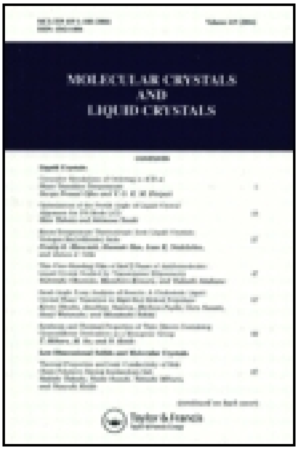

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Infrared Photoinduced Change of Liquid Crystal Domains for a Columnar Mesophase

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Infrared Photoinduced Change of Liquid Crystal Domains for a Columnar Mesophase

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Infrared photoinduced change of liquid crystal domains was investigated for a hexagonal columnar phase of a triphenylene derivative. A uniform change of domains was observed when an infrared laser beam corresponding to the wavelength range with the absorption band of triphenylene core was irradiated. The texture change means that a change of the molecular alignment occurred and it seems that the direction of columns depends on the direction of the incident laser beam. It could provides a novel technology to control the alignment of liquid crystals.

Keywords: discotic liquid crystal; free electron laser; infrared; alignment; columnar phase

INTRODUCTION

Discotic liquid crystals is a well-known example of supramolecular self-assembled systems[1]. The columnar arrangements of disc-shaped mesogens formed by triphenylene, porphyrin and phthalocyanine analogues are a promising architecture for functional materials with some potentials in applications such as one-dimensional conductors, photoconductors, molecular wires and fibers, light emitting diodes and photovoltaic cells[2-9]. In such devices, the orientation and the alignment of the molecules are essentially important for expected functions. The molecular alignment behavior and controllability are quite essential in device fabrications for such applications.

One of characteristic features of liquid crystals, especially for nematic liquid crystal is the better controllability of molecular alignment by external field effects. The nematic molecular alignment can be easily switched even by a slight external electric field. Magnetic field is also effective for molecular alignment switching, but so slow response and not so easy operation of strong magnetic field with the order of Tesla make this method uninteresting[10]. Furthermore, photoswitching techniques of liquid crystal alignment have been extensively studied to obtain a photoinduced change of molecular alignment in a nematic film[11-13]. At present, a rubbed polyimide-coated substrate is widely used to obtain homogeneous alignment of rod-like liquid crystals. However, some trials such as the usage of surface effect and shear flow were made to obtain uniform aligned discotic liquid crystals[14-17]. Recently, Ichimura *et al.* reported a UV-Vis photoalignment of a discotic liquid crystal in the discotic nematic phase on an azobenzene monolayer film by *trans-cis* photoisomerization[18,19]. The results indicate that it is possible to control the optical properties of liquid crystals by photons and furthermore that these methodologies are quite interesting from a viewpoint of device fabrication technology using organic thin films. However only a few results of molecular alignment switching of a discotic liquid crystal have been reported so far and this has been obtained by external magnetic field effect[20].

Recently, a linac-driven free electron laser (FEL) system covering a wide range of spectrum from ultraviolet to far-infrared has been developed[21]. Any trials to control the molecular alignment of a columnar mesophase have not been carried out by use of an infrared light which enable us to activate a specified local part of the molecule with the vibrational excitation in a mesophase. All studies of photoalignment of liquid crystals have been focused on the application of ultraviolet and/or visible light, as it could provide a clean and fast fabrication process of organic thin film devices. A possibility to control molecular alignment and domains of liquid crystals by use of infrared light has not been examined so far, where selective vibrational excitation process is probably related.

Recently, we found the infrared photoinduced alignment change of a discotic liquid crystal for a columnar phase[22]. In this communication, the results about molecular alignment change of a columnar mesophase induced by vibrational excitation is reported.

EXPERIMENTAL

The sample used in this work was 2,3,6,7,10,11-hexakishexyloxy-triphenylene, abbreviated as C6OTP, whose chemical structure and phase transitions are shown in Figure 1.

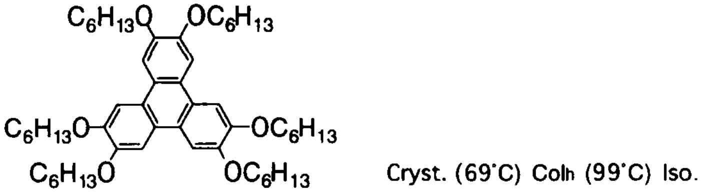

FIGURE 1 Molecular structure and phase transitions of C6OTP.

