Orientation of a photo-sensitive polymeric monolayer studied by second-harmonic generation

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Abstract. We determine the orientational distribution functions of azo-side-chain polymeric monolayers before and after the photo-irradiation by optical surface second-harmonic generation (SHG). The polymeric monolayer, composed of azo-dye-labeled polyamic acid (long alkyl) amine salt, is prepared by the Langmuir–Blodgett technique. Oblique incident surface SHG measurement from the monolayer provides the nonlinear-optical tensor components related to the orientational distribution functions of the azo-side-chain. The analysis of experimental results shows that the point symmetry of the azo-pendent unit in the monolayer changes from $C_{\infty v}$ to C_{1v} by the photo-isomerization process, with the azobenzene conformation retained as trans-isomer.

The photo-isomerization process of azobenzene derivatives with photon energies corresponding to their electronic excitation has been extensively studied from the fundamental and applicational viewpoints [1–3]. In this process, azobenzene molecules oriented parallel to the incoming electric field vector are excited in preference, whereas those with a perpendicular orientation do not undergo photo-isomerization [4–6]. Thus the prolonged irradiation of randomly oriented azobenzene molecules with a polarized UV light eventually results in the alignment of the molecules in the direction perpendicular to the polarization through multiple trans-cis isomerizations [7–9].

Recently, various forms of organization of polymeric thin films, such as Langmuir–Blodgett (LB) films and including photo-isomerizable azobenzene groups, have been investigated [10–15]. From the viewpoint of application, photo-reorientational effects may be used for high-density information storage [16, 17], optical holograph [5], and optical switching devices with photo-assisted electro-poling [18–20]. Further application includes the induced orientational changes of the nematic and ferroelectric liquid crystal (LC) phases by the photochromic transformation of doped azobenzene molecules [21, 22]. In particular, it has been successfully

shown that photo-treated polymer films containing azobenzene units align the LC molecules homogeneously when the films are exposed to linearly polarized light [11, 23–26]. This effect is mainly due to the possibility of the optical control of the homogeneous LC alignment rather than through a mechanical modification of polyimide films on substrates, such as by the rubbing method, which may produce the problems of contamination and static electricity [27–31].

In this application, understanding the exact orientation of azobenzene isomer units is of great importance in the practical design of various LC devices, because the orientation of azobenzene affects the surface alignment of LC molecules at the interface between the alignment layer and the LC molecules. Recently, the orientational changes of azobenzene units have been observed in LB films of azobenzene-labeled polyamic acid after an imidization process by using surface second-harmonic generation (SHG) [32]. However, it has not yet been clearly shown how the azobenzene isomer units are oriented in the photo-isomerizable alignment layer after the photo-irradiation process. In this respect, it is important to clarify the surface orientation and identify the isomer state of the photo-processed alignment layer, highly useful in controlling LC alignment.

In the present paper, we report how we have studied the symmetry and orientational structures of an azobenzene-labeled polyamic acid LB film in order to understand the changes in orientational distribution of the azobenzene units before and after the photo-isomerization processes. First of all, by monitoring the polarized UV–VIS absorption spectral change, we analyzed the effect of anisotropic alignment of azobenzene chromophores through the trans/cis/trans isomerization on the irradiation. Next, for the surface-orientational study, the surface SHG [33–35] measurement was adopted in order to measure the nonlinear optical (NLO) susceptibility tensor components, from which the optical point symmetry of the LB film was determined. From the NLO coefficients, the orientational distributions of the azobenzene-pendent unit in the LB monolayer before and after the photo-isomerization process were found by means of the maximum entropy method. Then the magnitude of the molecular hyperpolarizability was deduced from the meas-

urement so as to identify the isomer state of the pendent azobenzene-units after irradiation. Finally, we report how we showed that LB films align the nematic LC molecules homogeneously when the films are exposed to linearly polarized light.

1 Polarized absorption spectra

The photo-isomerizable polymer employed for this study was polyamic acid containing an SHG-active pendent azo dye and (long alkyl) amine N-icosylpyrrolidine (Azo-PA), with the chemical structure shown in Fig. 1. A 0.1 mM solution of Azo-PA dissolved in N, N-dimethylacetamide (DMAC) was prepared so that it could serve as a spreading solution. At the surface pressure of 15 dyne/cm, a closely packed Z-type LB monolayer was deposited onto a quartz substrate by the conventional vertical deposition method, resulting in a surface molecular density, N_s of $0.5 \times 10^{14} \, \text{cm}^{-2}$.

