Optically Inscribed Grating in Azo-Carbazole Dye: Concentration Dependence*

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Investigation for the operation mechanism in writing and reading processes are necessary in order to realize practical 3D devices with azo-carbazole dyes which are promising candidates for real-time 3D displays. We made dynamical studies of four-wave mixing and two-beam coupling for dyes 3-[(4-nitrophenyl)azo]-9H-carbazole-9-ethanol (NACzEtOH) and Disperse Red (DR1) doped in a polymer and investigated their dependence on dye concentration. Results indicated the important roles of birefringence on the holographic response and stable but erasable characteristics of the gratings in the azo-carbazole. [DOI: 10.1380/ejssnt.2015.69]

Keywords: Non-linear optical method; Visible/ultraviolet absorption spectroscopy; Photochemistry; Aromatics; Amorphous thin films; Holography; Azocarbazole; Photoisomerization

I. INTRODUCTION

Azo compounds have been attracting attention due to the potential for real-time 3D displays utilizing their fast and huge optical responses caused by photoisomerization process [1–3]. Recently, azo-carbazole compounds have been studied also due to their high performance as rewritable holographic/stereographic 3D displays in the form of the polymer films containing the highly concentrated dyes [4–8]. It is necessary to elaborate the precise grating formation and erasure processes in order to realize efficient holographic system. Performance as holography would be basically determined by the depth and phase of the modulation induced by photoisomerization and following processes of which characteristics must strongly depend on optical absorbance, concentration of chromophore and sample thickness. Therefore, in this study, we investigated the dynamic properties of grating and their dependence on molecular concentration which should reflect the intermolecular interaction among dyes or between dye and host. We employed an azo-carbazole dye, 3-[(4-nitrophenyl)azo]-9H-carbazole-9-ethanol (NACzEtOH, Fig. 1) which was doped in poly(methyl methacrylate) (PMMA) films and compared it to the most well-known azo dye, Disperse Red 1 (DR1, Fig. 1). Measurements for optical absorption and diffraction from the grating formed by two interfering beams (non-degenerate four-wave mixing: FWM) were made. Quantitative estimation for the optical constant modulation was made based on the results from two-beam coupling experiment (TBC).

II. EXPERIMENTS AND ANALYSIS

Synthesis of NACzEtOH was already given in a preceding paper and DR1 was used as purchased [6]. PMMA was provided from Sigma-Aldrich and its molecular weight was about $10^6$. Thin films were prepared by spin coating from dimethylformamide solutions including both ingredients. The thickness of films were adjusted so that the peak absorbance values ranged in 0.7–1.4. All fabricated samples are listed in Table I with their thicknesses.

Grating inscription was carried out by a FWM setup shown in Fig. 2(a), where a continuous wave frequency-doubled Nd:YAG laser (532 nm) was used for excitation and a He-Ne laser (633 nm) was for monitoring the intensity of the first-order diffraction. Incident angle of the green beams was 5.6 degree from the sample normal, and that of the red laser was adjusted to be 6.3 degree in order to satisfy the Bragg’s condition. Beam intensity was 40 mW/cm$^2$ for each of the two excitation beams and 150 mW/cm$^2$ for the monitor beam. All beams were p-polarized (horizontal in lab. frame). Diffraction light was detected by a photodiode and stored in a digital oscilloscope. After the grating inscription for a certain period, diffraction was being measured under no illumination of the excitation beam or under one green beam, in order to monitor natural decay and erasure process, respectively.

For the evaluation of grating properties at the writing wavelength, we also made TBC experiment giving the magnitudes of real and imaginary parts of refractive index modulation observed at 532 nm. Experimental setup for the TBC is depicted in Fig. 2(b). In this measurement, two beams were injected to inscribe a grating at first as the same way made in FWM. After the inscription, the sample was translated quickly to the direction perpendicular to the laser beams (horizontally in lab.). Intensities of transmitted light beams were sinusoidally modulated.

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FIG. 1. Molecular structures of NACzEtOH and DR1.
TABLE I. Samples used in this study and their thickness.

<table>
<thead>
<tr>
<th>Dye(wt%)/PMMA</th>
<th>Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NACzEtOH(30)</td>
<td>0.5</td>
</tr>
<tr>
<td>NACzEtOH(10)</td>
<td>1.6</td>
</tr>
<tr>
<td>NACzEtOH(5)</td>
<td>3</td>
</tr>
<tr>
<td>NACzEtOH(3)</td>
<td>5.5</td>
</tr>
<tr>
<td>NACzEtOH(1)</td>
<td>9</td>
</tr>
<tr>
<td>DRI(20)</td>
<td>1.25</td>
</tr>
<tr>
<td>DRI(10)</td>
<td>1</td>
</tr>
<tr>
<td>DRI(5)</td>
<td>4</td>
</tr>
<tr>
<td>DRI(3)</td>
<td>6</td>
</tr>
</tbody>
</table>

FIG. 2. (a) Experimental setup for grating inscription and reading (non-degenerate FWM). (b) Alignment for two beam coupling experiment (TBC). HM: half mirror, M: mirror, MS: mechanical shutter, PD: photodetector.

