Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2010

Mol. Cryst. Liq. Cryst., Vol. 397, pp. 59/[359]–65/[365], 2003

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390213717

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AN INFRARED TECHNIQUE FOR ALIGNMENT CONTROL OF DISCOTIC LIQUID CRYSTALS: A POSSIBLE FABRICATION TECHNOLOGY FOR ORGANIC MICRO/NANO ELECTRONIC DEVICES

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An infrared technique for molecular alignment control of discotic columnar liquid crystals is described. The liquid crystal domain change was induced in hexagonal columnar mesophase by infrared irradiation with a vibrational excitation of the chemical bonds in the triphenylene mesogen. In the new domain a uniform alignment of molecules was attained and the behaviour is essentially related to the polarisation of the incident beam. Also the new domain is quite stable, though depending on temperature. However, such a new domain formation was not observed in the discotic nematic phase.

Keywords: discotic liquid crystal; columnar mesophase; infrared laser; vibrational excitation; free electron laser

The authors thank METI and AIST for the financial support of this research project.

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INTRODUCTION

Since the discovery of discotic liquid crystals, a variety of disc-shaped mesogens have been synthesized and their mesomorphic behaviour was revealed [1]. Recently, some attention has been paid to the discotic liquid crystal, as an interesting candidate for organic semiconductors because of the fast mobility due to the molecularly stacked columnar structure in the mesophase [2,3]. The columnar mesophase of disc-shaped molecules possessing an extended π-conjugation system usually shows high viscosity owing to a strong intermolecular interaction based on its higher order of molecules as well as its extended π-conjugation system. This makes it very difficult to have a liquid crystalline film with a uniform alignment of molecules.

One of the important technologies for the applications of organic self-assembled systems to a part of functional devices is micro-/nano fabrications of molecular aggregations and liquid crystalline materials are promising candidates for this because of the relatively easy controllability of the alignment. For nematic and smectic A phases which are typical liquid crystalline phases with the relatively lower viscosity, some useful methods were developed to obtain such films with a uniform alignment. This has been successfully used in the LCD industries as an important process of device fabrication. However, no methodologies have been shown to realize the liquid crystal alignment control for highly ordered, thus highly viscous mesophases.

Recently, we reported the first observation of alignment change of a hexagonal columnar (Col_h) mesophase induced by vibrational excitation in use of Free Electron Laser (FEL) [4]. This phenomenon seems to be induced by the thermodynamically non-equilibrium state owing to the relaxation of vibrationally excited state of molecules by a successive irradiation of the laser pulses, which are followed by self-assembling as a nature of liquid crystalline molecules. However, it was found that only the turbulence of domains occurs by the incidence for lower ordered/low viscous liquid crystals such as nematic and smectic A phases [5]. Furthermore, it was also indicated that the direction of columns in the irradiated area is in relation to the incident beam direction [6].

In this work, the proposed mechanism of domain change in columnar liquid crystal is shown and some possible applications of this technique are considered with an evidence of a simple micro-sized structure in the film of columnar mesophase.

EXPERIMENTAL

A typical mesogenic compound (C6OTP) showing hexagonal columnar mesophase (Col_h phase) between 69°C and 99°C [7], was used for the

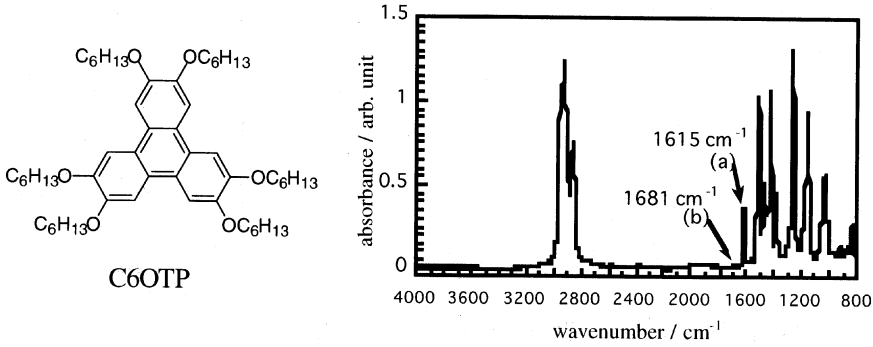

FIGURE 1 The mesogen used for the experiments which shows Col_h mesophase and its IR spectrum at 90°C.

experiments (Fig. 1). The compound is sandwiched by two BaF_2 plates and this cell was set in the temperature-controllable hot-stage (Mettler FP-5 and FP-52) which is put on the stage of the polarizing microscope (Olympus BH2). The domain change was observed under crossed polarisers (Fig. 2). The infrared laser incidence was introduced into the cell slantwise because of a spatial condition around the microscope. Thus, the observed domain change had an ellipsoidal shape.