The photo-isomerization for the Azo-PA LB film was achieved by linearly polarized irradiation at $\lambda = 488 \, \text{nm}$, close to the resonance absorption wavelength (470 nm) of the Azo-pendent group at room temperature of 25 °C (irradiation intensity $1 \, \text{W/cm}^2$ and irradiation time 10 min). The polarization of the irradiation was set to the y-axis, which was set perpendicular to the dipping direction (x-axis) of the LB sample.

Figure 2 shows the changes in the absorption spectra before and after the irradiation process. The spectra were measured in the two directions parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the y-direction. Prior to irradiation, there was no difference between $A_\parallel$ and $A_\perp (= A_0)$, suggesting that the orientation of azo-pendent groups is azimuthally isotropic. After irradiation, however, the changes in the absorption are clearly observed, the absorption peaking in $A_\perp$ at 470 nm, a value greater than that in $A_\parallel$. This indicates that a number of azo-pendent units had been reoriented perpendicular to the polarization direction of irradiation. Moreover, the unpolarized absorption A_{unpol} had decreased, indicating a partial reorientation of the azo-pendent groups into the surfaces normal direction (the z-direction).

This behavior is consistent with the photo-reorientation of azobenzene units as previously reported [27]. In these polar-
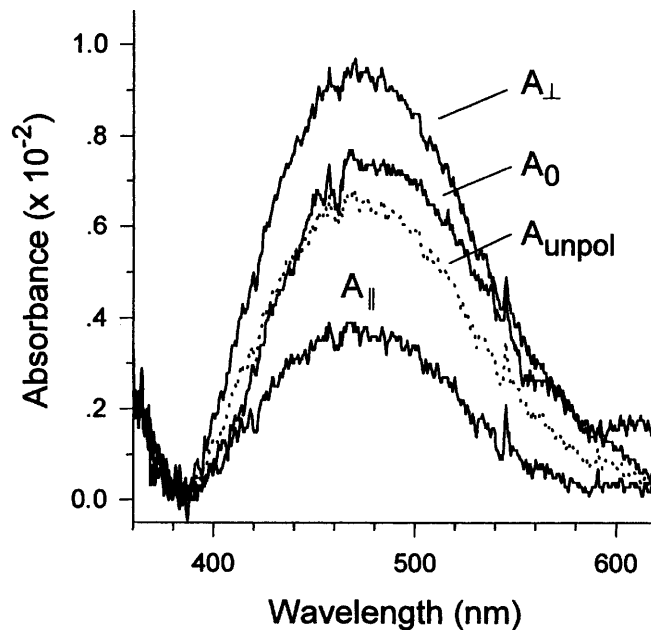

Fig. 2. Absorption spectra of an Azo-PA monolayer film before (A_0) and after the irradiation ($\lambda = 488 \, \text{nm}$, y-polarized). The past-irradiation results are given by $A_\parallel$: y-polarized; $A_\perp$: x-polarized; and A_{unpol}: unpolarized

ized UV-VIS absorption spectra, however, information on the exact optical point symmetry and orientation distribution, as well as the isomer state of azo-pendent units, are not explicit.