due to the interference of diffracted and transmitted parts from two injected beams. Employing Kogelnik’s theory for thick gratings characterized by sinusoidal function, relationship among the beam intensity and refractive index change can be formulated as the following expressions under the assumption that diffraction efficiency is much less than unity [6, 9, 10]. In the derivation, we assumed the equivalent intensity for both incident beams, and intensity was normalized by the incident intensity.

\[ I_1 + I_2 \cong 2e^{-2cz}[1 - 2dz \cos \varphi_A] \]  

\[ I_1 - I_2 \cong 4e^{-2cz}bz \sin \varphi_P \]  

Here, \( \varphi_A \) and \( \varphi_P \) indicate the phase of induced grating relative to light intensity fringe. The direction of the propagation is assumed to be parallel to \( z \) coordinate axis. The real and imaginary parts of the optical constant modulation \( \Delta n + i\Delta \kappa \) are related to the parameters \( b \) and \( d \) through the following relationships.

\[ b = \frac{\pi}{\cos \theta} \frac{\Delta n}{\lambda_0} \]

\[ d = \frac{\pi}{\cos \theta} \frac{\Delta \kappa}{\lambda_0} \]

where \( \lambda_0 \) means wavelength and \( \theta \) indicates the incident angle. Effect from a homogeneous absorption constant given by the equation

\[ c = \frac{2\pi}{\cos \theta} \frac{\kappa}{\lambda_0} \]

does not influence on the analysis. Here, \( \kappa \) indicates the extinction coefficient of the material. Linear translation of the sample is equivalent to the continuous change of the phases, leading to sinusoidal modulation for both signals. Addition and subtraction between two intensities will give modulations \( \Delta n \) and \( \Delta \kappa \).

When strong absorption exists, \( \Delta n \) and \( \Delta \kappa \) depend on the depth from the incident surface. In such a case, we assumed that the distributions were given by the following expressions.

\[ n(z) = n_0 + \Delta n_0 \exp^{-z/l} \]

\[ \kappa(z) = \kappa_0 + \Delta \kappa_0 \exp^{-z/l} \]

Here subscript 0 is introduced in order to distinguish the modulation from those defined in eqs. (3) and (4). The parameter of characteristic absorption length

\[ l = \frac{\lambda_0}{4\pi\kappa_0} \]
FIG. 3. Absorption spectra for (a) NACzEtOH/PMMA and (b) DR1/PMMA. Vertical scale is normalized in order to compare these spectral shapes. Absorbance at peak wavelengths were 0.96, 1.19, 0.87, 1.18 and 0.67 for 30, 10, 5, 3 and 1wt% samples of NACzEtOH, and 1.44, 1.02, 1.04 and 0.90 for 20, 10, 5 and 3wt% films of DR1, respectively.

can be used to convert the device length $z$ to the following effective length parameter $\zeta$.

$$\zeta = l(1 - \exp^{-z/l})$$

By using $\zeta$ instead of $z$ in eqs. (1) and (2), the values $\Delta n_0$ and $\Delta \kappa_0$ can be evaluated by the same calculations.

III. RESULTS AND DISCUSSIONS

Normalized absorption spectra for both materials are given in Fig. 3. They show that NACzEtOH has a peak at around 430 nm and DR1 does at 490 nm in these concentration ranges. Although the concentration dependence was not remarkable for both cases, the most highly concentrated azocarbazole had a shoulder in long wavelength side. On the other hand, peak-shift to the blue side was observed for concentrated DR1 samples. Usually such shift would be attributed to molecular aggregation in condensed systems. However, the dye concentrations of our samples were much higher than conventional solutions where dimerization and aggregation have been discussed. Therefore, the origin of the shift could be related to the change of molecular packing which has been typically caused by crystalline polymorphism, resulting in color variation.

In our typical FWM experimental condition, samples were excited for 5 minutes while the diffraction intensity was monitored by the photodetector. Erasure process was observed from the diffraction intensity after blocking one excitation beam by a mechanical shutter, while naturally decaying behavior was measured after blocking both beams. Rise process of the grating in NACzEtOH (1wt%, 3wt%, 5wt%, 10wt%, 30wt%)/PMMA and in DR1 (3wt%, 5wt%, 10wt%, 20wt%)/PMMA are shown in Fig. 4. Initial growing behavior strongly depended on the concentration for NACzEtOH. The most diluted sample gave quick rise and kept steady value, while more concentrated films (3–10wt%) indicated gradual increase of diffraction intensity up to 0.02–0.035% after 5 minutes. The sample of 30wt% showed an unusual evolution, that is, once increased to some maximum value then reduced, approaching to 0.003–0.005% of which value was almost the same to the final value for the 1.0wt% sample. This singular time dependence had reproducibility, but only observable for highly concentrated spin coated thin films incorporating NACzEtOH. On the other hand, DR1 indicated in Fig. 4(b) did show relatively fast increase to maximum values, and the most concentrated specimen gave the highest diffraction yield as anticipated. The higher efficiency for DR1 could be partially attributed to higher optical densities at the excitation wavelength.

