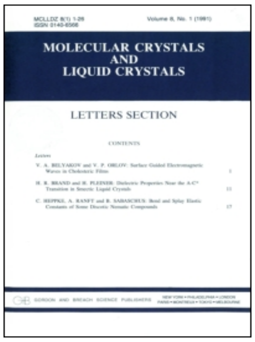

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Supramolecular discotic nematic liquid crystals built through simple hydrogen bonding between 1,3,5-tris(4-hydroxyphenyl) benzene and stilbazole derivatives

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ABSTRACT
New supramolecular discotic nematic liquid crystals have been prepared simply through hydrogen bonding between the non-mesogenic core of 1,3,5-tris(4-hydroxyphenyl)benzene and the peripheral arms of stilbazole derivatives with different alkyl chain lengths. The discotic mesophases formed by simple hydrogen bonding were examined by POM, DSC, and XRD. The nematic columnar and discotic nematic mesophases were observed depending on the length of alkyl chains around the aromatic core by introducing the curved structure in three arms of supramolecular discotic mesogens. Our controlled methodology will be helpful for providing a convenient and effective way to prepare the rarely found discotic nematic liquid crystals.

KEYWORDS
Liquid crystal; nematic mesophase; self-assembly; simple hydrogen bonding; supramolecule

Introduction

Since the discovery of discotic liquid crystals (DLCs) by Chandrasekhar et al. [1], DLC materials have attracted considerable attention owing to their potential use in electronic conductors, photovoltaics, organic light emitting diodes, and compensation layer in liquid crystal displays [2–5]. In general, discotic molecules, which are composed of a disc-shaped aromatic core and peripheral flexible alkyl groups, exhibit nematic or columnar mesophases through molecular self-assembly. While most of the DLC materials show columnar mesophases such as hexagonal, rectangular, and oblique columnar phases owing to the strong intermolecular interactions between aromatic cores, those displaying nematic LC properties are rarely found in recent years [6]. In the nematic columnar (N_C) phase, the discotic molecules stack to form short columns, and the columns have only an orientational order [7]. The discotic nematic (N_D) phase forms a nematic arrangement of discs [8]. In the nematic lateral (N_L) phase, the molecules associate into supramolecular assemblies with the short lateral order in a nematic arrangement [9].

Among the noncovalent interactions, hydrogen bonding is a simple and powerful tool to construct supramolecular architecture because of its remarkable strength and high directionality [10]. The structure of DLC materials can be readily controlled by employing suitable hydrogen bonding building blocks. We previously reported that supramolecular DLCs

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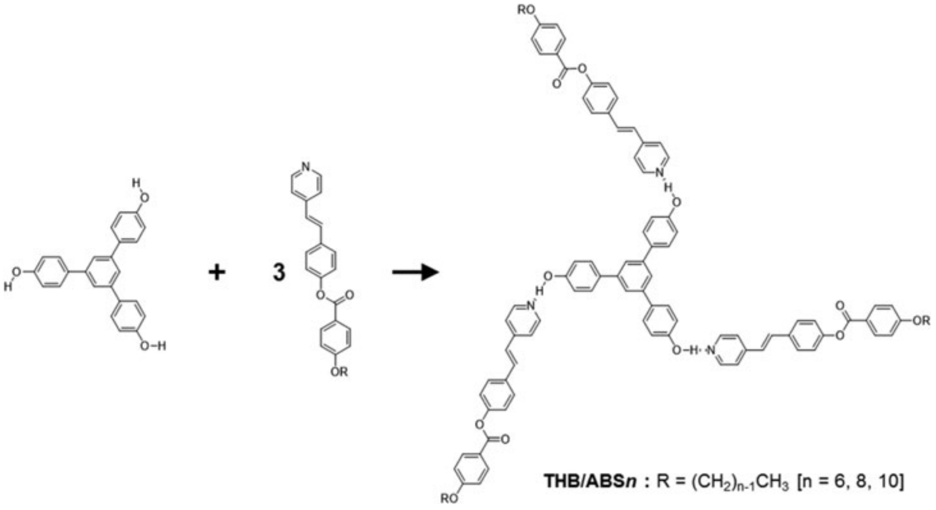

Figure 1. Preparation of supramolecular discotic nematic liquid crystals.

formed by single hydrogen bonding between phenol and pyridine moieties can exhibit discotic mesophases [11,12]. In the present study, we have prepared a new type of supramolecular discotic nematic liquid crystals formed through hydrogen bonding between 1,3,5-tris(4-hydroxyphenyl)benzene (THB) as a core molecule and 4-(4-alkoxybenzoyloxy)-4′-stilbazole (ABS*n*) with systematically varied alkyl chain lengths (*n*) as peripheral units, as shown in Fig. 1, and investigated their liquid crystalline properties using polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). It is expected that THB core and three ABS*n* peripherals can be self-assembled into supramolecular discs with a nonlinear arm structure and consequently the discs form the less-ordered nematic phases due to the lack of symmetry in aromatic core.

