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Photoinduced reorientation of azo-dyes covalently linked to a styrene copolymer in bulk state

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Abstract

Polarized light-induced orientation in azo-dyes covalently bonded to styrene copolymer (Azo–PSCMS) was investigated by using polarized UV–VIS spectroscopy. It was found that thermal isomerization and photoisomerization was slower and a photoinduced dichroism was larger than azo-dyes doped in polystyrene. The covalent linkage to a polymer chain may suppress both the mobility required for the isomerization and the rotational diffusion of the azo-moiety. The *trans* → *cis* photoisomerization was induced by ultraviolet (UV) light, whereas light with visible wavelength was used to drive the *trans* ↔ *cis* photoisomerization. A high repetition of *"trans–cis–trans"* isomerization cycles achieved under visible light plays an important role for the photoinduced reorientation. Therefore, the high repetition of the *"trans–cis–trans"* cycle and suppression of the rotational diffusion by the covalent linkage to a polymer are the two important factors for the photoinduced reorientation of azo-dyes in bulk polymer matrix.

Keywords: Photoinduced reorientation; Dichroism; Covalent linkage; Azo-dyes; Polystyrene

1. Introduction

Polarized light-induced anisotropy of polymers doped with azo-dyes has been studied by Todorov and coworkers [1,2] for transient polarization holography since 1980s. More recently, this phenomenon was also observed with polymers containing photochromic compounds other than azo-dyes such as diarylethene [3] and anthracene derivatives [4,5]. The change in molecular orientation associated with these chemical reactions plays a key role in the generation of optical anisotropy. Due to the selectivity and particularly the reversibility of these chemical reactions, the potential of applying these photoinduced effects has been demonstrated for fabrication of optical switches and photo-alignment of liquid crystals [6–12]. In order to efficiently control the polarized light-induced anisotropy, it is essential to understand the dynamics of photoisomerization as well as thermal isomerization of azo-dyes in the bulk state of polymers.

Azo-dyes exist in two spatial forms: *trans* and *cis* isomers. The former is energetically more stable than the latter and the transformation between them can be induced by light irradiation. The conversion *cis* → *trans* is also possible under heating due to the instability of the *cis* isomers. The isomerization rate and the photoequilibrium strongly depend on the chemical structure of the azo-dye and the polymer matrix. Depending on the ability of the electron donor (D) and acceptor (A) substituted on the two phenyl groups, Rau [13] classified azo-dyes into three groups: (i) azobenzene type, (ii) aminoazobenzene type, and (iii) pseudo stilbene type. In the case of (i), i.e. azobenzene type without D or A substituents, the absorption peak corresponding to π–π^* transition appears around 350 nm and their thermal isomerization is very slow (more than 1 day at ambient temperature). For the type (ii) with the D group on the *para* position of the phenyl ring, the absorption peak assigned as π–π^* transition appears at wavelengths (ca. 400 nm) longer than

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that of type (i). Their thermal isomerization is faster (several hours). Finally, the type (iii) with D and A substituents on the *para* position of each phenyl group (the so-called push–pull type) exhibits a maximum absorption attributed to π–π^* transition in the visible region (longer than 400 nm). Their thermal isomerization is much faster (several minutes or seconds) than type (ii) and strongly depends on the polarity of the environments.

Recently, we have reported the influence of the polymer matrix [14] and the azo-structure [15] of a push–pull type on the photoinduced anisotropy. The molecular motion of these particular dyes was evaluated by using the time-dependent orientation factors obtained from polarized UV–VIS and FTIR spectroscopy [16,17]. For a large number of polymer matrices without specific interactions with the dyes [14,15], it was found that the *trans* → *cis* photoisomerization of azo-dyes which have asymmetric structures with respect to the azo (–N=N–) bond, is driven by the rotation of the phenyl moieties with smaller sizes. Furthermore, the photoinduced anisotropy ratio in polystyrene was found to be smaller than that in methacrylate polymers. These results are in good agreement with the data obtained by positron annihilation lifetime spectroscopy [18,19], indicating that photoinduced anisotropy is controlled by free volumes of polymer matrices [20]. Photochemistry of azo-dyes in polymer solids had been studied with great detail taking into account the effects of free volume and physical aging [21–23,35]. In particular, Sung and coworkers [21,22] has studied the photoisomerization of azobenzene chemically labeled at different locations on a polystyrene chain and compared with the case of free probe. Our main concern in this study is the physical mechanism of photoinduced reorientation of azo-dyes undergoing photoisomerization induced by polarized light. Reorientation process means a phenomenon where the polarized-light irradiation changes the direction of transition moment of the *trans* molecule, and aligns them perpendicularly to the polarization direction of the exciting light. Since it is known that the reorientational process of azo-dyes are affected by both their rotational diffusion and the *trans* → *cis* → *trans* isomerization cycles [24–28], it is important to elucidate the effect of linkage of the dyes to polymer chains on the photoinduced anisotropy. In this paper, the photoinduced reorientation process of the azo-dye of type (i) chemically bonded to a styrene copolymer chain was examined upon irradiation with UV or visible light. The results are discussed by comparing with those obtained with the case using free-dyes.

2. Experimental

2.1. Synthesis and characterization

The copolymer (PSCMS) of styrene (Wako, Japan) and (chloromethyl) styrene (Tokyo Kasei) was synthesized by free radical polymerization in distilled benzene at 60°C over 60 h in vacuo with α,α'-azobis(isobutyronitrile) (Aldrich, crystallized twice in ethanol) used as initiator. Prior to the labeling reaction, the copolymer was reprecipitated twice with toluene as good solvent and methanol as non-solvent. As far as observed by small-angle X-ray scattering in the bulk state, PSCMS is a random copolymer without microphase separation. The chlorine content is ca. 12 mol% as identified by elemental analysis.

