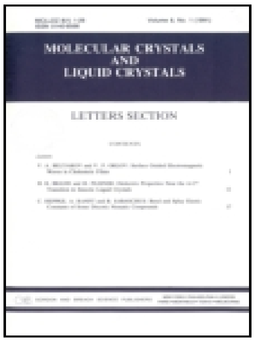

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Fabrication of π-Conjugated Polymers with Stable Columnar Order from Hydrogen-bonded Discotic Liquid Crystals Containing Diacetylene and Acrylate Moieties

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New cross-linked conjugated polydiacetylenes with stable columnar order have been fabricated by using hydrogen-bonded discotic liquid crystals (DLCs) containing photoreactive diacetylene and acrylate moieties. The polymerizable DLC exhibiting columnar mesophase has been prepared simply through hydrogen bonding between a phloroglucinol core and pyridine derivatives containing two photoreactive groups. Photopolymerization of the hydrogen-bonded DLCs in the LC state yielded cross-linked conjugated polydiacetylenic columns in which the diacetylene and acrylate groups were selectively polymerized. Our controlled methodology will provide a promising way to fabricate supramolecular π-functional polymeric materials for plastic optoelectronic devices.

Keywords Columnar phase; conjugated polymer; discotic liquid crystal; hydrogen bonding; photopolymerization

Introduction

π-Conjugated polymeric materials have received growing interest for their advanced applications in chemical sensors, organic solar cells, and optoelectronics [1–3]. For the construction of these functional materials, the fixation of liquid crystal (LC) order by polymerization is promising because the organized conjugations in polymers are stable over a wide temperature range. LC molecules with photoreactive groups can be aligned macroscopically in the LC state, and then polymerization will yield ordered functional polymers maintaining the stable LC order. The various LC phases including the nematic, smectic, and columnar mesophases have been successfully utilized in this process [4–6].

The concept of self-assembly in organized π-functional materials has attracted much attention because of the ease of processing [7]. Among the noncovalent interactions, hydrogen bond is a powerful tool to create self-assembled superstructures due to its high strength

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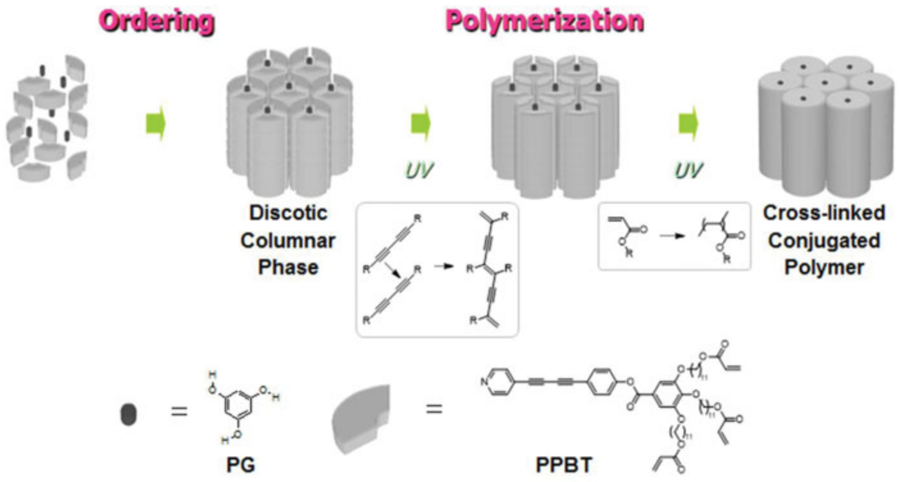


Figure 1. Fabrication of π-conjugated polymers with stable columnar order from hydrogen-bonded DLCs.

and directionality [8]. By choosing suitable hydrogen bonding donors and acceptors, the superstructure of organized supramolecular assemblies can be readily controlled.

We previously reported that single hydrogen-bonded discotic liquid crystals (DLCs) can form nematic columnar and hexagonal columnar mesophases [9]. By taking advantage of this simple and effective way to prepare the supramolecular DLCs, we now report on the fabrication of new π-conjugated polymers with stable columnar order from hydrogen-bonded DLCs. A polymerizable DLC has been prepared by single hydrogen bonding between a phloroglucinol (PG) core and pyridine derivatives containing photoreactive diacetylene and acrylate moieties. Conjugated polymers maintaining stable columnar order have been fabricated by in-situ photopolymerization of two photoreactive groups in the LC state, as shown in Fig. 1. The liquid crystalline properties and photopolymerization behavior of supramolecular DLC have been characterized and discussed in detail.

