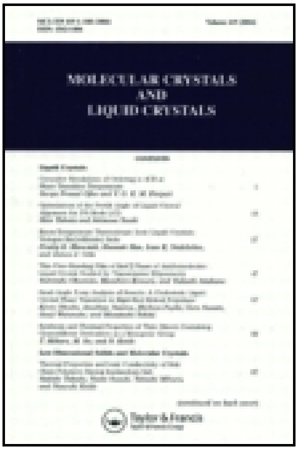

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A Novel Technique for the Alignment Control of Highly Ordered Liquid Crystals Based on Vibrational Excitation of Chemical Bond by Polarized Infrared Laser

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A Novel Technique for the Alignment Control of Highly Ordered Liquid Crystals Based on Vibrational Excitation of Chemical Bond by Polarized Infrared Laser

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Recent findings were briefly described for the liquid crystal alignment change under the polarized infrared laser irradiation using an free electron laser (FEL), which causes the excitation of vibrational mode of chemical bond in the mesogen. For hexagonal columnar (Col_h) mesophase of hexahexyloxytriphenylene (C6OTP), a new domain with a certain uniformity of molecular alignment could be attained, in which one can control the director orientation in the combination of the polarization direction of the incidence and the direction of the transition dipole moment for the vibrational excitation. This phenomenon is not observed for the relatively lower-ordered liquid crystals with the lower viscosity such as discotic nematic (N_D) phase as well as nematic (N) and smectic A/C (SmA/SmC) phases of calamitics. It could be expected that the polarized infrared irradiation gives a novel technique of domain control of the highly viscous mesophase, which is applicable to a fabrication of organic devices by use of liquid crystalline materials for electronics.

Keywords: columnar mesophase; molecular alignment control; organic electronic device; vibrational excitation

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INTRODUCTION

The alignment control of liquid crystals is one of the most essential issues for the device applications because of the highly anisotropic properties of liquid crystalline materials. It has a rather long history over at least 30 years for nematic liquid crystals being applied to the display devices [1]. Also found the development of successful techniques in the alignment control for ferroelectric liquid crystals (chiral SmC phase) [2]. However, these techniques are good only for lower ordered, thus lower viscous liquid crystals such as N, SmA and SmC phases and for the more highly ordered phases, any reliable techniques has not been developed.

On the other hand, the characteristic structure of columnar mesophase (molecular stacking) of disotic liquid crystals have been drawn much attention as an interesting architecture of self-assembled systems for charge and energy migrations in electronic process along the axis. In particular, the studies of discotic liquid crystals in these years have shown some of the interesting features as a novel electronic material of organics such as semiconductors since the discovery of fast mobility of the charged carriers ($10^{-1}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$) in columnar mesophase, which is comparable to that of a-silicon [3]. Also the recent studies have found novel systems of largely extended π-electronic conjugation for liquid crystalline semiconductors such as hexabenzocolonenes [4].

However, it is not so difficult to imagine that one has to face with a problem in the application of these materials to functional devices, meaning a certain difficulty of the alignment control of liquid crystal domains and films arises because of the high viscosity resulting from the strong intermolecular interactions based on both of the relatively large π-electronic conjugation structure of the molecular core and the relatively higher order of molecular orientations, as compared to those of the conventional liquid crystals such as N and SmA/C phases. In fact, the recent studies show only a few successful results in obtaining a well-controlled alignment of disc-shaped mesogenic molecules (liquid crystalline semiconductors) in device structure, whilst recent research and developments of organic electronic devices have shown a remarkable progress in their fabrication techniques in which crystalline and amorphous states of organic materials are used [5]. For example, a room-temperature hexabenzocolonene mesogen shows a spontaneous alignment behavior of molecules for planar one on a polytetrafluoroethylene (PTFE) film coated by friction transfer technique which enables us to bridge the two electrodes to give the performance as Field Effect Transistor (FET) [6]. Also a novel approach of chemical structure modification of mesogens has been reported in which the introduction of fluoroalkylated chain into the peripheral parts of a triphenylene to show the strong tendency of spontaneous homeotropic alignment on a variety of substrate surface for the Col_h mesophase [7]. These approaches to get the well-controlled alignment of Col_h mesophase might be strongly dependent on the chemical structure as well as the mesomorphic properties of mesogen and thus, a novel technique would strongly be required to have the independent nature of such characters of mesogenic molecules.

In these years, it was found that polarized infrared laser irradiation of Col_h mesophase of a typical columnar mesogen derived from triphenylene causes an alignment change to form a new domain with a certain uniformity of the alignment and this phenomenon is by way of the excitation of the selected vibrational mode of a chemical bond [8–11]. Recent studies on this phenomenon have also shown that this is a possible fabrication technique to form a certain area of a uniform domain in a Col_h mesophase film [12,13].

