

Dynamics of a cyanobiphenyl liquid crystal

S. Morino^a, H. Takahashi^b and K. Horie^b

^aPhotofunctional Chemistry Division, Research Laboratory of Resources Utilization, The Tokyo Institute of Technology, Nagatsuda-cho 4259, Midori-ku, Yokohama 226, Japan

^bDepartment of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan

Ordering and disordering processes during photoirradiation were investigated for a quinizarin/8OCB composite. Disorder of LC molecules occurred during irradiation. It is suggested that this disordering process is induced by not only thermal vibrations but some motions of photoexcited molecules.

Introduction

These days, there seems to be increasing interest in molecular dynamics during deactivation processes of photoexcited molecules. Photons of visible or ultraviolet light have large energy considering the energy of thermal vibrations. It is thought that photons are converted to phonons during deactivation, however, detailed pictures have not been obtained.

Liquid crystals (LC) are widely known materials and have interaction and continuity between liquid crystalline molecules. There is interest on molecular dynamics of liquid crystals from both scientific and industrial aspects.

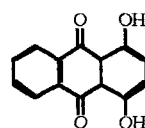
Here, we consider a dye/LC composite. On irradiation to dye molecules, deactivation processes could cause disordering/ordering of LC, and we could observe thermal deactivation process through changes in birefringence of liquid crystals. We could even expect that the molecular motions of photoexcited molecules would be amplified by LC. Next, considering molecular dynamics of LC, energy of absorbed light perturbs motions of LC molecules, and it would be possible to investigate interactions

and molecular dynamics of LC molecules during observation of their ordering/disordering process.

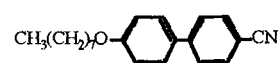
In this study, ordering and disordering processes during photoirradiation were investigated for a dye/LC composite. Molecular motions of photoexcited dye molecules and LC molecules will be discussed.

Materials

An LC of 8OCB and a dye of quinizarin ($\lambda_{max} = 480 \text{ nm}$) were used. The 8OCB and quinizarin were mixed over 360K. Rubbed and unrubbed samples were prepared for measurements. For rubbed samples, polyimide coated-quartz substrates were used after rubbing, for unrubbed samples, quartz substrates were used without any treatments.



quinizarin



4-octyloxycyanobiphenyl (8OCB)

Figure 1. Chemical structures of 8OCB and quinizarin

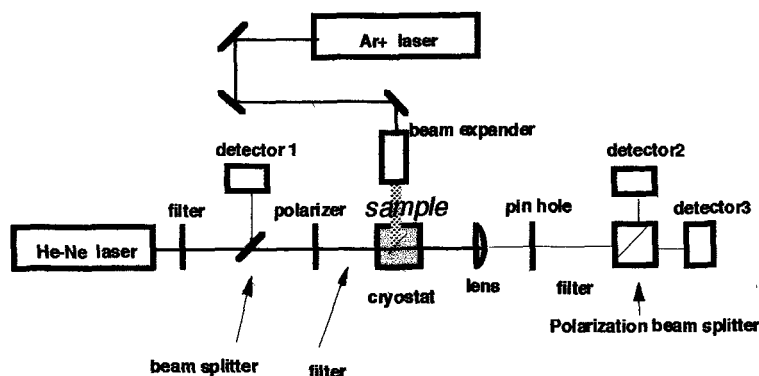


Figure 2. Experimental setup of birefringence measurements

Measurements

The experimental setup of retardation measurements is shown in figure 2. To confirm axes of birefringence, transmitted light intensity was measured while rotating the polarizer and the analyzer synchronously. As the need arise, photoirradiation can be carried out. The light source was an Ar⁺ laser. Two lines at 514.5nm and 488 nm were irradiated. The light power was 50mW/cm².

Results and discussions

Thermal property of 8OCB was previously reported. This LC shows crystal, smectic A, nematic and isotropic phases. Phase transition temperatures of T_{CSA}, T_{SAN}, T_{NI} are 327K, 337K, 353K. We have confirmed that the mixture of quinizarin and LC shows the same phase transition temperatures by using orthoscope observation.

