저분자 불소기 액정의 분자 배향 및 상변화관찰

윤동기, 최명철[1,2], 김윤호, 김만원[1], 정희태*
한국과학기술원 생명화학공학과, [1] 한국과학기술원 물리학과, [2] MRL, UCSB
(heetae@kaist.ac.kr*)

Molecular Ordering and Phase Behavior of Low Molecular Weight Perfluorinated Liquid Crystal

Dong Ki Yoon, Myung Chul Choi[1,2] , Yun Ho Kim, Mahn Won Kim[1], and Hee-Tae Jung*
Department of Chemical and Biomolecular Eng., KAIST, [1]Department of Physics, KAIST,
[2]MRL, UCSB
(heetae@kaist.ac.kr*)

Introduction

Supramolecular monodendrons and dendrimers provide the most powerful synthetic building blocks available for the construction of giant macromolecular and supramolecular nanoscopic architecture systems with well defined and precise shape, complex architecture, and functionality by using specifically designed monodendrons and dendrimers.[1-5]

In this study, first of all, we have studied the synthesis, phase behaviors and morphology of a linear supramolecule which self-assemble into thermotropic lamella mesophases via the combination of π-π stacked arrangement, the fluorophobic effect and hydrogen bonding. The structural analysis of the dendritic molecule was determined by investigating the anisotropic properties by polarized light microscopy (PLM) with presence of magnetic field. Moreover, we present a dramatic development of orientation in supramolecular cylinders by an applied magnetic field. To elucidate the orientation by an applied magnetic field, small angle neutron scattering (SANS) experiment was performed and subsequent PLM images show perfect ordering of molecules. We account for these observations on the basis of the competing diamagnetic moments of aromatic moiety of the materials.his is the standard font and layout for the individual paragraphs.

Experimental &Results

1H,1H,2H,2H,3H,3H,4H,4H-perfluorododecyl bromide (**1**) was synthesized according to the method previously reported.[6,7] The targeted compound(**2**) was prepared via a two step alkylation from **1** and ethyl 4'-hydroxy-4-biphenyl carboxylate, followed by reaction with $LiAlH_4$ and $SOCl_2$ for reduction and chlorination, respectively, and finally alkylation with methyl 3,4,5-trihydroxy benzoate. (Fig. 1.)The pristine yellowish solid was purified by column chromatography (silica gel, $CHCl_3$) to afford **2** as a white powder. All intermediates and targeted product were confirmed by ^{1}H-NMR spectroscopy.