Its preparation, purification and mesomorphic characterization have been presented and discussed in detail by others[23]. A hexagonal columnar mesophase appeared between the melting and clearing points. The FT-IR spectrum of C6OTP film is shown in Figure 2.

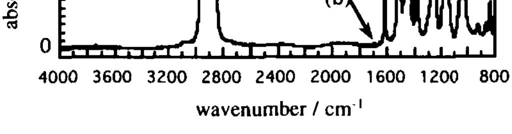

FIGURE 2 FT-IR spectrum of C6OTP.

The absorption peak at 1615 cm^{-1} is assigned to an aromatic C-C stretching vibration of the triphenylene core part. The C6OTP film was prepared between two BaF_2 substrates and mounted on the hot stage (Linkam LK-600 FT-IR), which was attached to an optical polarizing microscope (Olympus BH-2). The temperature of the film was changed from 105 °C to 50 °C, which corresponds to the range between the crystalline phase and the isotropic one involving the hexagonal columnar mesophase.

A schematic representation of the experimental setup is shown in Figure 3. The infrared FEL was guided through a pipe line and a mirror chamber in the experimental room from FEL emission facility. The guided FEL beam was focused in its size to about 0.5 mm in diameter by ZnSe lenses and concave mirrors. The sample on the hot stage of microscope was irradiated by the FEL beam through a multi-jointed manipulator. The microscopic image of the texture can be captured to a video recorder using a CCD camera (Keyence VH-6300C).

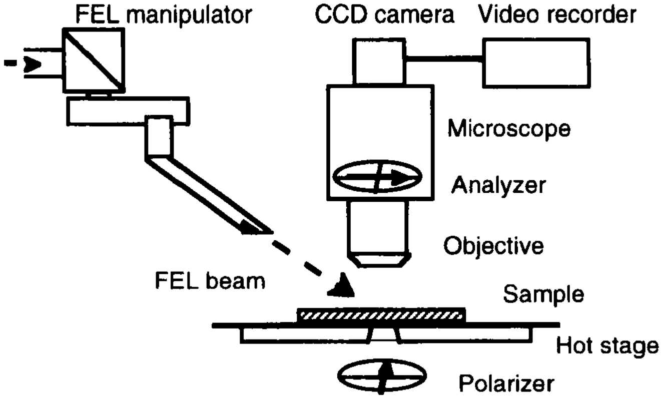

FIGURE 3 Schematic representation of the experimental setup.

The FEL has a complex pulse structure, which consists of a train of macropulses, which themselves contain a train of 300-400 ultrashort micropulses. The width of the macropulses is about 15 μs and the repetition rate is 10Hz. The separation between micropulses is 45 ns. The width of a micropulse is estimated to be less than 10 ps. The peak power of a micropulse is in the order of MW. Although the peak power is very high, the duty factor is as low as 3 × 10^{-8}. Thus, the average power is very low and kept on 10 mW in this experiment. The position of the irradiating FEL beam spot was confirmed by color change of a thermosensitive paper on the stage.

RESULTS AND DISCUSSIONS

Figure 4(a) and 4(b) show the texture of the C6OTP film at 97 °C with irradiation of the pulsed FEL beam with a wavelength of 1615 cm^{-1} (6.19 μm) and 1681 cm^{-1} (5.95 μm), respectively. A bright area appeared in the former case, while no change of the texture was observed in the latter one. No change was observed for the texture when the irradiating infrared light was corresponding to the wavelength range without any absorption bands of C6OTP. This means that the texture change was not on account of the radiation pressure and no signs of the laser ablation were observed.

The oval shape of the changed area in the texture was due to slantwise irradiation by the FEL beam. After a few seconds from the beginning of the FEL irradiation, the irradiated spot changed to bright from dark in the texture. The bright area was incessantly and dynamically changing during the FEL beam irradiation. In particular, the central part of the bright area in the texture showed a rapid and dinamical change. This may indicates that the molecules are quite mobile in the thermally disturbed domain. Following the generation of a thermodynamically non-equilibrium state in the irradiated area, the molecules align in the new direction probably due to the irradiating infrared laser beam. The mechanism of the liquid crystal alignment induced by FEL beam is unclear present. Further irradiation of FEL pulses created a uniform alignment of molecules. The change in the polarizing microscopic texture indicates that switching of the columnar axis from perpendicular to sideward to the substrate occurred. After the FEL irradiation experiments, the phase transition temperatures of the sample were not changed at the level of our detection. This implies the vibrational excitation and the following thermodynamical process did not cause any significant chemical damage to the material. The results clearly show that the columnar alignment of the discotic liquid crystal was changed from perpendicular to sideward to the substrate. The new domains of columnar alignment induced by the FEL irradiation was remained for at least one hour and it was broken into fine domains on crystallization at 51.4 °C.

