Out-of-Plane Photoreorientation of Azo Dyes in Polymer Thin Films Studied by Surface Plasmon Resonance Spectroscopy

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ABSTRACT: The out-of-plane photoreorientation in azo dye modified polymer thin films was investigated by surface plasmon resonance spectroscopy (SPR) and optical waveguide spectroscopy (WS). A styrene copolymer with covalently linked azo dye derivatives was used in order to measure changes in the molecular orientation during irradiation with polarized visible light. The covalent linkage of the azo moiety to polymer chain is found to be efficient in the reorientation process due to the suppression of the rotational diffusion. The measurement by four kinds of optical arrangement in SPR and WS results in the determination of the three independent refractive index components. Using this powerful technique for the evaluation of photoreorientation processes in polymer thin films, especially orientation normal to the film, we found that azo molecules preferentially align with the direction normal to the film plane.

Introduction

Polarized light induced anisotropy in polymers including azo dyes has been studied by Todorov and coworkers[1,2] since the 1980s. This type of optical anisotropy was also observed with polymers containing photochromic compounds other than azo dyes.[3−5] Despite the variety of materials, the polymers including azo dyes have attracted our interest as one of the most representative materials that shows efficient photoinduced orientation. Azo dyes exist in two isomeric forms: *trans* and *cis* isomers. The isomerization rate and the photostationary state strongly depend on the chemical structure of the azo dye and of the polymer matrix.[6] The photochemistry of azo dyes in polymer solids has been studied in great detail, taking into account the effects of free volume and physical aging.[7−10] The change in the molecular orientation associated with these chemical reactions plays a key role in the generation of optical anisotropy. The potential of applying these photoinduced effects has been demonstrated in optical switching and by the photoalignment of liquid crystals.[11−17]

The large anisotropy that can be achieved by this reorientation process was previously reported in DR1-dye ($NO_2-C_6H_4-N{=}N-C_6H_4-N(CH_2CH_3)CH_2CH_2OH$) doped PMMA.[18,19] “Reorientation process” means a phenomenon by which the irradiation with polarized light changes the direction of the transition dipole moment of the *trans* molecule and aligns them perpendicularly to the polarization direction of the excitation light. Photoinduced reorientation has also been studied in various polymer films containing azo moieties, e.g., in Langmuir−Blodgett−Kuhn films,[20] liquid crystalline polymers,[21] polyglutamates,[22] and polyimides.[23] Recently, we have described the photoinduced anisotropy in the bulk state of polymers doped with a push−pull type of azo derivatives[24−26] and with covalently linked azo dyes.[27,28] Since it is known that the reorientational process of azo dyes is affected by both their rotational diffusion and the *trans*−*cis*−*trans* isomerization cycles,[20b,21a,22,23] the linkage of the dyes to polymer chains is found to effectively control the photoinduced anisotropy by suppressing the rotational diffusion.

In this study, the photoinduced reorientation process was examined by surface plasmon resonance spectroscopy (SPR) and by optical waveguide spectroscopy (WS)[29,30] using thin films of a styrene copolymer with chemically bonded azo dyes; for this system the photoreorientation studied by polarized UV−vis absorption spectroscopy has been reported.[27] SPR and WS are very useful techniques in order to clarify the molecular orientation in polymer thin films, especially the out-of-plane orientation. Four kinds of optical arrangement in SPR and waveguide modes as explained later (see Figure 3) allows for the independent evaluation of the three refractive indices in the X, Y, and Z directions. The out-of-plane orientation has been reported in LBK films composed of hairy-rod polymers with azo dye side groups.[20b,31] The azo dye covalently attached to the polymer was found to align with the out-of-plane direction upon irradiation. Recently, the out-of-plane photoreorientation was also studied using liquid crystalline polymers with an azo moiety as a side chain.[32,33] It was found that the out-of-plane orientation is very important in the correct analysis of the photoinduced reorientation mechanism. However, marked out-of-plane reorientation was never observed in spin-cast films of polymers that do not show liquid crystallinity. It is possible that this is due to different conditions from those used in this study, e.g., the transition state in photoisomerization, the chemical structure of polymers and azo dyes, the content of azo dyes in polymers, and so on. Our main concern in this report is the discussion of photoinduced reorientation in the direction normal to the film plane (out-of-plane, Z direction) in polymer thin films containing an azo dye, which shows, however, no liquid crystallinity. The physical properties of a thin polymer film with a thickness below 100 nm have been found to

