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Local environment dependence of photoinduced anisotropy observed in azo-dye-doped polymer films

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Abstract

Polymer matrix dependence of polarized light-induced anisotropy of the push–pull azo dye, Disperse Orange 3 (DO_3; NO_2–C_6H_4–N=N–C_6H_4–NH_2), was investigated by UV–Vis and polarized FTIR spectroscopies. The orientation factors obtained by these spectroscopic methods helped us to understand the dynamics of DO3 in polymers. In methacrylate polymers and polystyrene (PS), the *trans* forms of DO3 are apt to isomerize to *cis* forms by the motion of *p*-NH_2–C_6H_4 group side, because the relative volume of the *p*-NH_2–C_6H_4 group is considered to be small compared with that of the *p*-NO_2–C_6H_4 group. The large photoinduced anisotropy of DO3 (*trans* and *cis* isomers) was found in poly(methyl methacrylate) (PMMA). The small free volume in PMMA is considered to inhibit the rapid rotational motion of DO3 molecules. The free volume provides the primary effect on the polarized light-induced anisotropy, but the local polarity effect of matrices cannot be ignored for the anisotropy of DO3. In the less polar PS with the larger free volume, the anisotropy for *cis* isomers depends on the motion of NH_2 groups, which do not interact with polymers so much.

Keywords: Photoinduced anisotropy; Azo-dye-doped polymer; Polarized FTIR

1. Introduction

Azo dyes have been attractive materials for many researchers who study the various kinds of optical properties such as the second-order nonlinear optical effect [1,2] and polarized light-induced anisotropy [3–8]. The reasons can be summarized as follows: (1) existence of two kinds of isomers, i.e. *trans* and *cis*, and possibility of isomerization by irradiating the light with an appropriate wavelength; (2) variety of azo compounds including the molecules which exhibit the liquid crystallinity [9–13]; (3) dependence of absorption peak wavelength and isomerization rate on the combination of azo dyes and matrices [14]; and (4) large polarity in azo molecules with electron donor and acceptor substituents (push–pull type). The push–pull azo molecules in side-chain or main-chain polymers can be oriented by an applied electric field, so that large second-order nonlinear optical susceptibilities can be obtained [1,2].

A polarized light-induced anisotropy [3–8] has been observed in polymer films doped with photosensitive molecules. Since the 1980s Todorov and coworkers [15,16] have studied photoinduced anisotropy in polymer films doped with azo dyes for transient polarization holography utilized as a real-time recording. The polarized light-induced anisotropy has also been observed in the mixture of azo dyes and liquid crystals [9–13], which is expected to be utilized as optical switching materials. Orientation of azo dyes induced by irradiating the polarized light is considered to be a driving force for the alignment of the liquid crystals. Recently, as a promising application of photoinduced anisotropy, the photofabrication of surface relief polarization gratings in polymer thin films has been studied by Natansohn and coworkers [17,18] and Tripathy and coworkers [19,20]. The polarization dependent surface relief grating is one of the surface relief gratings fabricated using simple interference of two coherent laser beams. The gratings are observed in side-chain or main-chain polymers containing azobenzene groups. The interval between gratings can be controlled around sub-micron and micron orders. As described above, the photoinduced anisotropy of azo dyes has been attempted to apply to various optical devices. However, the physical mechanisms of the photoinduced anisotropy have not been clarified yet. In order to comprehend the mechanisms, it is essential to examine the dynamics of photosensitive molecules. Therefore, understanding the molecular motion at each process must give promise of the development of these applications.

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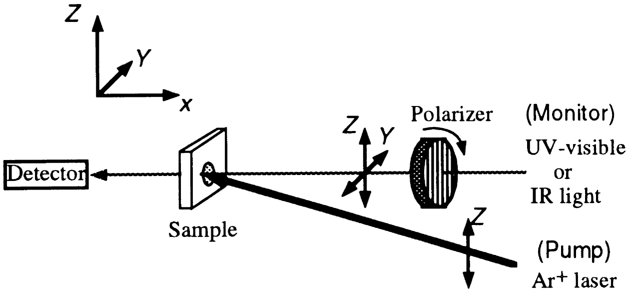

Fig. 1. The optical arrangement for polarized UV–Vis and FTIR measurements. The polarization direction of pump light was defined as the *Z*-direction. The absorbance in the polarized spectroscopy was obtained by rotation of polarizer in the *Z*- and *Y*-directions which are parallel and perpendicular to the polarization direction of pump light, respectively.