Experimental

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a JASCO FT/IR-200 spectrometer. DSC experiment was performed on a TA DSC 2010 at scan rate of 10°C min^{-1} under nitrogen atmosphere. The phase transition temperatures were determined from the peak maximum. POM measurements were conducted on a Leica MPS 30 microscope equipped with a Mettler FP82HP hot stage and a Mettler FP90 control unit. XRD patterns were obtained from 8C1 synchrotron X-ray beam line at the Pohang Accelerator Laboratory (PAL) in Pohang, South Korea using a home-made heating stage. Cu Kα radiation ($\lambda = 1.54$ Å) was used for X-ray experiments.

Preparation of supramolecular discotic complexes

The three stilbazole derivatives of ABS*n* with different lengths of alkyl chains, which were 4-(4-hexyloxybenzoyloxy)-4′-stilbazole (ABS6), 4-(4-octyloxybenzoyloxy)-4′-stilbazole (ABS8), 4-(4-decyloxybenzoyloxy)-4′-stilbazole (ABS10), were synthesized according to previous report [12]. The discotic complexes were prepared by dissolving THB core with

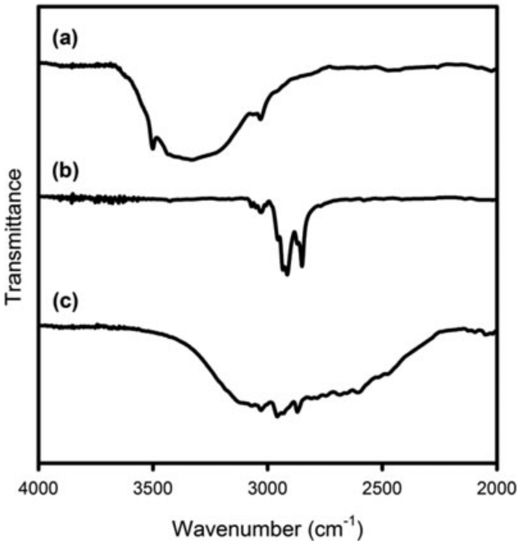

Figure 2. FTIR spectra of (a) THB core, (b) ABS8, and (c) THB/ABS8 complex.

the peripheral ABS*n* (1/3 mol/mol) in anhydrous acetone under sonication for 1 hr and subsequently evaporating the solvent slowly at reduced pressure.

Results and discussion

Infrared studies

The formation of supramolecular discotic complexes was confirmed by FTIR spectroscopy. Figure 2 shows the FTIR spectra of pure THB, ABS8, and the discotic complex between THB and ABS8 (THB/ABS8) in KBr discs of neat powders at room temperature. For unmixed THB, a broad stretching band of O-H corresponding to self-hydrogen bonding of the hydroxyl groups in THB was observed at around 3330 cm^{-1}. For THB/ABS8 complex, a new broad stretching band of O-H was found at a lower wavenumber of about 2800 cm^{-1}, which appears to be the result of stronger hydrogen bonding between phenol and pyridine moieties in the complex. These results indicate that intermolecular hydrogen bonds between THB and ABS*n* are formed to a large extent. Our FTIR spectral results were in accord with the literature [13].

Mesophase behaviors

The mesomorphic properties of THB/ABS*n* complexes were examined by DSC and POM measurements. The THB core molecule is non-mesogenic and simply melts at 233°C. The stilbazole derivatives of ABS*n* showed wide temperature ranges of enantiotropic smectic phases typically between 80 and 170°C [14]. The phase transition behaviors of THB/ABS*n* complexes, summarized in Table 1, were different from those of the peripheral ABS*n*. The discotic complexes exhibited monotropic mesophases and lower mesophase transition temperatures of around 150°C than pure ABS*n*. The enthalpies of clearing transition were relatively small (about 3.0 J g^{-1}), suggesting a lower order in the mesophase. It is reported that the angular mesogenic structures of hydrogen-bonded supramolecules induce monotropic mesophases and low transition temperatures [15]. In the case of THB/ABS*n* complexes, a nonlinear arm

Table 1. Thermal properties of supramolecular discotic complexes.

	Phase transition behavior[a]	
Complex	Heating	Cooling
THB/ABS6	120.0 (59.9) Cr→I	150.9 (3.6) I→N_C
THB/ABS8	128.2 (120.4) Cr→I	152.8 (3.2) I→N_C
THB/ABS10	103.4 (99.0) Cr→I	147.2 (2.8) I→N_D

[a] Transition temperatures (°C) and enthalpies of transition (J g^{-1}, in parentheses) on heating and cooling at the scan rate of 10°C min^{-1}. Cr, crystalline; N_C, nematic columnar; N_D, discotic nematic; I, isotropic.

structure of discotic mesogen formed by hydrogen bonding could lead to similar phase transition behaviors to the literature. Optical analysis by POM in the mesophase temperature range after cooling from the isotropic melt showed clearly birefringent textures of liquid crystals in Fig. 3. In THB/ABS*n* complexes, Schlieren textures were observed on slow cooling from the isotropic state. These Schlieren textures and low enthalpies of clearing transition indicate the formation of nematic phases. The precise structure of nematic arrangement will be further characterized by XRD.