At first, we have confirmed the initial states of prepared samples. Figure 3 shows the intensity of transmitted light while rotating the polarizer and the analyzer. For a rubbed sample (Figure 3 (a)), the minimum intensity of transmitted light is zero when the plane of polarization is parallel or perpendicular to the rubbing direction. It is concluded monodomain texture was formed. For an unrubbed

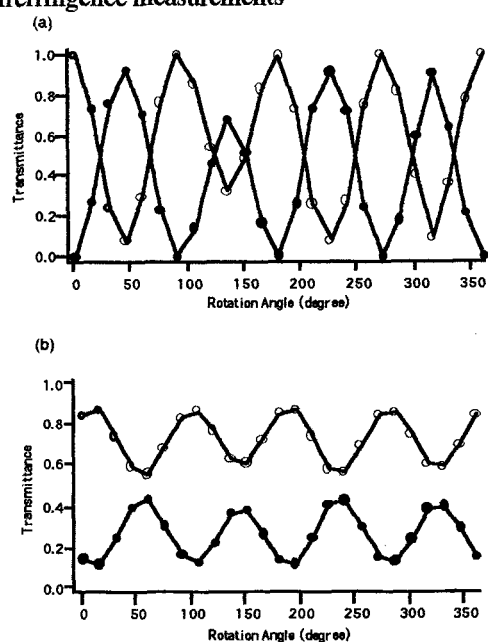


Figure 3. Rotation angle dependence of transmitted light. (a) rubbed sample at 344.8K, (b) unrubbed sample at 344K. Open circles are for transmitted light intensity when planes of polarization of polarizer and analyzer are parallel, and filled circles are for those when planes of polarization of polarizer and analyzer are perpendicular.

sample (Figure 3(b)), 4 weak peaks were observed, which proves that birefringence is not zero. Hence, there is no angle where the transmitted light intensity is zero. Therefore it is concluded that unrubbed samples have polydomain texture.

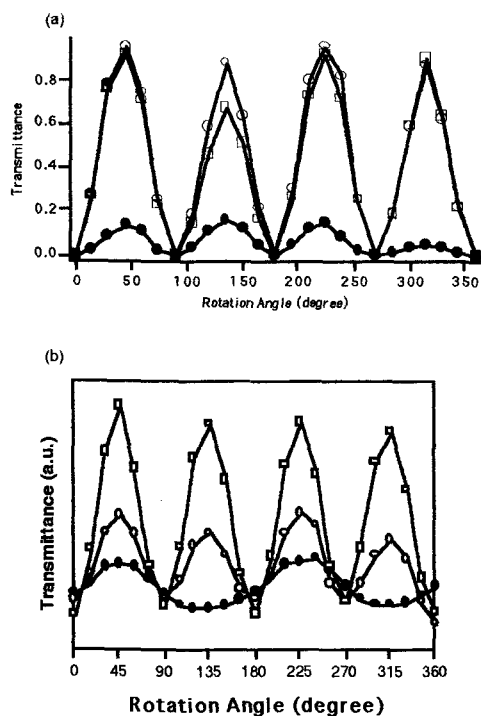


Figure 4. Rotation angle dependence of transmitted light intensity. Open squares for transmitted light intensities before irradiation, filled circles for those during photoirradiation, open squares for those after irradiation. Rubbed sample at 344.8K (a). Unrubbed sample at 344K(b)

Next, we have carried out the same experiments during irradiation of an Ar^+ laser (Figure 4). Irradiating to a rubbed sample, intensities of peaks decreased. Comparing this change with the change in birefringence during heating, we have concluded that birefringence decreased while irradiation. Irradiating to an unrubbed sample, 4 peaks had disappeared, and 2 weak peaks appeared instead. These new peaks were due to the angular dependence of incident laser beam, and did not depend on LC textures. However, transmitted light intensity is not zero. Therefore, it is concluded that the LC kept LC phase and birefringence was retained, and is also concluded that uniform angular distribution of directors were formed.

There are two possible explanations for decrease in birefringence while irradiation: One is that motions

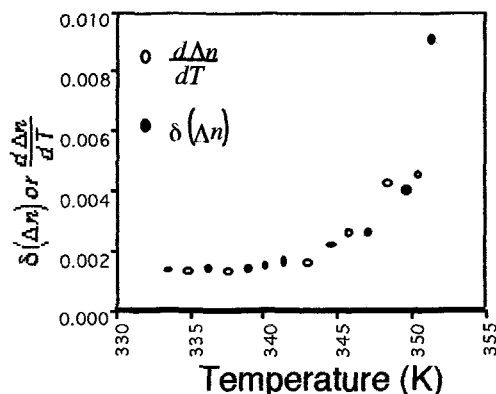


Figure 5. Temperature dependence of photoinduced refractive index change (δn) and birefringence (Δn) differentiated against temperature.