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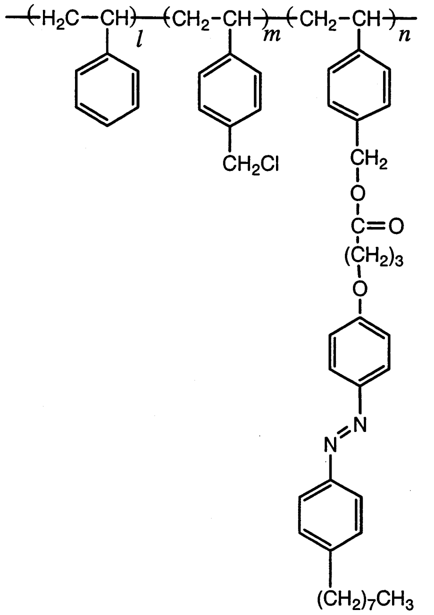

Figure 1. Chemical structure of the Azo-PSCMS copolymer (l:m:n = 88:4.3:7.7).

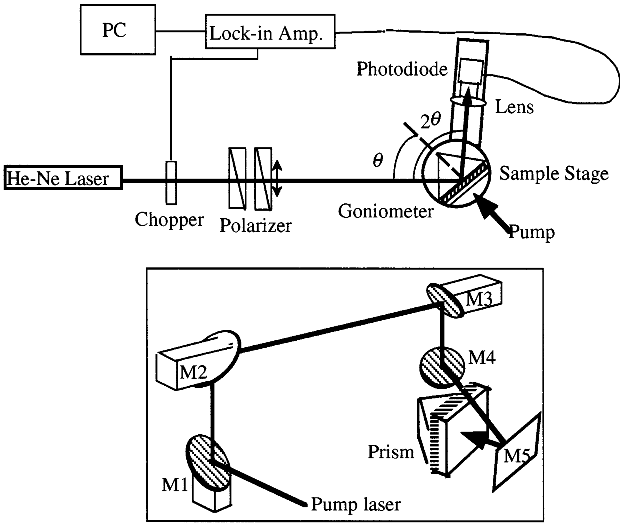

Figure 2. Optical arrangement for SPR and WS in situ measurement. Below: inset shows the optical arrangement for the pump laser (composed of five mirrors). The mirrors of M3 and M4 are adjusted as that the propagation axis of the pump light coincides with the rotational axis of the sample stage.

deviate significantly from that in the bulk state, even in spin-cast films.[34,35] The glass transition temperature, which is a measure of the molecular mobility, has been shown to decrease as the film decreases in thickness to below 100 nm.[34] The properties of films about 100 nm thickness used in this study can be considered to be identical to those in the bulk state; however, the surface characteristic may begin to emerge effectively. The combination of SPR and WS is a powerful method to investigate not only the in-plane but also the out-of-plane reorientation in such a thin film.

Experimental Section

Sample. The copolymer (PSCMS) of styrene (Wako, Japan) and (chloromethyl)styrene (Tokyo Kasei) was synthesized by free radical polymerization, and the copolymer was labeled with 4-octyl-4′-(3-carboxytrimethyleneoxy)azobenzene (Dojindo Laboratories, Japan) according to a procedure described previously[27,36] (Azo-PSCMS). The label content of the dye was approximately 7.7 mol % with respect to the repeat units of the copolymer (Figure 1). The glass transition temperature of the Azo-PSCMS is 86 °C as determined by DSC. Thin films were prepared from toluene solutions on glass substrates (BK7 or LaSFN9) covered with gold by spin-coating. The films were annealed at 80 °C for more than 10 h prior to the measurements and also after measuring the orientation induced by polarized light irradiation.

