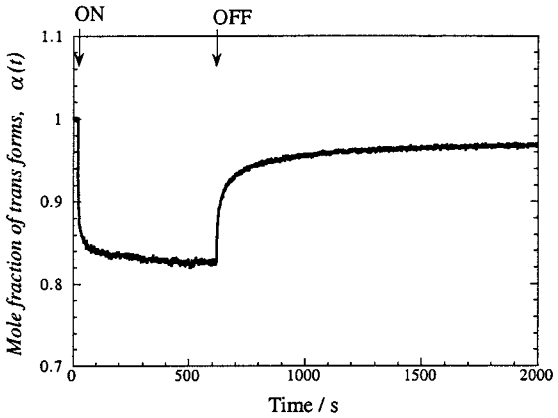

Figure 4. Variation of mole fraction of trans isomers, α(*t*), when Ar^+ laser was turned on and off.

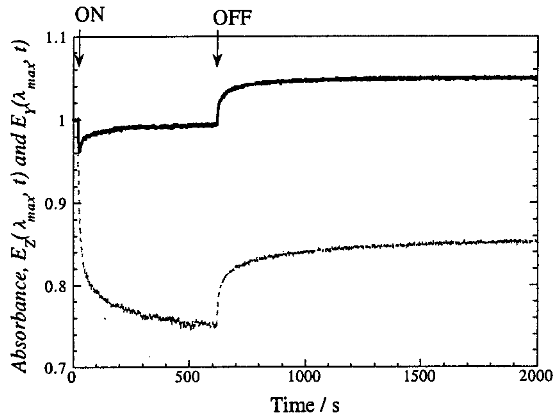

Figure 5. Variation of dichroism observed by UV−vis spectroscopy, $E_Z(\lambda_{\max},t)$ (· · ·) and $E_Y(\lambda_{\max},t)$ (—).

However, such a difference shown in the isomerization time between two samples is not as large as the difference in a photoinduced dichroism described in the following section.

Polarized Light-Induced Dichroism Observed by UV−vis Spectroscopy. Figure 5 shows dichroism measured by polarized UV−vis spectroscopy. The dichroism should be induced by at least two factors; one is the photoselective isomerization (photobleaching) of trans molecules by polarized-light irradiation, and the other is the reorientation of trans molecules during the continuous isomerization cycle. If the dichroism is caused by only photobleaching without the thermally rotational diffusion of trans molecules, the expected dichroism can be calculated from experimental value, α(*t*), according to the method descrbed in the Appendix.

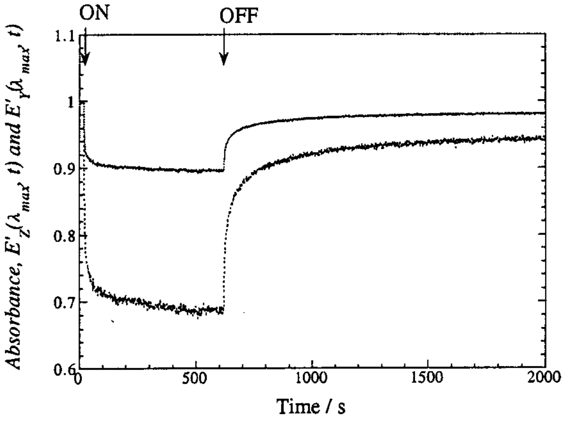

Figure 6. Theoretical dichroism obtained by only photobleach process (see Appendix): $E'_Z(\lambda_{\max},t)$ (· · ·) and $E'_Y(\lambda_{\max},t)$ (—).

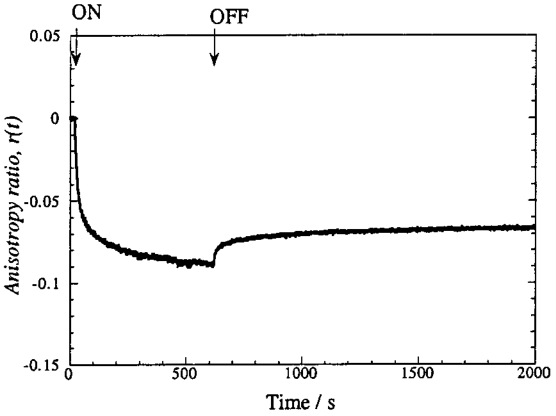

Figure 7. Variation of anisotropy ratio, $r(t)$, obtained from UV−vis absorbance.

