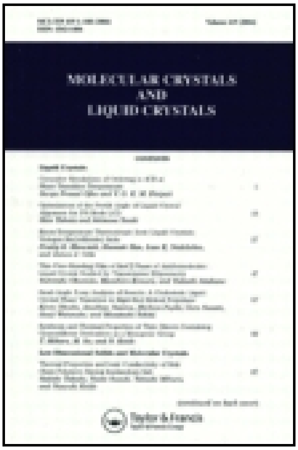

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Change of DLC Domains by IR Irradiation for a Plastic Columnar Mesophase

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In this study, alignment change of liquid crystal domains induced by infrared irradiation was investigated for a plastic hexagonal columnar mesophase of a liquid crystalline triphenylene derivative. A uniform and anisotropic alignment change of domains was observed when polarized infrared light corresponding to the wavelength of the aromatic C–C stretching absorption band of triphenylene core was irradiated. The results strongly imply that the infrared irradiation is a possible technique for device fabrication by use of plastic columnar mesophase as a liquid crystalline semiconductor.

Keywords: alignment control; columnar phase; discotic liquid crystal; infrared; polarized light

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INTRODUCTION

Columnar liquid crystals, especially for discotic liquid crystals, have been drawing much attention as novel organic semiconductors such as one-dimensional conductors, photoconductors, molecular wires and fibers, light emitting diodes and photovoltaic cells in these years [1–4]. Discotic liquid crystals have shown some interesting features for their electronic properties such as charge migration phenomena along a columnar axis [5–10]. In addition, recent studies as for photopolymerization of liquid crystals indicate that such a molecular order of discotic liquid crystal could remain in polymer solid film [11], leading to a sophisticated invention of optical compensator for wider view angle of liquid crystal display [12,13]. These results imply that discotic liquid crystals are good candidates for organic thin film devices if their alignment is well controlled.

In order to obtain a higher performance in molecular materials, an appropriate long-range order of molecules is an essential requirement. Uniformity of molecular alignment in the film is also an important issue in device fabrication with the thin film. However, it is well known that the control of molecular alignment is somewhat difficult to achieve for a crystalline solid and therefore liquid crystals have received much attention as materials, of which one can control the molecular alignment. Surface effects and shear flow have often been used in order to obtain a uniformly aligned phase of discotic liquid crystals for studies of their potential application as novel optoelectronic functional materials [14–19]. All the studies of photoalignment of liquid crystals have focused on the application of ultraviolet and/or visible light, since this could provide a clean and fast fabrication process for organic thin film devices [20–22]. However, only a few results of molecular alignment controlling in columnar phases of discotic liquid crystals were reported so far, due to the higher viscosity and order as compared to those of the nematic liquid crystals. Some experiments have been reported to get uniaxial planar and homeotropic alignment of columnar mesophases and a few successes were attained by usage of polytetrafluoroethylene (PTFE) coated by friction transfer technique [23] and the introduction of fluoroalkylated chain into peripheral parts of triphenylene [24] for planar and homeotropic alignment, respectively.

Recently the technology of free electron lasers (FEL) has been extensively developed and this can provide some special analytical techniques to materials and their related phenomena [25]. The FEL has a specific characteristic for a laser system in that we can obtain a highly tuned pulsed laser beam with variety of wavelength from ultraviolet to far-infrared (0.3–20 μm).

In the previous work [26–29], the possibility of controlling the molecular alignment and domains of liquid crystals using infrared light, relating to selective excitation of vibrational processes, has been examined. We have found the first results on molecular alignment change for a columnar mesophase by vibrational excitation.

In this work, we show that an anisotropic alignment change for a plastic columnar mesophase could be controlled by vibrational excitation with polarized infrared irradiation.

EXPERIMENTAL

The compound used in this work is a typical columnar discotic liquid crystal, 2,3,6,7,10,11-hexabutyloxytriphenylene (C4OTP), as shown in Figure 1. Its preparation, purification and mesomorphic characterization have been presented and discussed in detail by others [30,31]. A plastic hexagonal columnar (Col_{hp}) mesophase appeared between the melting and clearing points (C 90°C Col_{hp} 145°C Iso). C4OTP film was prepared between two BaF_2 substrates which have high transparency in infrared region, with 2-μm silica beads spacer and mounted on a hot stage (Linkam LK-600 FT-IR), which was attached to an optical polarized microscope (Olympus BX-51P). The BaF_2 substrates used were polished substrates. The microscopic texture was recorded using a CCD camera (Keyence VH-6300C) with a commercially available S-VHS video recorder. FT-IR spectrum of C4OTP film at 140°C was shown in Figure 2. The absorption peak at 1615 cm^{-1} is assigned to an aromatic C$-$C stretching vibration of the triphenylene.