2 Second-harmonic generation measurements

Next, the surface-specific SHG measurements were made in order to clarify the surface structure of photo-processed LB film. A fundamental light beam ($\lambda = 1064 \, \text{nm}$) from a Q-switched Nd:YAG pulsed laser (pulse width 12 ns, repetition rate 10 Hz, pulse energy 8 mJ) was employed. The unfocused beam, with a diameter of approximately 8 mm, was incident on the glass side of the LB sample with an angle of incidence of 45° (once the polarization of the incident beam had been selected). The transmitted SHG output from the LB film was detected for both p and s polarizations. The SHG signal from
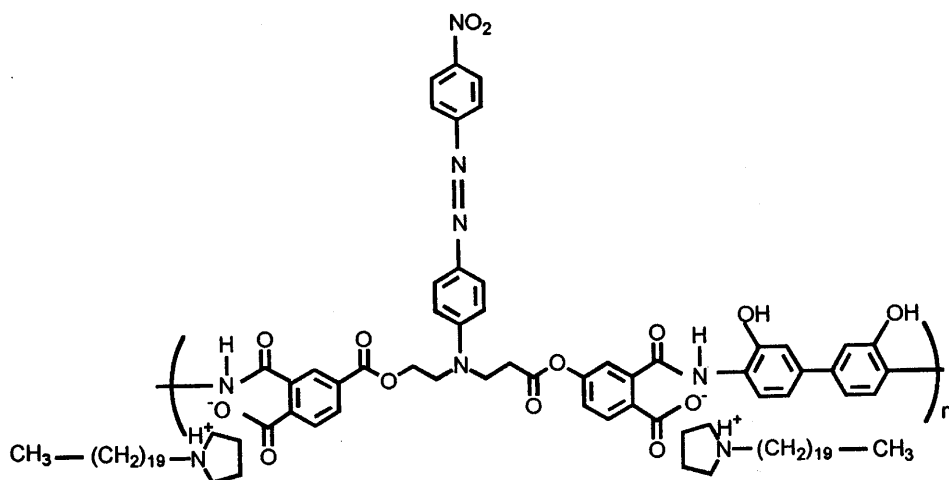

Fig. 1. Chemical structures of polyamic acid containing a pendant azo dye and (long alkyl) amine N-icosylpyrrolidine (Azo-PA)

the sample was measured in four different polarization combinations while the film was being rotated around the surface normal: $p-p$, $p-s$, $s-p$, $s-s$, where the former and the latter symbols stand for the polarization directions of the polarizer and the analyzer respectively. The SHG wavelength (532 nm) was close to that for resonance of the azo-pendent group, and therefore in all cases the SHG background of the substrates was negligible. All measurements were performed at a temperature of 25 °C, i.e. around room temperature.

The photo-induced anisotropic orientational distribution in LB film is not stable and fades away upon prolonged storage. This situation was studied by fabricating a nematic LC cell with plates coated with LB monolayers that were irradiated with the polarized light and stored for several days in the dark before cell assembly. No homogeneous alignment was observed for the cell after seven days, in contrast to the high stability exhibited by homogeneous alignment induced by LB films when a cell is fabricated just after irradiation. However, the anisotropic orientation induced by polarized light was found to be stable enough to measure surface SHG.

Let us now examine the geometry of the surface SHG experimental setup. In the laboratory coordinates denoted by (X, Y, Z) in Fig. 3, the incident angle $\theta_1(\omega)$ represents the rotation of the sample with respect to the z-axis, i.e. the angle between the surface normal of the sample and the propagation direction of the incident light. The angle ϕ denotes the azimuthal angle for rotation with respect to the surface normal in the samples coordinates (x, y, z), where the y-axis represents the direction of the polarization of irradiation for the photo-treatment process, x is perpendicular to the y-axis in the incident plane, and z is the normal direction of the film surface. To get consistent experimental results of surface SHG from the monolayer before and after the photo-
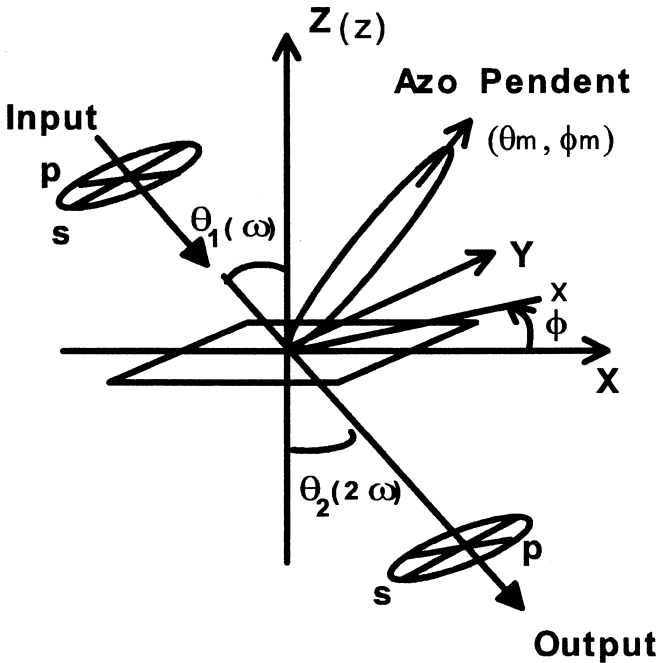
irradiation, we set the incident angle of photo-irradiation for photo-isomerization to be 45° in the $X-Z$ plane without perturbing surface SHG experiments.

