Photoinduced Birefringence in Poly(malonic ester) Containing *p*-Cyanoazobenzene with Photoexcitation of cis Conformer

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Photoinduced birefringence in a poly(malonic ester) containing two symmetrical *p*-cyanoazobenzene groups has been investigated using two pumping beams with different wavelengths of 365 and 488 nm, which are assignable to the absorption wavelengths of trans and cis conformers of azobenzene, respectively. We observed unexpected photoinduced birefringence even by the pumping beam of 488 nm as large as that by 365 nm. To describe such specific phenomenon, we measured the magnitude and direction of the induced birefringence by means of a new experimental setup, adding $\lambda/4$ waveplate between the polymer film and the analyzer of conventional a pair of crossed polarizers setup. The measurement of the photoinduced phase retardation by simultaneous illumination with two perpendicularly polarized beams of 365 and 488 nm supports the fact that there is another process for the photoinduced birefringence besides a typical trans—cis photoisomerization of azobenzene.

Introduction

Recently, polymeric materials have been suggested as the most promising materials for optical data storage and optical information process applications.^{1–3} There are many organic photoresponsive materials, including photopolymers, photorefractive polymers, LB films, and the polymers containing azobenzene group in the side-chain or main-chain. Among them, in particular, the azobenzene containing side-chain polymers have been studied intensively due to their large nonlinearity and reversibility in data storage.

In general, storage or processing of an optical information in the azo-polymers results from the photoinduced birefringence caused by the alignment of azobenzene mesogenic group. As is well-known, the alignment occurs as a result of the angular selective trans-cis and cis-trans photoisomerization of azobenzene group or its thermal isomerization.³⁻⁵ The isomerization from rod-shaped trans conformer of azobenzene to bent-shaped cis one takes place only by the photochemical excitation, whereas both photochemical excitation and thermal relaxation can drive the cis-trans isomerization. The orientational photoinduced birefringence procedure is represented simply as follows: The linearly polarized pumping beam illuminating on the polymer film converts the trans conformer to the cis one, which is proportional to the square of the cosine of the angle θ between the polarization axis of pumping beam and the symmetry axis of rod-shaped trans conformer. The photoexited cis conformer goes back to trans conformer with nonangular selectivity by means of thermal relaxation or photochemical process. As a result of repetitive cycles of trans-cis-trans isomerization, anisotropic angular distribution of trans conformer is induced by the illumination of the linearly polarized light.⁶

We have reported an abnormal phenomenon in the relaxation process of photoinduced birefringence, which could not be

explained by the conventional theory for the photochemical or thermal isomerization. We proposed a new interpretation for the relaxation process on the basis of elastic force between neighboring molecules in our previous paper.⁷

In the present article, we reports the photoinduced birefringence in poly(malonic ester) containing *p*-cyanoazobenzene group using two pumping beams with different wavelengths of 365 and 488 nm, which are assignable to $\pi - \pi^*$ transition of the trans conformer of azobenzene and $n - \pi^*$ transition of the cis form, respectively.^{8,9} Unexpected photoinduced birefringence was observed by the pumping beam of 488 nm. To describe such specific phenomenon, a novel experimental setup was introduced and the results were analyzed on the basis of the conventional photoisomerization theory.

Experiments

As optical recording media, novel liquid crystalline (LC) sidechain poly(malonic ester) was prepared according to the reported procedure shown in Figure 1.10 New thermotropic LC malonic ester compound (MCN) was first synthesized by reacting in chloroform for 48 h at 5 °C malonyl dichloride and mesogenic alcohol (mp 142 °C) with p-cyanoazobenzene. The yield and melting temperature of the MCN were 46% and 95 °C, respectively. It was observed by means of differential scanning calorimetry for the MCN monomer to show a smectic structure on both heating and cooling cycles. The phase transition temperatures to LC state appeared at 63 and 90 °C, respectively, on the heating and cooling cycles. The isotropization temperatures were 95 and 55 °C, respectively. In the phase transition temperatures, a large value of supercooling between the heating and cooling cycles might be due to the rapid cooling rate (average rate: 30 °C/min) of the equipment and also to the complicated structural change with temperature of the monomer.