We reported how the orientation factors are useful to discuss the dynamics of azo dyes, Disperse Orange 3 (DO3; $NO_2–C_6H_4–N=N–C_6H_4–NH_2$), in poly(methyl methacrylate) (PMMA) in the previous paper [21]. We have also established the method for evaluating the photoinduced anisotropy of push–pull azo dyes in terms of the orientation factors [21,22] obtained from UV–Vis and polarized FTIR spectroscopy. In this paper, the method is applied to studying the polymer matrix dependence of photoinduced anisotropy. As the polymer matrix effect, the free volume and the local polarity surrounding the DO3 molecules are expected. In order to investigate how the matrices influence the dynamics of DO3 molecules, several kinds of poly(alkyl methacrylate)s and polystyrene (PS) were used as polymer matrices. Firstly, we discuss the matrix dependence of the thermal isomerization. DO3 molecules taking stable *trans* forms isomerize to *cis* forms by irradiating the visible light, but the unstable *cis* forms reisomerize thermally to the *trans* forms. The thermal isomerization rate of push–pull azo dyes in the solvents has been known to depend on the isomerization mode, which is controlled by the solvent polarity. Even in the polymer matrices, the similar effect of local matrix polarity should be expected. The matrix polarity effect is considered to originate from the interaction between ester groups of methacrylate polymers and azo dyes. Secondly, the free volume effect on photoinduced anisotropy is investigated by comparing the orientation factors in poly(*n*-alkyl methacrylate)s. Methacrylate polymers with the different length of alkyl side-chain have the different glass transition temperature (T_g) and the different free volume. In such methacrylate polymers, the free volume is known to be larger as alkyl chain is longer [23], so the free volume effect on the photoinduced anisotropy can be understood clearly by using poly(*n*-alkyl methacrylate)s as the matrices. Finally, the polarity effect on photoinduced anisotropy is discussed by comparing the orientation factors of DO3 in polar matrix such as poly(propyl methacrylate), (PPMA, *n*-alkyl type) with those in less polar matrix such as poly(isopropyl methacrylate) (PiPMA, branched-alkyl type) and PS. The free volume of PiPMA and PS is larger than that of *n*-alkyl methacrylate polymers [23–25] and the polarity of PiPMA and PS is lower. The comparison should help us to understand the polarity effect on photoinduced anisotropy of DO3.

2. Experimental

2.1. Materials

A push–pull azo dye, DO3 (Aldrich), was used as a photosensitive molecule. A series of methacrylate polymers, poly(methyl methacrylate) (PMMA, Aldrich, $M_w = 120,000$, $T_g \sim 114°C$), poly(ethyl methacrylate) (PEMA, Aldrich, $M_w = 515,000$, $T_g \sim 63°C$), poly(propyl methacrylate) (PPMA, Scientific Polymer Products, $M_w = 250,000$, $T_g \sim 35°C$), and poly(isopropyl methacrylate) (PiPMA, Aldrich, $M_w = 100,000$, $T_g \sim 85°C$), and polystyrene (PS, Aldrich, $M_w = 239,700$, $T_g \sim 110°C$) were used as matrices. The cast films of these polymers doped with DO3 were prepared from chloroform solution. The thickness of the films was less than 20 μm. The dye concentration was about 1 wt%. The films were heated for several hours for annealing at the temperature of 5°C below T_g for each polymer. The residual chloroform in the films was examined by FTIR spectroscopy, using the absorption band at 665 cm^{-1} assigned to C–Cl stretching vibrational mode. From this band, the content of the residual chloroform was so little that the residual chloroform is not considered to affect the photoinduced anisotropy.

2.2. Measurements

Linearly polarized continuous-wave light (488 nm) from the Ar ion laser was used to induce the photoisomerization from *trans* to *cis* isomers and the optical anisotropy observed in both UV–Vis and infrared absorptions. The optical arrangement is shown in Fig. 1. The optical power of Ar ion laser was 4 mW/cm^2 at the sample position. Polarized spectra were observed in the parallel (*Z*) and perpendicular (*Y*) directions to the polarization direction of an Ar ion laser.

The variations of polarized UV–Vis absorbances, $E_Z(\lambda)$ and $E_Y(\lambda)$, were measured at λ_{max} in the DO3/polymer films by Shimadzu UV-2500PC spectrometer. They were observed at room temperature (23°C) before irradiation, during irradiation, and after irradiation with polarized light. Before irradiation, all the DO3 molecules are considered to take *trans* forms. In push–pull azo dyes, it has been known that the UV–Vis absorption peaks at λ_{max} correspond to the $\pi\pi^*$ transition of the *trans* isomer. *Cis* molecules formed by the irradiation have little absorption around λ_{max} of the *trans* isomer. Therefore, the variation of mole fraction of *trans* forms by the isomerization, α, can be obtained by monitoring the absorbance at λ_{max} and normalizing it to the initial absorbance before irradiation. In the

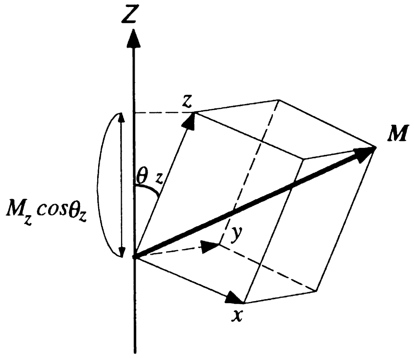

Fig. 2. *Z*-axis is an axis of laboratory-fixed coordinates (*X*,*Y*,*Z*). The electric transition moment, **M**, is represented in the molecular axis (*x*,*y*,*z*).

case of the isomerization by linearly polarized light, the optical anisotropy is induced in a film plane, so the α value can be obtained with $\{E_Z(\lambda_{\max}) + 2E_Y(\lambda_{\max})\}/3$.