For a rod-like molecule such as the azo-pendent group, the second-order hyperpolarizability is dominated by a single element $\beta_{\xi\xi\xi}$ along the long ξ-axis of the chromophore [36]. Then the monolayer of such molecules on a surface has a nonlinear susceptibility tensor $\boldsymbol{\chi}^{(2)}$ [33, 34] given by

$$\chi_{ijk}^{(2)} = N_s < (\boldsymbol{i} \cdot \boldsymbol{\xi})(\boldsymbol{j} \cdot \boldsymbol{\xi})(\boldsymbol{k} \cdot \boldsymbol{\xi}) > \beta_{\xi\xi\xi}^{(2)}, \tag{1}$$

where N_s is the surface molecular density, $(\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k})$ refer to the unit vector of the samples coordinates (x, y, z), and the angle brackets denote the orientational average weighted by a distribution function F.

An ensemble of rod-like molecules can be described in terms of a $\boldsymbol{\chi}^{(2)}$ tensor of only six independent components in general:

$$\chi_1 = \chi_{zzz} = N_s \langle \cos^3 \theta_m^{(2)} \rangle \beta_{\xi\xi\xi}^{(2)}, \tag{2}$$

$$\chi_2 = \chi_{xxx} = N_s \langle \sin^3 \theta_m \cos^3 \phi_m \rangle \beta_{\xi\xi\xi}^{(2)}, \tag{3}$$

$$\chi_3 = \chi_{zyy} = \chi_{yzy} = \chi_{yyz}$$
$$= N_s \langle (\cos \theta_m - \cos^3 \theta_m)(1 - \cos^2 \phi_m) \rangle \beta_{\xi\xi\xi}^{(2)}, \tag{4}$$

$$\chi_4 = \chi_{zxx} = \chi_{xzx} = \chi_{xxz}$$
$$= N_s \langle (\cos \theta_m - \cos^3 \theta_m) \cos^2 \phi_m \rangle \beta_{\xi\xi\xi}^{(2)}, \tag{5}$$

$$\chi_5 = \chi_{zxz} = \chi_{zzx} = \chi_{xzz}$$
$$= N_s \langle (\sin \theta_m - \sin^3 \theta_m) \cos \phi_m \rangle \beta_{\xi\xi\xi}^{(2)}, \quad \text{and} \tag{6}$$

$$\chi_6 = \chi_{xyy} = \chi_{yxy} = \chi_{yyx}$$
$$= N_s \langle \sin^3 \theta_m (\cos \phi_m - \cos^3 \phi_m) \rangle \beta_{\xi\xi\xi}^{(2)}, \tag{7}$$

where θ_m is the polar angle between the molecular ξ-axis and the samples coordinate z-axis and ϕ_m is the azimuthal angle between ξ-axis and the x-axis. The six independent NLO coefficients of $\boldsymbol{\chi}^{(2)}$ are determined by measuring the SHG intensity from the monolayer as a function of sample rotation about its surface normal.

Figure 4a and b show the SHG results from the monolayers before and after irradiation, respectively, for four different polarization combinations. The radial length represents the square root of SHG intensity and the azimuthal angle is the angle between the x and X directions. In the case of the Azo-PA monolayer before irradiation, the s-polarized SHG signals are not allowed and the p-polarized signals are isotropic, as shown in Fig. 4a. From the theoretical best fit to the experimental data, assuming C_{1v} symmetry (filled circles in the figure) with appropriate local field factors [34], we were able to determine the relative values of $\boldsymbol{\chi}^{(2)}$ elements to be given by $\chi_1 : \chi_2 : \chi_3 : \chi_4 : \chi_5 : \chi_6 = 1 : 0 : 0.83 : 0.83 : 0 : 0$. Here, it is noted that $\chi_2 = \chi_5 = \chi_6 = 0$ and $\chi_3 = \chi_4$, which indicates that the Azo-PA LB film exhibits $C_{\infty v}$ symmetry.