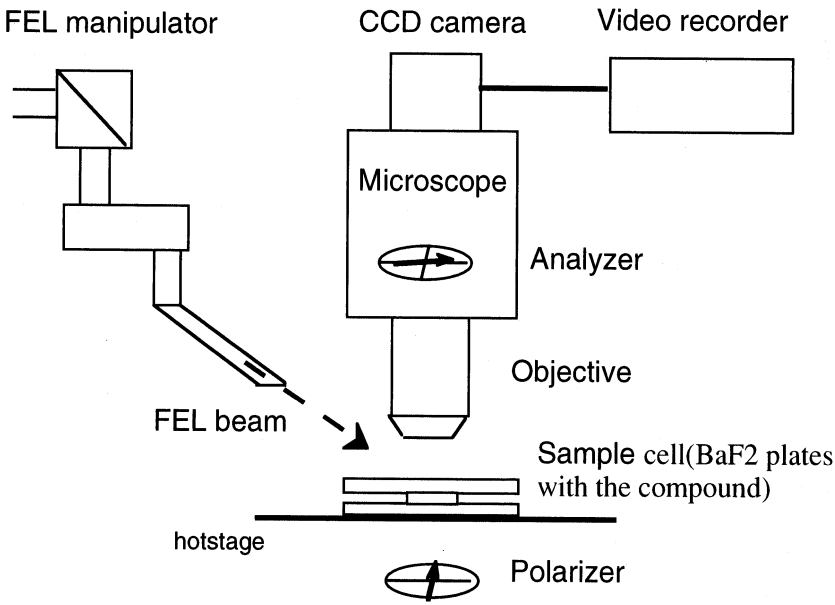

FIGURE 2 Schematic representation of the experimental set-up.

The infrared pulsed beam was provided by Free Electron Laser (FEL) System by which one can obtain a tuned beam in wavelength. The beam power was 10 mW with *ca*. 10% of fluctuations and it is linearly polarised at the incident edge of manipulator. The details of FEL was reported elsewhere [8].

RESULTS AND DISCUSSION

The liquid crystal domain change caused by the vibrational excitation of a C=C stretching mode of the triphenylene skeleton is shown in Figure. 3. C6OTP was found to have a strong tendency of homeotropic alignment between two BaF_2 substrates.

In the incidence at 1615 cm^{-1} (C = C stretching vibrational mode of triphenylene), the area absorbing the incidence gradually changes to be bright, whilst the incidence at 1625 cm^{-1} (almost no absorption range) did not give any change of the homeotropic domain as shown in Figure. 3. The domain change takes place only in the incidence at the wave number

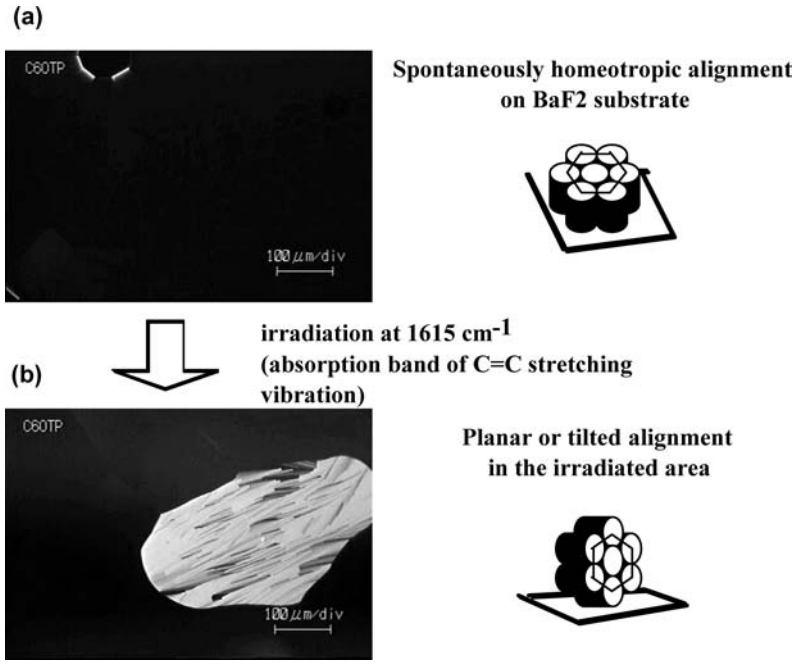

FIGURE 3 Infrared-incident induced domain change in a homeotropic film of Col_h mesophase

corresponding to the absorption band. The incidence to excite other bands leads to the same behaviour detectable under the microscope. It was revealed that the new domain formed by the infrared incidence has an optically uniform property evidenced by the rotation of the microscopic stage, where one can see the repetitive change between dark and bright views by 45° of the rotation angle. This indicates that the molecular alignment in the new domain is almost uniform in the scale of wavelength in the visible region.