Figure 6 shows the expected dichroism. When the experimental value of $\Delta E(t)^{\mathbf{PU}} = E_Y(t) - E_Z(t)$ as elucidated by using Figure 5 is compared with the $\Delta E(t)_{\mathrm{PB}}{}^{\mathbf{PU}}$ calculated by the photobleaching process shown in Figure 6, the $\Delta E(t)^{\mathbf{PU}}$ value of 0.24 is larger than the $\Delta E(t)_{\mathrm{PB}}{}^{\mathbf{PU}}$ value of 0.20. On the other hand, in the most polymer systems doped with push−pull azo dyes except for DR1 in PMMA,[7] the dichroism, $\Delta E(t)^{\mathbf{Dope}}$, is smaller than that calculated by photobleaching process, $\Delta E(t)_{\mathrm{PB}}{}^{\mathbf{Dope}}$. In our previous study[24] on the dichroism of DO3-doped PMMA, $E_Y(t) = 0.87$ and $E_Z(t) = 0.71$ (i.e., $\Delta E(t)^{\mathbf{Dope}} = 0.16$) were observed in the photostationary state. Then, using the $\alpha(t)$ of 0.82, the dichroism induced by only photobleaching without thermal diffusion was obtained as $E_Y(t) = 0.89$ and $E_Z(t) = 0.67$ ($\Delta E(t)_{\mathrm{PB}}{}^{\mathbf{Dope}} = 0.22$). Experimental value of $\Delta E(t)^{\mathbf{Dope}}$ was smaller than $\Delta E(t)_{\mathrm{PB}}{}^{\mathbf{Dope}}$, which means a quick diffusion of azo molecules. On the contrary, larger $\Delta E(t)^{\mathbf{PU}}$ than $\Delta E(t)_{\mathrm{PB}}{}^{\mathbf{PU}}$ may mean the existence of reorientation process of azo molecules under little thermal diffusion.

Further, introduction of an anisotropy ratio, r, may help us to comprehend the difference in the rate between reorientation and isomerization. The anisotropy ratio, r, can be estimated with $E_Z(\lambda_{\max})$ and $E_Y(\lambda_{\max})$ obtained by the polarized UV−vis spectroscopy, i.e., $r(t) = (E_Z(\lambda_{\max},t) - E_Y(\lambda_{\max},t))/(E_Z(\lambda_{\max},t) + 2E_Y(\lambda_{\max},t))$. The $r(t)$ value in the photostationary state was −0.09 as shown in Figure 7. When excitation light was turned on, the $r(t)$ changes more slowly than the $\alpha(t)$, as can be seen from a comparison of Figure 7 with Figure 4. The reorientation behavior of azo moieties is considered to be slower than isomerization behavior. Therefore, we cannot understand the behavior of $r(t)$ by only photobleaching process, and the existence of reorientation process with little rotational diffusion is plausible in order to explain the $r(t)$. After turning the light off, $r(t)$ did not recover to random orientation, and it kept around −0.07. The remaining anisotropy can be erased by irradiation with nonpolarized light or heating the sample. As expected from higher T_g than the room temperature (23 °C), the main chain should be difficult to move at room temperature after turning the light off. Therefore, the photoinduced orientation of azo moieties may be difficult to change.

On the other hand, it is difficult to discuss the photoinduced orientation process of the cis isomers by this method, because of too small absorbance. To discuss the reorientation process of azo molecules from the point of both trans and cis isomers, orientation factors obtained by polarized FT-IR technique are available.

