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A Simple Method for the Monitoring of Photo-induced Alignment of the Azobenzene Molecules in a Poly(malonic ester)

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Abstract

A simple method for real-time monitoring the molecular orientation in a polymeric film was suggested. This method was examined in the polarization holograms by two recording beams on a poly(malonic ester) containing disperse red 1. The spatial distributions of the photo-induced alignment were measured and analyzed at various polarization states of two recording beams. As the result, the directions of molecular alignments could be identified easily by our method.

1. Introduction

Many research groups have been interested in polymers containing azobenzene molecules, because it has the merits of fabrication, high birefringence, and reversibility for optical data storage [1]. The origin of optical data storage in the azobenzene polymers is based on the photo-induced alignment of azobenzene molecules [2]. Therefore, dynamic behavior of the alignment of the azobenzene molecule is an important factor for improving the performance of the azobenzene polymer as optical data storage medium. Several methods have been used for investigating the photo-induced birefringence and surface relief grating (SRG), such as polarization double-exposure holographic interferometry, microscope, AFM and SEM. But, these methods have some problems for the real-time investigation on the photo-induced alignment.

In this paper, a simple method for real-time monitoring of the photo-induced molecular alignment in a photo-isomerization polymer was suggested. The spatial distribution of induced birefringence was measured for the various polarization states of two recording beams, and the intensity profiles were compared with each other. Finally, the directions of alignments of azobenzene groups were analyzed and determined.

2. Experimental

An experimental setup for obtaining the image of the photo-induced birefringence *in situ* and analyzing the direction of alignment of azobenzene groups was prepared (Fig. 1). The polymer used in our experiment was a poly (malonic ester) (PDR1) with two symmetrical disperse red 1. The synthesis procedure and the absorption spectrum of the polymeric film are described in Ref. [3]. The sample was irradiated with two recording beams from a Nd:YAG laser(532 nm) for generating periodic photo-induced birefringence. The angle between the two beams was about 2.5°. A He-Ne laser(633 nm) was used for obtaining the image of the photo-induced birefringence. On the path of He-Ne laser, there was a pair of crossed polarizers which optic axes were orthogonal each other. [4] The

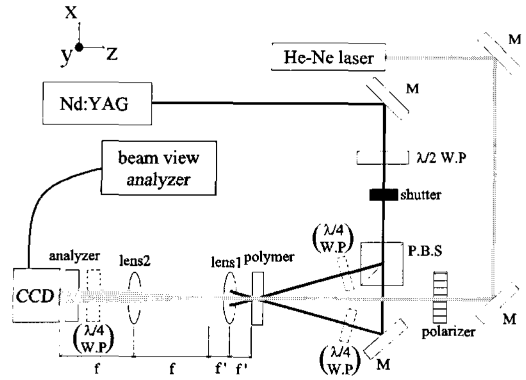

Fig. 1. Experimental setup.

detected periodic birefringence was captured with a CCD camera, and stored by a beam view analyzer (Coherent, cohu-4800). 4-f system was used for obtaining a magnified image (about 30 times) of original one and transporting the pattern from the polymer film to the CCD camera. A $\lambda/4$ waveplate was inserted between the polymer film and the analyzer in order to get additional information for the alignment direction of molecule [4,5].

For simplicity, some abbreviations are used; p_{0°, p_{90°, p_{left}, and p_{right} represent the polarization state of recording beam, and the subscripts mean that the polarization states are linearly (parallel and perpendicular with x-axis) polarized and circularly (left and right) polarized, respectively. θ_{anal}, θ_{pol} and $\theta_{w.p.}$ represent the angles between x-axis and the directions of the analyzer, the polarizer and the fast axis of $\lambda/4$ waveplate, respectively. The direction of alignment of azobenzene groups expressed as A_{0°, A_{90°, A_{45°, A_{-45° and A_{random}, and the subscripts represent the angles between the direction of alignment and the x-axis.