The copolymer labeled with azobenzene derivatives was synthesized according to the procedure described previously [29]. Namely, the copolymer PSCMS containing chloromethyl groups was reacted with the potassium salt of 4-octyl-4′-(3-carboxytrimethyleneoxy)azobenzene (O-Azo; Dojindo Laboratories, Japan) in anhydrous dimethylformamide (Aldrich) at 65°C over 8 h. Subsequently, the reacting solution was poured into iced water and the resulting polymer (Fig. 1) was reprecipitated twice using tetrahydrofuran as good solvent and methanol as non-solvent. The weight-average molecular weight ($M_w = 3.2 \times 10^5$) was determined by intrinsic viscosity with toluene as solvent at 30°C [30]. Its polydispersity M_w/M_n is 2.0 as measured by gel permeation chromatography. The label content of the dye was approximately 7.7 mol% with respect to the repeat units of copolymer. The glass transition temperature of the Azo–PSCMS is 86°C as determined by DSC. For comparison, the polystyrene films doped with O-Azo were also prepared at a concentration of ca. 2 wt.%. The average molecular weight, M_w, of the polystyrene matrix (Aldrich) is 239,700 and its T_g is 110°C. They were prepared from chloroform solutions on glass substrates by spin-coating method. The thickness of the films was about 200–100 nm.

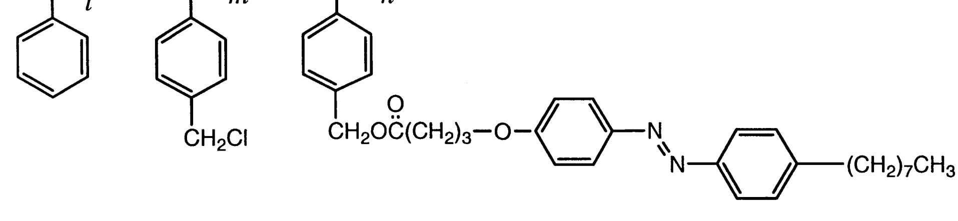

Fig. 1. Chemical structure of the Azo–PSCMS copolymer (l:m:n = 88:4.3:7.7).

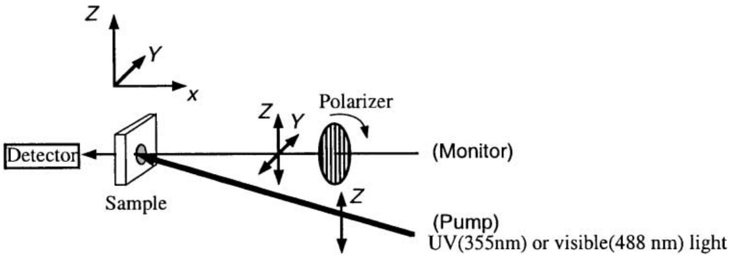

Fig. 2. Optical arrangement for measuring UV–VIS spectra in situ under irradiation.

The films were annealed at 80°C for several hours, prior to measurements.

2.2. Measurements

Linearly Z-polarized UV light with the wavelength 355 nm was generated by passing the light from a Xe lamp (Ushio SP-V) through a polarizer (Glan Laser Prisms, Sigma Koki) and appropriate optical filters. On the other hand, linearly Z-polarized visible light at 488 nm was obtained from the 488 nm line of an Ar^+ laser (Spectra-Physics Model 161C). Polarized UV–VIS spectra of the dye were taken along the directions parallel (Z) and perpendicular (Y) to the polarization direction of the excitation light by using a spectrometer (Shimadzu UV-2500 PC). The optical arrangement was shown in Fig. 2. The optical power of the exciting light at 488 and 355 nm was measured at the sample position before irradiation.

The irradiation time dependence of the absorbances, $E_Z(\lambda, t)$ and $E_Y(\lambda, t)$, at $\lambda_{\max}$ of the azo-dyes along the Z- and Y-directions, was measured before, during, and after irradiation at room temperature (23°C). Before irradiation, all the azo-molecules are considered to exist in the *trans* forms. This absorption peak corresponds to the π–π^* transition of the *trans* isomer. The direction of the π–π^* transition moment of the *trans* isomer is almost parallel to the long axis of the molecule [31–33]. With the optical arrangement shown in Fig. 2, the absorbance, $E(\lambda)$, can be obtained from $\{E_Z(\lambda) + 2E_Y(\lambda)\}/3$.