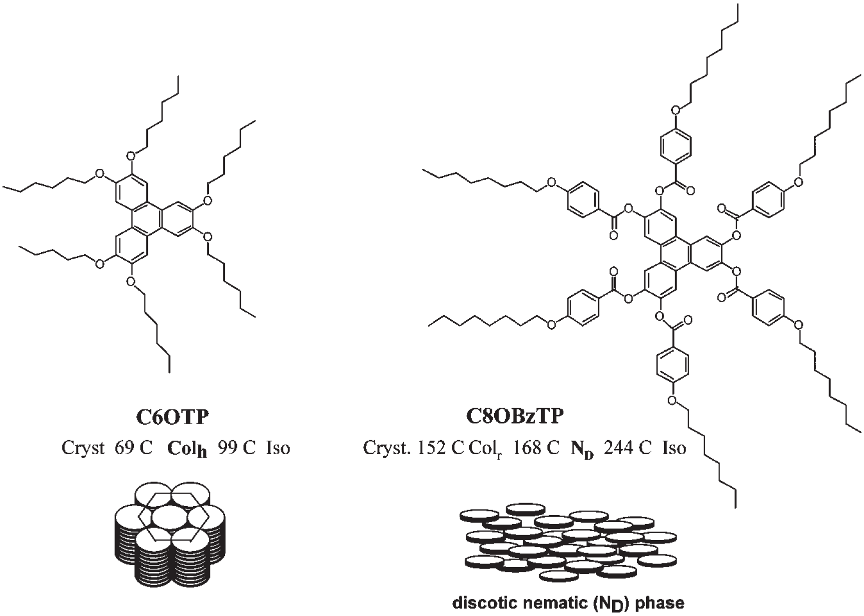
In this article, some evidences of reorientation to form liquid crystalline domains with uniform alignment of molecules under the polarizing infrared irradiation are shown to discuss the possibility of the polarized infrared technique as a novel tool for the device fabrication using highly ordered mesophases as an important component for the performance.

EXPERIMENTAL

The mesogenic compounds used in this work and their phase transition temperatures are shown in Scheme. The infrared irradiation was carried out using Free Electron Laser (FEL) in Osaka University, which is wavelength-tunable laser system based on Synchlotron radiation [14]. The incident beam power was ca. 10–8 mW as an averaged one because of some fluctuation of the generated laser beam. The beam power profile essentially has Gaussian-type distribution and for the irradiation, it was focused by ZnSe lense to give the cross section with ca. 0.5 mm of the diameter. The change of the liquid crystalline textures was observed using a polarizing microscope under crossed polarized condition and the phenomenon was detected by CCD camera to record in video tapes as a motion picture by a video recorder. The details of the experiments are described in Ref. [9].

RESULTS AND DISCUSSION

Figure 1 shows the first observation of the texture change of the Col_h mesophase of C6OTP under the successive irradiation, where the



SCHEME

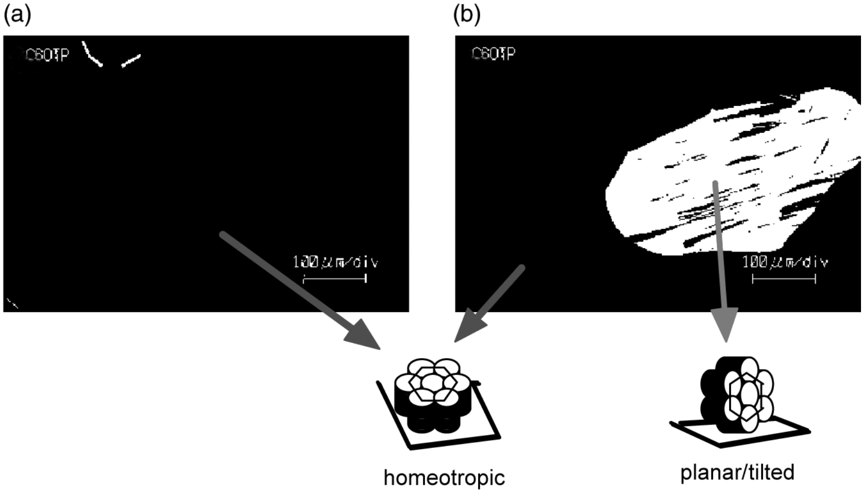


FIGURE 1 Texture change of Col$_h$ mesophase for C6OTP (90°C) under the infrared irradiation to excite the C−C stretching mode of the triphenylene ring (1615 cm^{-1}). (a) Before the irradiation, a homeotropic alignment was spontaneously formed on cooling from the isotropic phase. (b) After the successive irradiation, a new domain with an ellipsoidal shape comes out against the homeotropic area.