Polarized Light-Induced Orientation Estimated by Orientation Factors. Figure 8a,b shows the polarized infrared spectra of urethane polymer with the push−pull azo dyes at the side chain before irradiation and during irradiation in the wavenumber range of 1850−1250 cm^{-1}. We utilized three vibrational bands assigned to symmetric (ν_s(NO$_2$), 1340 cm^{-1}) and antisymmetric (ν_{as}(NO$_2$), 1516 cm^{-1}) stretching modes of NO$_2$ and the C−N stretching mode of C−dialkylamino (ν(C−N), 1311 cm^{-1})[30,31] for the present analysis. The orientation factors described by eq 4 were determined by the following procedure. The six infrared data, $E_Z(\nu_s(\mathrm{NO_2}))$, $E_Z(\nu_{as}(\mathrm{NO_2}))$, $E_Z(\nu(\mathrm{C{-}N}))$, $E_Y(\nu_s(\mathrm{NO_2}))$, $E_Y(\nu_{as}(\mathrm{NO_2}))$, and $E_Y(\nu(\mathrm{C{-}N}))$, were utilized as the $E_F(a)$ values in eq 5. Further, the $\alpha(t)$ value was obtained by UV−vis absorption. To determine the absorbance, $A_f(a)$, in the molecular framework, we defined the molecular-fixed coordinates for the trans and cis isomers, as shown in parts a and b of Figure 9, respectively.[22] Thus, the orientation factors for each isomer can be estimated by solving the simultaneous equations for the three bands as follows:

$$\begin{aligned}
E_F(\nu_s(\mathrm{NO_2})) &= \alpha\sum_f K_{Ff}{}^{(t)} A_f(\nu_s(\mathrm{NO_2}))^{(t)} + {} \\
&\qquad (1-\alpha)\sum_f K_{Ff}{}^{(c)} A_f(\nu_s(\mathrm{NO_2}))^{(c)} \\
E_F(\nu_{as}(\mathrm{NO_2})) &= \alpha\sum_f K_{Ff}{}^{(t)} A_f(\nu_{as}(\mathrm{NO_2}))^{(t)} + {} \\
&\qquad (1-\alpha)\sum_f K_{Ff}{}^{(c)} A_f(\nu_{as}(\mathrm{NO_2}))^{(c)} \\
E_F(\nu(\mathrm{C{-}N})) &= \alpha\sum_f K_{Ff}{}^{(t)} A_f(\nu(\mathrm{C{-}N}))^{(t)} + {} \\
&\qquad (1-\alpha)\sum_f K_{Ff}{}^{(c)} A_f(\nu(\mathrm{C{-}N}))^{(c)} \quad (7)
\end{aligned}$$

The molecular axes for the trans isomer were chosen so that the molecule takes a planar structure in the y_t−z_t plane. The relationship $K_{Zx}{}^{(t)} = K_{Zy}{}^{(t)}$ can be assumed since the direction of $\pi\pi^*$ transition moment is parallel to the z_t axis in the present molecular framework. The cis molecule is assumed to take a structure with the two-phenyl ring planes perpendicular to each other as shown in Figure 9b. Their assumption was proved to be valid in our previous work.[24]

The time variation of the $K_{Zz}{}^{(t)}$ and $K_{Zf}{}^{(c)}$ (f: x, y, z) obtained here are shown in Figure 10a,b. In Figure 10a,

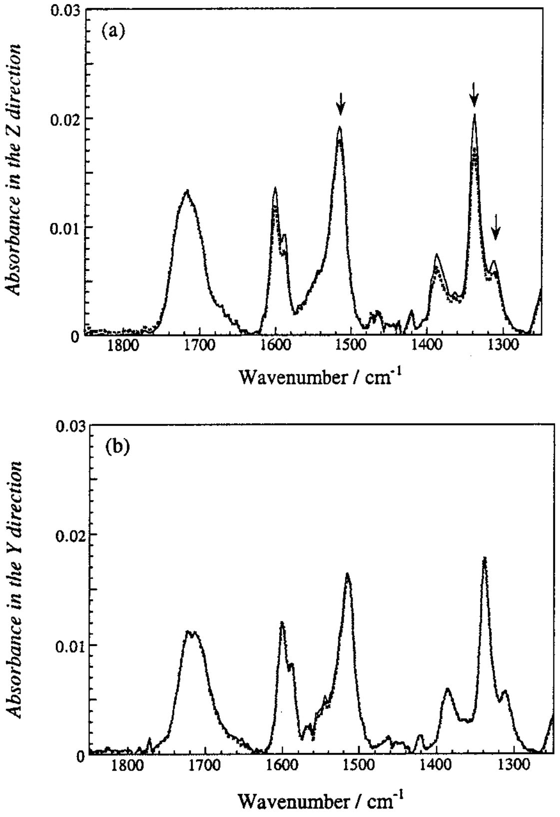

Figure 8. Polarized FT-IR spectra of a sample observed in the *Z* direction (a) and in the *Y* direction (b) before irradiation (—) and during irradiation (· · ·).

