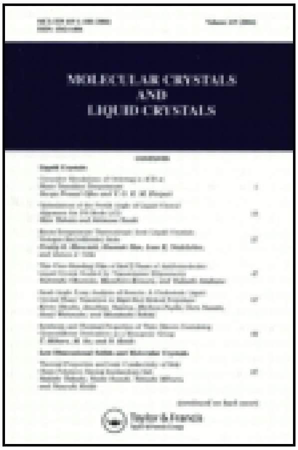

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Photoinduced Reorientation of Liquid Crystals Doped with a Mesogenic Oligothiophene

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Photoinduced Reorientation of Liquid Crystals Doped with a Mesogenic Oligothiophene

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We studied the dynamic behavior of director-reorientation induced by linearly polarized light in an oligothiophene-doped liquid crystal (LC) by transmission-mode analyses and the Z-scan measurement. An in-plane reorientation process occurred and LC molecules tended to reorient parallel to the polarization of incident light in the case of low-intensity irradiation. The thermal effect due to absorption affects the reorientation behavior largely in the case of high-intensity irradiation.

Keywords: Liquid crystal; Oligothiophene; Guest-Host system; Reorientation; Linearly polarized light

INTRODUCTION

Photo-manipulation of the liquid crystal (LC) alignment has attracted increasing attentation in recent years due to its large optically induced birefringence. It has been known for decades that transparent LCs tend to reorient parallel to the electric field of light when irradiated with linearly polarized light [1,2]. This is responsible for the largest optical

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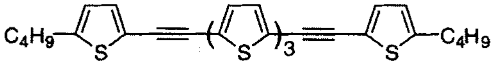
nonlinearity in any known materials. However, the high light intensity required for reorientation limits its development in applications. On the other hand, recent researches have revealed that a small amount of dyes dissolved in LCs, which makes the system light absorbing, may strongly increase the photoreorientation efficiency [3,4]. Depending on the structure of dyes, the reorientation efficiency is more or less [3], and host LCs may reorient either parallel or perpendicular to the polarization of incident light [4]. The accepted mechanism attributes the dye-induced reorientation to changes in physical or chemical properties of dye molecules upon irradiation, which in turn affect the LC alignment through guest-host interaction [5].

Many dyes have been used to evaluate the dye-induced reorientation effect [3-5]. Anthraquinone and azobenzene dyes are both proved to be effective in certain guest-host systems. In our work aimed at developing effective materials for dye-induced reorientation, we synthesized an oligothiophene, 5,5"-bis-(5-butyl-2-thienylethynyl)-2,2':5',2"-terthiophene (TR5) (Fig. 1, top), as the photoactive dopant [6]. By self-diffraction measurements, it was found that TR5 could strongly decrease the threshold light intensity for optical Freedericksz transition at very low doping concentrations. We attributed its high efficiency for reorientation to the photoinduced change in molecular polarizability, which is related to the high π-electron delocalization in oligothiophenes. In this paper, the dynamic photoinduced reorientation behavior in a TR5-doped LC was studied by transmission-mode analyses. The reorientation direction was determined by the Z-scan measurement.

EXPERIMENTAL SECTION

TR5 was synthesized as reported previously [6]. It shows nematic and monotropic smectic phases in mild temperature regions [6]. 4-Cyano-4'-pentylbiphenyl (5CB) was chosen as an LC host and TR5 was doped at a concentration of 0.22 mol%, then the mixture was put into sample cells that had been treated with lecithin for homeotropic alignment. Fig. 1 shows the schematic illustration of the optical setup used for transmission-mode analyses. A 100-μm-thick sample cell was used, which showed absorbance of 0.27 at 488 nm and no absorbance at 633 nm. The initial LC director was in the horizontal plane. Reorientation was induced by a laser beam at 488 nm from an Ar^+ laser with an incident angle of 30°, which was linearly polarized in the horizontal plane, the beam diameter being 1.2 mm. The change in the transmittance of a normally incident He-Ne probe laser (633 nm) through a pair of crossed polarizers, with the sample cell between them, was recorded as a function of irradiation time. Probe polarizations were set to be parallel, perpendicular and 45° with respect to the horizontal plane, which are referred in the following discussion as parallel-, perpendicular-, and 45°-probe-polarizations, respectively. All measurements were performed at room temperature (20 °C).



