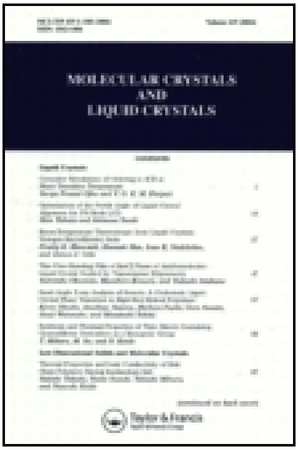

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Alignment Behavior of Discotic Nematic and Rectangular Columnar Mesophases on Self-Assembled Monolayers of Alkanethiol and Asymmetrical Alkyl Disulfide

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ALIGNMENT BEHAVIOR OF DISCOTIC NEMATIC AND RECTANGULAR COLUMNAR MESOPHASES ON SELF-ASSEMBLED MONOLAYERS OF ALKANETHIOL AND ASYMMETRICAL ALKYL DISULFIDE

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Alignment behavior of a discotic liquid crystalline triphenylene (C8OBTP) on substrates coated with self-assembled monolayers (SAMs) of alkanethiol and asymmetrical alkyl disulfide was investigated by polarized microscopy. Discotic nematic (N_D) and rectangular columnar (Col_r) phases of C8OBTP shows a different alignment behavior depending on the element of SAMs. C8OBTP exhibits a fan-shaped texture on an alkanethiol SAM in Col_r phase, while it has a tendency to show a planar alignment on asymmetrical alkyl disulfide SAM. The different elements of the SAM could influence the alignment behavior of discotic liquid crystal distinctly even in columnar mesophase which has highly self-cohesive forces of systems.

Keywords: alignment; alkanethiol; asymmetrical disulfide; columnar mesophase; discotic liquid crystal

INTRODUCTION

The control of the anisotropic structures for the functional materials is of importance the enhancement of properties such as electric conduction,

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electronic transportation, refractive index and optical polarization [1]. 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 a field of matter that posses anisotropic molecular order and fluidity which one can control the molecular alignment easily.

One of characteristic features of liquid crystals, especially for nematic liquid crystal is the good controllability of molecular alignment exerted by the surface treatment. At present, a rubbed polyimide film is widely used to obtain a homogeneous alignment of rod-like liquid crystal systems [1]. Since the alignment of liquid crystal molecules is critically determined by the nature of an outmost surface layer of substrates, the monolayers are used to analyze the relationship between structure of monolayers and the mode of liquid crystal alignment. For rod-like liquid crystals, representative procedures to provide liquid crystal aligning monolayers include the chemisorption of silylating reagents [2,3], and self-assembled monolayer (SAM) deposition of alkanethiols on gold [4–6].

On the other hand, discotic liquid crystal has shown some interesting features for their electronic properties like charge migration phenomena along a columnar axis [7–11]. In addition, recent studies for photoplolymerization of liquid crystals indicate such a molecular order of discotic liquid crystal could remained in polymer film [12–14], leading to a sophisticated invention of optical compensator for wider view angle of liquid crystal display [13,14]. These imply that discotic liquid crystals are a good candidate for organic thin film devices if their alignment is well composed.

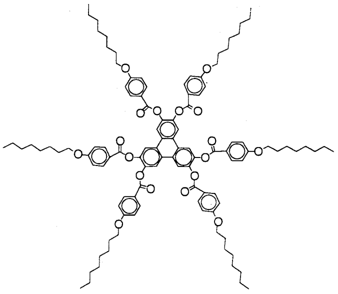
Surface effects and shear flow have often been used in order to obtain uniformly aligned films of discotic liquid crystals for studies of their potential as novel optoelectronic functional materials [14–19]. The monodomain oriented discotic liquid crystal without defect has been obtained in N_D phase by the substrates coating liquid crystal alignment films typically used for rod-shaped liquid crystals, according to the alignment regulation force of the alignment film probably due to lower viscosity of nematic discotics. Recently, UV-vis photoalignment of discotic liquid crystals in also N_D phase by using photoreactive monolayer films has been reported to indicate that it is possible to control the optical properties of liquid crystal devices by photons [20,21]. However, only few results of molecular alignment controlling in columnar phases of discotic liquid crystals were reported so far using infrared laser irradiation [22,23] or surface effect [24]. For columnar phases, the highly cohesive forces of discotic molecules causes the formation of the multidomain structure rather than the monodomain structure [14,19].

In this work, alignment behavior of 2,3,6,7,10,11-hexa(4-octyloxybenzoyloxy) triphenylene (C8OBTP) on SAMs consisting of a hexadecanethiol (C16) and an asymmetrical alkyl disulfide, butyl hexadecyl disulfide (C4C16), was investigated by polarized microscopy. SAMs were prepared on glass plates which was coated with gold film formed by sputtering.

