Anisotropic Alignment Change of Columnar Liquid Crystal by Polarized Infrared Irradiation

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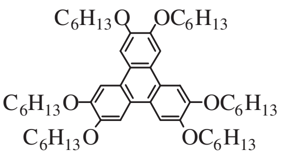
Infrared photoinduced alignment change of liquid crystal domains was investigated and a uniform and anisotropic change of domains was observed. The texture observation and polarized microscopic IR spectra show that a change of the molecular alignment occurred and the direction of columns depends on the polarizing angle of an irradiating infrared light.

Recent studies on electronic properties of the highly ordered mesophase materials have revealed that they are good candidates as organic semiconductor for electronic devices because of the fast charge carrier mobility[1] as well as the anisotropic conduction property.[2] In columnar mesophase where disc-shaped molecules stack to each other to form columnar structure, a fast carrier mobility (ca. $10^{-1}\,\mathrm{cm^2V^{-1}s^{-1}}$) by electronic process of carrier transportation was found, and this is comparable to those of organic single crystal and amorphous silicon.[3] In order to apply this new property of liquid crystals to electronic functional devices, an appropriate technique for the alignment control on substrate is necessary. Studies to obtain a reasonable controllability for liquid crystal alignment have been extensively carried out for the conventional rod-like systems exhibiting nematic and smectic phases with surface modifications of substrates and photoirradiation. Furthermore, in these years these were extended to the unconventional liquid crystalline systems such as discotics.[4] However, the great success in these methods is shown almost only for the relatively lower ordered phase and they are not available for the higher ordered mesophase such as columnar one especially, columnar mesophase formed by extended π-conjugated systems, while the semiconduction properties of such liquid crystals are getting more and more important topic for future technology.

Recently, in a series of experiments for hexagonal columnar ($\mathrm{Col_h}$) phase of a well-known discotics mesogen, 2,3,6,7,10,11-hexahexyloxytriphenylene (C6OTP),[5] by use of free electron laser (FEL), we found that the homeotropic domain where the columnar axis aligns perpendicular to the substrate could be changed to domains with a planar or tilted alignments of columns by the excitation of C=C stretching vibration of triphenylene.[6] Considering that all of the photonic techniques applied to the alignment control for the lower ordered systems are realized with UV and visible light, this phenomenon is expected to provide a novel technique for the alignment control of highly ordered and thus highly viscous liquid crystals.

In this work, in order to reveal the relationship between the aligned azimuth angle of the columnar axis and the polarization of the infrared incidence was investigated for C6OTP as shown in Scheme 1.

A hexagonal columnar mesophase appeared between the melting and clearing points. C6OTP film was prepared between two $\mathrm{BaF_2}$ substrates which have high transparency in infrared region, with 2 µm silica-beads as spacer and mounted on a hot stage. The microscopic texture was recorded using a CCD camera which was attached to an optical polarizing microscope. The cell was heated to 105 °C at which the compound melts into the isotropic liquid and cooled down to 94 °C to form domains of $\mathrm{Col_h}$ phase. A homeotropic alignment was spontaneously attained between two $\mathrm{BaF_2}$ plates. The incident IR-FEL beam comes normal to the cell through an IR-polarizer. The pulse sequence of FEL consists of a train of macropulses, which themselves contain a train of 300–400 ultrashort micropulses and their beam quality is likely to fluctuate.[7] This actually makes the detailed and quantitative analyses of this phenomenon far difficult. The IR-FEL beam average power was kept on 8 mW in this experiment. The IR-FEL beam was focused to about 0.5 mm in diameter by ZnSe lens. The polarization property and pulse sequence of a FEL beam is shown in Figure 1 and it shows a linear polarization. A microscopic IR absorption dichroism was measured by a microscopic FT-IR spectrophotometer.



Cryst. (69 °C) $\mathrm{Col_h}$ (99 °C) Iso.

Scheme 1.

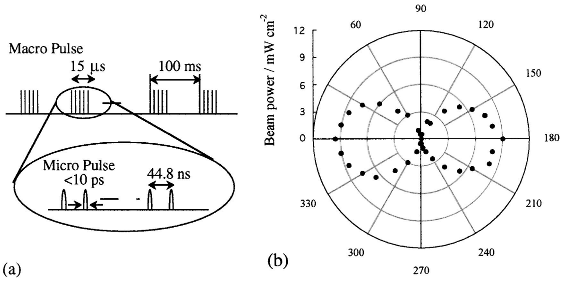


Figure 1. (a) The FEL pulse profile. (b) Polarization property of a FEL beam intensity.

By the incidence at $1615\,\mathrm{cm^{-1}}$ of which wavenumber corresponds to a C=C stretching vibration band of the triphenylene core, the area under the incidence gets bright and the molecular alignment is essentially in a uniform way as shown in Figure 2. This domain newly formed was quite stable and could be maintained for a few hours to days by keeping the temperature in the mesophase region. Every 45° rotation of the microscopic stage gave rise to an alternately and periodic appearance of darkness for this domain under cross Nicol condition. This means a uniform alignment of molecules is obtained and it is almost planar alignment where the columnar axis lies on the substrate surface.

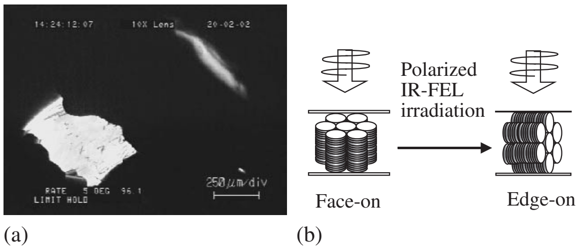


Figure 2. (a) Microscopic textures observed for a C6OTP film after IR-FEL irradiation by 1615 cm^{-1} infrared and (b) a schematic reperesantation of alignment change of C6OTP.