compound was sandwiched by two BaF_2 substrates. It was a new finding that between the BaF_2 substrates, C6OTP shows strong tendency to give a homeotropic alignment and after the successive irradiation of the incident beam at 1615 cm^{-1} corresponding to the absorption band of C–C stretching mode of the aromatic triphenylene ring, a new domain was formed with a almost ellipsoidal shape in the homeotropic domain. The resulting ellipsoidal shape of the new domain is due to the slantwise irradiation of the beam. The new domain has almost uniformity of the molecular alignment, indicated by the periodic change of the brightness in the texture under rotating the microscopic stage. This is not a phenomenon with quick formation of new domain under the irradiation. It requires a certain time ($\sim$10 sec) for the beginning of the texture change and this waiting time depends on the temperature at which the irradiation is carried out and one can see the higher temperature in irradiation leads to the shorter time. The irradiation at 1681 cm^{-1} where the molecules have almost no absorption of the incident photon energy, never give rise to any change of the original domain. This means that the photon absorption to excite the vibration mode of chemical bond is necessary for the domain change of liquid crystal. This is indeed quite reasonable, considering the fact that the excited state relaxes to the ground state within a time scale of pico second order accompanied with the thermal energy which is diffused by way of through-bond and molecular collisions in a condensed matter. This strongly implies the thermal injection into the system followed by the relaxation of the vibrational excited state concerns with the formation of new domain having a uniform alignment of molecules. In addition, the change of the irradiation power affect the size of perturbed domain and the less power gets the smaller area of turbulence in the texture. This also supports that the thermal energy injection followed by the vibrational excitation is involved in this phenomenon.

Here, it is noteworthy to enphasize that the newly formed domain could have rather long lifetime, dependent on the temperature where the higher temperature leads to the shorter lifetime. This fact is interesting when one sees the contrast behavior in N_D phase shown by C8OBzTP. The irradiation to C8OBzTP at 1615 cm^{-1}, which is the wavenumber corresponding to the band of the C–C stretching mode of the aromatics, does cause only dynamic turbulence of the texture (Fig. 2) and this turbulence immediately stops to go back to the original homeotropic alignment of domain when the irradiation is cut off. The N_D mesophase exhibited by C8OBzTP also shows strong tendency for homeotropic alignment between BaF_2 substrates. For N_D phase, there was no evidence that new domains with the

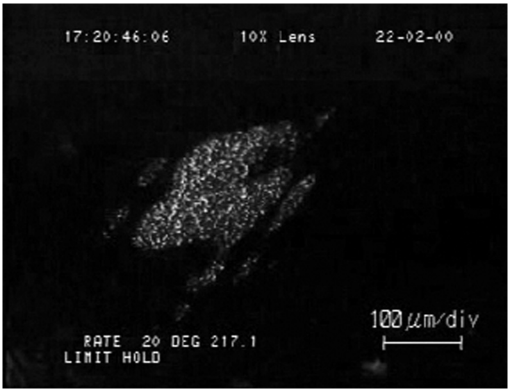


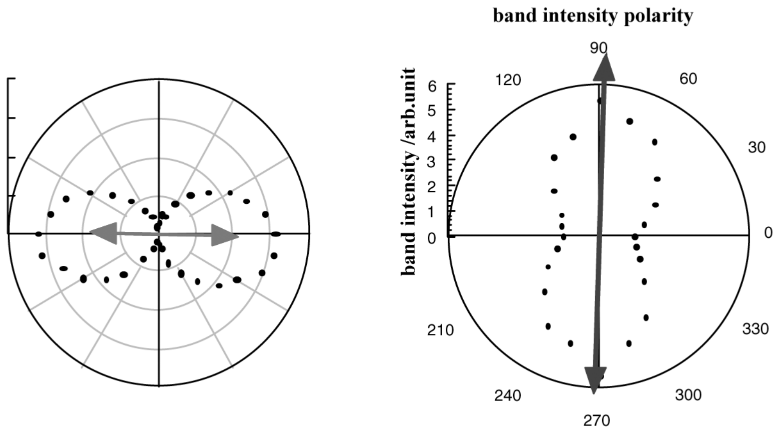
FIGURE 2 A dynamic turbulence of the homeotropic texture of N_D phase (217°C) under the irradiation at $1615\,cm^{-1}$ (C–C stretching mode of the aromatics). The bright area is a dynamic turbulence of domain texture.

uniformity are formed in a stable manner like Col_h mesophase as described above. This is probably due to the far lower viscosity of N_D phase, meaning the alignment is strongly subject to the substrate surface (surface anchoring determining the alignment). This behavior was also observed for N and SmA/C phases of a calamitic liquid crystal [15].