3. Results and discussions

3.1. Isomerization process

3.1.1. Thermal isomerization

As indicated by the solid lines in Fig. 3, the maximum absorption of the *trans* isomer in Azo–PSCMS is located at 352 nm that is the same as observed with the case of O-Azo doped in polystyrene. Upon the irradiation with the UV light (0.68 mW/cm^2) over 1 h, the mole fraction of the *cis* isomer in Azo–PSCMS is ca. 0.97 as illustrated by the broken line in Fig. 3. The mole fraction, α, of the *trans* isomer in the isomerization process was obtained after subtracting the contribution of the *cis* isomer from the normalized absorbance at $\lambda_{\max}$, $E(\lambda_{\max})$. As soon as the UV light is turned off, the *cis* form is thermally converted to *trans* form and α increases. The variations of α with time are shown in Fig. 4 for the Azo–PSCMS and the doped polystyrene, respectively. For

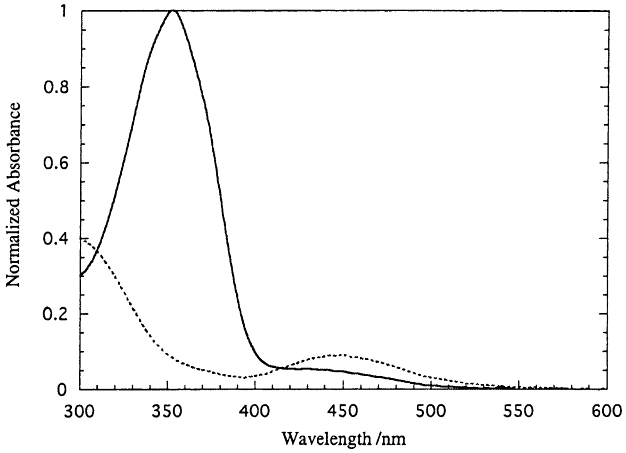

Fig. 3. UV–VIS spectra of Azo–PSCMS obtained before irradiation (solid line) and after irradiation (broken line) with UV light over 1 h.

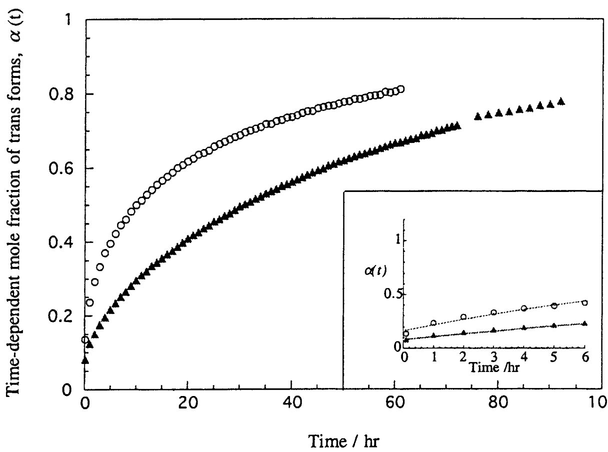

Fig. 4. Time-evolution of the mole fraction of the *trans* isomer observed for the *cis* → *trans* thermal isomerization process after UV irradiation (the optical power 0.68 mW/cm^2, irradiation time 1 h): Azo–PSCMS (▲), and O-Azo doped in polystyrene (○). Inset shows the result of fitting the curves to the first-order kinetics.

most cases, the kinetics of isomerization in the bulk state of polymer does not proceed homogeneously [21–23]. As a result, the reaction does not follow the first-order kinetics. One way of analysis of the reaction is fitting the early stage of the reaction to the first-order kinetics and using the rate constant as a measure for the reaction rate [34–36]. Thus, the early stage of the time-dependent α values corresponding to 6 h after turning the UV light off was fitted to the following Eq. (1)

$$\frac{\mathrm{d}[cis]_t}{\mathrm{d}t} = -k_{(c-t_{\mathrm{Th}})}[cis]_t,$$
$$[trans]_t = 1 - [cis]_0 \exp(-k_{(c-t_{\mathrm{Th}})}t) \qquad (1)$$

where t is time, and $[cis]_t$ and $[trans]_t$ are, respectively the concentration of *cis* and *trans* isomers. $k_{(c-t_{\mathrm{Th}})}$ is the rate constant of *cis* → *trans* thermal isomerization. According to the fitting as shown by inset in Fig. 4, $k_{(c-t_{\mathrm{Th}})}$ is found to be 8×10^{-6} and $2 \times 10^{-5}\,\mathrm{s}^{-1}$ for the Azo–PSCMS and the doped polystyrene, respectively. Namely, the thermal isomerization rate for the Azo–PSCMS is smaller than that for the O-Azo doped in polystyrene. The chemical bonding of O-Azo to the polymer chain should be responsible for the restriction of *cis* → *trans* isomerization.

Ar^+ laser irradiation induces *trans* → *cis* and also *cis* → *trans* photoisomerization via n–π^* transition, because the absorption peak of the *trans* isomer in the visible range overlaps with the absorption peak for the *cis* isomer. Upon irradiation over 20 min with an Ar^+ laser (11 mW/cm^2 at 488 nm), the α value reaches a constant. Fig. 5 shows the variation of α after turning the Ar^+ laser light off. By fitting the early stage of α to the first-order kinetics as shown in the inset of Fig. 5, it was found that the rate constants ($k_{(c-t_{\mathrm{Th}})}$) for the Azo–PSCMS and the doped polystyrene are 1×10^{-5} and $2 \times 10^{-5}\,\mathrm{s}^{-1}$, respectively. These kinetic data are almost the same as those obtained after irradiation with the UV light. These results indicate that the *cis* → *trans* thermal isomerization is independent of the generation mechanism of the *cis* isomer.

