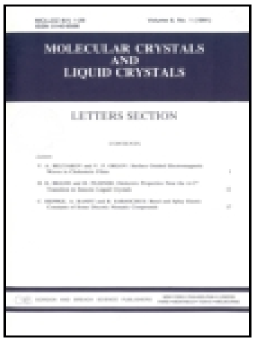

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ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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**To cite this article:** Seung Jun Lee, Jae Young Jho & Jun Hyup Lee (2015) Preparation of Stable Anisotropic Films with Columnar Order from Polymerizable Star-shaped Supramolecular Liquid Crystals, Molecular Crystals and Liquid Crystals, 621:1, 175-181, DOI: 10.1080/15421406.2015.1096468

**To link to this article:** http://dx.doi.org/10.1080/15421406.2015.1096468

*Mol. Cryst. Liq. Cryst.*, Vol. 621: pp. 175–181, 2015
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1096468

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# Preparation of Stable Anisotropic Films with Columnar Order from Polymerizable Star-shaped Supramolecular Liquid Crystals

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*We have fabricated new stable anisotropic films with columnar order using star-shaped supramolecular liquid crystals as photoreactive monomers. The polymerizable supramolecular liquid crystal exhibiting a hexagonal columnar mesophase has been prepared simply through hydrogen bonding between a phloroglucinol core and pyridine derivatives containing acrylate groups in the alkyl chain. Photopolymerization of the supramolecular monomer in the liquid crystalline state yielded cross-linked anisotropic polymer networks with columnar order. The controlled approach in the present study opens a new way to design and prepare stable anisotropic materials for potential electronic and optical applications.*

**Keywords** Anisotropic polymer; hexagonal columnar; hydrogen bonding; photopolymerization; star-shaped liquid crystal

## Introduction

In recent years, polymerizable liquid crystals (LCs) have received much attention for their applications as nanostructured polymers, optically anisotropic films, and microscopic patterning materials [1–3]. The polymerization of LCs in the LC state can provide a method to obtain functional polymers with ordered LC structures. Especially, the discotic liquid crystals (DLCs) can form columnar structures, offering the excellent charge transporting properties [4]. A limited number of studies on the polymerization of DLCs in the columnar state have been reported to date [5–7]. All of these studies utilized covalently bonded discotic systems involving polymerizable groups. However, polymerizable DLCs formed with complicated aromatic rings are difficult to be prepared by conventional synthetic method using covalent bonds.

Recently, it has been reported that supramolecular DLCs exhibiting the various types of nematic or columnar mesophases can be readily obtained via hydrogen bonding between phenolic group and pyridine moieties [8]. Taking advantage of this methodology for

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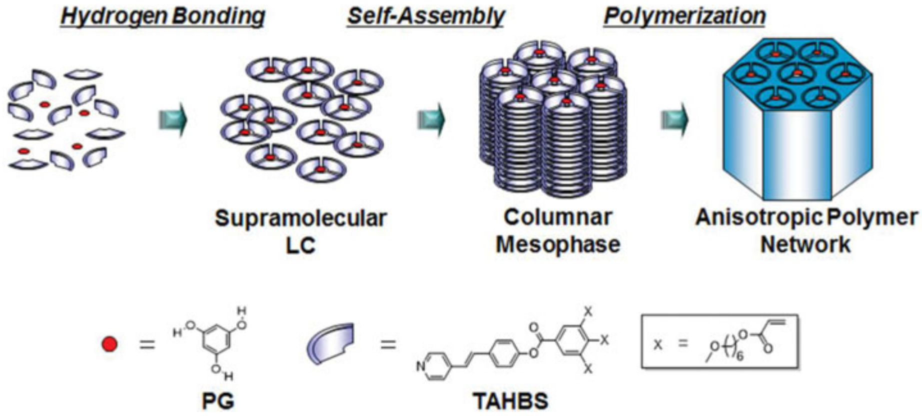


**Figure 1.** Schematic illustration of polymerization of star-shaped supramolecular LCs.

DLC materials, we now report a new way to fabricate stable anisotropic polymers with columnar order using star-shaped supramolecular LCs as photoreactive monomers. A new polymerizable LC has been prepared simply through single hydrogen bonding between a phloroglucinol (PG) core and pyridine derivatives including acrylate groups in the alkoxy chain. We attempted to photopolymerize the supramolecular monomer in the LC state to obtain cross-linked anisotropic polymer networks with columnar order, as shown in Fig. 1. The mesophase properties and photopolymerization behavior of supramolecular monomer were investigated by Fourier transform infrared (FTIR) spectroscopy, polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD).