Figure 1. Synthesis route for poly(malonic ester), PCN.

It, however, is not clear yet and need to examine in more detail. The LC structure of the MCN was found by means of optical polarizing microscopy to show a focal-conic texture. The MCN was then condensed with 1,6-dibromohexane in tetrahydrofuran in the presence of sodium hydride at 65 °C for 48 h to give poly(malonic ester) (PCN) with two symmetrical azo dye mesogens in the side chain. The polymeric thin film (ca. 0.8 μ m) was cast from the polymer solution (5 wt %) in CHCl₃ onto a glass plate for 30 s using a spin coater.

During illumination of the pumping beam, the change of absorption spectrum of the prepared polymer film was measured using optical multichannel analyzer (OMA), which is composed of monochromator, charge-coupled display (CCD) as a photodetector and sufficiently attenuated Xe-lamp as a reading light source. The spectral resolution of the used OMA was 2 nm.

We employed a standard two-crossed polarizers setup for measuring the photoinduced birefringence in the polymer film.⁶ The color-filtered Xe-lamp and Ar^+ ion laser were used as pumping beams of 365 and 488 nm, respectively. The model of the color filter was UG.11 from Newport Company. The wavelength of the reading beam from He–Ne laser, 633 nm, is far from the absorption bands of the PCN film. The transmittance of the reading beam passing through two crossed polarizers and a polymer film placed between them was measured with a photodiode.

Temporal evolution of concentration of trans conformer in the pumping process was obtained by measuring the absorbance of the polymer film at 365 nm with exposure time. The colorfiltered Xe-lamp was used as both pumping and reading beams. To avoid any photochemical effect caused by the reading beam on the film, the intensity of the reading beam was attenuated with ND filter. On the other hand, Ar^+ ion laser of 488 nm was used as the other pumping beam with different wavelength.

By the conventional two-crossed polarizers setup, only the magnitude of birefringence can be measured without the directional information of fast-axis of a induced birefringence, but the directional information is very important for investigating the mechanism of photoinduced birefringence in the azo polymer film. Thus, the modified experimental setup was prepared to obtain the information of both magnitude and direction. That is, a quarter waveplate was added between the polymer film and the analyzer of the conventional two-crossed polarizers setup, as shown in Figure 2. The optic axis of the quarter waveplate was adjusted by 5° with respect to the polarization axis of the analyzer. Two pumping beams with different wavelengths of 365 and 488 nm were used for simultaneous illumination on the polymer film.

Results and Discussion

Figure 3 shows the change of the absorption spectrum of PCN film during the irradiation of pumping beam at 365 and 488 nm. The absorption spectrum was measured by means of OMA. The PCN film has two broad absorption bands. As is wellknown, the larger absorption band around 362 nm is due to the trans conformer of azobenzene and the much smaller one around 450 nm is due to the cis one. The color-filtered Xe-lamp with center wavelength of 365 nm and Ar⁺ laser beam of 488 nm were used for pumping trans and cis conformers of azobenzene, respectively. As shown in Figure 3a, the absorption band of trans conformer rapidly decreased with the irradiation time of the pumping beam of 365 nm. However, the band of cis one increased gradually with increasing the exposure time. Photostationary state of the concentration of trans and cis forms was approached after irradiating over 30 s. On the other hand, when the pumping beam of 488 nm was irradiated, the absorption bands of both trans and cis conformers remained unchanged as



Figure 2. Experimental setup for measurements of the photoinduced phase retardation of PCN thin film. The inset shows the angle δ between the fast axis of $\lambda/4$ waveplate and the polarization axis of analyzer.



Figure 3. UV absorption spectra of the PCN film after irradiation by pumping beams of (a) 365 and (b) 488 nm.

shown in Figure 3(b). These results mean that the initial concentration of unstable cis conformer is very low, and also that the rate constant of photochemical trans—cis transition by the pumping beam of 488 nm is fairly small.