3.1.2. Photoisomerization

Photoisomerization process induced by irradiation with UV light (0.68 mW/cm^2) can be also described by the time-dependent mole fraction of *trans* isomer, $\alpha(t)$. Fig. 6a shows the variation with time of $\alpha(t)$ obtained with Azo–PSCMS. The experimental data corresponding to the O-Azo doped in polystyrene are indicated in Fig. 6b. It was found that the variation of $\alpha(t)$ of the Azo–PSCMS is slower than that of the O-Azo doped in polystyrene by comparison between Fig. 6a and b. Moreover, the α value of the Azo–PSCMS (0.03) is smaller than that of the doped polystyrene (0.12) at the photostationary state for 1 h of irradiation. The smaller $\alpha(t)$ value observed for the

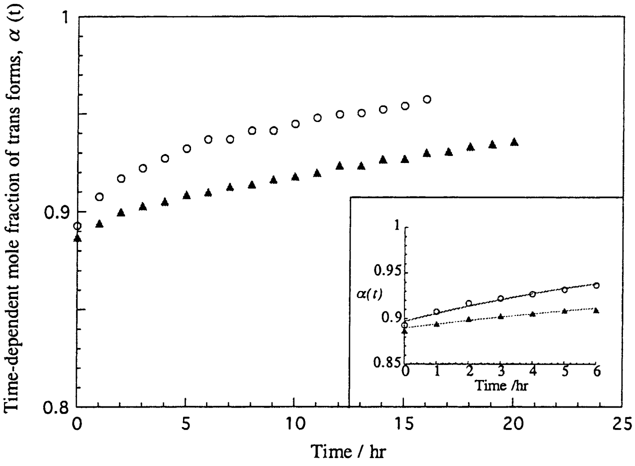

Fig. 5. Time-evolution of the mole fraction for the *trans* isomer observed for the *cis* → *trans* thermal isomerization process after irradiation with visible light (the optical power 11 mW/cm^2, irradiation time 20 min): Azo–PSCMS (▲), and O-Azo doped in polystyrene (○). Inset shows the result of fitting the curves to the first-order kinetics.

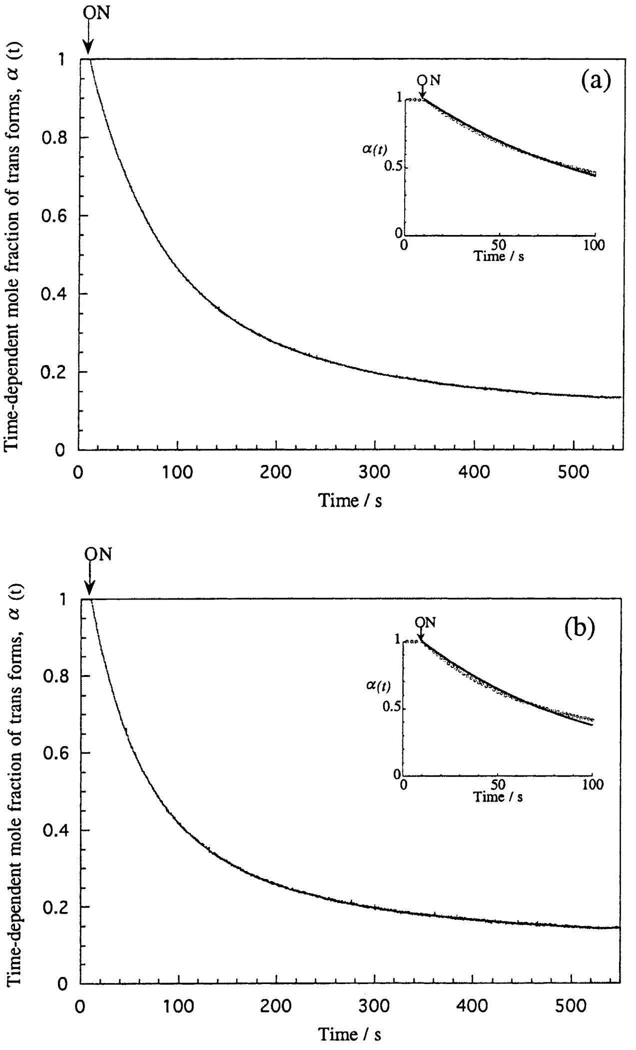

Fig. 6. Time-evolution of the mole fraction for the *trans* isomer observed for the photoisomerization process induced by UV light irradiation (0.68 mW/cm^2): (a) Azo–PSCMS, and (b) O-Azo doped in polystyrene. Inset shows the result of fitting the curves to the first-order kinetics.

Azo–PSCMS is considered to be due to the slower thermal isomerization ($c - t_{\mathrm{Th}}$). It should be noted that under UV irradiation, there exist three isomerization processes, i.e. (1) *trans* → *cis* photoisomerization ($t - c_{\mathrm{UV}}$), (2) *cis* → *trans* photoisomerization ($c - t_{\mathrm{UV}}$), and (3) *cis* → *trans* thermal isomerization ($c - t_{\mathrm{Th}}$). The possibility of $c - t_{\mathrm{UV}}$ is very low compared to the $t - c_{\mathrm{UV}}$ process and therefore can be neglected, because the mole extinction coefficient of the *cis* form at 355 nm is smaller than 0.04% of the *trans* isomer [13,37]. If the variation of $\alpha(t)$ is fitted at an early stage (irradiation over 100 s) to the first-order kinetics as described by Eq. (2),

$$\frac{\mathrm{d}[cis]_t}{\mathrm{d}t} = k_{(t-c_{\mathrm{UV}})}[trans]_t - k_{(c-t_{\mathrm{Th}})}[cis]_t,$$

$$[trans]_t = \frac{k_{(t-c_{\mathrm{UV}})}}{k_{(t-c_{\mathrm{UV}})} + k_{(c-t_{\mathrm{Th}})}} \times \exp\{-(k_{(c-t_{\mathrm{Th}})} + k_{(t-c_{\mathrm{UV}})})t\} + \frac{k_{(c-t_{\mathrm{Th}})}}{k_{(t-c_{\mathrm{UV}})} + k_{(c-t_{\mathrm{Th}})}}, \qquad (2)$$