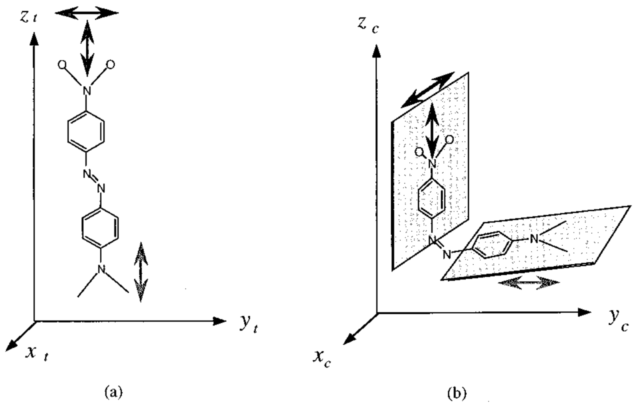

Figure 9. Molecular axes for a trans isomer (a) and a cis isomer (b).

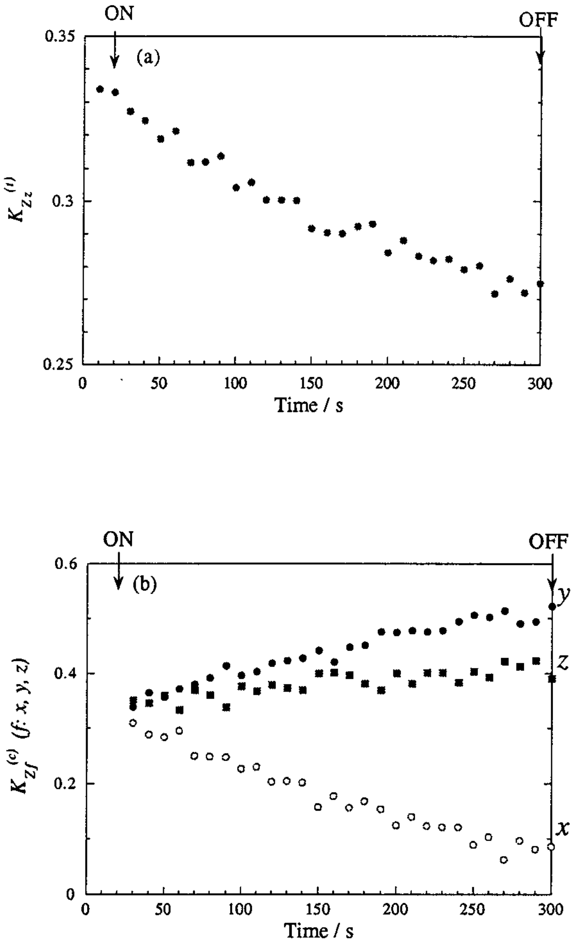

Figure 10. Orientation factors: $K_{Zz}^{(t)}$ for trans (a) and $K_{Zf}^{(c)}$ for cis (*f*: *x* (○), *y* (●), *z* (■)) (b).

$K_{Zz}^{(t)}$ values in the trans isomers should be $^1/_3$ when the system is isotropic before irradiation. The $K_{Zz}^{(t)}$ values gradually decrease from $^1/_3$ after turning the light on. 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. Then, $K_{Zz}^{(t)}$ values continue to decrease even in the stationary state for the concentration of trans molecules during the irradiation for 140 s.