After irradiation, the SHG profiles from the monolayer have dramatically changed. Unlike the unirradiated case, the irradiated Azo-PA film generates s-polarized SHG signals and p-polarized signals that are anisotropic, as shown in Fig. 4b. The anisotropic SHG responses under rotation directly reflect the symmetry properties of the photo-irradiated monolayer. Moreover, the different SHG responses
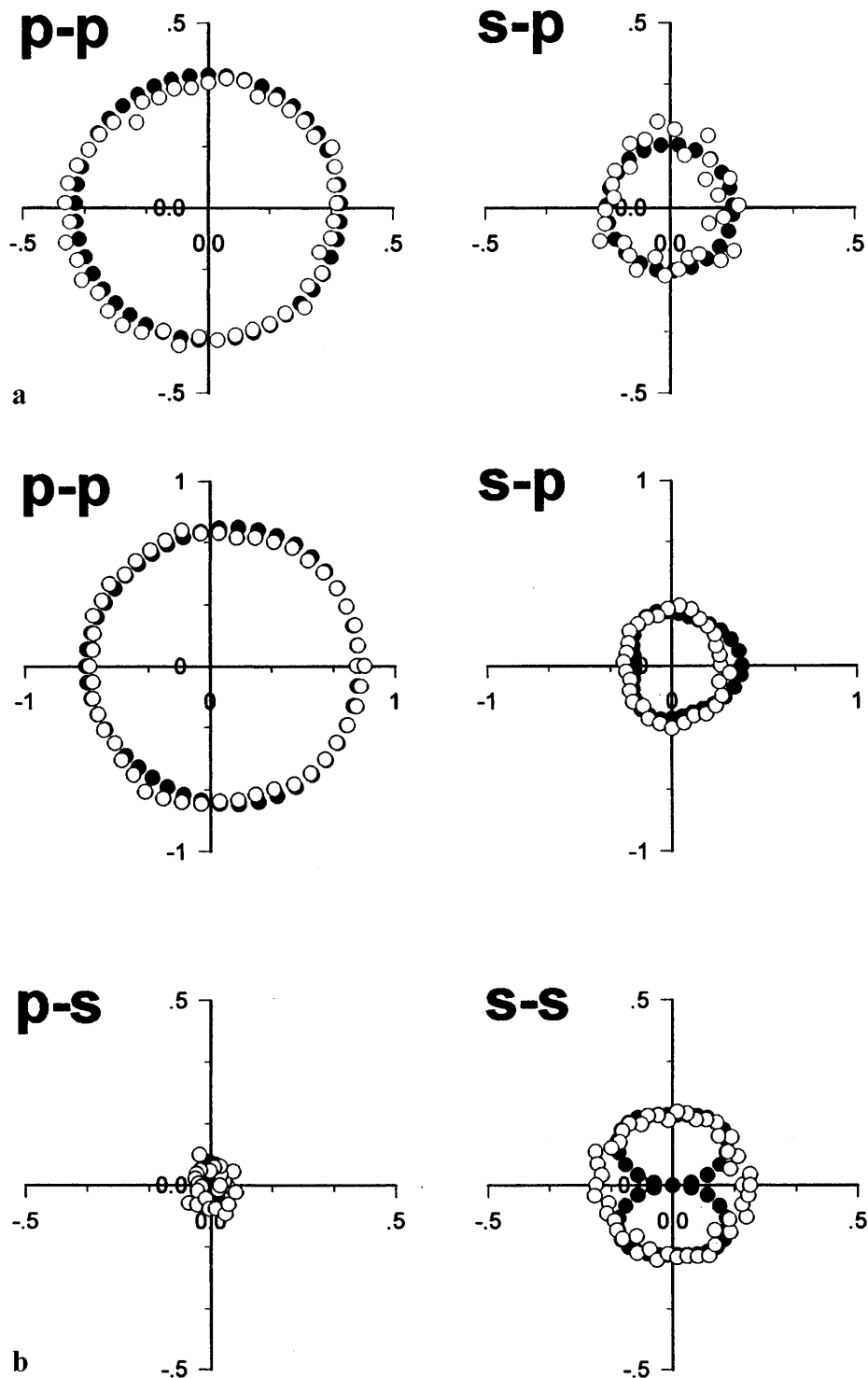

Fig. 3. Geometry of the experimental setup for surface SHG used in this study. (X, Y, Z) are the laboratory coordinates and $\theta_1(\omega)$ is the incident angle between the surface normal and the propagation direction of the incident light. ϕ denotes the azimuthal angle of rotation with respect to the surface normal

