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Small Angle Neutron Scattering Studies of Discotic Liquid Crystals under External Magnetic Fields

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1. Introduction

The columnar discotic liquid crystals (DLCs), which consist of disc-shaped molecules with an aromatic core and side chains, show one dimentional conductivity along overlapping π orbitals of stacked cores[1]. Therefore, DLCs have been investigated for applications such as FETs[2], photovoltaics[3], and LEDs[4]. For practical applications, uniaxial alignment of the columnar DLC in a large scale is crucial.

Various alignment techniques for columnar DLCs have investigated during two decades. In general, the techniques utilize interfacial interactions[5], shear forces[6], external fields[7], temperature[8] and concentration gradient[9], most of which are coupled with substrate effects.

Magnetic alignment is one of the most efficient methods to produce ordered molecular materials in a bulk scale. The free energy of magnetic alignment for DLCs can be expressed as $\Delta G_{align} = -1/2\ \Delta\chi(\mathbf{H}\cdot\mathbf{n})^2$, where $\Delta\chi$ is the anisotropy of magnetic susceptibility, **H** is an applied magnetic field, and **n** is the columnar director[10]. Due to the large diamagnetic anisotropy of the aromatic core ($\Delta\chi < 0$), the columnar DLCs align perpendicular to the applied magnetic field.

In this study, we introduce an simple method for uniaxial alignments of DLCs by rotating samples under applied magnetic fields, with the rotation axis being perpendicular to the fields [11]. In the absence of an external magnetic field, the columnar directors of DLC domains are randomly oriented (Fig. 1a). When a static magnetic field is applied, they align with their directors normal to the field. Within the plane normal to the field, however, the columnar directors are randomly distributed (Fig. 1b). Upon a rotating magnetic field, the only columns with their directors normal to the field are parallel to the axis of field rotation and uniaxially aligned columnar DLC phases may be produced (Fig. 1c).

We employed cobalt octa(*n*-alkylthio)porphyrazine (Fig.1 inset, *n*-alkyl = C_xH_{2x+1}, x = 10, 12, 14). To opmimize the magnetic alignment of CoSx, the magnetic responses of CoSx with different side chain length were compared and the optimal rotation speed for uniaxial alignment were identified. The columnar orientations and ordered structures were directly observed by small angle neutron scattering (SANS).

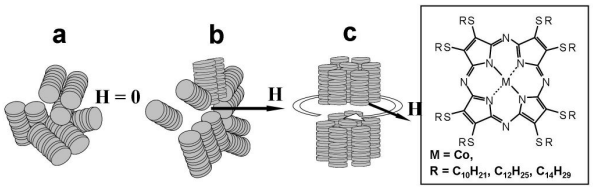

Figure 1. A concept of the uniaxial alignment using a rotating magnetic field **H**. The schematics of columnar domain distributions, (a) in the absence, (b) in the presence of a static magnetic field, and (c) in the presence of a rotating magnetic field are described.

2. SANS measurement

SANS measurements were performed the 9 m SANS instrument at the High-flux Advanced Neutron Application Reactor (HANARO) of the Korea Atomic Energy Research Institute in Daejeon, Korea. and the 30 m instruments (NG3 and NG7) at the NIST Center for Neutron Research (NCNR) in Gaithersburg, MD, USA. The scattering intensities were measured using a 2D detector as a function of scattering vector Q, $|Q| = 4\pi \sin\theta/\lambda$ where λ is the wavelength and 2θ is the scattering angle. The Q range used in this study was 0.025 $Å^{-1}$– 0.48 $Å^{-1}$.

3.Results and Discussion

3.1 Phase Behavior of CoSx

The phase transition and degradation temperatures of CoSx (x = 10, 12, 14) were identified by Differential scanning calorimetry (DSC) and Thermogravimetric Analyzer (TGA) respectively. As the side chain length increases, the transition temperature from the isotropic phase to the liquid crystalline (LC) phase decreases and the temperature range of the LC phase becomes narrower.

Table 1. Phase transition temperatures of CoSx.