it was found that the rate constant, $k_{(\mathrm{t}-c_{\mathrm{UV}})}$, is $9 \times 10^{-3}\,\mathrm{s}^{-1}$ for the Azo–PSCMS and $1.1 \times 10^{-2}\,\mathrm{s}^{-1}$ for the doped polystyrene as shown in the inset of Fig. 6a and b, with $k_{(c-t_{\mathrm{Th}})}$ taken as 1×10^{-5} and $2 \times 10^{-5}\,\mathrm{s}^{-1}$, respectively. Namely, the difference in $k_{(t-c_{\mathrm{UV}})}$ between the Azo–PSCMS and the doped polystyrene was found to be insignificant compared to the difference in $k_{(c-t_{\mathrm{Th}})}$. The result indicates that thermal reversible process may be more sensitive to the difference in free volumes involved in the isomerization.

Fig. 7a and b show the time-dependent mole fraction of *trans*-forms, $\alpha(t)$, in Azo–PSCMS and in the doped polystyrene upon irradiation with an Ar^+ laser with the optical power 11 mW/cm^2. Under these irradiation conditions, there exist three competing isomerization processes, i.e. (1) *trans* → *cis* photoisomerization ($t - c_{\mathrm{Ar}}$), (2) *cis* → *trans* photoisomerization ($c - t_{\mathrm{Ar}}$), and (3) *cis* → *trans* thermal isomerization ($c - t_{\mathrm{Th}}$). The early stage (the first 100 s of irradiation) of the time-dependent $\alpha(t)$ was fitted to the first-order kinetics:

$$\frac{\mathrm{d}[cis]_t}{\mathrm{d}t} = k_{(t-c_{\mathrm{Ar}})}[trans]_t - k_{(c-t_{\mathrm{Ar}})}[cis]_t - k_{(c-t_{\mathrm{Th}})}[cis]_t,$$

$$[trans]_t = \frac{k_{(t-c_{\mathrm{Ar}})}}{k_{(t-c_{\mathrm{Ar}})} + k_{(c-t_{\mathrm{Ar}})} + k_{(c-t_{\mathrm{Th}})}} \times \exp\{-(k_{(t-c_{\mathrm{Ar}})} + k_{(c-t_{\mathrm{Ar}})} + k_{(c-t_{\mathrm{Th}})})t\} + \frac{k_{(c-t_{\mathrm{Ar}})} + k_{(c-t_{\mathrm{Th}})}}{k_{(t-c_{\mathrm{Ar}})} + k_{(c-t_{\mathrm{Ar}})} + k_{(c-t_{\mathrm{Th}})}}, \qquad (3)$$

the photoisomerization rate constants, $k_{(t-c_{\mathrm{Ar}})}$ and $k_{(c-t_{\mathrm{Ar}})}$, are 8×10^{-3} and $1 \times 10^{-1}\,\mathrm{s}^{-1}$, respectively, for the Azo–PSCMS. Here, $k_{(c-t_{\mathrm{Ar}})}$ is about 10 times larger than $k_{(t-c_{\mathrm{Ar}})}$. The molar extinction coefficient and the quantum yield of the *cis* isomer are partially responsible for this observation. The optical power of irradiation may also contribute to the result. Thus, irradiation with an Ar^+ laser greatly contributes to *trans* → *cis* → *trans* photoisomerization cycles. On the other hand, $k_{(t-c_{\mathrm{Ar}})}$ and $k_{(c-t_{\mathrm{Ar}})}$ are, respectively 1×10^{-2} and $1 \times 10^{-1}\,\mathrm{s}^{-1}$ for the doped case. These rate constants are not significantly different between these two samples, suggesting that the difference in the rates of thermal isomerization is so sensitive considerably to the free volumes of a polymer segments involved in the reaction.

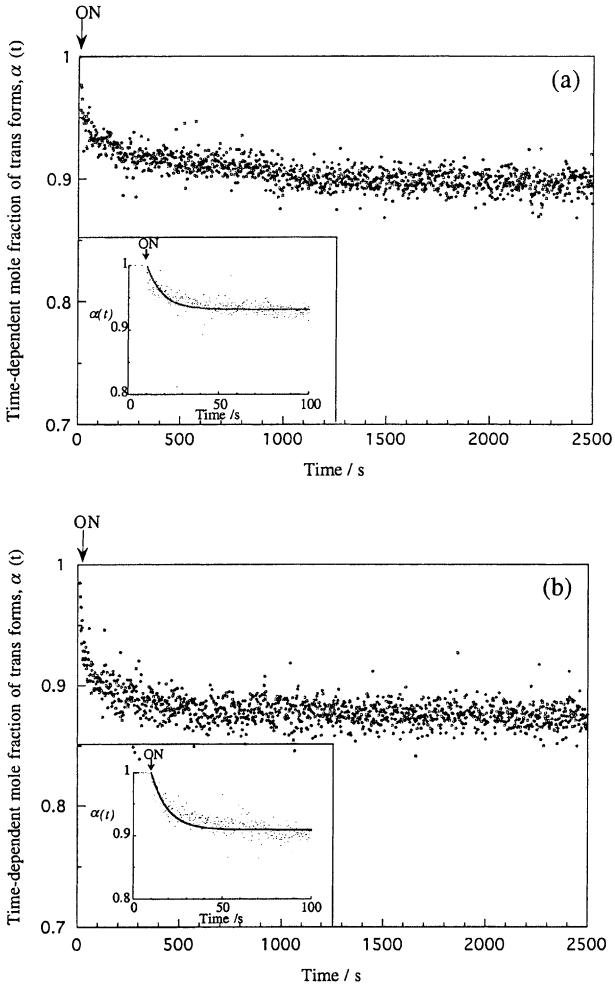

Fig. 7. Time-evolution of the mole fraction for the *trans* isomer observed for the photoisomerization process induced by visible light irradiation (11 mW/cm^2): (a) Azo–PSCMS, and (b) O-Azo doped in polystyrene. Inset shows the result of fitting the curves to the first-order kinetics.