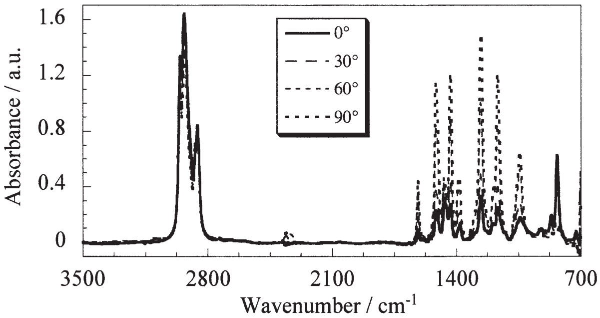


Figure 3. Polarized microscopic IR absorption spectra of C6OTP film for which alignment has been changed by infrared irradiation.

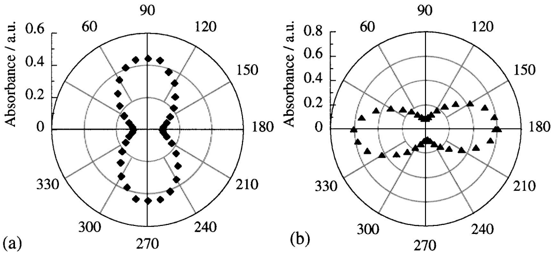


Figure 4. Angle dependency of microscopic polarized infrared absorption intensity at (a) 1615 cm^{-1} (C=C aromatic stretching vibration) and (b) 839 cm^{-1} (C–H aromatic out-of-plane vibration) of C6OTP film.

The polarized microscopic IR absorption spectra for the domain changed by infrared irradiation was measured (Figure 3) to confirm that the molecular plane aligns normal to the plane formed by electric wave of the incident beam. The angle of the absorption maxim at the peak of 1615 cm^{-1} (assigned to the C=C aromatic stretching vibration of triphenylene ring) is perpendicular to the polarization direction of irradiated IR-FEL beam as shown in Figure 4. On the contrary, the angle of the absorption maximum at the peak of 839 cm^{-1} which is assigned to the C–H aromatic out-of-plane vibration is parallel to the polarization direction of incidence. This indicates that the plane of discotic molecules aligns perpendicular to the plane of polarization of incidence. In other words, the results indicate that the relation between the polarizing direction of the incident infrared light and the azimuthal direction of the columnar axis is parallel. These are consistent with the polarizing microscope observation. The direction of in-plane columnar axis is controlled by the angle of polarization plane of infrared incidence.

Furthermore, this relation can be also confirmed by the incidence at another wavenumber of incidence which corresponds to an absorption for exciting another vibrational mode or another chemical bond. The incidence was carried out at 1166 cm^{-1} which corresponds to the wavenumber of the absorption for C–O–C stretching asymmetric vibration of the linkage ether group to give the same manner of the molecular alignment behavior where the triphenylene plane is likely to align normal to the substrate.

The whole mechanism of this phenomenon is still unknown in part. However, the following is a possible model of alignment mechanism. The relaxation process from a vibrational excited state gives the corresponding thermal energy into the system and this injection of energy seems to cause the transient turbulence of columnar structure. This means each fragment of columnar structures is relatively mobile than that before the incidence. If some fragments of columns occasionally align in a way such that the molecules are no longer excited as the transition moment of the vibrational excitation is perpendicular to the electric component of polarizing beam, although the continuous incidence makes such a dynamic state. The cycle of anisotropic heating could lead to the creation of a uniform alignment of molecules. This technique could provide a novel technology to control the columnar alignment of viscous systems of liquid crystals.

References

1 D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher, and K. Siemensmeyer, *Phys. Rev. Lett.*, **70**, 457 (1993); M. Funahashi and J. Hanna, *Phys. Rev. Lett.*, **71**, 602 (1997); A. M. Craats, J. M. Warman, K. Müllen, Y. Geerts, and J. D. Brand, *Adv. Mater.*, **10**, 36 (1998); N. Mizoshita, H. Monobe, M. Inoue, M. Ukon, T. Watanabe, Y. Shimizu, K. Hanabusa, and T. Kato, *Chem. Commun.*, **2002**, 428.

2 N. Boden, R. J. Bushby, and J. Clements, *J. Chem. Phys.*, **98**, 5920 (1993).

3 D. Adam, P. Schuhmacher, J. Simmerer, L. Haussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf, and D. Haarer, *Nature*, **371**, 141 (1994).

4 K. Ichimura, *Chem. Rev.*, **100**, 1847 (2000); M. Okazaki, K. Kawata, H. Nishikawa, and M. Negoro, *Polym. Adv. Technol.*, **11**, 398 (2000); H. Monobe, H. Azehara, Y. Shimizu, and M. Fujihira, *Chem. Lett.*, **2001**, 1268; K. Kawata, *Chem. Rec.*, **2**, 59 (2002).

5 C. Destrade, M. C. Mondon, and J. Malthete, *J. Phys.*, **40**, 17 (1979).

6 H. Monobe, K. Awazu, and Y. Shimizu, *Adv. Mater.*, **12**, 1495 (2000); H. Monobe, K. Awazu, and Y. Shimizu, *Mol. Cryst. Liq. Cryst.*, **364**, 453 (2001); Y. Shimizu, H. Monobe, M. Heya, and K. Awazu, *Jpn. J. Appl. Phys.*, **41**, Suppl. 41-1, 104 (2002).

7 H. Horiike, T. Tsubouchi, K. Awazu, M. Asakawa, and M. Heya, *Jpn. J. Appl. Phys.*, **41**, Suppl. 41-1, 10 (2002).

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