X	T_m (ºC) Heating/cooling	T_i (ºC) Heating/cooling	T_d (ºC)
10	64 / -*	178 / 165	229
12	80 / 51	127 / 116	250
14	77 / 41	124 / 98	233

T_m : Phase transition temperature from solid to LC phase.
T_i : Phase transition temperature from LC to liquid phase.
T_d : Degradation temperature.

3.2 Magnetic Alignment and Response of CoSx

In order to compare magnetic response of CoSx with different side chain lengths, CoSx (x = 10, 12, 14) were heated to their isotropic phases and cooled down to their LC phases under various magnetic fields (0.2-1.1 T) and the orientational orderings of the columnar LC phases were measured by SANS. the 2D SANS data, measured in the presence of a magnetic field (1.0 T), clearly indicates that the domain directors are oriented perpendicular to the applied field while the directors have random orientation in the absence of a magnetic field. Similar behavior was observed for CoS12 but the scattering pattern of CoS14 was much less anisotropic.

The magentic responses of CoSx were compared quantitatively using the FWHM of domain director distribution[12]. The FWHM of annularly averaged SANS intensity, I(ϕ), for CoS10 and CoS12 decrease rapidly with field and then saturate to ~42º at ~0.5 T and 50º at ~0.6 T. In the case of CoS14, however, the FWHM is very broad ca. 120º even at 1.13 T. These results reveal that the saturating magnetic field strength for the alignment increases with the side chain length x, which may be attributed to the entropy increase with the side chain length.

3.3 Uniaxial Alignment of CoSx

Considering good magnetic response and low isotropic phase transition temperature which is free from degradation, We determined to apply the uniaxial alignment technique to CoS12. Uniaxial alignment of CoS12 was obtained by cooling and rotating samples from the isotropic phase in the presence of an applied magnetic field of 1.0 T. The rotation axis was perpendicular to the magnetic field direction, and a series of rotation speeds were tested.

The SANS pattern (Fig. 2a), which was measured with the neutron beam direction perpendicular to the rotation axis, shows a very sharp anisotropy. On the other hand, the pattern, which was measured with the neutron beam direction parallel to the rotation axis, shows an isotropic pattern (Fig. 2b). These results clearly indicate that the columnar domains are uniaxially aligned parallel to the sample rotation axis which is perpendicular to the field. The uiaxial alignments were tested with various sample rotation speeds (2–250 rpm), for CoS12 in the presence of an applied field of 1.0 T. The FWHM of the columnar domain director distribution decreased initially but, after reaching the lowest value 24.5° at 5-10 rpm, it slightly increased rather than reaching an asymptote. which was almost a factor of 2 smaller than that of CoS12 aligned without sample spinning. The increase of the FWHM at higher rotation rates may be attributed to the disturbance induced by the combined effects of centrifugal force. The rotation rates of 5-10 rpm are quite slow and readily achievable. The uniaxial alignment method presented here provides for easy and straightforward access to fabricating uniaxially aligned columnar discotic liquid crystal materials in over a bulk length scale.

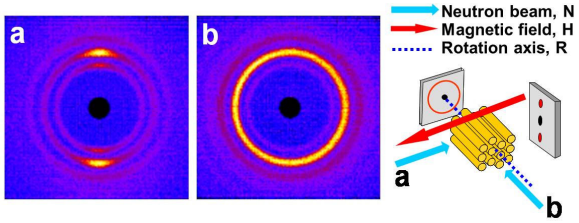

Figure 2. 2D SANS patterns of uniaxially aligned CoS12. The samples were spun at 5 rpm under a magnetic field 1.0 T. The measurements were performed at room temperature, i.e. the solid phase. The inset describes the induced orientations of columnar directors and the neutron beam directions against the sample orientation during SANS measurements.

3. Conclusion

In summary, we have investigated the magnetic responses and aligned structures of CoSx (x=10, 12, 14) using SANS. Upon cooling from the isotropic phase to the columnar LC phase under a magnetic field (0.4 – 1.1 T), the columnar directors of CoSx point randomly in the plane perpendicular to the external magnetic field. The magnetic field strength required for the alignment increases with the side chain length x. When the samples were rotated under an applied magnetic field of 1.0 T, the columnar directors of CoS12 were uniaxially aligned parallel to the rotation axis which is perpendicular to the external field. The optimal sample rotation speed for CoS12 was found to be 5-10 rpm.

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