Surface Plasmon Spectroscopy and Waveguide Spectroscopy. The principles of surface plasmon resonance spectroscopy (SPR) and optical waveguide spectroscopy (WS) have been described in other papers in detail.[29,30] The optical arrangement for SPR and WS as used in this study is shown in Figure 2. This arrangement is called an ATR (attenuated total reflection)−Kretschemann setup. The substrate is brought in optical contact with a prism of the same material. Two kinds of substrates, BK7 glass and LaSFN9 glass (high refractive index glass), were used for the measurements of WS and SPR, respectively. For the BK7 substrate, a Cr layer of about 2 nm thickness was evaporated before the Au layer with the thickness of 47 nm was depositted. For the LaSFN9 substrate, only the Au layer was evaporated at a thickness of about 45 nm. A He−Ne laser (wavelength 632.8 nm) was used as the probe light. Linearly p- and s-polarized light of the He−Ne laser was used for SPR and WS measurements, respectively. The polarization and intensity were controlled by the combination of two polarizers. The computer-controlled $\theta-2\theta$ goniometer was utilized to rotate the sample stage at θ and the detector at 2θ. The reflection signal was monitored by a lock-in amp (Seiko EG&G, model 5210) synchronized with the signal from light chopper (Seiko EG&G, model 197).

The irradiation (pump) light with $\lambda = 488$ nm was obtained from an Ar ion laser (Spectra-Physics). Before any SPR measurement, the optical power of the pump light was adjusted to 12.0 mW/cm^2 at the sample position by ND filters. The propagation direction of irradiation light was arranged to be normal to the film plane by using five mirrors as shown

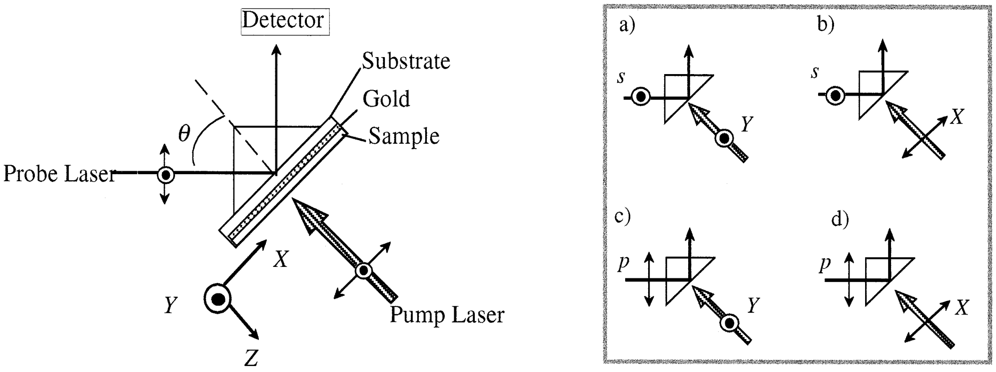

Figure 3. Four kinds of optical arrangements for polarized light irradiation: (a) waveguide mode under the irradiation of Y-polarized light, (b) waveguide mode, X-polarized light, (c) SPR mode, Y-polarized light, (d) SPR mode, X-polarized light.

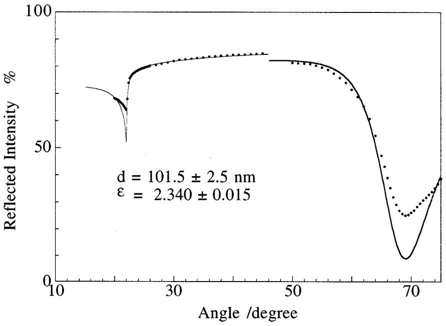

Figure 4. SPR and waveguide spectra of Azo-PSCMS before irradiation (broken line) and simulation curve (solid line).

in Figure 2. Therefore, the incident angle of the Ar ion laser light was always 0° independent of θ. Two orientations of the linearly polarized light (X- and Y-) of the Ar ion laser were prepared by a $\lambda/2$ plate and a polarizer. They were combined with s- (waveguide mode) and p-polarization (SPR mode) of the He−Ne laser light to give the four optical arrangements as shown in Figure 3 necessary to evaluate the three independent refractive indices and the film thickness. All spectra were measured at room temperature (23 °C).