Temporal evolution of the concentration of trans conformer in the pumping process was measured through the absorbance of the polymer film at 365 nm. The photoinduced birefringence in our PCN film mainly results from the reorientation of trans form, so that the angular distribution of the concentration of trans conformer in pumping process offers a molecular dynamics of the trans conformer of azobenzene. In other words, we can easily estimate the angular distribution of the concentration of trans conformer from Figure 4. The absorbance of PCN film was measured with the exposure time, while the polarization axis of the linearly polarized reading beam is rotated discretely from 0 to 90° with respect to that of the pumping beam. As the pumping beam of 365 nm was illuminated, the absorbance curves totally decreased due to the large photochemical transcis isomerization rate and they showed an angular sinusoidal distribution of trans conformer, which is responsible for the birefringence of the polymer film. On the other hand, as the pumping beam of 488 nm was illuminated, the absorbance curves decreased at the parallel direction to the polarization axis of the pumping beam, but increased at the perpendicular direction. The average absorbance of all angles did not change during illumination of the pumping beam of 488 nm. Hence, this supports that the photochemical trans-cis isomerization occurred very weakly at the wavelength of pumping beam.

Figure 5 shows the photoinduced birefringence of the PCN film measured by pumping beams of 365, 488 and 514.5 nm. The pumping beams of 488 and 514.5 nm as well as 365 nm induced the optical birefringence. It is noticeable that the magnitude of the induced birefringence by the pumping beam



Figure 4. Time evolution of the absorbance of the PCN film with angle between the polarization axes of the pumping and reading beams, during pumping at (a) 365 and (b) 488 nm. The angle increased from 0° to 90° by 10° .



Figure 5. Photoinduced birefringence in pumping at 365, 488 and 514.5 nm onto the PCN film. The intensity of the pumping beams was 2 mW/cm².

of 488 nm is comparable to that by the pumping beam of 365 nm: The photoinduced birefringence by the pumping beam of 365 nm matches well with the conventional trans-cis photoisomerization theory of azobenzene. However, in the case of pumping at 488 and 514.5 nm, those results were beyond our expectation. Since the energy of the pumping beam at 488 and 514.5 nm is lower than the energy required for $\pi - \pi^*$ transition of a trans conformer of azobenzene, it is impossible for the trans form to be excited to the cis one by illuminating with those pumping beams.^{8,9} Nevertheless, the illumination at 488 and 514.5 nm produced the photoinduced birefringence resulting from the alignment of trans conformer, without the repetitive cycles of trans-cis-trans isomerization. But we cannot confirm that any trans-cis photoisomerization did not occur at all by



Figure 6. Photoinduced phase retardation of the PCN thin film. Curve A is irradiated at 365 nm (45°), curve B at 488 (-45°), curve C at 365 (45°), and 488 nm (-45°), and curve D is calculated from the sum of curves A and B.

the pumping beam of 488 nm, although the wavelength of the pumping beam was out of the absorption band of trans conformer.

Consequently, we are not sure whether the explanation on the basis of a typical photoisomerization theory of azobenzene is right or not. To describe the unexpected results, we designed new experimental setup shown in Figure 2 by adding a $\lambda/4$ waveplate and a pumping beam with different wavelength and polarization into the conventional two-crossed polarizers setup. When the birefringence was induced by pumping beam with the polarization axis of 45° or -45° , the transmitted intensity increases or decreases, respectively. The transmittance can be represented by¹¹

$$\frac{I_{\text{out}}}{I_{\text{in}}} = \frac{1}{2} \left(2\sin^2 \frac{\Gamma}{2} + \sin\Gamma\sin 2\delta + \sin^2 2\delta\cos\Gamma \right)$$
(1)

where δ is the angle between the optic axis of the $\lambda/4$ waveplate and the polarization axis of the analyzer, and Γ is the phase retardation occurred through the polymer film and it is defined as the difference of the phase delays in $\Gamma = (n_s - n_f)\omega l/c$.¹¹

The polarization axis of the pumping beam of 365 nm was 45° with respect to the polarization axis of the analyzer and that of the other pumping beam of 488 nm was -45° . The pumping beams will reorient the mesogenic azobenzene groups in the PCN film perpendicularly with respect to their polarization axis. Thus, if the two pumping beams illuminate simultaneously on the film, the main direction of the reoriented mesogenic groups will be determined by the competition reaction between the two pumping beams.