3.2. Photoinduced anisotropy

3.2.1. Anisotropy induced by irradiation with UV light

The time-dependent photoinduced dichroism, $\Delta(t)$, is defined as

$$\Delta(t) = E_Y(t) - E_Z(t) \qquad (4)$$

Fig. 8a and b show the $\Delta(t)$ for the Azo–PSCMS and the O-Azo doped in polystyrene, respectively. According to Morita and Tran-Cong [5], the behavior of the dichroism,

$\Delta(t)$, can be controlled by the ratio of reaction rate k to the diffusion rate D. When the reaction rate is very small and the reactant is not exhaustedly consumed (the case (A)), the dichroism $\Delta(t)$ increases at an early stage, and then reaches a constant. On the other hand, when the reaction is very fast and the reactant is exhaustedly used (the case (B)), a curve of $\Delta(t)$ displays a maximum. Because a maximum exists in both samples, the photoinduced anisotropy can be regarded as the case (B). However, the quantitative analysis is not straight forward for the case of polymer because the mean-field kinetics of the reaction was assumed in the theory. A theoretical model taking into account the reaction inhomogeneity would be in need for tackling polymer systems. As shown in Fig. 8a, the large dichroism 0.23 was observed in the Azo–PSCMS after irradiation over 78 s. This result is in contrast with the value, 0.15, obtained for the doped polystyrene after 70 s of irradiation as depicted in Fig. 8b. These results suggest that the chemical linkage between the azo-moiety and the polymer chain did suppress the orientation relaxation of the O-Azo molecule.

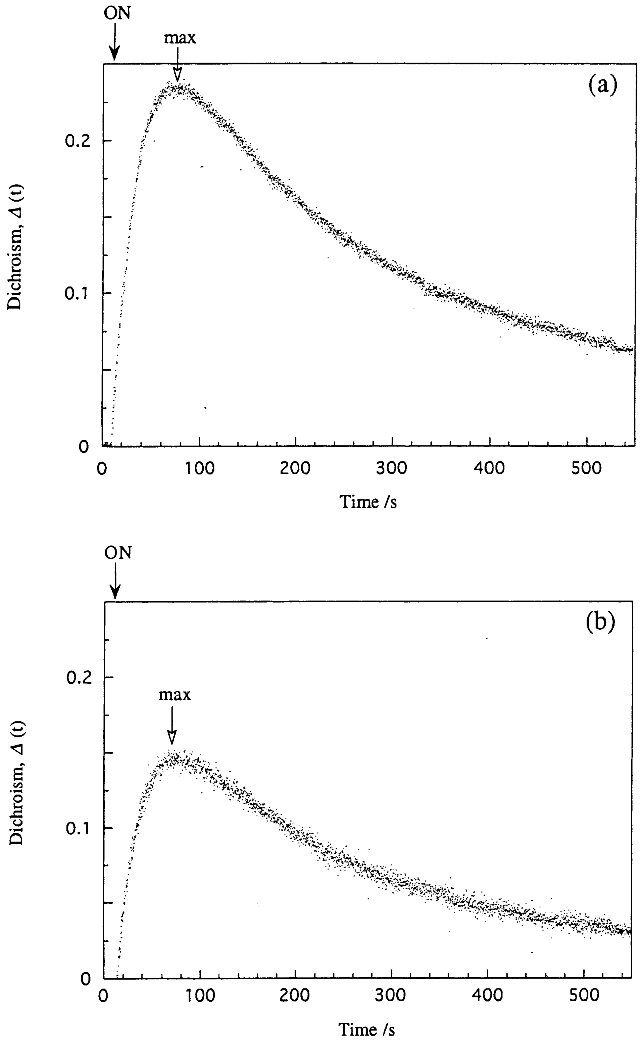

Fig. 8. Time-dependent dichroism ($\Delta(t) = E_Y(t) - E_Z(t)$) of: (a) Azo–PSCMS, and (b) O-Azo doped in polystyrene in the photoisomerization process induced by UV light irradiation (0.68 mW/cm^2).