Results and Discussion

SPR and Waveguide Spectra before Irradiation. Before irradiation, the film is (optically) isotropic, and the three independent refractive indices, n_Z, $n_{\parallel}$, and $n_{\perp}$, are identical to each other ($n_Z = n_{\parallel} = n_{\perp} = n_0$). n_Z means the refractive index in the direction normal to the film plane, i.e., Z direction (see Figure 3). $n_{\parallel}$ and $n_{\perp}$ correspond to the two in-plane refractive indices, and the subscripts indicate the relation to the polarization axes of the pump beams, respectively. The former is the refractive index parallel to the polarization direction of pump light, and the latter is that perpendicular to it. If polarized light is incident on the Azo-PSCMS film, an optical anisotropy is induced within the polymer, and the refractive indices are not equivalent to each other any more.

Figure 4 shows the SPR and waveguide spectra of an Azo-PSCMS sample before irradiation. Using a Fresnel's simulation program, the film thickness, d, and the isotropic dielectric constant, ϵ ($= n^2$, n: refractive index), can be obtained. We evaluated the value of n_0 for Azo-PSCMS as 1.530 ± 0.005 at the initial condition ($\epsilon_0 = 2.340 \pm 0.015$). As seen in Figure 4, the experimentally determined dips are not as sharp as the simulation curves (shown in solid lines) because of the inhomogeneity of the polymer film. However, the position of dips is the relevant feature and can be used to evaluate the parameters. The solid lines illustrated in Figure 5a,b show the waveguide mode before irradiation. They were observed in the arrangement of Figure 3a,b. Using the value of $n_0 = 1.530$, each film thickness was evaluated as 139.9 nm ± 2.5 nm (for Figure 5a) and 138.5 ± 2.5 nm (for Figure 5b). The solid lines in Figure 5c,d show the surface plasmon mode before irradiation. They were observed in the arrangement of Figure 3c,d. It was also evaluated as 107.5 ± 2.5 and 108.5 ± 2.5 nm, respectively.

SPR and Waveguide Spectra during Irradiation. As illustrated by the broken lines in Figure 5a−d, the minimum position changed upon irradiation by the pump beam. All the broken lines show the reflectance spectra after irradiation for 60 min in each optical arrangement. Figure 6 shows the UV−vis absorption spectra of spin-coated Azo-PSCMS film on BK7 glass measured by a Perkin-Elmer Lambda 9. The film

