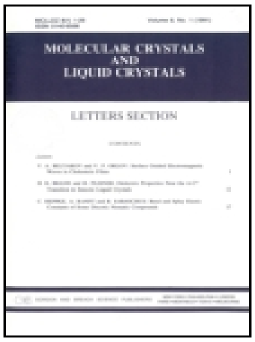

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Preparation and Polymerization of Polymerizable Discotic Liquid Crystals Containing Hydrogen Bonds and Their Behavior in Nanochannels

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New photopolymerizable discotic liquid crystal was prepared by hydrogen bonds between a phloroglucinol core and peripheral 4-(4-alkoxyphenyl)pyridines containing acrylate unit. The liquid crystalline order of discotic mesophase was perfectly maintained by photopolymerization in the presence of photoinitiator during very short time of 10 sec. When the discotic complex was inserted into anodic aluminum oxide (AAO) nanopores, hydrogen bonds in the complex were broken probably due to the strong interaction between peripheral pyridine moieties and AAO surface inducing structural change in columnar order to the lamellar order.

Keywords Anodic aluminum oxide; discotic liquid crystal; hydrogen bonding; nanochannel; photopolymerization

Introduction

Since the discovery of discotic liquid crystal (DLC) by Chandrasekhar et al. in 1977 [1], DLCs have been investigated for the applications in hole and electron transport materials, compensation layer of liquid crystal display, and nanostructured liquid crystalline polymers [2–4]. For the formation of stable nanostructure, it is necessary to fix the long-range order of DLCs by polymerization process. General method for preparing nanostructured LC polymers is the incorporation of photo-reactive groups such as acrylate or diacetylene moieties into the LC molecules and in-situ photopolymerization in the LC state by UV irradiation [5, 6]. Especially, the employment of columnar mesophases in this process can offer high charge carrier properties along columnar direction. Moreover, the macroscopic alignment of DLC molecules may widen the application range of columnar DLCs. Recently, it was reported that covalently bonded triphenylene derivative can be aligned on a macroscopic scale using ordered porous alumina templates [7].

Here we report on the polymerization of photo-reactive hydrogen-bonded DLC and its nanoscopic behavior in the confined geometry of nanoporous anodic aluminum oxide (AAO). A new photopolymerizable DLC was prepared via intermolecular hydrogen bonds

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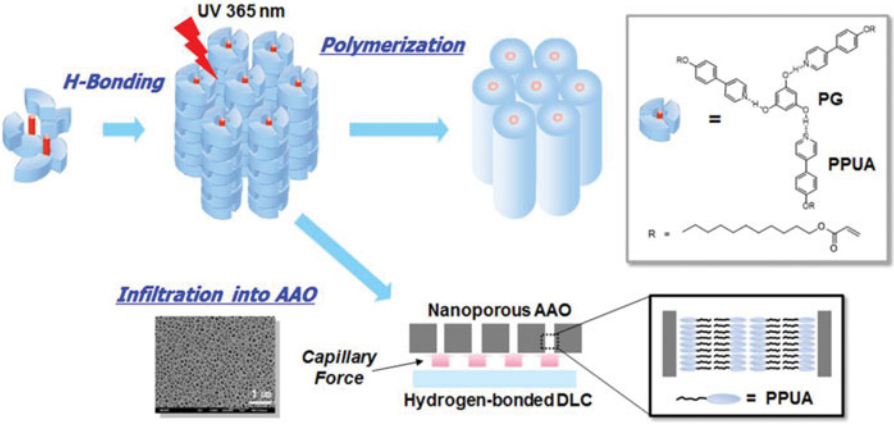


Figure 1. Schematic illustration of photopolymerization of hydrogen-bonded DLC and its infiltration into AAO.

between a phloroglucinol (PG) core and peripheral 4-(4-alkoxyphenyl)pyridines containing acrylate unit at the end of alkyl chain. The photopolymerization was carried out in the LC state by UV irradiation in order to fabricate stable hydrogen-bonded DLC polymer with columnar structure. We attempted to insert the photo-reactive DLC into AAO nanochannels in order to investigate the influence of confined geometry on the mesophase structure. Overall fabrication process is described in Fig. 1.

