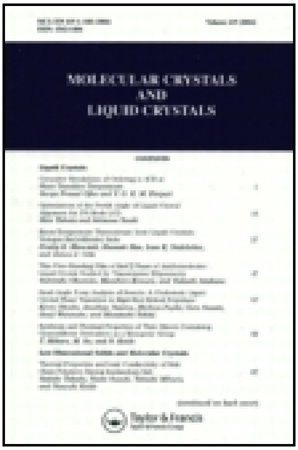

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Photo-Isomerization Effects on Orientations of Azobenzene-Labeled Polymer Films Measured by Second Harmonic Generation

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PHOTO-ISOMERIZATION EFFECTS ON ORIENTATIONS OF AZOBENZENE-LABELED POLYMER FILMS MEASURED BY SECOND HARMONIC GENERATION

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Abstract We have studied the changes in the orientational distribution functions of azobenzen-labeled polyamic acid monolayers before and after photoisomerization by measuring optical second-harmonic generation (SHG). From the surface SHG data, we determined the nonlinear-optical tensor components of the monolayers before and after the photo-isomerization. It is found that the point symmetry of the azo-pendant units in the monolayer changes from $C_{\infty v}$ *to* C_{1v} by the photo-isomerization.

INTRODUCTION

Photo-sensitive polymers have been extensively studied because of their considerable interests from both fundamental and practical viewpoints such as optical information storage, holography, and optical switching devices.[1] Among them, the use of photoisomerizable polymers containing azobenzene (Azo) units has stimulated a significant interest.[2] This is mainly due to the possibility of the optical control of the orientation of Azo units through the multiple trans-cis photo-isomerization process.

However, the surface structure of photo-processed polymer is not clearly presented yet. In the present work, we have investigated the microscopic surface structure of photo-processed Langmuir-Blodgett (LB) monolayer by using surface second harmonic generation (SHG)[3].

EXPERIMENTAL

The polymer used for this study is a poly(amic acid) containing pendent azo-dye and (long alkyl) amine (N-icosylpyrrolidine) (Azo-PA)[4]. Azo-PA monolayers were deposited onto quartz substrates with an LB technique. A closely packed monolayer was deposited into Z-type layer on the substrate. The photo-isomerization was achieved by irradiation of a linearly polarized (x-axis) 488 nm light from Ar-ion laser.

The SHG experiments were performed using a fundamental beam (1064 nm) of a Q-switched Nd:YAG pulsed laser with a pulse energy of 8 mJ. The incident beam was directed onto the LB sample at an incident angle of 45°. All sample preparations and measurements were performed at room temperature of $25°C$.

RESULTS AND DISCUSSION

For a rod-like molecule as the pendanting Azo unit, the second-order polarizability is dominated by a single element $\beta_{\xi\xi\xi}$ along the long axis, ξ, of the chromophore.[3] An ensemble of rod-like molecules can be described in terms of a $\chi^{(2)}$ tensor of only six independent components for the general C_{1v} configuration. The six independent NLO coefficients of $\chi^{(2)}$ are determined by measuring the SHG intensity as a function of sample rotation about its surface normal for four different input-output polarization combinations, p-p, p-s, s-p, and s-s.

Before the photo-isomerization, it is observed that the s-polarized SHG signals from the Azo-PA monolayer are forbidden and the p-polarized signals are isotropic. From the experimental data, we determine the relative values of $\chi^{(2)}$ elements to be : $\chi_1 : \chi_2 : \chi_3 : \chi_4 : \chi_5 : \chi_6 = 1 : 0 : 0.83 : 0.83 : 0 : 0$, which indicates that the Azo-PA LB film exhibits $C_{\infty v}$ symmetry.

After the photo-process, the SHG profiles have dramatically changed. Unlike the unirradiated case, the irradiated film generates s-polarized SHG signals and the p-polarized signal are anisotropic. We determine the relative values of $\chi^{(2)}$ elements to be : $\chi_1 : \chi_2 : \chi_3 : \chi_4 : \chi_5 : \chi_6 = 1 : 0.21 : 0.43 : 0.50 : 0 : 0.14$. Therefore, it is clear that the photo-process by the linearly polarized light transforms the Azo-pendant units from $C_{\infty v}$ to C_{1v} symmetry.

We then determine and plot the complete orientational distribution function (ODF) $f(\theta_m, \phi_m)$ in Fig. 1 using the maximum entropy method[5]. Here, θ_m is the polar angle between molecular axis ξ and the normal direction (z axis) of the film and ϕ_m is the azimuthal angle between ξ and x axis.

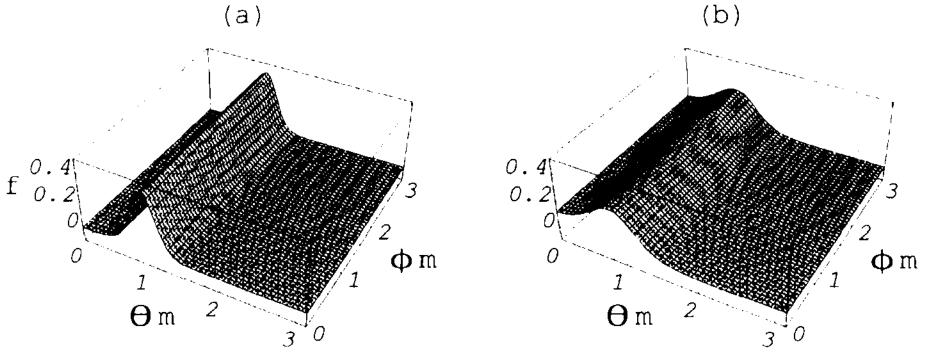

FIGURE 1 The ODF of Azo units before (a) and after (b) the photo-process.

In the case of Azo-PA monolayer before the photo-process (Fig. 1 (a)), the Azo units exhibited an azimuthally isotropic distribution. The major molecular tilt angle distributions are found at $\theta_m = 54.7°$ with a half-width $\Delta\theta$ of 25°. After the photo-process, the Azo units exhibit an anisotropic distribution (Fig. 1 (b)). As shown in the Figure, the Azo-pendants are effectively aligned along the x-axis, perpendicular to the polarization of the irradiated light. It is also found that the molecular tilt of Azo units are unsymmetrically centered at $\theta_m = 50.4°$ with $\Delta\theta$ of 53° and $\theta_m = -42.3°$ with $\Delta\theta$ of 66°.

The value of $\beta_{\xi\xi\xi}$ of Azo-pendant units can be deduced from the microscopic and macroscopic relation of NLO coefficients.[5] Before the photo-process, $\beta_{\xi\xi\xi}$ of Azo-pendent is estimated nearly 3.5×10^{-29} esu. We consider that this value comes from the trans-isomer units because a trans-isomer is more stable than a cis-isomer under the room temperature. After the process, the estimated $\beta_{\xi\xi\xi}$ value is 3.8×10^{-29} esu, which is nearly the same as the value before the process. This indicates that the final isomer state of the Azo unit is trans-isomer after the process, because $\beta_{\xi\xi\xi}$ value of the cis-isomer is known to be about 1/5 times lower than that of the trans-isomer[6].

CONCLUDING REMARKS

We have studied the surface SHG from the LB monolayers of photo-isomerizable polyamic acid before and after the photo-process. It is found that the irradiation of linearly polarized light on the monolayer transforms the symmetry group of the azo-pendent from $C_{\infty v}$ to C_{1v}. The orientational distribution function of the azo-pendent group is also determined quantitatively. It is also found that the trans-isomer is the final mode of azobenzene units after the photo-process.

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