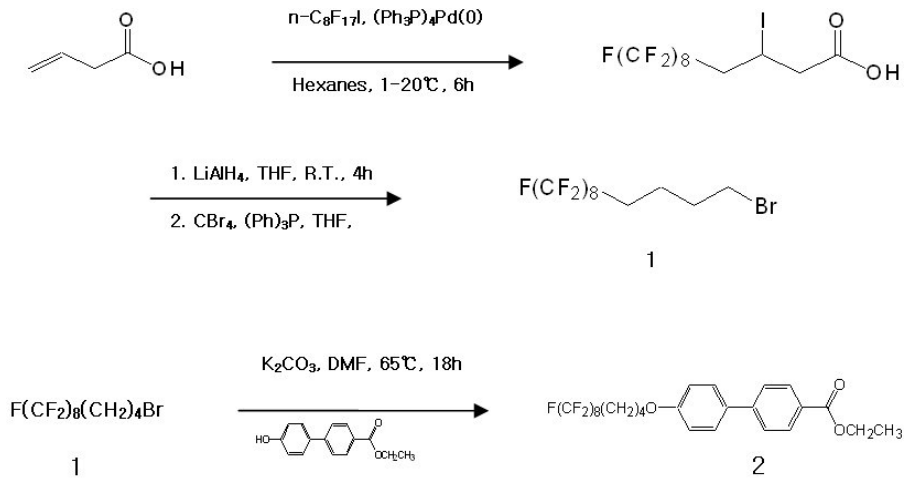

Fig. 1. Synthesis of the material

The thermotropic phase behavior was characterized by polarized light microscopy (PLM). The anisotropic optical textures were observed on a polarized optical microscopy (Leica, Model DMLB), equipped with a hot stage (Mettler FP82 HT). Based on the optical birefringence between cross polarizer and analyzer, this material exhibits one of the characteristic textures of lamella mesophases because of high viscous and birefringent characteristics.(Fig. 2.) Especially, sample prepared between glasses shows typical line structure, which means the director of lamellar sheets, is well aligned with glasses. When a magnetic force was applied to the sample, optical large domains are oriented perpendicular to the field direction, which means the direction of lamella is parallel with the field.

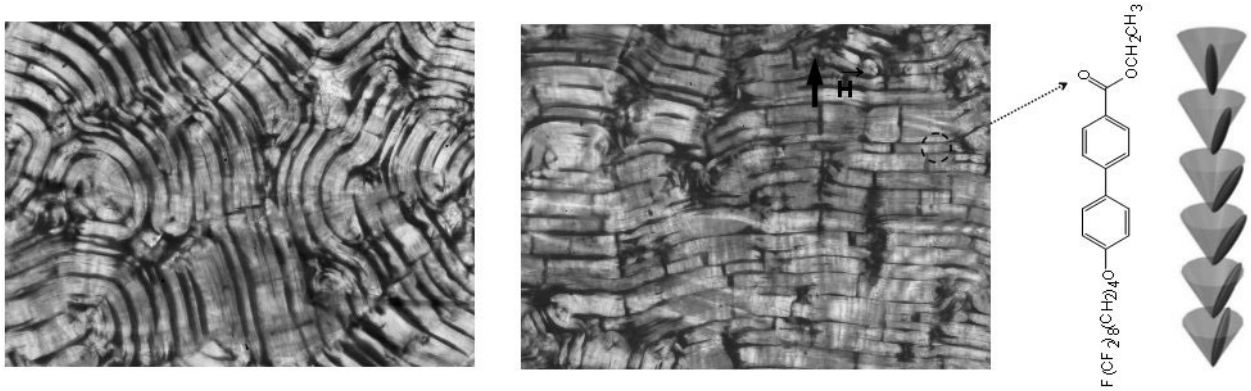

Fig. 2. PLM images of liquid crystalline film between two glass slips. (right) with magnetic field applied during thermal annealing (cooling from 200^{o}C with -1^{o}C/min); (left) without field.

For examination of the orientational ordering by an applied magnetic field, SANS studies were performed as the material was cooled from the disordered state into the ordered state under the

influence of a magnetic field. The samples were heated to isotropic temperature (disordered state) then, the samples were cooled down below the disorder-to-order transition temperature under a magnetic field of 1 T.

SANS experiments was conducted by neutrons with a wavelength of 8.0Å at HANARO (KAERI) for Neutron Research. Prepared sample under magnetic field was loaded to a copper-supported quartz cell. The sample positioned in the neutron beam line, between the poles. The sample cooled without an applied field shows the azimuthally isotropic diffraction intensity in the 2-D SANS pattern, while the diffracted intensity was limited to a specific range in azimuthal angle in the magnetic field induced sample. (Fig. 3.) This symmetric 2-D SANS pattern means that the compulsory one-dimensional reorientation occurs under a magnetic field. The strong arcs of the pattern indicate alignment of the lamella nanostructures perpendicular to the magnetic field vector. This anisotropic scattering pattern performed under magnetic field and has not changed for a long time (~several months) after being held. Synchrotron X-ray scattering measurements were performed to further confirm the molecular ordering and orientation within the lamella at the 4C1 (SAXS), 4C2 (SAXS2), and 3C2 (XRD) beam lines of the Pohang Accelerator Laboratory (PAL). A small amount of magnetically aligned sample was sealed with imide films, and analyzed in transmission mode with a 2-D detector. The scattering maxima of arcs at small angles and wide angles were orthogonal to each other. Equatorial arcs at small angles represent the repeat distance of the material, indicating that the lamella sheets are aligned perpendicular to the magnetic fields. On the other hand, meridional arcs at wide angles represent the separation distance between the stacked molecules oriented parallel to the magnetic field. This XRD result further confirms that the alignment is induced as a result of the diamagnetic character of the aromatic system of the lamella structure.