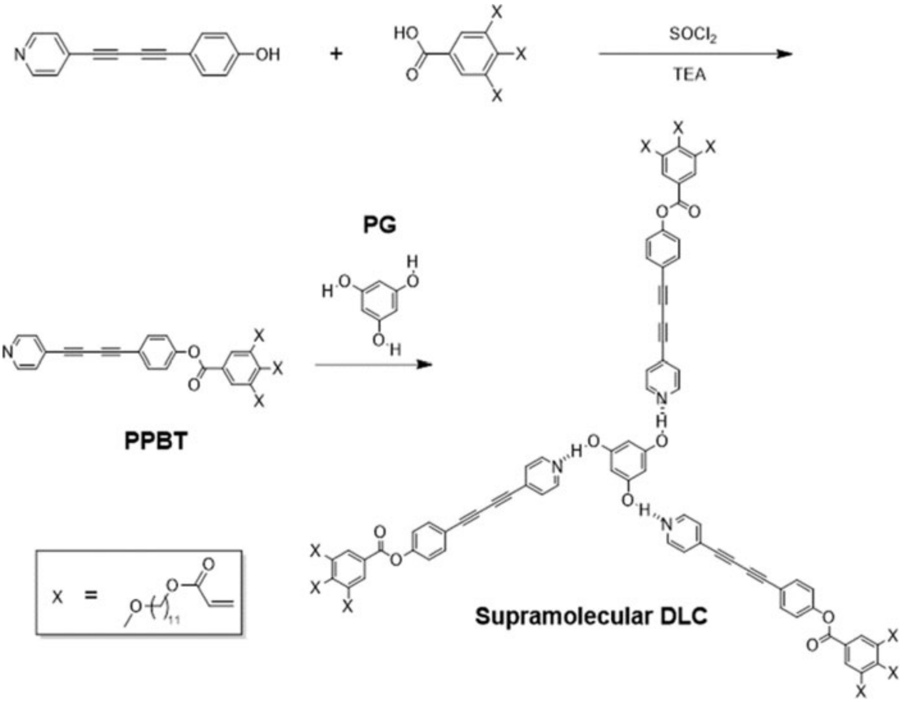
Experimental

Measurements

^{1}H NMR spectra were measured with JEOL JNM-LA 300 spectrometer (300 MHz). FTIR experiment was conducted on a JASCO FT/IR-200 spectrometer. Differential scanning calorimetry (DSC) was carried out with TA DSC 2010 under a nitrogen atmosphere with heating and cooling rates of 10 °C min^{-1}. The phase transition temperature was obtained from the peak maximum. Polarized optical microscopy (POM) was conducted with Leica LABORLUX 12 POLS microscope fitted with Mettler FP82HP hot stage and Mettler FP90. Small-angle X-ray scattering (SAXS) patterns were measured with Bruker AXS NanoSTAR equipped with a temperature controller. Wide-angle X-ray scattering (WAXS) was conducted on a Bruker AXS GADDS fitted with heating accessory. Cu Kα radiation ($\lambda = 1.54$ Å) was utilized for all XRD experiments. UV-vis spectra were obtained from Perkin Elmer Lambda 20.

Preparation and Photopolymerization of Supramolecular DLC

The peripheral pyridine derivative, 11,11′,11″-(5-((4-(pyridin-4-yl-buta-1,3-diynyl)phenoxy)carbonyl)benzene-1,2,3-triyl)tris(oxy)tris(undecane-11,1-diyl) triacrylate (PPBT) was synthesized in accord with a standard literature procedure, as described in Scheme 1 [6, 10]. The analytical data are given below.



Scheme 1. Synthesis of the pyridine derivative PPBT and preparation of the polymerizable supramolecular DLC.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.62 (d, 2H), 7.62 (d, 2H), 7.40 (m, 4H), 7.22 (d, 2H), 6.41 (d, 3H), 6.12 (dd, 3H), 5.80 (d, 3H), 4.17–4.02 (m, 12H), 1.86–1.26 (m, 54H). MS (*m*/*z*): 1043.6 (M^+). Anal. Calcd. for $C_{64}H_{85}NO_{11}$: C, 73.60; H, 8.20; N, 1.34. Found: C, 73.85; H, 8.21; N, 1.07.

The polymerizable supramolecular DLC was obtained by dissolving the phloroglucinol core and PPBT peripherals in a molar ratio of 1 : 3 in anhydrous acetone and then evaporating the solution slowly under reduced pressure. Thin films of the DLC monomer were prepared on quartz plates or polyimide films by melting casting. After these samples were placed on a heating stage (a Mettler FP82HP with a Mettler FP90 control unit), photopolymerization in the LC state was performed by UV irradiation under nitrogen with a UV lamp (UVP XX-15S, 20W) at 59°C for 5 h.