EXPERIMENTAL

Figure 1 shows chemical structure of liquid crystalline triphenylene, C8OBTP. C8OBTP shows three enantiotropic phase transitions [25]. The two mesophases, Col_r and N_D phases appear (C 150 Col_r 167 N_D 238 Iso). During these experiments, the phase transition temperatures of the sample were not changed in the detectable level. Figure 2 shows chemical structures of alkanethiol and asymmetrical alkyl disulfide of which consist SAMs using in this work. C4C16 was synthesized from the corresponding thiols of butanethiol and hexadecanethiol by iodine oxidation [26]. The resulting disulfide was separated and purified by high performance liquid chromatography.

The C8OBTP films were prepared on glass substrates with two types of SAM on sputtered gold film. The gold-coated substrates were prepared by the following method [27]. Micro-cover glass plates obtained from Matsunami Glass Industry were cleaned using an ozone cleaner (Nippon Laser & Electronics Lab.) for 30 min. Gold films (ca. 10 nm) were deposited on the cleaned cover glass plates with a Hitachi E-1030 ion sputter coater



C8OBTP

	crystal		Col_r		N_D		isotropic
T / °C		150		167		238	
ΔH / kJ mol^{-1}		21		6		0.5	

FIGURE 1 Molecular structure and phase transitions of C8OBTP.

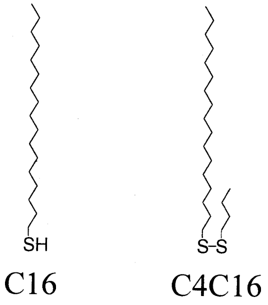


FIGURE 2 Molecular structure of C16 alkanethiol and C4C16 asymmetrical disulfide.

using an argon plasma at about 10 Pa, 15 mA with a deposition rate of about 6 nm min^{-1} for 100 sec. The SAMs were obtained by immersing the resulting gold-coated substrates into ethanol solution of corresponding thiol or disulfide for 12 hours at 1 mmol dm^{-3}. C8OBTP was spin-coated on these substrates by 1 wt% 2-butanone solution. In this study, the film of the discotic liquid crystal only contacted with the substrate coated with SAM on one side and the other side was open in the air. The thickness of the discotic film was estimated about 0.9 ~ 1 μm by AFM topographic measurement. The textures of C8OBTP films were observed by a polarized microscope (Olympus, BH-2) fitted with a hot stage (Linkam, LK-600 FTIR). All the texture observation of C8OBTP films were carrier out in the cooling process by the rate of 5°C min^{-1} from the isotropic phase of the sample.

RESULTS AND DISCUSSIONS

The textures of N_D phase of C8OBTP film at 230°C show a typical nematic schlieren texture on a gold substrate and on a C16 SAM, while the larger area of a planar texture was observed on a C4C16 SAM as shown in Figures 3(a), (b), and (c), respectively. The texture on substrate with a C4C16 SAM shows that the number of point defect is small and the area of planar alignment is broad, while those have many defects and no tendency to align uniformly on bare gold and C16 SAM substrate. On the other hand, in the case of substrate modified with C16 SAM, a remarkable difference was seen that the domain size is smaller than that on substrate without SAM. Rod-shaped liquid crystal could visualized a micropatterned SAM consist of -CH_3 and -COOH terminated alkanethiols [28]. In this study, alignment of C8OBTP molecules could be inferred to the orientational state of alkyl chains of SAM molecules on the substrate. It is known that

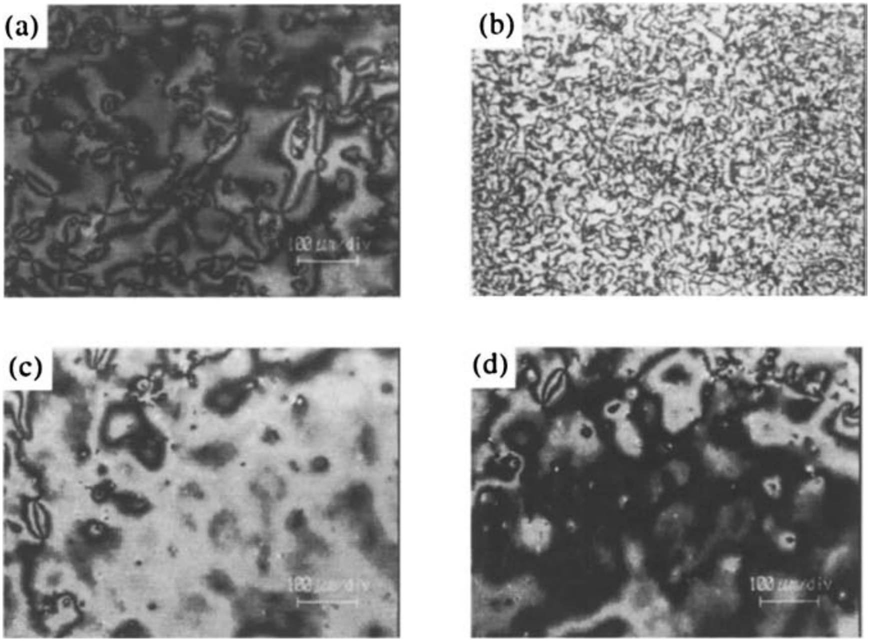


FIGURE 3 The textures of C8OBTP film in N_D phase, cooled from the isotropic phase on the substrate with (a) sputtered gold film, (b) hexadecanethiol (C16), and (c) butyl hexadencane disulfide (C4C16), and (d) after the sample was rotated by 45° clockwise around the optical axis from (c).

