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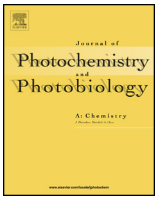

Disorder/reorientation dynamics of 4-methoxybenzylidene-4-*n*-butylaniline observed by heterodyne transient grating method

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ABSTRACT

Molecular dynamics of 4-methoxybenzylidene-4-*n*-butylaniline (MBBA) in a liquid crystal cell after the perturbation of a UV pulse was observed using the polarization dependent heterodyne transient grating (HD-TG) method. The response of a refractive index change showed different signs depending on the probe polarization, and each response was composed of 4 exponential components. These components were assigned to disordering, 2 types of ordering, and molecular diffusion, judged from the sign of the refractive index change and the dependence on the grating spacing and the pump intensity. The time constants for the disordering and the ordering processes drastically increased for the pump intensity above 0.10 mJ/pulse. To explain the threshold, we proposed that disordering/ordering of domains were observed for the higher pump intensities, while an individual molecule is subject to disordering/ordering for the lower pump intensity.

1. Introduction

Because of the orientation property, liquid crystals (LCs) show characteristic physical properties; their thermal, mechanical, optical, and electrical properties are highly anisotropic [1–3]. LC is commercially used for the display by switching its molecular orientation electrically and also it is expected for an optical recording material. The basic physical properties of LC such as the response speed and orientation are critical for actual devices. To obtain the dynamic response of LC, the reorientation, after the orientation is once disturbed, was monitored and the processes were studied.

4-Methoxybenzylidene-4-*n*-butylaniline (MBBA) is a frequently used sample as a nematic LC. It undergoes trans to cis photoisomerization by a photoirradiation with a wavelength of 300–400 nm, and the molecular conformation is changed. It disturbs the alignment of LC, and is followed by the reorientation processes. Since the orientation change in LC involves a refractive index change, the processes were observed by the transient grating (TG) method [4–14], which is a method for the dynamics measurement of a photoinduced physical or chemical change via the refractive index change.

In the TG method, a stripe pattern of light is irradiated to a sample, which induces a photo-induced change like the same pattern, causing the refractive index change (TG), and the TG is monitored by a diffraction of another probe light. MBBA [4,6–10,12] and p-pentyl-p′-cyanobiphenyl (5-CB) [5,6,11] have been studied intensively by the TG method. In these studies, generation of standing sound wave [8,9,12], anisotropy of thermal diffusion [8,9], a reorientation process caused by molecular rotational relaxation [5,7,11], and molecular diffusion [4,7,9,10] have been studied.

The reorientation process is explained by the change in the order parameter, which is an indicator of the collective orientation of LC molecules [6]. Typically the molecular orientation time is believed to be on the order of milliseconds [5,7–9]. On the other hand, we have developed the heterodyne transient grating (HD-TG) method [15,16]; featuring a simple optical setup and highly sensitive detection using the amplification by the heterodyne technique. Similar techniques have been developed by other groups, too [17–20]. Compared with the conventional TG method, the HD-TG method is superior in the distinction of the sign of the refractive index change, which allows easier assignment of the signal component especially for the LC sample [21,22], which have a different sign of the polarization (refractive index) depending on the configuration of the directions between the light polarization and the sample orientation. In this study, the HD-TG method was applied to a MBBA sample in a LC cell, and it was observed that transient responses depended on the probe polarization and

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pump intensity with respect to the LC orientation and we discussed its origin.

2. Theory

A brief introduction of the HD-TG technique is shown in Fig. S1 (Supporting information). Conventionally when photoexcited chemical species are generated, the HD-TG response showed an exponential decay including the diffusion and decay of the species, and the time constant is composed as,

$$\frac{1}{\tau} = D\left(\frac{2\pi}{\Lambda}\right)^2 + \frac{1}{\tau_r} \tag{1}$$

where D is the diffusion coefficient of chemical species, Λ is the grating spacing, and τ_r is the time for the lifetime of the species. When τ_r is much shorter than the diffusion process, the first term on the right side is neglected and the time constant directly reflects the lifetime. When the photo-generated species decays as they diffuse, it is called the species grating [1]. The plot of τ^{-1} as a function of q^2 ($q = (2\pi/\Lambda)$ is controllable by the grating spacing) gives the diffusion coefficient and lifetime as the slope and y-intercept, respectively [2]. If the τ^{-1} does not depend on q, it means the response is not caused by the diffusion of chemical species or heat, but by the decay of transient states or structure, and the latter is typically observed in the case of LC.