Figure 6 shows the photoinduced phase retardation curves at various pumping conditions. When the pumping beam of 365 nm was illuminated on the PCN film, the phase retardation increased gradually with positive sign, as shown in Figure 6A. By the pumping beam of 488 nm, the phase retardation decreased with negative sign (Figure 6B). The sign, positive or negative, of the phase retardation indicates the direction of the mesogenic azobenzene groups. As mentioned earlier, it is well-known that the photoinduced birefringence occurs through the repetitive trans–cis–trans isomerization cycles. The birefringence induced by the pumping beam of 488 nm is attributed to large optical cis–trans isomerization rate and very small trans–cis isomerization rate. On the other hand, the birefringence by 365 nm is attributed to large optical trans–cis isomerization rate with the angular selectivity and large (or not small) cis–

trans one. Thus, when the two pumping beams were illuminated simultaneously on the PCN film, the large trans-cis isomerization rate by pumping at 365 nm and the large cis-trans isomerization rate by pumping at 488 nm could be expected. In this case, the main direction of the aligned azobenzene group would be determined by the competition of the optical transcis isomerization rate derived from each pumping beam. Although the intensity of the pumping beam of 365 nm was the same as that of 488 nm, the trans-cis isomerization rate derived from the 365 nm should have a much larger value than that from the 488 nm, because the absorbance of the trans conformer of azobenzene at 365 nm is over 10 times higher than that at 488 nm. Therefore, it is obvious that the main direction of the aligned azobenzene group has to be perpendicular to the polarization axis of the pumping beam of 365 nm and the magnitude of the phase retardation should remarkably increase rather than that induced only by the pumping beam of 365 nm. However, the photoinduced phase retardation by the two pumping beams was nearly zero, as shown in Figure 6. It is impossible to explain the above results utilizing the mechanism of the repetitive trans-cis-trans isomerization. The phase retardation for the simultaneous pumping with the two beams was nearly the same to the numerical sum of the phase retardations induced independently by each pumping beam.

Unfortunately, it is not clear yet what the photoreorientation mechanism induced by pumping at 488 nm proceeds exactly. As far as we know, the mechanism seems to be related with the permanent and field-induced dipole moment of azobenzene molecules and the photomolecular resonant interaction. In liquid crystal molecules, the Freedericksz transition is a typical photomolecular interaction, but it exhibits large threshold pumping intensity of around 150 W/cm². ¹² Recently, it has been reported that the threshold pumping intensity for the Freedericksz transition decreases greatly in azobenzene doped polymers.¹³ We need to carry out the studies on the interaction between the molecule and optical field to establish the mechanism of the birefringence induced by pumping at the absorption band of cis conformer of azobenzene.

Conclusion

We investigated the photoinduced birefringence of poly-(malonic ester) containing p-cyanoazobenzene group by the pumping beams at 365 and 488 nm, which are responsible for the photoexcitations of trans and cis conformers of azobenzene, respectively. From the measurements of the change of absorbance in pumping at 365 and 488 nm, the optical trans-cis isomerization rate by pumping at 488 nm was found to be very small. Nevertheless, the birefringence was induced by pumping not only at 365 nm, but also at 488 and 514.5 nm. According to the trans-cis photoisomerization theory, the trans-cis-trans cycles could be occurred due to large rate constant of optical cis-trans isomerization, although trans-cis isomerization is very weak. In the measurement of the photoinduced phase retardation by simultaneous illumination with two perpendicularly polarized beams of 365 and 488 nm, the magnitude of phase retardation was very small and the main direction of the aligned mesogenic azobenzene group was not perpendicular to the polarization of the pumping beam of 365 nm unlike our expectation. These results cannot be explained by the mechanism of the trans-cis-trans photoisomerization reported so far. Such an unexpected phenomenon for the reorientation effect of the mesogenic group is not clear yet, but it seems to be related with the permanent and field-induced dipole moment of azobenzene molecules and the photomolecular resonant interaction.

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