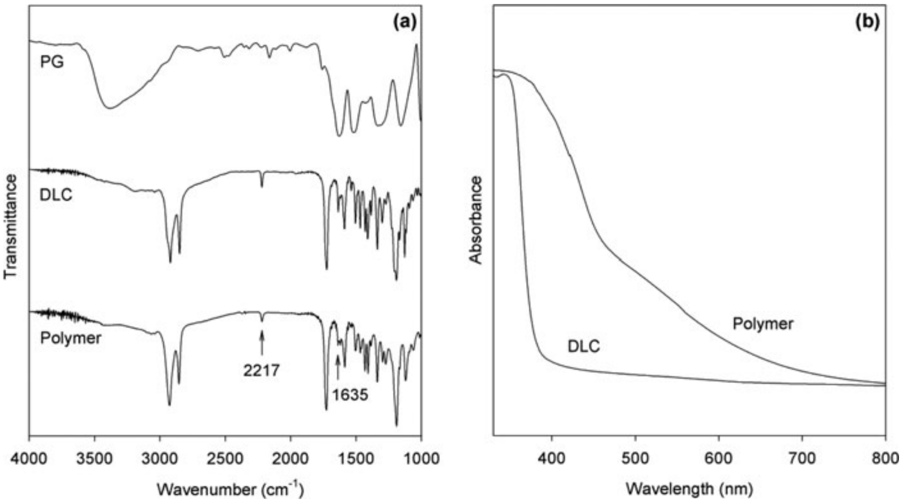


Figure 2. (a) FTIR spectra and (b) UV-vis absorption spectra of supramolecular DLC and the resulting polymer after UV irradiation.

Results and Discussion

Liquid Crystalline Properties of Polymerizable Supramolecular DLC

The formation of hydrogen bonds in supramolecular DLC was examined by FTIR spectroscopy. While PG core showed a broad stretching band of OH group at 3370 cm^{-1} corresponding to self-hydrogen bonding between hydroxyl groups, a new OH stretching band of supramolecular DLC was observed at a lower wavenumber of about 2900 cm^{-1}, which is ascribed to the strong hydrogen bonding between a PG core and peripheral PPBTs in the supramolecular DLC, as shown in Fig. 2(a). Spectral features of our study were in accord with the literature [11].

The phase transition behaviors of supramolecular DLC were summarized in Table 1. The supramolecular DLC exhibited a monotropic transition at 66°C on cooling. The enthalpy of isotropic-mesophase transition was relatively high (4.0 J g^{-1}), suggesting ordered LC phases. In POM measurements, a birefringent fine texture of small domains was observed at 60°C on cooling. The mesophase structure of supramolecular DLC was further characterized by XRD, as shown in Fig. 3. A strong reflection at 35.3 Å corresponding

Table 1. Thermal properties of PPBT and supramolecular DLC complex

	Phase transition behavior[a]									
Compounds	Heating					Cooling				
PPBT	Cr	38(22.8)	Cr	69(35.7)	I	I	53(31.9)	Cr		
Complex	Cr	23(163.5)	Cr	58(125.7)	I	I	66 (4.0)	Col	48(29.6)	Cr

[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.

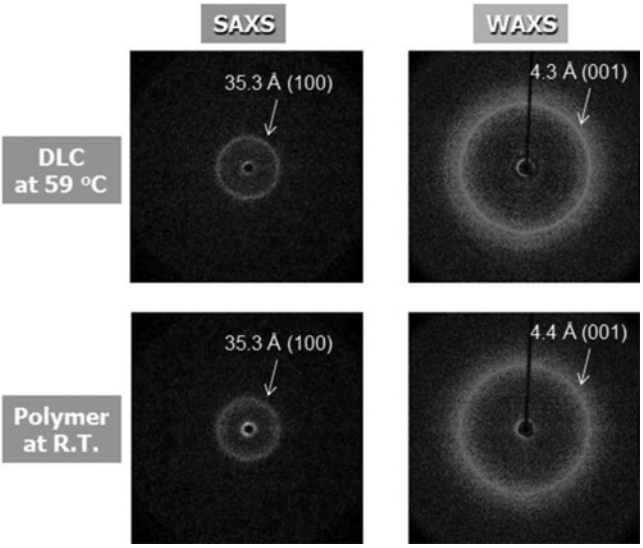


Figure 3. SAXS and WAXS patterns of supramolecular DLC at 59°C and the polymer at room temperature.

to the (100) reflection was detected in the SAXS, which is attributed to the average distance between columns. A narrow reflection at 4.3 Å and a broad halo were displayed in the WAXS, corresponding to the average distance between discs within a column and disordered alkyl chains, respectively. These reflection patterns indicate the formation of a discotic columnar mesophase with regular stacking of discs.