The FTIR spectra of the DO3/polymer films were measured at room temperature (23°C) using a Bio-Rad FTS-175C IR spectrometer equipped with MCT detector. The IR spectra of polymers without DO3 were also measured as references in order to observe quantitatively (by spectral subtraction) the infrared absorption bands of DO3. Wavenumber resolution was $4\ \mathrm{cm}^{-1}$. Polarized FTIR spectra were observed using the polarizer (KRS-5). All interferograms were collected for every 10 s before irradiation, during irradiation, and after irradiation with linearly polarized light.

3. Analysis

In our previous paper [21], it was described how the molecular orientation induced by polarized light can be discussed by the orientation factors. We have established the method for determining the orientation factors. Since details were described in the previous paper [21], the process of determination is briefly explained here. The molecular orientation in the laboratory-fixed coordinates ($F = X, Y, Z$) can be represented by the matrix of orientation factors, **K**, which indicates the statistically averaged alignment of molecules within the molecular-fixed coordinates ($f = x, y, z$) [22]. The absorption probability of a band (a) along the *Z*-axis is represented by the dot product of the *Z*-polarized light, $\mathbf{e}_Z$ (unit vector), and an electric dipole transition moment, $\mathbf{M}(a)$, as described 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 $\langle\ \rangle$ means the statistical average and the terms of $M_f^2(a)\langle\cos^2\theta_f\rangle$ correspond to the square of the projection of the *f*-components of $\mathbf{M}(a)$ onto the *Z*-axis (Fig. 2), and 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. Here, the orientation factor, K_{Zf} is defined as

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

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

$$E_F(a) = \sum_f K_{Ff}A_f(a) = K_{Fx}A_x(a) + K_{Fy}A_y(a) + K_{Fz}A_z(a). \quad (3)$$

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

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

Azo compounds can take two isomers: *trans* and *cis*. The *F*-component of observed absorbance of a vibrational band (a), $E_F(a)$, can be expressed as the sum of the absorbance of the *trans* and *cis* isomers using the mole fraction of the *trans* isomer, α,

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

The orientation factors can be estimated for each isomer by solving the above simultaneous equations for several different bands.

4. Results and discussion

4.1. Polarity effect on isomerization

The dynamics of DO3 in polymer matrices should include two processes, the isomerization and the molecular rotation. The local polarity surrounding DO3 is considered as one of the polymer matrix effects on the isomerization of DO3 molecules. The local polarity depends on the polymer structure, i.e. if the polymer has polar substituted groups or how large the steric hindrance around the polar substituent is. The ester group in methacrylate polymers should play a role as the polar group for DO3 molecules. Therefore, the interaction between the ester groups and amino groups of DO3 is expected in the methacrylate polymers. However, the interaction in branched-alkyl methacrylate polymers is predicted to be not so strong as that in *n*-alkyl methacrylates because the bulky branched-alkyl chains may block the approach of DO3 molecules to ester groups. Moreover, the local polarity in PS without ester group is considered

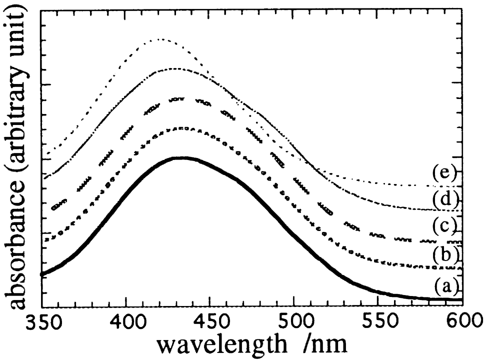

Fig. 3. The UV–Vis spectra of DO3 in (a) PMMA (—), (b) PEMA (···), (c) PPMA (–––), (d) PiPMA (···–) and (e) PS (- - -).

to be smaller than that in methacrylate polymers. The local polarity effect on thermal isomerization can be shown by UV–Vis and FTIR spectra as described later.

The direction of the $\pi\pi^*$ transition moment of the *trans* isomer aligns with the molecular long axis [26–28]. As shown in Fig. 3, each λ_{max} is observed around 420–430 nm for the DO3 in polymers used in this study. For DO3 in PiPMA and PS, the blue-shifts of λ_{max} were observed in UV–Vis spectra. It has been known that the blue-shift of λ_{max} occurs [14,29] in less polar solvents because of the weak interaction between the DO3 molecules and the solvents. The blue-shift observed in polymer matrices may also suggest the lower local polarity surrounding DO3 [14].