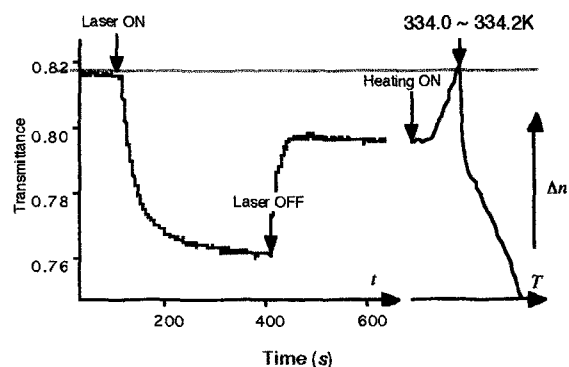


Figure 6. Transmittance during photoirradiation and heating. Photoirradiation was carried out from 80s to 400s. Heating started where the second X starts.

of photoexcited dye molecules are activated during deactivation, which changes LC alignment. (Photon mode) Another is that the change is simply due to the change in temperature during irradiation. (Heat mode)

Further experiments were carried out to distinguish the contributions of photon mode and heat mode. The birefringence (Δn) at some temperatures and its changes (δn) while irradiation were measured. Figure 5 shows the temperature dependence of $\Delta n/dT$ and $\delta n/dT$. Both are approximately the same. Assuming that all changes are due to temperature changes, the photoinduced change in temperature would be estimated to 1K.

Birefringence and its changes while irradiation were also measured some temperatures during heating from crystal phase and during cooling from isotropic phase. At S_A phase, the values of birefringence were different before and after irradiation in heating process(Figure 6).

Furthermore, birefringence increased when heating was started while birefringence ordinary decreases during heating. It reaches the same value as the value before irradiation when temperature increased ca. 0.2~0.4K. It may be suggested that distortion of LC textures is formed during photoirradiation and retained even after irradiation. Here, the temperature where the value of birefringence reaches the value before irradiation may be regarded as the temperature during irradiation.

Two values of temperature, 1K and 0.2~0.4K, have been estimated and do not coincide. At least changes of 0.2~0.4 K would occur. However, changes in birefringence corresponding to the change in temperature of 1K could contain the contribution of disordering of LC molecules induced by photon mode.

Irradiating time dependence of birefringence was also measured at some temperatures. Values of decay time during and after irradiation were obtained by least square fitting, and shown in figure 7. Below 342K, decay curves while irradiation fits well with the double exponential function only in heating process. For other measurements below 342K, single exponential function fits well. Double exponential function gives good results for decay curves during and after irradiation over 342K in both heating and cooling process. The time constants of short decay are 10~20s, and those of long decay are longer than 40s. The temperature of 342 K does not correspond to any phase transition temperatures. LC shows N phase at this temperature. There may be a molecular motion activated over 342K. We could not identify the origin of short and long decays, and are going to carry out further investigations.

Conclusion

We have investigated the ordering and disordering processes during photoirradiation for a quinzarin/8OCB composite. Disordering of LC molecules occurred during irradiation. It is suggested that this disordering process is induced by not only thermal vibrations but some motions of photoexcited molecules. It is suggested that molecular motion were activated over 342K in nematic phase from analyses for time constants of ordering and disordering processes.

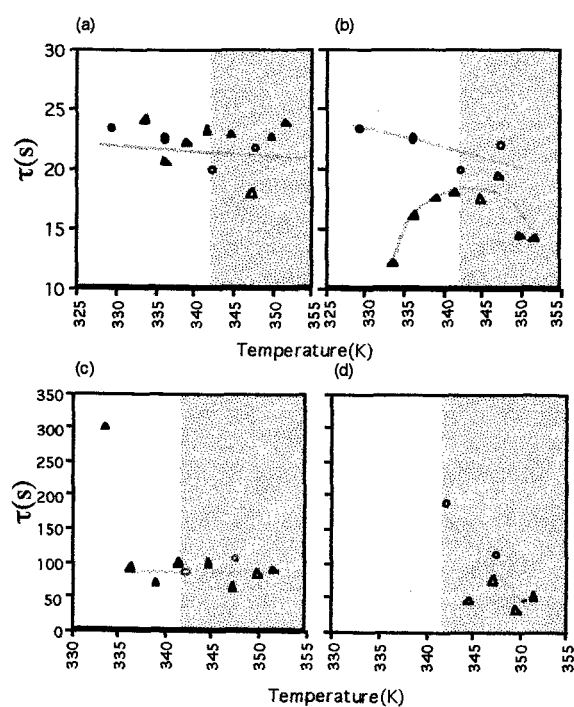


Figure 7. Time constants of decay curves. Short decay during irradiation (a), short decay after irradiation (b), long decay during irradiation (c), short decay after irradiation(d). Open and filled triangles are time constants in heating, Open and filled circles are for time constants in cooling.