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

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Alignment behavior of a discotic liquid crystalline triphenylene (C8OBT) on substrates coated with self-assembled monolayers (SAMs) of alkanethiol and asymmetrical disulfide was investigated by polarized microscopy. Discotic nematic (N_D) and rectangular columnar (Col_r) phases of C8OBT shows a different alignment behavior depending on the element of SAMs. C8OBT exhibits a fan-shaped texture on an alkanethiol SAM in Col_r phase, while it shows a planar alignment on a SAM of asymmetrical disulfide.

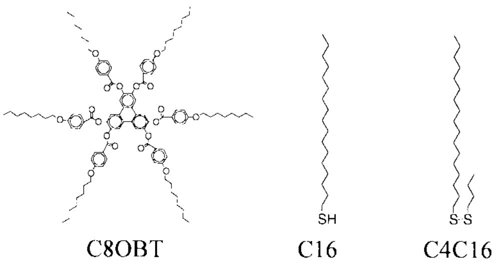
In order to obtain a higher performance in molecular materials, an appropriate long-range order of molecules is an essential requirement. Uniformity of molecular alignment in the film is also an important issue in device fabrication with the thin film. However, it is well known that the control of molecular alignment is somewhat difficult to achieve for a crystalline solid and therefore liquid crystals have received much attention as a field of matter where one can control the molecular alignment.

One of characteristic features of liquid crystals, especially for nematic liquid crystal is the good controllability of molecular alignment exerted by the surface. 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.[7–9] In addition, recent studies for photopolymerization of liquid crystals indicate such a molecular order of discotic liquid crystal could remain in polymer solid film,[10] leading to a sophisticated invention of optical compensator for wider view angle of liquid crystal display.[11] These imply that discotic liquid crystals are a good candidate for organic thin film devices if their alignment is well controlled.

Surface effects and shear flow have often been used in order to obtain uniformly aligned phase of discotic liquid crystals for studies of their potential as novel optoelectronic functional materials.[12–16] Recently, UV–vis photoalignment of discotic liquid crystals in 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.[17,18] However, only few results of molecular alignment controlling in columnar phases of discotic liquid crystals were reported so far due to the highly cohesive forces of systems.[19]

In the present work, alignment behavior of 2,3,6,7,10,11-hexa(4-octyloxybenzoyloxy)triphenylene (C8OBT) on SAMs consisting of a hexadecanethiol (C16) and an asymmetrical disulfide, butyl hexadecyl disulfide (C4C16), was investigated by polarized microscopy. SAMs were prepared on glass plates which were coated with gold film formed by sputtering.



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

Scheme 1.

C8OBT shows three enantiotropic phase transitions. The two mesophases, Col_r and N_D phases appear.[20] During these experiments, the phase transition temperatures of the sample were not changed in the detectable level. C4C16 was synthesized from the corresponding thiols by iodine oxidation.[21] This disulfide was purified by high performance liquid chromatography.

The C8OBT films were prepared on glass substrates with sputtered gold film and two types of SAMs. Gold-coated glass plates were prepared by sputtering with 10 nm of film thickness. SAMs were obtained by immersing the gold-coated substrates into ethanol solution of corresponding thiol and disulfide (1 mmol dm^{-3}) for 12 h. C8OBT was spin-coated on these substrates by 1 wt% 2-butanone solution. In this study, the film of the discotic liquid crystal contacted only with the alignment film on one side and the nother side was open to the air. The thickness of the discotic film was estimated about 1 µm by AFM measurement. The textures of C8OBT films were observed by a polarized microscope with a hot stage.

The textures of N_D phase of C8OBT 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 1(a), (b), and

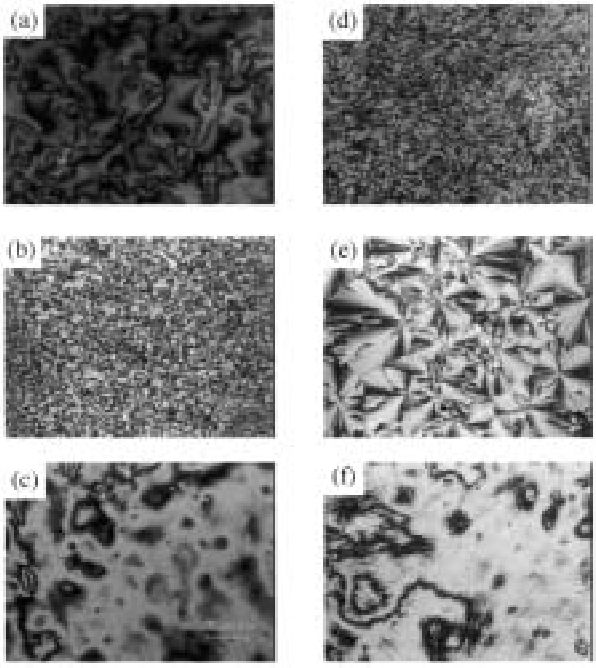


Figure 1. Textures of C8OBT film in discotic nematic phase on (a) sputtered gold film, (b) hexadecanethiol (C16), and (c) butyl hexadecyl disulfide (C4C16) SAMs and in rectangular columnar phase on (d) sputtered gold film, (e) C16, and (f) C4C16.

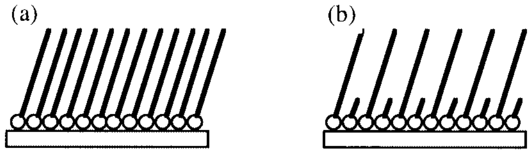


Figure 2. Schematic illustrations of SAMs (a) covered with C16 and (b) covered with C4C16 mixed homogeneously.

(c). 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 on gold and C16 SAM have many defects and no tendency to align uniformly. On the other hand, in the case of C16 SAM, a remarkable difference was seen that the domain size is smaller than that on substrate without SAM. Alignment of C8OBT could be inferred to the orientational state of alkyl chains of SAM molecules. It is known that adsorbed alkanethiol and disulfide molecules packed closely in the homogeneously mixed SAM as illustrated in Figure 2 from electrochemical analysis.[22] Further investigation of the minutely orientational order of monolayer is required for detailed analysis. In addition, C8OBT molecules has tendency of oblique alignment at the interface of the air in N_D phase.[15] In fact, it shows a typical nematic schlieren texture on both SAMs for thicker films probably because of hybrid alignment of molecules. The thickness of discotic film is important for alignment of molecules in these cases.

The texture of $\mathrm{Col_r}$ phase at 160 °C shows a fan-shape texture on C16 SAM (Figure 1(e)), while it shows a polydomain texture on bare gold surface (Figure 1(d)). This indicates that the number of point defect on C16 SAM is smaller and the size of domains is larger than that on the substrate without SAM. On the other hand, a planar alignment textures was observed in the broad area when C8OBT film was on C4C16 SAM (Figure 1(f)). The alkyl–alkyl interaction of liquid crystal 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 disulfide SAMs.

These indicate that the monolayer of SAMs could give a significant effect on the alignment behavior of discotic liquid crystals even in columnar phase and it could be applicable for fabricating organic thin film devices.

This is the first report for alignment control of discotic liquid crystal, especially for rectangular columnar mesophase 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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