TR5

Sample cell

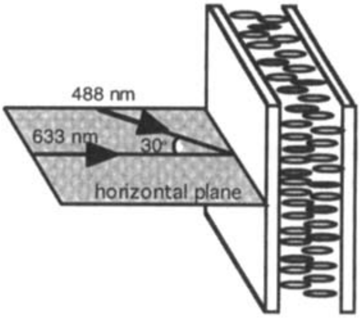


FIGURE 1 Top: Structure of TR5; Bottom: Schematic illustration of the optical setup used for transmission-mode analyses.

The Z-scan measurement was carried out with a similar method to that in the literature [4]. In the measurement, the same pumping laser as above was used and the output was kept constant. The pumping laser was focused onto the 20-μm-thick homeotropic sample cell by a lens (f = 7 cm) with an incident angle of 30°, and the intensity of the central part of the laser beam was monitored after the sample cell in the far field by translating the sample along the optical axis of the laser beam (Z-direction).

RESULTS AND DISCUSSION

Transmission-Mode Analyses

In-plane reorientation process

The result of transmission-mode analyses was strongly dependent on the pumping intensity and the probe polarization. Fig. 2a shows a typical result at relatively low irradiation intensity (1.77 W/cm^2). Before photoirradiation, the homeotropic sample cell showed no birefringence, and the probe beam could not transmit the crossed polarizers. After pumping light (488 nm) was turned on at 10 s, the growth of transmittance could be observed by the 45°-probe-polarization. The transmittance increased until a photostationary state in about 40 s after turning on the pumping beam, and decreased to 0 in about 10 s after turning off the pumping beam, which is typical for LC reorientation. The increase in transmittance is a result of change in the probe polarization due to the LC birefringence induced by photoirradiation.

Parallel- and perpendicular-probe-polarizations always showed similar dynamic behavior of transmittance during the reorientation process, and in cases of low-intensity irradiation, no transmittance could be observed by them (Fig. 2a), indicating that their polarizations changed little during the LC reorientation process. Considering the birefringence character of LCs, this means that LC molecules should reorient in the horizontal plane or in the vertical plane containing the initial LC director, which would unchange the parallel- and perpendicular-probe-polarizations.

Diffraction and thermal effects

When the irradiation intensity was up to about 5.31 W/cm^2, reorientation behavior changed. Fig. 2b shows a typical result. One can see that an in-plane reorientation process also existed at the early stage of photoirradiation. However, with the 45°-probe-polarization, the transmittance first increased until a maximum in about 10 s after turning on the pumping beam, and then decreased upon further irradiation. At the time of 27 s described in Fig. 2b, it seemed that another process was involved, and simultaneously, significant transmittance was detected by parallel- and perpendicular-probe-polarizations. In addition, an obvious transient peak appeared at the just beginning of photoirradiation in the case of the 45°-probe-polarization as shown in the inset of Fig. 2b.

By directly observing the optical pattern of pumping light after the

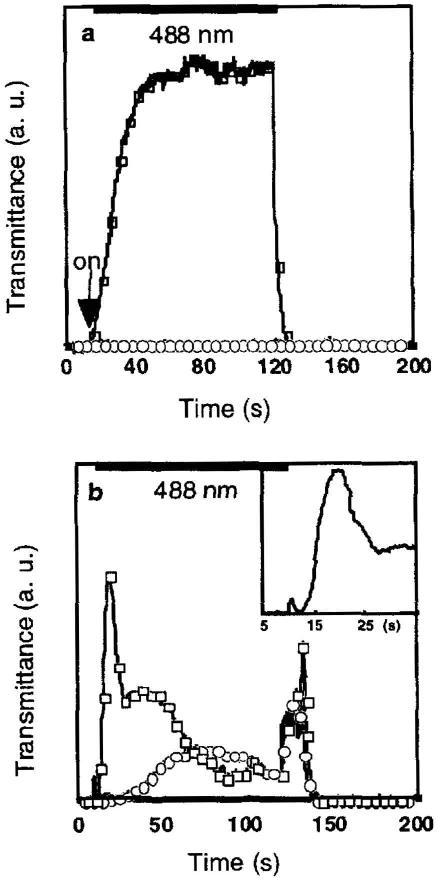


FIGURE 2 Change in the transmittance through TR5-doped 5CB as a function of irradiation time for the 45°-probe-polarization (□) and the parallel-probe-polarization (○) at irradiation intensiy of 1.77 W/cm^2 (**a**) and 5.31 W/cm^2 (**b**). Pumping light was turned on at 10 s and turned off at 120 s. The inset of Fig. 2**b** is the magnified illustration of an early stage for the 45°-probe-polarization.