The mole fractions of *trans* isomers, α values, began to decrease by irradiation. They kept constant in the photostationary state during irradiation. The α values in the photostationary state were 0.82 (PMMA), 0.80 (PEMA), 0.76 (PPMA), 0.79 (PiPMA) and 0.81 (PS). On turning the light off, the α values increased and finally recovered to 1. The variations of absorbance in PPMA, PiPMA and PS after irradiation are shown in Fig. 4. The reisomerizations to the *trans* form in PiPMA and PS were slower than that in PPMA. The rates in *n*-alkyl methacrylates, i.e. PMMA, PEMA and PPMA, were almost the same (they were not shown in this paper). In the case of DO3 in PS, it takes about 1 h for the 90% recovery. For the push–pull azo dyes in any polar solvents, *cis* molecules generally isomerize not only via slow inversion processes, but also by rapid rotation processes, because the polar solvents promote the charge separation [30–32] in the push–pull azo dyes. The thermal isomerization rate in polymer matrices is considered to reflect the isomerization mechanisms depending on the local polarity in the matrices similar to that in solvents. The result of slower reisomerization in PiPMA and PS also supports the less polar environment surrounding DO3 molecules than that in *n*-alkyl methacrylates as well as the result of the blue-shift of λ_{max}.

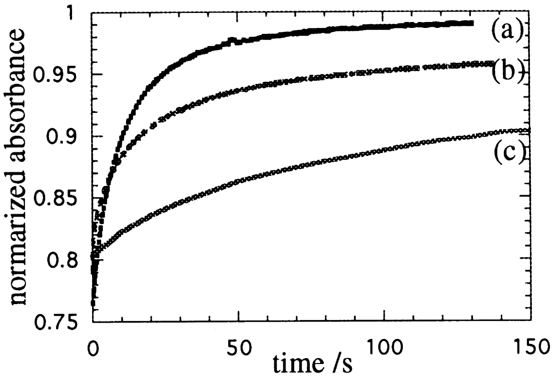

Fig. 4. After irradiation for 120 s of laser light, the absorbance variation of DO3 was measured at λ_{max} in each UV–Vis spectrum (as shown in Fig. 3). The absorbance was normalized to each initial value before irradiation. The polymer matrices are (a) PPMA, (b) PiPMA and (c) PS.

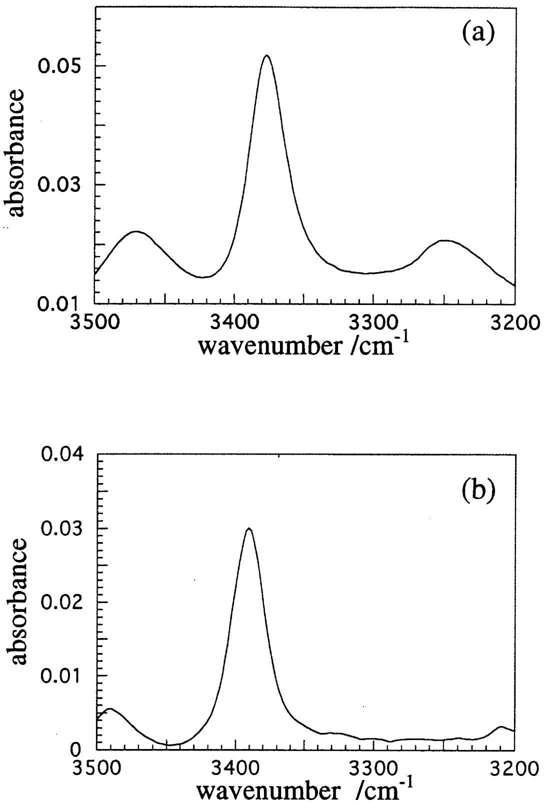

Fig. 5. The FTIR spectra of (a) DO3/PMMA and (b) DO3/PS. Some NH_2 vibrational bands are observed in this frequency range.

The FTIR spectra also support the interaction between ester groups in methacrylate polymers and amino groups in DO3. The FTIR spectra of DO3 in PMMA and PS are shown in Fig. 5a and b, respectively, in which the three absorption peaks related with the amino group are observed in the range 3200–3500 cm^{-1}. Two peaks at higher frequencies are assigned to antisymmetric and symmetric vibrational bands of the free amino group and the other is assigned to the vibrational band of the amino group interacting with matrix. The former two bands in PMMA are observed at lower frequencies than those in less polar polymers such as PS (Fig. 5a and b). The latter band was found in methacrylate polymers, but it was not found in PS and in less polar solvents such as benzene. These results