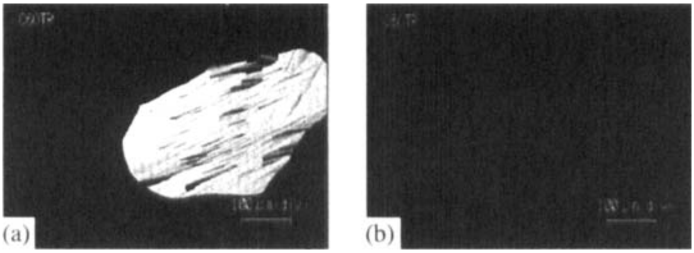

FIGURE 4 Polarizing microscopic textures observed for a C6OTP film at 97 °C under FEL irradiation at (a) 1615 cm^{-1} and (b) 1681 cm^{-1}. The texture before FEL irradiation was that of the homeotropic alignment of Col$_h$ phase (the columnar axis is perpendicular to the substrate), similar to (b).

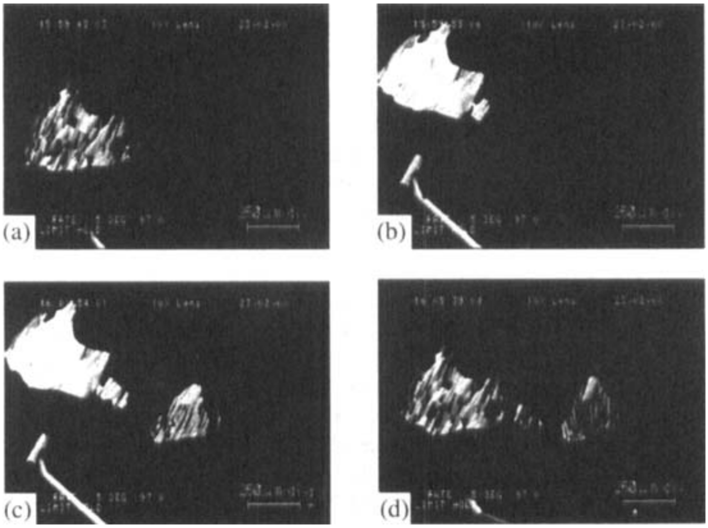

FIGURE 5 Polarizing microscopic textures observed for a C6OTP film at 97 °C of two different direction of the incident FEL beam. (a) after the first FEL irradiation, (b) the sample was slightly rotated by 15°, (c) after second FEL irradiation, and (d) the sample was re-rotated to the previous position.

Figures 5 shows the textures of C6OTP film irradiated by different two directions of the incident FEL beam. Figure 5(a) shows the texture after irradiating the FEL beam, Followed by the clockwise rotation of the sample by 15° on the stage as shown in Figure 5(b). The texture resulted in the second FEL irradiation was shown in Figure 5(c). Figure 5(d) shows the texture observed after a re-rotation to the previous position of the sample. The optical axes of the changing areas in the texture were different each other depending on the direction of incident FEL beam in the film plane. This indicates that the direction of the columnar axis depends on the direction of the incident FEL beam.

As pulsed FEL photons are absorbed by mesogenic molecules, the molecular fluctuations became more vigorous. This generates a thermodynamical non-equilibrium state in the system. Following the liberation of the thermal energy from the excited state, the mesogens form columns which are aligned to a new direction, which is probably dependent on either the direction and/or the polarizing angle of the incident laser beam.

In this method, it is possible to select a chemical bond to be excited by tuning the wavelength of the laser pulse for various infrared absorption bands of the mesogens. Therefore this method could be good for all mesophases, especially for viscous mesophases with a high order of molecules. The procedure seems to be applicable to the generation of a homogeneous alignment from a homeotropic state for C6OTP by using infrared irradiation into the band assigned to an aromatic C-C stretching vibration. In addition, it may be applicable for not only switching the columnar axis of columnar discotics, but also controlling liquid crystal alignment in device fabrications such as producing a conductive line and/or define some other structures in a liquid crystal film as a part of a organic sheet device.

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