X-ray diffraction

Figure 4 shows temperature-dependent XRD patterns of THB/ABS*n* complexes. The X-ray diffraction at room temperature exhibited numerous reflections characteristic of crystalline phases, while reduction of the temperature from isotropic state to the liquid crystalline region produced only characteristic reflections corresponding to nematic mesophases. THB/ABS6 and THB/ABS8 complexes showed a single peak at 32.1 and 34.6 Å, respectively, corresponding to the (100) reflection in the small-angle region (Fig. 4(a) and 4(b)). No higher order reflections point to the absence of long-range order in mesophase. In the wide-angle region, a broad halo was observed at 4.4 Å, resulting from the average distance between flexible alkoxy chains. These diffraction patterns and the Schlieren textures of THB/ABS6 and THB/ABS8 indicate the formation of a nematic columnar (N_C) mesophase with a nematic arrangement of short columns [7]. In the case of THB/ABS10 complex, no reflection in the small-angle

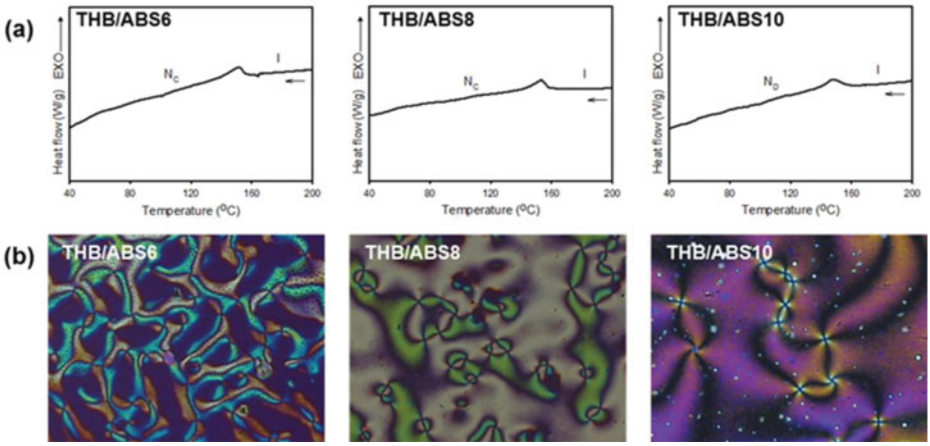

Figure 3. (a) DSC thermograms and (b) polarized optical micrographs of THB/ABS*n* complexes on cooling. The POM images of THB/ABS6, THB/ABS8, and THB/ABS10 were obtained at 151°C, 152°C, and 144°C, respectively (200×).

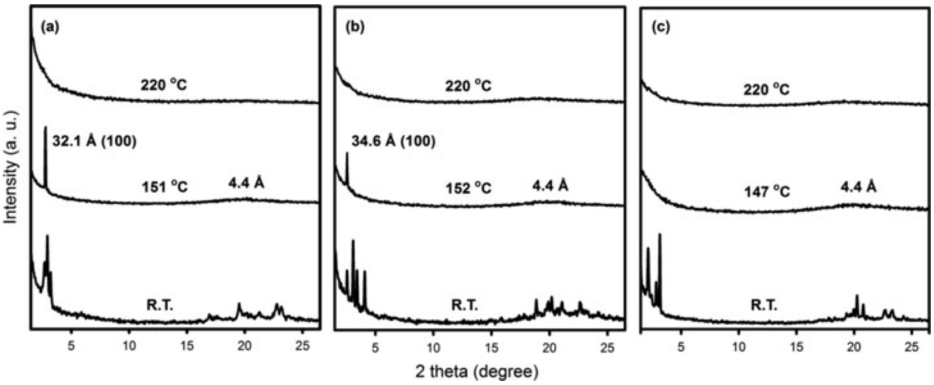

Figure 4. Temperature-dependent XRD patterns of (a) THB/ABS6, (b) THB/ABS8, and (c) THB/ABS10.

region and only a broad halo ascribed to disordered alkyl chains in the wide-angle region were detected, as shown in Fig. 4(c). Commonly, the discotic nematic phase exhibits a broad peak or no reflection in the small-angle region due to only an orientational order of discs [8]. Thus, the mesophase of THB/ABS10 is identified as a discotic nematic (N_D) phase. It is supposed that the conformational disorder of long alkyl chains attached to the nonlinear arms of a supramolecular disc may reduce the packing efficiency of asymmetric discotic core and consequently lead to the formation of a discotic nematic phase.

Conclusions

New supramolecular discotic nematic liquid crystals were prepared simply through hydrogen bonding between a non-mesogenic THB core and the peripheral arms of stilbazole derivatives with different number of alkyl chains, and their self-assembly behavior was examined. The THB/ABS6 and THB/ABS8 complexes showed nematic columnar mesophases, while THB/ABS10 complex formed discotic nematic mesophase. These observations suggest that careful designs such as asymmetric discotic core or long alkyl chains could prevent columnar stacking of discs, leading to nematic mesophases. The proposed approach in this study provides a simple and powerful method for preparing the discotic nematic liquid crystals for display applications such as the active switching component or optical compensation film.

Acknowledgments

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