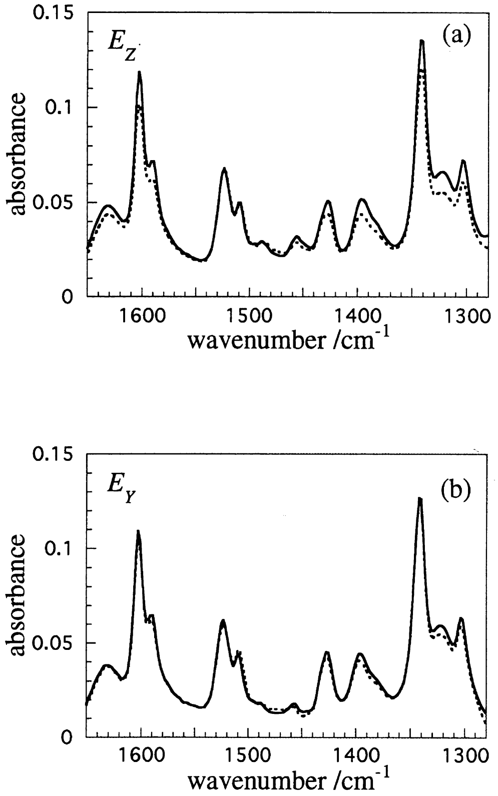

Fig. 6. The polarized FTIR spectra of DO3/PMMA before irradiation (—) and during irradiation (- - -) by laser. They were measured in the (a) Z-polarization direction and (b) Y-polarization direction.

support the presence of dipole–dipole interaction between the amino group and the ester group in methacrylate polymers [29,33]. However, the absorbance of these bands is so small that it is difficult to estimate the difference of absorbance quantitatively. Moreover, it is difficult to observe clear difference in the infrared spectra between *n*-alkyl methacrylates and branched-alkyl methacrylate.

4.2. Free volume effect on polarized light-induced anisotropy

The free volume in polymers is considered as one of the polymer matrix effects on polarized light-induced anisotropy. This effect is investigated by comparing the orientation factors of DO3 molecules in *n*-alkyl methacrylates. Orientation factors were determined by the experimental results of polarized FTIR spectra and the definition of the molecular-fixed coordinates. Fig. 6 shows the polarized infrared spectra of DO3 in PMMA before irradiation and during irradiation in the wavenumber range 1650–1280 cm^{-1}. Three vibrational bands assigned [34,35] to symmetric (NO_2^s, 1341 cm^{-1}) and antisymmetric (NO_2^{as}, 1523 cm^{-1}) stretching modes of NO_2, and the C–N stretching mode of C–NH_2 (C–N, 1303 cm^{-1}) are found to be useful for determining the orientation factors. The variation of absorbances of the three bands in each polymer (it was not shown in this paper) was measured when the polarized light was turned on and off. The variation of the absorbances in PMMA was the largest in *n*-alkyl methacrylate polymers used in the present study.

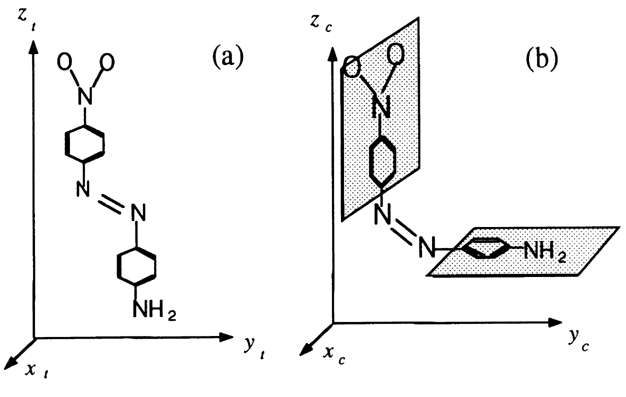

Fig. 7. The molecular axes for (a) *trans* and (b) *cis* isomers.

In order to determine the orientation factors, we defined the molecular-fixed coordinates for the *trans* and *cis* isomers, respectively [21], as shown in Fig. 7a 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 $K_{Zx}^{(t)} = K_{Zy}^{(t)}$ 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 Fig. 7b. 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 y_c-axis. It was shown in the previous paper [21] that this assumption can be justified because the determined orientation factors are almost the same in both cases as the plane formed by p-NO_2–C_6H_4 is put on z_c–y_c plane and on z_c–x_c plane.