sample in the far field, we found that the optical pattern first developed into multiple diffraction rings in about 10 s after turning on the pumping beam, which, however, became ambiguous and was strongly scattered in the far field after irradiation for about 20 s. The multiple diffraction rings showed similar characters to those observed in reference [6], which is a result of ununiform LC director reorientation induced by laser [2]. It is reasonable that the scattering of the pumping light resulted from the formation of isotropic droplets due to the thermal effect of absorption. Comparing the time scale of the formation of different optical patterns with the result of transmission-mode analyses, the decrease in transmittance observed by the 45°-probe-polarization during photoirradiation described in Fig. 2b could be attributed to light diffraction and scatting effects, and the transmittance observed by parallel- and perpendicular-probe-polarizations was a result of light scatting due to the thermal effect.

The transient process

As mentioned above, another interesting feature in Fig. 2b is that an obvious transient peak with the characteristic time of 2 s was observed by the 45°-probe-polarization just after the pumping light was turned on. In fact, this transient peak could also be observed at low-power irradiation but was very weak. The transmittance maximum of this process increased with an increase of irradiation intensity. This transient process also showed anisotropic dependence on probe polarizations since it could not be detected by parallel- and perpendicular-probe-polarizations, indicating that it was corresponding to an in-plane reorientation process. The mechanism for this transient jump is unclear at present. Its fast relaxation time suggests that it might result from thermally induced reorientation effects [7,8]. It is noteworthy that in another transmission-mode analysis experiment in a similar condition except that the diameter of irradiation light was doubled by a lens, we obtained similar results to those discussed above but without the transient process, indicating that the transient process may also be related to the intensity distribution of pumping light.

The transmission-mode analysis was also performed with an undoped 5CB sample cell, and transmittance could not be detected by any probe-polarizations even at the irradiation intensity as high as 10.36 W/cm^2. This confirmed that the phenomenon described above resulted from the photo excitation of TR5.

The Z-Scan Measurement

In order to confirm the reorientation direction, the Z-scan measurement was performed. In the measurement, a low output of the pumpimg laser was used and we neglected the thermal effect. A typical self-focusing phenomenon was observed for TR5-doped 5CB as shown in Fig. 3. That is, the detected intensity exhibited a minimum at a sample position between the lens and the focal point, and a maximum behind the focal point, indicating that LC molecules tend to reorient parallel to light electric field [4]. Combining the result of transmission-mode analyses, we thus concluded that the director of TR5-doped 5CB tended to reorient parallel to the light polarization in the horizontal plane upon proper irradiation. However, we would like to point out that it is difficult to determine the reorientation direction of the transient process described in Fig. 2b by the Z-scan measurement because of its short relaxation time. Further researches are needed to confirm the mechanism for this process.

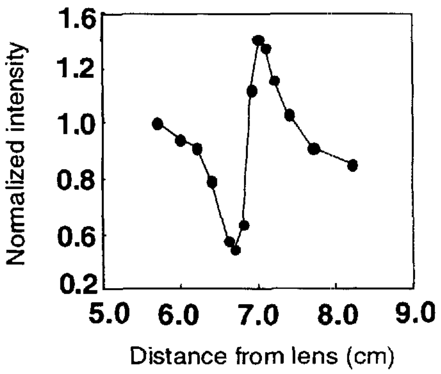


FIGURE 3 Z-scan curve for TR5-doped 5CB. X-axis is the distance between the sample cell and the focal lens. The light intensity of the pumping beam before the focal lens was 0.01 W/cm^2.

CONCLUSION

We showed that reorientation of LCs could be induced in an oligothiophene-doped LC by low-power photoirradiation. The reorientation behavior was strongly dependent on irradiation intensity. An in-plane reorientation process was observed and LC molecules tended to reorient parallel to the light polarization.

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