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Fig. 4a,b. Square root of SHG intensities from the Azo-PA monolayer film before (**a**) and after (**b**) the photo-irradiation process. *Open circles* are experimental data and *filled circles* are the theoretical fits. *p-p* means a *p*-in-*p*-out polarization combination, etc

for $\phi = 0°$ and $\phi = 180°$ reflect directly the preferential alignment of the azo-pendent units along the x-axis. The best-fitted theoretical data under C_{1v} symmetry is plotted by filled circles in Fig. 4b. From the fit, we determine the relative values of $\chi^{(2)}$ elements to be given by $\chi_1 : \chi_2 : \chi_3 : \chi_4 : \chi_5 : \chi_6 = 1 : 0.21 : 0.43 : 0.50 : 0 : 0.14$.

Therefore, it is clear that the photo-irradiation process by the linearly polarized (y-direction) 488 nm light transforms the azo-pendent units from $C_{\infty v}$ to C_{1v} symmetry, with the preferred direction along the x-axis.

3 Orientational distribution function

With the NLO coefficients determined above, it is possible to estimate the orientational distribution function $F(\theta_m, \phi_m)$ of the molecules by using the maximum entropy method [37,38]. The complete orientational distributions as a function of θ_m and ϕ_m for the azo-pendent units are plotted in Fig. 5. In the case of the Azo-PA monolayer before the irradiation process, the azo-pendent units exhibited an azimuthally isotropic distribution (Fig. 5a left and right). If

surface anisotropy order parameters measuring the in-plane orientational distribution, $\langle\cos 2\phi_m\rangle$ and $\langle\cos\phi_m\rangle$, are introduced, we have that $\langle\cos 2\phi_m\rangle$ describes the degree of in-plane ordering intermediate between completely isotropic (0) and completely ordered (1), and $\langle\cos\phi_m\rangle$ represents the parallel/antiparallel asymmetry of orientation for the azo pendent units. For isotropic distribution $\langle\cos\phi_m\rangle$ is zero, and for complete parallel ordering $\langle\cos\phi_m\rangle$ is 1. We find both order parameters are zero when corresponding to the isotropic orientations. It is thus confirmed that the orientation of parallel/antiparallel to the x-direction is symmetric for the azo pendent units.

Other surface order parameters, relating to the polar angle distributions of azo pendent units, are $\langle\cos\theta_m\rangle$ and $\langle\cos^2\theta_m\rangle$, corresponding to the polar and axial order parameter with respect to the surface normal direction (z). For the mono-layer before irradiation, the obtained value of $\langle\cos\theta_m\rangle$ is 0.56, $\langle\cos^2\theta_m\rangle$ is 0.33, and the major molecular tilt angle is found at $\theta_m = 54.7°$ with a half-width $\Delta\theta$ of 25°. Therefore, it is clear that the orientation of azo pendent units is more highly polar-ordering than axial-ordering.

After the irradiation process, the azo pendent units exhibit an azimuthally anisotropic distribution (Fig. 5b left and right). As shown in the figure, the azo pendents are effectively aligned along the x-direction ($\phi_m = 0°$ and $\phi_m = 180°$), perpendicular to the polarization of the irradiated light. The surface anisotropy order parameter $\langle\cos 2\phi_m\rangle$ and $\langle\cos\phi_m\rangle$ for azo pendent units are increased from zero to nearly 0.20 and 0.10, respectively. These values clearly indicate that a significant number of azobenzene units are reoriented and realigned parallel to the x-direction after the photo-isomerization process. Moreover, it is found that the molecular tilt of azo-pendent molecules is asymmetrically centered at $\theta_m = 50.4°$ with $\Delta\theta$ at 53° and at $\theta_m = -42.3°$ with $\Delta\theta$ of 66°. This is quite different from the molecular tilt before irradiation. It is also found that the surface polar angle order parameters are also increased, with $\langle\cos\theta_m\rangle = 0.56$ and $\langle\cos^2\theta_m\rangle = 0.41$. These results indicate that the azo pendent units after irradiation are more highly axially ordered than those before irradiation. Therefore the LC molecules may effectively align along the x-direction.