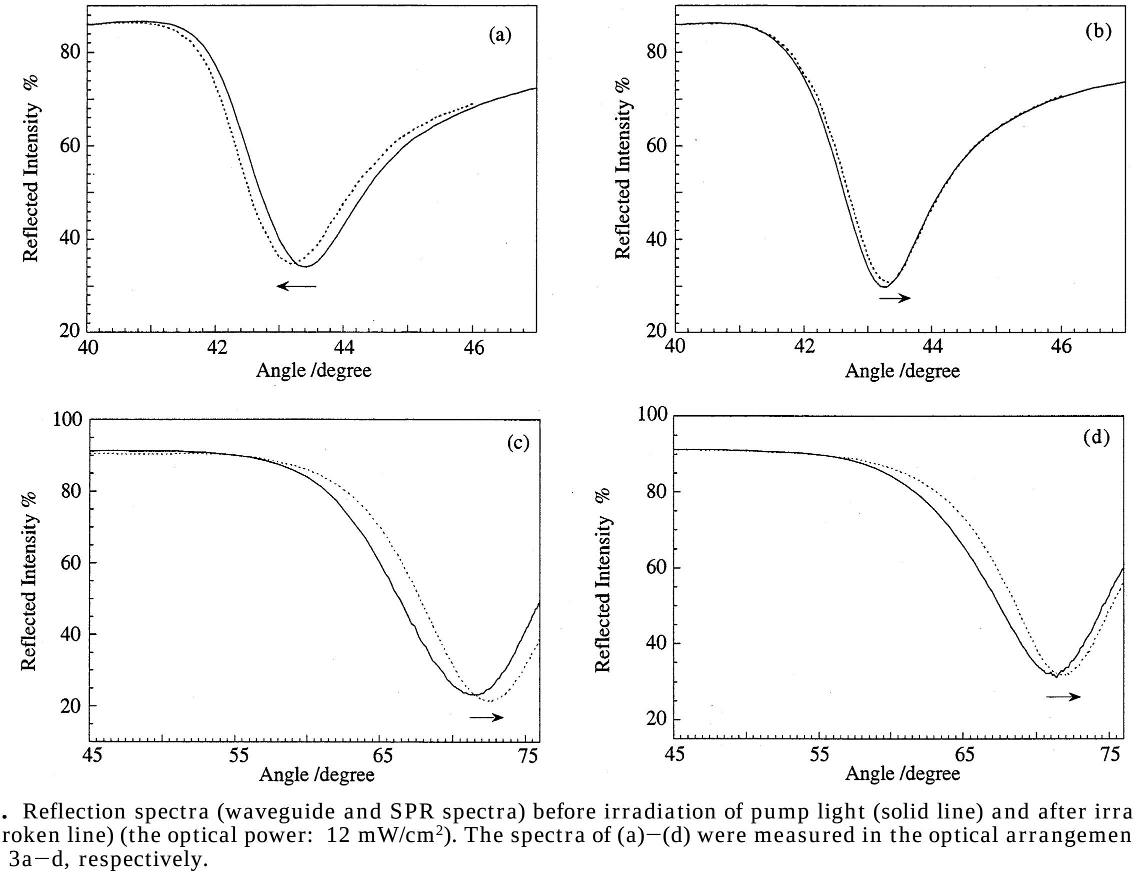

Figure 5. Reflection spectra (waveguide and SPR spectra) before irradiation of pump light (solid line) and after irradiation for 60 min (broken line) (the optical power: 12 mW/cm^2). The spectra of (a)−(d) were measured in the optical arrangement as shown in Figure 3a−d, respectively.

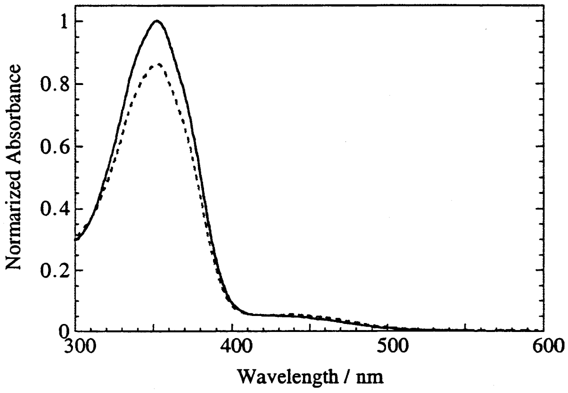

Figure 6. UV–vis absorption spectra in Azo-PSCMS with the thickness of about 120 nm before irradiation (solid line) and after irradiation for 60 min by Ar$^+$ laser (12 mW/cm^2) (broken line).

thickness was about 120 nm. The solid line and the broken line represent the absorption spectra before irradiation and after irradiation for 60 min by an Ar ion laser, respectively. They were normalized to the maximum absorbance at $\lambda_{\max}$ before irradiation. By irradiation for 60 min, 15% of the *trans* molecules isomerize to the *cis* molecules. Upon irradiation for 20 min with an Ar ion laser, the isomerization ratio was also found to reach a constant value of photoequilibrium due to the high repetition of *trans*–*cis*–*trans* photoisomerization cycles.[27] However, the reorientational behavior gradually developed by irradiation for 60 min because these photoisomerization cycles induced by the illumination with visible light play an important role for the photoinduced reorientation. The time evolution of the reflected intensity detected at a fixed angle corresponds to the kinetics of the molecular orientation of the azo dyes. Figure 7a–d shows the kinetics data observed at fixed angles in the four optical arrangements shown in Figure 3. The time evolution of the reflected intensity depicted in Figure 7a–d was observed at 42.6° (a), 42.5° (b), 65.2° (c), and 66.5° (d). Only the trace depicted in Figure 7a gradually decreases during irradiation with the pump. This means that the trans isomers were excited selectively in the *Y* direction (parallel to the polarization of the pump). On the other hand, the other three traces in Figure 7b–d gradually increase. In particular, the two traces shown in Figure 7c,d indicate almost the same behavior. Therefore, the orientational behavior is considered to develop simultaneously in the in-plane and the out-of-plane directions. This is different from the out-of-plane oirentational process reported for liquid crystalline polymers.[32] There, the subsequent out-of-plane orientation after the in-plane orientation due to a long period of irradiation by a Hg–Xe lamp was reported.