Experimental

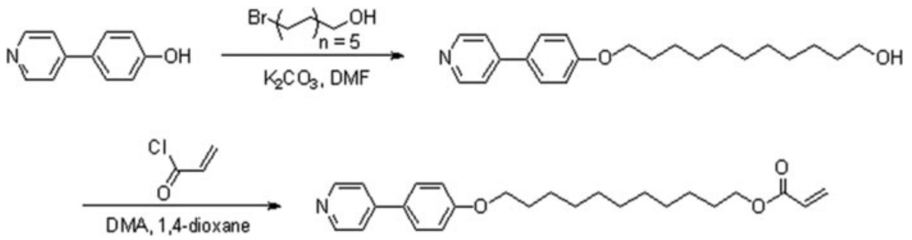
Measurements

^{1}H NMR spectra were measured with JEOL JNM-LA 300 spectrometer (300MHz). FT-IR spectroscopy was carried out on Perkin Elmer Spectrum 2000 spectrometer. Raman spectra were obtained from HORIABA T64000 spectrometer. Differential scanning calorimetry (DSC) was conducted on a TA DSC 2920. The heating and cooling rate was 10°C min^{-1}. Polarizing optical microscopy (POM) was performed on Leica Leitz Laborlux 12 POLS fitted with Mettler FP82HP and Mettler FP90. X-ray diffraction (XRD) experimets were performed on Bruker AXS GADDS equipped with a heating controller.

Preparation of Polymerizable Hydrogen-bonded DLC

The peripheral 4-(4-alkoxyphenyl)pyridine with acrylate unit at the end of alkyl chain, 11-(4-(pyridine-4-yl)phenoxy)undecyl acrylate (PPUA) was synthesized in accordance with the procedure in literature, as shown in Scheme 1 [8]. The analytical data are given below.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.70 (d, 2H, aryl), 7.60 (d, 2H, aryl), 7.65 (d, 2H, aryl), 7.01 (d, 2H, aryl), 6.43 (d, 1H, $\text{-CH} = \text{CH}\underline{\text{H}}'$), 6.05 (dd, 1H, $\text{-C}\underline{\text{H}} = \text{CHH}'$), 5.80 (d, 1H, $\text{-CH} = \text{C}\underline{\text{H}}\text{H}'$), 4.15 (t, 2H, $\text{-O(CH}_2)_{10}\text{C}\underline{\text{H}}_2\text{O-}$), 4.06 (t, 2H, $\text{-OC}\underline{\text{H}}_2\text{(CH}_2)_{10}\text{O-}$), 1.74 (m, 2H, $\text{-OCH}_2\text{C}\underline{\text{H}}_2\text{(CH}_2)_9\text{O-}$), 1.57 (m, 2H, $\text{-O(CH}_2)_9\text{C}\underline{\text{H}}_2\text{CH}_2\text{O-}$), 1.43 (m, 2H,



Scheme 1. Synthesis of the peripheral PPUA.

$-O(CH_2)_2C\underline{H}_2(CH_2)_8O-$), 1.29 (m, 6H, $-O(CH_2)_3C\underline{H}_2(CH_2)_3C\underline{H}_2C\underline{H}_2(CH_2)_2O-$), 1.26 (m, 6H, $-O(CH_2)_4C\underline{H}_2C\underline{H}_2C\underline{H}_2(CH_2)_4O-$). MS ($m/z$): 395.3 ($M^+$).

The polymerizable hydrogen-bonded DLC (PG/PPUA) was prepared by dissolving PG and peripheral PPUA in a molar ratio 1:3 in anhydrous acetone and then removing the solvent slowly at a reduced pressure.

Photopolymerization of Hydrogen-bonded DLC and Insertion into AAO

After a small amount of hydrogen-bonded DLC was placed on a heating stage (a Mettler FP82HP with a Mettler FP90 control unit), photopolymerization was carried out in the LC state by UV irradiation under nitrogen with a UV lamp (UVP B-100AP, 115V, 60Hz). In the case of DLC mixtures containing photoinitiator, Irgacure 651® was used in the concentration of 5 wt. %. The DLC insertion experiment was performed by infiltrating nanoporous AAO (Whatman® Anodisc, pore diameter = 100 nm, thickness = 90 μm) in the LC state using capillary force.

Results and Discussion

Liquid Crystalline Properties of Polymerizable Hydrogen-bonded DLC

To examine the formation of intermolecular hydrogen bonds between a PG core and peripheral PPUA, FT-IR spectroscopy was performed. In the case of PG, a broad stretching band of hydroxyl group centered at about 3370 cm^{-1} was observed in the range of 3600 to 2900 cm^{-1}, which means the self-hydrogen bonding of OH groups. Hydrogen-bonded DLC exhibited a new stretching band of OH group centered at a lower wavenumber of