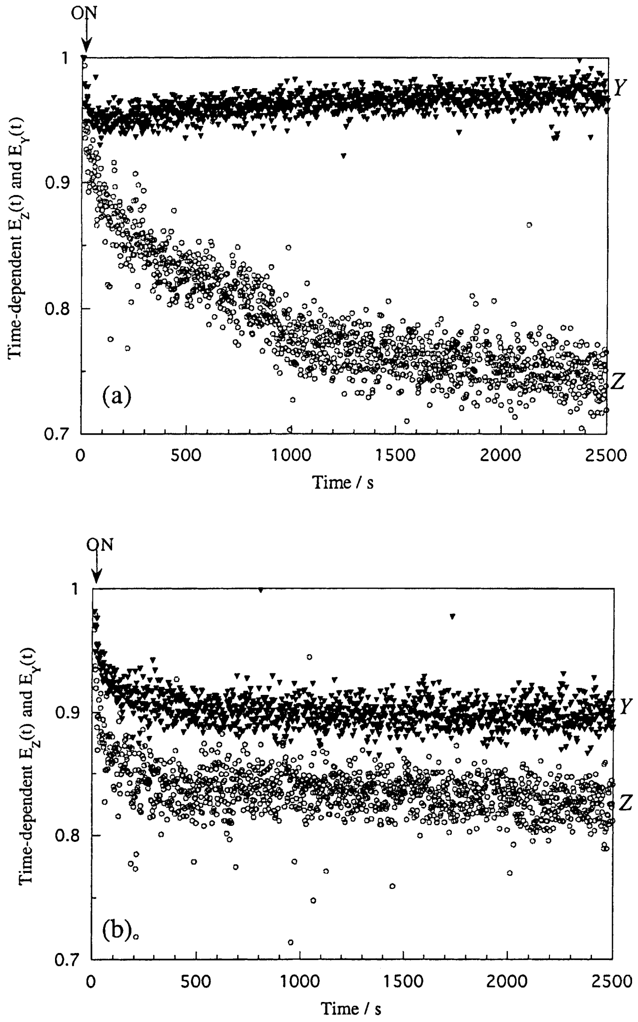

Fig. 9. Time-dependent $E_Y(t)$ (▲), and $E_Z(t)$ (○) of: (a) Azo–PSCMS, and (b) O-Azo doped in polystyrene in the photoisomerization process induced by visible light irradiation (11 mW/cm^2).

3.2.2. Anisotropy induced by irradiation with visible light

The difference was found between the dichroism of Azo–PSCMS and the doped polystyrene as illustrated in Fig. 8a and b. It indicated that the photoinduced anisotropy of azo-dyes in polymer matrix is controlled by the ratio (k/D) as predicted by the case (B) of the rotational diffusion-controlled reaction model [5]. However, more remarkable difference in dichroism ($E_Y(t) - E_Z(t)$) between two samples was induced by irradiation with Ar$^+$ laser as shown in Fig. 9a and b. The value of $E_Y(t)$ in Azo–PSCMS decreases at first stage (up to 60 s) during irradiation, and the dichroism in the Azo–PSCMS gradually increases with irradiation time, even when the photostationary state was achieved after 1000 s of irradiation as shown in Fig. 7a. 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 continuous isomerization cycle. During irradiation for 2500 s, the $\Delta(t)$ value of 0.24 is definitely larger than the $\Delta(t)$ of 0.07 in polystyrene doped with O-Azo. It means a quickly rotational diffusion of azo-molecules in polystyrene doped with O-Azo. On the contrary, larger $\Delta(t)$ means the existence of effective reorientation process of azo-molecules. Reorientation process has been considered as a phenomenon where the polarized-light irradiation changes the direction of transition moment of the *trans* molecule, and aligns them perpendicularly to the polarization direction of the exciting light. This reorientation process has been observed in the DR1-dye (NO_2–C_6H_4–N=N–C_6H_4–N(CH_2CH_3)CH_2CH_2OH) doped in PMMA [38,39] and the push–pull azo-dye covalently bonded to polymers [27]. Since the thermal isomerization rate of the push–pull azo-dyes is about 10^3–10^4 times faster than the azo-derivatives used in this study [13], a large number of *trans–cis–trans* isomerization cycles can be expected during irradiation for the push–pull azo-dyes. This repeating cycle has been considered to be one of the necessary conditions for the reorientation process. The small *trans–cis–trans* cycles would be responsible for the lack of the reorientation process in the Azo–PSCMS irradiated with UV light.

On the other hand, upon irradiation with visible light, the repeating rate of the *trans–cis–trans* isomerization cycles for the O-Azo doped polystyrene may be as high as the case of Azo–PSCMS. The photoinduced anisotropy was measured at room temperature. Although both samples were kept in the glassy state, the reorientation process of the dye was observed only in Azo–PSCMS excited (irradiated) by polarized light of an Ar^+ laser. The fact implies that the rotational diffusion of the O-Azo molecule may be too fast to make the reorientation process possible. We, therefore, conclude that the reorientation process is due to the chemical linkage of the azo-dye to the polymer chain via a flexible alkyl chain. In conclusion, to enable the reorientation of the azo-dyes in polymer matrix, both the restriction of rotational diffusion and the number of *trans–cis–trans* cycles upon irradiation are necessary.

4. Conclusion

Azo-dyes are promising materials for new optical switching elements and for photo-alignment of liquid crystal. In spite of their important applications, the relationships between the molecular structure and the orientation behavior have not been clarified sufficiently. In this study, the polarized light-induced anisotropy of azo-moieties chemically attached on polystyrene chains and dispersed in polystyrene matrix was measured and analyzed by using polarized UV–VIS spectroscopy. The findings are as follows: (1) compared to the O-Azo doped in polystyrene, Azo–PSCMS exhibits a large photoinduced dichroism due to the suppression of rotational diffusion; (2) the reorientation of azo-dyes was not observed with UV irradiation and was only obtained with visible light. The results shown here indicate that by choosing an appropriate wavelength for excitation so that both isomers are able to absorb, reorientation can occur due to the high repetition rate of the “*trans–cis–trans*” cycle. The suppression of the dye diffusion by the covalent linkage to polymer chain and the high repetition rate of the cycle “*trans–cis–trans*” play a key role in the induction of reorientation of the azo-dye.