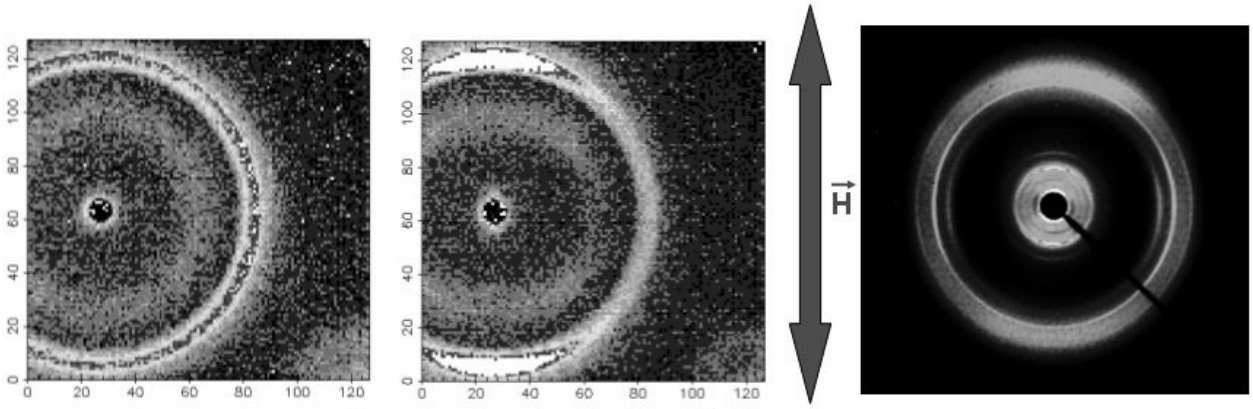

Fig. 3. SANS pattern of liquid crystalline film between two glasses. (right) with magnetic field applied during thermal annealing (cooling from 200°C with -1°C/min); (center) without field. 2-d XRD pattern shows lamella sheets are aligned perpendicularly to magnetic field, while every single molecule is parallel with the field.

That is caused by interaction between aromatic group and magnetic field. This magnetic alignment relates the induced magnetization M to the strength of the magnetic field, simply it can be depicted:

$$M\alpha = \mu_0^{-1} \chi_{\alpha\beta}^{mag} B\beta \quad (1)$$

where magnetic induction B, μ_0 is the permeability of free space and $\chi_{\alpha\beta}$ is a volume susceptibility.[8] The magnetic contribution to the free energy density becomes:

$$g_{mag} = -\int B_\alpha dM_\alpha = \mu_0^{-1} \int B_\alpha \chi_{\alpha\beta} dB_\beta$$
$$= g_0 - \frac{1}{2}\mu_0^{-1} \chi_{\alpha\beta} B_\alpha B_\beta \qquad (2)$$

Conclusion

To establish the identity of the magnetic switching property of this molecule, we compared the scattering patterns of the isotropic phase obtained in the presence and absence of a magnetic field. Magnetically aligned sample was heated to their corresponding isotropic temperature without a magnetic field, then cooled down to room temperature slowly. As we expected, 2-D SANS pattern of sample cooled without an applied field shows the azimuthally isotropic diffraction intensity like Fig 4a. This is thought to be due to the molecules in the isotropic phase existing as fractional dendrimers, and they are self-assembled to inherent morphology when it is cooled down. Because it takes very short time to change molecular ordering with magnetic field, this material system has potential for future switching material.

References

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