adsorbed alkanethiol and alkyl disulfide molecules packed closely in the homogeneously mixed SAM as illustrated in Figure 4 from electrochemical analysis [29,30]. Further investigation of the minutely orientational order of monolayer and topology of gold substrate is required for detailed analysis. In addition, C8OBTP molecules has tendency of obliquely alignment at the interface of the air in N_D phase [14,18]. In fact, it shows a typical nematic schlieren texture on both SAMs for thicker films probably in a result of hybrid alignment of discotic molecules. The thickness of discotic film is important for alignment of molecules in these cases.

As shown in Figure 5, the textures of Col_r phase at 160°C shows a fan-shape texture on C16 SAM (Fig. 5(b)), while it shows a polydomain texture on bare gold surface (Fig. 5(a)). This indicates that in the case of C16 SAM the number of point defect is smaller and the size of domains is larger than that on the substrate without SAM. This may be arisen from the growth rate of columnar structures at phase transition temperature from N_D phase. On the other hand, a planar alignment textures was observed in the broad area when C8OBTP film was on the substrate

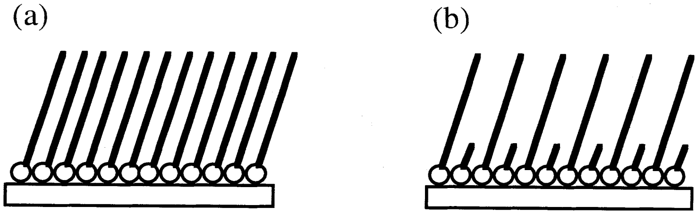


FIGURE 4 Schematic illustrations of SAMs (a) covered with C16 and (b) covered with C4C16 mixed homogeneously.

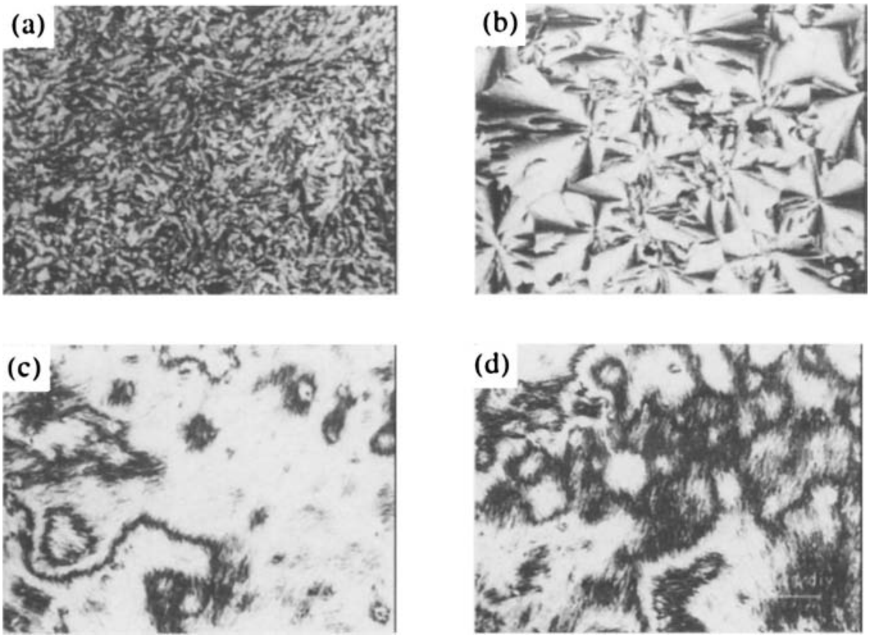


FIGURE 5 The textures in Col$_r$ phase (160°C) of C8OBTP, cooled from N$_D$ phase on the substrate with (a) sputtered gold, (b) C16 SAM, and (c) C4C16 SAM, and (d) after the sample was rotated by 45° counterclockwise around the optical axis from (c).

modified with C4C16 SAM (Fig. 5(c)). In contrast, the effect of the C4C16 SAM is to induce alignment of the discotic core perpendicular to the substrate. The alkyl-alkyl interaction of discotic liquid crystalline molecules with substrate surface could be evaluated. The results imply that the alignment of discotic liquid crystal molecules is affected by the morphological state of monolayer between an alkanethiol and an asymmetrical alkyl disulfide SAMs.

CONCLUSION

These indicate that the monolayer of SAMs could give a significant effect on the alignment behavior of discotic liquid crystal even in columnar mesophase and it could be applicable for fabricating organic thin film devices. It is found that alignment control of discotic liquid crystal, especially for rectangular columnar mesophase was exerted by SAM. Our results indicate that the different elements of the SAM could influence the alignment behavior of discotic liquid crystal distinctly even in columnar mesophase which has highly self-cohesive forces of systems.

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