For the cis isomer, the $K_{Zf}^{(c)}$ value is indefinite at the initial stage (time: 0), because there is no cis molecule before irradiation. The $K_{Zf}^{(c)}$ value is defined as an average value by $\langle\cos^2\theta_f\rangle$ of cis molecules as written in the Analysis section. $K_{Zf}^{(c)}$ is considered to reflect the averaged motion of azo molecules during the isomerization cycles. A trans molecule with the transition moment parallel to the polarization direction of the laser light is excited selectively. If the excited trans molecule isomerizes to cis form without fixing a specific position into the molecule or the rotational diffusion of a molecule is very fast even in polymer matrices, the cis molecules should never orient toward a certain direction and the anisotropy should not be observed. However, the polarized light-induced anisotropy of the cis forms is shown in Figure 10b. Therefore, the trans molecule is considered to isomerize to the cis form by the motion of the mobile side.[22] During irradiation, the $K_{Zy}^{(c)}$ values became larger than $K_{Zx}^{(c)}$ and $K_{Zz}^{(c)}$ values (Figure 10b). The larger $K_{Zy}^{(c)}$ values indicate that there are a large number of cis molecules with a small angle between the *Z* and the y_c axes. In other words, in the cis form, *p*-NR_2−C_6H_4 (R: −CH_2CH_2−) has a tendency to align with *Z*-axis by the motion of NO_2 group side in the isomerization process. The dialkylamino side is covalently bonded to urethane main chain, and the chemical bond should restrict the motion of azo molecule including the rotational diffusion. The $K_{Zy}^{(c)}$ values also continue to increase during the irradiation for 140 s. Such a behavior means the photoinduced reorientation of the cis molecules. The reorientation process of the cis molecules is found to be essential to the reorientation of the trans molecules. During trans−cis−trans isomerization cycles where trans forms excited by photoselection isomerize to cis forms and the cis forms thermally reisomerize to trans forms, both the trans and the cis forms gradually change the alignment from the original ones before the irradiation.

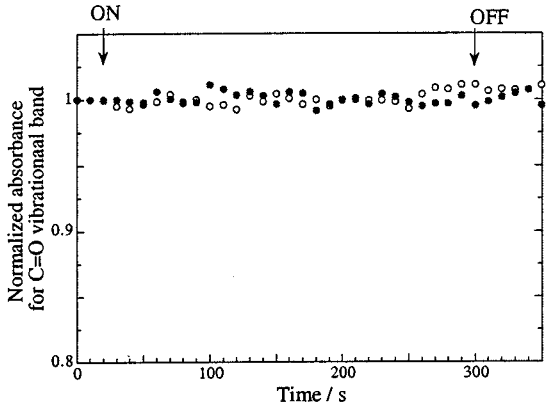

Figure 11. Variation of absorbance for the C=O vibrational band observed in the Z (●) and the Y (○) directions.

During the reorientation process of azo moieties under the polarized-light irradiation, the motion of urethane main chain was examined by polarized FT-IR spectra. The variation of the absorbance at 1720 cm^{-1} assigned to C=O vibrational band is shown in Figure 11. The dichroism was not observed in IR absorbance for C=O, and also the orientation of C=O is unchanged by irradiation. This indicates the urethane bond in a main chain does not move together with azo moieties during polarized light irradiation. Considering the T_g of the urethane polymer used in this study, only the alkyl chain directly bonded to an azo moiety may move together with reorientational behavior of azo moieties.

Thus, the reorientation can be controlled by polarized-light irradiation. The chemical bonding to polymer main chain was found to contribute to photoinduced reorientation of both the trans and cis forms of azo molecules.

Conclusion

We have observed the polarized-light induced anisotropy in polymer films doped with azo dyes by polarized UV–vis and FT-IR spectroscopies. The relationships between the molecular structure and the orientational behavior have been studied in doped systems. However, in this study, the large polarized light-induced anisotropy ratio was observed in push–pull azo dyes covalently linked to a polyurethane. A reorientation process of the azo moiety was observed by polarized UV–vis spectroscopy. It was found that much more trans forms can isomerize to cis forms by the motion of the p-NO_2–C_6H_4 group than by the motion of the p-dialkylamino-C_6H_4 group, by the analysis of orientation factors obtained from the polarized FT-IR measurement. Further, reorientation process is observed in not only the trans forms but also the cis forms. During trans–cis–trans isomerization cycles where trans forms excited by photoselection isomerize to cis forms and the cis forms thermally reisomerize to trans forms, both the trans and cis forms gradually change the alignment from the original one before irradiation. Restriction of the rotational diffusion by covalently bonding was found to be one of the important factors which induce the reorientation process under the polarized-light irradiation. This study clarified the relationship between the orientational behavior and the bonding effect in the system of push–pull azo dyes covalently bonded to a polymer.