As shown in these figures, it is clear that there exists asymmetry of orientational distribution between x and $-x$ after irradiation, and there are two possible explanations for this. One is the formation of aggregates of the azobenzene moiety during the photo-isomerization. However, we used
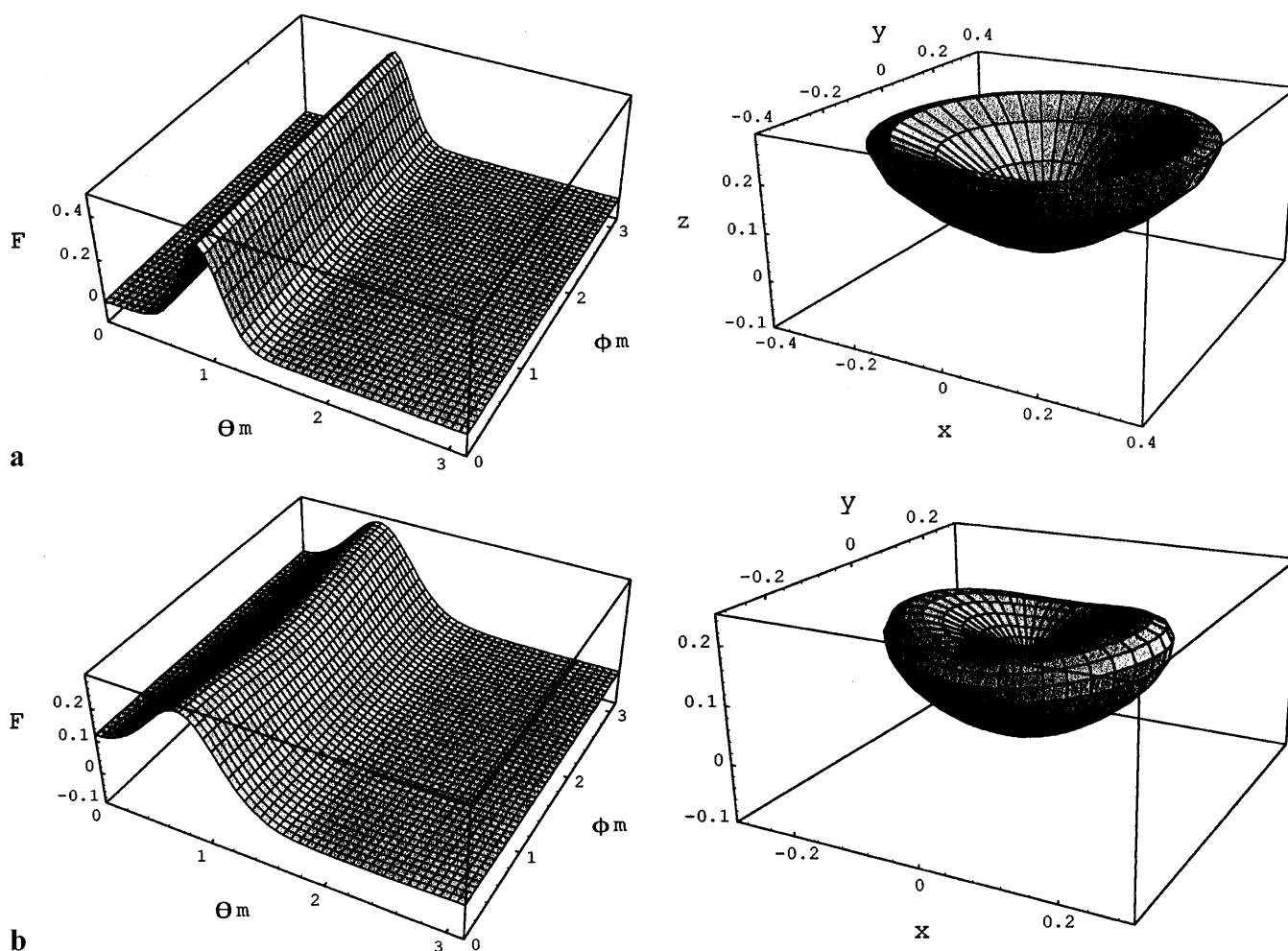