References

[1] T. Todorov, L. Nikolova, N. Tomova, V. Dragostinova, Opt. Quantum Electron. 13 (1981) 209.
[2] V. Mateev, P. Markovsky, P. Nikolova, T. Todorov, J. Phys. Chem. 96 (1992) 3055.
[3] H. Ishitobi, Z. Sekkat, S. Kawata, Chem. Phys. Lett. 316 (2000) 578.
[4] Q. Tran-Cong, T. Kumazawa, O. Yano, T. Soen, Macromolecules 23 (1990) 3002.
[5] A. Morita, Q. Tran-Cong, Phys. A 242 (1997) 377.
[6] T. Ikeda, T. Sasaki, K. Ichimura, Nature 361 (1993) 428.
[7] T. Ikeda, O. Tsutsumi, Science 268 (1995) 1873.
[8] A. Shishido, O. Tsusumi, A. Kanazawa, T. Shiono, T. Ikeda, N. Tamai, J. Am. Chem. Soc. 119 (1997) 7791.
[9] K. Ichimura, Chem. Rev. 100 (2000) 1847.
[10] K. Ichimura, in: J.C. Crano, R.J. Guglielmetti (Eds.), Organic Photochromic and Thermochromic Compounds, Vol. 2, Kluwer Academic Publishers, New York, 1999 (Chapter 1).
[11] S. Hvilsted, F. Andruzzi, P.S. Ramanujam, Opt. Lett. 17 (1992) 1234.
[12] S. Hvilsted, F. Andruzzi, C. Kulinna, H.W. Siesler, P.S. Ramanujam, Macromolecules 28 (1995) 2172.
[13] H. Rau, in: J.F. Rabek (Ed.), Photochemistry and Photophysics, Vol. 2, CRC Press, Boca Raton, FL, 1990 (Chapter 4).
[14] K. Tawa, K. Kamada, T. Sakaguchi, K. Ohta, Polymer 41 (2000) 3235.
[15] K. Tawa, K. Kamada, K. Ohta, J. Photochem. Photobiol. A: Chem. 134 (2000) 185.
[16] K. Tawa, K. Kamada, T. Sakaguchi, K. Ohta, Appl. Spectr. 52 (1998) 1356.
[17] J.E. Michi, W. Thulstrup (Eds.), Spectroscopy with Polarized Light, VCH, New York, 1986.
[18] H.-L. Li, Y. Ujihara, S. Tanaka, T. Yamashita, K. Hone, J. Radioanal. Nucl. Chem. 210 (1996) 543.
[19] H.-L. Li, Y. Ujihara, A. Nanasawa, J. Radioanal. Nucl. Chem. 210 (1996) 533.
[20] D. Anwand, W. Müller, B. Strehmel, K. Schiller, Makromol. Chem. 192 (1991) 1981.
[21] C.S.P. Sung, I.R. Gould, N.J. Turro, Macromolecules 17 (1984) 1447.
[22] W.-C. Yu, C.S.P. Sung, R.E. Robertson, Macromolecules 21 (1988) 355.
[23] I. Mita, K. Horie, K. Hirao, Macromolecules 22 (1989) 558.
[24] Th. Geue, A. Ziegler, J. Stumpe, Macromolecules 30 (1997) 5729.
[25] P.S. Ramanujam, C. Holme, S. Hvilsted, M. Pedersen, F. Andruzzi, M. Paci, E.L. Tassi, P. Magagnini, U. Hoffman, I. Zebger, H.W. Siesler, Polym. Adv. Tech. 7 (1996) 768.
[26] Z. Sekkat, M. Büchel, H. Orendi, H. Menzel, W. Knoll, Chem. Phys. Lett. 220 (1994) 497.
[27] Z. Sekkat, J. Wood, F. Aust, W. Knoll, W. Volksen, R.D. Miller, J. Opt. Soc. Am. B 13 (1996) 1713.
[28] Z. Sekkat, P. Prêtre, A. Knoesen, W. Volksen, Y. Lee, R. Miller, J. Wood, W. Knoll, J. Opt. Soc. Am. B 15 (1998) 401.
[29] A. Imagawa, Q. Tran-Cong, Macromolecules 28 (1995) 8388.
[30] S. Kondo, T. Ohtsuka, K. Ogura, J. Macromol. Sci. Chem. A 13 (1979) 767.

[31] J.G. Radziszewski, J. Michl, J. Am. Chem. Soc. 108 (1986) 3289.
[32] J.G. Radziszewski, I. Michi, J. Chem. Phys. 82 (1985) 3527.
[33] D.L. Beveridge, H.H. Jaffé, J. Am. Chem. Soc. 88 (1966) 1948.
[34] T. Naito, K. Horie, I. Mita, Macromolecules 24 (1991) 2907.
[35] T. Naito, K. Horie, I. Mita, Eur. Polym. J. 12 (1990) 1259.
[36] Z. Sekkat, J. Wood, W. Knoll, J. Phys. Chem. 99 (1995) 17226.
[37] P.D. Wildes, J.G. Pacifici, G. Irick Jr., D.G. Whitten, J. Am. Chem. Soc. 93 (1971) 2004.
[38] M. Dumont, Z. Sekkat, R.L. Säibi, K. Nakatani, J.A. Delaire, Nonlinear Opt. 5 (1993) 395.
[39] T. Buffeteau, F.L. Labarthet, M. Pézolet, C. Sourisseau, Macromolecules 31 (1998) 7312.