## Experimental

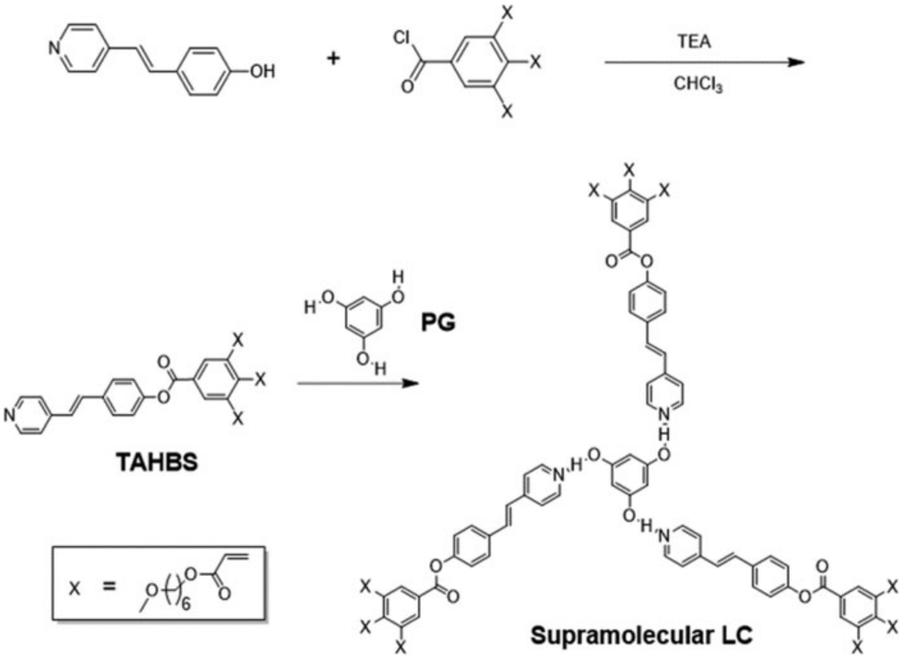
### *Measurements*

$^1$H NMR and $^{13}$C NMR (300 MHz) spectra were obtained from JEOL JNM-LA 300 spectrometer. FTIR experiment was conducted on JASCO FT/IR-200 spectrometer. DSC was carried out on TA DSC 2010 under nitrogen atmosphere at scan rate of 10°C min$^{-1}$. The phase transition temperature was chosen from the peak maximum. POM was conducted on Leica LABORLUX 12 POLS microscope fitted with Mettler FP82HP hot stage and Mettler FP90 control unit. XRD patterns were recorded on Bruker AXS X-ray diffractometer system equipped with HI-STAR detector and heating accessory using Cu K$\alpha$ radiation ($\lambda = 1.54$ Å).

### *Preparation and Polymerization of Star-shaped Supramolecular LC*

The pyridine derivative, 3,4,5-tris(6-(acryloyloxy)hexyloxy)benzoate-stilbazole (TAHBS) was synthesized according to the procedure reported in literature, as described in Scheme 1 [9,10]. The analytical data are given below.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.59 (d, 2H, $NC_5H_4$), 7.60 (d, 2H, $NC_5H_4$), 7.41 (s, 2H, $O_3C_6H_2COO$), 7.38 (d, 2H, $OC_6H_4CH=$ ), 7.32 (d, 1H, $NC_5H_4CH=$ ), 7.23 (d, 2H, $OC_6H_4CH=$ ), 7.00 (d, 2H, $OC_6H_4CH=$ ), 6.40 (d, 3H, $HHC=CH$-), 6.12 (dd, 3H, HHC



**Scheme 1.** Synthesis of the pyridine derivative TAHBS and preparation of the polymerizable supramolecular LC.

= C*H*CH$_2$-), 5.81 (d, 3H, H*H*C = CH-), 4.15 (m, 6H, CH$_2$ = CHCOOC*H*$_2$), 4.05 (m, 6H, OC*H*$_2$CH$_2$), 1.85-1.30 (m, 30H, OCH$_2$(C*H*$_2$)$_5$O). $^{13}$C NMR (300 MHz, CDCl$_3$): $\delta$ 25.7, 25.5, 25.7, 28.8, 28.9, 29.3, 30.1, 64.5, 64.6, 69.4, 73.8, 108.8, 116.0, 120.8, 123.8, 127.5, 129.0, 130.2, 130.9, 133.4, 143.4, 145.2, 150,1, 153.1, 158.5, 166.4, 172.1. MS (*m*/*z*): 811.4 (M$^+$).