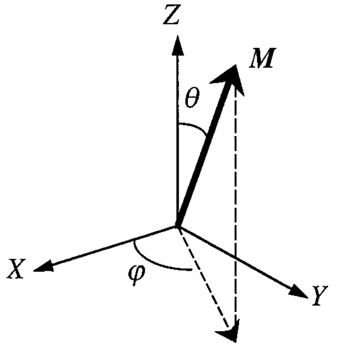

Figure 12. Transition moment expressed by a tilt angle to the Z-axis and a rotational angle to the X-axis.

Appendix

As shown in Figure 12, a molecule with an electric dipole transition moment, $\mathbf{M}$, can be expressed using θ (the tilt angle to the Z-axis) and φ (the rotational angle to the X-axis) in the laboratory-fixed coordinates. When a lot of molecules randomly distribute, the observed absorbances, $E_{X0}(\theta,\varphi)$, $E_{Y0}(\theta,\varphi)$, and $E_{Z0}(\theta, \varphi)$, are equivalent to each other before irradiation. When the Z-polarized light is irradiated, a molecule is excited to an upper level by absorbing the Z-polarized light. Three absorption components by $\mathbf{M}$, $i_X(\theta,\varphi)$, $i_Y(\theta,\varphi)$, and $i_Z(\theta,\varphi)$, are described as

$$i_X = p \sin^2\theta \cos^2\varphi, \quad i_Y = p \sin^2\theta \sin^2\varphi, \quad i_Z = p \cos^2\theta \tag{A1}$$

where p is constant. Here, the observed absorbance, $E_F(\theta,\varphi)$ (F: X, Y, Z), decreases from $E_{F0}(\theta,\varphi)$, because some molecules vanish due to excitation and the following isomerization from their original ground states by absorbing the Z-polarized light. The absorption probability of the Z-polarized light by $\mathbf{M}$ is independent of φ; i.e., the statistical average of $\cos^2\varphi$ described in eq A1 is $^1/_2$. Therefore, the Z-polarized light irradiation induces the uniaxial orientation ($E_X(\theta) = E_Y(\theta)$) under the condition of no rotational diffusion of the molecules.

$$\begin{aligned} E_X(\theta) &= E_{X0}(\theta) - {}^1/_2P' \sin^2\theta \\ E_Y(\theta) &= E_{Y0}(\theta) - {}^1/_2P' \sin^2\theta \\ E_Z(\theta) &= E_{Z0}(\theta) - P' \cos^2\theta \end{aligned} \tag{A2}$$

where P' can be dependent on time. The statistical average of $\cos^2\theta$ ($0 < \theta < \pi/2$) is given by

$$\langle\cos^2\theta\rangle = \left(\int_0^{\pi/2}\cos^2\theta\, f(\theta)\, d\theta\right) / \left(\int_0^{\pi/2} f(\theta)\, d\theta\right) \tag{A3}$$

where $f(\theta)$ is orientation distribution function which satisfies the normalization condition ($\int_0^{\pi/2} f(\theta)\, d\theta = 1$). $f(\theta)\, d\theta$ can be expressed by $3 \cos^2\theta \sin\theta\, d\theta$ in consideration of angular distribution under photoselection.[23,32] Therefore, the statistical average $\langle\cos^2\theta\rangle$ is 0.6. Using this value, the averaged absorbances, E_Z and E_Y, can be written by

$$E_Z = E_0 - 0.6P', \quad E_Y = E_0 - 0.2P' \tag{A4}$$

The time variation of mole fraction, $\alpha(t)$, which is obtained by $\{(E_Z(t) + 2E_Y(t))/3\}$, can be expressed by (E_0

$- {}^{1}/_{3}P'(t)$) using eq A4. When the absorbance is normalized to the initial absorbance before irradiation, $E_0 = 1$. Therefore, the polarized-light induced orientation is described as

$$\begin{aligned} E_Z(t) &= 1 - 0.6 \times 3(1 - \alpha(t)) \\ E_Y(t) &= 1 - 0.2 \times 3(1 - \alpha(t)) \end{aligned} \tag{A5}$$

Thus, two curves shown in Figure 6 were depicted on the basis of eq A5, using the experimental result of $\alpha(t)$.

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