The pulse sequence of FEL consists of a train of macropulses, which themselves contain a train of 300–400 ultrashort micropulses as shown in Figure 3(a). The beam quality such as power is likely to fluctuate [32]. This actually makes it difficult to analyze these phenomena in the detailed and quantitative ways. The width of the macropulses is

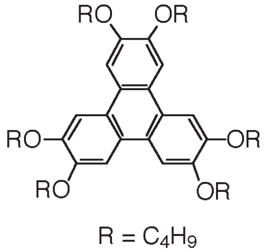

FIGURE 1 Molecular structure of hexabutyloxytriphenylene (C4OTP).

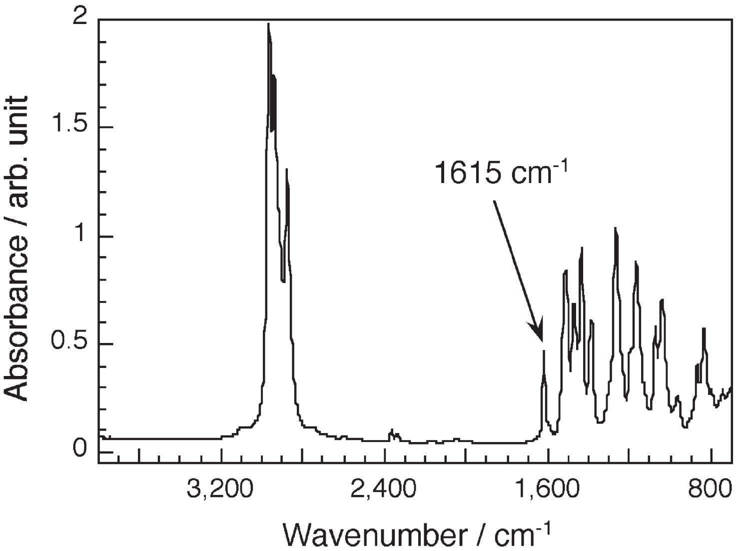

FIGURE 2 FT-IR absorption spectra of C4OTP film in Col_{hp} (140°C).

about 15 μs and the repetition rate is 10 Hz. The average power of FEL beam was ca. 4 mW in these experiments. The beam was focused to about 0.5 mm in diameter by ZnSe lens at the end of a FEL manipulator. The polarization property of the FEL beam is shown in Figure 3(b), to be a linear polarization. A schematic representation of the

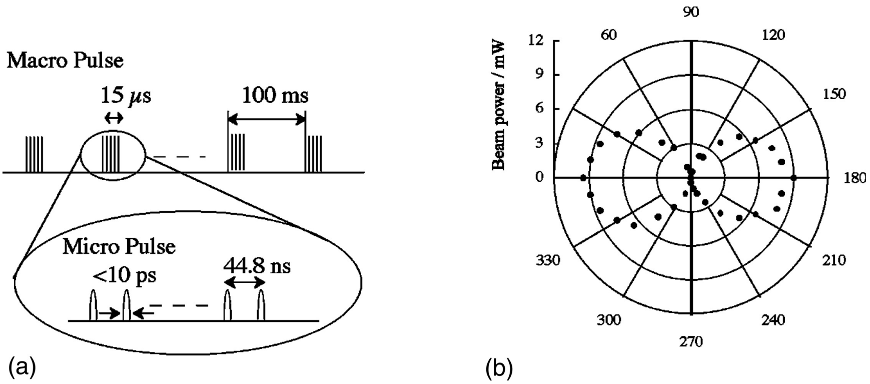

FIGURE 3 (a) The FEL temporal beam profile. The FEL has two pulse structures: micro- and macro-pulses. (b) Polarization property of an FEL beam intensity.

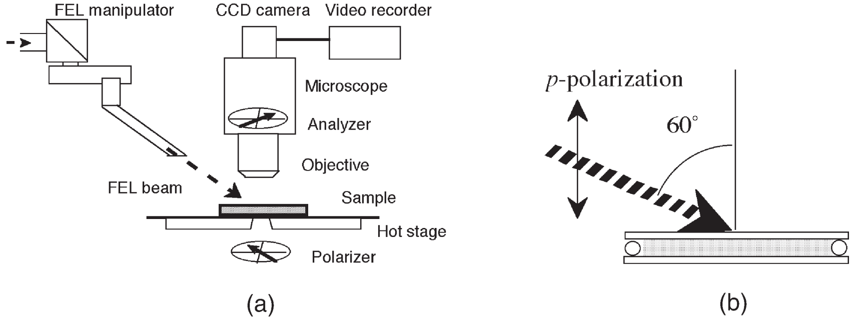

FIGURE 4 Schematic representation of (a) setup for FEL irradiation and (b) incident IR FEL beam.

experimental setup for a slantwise configuration for the irradiation is shown in Figure 4.