The star-shaped supramolecular LC was prepared by dissolving PG and TAHBS in a molar ration of 1:3 in anhydrous tetrahydrofuran and subsequently evaporating the solution slowly under reduced pressure. Thin films of supramolecular monomer (about 0.5–1 $\mu$m thickness) were fabricated by melting a small amount of monomer mixtures containing 1 wt.% of Irgacure 651® photoinitiator on the glass slide and placing it on a heating stage. Polymerization of the supramolecular monomer in the LC state was carried out by UV irradiation under nitrogen with a UV lamp using an intensity of 15 mW cm$^{-1}$ (UVP XX-15S with IR cut-off filter, 100W).

## Results and Discussion

### *Mesomorphic Properties of Polymerizable Supramolecular LC*

Figure 2(a) shows FTIR spectra of PG core, peripheral TAHBS, and supramolecular LC. For PG, a broad stretching band of O-H corresponding to self-hydrogen bonding between hydroxy groups was found at 3370 cm$^{-1}$. For the supramolecular LC, a new broad stretching band of O-H was detected at a lower wavenumber of about 2900 cm$^{-1}$, which is the result of strong hydrogen bonding between phenol and pyridine moieties in the complex. These

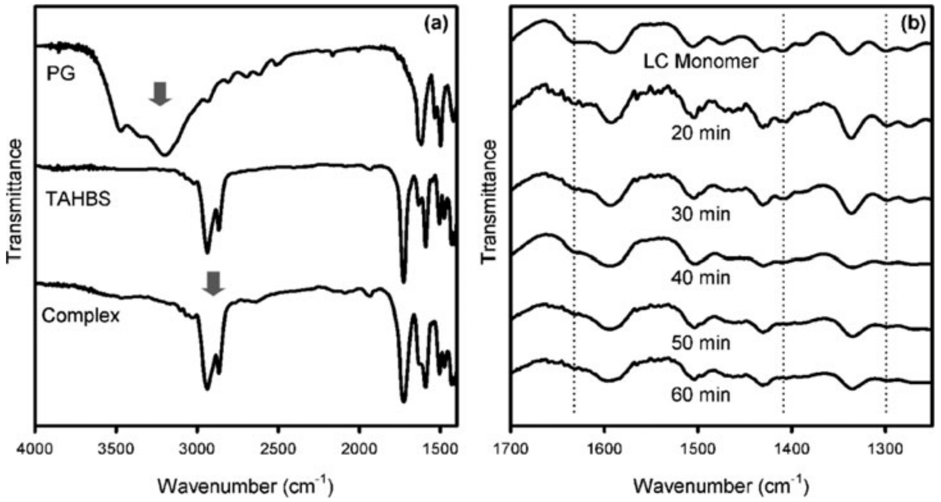


**Figure 2.** FTIR spectra of (a) supramolecular LC and (b) polymers after UV irradiation during 60 min.

results indicated the successful formation of supramolecular LC complex and spectral features were in accordance with literature [11].

The mesophase properties of supramolecular LC were studied by DSC, POM, and XRD. While the peripheral TAHBS exhibited only melting and crystallization transitions, an enantiotropic mesophase was formed in the supramolecular LC, as shown in Table 1 and Fig. 3(a). In POM experiments, a small mosaic-like fine texture was observed below 48°C as shown in Fig. 3(b), which is characteristic of ordered LC phases. The mesophase structure of the supramolecular LC was examined in detail by XRD. At the mesophase temperature of 30°C, supramolecular LC exhibited a high-intensity peak (46.0 Å) and two lower-intensity peaks (27.0 and 22.5 Å) in the small-angle region, with a reciprocal spacings ratio of about $1{:}3^{1/2}{:}2$ (Fig. 4(a)). These peaks were assigned to the (100), (110), and (200) reflections, respectively, from the hexagonal arrangement with a lattice constant of 53.1 Å. The broad halo at around 4.2 Å was attributed to the disordered alkyl chains. This reflection pattern is characteristic of hexagonal columnar mesophase. The observed intercolumnar distance of 53.1 Å was significantly smaller than the estimated diameter of about 64 Å in the fully stretched state. It is assumed that a pair of E-shaped mesogens

**Table 1.** Thermal properties of TAHBS and supramolecular LC complex

| | Phase transition behavior[a] | |
|---|---|---|
| Compounds | Heating | Cooling |
| TAHBS | Cr 63 (63) I | I 37 (63) Cr |
| Complex | g 10 Col 58 (0.8) I | I 48 (0.6) Col 25 g |

[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; Col, columnar; I, isotropic; g, glassy.