Here, the free volume effects on polarized light-induced anisotropy of DO3 were investigated by determining orientation factors in PMMA, PEMA and PPMA, where the glass transition temperature (T_g) can be a guide to predict the relative size of the free volumes. Li et al. [23] have studied the mean free volume and the fraction of free volume in methacrylate polymers by the positron annihilation lifetime spectroscopy (PALS) and reported that the mean free volume and the fraction of free volume increase as the alkyl chain is longer (the T_g is lower).[1] The determined values of $K_{Zz}^{(t)}$ and $K_{Zf}^{(c)}$ $(f: x, y, z)$ are shown in Fig. 8a–f. In the *trans* isomers, the $K_{Zz}^{(t)}$ values in three kinds of polymers are smaller than $\frac{1}{3}$ during irradiation, and they recover to $\frac{1}{3}$

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[1] The treatment of the free volume in a polymer should be taken care of, because the free volume has the wide distribution in the size and fraction. The scale of the free volume evaluated by PALS is not the same as that required for the isomerization of the molecules like azo-dyes. The radius of the free volume in methacrylate polymers obtained by PALS is about 0.3 nm, whereas the isomerization of an azo-dye needs the volume with the radius of around 0.5 nm. However, the data obtained by PALS can be used as the useful guide of the scale when the free volume effect for the isomerization and the rotation of the azo molecules is considered.

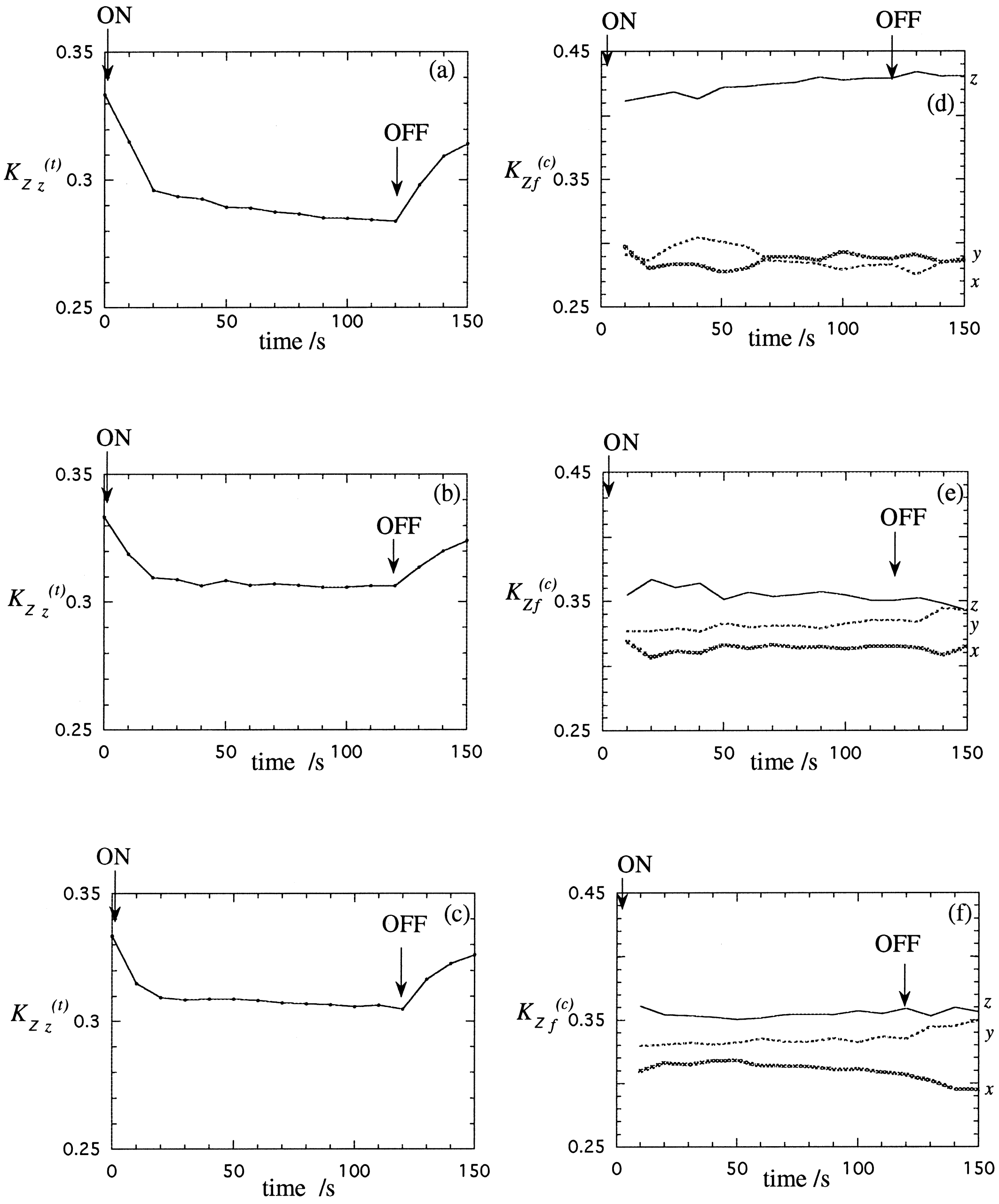

Fig. 8. The orientation factors, $K_{Zz}^{(t)}$, for the DO3 *trans* form in (a) PMMA, (b) PEMA and (c) PPMA, and $K_{Zf}^{(c)}(f,x,y,z)$ for the *cis* form in (d) PMMA, (e) PEMA and (f) PPMA. The laser was turned on at 0 s, and turned off at 120 s.

on turning the light off. 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. Among the polymers treated in this study, the $K_{Zz}^{(t)}$ value in PMMA was the smallest, i.e. the anisotropy was the largest during irradiation (Fig. 8a). The rotational motion of *trans* isomers is considered to be restricted into a small free volume. During irradiation, the larger $K_{Zz}^{(t)}$ values in PEMA and PPMA compared with that in PMMA indicate that the *trans* isomers rotate easily in polymers with lower T_g. After irradiation, the recovery of $K_{Zz}^{(t)}$ in PPMA is faster than that in other polymers (Fig. 8c).