The alignment of the LC cell, the directions of the pump and probe light polarizations are shown in Fig. 1. In the TG signal, the refractive index change is induced by the third-order nonlinear polarization, which is given by, for example,

$$P_x = \chi^{(3)}_{xxyy} E_{x,\text{probe}} E_{y,\text{pump}} E_{y,\text{pump}} \tag{2}$$

In this case, the polarization in the x direction is induced by the probe polarization in the x direction and the pump polarization in the y direction. In our measurements, the refractive index change was observed by the probe in the x or y direction. The index changes, Δn_x, Δn_y for each probe polarization in case of the pump polarization parallel to the liquid crystal director are expressed as [9]

$$\Delta n_x = \frac{\varepsilon_0}{n_x} E_y E_y \tag{3}$$

$$\Delta n_y = \frac{\varepsilon_0(\chi^{(3)}_{yyyy} + \chi^{(3)}_{yxyy})}{n_y} E_y E_y \tag{4}$$

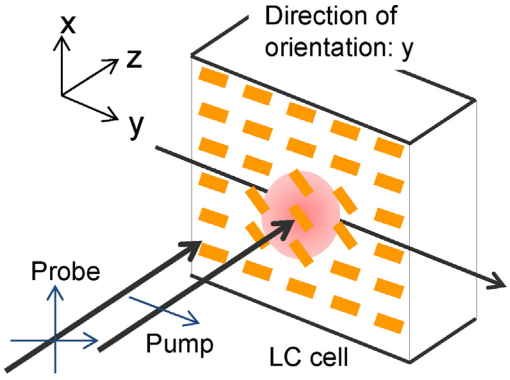

Fig. 1. The sample and optical configuration are shown. The sample is a MBBA and it is put into a LC cell, whose director axis is in the y-direction. The polarizations of the pump and probe beams are shown. The polarization of pump light is parallel to the director axis and the probe polarization direction was controlled.

Typically, $\chi^{(3)}_{yyyy} \gg \chi^{(3)}_{yxyy}, \chi^{(3)}_{xyyy} > \chi^{(3)}_{xxyy}$ is accepted. The index change is divided into 3 parts depending on the physical origins as

$$\Delta n(t) = \Delta n_T(t) + \Delta n_\rho(t) + \Delta n_S(t), \tag{5}$$

where the terms in the right side corresponds to the index change due to temperature, density, and order parameter. The Δn_T term is known to be small usually. The Δn_ρ term is expanded to

$$\Delta n_\rho(t) = \left(\frac{\partial n}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial T}\right) \Delta T(t) \tag{6}$$

Then, the temporal response of this signal corresponds to the thermal grating of the liquid crystal. For most of LCs, $(\partial n/\partial \rho)_T > 0$ and $(\partial \rho/\partial T) < 0$ and then the index change is negative, and also the sign is not dependent on the polarization of the probe. The $\Delta n_S(t)$ term is the main cause of the disordering and reorientation dynamics of the liquid crystal, and it can be expanded into,

$$\Delta n_S(t) = \left(\frac{\partial n}{\partial S}\right)_\rho \Delta S(t) \tag{7}$$

We found a mistake in a few papers which says that this component is proportional to $\Delta T(t)$. Although this is true for the static condition, we observed several steps in the refractive index change due to the change in the order parameter even after the heat dissipation, and it means that the change in the order parameter and temperature behaved differently in the temporal response. For an oval molecule aligned in the direction of y-axis, the index change for the x and y polarized light is, [9]

$$\frac{\Delta n_{S,y}}{\Delta n_{S,x}} = \frac{\alpha_y}{\alpha_x} = -2, \tag{8}$$

where α_x and α_y are the polarizability in x and y directions. This is the reason why the sign of the signal for different polarization of the probe lights is reversed for a LC sample. Since this is the case for an ideal oval molecule, the actual ratio would be smaller than 2. The order parameter is defined as

$$S\left(\theta\right) = \frac{1}{2}\left(3\left\langle \cos^2\theta \right\rangle - 1\right), \tag{9}$$

where θ is defined as the angle between the director and the molecular axis, and $\left\langle \cos^2\theta \right\rangle$ indicates the average of $\cos^2\theta$. Looking into (9), the change in the order parameter is caused by 2 factors; the θ change, and the ordering change because disordering reduces the average of $\cos^2\theta$ even for the same θ.

Furthermore, our polarization dependent measurements revealed that the molecular motion depends not only on the angle to the director axis (y-axis), but also the angle to the perpendicular axis to the director (x-axis). Thus Eq. (7) is changed into,

$$\Delta n_{S,x}(t) = \left(\frac{\partial n_x}{\partial S_\theta}\right)_\rho \Delta S_\theta(\theta(t)) + \left(\frac{\partial n_x}{\partial S_\varphi}\right)_\rho \Delta S_\varphi(\varphi(t)) \approx \left(\frac{\partial n_x}{\partial S_\theta}\right)_\rho \Delta S_\theta(\theta(t)) \tag{10}$$

$$\Delta n_{S,y}(t) = \left(\frac{\partial n_y}{\partial S_\theta}\right)_\rho \Delta S_\theta(\theta(t)) + \left(\frac{\partial n_y}{\partial S_\varphi}\right)_\rho \Delta S_\varphi(\varphi(t)) \approx \left(\frac{\partial n_y}{\partial S_\varphi}\right)_\rho \Delta S_\varphi(\varphi(t)) \tag{11}$$

where S_φ is the order parameter for the x axis, and φ is the angle between the x axis and the molecular orientation.

3. Experiment

Fig. 1 shows the sample and optical configuration; the directions of the pump and probe polarizations and the orientation of the sample. MBBA (Tokyo Kasei) was purchased and used without further purification (Fig. 2). The sample was put into a LC cell (E.H.C) with a sample thickness, ca. 3 ± 0.5 μm, where polyimide films are rubbed in y direction on both sides of the cell.