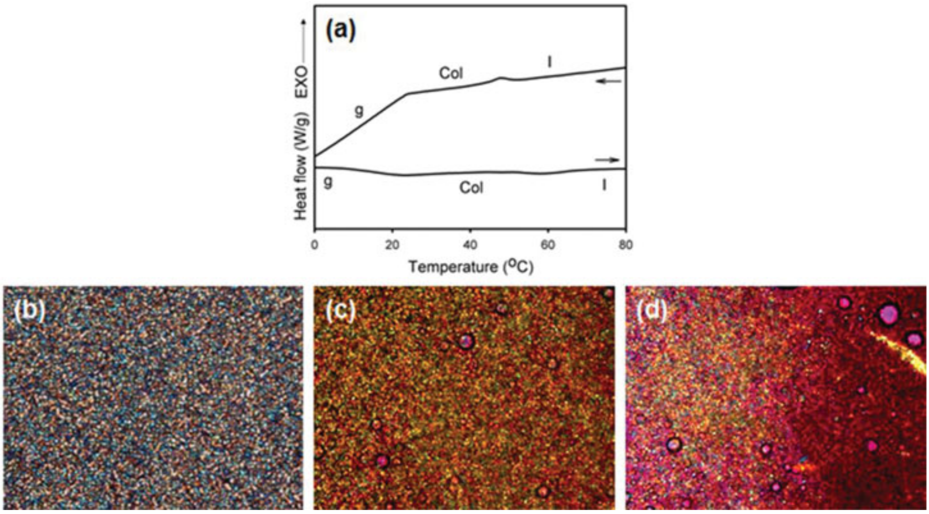


**Figure 3.** (a) DSC thermograms of supramolecular LC and polarized optical micrographs of (b) supramolecular LC at 30°C on cooling, and the polymers at (c) 25°C and (d) 80°C (200×). Col, columnar; I, isotropic; g, glassy.

would be assembled with opposite directions to reduce free spaces between arms, leading to compact aggregation of columns in the hexagonal columnar phase, as shown in Fig. 4. A similar XRD result was obtained for star-shaped supramolecular LC with no photoreactive moieties by our group [12].

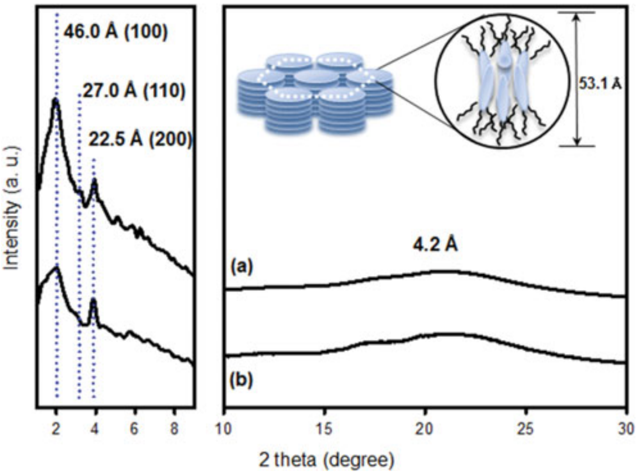


**Figure 4.** XRD patterns of (a) supramolecular LC at 30°C and (b) the polymer at room temperature.

### *Photopolymerization of Supramolecular LC*

The polymerization behavior of supramolecular LC was examined by FTIR spectroscopy, as shown in Fig. 2(b). Before UV irradiation, the supramolecular LC showed three characteristic bands at 1636, 1411, and 1294 $cm^{-1}$ corresponding to the acrylate moieties. After irradiation for 60 min, these three bands have almost completely disappeared. This means that the cross-linked polymer was formed by polymerization of acrylate groups in the alkyl chains. The similar spectral features were obtained for other study using the acrylate groups [13].

The morphological changes in optical textures after UV irradiation were studied by POM. After irradiation, the domain size of texture was slightly reduced, with the texture type remaining almost the same (Fig. 3(c)). This texture of polymer film was stable up to 80°C (Fig. 3(d)). This suggests that the liquid crystalline structure of supramolecular LC was not perfectly maintained after polymerization, but molecular order in the anisotropic polymer was still similar up to high temperature.

The structure of anisotropic polymer after UV irradiation was investigated by XRD. The resulting polymer showed similar XRD pattern to that of the supramolecular LC, although the (100) reflection was somewhat broadened and the position of (110) reflection changed slightly (Fig. 4(b)). This means that the columnar order in the supramolecular LC was maintained by photopolymerization.

## Conclusions

New stable anisotropic films with a columnar order have been fabricated by using star-shaped supramolecular LCs as photoreactive monomers. The photopolymerization in the LC state under UV irradiation yielded cross-linked anisotropic polymer maintaining the stable columnar LC order over a wide temperature range. Our findings in the present study could contribute to the development of anisotropic polymers for future optoelectronic applications.

## Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2014R1A1A2057947).

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