Further experiments recently carried out revealed one interesting relation between the polarizing direction of the incident beam and the direction of the transition moment of the vibrational excitation. Figure 3 shows the relation between the polarizing direction of the beam and the distribution of the band intensity for the C–C stretching mode ($1615\,cm^{-1}$). It is clearly seen that the triphenylene mesogens align in a way that the molecules no longer absorb the incident photon. The new uniform domain has a planar alignment of molecules (the columnar axis parallel to the substrate surface), meaning the initial homeotropic alignment was changed to the planar one [12].

Furthermore, the irradiation at $839\,cm^{-1}$ (C–H wagging out-of-plane mode) to the planar domain formed by the irradiation at $1615\,cm^{-1}$ under the same direction of the incident polarization resulted in realizing the initial homeotropic alignment (return to the initial state of alignment).

These results mean this technique of polarizing infrared laser irradiation could provide a novel method to control the alignment of highly viscous liquid crystals. In our recent experiments, a H-shaped uniform domain with a planar alignment was successfully obtained



polarization at 1615 cm^{-1}
(C=C str. mode of the triphenylene core)

band intensity distribution of the C-C stretching mode

FIGURE 3 The observed distribution in the band intensity of the C–C stretching mode of the triphenylene core, which directly shows the perpendicular reorientation against the polarizing direction of incident beam. The irradiation and spectral measurements were carried out at 90°C (Col$_h$ mesophase).

in the homeotropic film of Col$_h$ mesophase for C6OTP mesogen (Fig. 4) [13]. This makes it expected that one can prepare a polymer film with a liquid crystalline order by the following photo polymerization after

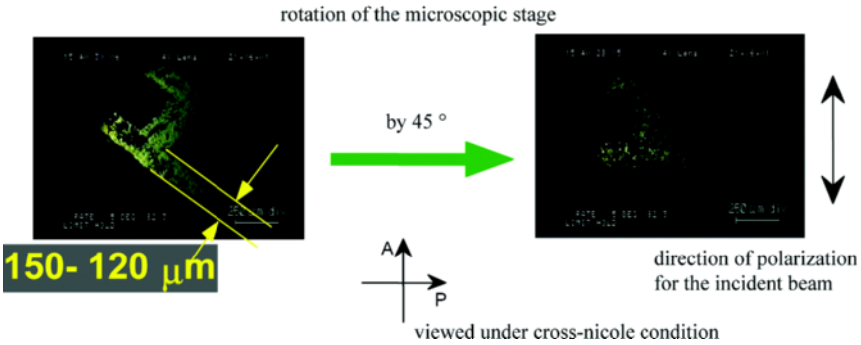


FIGURE 4 A H-shaped domain fabricated by the manual scanning of the polarized infrared beam (1615 cm^{-1}) at °C. The rotation of the microscopic stage indicates the domain has an almost uniform alignment of molecules, though some parts are not probably due to the fluctuation of beam power and quality.

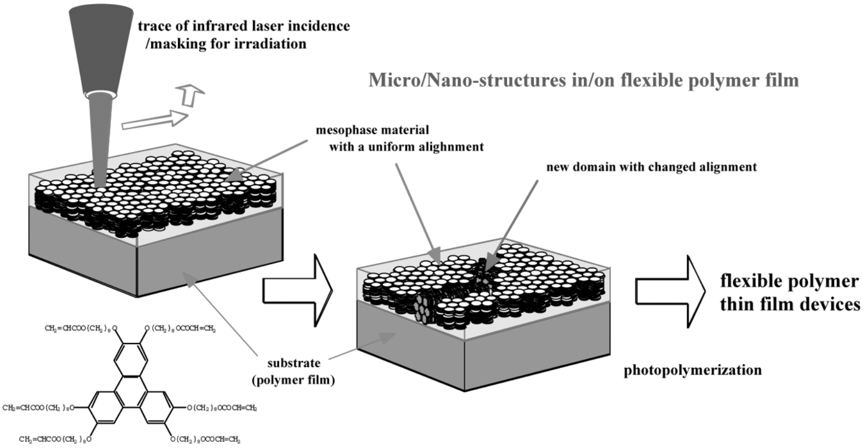


FIGURE 5 A schematic representation of a novel technique for the processing of functionalized polymer film by use of highly ordered mesophase materials.

the infrared treatment, where some domains with uniformity of the molecular alignment independently exist in one sheet of the film like a circuit in a thermally stable manner (without no phase transitions in a certain range of temperature), when considering the local order parameters are changed in 70% decrease of the parameter by photopolymerization in discotic nematic phase [16,17]. The simple image of the novel technique is schematically drawn in Figure 5.

CONCLUSION

The infrared irradiation to excite a vibrational mode of chemical bond in a liquid crystalline phase with high viscosity was found to induce the alignment change to form a new domain with the uniformity of the alignment of which direction could be determined by the combination of the polarizing direction of the incident beam and the direction of the transition moment of the vibrational excitation for the molecular anisotropy in shape. This is expected to provide a novel technique for a device fabrication using highly viscous mesophase materials.

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