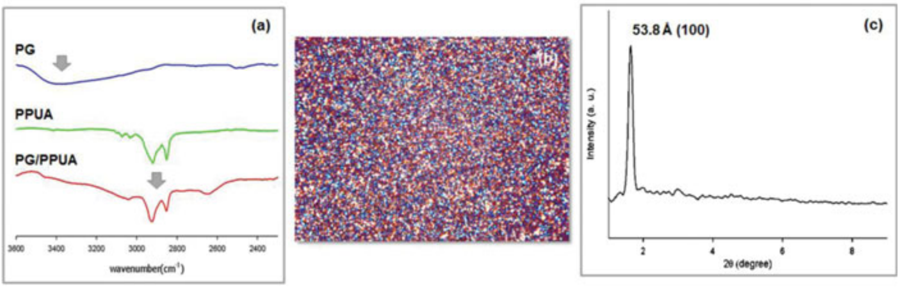


Figure 2. (a) FTIR spectra, (b) POM image at 65°C, and (c) XRD pattern at 65°C for hydrogen-bonded DLC.

Table 1. Thermal properties of PPUA and hydrogen-bonded DLC

	Phase transition behavior[a]	
Compounds	Heating	Cooling
PPUA	Cr 80.4 (57.6) I	I 44.1 (149.9) Cr
PG/PPUA	Cr 61.5 (9.8) Cr 73.6 (3.5) I	I 69.6 (6.3) Col

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

about 2900 cm^{-1} in the range of 3500 to 2500 cm^{-1}, indicating the formation of stronger hydrogen bonds between hydroxyl group of PG core and pyridine moieties of peripheral PPUA in the DLC complex, as shown in Fig. 2(a). Similar results were reported in the literature [9].

Table 1 shows the phase transition behavior of peripheral PPUA and hydrogen-bonded PG/PPUA complex. While the PPUA showed no liquid crystalline phases, monotropic mesophase was observed at 69.6°C upon cooling. POM observations revealed clearly birefringent fine texture at 65°C, as shown in Fig. 2(b). The mesophase structure of PG/PPUA DLC complex was further characterized by XRD. The XRD pattern at 65°C showed one sharp (100) reflection of 53.8 Å corresponding to the inter-columnar order in the discotic mesophase, as shown in Fig. 2(c). No higher order reflections were detected probably due to weak long-range interactions between columns resulting from a lot of free space inside hydrogen-bonded discotic mesogen. This XRD pattern suggests the formation of discotic columnar mesophase.

Photopolymerization of Hydrogen-bonded DLC and Its Infiltration into AAO

The extent of polymerization was monitored by Raman spectroscopy. The intensity of C=C stretching band at about 1600 cm^{-1} corresponding to acrylate group decreased gradually as photopolymerization proceeded in the absence of photoinitiator, as shown in Fig. 3(a) [10]. On the other hand, polymerization in the presence of photoinitiator gave rise to abrupt decrease in intensity of the C=C band after UV irradiation for only 10 sec, which shows

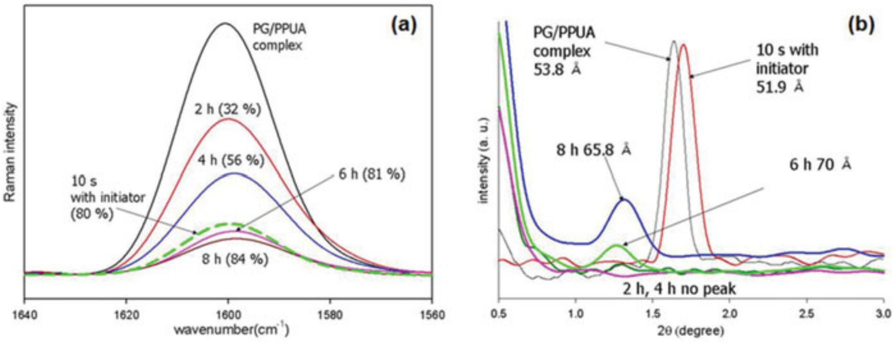


Figure 3. (a) Raman spectra and (b) XRD patterns of hydrogen-bonded DLC and the resulting polymers after UV irradiation.