Photopolymerization of Supramolecular DLC

The photopolymerization process of supramolecular DLC containing diacetylene and acrylate groups was examined by FTIR and UV-vis spectroscopy. Figure 2(a) shows FTIR spectrum of the resulting polymer after UV irradiation. For diacetylene groups, the absorbance of a weak band at 2217 cm^{-1} corresponding to asymmetric stretching vibration of carbon-carbon triple bonds has decreased by over 50% after irradiation. In the case of acrylate groups, the absorbance of a characteristic band at 1635 cm^{-1} corresponding to the stretching vibration of carbon-carbon double bond of the acrylic moiety decreased by over 50% after photopolymerization. These results suggest that the diacetylene and acrylate moieties in supramolecular DLC were selectively polymerized to a large extent by UV irradiation. The similar results were observed for other studies involving diacetylene or acrylate groups [6, 12].

In UV-vis spectroscopy, the supramolecular DLC had an absorption tail up to about 400 nm, as shown in Fig. 2(b). After UV irradiation, a dark red polymer was formed at room temperature with an absorption limit extending to about 750 nm. This broad red-shifted absorption with a long tail means the formation of conjugated polydiacetylene in which a broad distribution of conjugation lengths exists. These results suggest that 1,4-polymerization of diacetylene groups occurred along the column axis by UV irradiation.

The structure of the resulting conjugated polymer was examined by SAXS and WAXS experiments, as shown in Fig. 3. The SAXS pattern of the polymer showed a sharp peak

(35.3 Å) corresponding to the (100) reflection of discotic columnar mesophase, and also the WAXS pattern displayed a reflection at 4.4 Å and a broad halo resulting from the (001) reflection and average distance between alkyl chains of columnar structure, respectively. This reflection pattern was similar to that of the supramolecular DLC, suggesting that the diacetylene and acrylate moieties in supramolecular DLC were photopolymerized in the discotic columnar state and therefore the cross-linked conjugated polydiacetylene with stable columnar order was successfully fabricated.

Conclusions

π-Conjugated polymers with stable columnar order have been prepared using hydrogen-bonded DLC containing diacetylene and acrylate groups. Photopolymerization of the supramolecular DLC in the discotic columnar state yielded cross-linked conjugated polydiacetylene maintaining stable columnar order. Our controlled method provides an effective way to fabricate organized conjugated polymers for possible use in sensors, electronic conductors, and optoelectronics.

Acknowledgments

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References

[1] Bardeen, C. (2011). *Science*, *331*, 544.
[2] Rose, A., Zhu, Z., Madigan, C. F., Swager, T. M., & Bulovic, V. (2005). *Nature*, *434*, 876.
[3] Sessolo, M., & Bolink, H. J. (2011). *Adv. Mater.*, *23*, 1829.
[4] Schultz, J. W., & Chartoff, R. P. (1998). *Polymer*, *39*, 319.
[5] Baxter, B. C., & Gin, D. L. (1998). *Macromolecules*, *31*, 4419.
[6] Chang, J. Y., Yeon, J. R., Shin, Y. S., Han, M. J., & Hong, S. K. (2000). *Chem. Mater.*, *12*, 1076.
[7] González-Rodríguez, D., & Schenning, A. P. H. J. (2011). *Chem. Mater.*, *23*, 310.
[8] Steiner, T. (2002). *Angew. Chem. Int. Ed.*, *41*, 48.
[9] Lee, J. H., Jang, I., Hwang, S. H., Lee, S. J., Yoo, S. H., & Jho, J. Y. (2012). *Liq. Cryst.*, *39*, 973.
[10] Smith, R. C., Fischer, W. M., & Gin, D. L. (1997). *J. Am. Chem. Soc.*, *119*, 4092.
[11] Sato, A., Kato, T., & Uryu, T. (1996). *J. Polym. Sci. Part A: Polym. Chem.*, *34*, 503.
[12] Bacher, A., Erdelen, C. H., Paulus, W., Ringsdorf, H., Schmidt, H. W., & Schuhmacher, P. (1999). *Macromolecules*, *32*, 4551.