3. Results And Discussion

In this experiment, two cases of the polarization states of recording beams were examined. One was that the polarization states of recording beams were linear and orthogonal each other(p_{0° and p_{90°,) ; the other one was that those were circular and orthogonal each other(p_{left} and p_{right}). Fig. 2 shows the spatial distributions of the polarization states along the x-axis for the two cases. These were calculated by the polarization hologram theory. As shown in the figure, the polarization state is modulated at the period of $\ell/2\sin\theta$, where θ is the angle between the two recording beams. Because the azobenzene molecules in a photo-isomerization polymer reorient perpendicularly to the laser polarization direction, we can easily determine the spatial distribution of the molecular alignment by monitoring the transmitted intensity through the polarization hologram on the polymeric film.

The captured images at the various conditions in Fig. 3 in order to demonstrate how the aligned direction of azobenzene groups could be determined.

Fig. 2. The spatial distribution of the polarization state along the x-axis on the polymeric film.

Polarization states of the recording beams		Spatial distribution of the polarization states along the x- axis								
Beam 1	Beam 2	0	$\frac{\lambda}{16\sin\theta}$	$\frac{\lambda}{8\sin\theta}$	$\frac{3\lambda}{16\sin\theta}$	$\frac{\lambda}{4\sin\theta}$	$\frac{5\lambda}{16\sin\theta}$	$\frac{3\lambda}{8\sin\theta}$	$\frac{7\lambda}{16\sin\theta}$	$\frac{\lambda}{2\sin\theta}$
↕	↔	⤢	↺	↺	↺	⤡	↻	↻	↻	⤢
↻	↺	↕	⤢	⤢	⤢	↔	⤡	⤡	⤡	↕

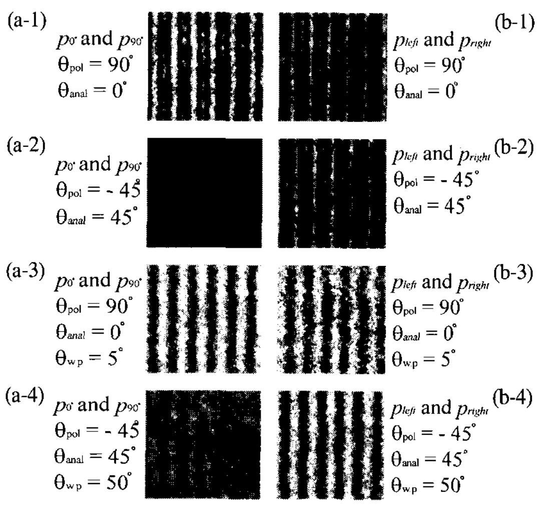

Fig. 3. The captured images by a CCD camera for various conditions : (a) the polarization states of recording beams were horizontal and vertical, and (b) the polarization states of recording beams were left and right circular.

Setup 1) θ_{pol} = 90° and θ_{anal} = 0° : The captured images of grating-a(p_{0° and p_{90°) and grating-b(p_{left} and p_{right}) are shown in Fig. 3. (a-1) and (b-1), respectively. The normalized intensity profiles of grating-a and grating-b are shown in Fig. 4. (a-1) and (b-1), respectively. In this setup, the directions of alignment were A_{45° or A_{-45° in the bright lines, and A_{random}, A_{0° or A_{90° in the dark lines. In these images, however, we cannot distinguish A_{random} from A_{0° (or A_{90°) and A_{45° from A_{-45°.

Setup 2) θ_{pol} = -45° and θ_{anal} = 45° : If the angles of polarizer and analyzer are modified to θ_{pol} = -45° and θ_{anal} = 45°, then we can identify whether A_{random} or A_{0° (or A_{90°). In this setup, the lines of A_{0° or A_{90° will be bright, since the alignment directions are at an angle of 45° with the direction of the analyzer. However, the lines of A_{random} will be dark. The captured images are shown in Fig. 3. (a-2) and (b-2). Those intensity profiles are shown in Fig. 4. (a-2) and (b-2). Therefore, the alignment directions of grating-a were A_{random} in the dark line of Fig. 3. (a-1), and A_{45° (or A_{-45°) in the bright line. The dark lines in Fig. 3. (b-1) became bright in Fig. 3. (b-2), and similarly the alignment directions of grating-b were A_{0° or A_{90° in the dark lines of Fig. 3. (b-1) and A_{45° or A_{-45° in the bright line.