In the *cis* isomer, $K_{Zf}^{(c)}$ does not have a definite value at time 0, because there is no *cis* molecule before irradiation. During irradiation, the $K_{Zz}^{(c)}$ values are found to be larger than $K_{Zx}^{(c)}$ and $K_{Zy}^{(c)}$ values in three methacrylate polymers (Fig. 8d–f). 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. Therefore, we can consider that a lot of *cis* isomers are formed by the easy motion of the p-NH_2–C_6H_4 group in isomerization process, probably because the relative volume of p-NH_2–C_6H_4 is smaller than that of p-NO_2–C_6H_4. However, in methacrylate polymers, some NH_2 groups of DO3 interact with ester groups of polymers, so the motion

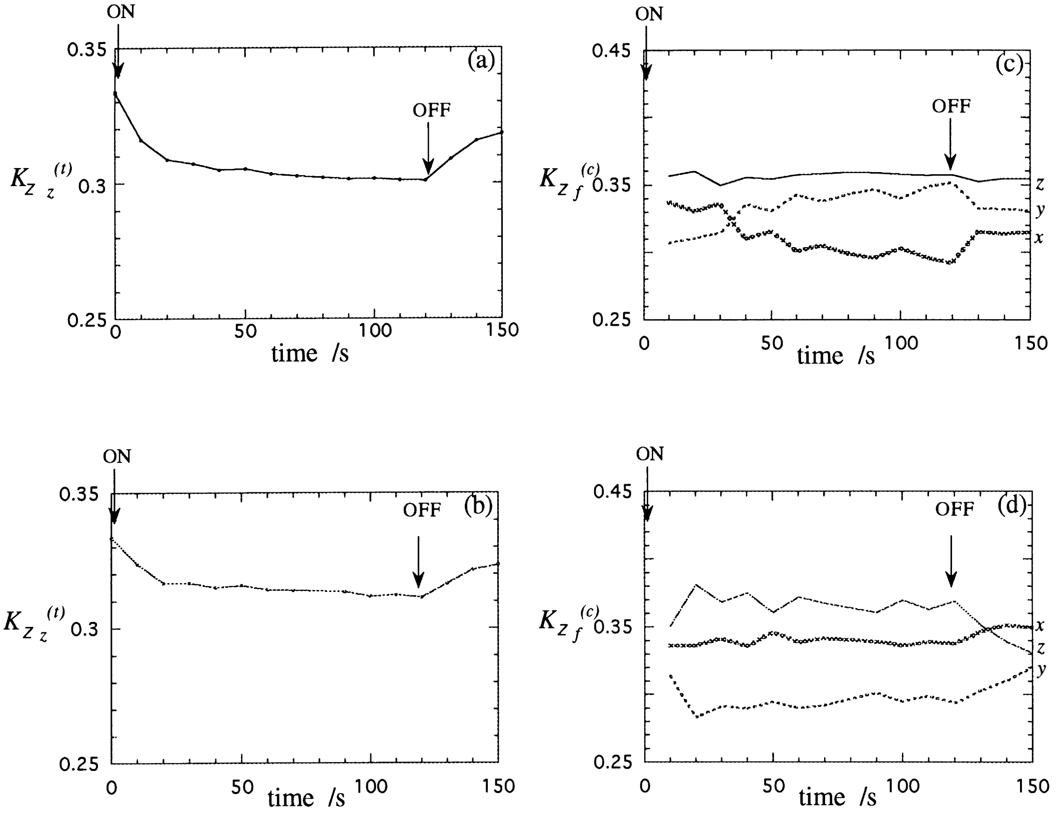

Fig. 9. The orientation factors, $K_{Zz}^{(t)}$, for the DO3 *trans* form in (a) PiPMA and (b) PS, and $K_{Zf}^{(c)}$ (f, x, y, z) for the *cis* form in (c) PiPMA and (d) PS. The laser was turned on at 0 s, and turned off at 120 s.