RESULTS AND DISCUSSIONS

The microscopic observations of a $\mathrm{Col_{hp}}$ phase emerge as a multidomain mosaic texture under the crossed Nicol condition when a 2-μm thick C4OTP film is cooled from isotropic phase to 141°C as shown in Figure 5(a). A rotation of the microscopic stage gave rise to an alternately and periodic appearance of darkness for the domains under crossed Nicol condition by every 45° as shown in Figure 5(b). This means that it is almost planar (edge-on) alignment where the columnar axis lies on the substrate surface in the center area of Figure 5.

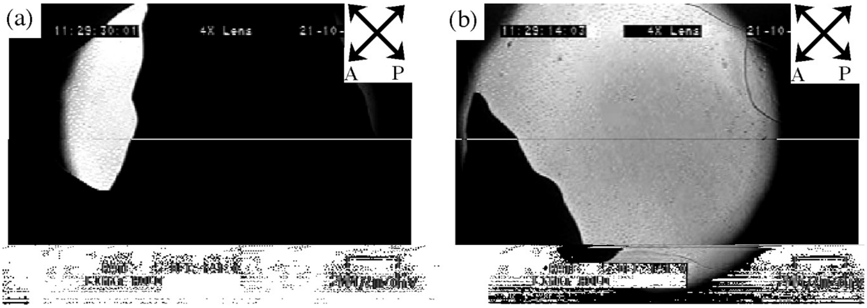

FIGURE 5 Microscopic textures observed for a C4OTP film at 141°C cooled from I.L. (a) before FEL irradiation and (b) after rotation of the sample on the stage by 45°counterclockwise.

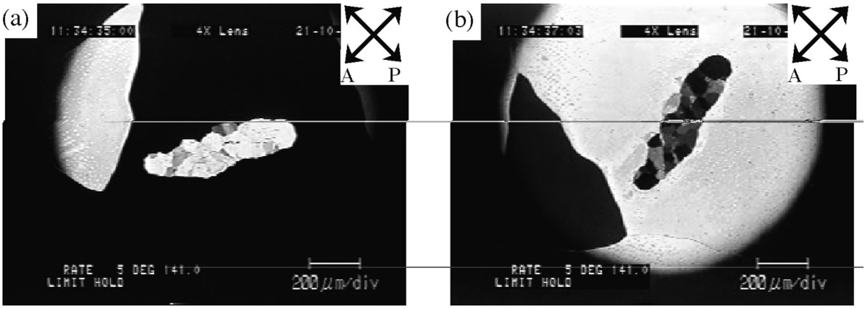

FIGURE 6 Microscopic textures observed for a C4OTP film at 141°C cooled from I.L. (a) after FEL irradiation from slantwise by 1615 cm^{-1} infrared pulses and (b) after rotation of the sample on the stage by 45° counterclockwise. The position of the film is same as that of Figure 5.

Figure 6(a) shows the texture of C4OTP film after irradiation by the pulsed infrared FEL with a wavelength of 1615 cm^{-1} which is absorbed by triphenylene core. The plane of polarization of the IR radiation irradiated was perpendicular to the substrates and parallel to the abscissa in the Figure 6(a). This newly formed domain was quite stable and could be maintained for more than several hours in the mesophase depending on the temperature. A rotation of the microscopic stage gave rise to an alternately and periodic appearance of darkness for this domain under crossed Nicol condition by every 45° as shown in Figure 6(b). This means a uniform alignment of columns is obtained in the newly formed domain. The sample used in the FEL irradiation experiments did not show any change of the phase transition temperatures checked by polarizing microscope observation. This implies that the vibrational excitation and the following thermal process did not cause any significant chemical damage of the compound.

According to our previous work [26–29], this phenomena could be interpreted as the following. First, the molecules become quite mobile in the thermally disturbed domain as a result of the absorption of infrared light by molecules. Following the generation of thermodynamically non-equilibrium states in the irradiated area, the molecules align in the new direction during the time before next pulse was irradiated due to the irradiating infrared light in order to attain a thermodynamically more stable state. It is assumed that the vibrationally excited state relaxes rapidly on a timescale of the order of pico second, followed by the thermal energy diffusion as a slower process. Further irradiation of FEL pulses created a uniform alignment of molecules. The change in polarized microscopic texture indicates that orientational change of the columnar axis in the plane occurred. The results clearly show that the direction of the columnar axis of the plastic columnar mesophase was uniformly changed to the new direction by vibrational excitation with polarized infrared irradiation.

CONCLUSION

It was found that infrared laser irradiation of $\mathrm{Col_{hp}}$ mesophase shown by a typical triphenylene mesogen causes alignment change to form a new domain with uniformity of alignment and this phenomena is by way of the excitation of the selected vibrational mode of a chemical bond. Recent studies on this phenomenon have also shown that a relationship was found for the directions of the polarization of incidence and the transition moment of the vibrational excitation. The results strongly imply that the infrared irradiation is a possible technique for device fabrication by use of plastic columnar mesophase as a liquid crystalline semiconductor.

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