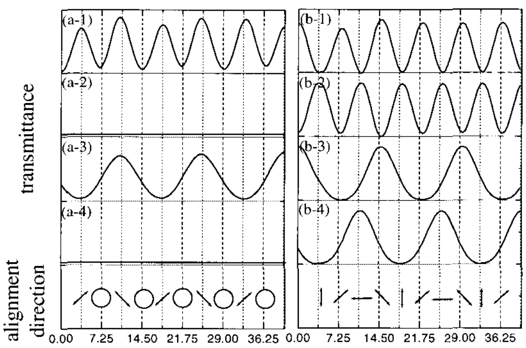

Fig. 4. The transmittances for various conditions : (a) as the polarization states of recording beams were horizontal and vertical, and (b) as the polarization states of recording beams were left and right circular.

With only the pair of the crossed polarizers, it is impossible to identify the alignment direction, whether 45° or -45°. For identifying these, the $\lambda/4$ waveplate inserted between the polymer film and the analyzer was used.

Setup 3) θ_{pol} = 90°, $\theta_{w.p.}$ = 5° and θ_{anal} = 0° : In this modified setup, if the angle between the alignment axis of azobenzene groups and the fast axis of $\lambda/4$ wave plate is bigger than the angle between the alignment axis and slow axis, the transmitted beam intensity passing through the analyzer increases. Therefore, if the alignment direction of azobenzene groups is A_{-45°, the transmitted beam intensity passing through the analyzer will increase, but decrease for A_{45°. The captured images with this modified setup are shown in Fig. 3. (a-3) and (b-3), and the intensity profiles of them are depicted in Fig. 4. (a-3) and (b-3), respectively. The patterns had a double spatial period ($\ell' \equiv 2\ell$) with respect to those in Fig. 4. (a-1) and (b-1). As a result, the bright lines were the areas of A_{-45°, and the dark lines were those of A_{45°.

Setup 4) θ_{pol} = -45° , $\theta_{w.p.}$ = 50° and θ_{anal} = 45° : In this setup, if the alignment direction of azobenzene groups is A_{0°, the transmitted beam intensity passing through the analyzer will increase, but decrease for A_{90°. The captured images are shown in Fig. 3. (a-4) and (b-4), and their intensity profiles are depicted in Fig. 4. (a-4) and (b-4), respectively. As a result, the bright lines were the areas of A_{0°, and the dark lines were those of A_{90°.

As described above, the formation of photo-induced birefringence can be monitored *in situ*, and the alignment directions of azobenzene groups can be determined within four measurements of the transmitted beam intensity. Finally, the distributions of alignment directions of azobenzene molecules for the two cases can be summarized, as the bottom of Fig. 4.

4. Conclusions

The image of photo-induced birefringence, caused by the reorientation of azobenzene groups, was obtained *in situ* with a CCD camera. The spatial distributions of polarization states for the two polarization states of recording beams were calculated. The formation of photo-induced birefringence was investigated in real time. The alignment directions of the azobenzene group were analyzed precisely within four measurements of the transmitted beam intensity. The intensity profiles of the images were compared with each other, and the directions of alignment of azobenzene groups were identified as following;

$\theta_{pol.} = 90°$ and $\theta_{anal.} = 0°$:
whether [$A_{45°}$ and $A_{-45°}$] or [$A_{0°}$, $A_{90°}$ and A_{random}]

$\theta_{pol.} = -45°$ and $\theta_{anal.} = 45°$:
whether [$A_{0°}$ and $A_{90°}$] or [A_{random}]

$\theta_{pol.} = 90°$ and $\theta_{anal.} = 0°$ and $\theta_{w.p.} = 5°$:
whether [$A_{45°}$] or [$A_{-45°}$]

$\theta_{pol.} = -45°$ and $\theta_{anal.} = 45°$ and $\theta_{w.p.} = 50°$:
whether [$A_{0°}$] or [$A_{90°}$]

Our results are applicable to the real-time study on the dynamic behavior of photo-induced birefringence and molecular alignment.

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