To evaluate the independent refractive indices, we simulated the four spectra shown in broken lines of Figure 5a–d. The refractive index (at $\lambda = 633$ nm) of the *trans* form is known to be higher than that of the *cis* isomer.[30] By irradiation for 60 min, the dip of waveguide mode shown in Figure 3a shifts to a lower angle and the dip in Figure 3b shifts to a higher angle. Despite the existence of cis molecules, the shift to higher angles is a very important phenomenon. It means that the in-plane azo molecules reorient in the direction perpendicular to the polarization of the pump light. This result is complementary to our previous data[27] that showed the increase of the absorbance observed in the direction perpendicular to it. In the waveguide mode, $n_{\parallel}$ and $n_{\perp}$ can be evaluated by the optical arrangement of parts a and b of Figure 3, respectively. Thus, the values of the refractive indices as described in Table 1 are calculated. After irradiation, the film thickness can

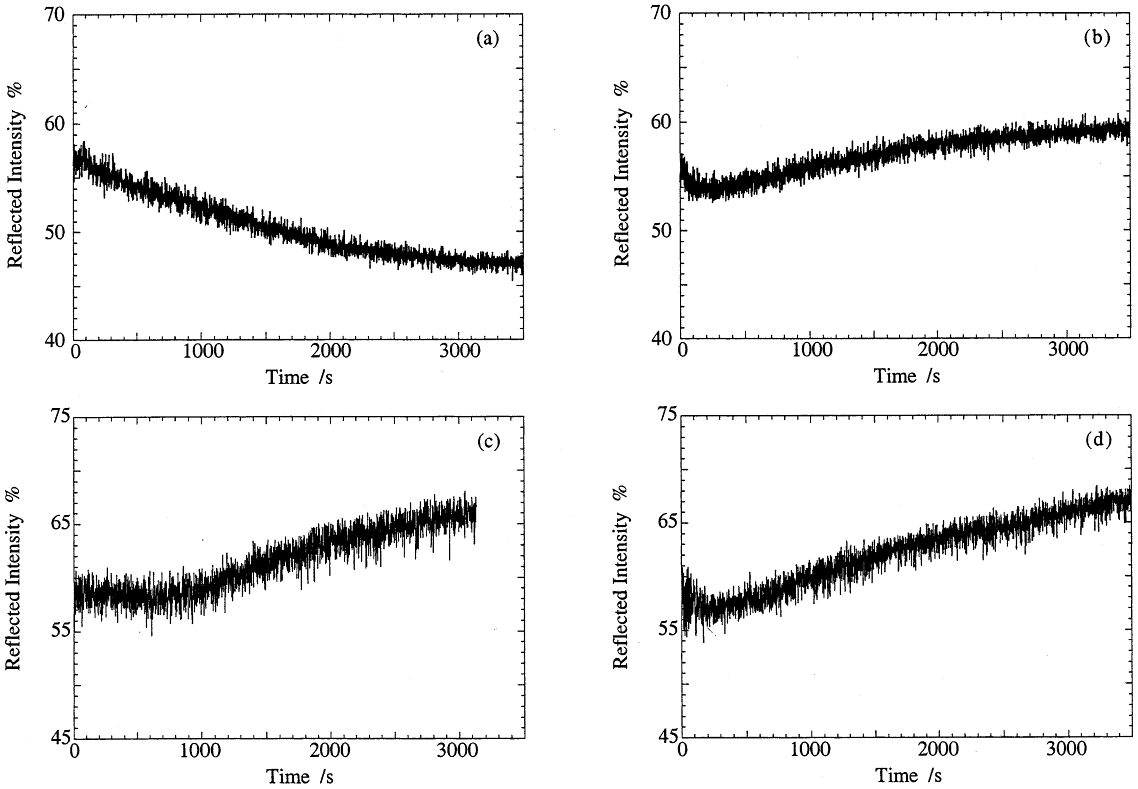

Figure 7. Time evolution of the reflected intensity induced by the polarized light irradiation (12 mW/cm^2). They were observed at fixed angles, i.e., (a) 42.6°, (b) 42.5°, (c) 65.2°, and (d) 66.5°, in the optical arrangement as shown in Figure 3a–d, respectively.

Table 1. In-Plane Refractive Indices Evaluated from WS

	$n_{\parallel}$	$n_{\perp}$
before irradiation	1.530 ± 0.005	1.530 ± 0.005
after irradiation	1.522 ± 0.005	1.530 ± 0.005

Table 2. Out-of-Plane Refractive Index Evaluated from SPR Using In-Plane Refractive Indices Described in Table 1

	n_Z
before irradiation	1.530 ± 0.005
after irradiation	1.535 ± 0.005

be assumed to be unchanged within experimental errors.

On the other hand, both dips of the SPR mode shown in Figure 5c,d shift to higher angles after irradiation for 60 min. These spectra depend on the combination of the refractive indices of (n_Z, $n_{\perp}$) or (n_Z, $n_{\parallel}$), respectively. Using the values described in Table 1, n_Z was determined. The values of n_Z evaluated from two spectra in Figure 5c,d were almost the same without contradiction. The obtained values are described in Table 2. The film thickness was found to be unchanged within experimental errors upon irradiation. The increase of n_Z corresponds to a structure in which azo molecules align normal to the direction of the surface plane (Z direction). SPR and WS allowed us to quantify this out-of-plane orientation. The mean refractive index, n, as evaluated by $(n_{\parallel} + n_{\perp} + n_Z)/3$ is 1.529 and is found to be slightly smaller than n_0 before irradiation. This can be considered to be reasonable taking into account the 15% isomerization from *trans* to *cis*.