Interestingly it was found that this new domain could remain for several minutes to hours depending on the temperature of the mesophase.

However, the similar experiments for a conventional calamitic system (FLNOC16hy) showed no alignment behaviour in both nematic and smectic A (SmA) phases, while the molecules are likely to align in a homeotropic way between BaF_2 plates. Also was observed the same behaviour for discotic nematic phase.

In the calamitic nematic phase, for example, it was observed that the incidence at $1715\,cm^{-1}$ caused transient and dynamic turbulence of homeotropic domains. However, this turbulence was ceased back immediately to the original homeotropic alignment (Fig. 4). This indicates the stress around the domain boundaries is not stronger than the surface anchoring force working between the molecules and BaF_2 substrate.

A series of these phenomena is obviously intensity-dependent for the incidence and also depends on the extinction coefficient of the vibrational

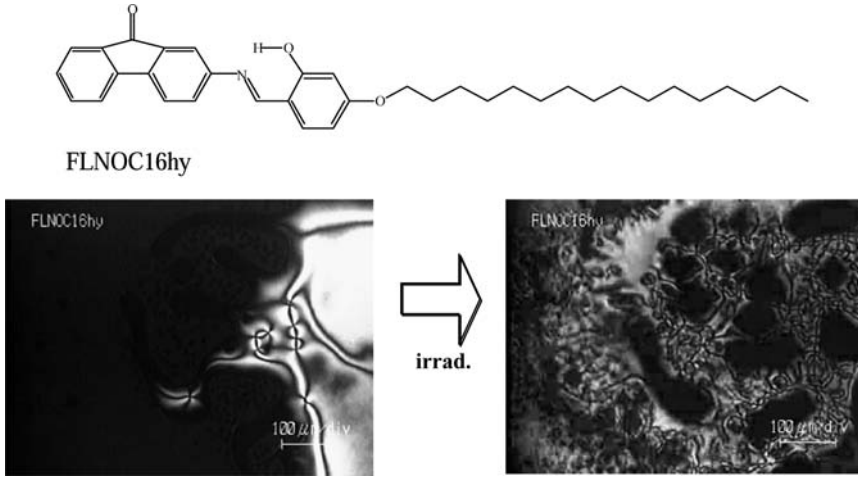

FIGURE 4 Turbulence of nematic domain in FLNOC16hy caused by the vibrational excitation of C = O stretching by the infrared incidence.

band because the disturbed area of the liquid crystal domain increases as the incident power is enhanced at the temperature.

In the case of Col_h mesophase of C6OTP, the relation between the polarising direction of the incident beam and the resultant alignment of discotic molecules has been recently revealed. Furthermore, a recent trial for the Col_h mesophase indicate that some line-drawings in a liquid crystalline film with a uniform homeotropic alignment could be successfully obtained using this technique, in which the averaged direction of columnar axis is parallel to the substrate plane (planar alignment). This may imply that image storage could be operated by this technique.

Infrared laser incidence to liquid crystalline systems involving a process of vibrational excitation and the relaxation seem to be useful for domain control of Col_h mesophase. Considering the results of discotic nematic as well as calamitic nematic and SmA/SmC phases, it is indicated that this technique is applicable to the alignment control of, highly ordered liquid crystalline phases.

SUMMARY

In the last few decades, alignment control of nematic liquid crystals have been extensively studied for an industrial technology in relation to the display devices and the controllability has been successfully attained by surface treatment and application of an external field. However, these techniques are not useful for highly viscous liquid crystalline phases and most of such phases have more highly ordered structure of the orientational order. Even for nematic and SmA/SmC phases, liquid crystalline molecules possessing some chemical structures providing strong intermolecular interaction tend to show relatively higher viscosity. Furthermore, considering that recent studies on liquid crystalline semiconductors have revealed that the highly ordered mesophase is suitable for obtaining a fast mobility and indeed, a plastic phase such as Helical phase [9], shows fast charged carrier mobility along the columnar axis [2] and columnar mesophase materials containing a largely extended π-electronic conjugation system tend to exhibit fast carrier mobility [10,11], this technique seems to be able to provide a new method to control the domain size and the molecular alignment within the domain for such highly viscous mesophases.

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