Decay and erasure processes were also compared for NACzEtOH and DR1 as shown in Fig. 5. We have already reported relatively slow decay and erasure for NACzEtOH

http://www.sssj.org/ejsnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejsnt/)
compared to DR1 in the range around 1 minute [6]. In this study, we investigated in longer time range as well as the concentration dependence for the two materials. The results for 10wt% samples are given in the figure as a representative since others loading 3 to 10wt% showed similar behaviors except for the diffraction intensity. The diffraction intensity for NACzEtOH showed fast decay in half a minute, while that of DR1 was much faster. Both materials indicated slower decay after the initial decrease, and the azo-carbazole gave relatively larger magnitude of the slow component. The most prominent difference between two materials was found in the comparison between the natural decay and erasure process as shown in the figure. Apparently, grating extinction was strongly accelerated with one beam illumination for NACzEtOH, while the difference was not so remarkable in DR1 especially in early time. There still remained diffraction even after 10 minute erasure for DR1, suggesting that more stable or persistent change had occurred in the material. In other words, the pattern formed in the azo-carbazole films was more controllable with external light.

As strange decaying behavior was observed in the growing process for 30wt% azocarbazole, it also gave different decaying, that is, much faster relaxation (one tenth of magnitude in the first minute). On the other hand, the most concentrated DR1 sample gave a curve similar to that for the 10wt% case. One possible explanation for the unusual behaviors of 30wt% azocarbazole was competition among more than two processes such as photo-orientation and surface relief grating (SRG) in the highly concentrated sample as previously reported by several scientists [11–13]. Indeed, no such behavior was observed in thick films sandwiched between glass plates to alleviate the SRG formation. However, observation with an AFM showed very shallow surface undulation with amplitude as small as 4 nm for the 30wt% azocarbazole sample, and other specimens for the both materials did not indicate surface modulation in AFM profiles. Because the observed SRG might not have been deep enough to give persistent signal in FWM trace, the details would be left for the future investigations.

Light diffraction can be caused not only by refractive index modulation but also with absorption change as utilized in amplitude holograms [14]. As long as the experiment was made with the probe light in transparent region such as 633 nm as described above, only refractive index change would contribute. However, because the change of absorption will reflect the states of molecules directly, it would be important to make a measurement at an absorbing wavelength via TBC experiment. As explained in the former section, it is possible to evaluate $\Delta n$ and $\Delta \kappa$ separately from the sum and difference of intensity of two beams during sample translation. Typical experimental results are shown in Fig. 6, giving traces with opposite phases for NACzEtOH (10wt%) and with mutually shifted phases for DR1 (10wt%). Because two traces are oppositely phased when $\Delta n$ is dominant and two phases are coincident if $\Delta \kappa$ is dominant, it was known that the refractive index modulation was dominant for the azocarbazole and both parts contributed for DR1. Intensities
FIG. 7. Concentration dependence of optical constant modulation formed with optical excitation in (a) NACzEtOH and (b) DR1 in PMMA.

in the figures are normalized with the initial intensity of the transmitted beams. The values larger than unity were the results of induced transparency assumingly caused by the molecular reorientation or conversion to cis states. The larger transmission change in DR1 did not necessarily mean bigger change of its absorption coefficient, but did the results of large absorption at initial instant. Indeed, the change of absorption $\Delta \alpha / \alpha$ was estimated to be about 0.4 for both cases.

Concentration dependences of these modulations are summarized in Fig. 7. High concentration increased the index modulations while the ratios of real and imaginary parts were constants, suggesting that the grating characteristics were determined only by the realignment of dopants. This inference seemed to contradict the temporal behavior in Fig. 4(a) supposedly showing multiple origins. One possible explanation is that all dynamical processes finally result in molecular alignment after 5 minute irradiation, even though they have different temporal responses. In order to clarify their details, another experimental technique would be necessary to evaluate $\Delta n$ and $\Delta \kappa$ separately and in situ.

Capability of erasure in the azo-carbazole by the excitation beam would be the reason for the good re-writability in high performance holography demonstrated by Tsutsumi et al. [7, 8]. And the dominance of birefringence over dichroism in the dye would be an important property for the azo-carbazoles. This fact and relatively slow growth rate suggest the incorporation of polymer chain for the birefringence. Our recent results on the several azo-carbazole derivatives supported the conjecture [15]. In order to probe the details of light induced molecular alignment, studies based on polarization holography are now on progress.

IV. CONCLUSIONS

In order to investigate the holographic characteristics for polymer films heavily doped with azo-carbazole dyes, temporal evolution of diffraction efficiency, magnitudes of refractive index modulation, and their dependence on the dye concentration were studies with FWM and TBC methods with comparison to DR1. The index modulation was roughly proportional to the dopant concentration. It was found that the refractive index change was dominant for NACzEtOH, while absorption modulation also contributed for DR1. Response speed of NACzEtOH was slower than that of DR1, while the grating formed in NACzEtOH was erasable under illumination of excitation light as opposed to DR1 where much stable pattern was formed. The good controllability of the azo-carbazole could be an important reason for the success of dynamic holography with this material.

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