of the *p*-NH_2–C_6H_4 groups should be restricted. In spite of the restriction, the experimental result suggests the easy motion of the *p*-NH_2–C_6H_4 group. If the DO3 had little interaction with polymer matrix, the difference between $K_{Zy}^{(c)}$ and $K_{Zz}^{(c)}$ values could be much larger. The matrix effect of this kind of interaction on the photoinduced anisotropy will be discussed in Section 4.3. The $K_{Zz}^{(c)}$ value in PMMA during irradiation is the largest among the values of three polymer matrices. The $K_{Zf}^{(c)}$ values were found to be almost the same between PEMA and PPMA because of the similar restriction of rotational mobility depending on the free volume. Even after turning the light off, the $K_{Zf}^{(c)}$ values do not change so largely. The *cis* molecules are not excited directly by the *Z*-linearly polarized light but formed via excited *trans* isomers. Therefore, the orientation of *cis* molecules does not reflect the light off so immediately. From the determination of orientation factors, we found that the free volume is one of the most important factors, which govern the photoinduced anisotropy of DO3 molecules.

4.3. Local polarity effect on polarized light-induced anisotropy

The free volume was found to provide a dominant effect for polarized light-induced anisotropy as described earlier. However, the local polarity can be considered as another matrix effect on photoinduced anisotropy especially for the polymers with the large free volume.

First, let us compare the orientation factors in PiPMA with those in PPMA. The temporal variations of $K_{Zz}^{(t)}$ and $K_{Zf}^{(c)}$ in PiPMA (Fig. 9a and c) are very similar to those in PPMA (Fig. 8c and f). The similarity in PiPMA and PPMA may be due to almost the same fraction of the free volume [23]. In spite of the difference in the polarity between PiPMA and PPMA as shown in Fig. 4, the local polarity dependence of the orientation by polarized light was not clearly observed from the comparison between PiPMA and PPMA.

In order to confirm the local polarity effect on the photoinduced anisotropy more clearly, the orientation factors in PS as a less polar matrix are compared with those in PPMA. Both polymers have larger free volumes than PMMA. In the *trans* isomers, $K_{Zz}^{(t)}$ values in PS also decrease during irradiation and the value in the photostationary state is the largest, i.e. the photoinduced anisotropy is the smallest, of all polymers used in this study (Fig. 9b). The larger free volume in PS [23–25] may make the molecular rotation of *trans* isomers easier. According to these results, the free volume effect is dominant for orientation of the *trans* isomers. On the other hand, in the *cis* isomers, we observed the difference of $K_{Zy}^{(c)}$ values between PS and PPMA (Figs. 9d and 8f), which can be explained only by taking onto account the local polarity effect. The small $K_{Zy}^{(c)}$ value indicates that there are fewer *cis* molecules with a small angle between the Z and the y_c-axes (see Fig. 7b). The smaller $K_{Zy}^{(c)}$ in PS means that the ratio of *cis* molecules formed by the motion of the p-NH_2–C_6H_4 group side is larger than the ratio in PPMA. The restriction of the p-NH_2–C_6H_4 motion in methacrylate polymers is ascribed to the presence of interaction between the NH_2 groups of DO3 and the matrix. Under the less polar environments with the large free volume such as PS, it is much easier for the p-NH_2–C_6H_4 groups to move on the isomerization processes than under the polar matrix with the large free volume such as PPMA. Though the free volume effect is primary for photoinduced anisotropy, the local polarity effect is also found to be important in the matrix with the large free volume.

5. Conclusion

The dynamic behavior of DO3 molecules isomerized by the linearly polarized light was observed by the polarized UV–Vis and FTIR spectroscopies. Several kinds of methacrylate polymers and PS were used as matrices in order to investigate the polymer matrix dependence of the polarized light-induced anisotropy. It was found that more DO3 molecules in all the matrices used in this study can isomerize by the motion of the p-NH_2–C_6H_4 group than by the motion of the p-NO_2–C_6H_4 group due probably to its relatively small volume. In PMMA, the anisotropies for both *trans* and *cis* molecules were found to be the largest in all the polymers used in present study. The small free volume in PMMA was considered to restrict the rotational motion of both *trans* and *cis* molecules. In PEMA and PPMA with lower T_g and larger free volumes, the anisotropies for both *trans* and *cis* molecules were found to be small because of easy rotation of DO3. The free volume effect was found to be the primary dominant factor for the polarized light-induced anisotropy. The UV–Vis and FTIR spectra indicate that the local polarity also contributes to the dynamics of DO3 molecules. The thermal isomerization rate depends on the isomerization mode influenced by the local polarity surrounding DO3 molecules. The local polarity effect on photoinduced anisotropy was also observed in the polymers with the large free volume, i.e. less polar matrix such as PS and polar matrix such as PPMA. The large difference of $K_{Zy}^{(c)}$ for *cis* molecules was observed between PS and PPMA. It is due probably to the fact that the mobility of the p-NH_2–phenyl group depends on the interaction between the NH_2 group and the polymers. The local polarity effect was also found to be an essential factor governing the photoinduced anisotropy of DO3 in the polymer matrix with the large free volume.

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