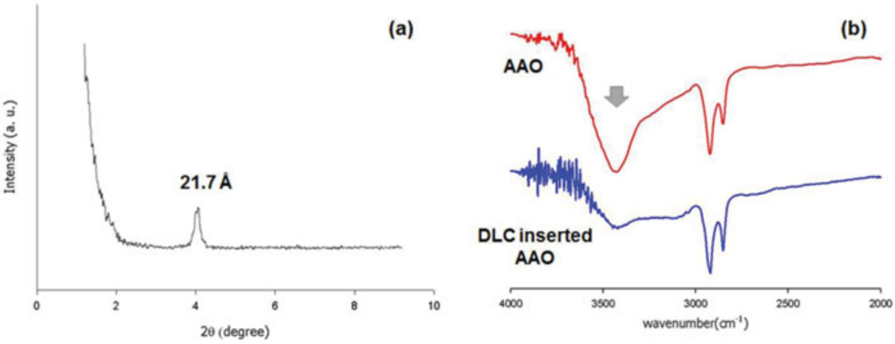


Figure 4. (a) XRD pattern and (b) FT-IR spectra for DLC inserted AAO.

the similar conversion to that for polymerization without photoinitiator during 6 h. This result indicates that UV irradiation in the presence of photoinitiator during very short time is more efficient in polymerization of hydrogen-bonded DLC in the LC state.

The structural changes in the resulting polymers after UV irradiation were studied by XRD. After UV irradiation for 10 s in the presence of photoinitiator, the XRD pattern of the polymer was similar to that of hydrogen-bonded DLC although the position of (100) reflection changed slightly due to radical reactions between acrylate groups, as shown in Fig. 3(b). In the case of UV irradiation without photoinitiator, the peak of the (100) reflection disappeared or its position changed greatly, which means that prolonged UV irradiation at elevated temperature causes structural change in the discotic columnar arrangement to a large extent, leading to failure in the fixation of mesophase structure. From these results, it is assumed that the liquid crystalline order of discotic columnar mesophase can be maintained by photopolymerization in the presence of photoinitiator during very short time.

In order to examine the influence of confined geometry in AAO nanochannels on the mesophase structure, we performed XRD experiments after infiltration of hydrogen-bonded DLC into AAO nanopores. As shown in Fig. 4(a), the position of (100) reflection in hydrogen-bonded DLC changed considerably to 21.7 Å in AAO, which is similar to molecular length of fully extended peripheral PPUA. Khaleel and Klabunde reported that porous high-surface-area alumina can absorb pyridine through coordination or hydrogen bonding between AAO surface and pyridine molecules [11]. In our case, it is supposed that pyridine moities of peripheral PPUA can be adsorbed on the AAO surface wall, which leads to breaking of hydrogen bonds in the hydrogen-bonded DLC. Figure 4(b) shows the evidence of hydrogen bond breakage in AAO. The large decrease in intensity of the surface hydroxy groups at about 3400 cm^{-1} was observed in the FT-IR spectrum of DLC inserted AAO, indicating the absorption of PPUA into AAO. From these results, we can conclude that hydrogen bonds in the DLC were broken due to the strong interaction between peripheral PPUA molecules and AAO surface inducing structural change in columnar order to the lamellar order.

Conclusions

New photopolymerizable discotic liquid crystal formed by hydrogen bonding between a phloroglucinol core and peripheral 4-(4-alkoxyphenyl)pyridines containing acrylate unit was prepared. The polymerization in the presence of photoinitiator for very short time provided stable hydrogen-bonded DLC polymer with columnar structure. The infiltration of hydrogen-bonded DLC into AAO nanopores yielded structural change in mesophase structure due to hydrogen bond breakage.

Acknowledgments

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References

[1] Chandrasekhar, S., Sadashiva, B. K., & Suresh, K. A. (1977). *Pramana*, *9*, 471.
[2] Watson, M. D., Fechtenkötter, A., & Müllen, K. (2001). *Chem. Rev.*, *101*, 1267.
[3] Kawata, K. (2002). *Chem. Rec.*, *2*, 59.
[4] Schenning, A. P. H. J., Gonzalez-Lemus, Y. C., Shishmanova, I. K., & Broer, D. J. (2011). *Liq. Cryst.*, *38*, 1627.
[5] Feng, X. S., & Pan, C. Y. (2002). *ChemPhysChem.*, *3*, 539.
[6] Chang, J. Y., Yeon, J. R., Shin, Y. S., Han, M. J., & Hong, S. K. (2000). *Chem. Mater.*, *12*, 1076.
[7] Steinhart, M., Zimmermann, S., Göring, P., Schaper, A. K., Gösele, U., Weder, C., & Wendorff, J. H. (2005). *Nano Lett.*, *5*, 429.
[8] Lee, J. H. (2014). *Liq. Cryst.*, *41*, 738.
[9] Sato, A., Kato, T., & Uryu, T. (1996). *J. Polym. Sci. Part A: Polym. Chem.*, *34*, 503.
[10] Edwards, H. G. M., Johal, K. S., Johnson, A. F. (2006). *Vib. Spectrosc.*, *41*, 160.
[11] Khaleel, A. A., & Klabunde, K. J. (2002). *Chem. Eur. J.*, *8*, 3991.