Fig. 5a,b. The orientational distribution function $F(\theta_m, \phi_m)$ of the azo-pendent units before (**a**) and after (**b**) the photo-irradiation process as a function of polar (θ_m) and azimuthal (ϕ_m) angles. Since the (ϕ_m, F) plane is a mirror plane of this monolayer, the half-region given by $\phi_m = \pi$ to $\phi_m = 2\pi$ is omitted. 3D graphs on the *right-hand side* are spherical polar plots of the 3D maps on the *left-hand side*

a dilute solution and transferred the monolayer on the substrate at the surface pressure just before the solid state monolayer; thus, it is considered that the azobenzene moiety could not aggregate during the photo-isomerization process. The other explanation of the asymmetry is an effect of inclined (45°) irradiation of polarized 488 nm light to the LB film. The azobenzene moieties tend to reorient in the plane perpendicular to the polarization of irradiated light. Thus, the azobenzene molecules orient preferably into the x direction. A detailed study of asymmetry dependence on the incident angle of irradiation for photo-isomerization is in progress and will be reported elsewhere in due course.

4 The isomer state

Finally, in order to identify the isomer state after the irradiation process, the values of the optical hyperpolarizability $\beta_{\xi\xi\xi}$ of azo pendent units were deduced from the relationship given in (1) between macroscopic χ and microscopic $\beta_{\xi\xi\xi}$. Before the irradiation process of the monolayer, the values of $\beta_{\xi\xi\xi}$ were estimated at nearly 4.1×10^{-28} esu, which is of the same order as the value (1.3×10^{-28} esu) of the Disperse Red azobenzene molecule [39]. We consider that this value comes from the trans-isomer of azobenzene pendent units because trans-isomer is more stable than cis-isomer at room temperature.

After the irradiation process, the estimated $\beta_{\xi\xi\xi}$ value is 4.4×10^{-28} esu, which is nearly the same as the value before the process. This indicates that the final isomer state of the azo-pendent unit is trans-isomer after the irradiation process, because the $\beta_{\xi\xi\xi}$ value of cis-isomer is about one-fifth lower than that of trans-isomer due to the conformational change [40]. To examine the utility of this photo-irradiation process, a nematic LC cell was fabricated with photo-irradiated monolayers as an LC alignment layer and it exhibited a good homogeneous alignment, as shown in Fig. 6.
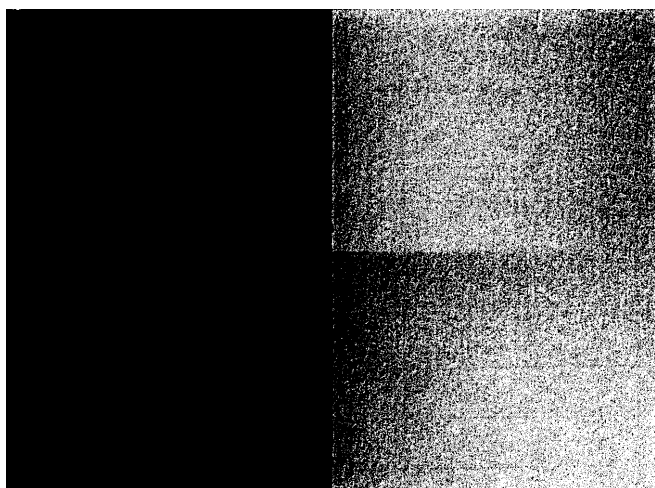

Fig. 6. Photographs of a cell containing nematic LC (ZLI-2293) with the photo-processed Azo-PA monolayers as an alignment layer between crossed polarizers. Azimuthal rotation angle $= 0°$ (*top-left, Dark*), 45° (*top-right, Bright*), 90° (*lower-left, Dark*), and 135° (*lower-right, Bright*)

5 Conclusions

In summary, we have studied the surface SHG from the LB monolayers of photo-isomerizable side-chain-substituted polyamic acid before and after a photo-irradiation process. We have found that the irradiation of linearly polarized light transforms the symmetry group of the monolayer film from $C_{\infty v}$ to C_{1v}. From the measured values of the second-order NLO coefficients, the complete orientational distribution function of the monolayer can be determined quantitatively.

From the orientational distribution function, we have found that azobenzene units of the polymer reorient along the preferred direction perpendicular to the plane of irradiation. We have also obtained the surface order parameters of the monolayer, which resemble the anisotropic properties of the monolayer film. Moreover, we have found that the trans-isomer is the final mode of azobenzene units after the photo-isomerization process.

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