The reorientation process should be induced by at least two factors: one is the photoselective isomerization (photobleaching) of *trans* molecules by the irradiation with polarized light, and the other is the reorientation of the *trans* molecules during the continuous isomerization cycle. We found that the azo molecules prefer to align with the direction normal to the film plane. In conclusion, the reorientation of the azo dyes even in polymer thin films strongly develops out-of-plane compared with that in-plane. The azo molecules may align with out-of-plane due to a surface effect. The mobility of azo molecules near surface is different from that of the bulk state. On the surface in such a thin film, the azo molecule is easy to diffuse, and therefore, in-plane orientation is not so effective compared with the out-of-plane one. To clarify this physical mechanism, a more detailed experiment about the film thickness dependence of photoinduced reorientation is in progress.

Conclusion

Polymers including azo dyes are known as one of the promising materials for new optical devices. The polarized light induced reorientation was previously reported in azo moieties chemically bonded to a styrene copolymer (Azo-PSCMS). The suppression of the rotational diffusion of azo molecules by the covalent linkage to the polymer chain and the high repetition rate of the cycle “*trans*−*cis*−*trans*” were found to play a key role in the inducing the reorientation of the azo dye. In this study, the reorientation process observed in Azo-PSCMS was studied by using the SPR and WS. Four types of optical arrangement in the SPR and WS techniques allowed us to understand the reorientation process via the independent three refractive indices in such a thin film of about 100 nm thickness. We found that Azo-PSCMS exhibits marked out-of-plane orientation compared with in-plane orientation. The out-of-plane orientation can be induced by the polarized light irradiation even in the thin film of polymer without liquid crystallinity. However, the mechanism of the out-of-plane orientation may strongly depend on the chemical structure of a polymer and of an azo dye.

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