Alignment of Lyotropic Liquid Crystalline Conjugated Polymers in Floating Films

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ABSTRACT: Directed alignment of polymer chains plays an indispensable role in charge transport properties. We focus not only on a specific method to induce the alignment but also on the design of a liquid crystalline (LC) conjugated polymer to take advantage of an intrinsic self-assembly characteristic. We synthesized a lyotropic LC conjugated polymer, CP1-P, having o-nitrobenzyl (ONB) esters as photocleavable side chains and adopted a floating film transfer method to induce the polymer chain alignment through a lyotropic LC phase transition. An optimum amount of a high boiling point solvent (1,2-dichlorobenzene) in chloroform turned out to be an important factor to maximize the polymer chain alignment. The hole transport mobility along the polymer chain alignment direction was 13–14 times higher than that in the direction perpendicular to the alignment. In addition, the removal of side chains resulted in the solvent resistivity while maintaining the alignment feature in organic thin-film transistors.

INTRODUCTION

Liquid crystalline (LC) conjugated polymers (CPs) combine benefits from both LC and CP properties. In other words, they not only possess the unique LC features of self-assembly and molecular alignment by external treatments but also show flexibility, solution processability, and structure tunability from the molecular design of CPs. A combination of these properties offers significant advantages for the development of highly aligned polymer films promoting efficient charge transport characteristics in organic electronics.1–4 Siringhaus et al. reported that enhanced mobilities were achieved in poly-9,9-diocetyl-fluorene-co-bithiophene (F8T2) by aligning polymer chains parallel to the charge transport direction.5 Another LC polyfluorene, (9,9-diocetylfluorene-co-benzothiaiazole) (F8BT), showed mobility anisotropies of 10–15 and 5–7 for hole and electron transport, respectively, when the conjugated backbones were aligned along the direction of nanolines formed by a nanoimprinting process.6 We also reported LC CP design rules and demonstrated a hole mobility of 0.86 cm2/Vs along the polymer alignment direction that is 1600 times faster than that perpendicular to the polymer alignment.7 Recently, Bridge and co-workers presented that different intermolecular interactions of lyotropic cyclopentadithiophene-based polymers contributed to the formation of macroscopically aligned polymer films by varying flexible side chains.8

Although many previous studies elaborated distinct advantages of LC that lead to a charge transport anisotropy in polymer films,6,8,9 the structural diversity remains a challenge because of the lack of systematic analysis on correlations between the molecular structure and LC behavior of CPs. In this work, a newly designed LC CP, poly[bis(5-(dodecyloxy)-2-nitrobenzyl) 1-(5-(2,5-di-2-furo-4-(thiophen-2-yl)phenyl)-thiophen-2-yl)-4H-cyclopenta[c]thiophene-5,5(6H)-dicarboxylate] (CP1-P), is being synthesized (Scheme 1). Specifically, this polymer has o-nitrobenzyl (ONB) ester side chain, which is one of the most commonly used photocleavable moieties,10–12 but has not been widely applied for lyotropic LC CPs. We confirmed that the polymer forms typical schlieren-like texture at a highly concentrated LC phase. This proves comparability of the photocleavable side chains with our previously reported design rule for LC CPs.7 Because of its LC character, the polymer showed a unique intermolecular interaction leading to a uniaxial alignment during the film formation process by the floating film transfer method (FTM).13–15 This method was first reported with poly(3-hexylthiophene) by Morita et al.16 It is similar to the Langmuir–Schaefer technique except that controlling a

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Surface-pressure to make a compact film is not required. To be specific, a small drop of hydrophobic polymer solution is put on the surface of subphase hydrophilic liquid and spread out rapidly over the liquid followed by a thin and uniform film formation. Several factors, such as temperature and viscosity of the hydrophilic liquid, solvent, and backbone structure, affect this film formation process have been investigated.\(^\text{17-19}\) Very recently, a modified FTM with a customized slider to provide a directional force has been also introduced using poly(3,3‴-didodecyl-quaterthiophene) (PQT-12), which is one of the widely studied polymers as the charge transporting layer in organic thin-film transistors (OTFTs).\(^\text{15}\)

We found an interesting new phenomenon in the solvent composition for FTM. Although it has been shown that using a high boiling point (BP) solvent induces strong self-assembly and large crystalline grains of polymer chains,\(^\text{20,21}\) the complete replacement of a low BP solvent with a high BP solvent resulted in negative impact on the polymer chain alignment in FTM.\(^\text{18}\) Instead, we systematically controlled the solvent composition by using a high BP solvent as an additive to provide adequate time for polymer chains to self-assemble while maintaining a low BP solvent as the primary solvent for CPs to undergo lyotropic LC phase transition. The precisely controlled amount of high BP solvent brings about a slow evaporation and uniform morphology without losing the alignment feature. This produces remarkably enhanced optical anisotropy and charge-carrier mobility compared to the case of polymer solutions without containing any high BP solvent. Moreover, the polymer chain alignment was essentially maintained after cleavage of ONB side chains, yielding solvent resistance, which can be useful for a solution-based multilayer processing in organic electronics.

### RESULTS AND DISCUSSION

An LC CP bearing photocleavable side chains (CP1-P) has been synthesized (Schemes 1 and S1). Our group reported previously a molecular design principle of lyotropic LC CPs, which states the following three points: (1) the interaction between sulfur and fluorine atoms, which is weak enough not to induce interpolymer aggregation, but will make chain planarization in a highly concentrated regime only; (2) introducing two bulky side chains to prevent interdigitation of the side chains between lamellar layers; (3) the tetrahedral carbon to minimize undesired massive interpolymer aggregation. A more detailed study to verify that these rules are not limited to a certain building block is being currently explored.
Together with the investigation on universal applicability of different building blocks in polymer main chains, we have been interested in modification on side chains without sacrificing LC properties. Even if incorporating side chains to CPs is a common strategy to make the polymers solution processable for OTFTs, the side chains do not contribute to charge transport properties because they are electrically insulating. For this reason, we assumed that removing side chains after a film formation might be beneficial for a more efficient charge transport. We chose ONB esters as photocleavable side chains not only because of their photo responsivity but also because of their bulkiness to provide sufficient solubility before the cleavage. The detailed synthetic process for the polymer is described in the Supporting Information.

The absorption profiles of CP1-P in solution and the solid state were almost identical, indicating that the polymer has a similar structural order in solution as in the film state (Figure S1). To remove the photo-labile ONB side chains, the spin-coated films on glass substrates were irradiated with UV light (365 nm). UV irradiation resulted in side chain cleavage and after chloroform (CF) rinsing, the absorbance intensity and absorption maxima of the conjugated polymer film remained intact because of the removal of the solubilizing side chains (Figure 1). The nonirradiated third layer having ONB side chains was completely removed by the same CF rinsing as shown in Figure 1a. The cleavage of side chains clearly displayed that it makes the polymers insoluble, enabling the deposition of consecutive layers from the same solvent without disrupting the bottom layers. Continuously, optical anisotropy of films prepared by another film formation method, FTM, was investigated (Figure 2). A uniaxial alignment of polymer chains perpendicular to the radial direction in a spreading polymer droplet on subphase liquid is induced by this method. The dichroic ratio (DR), defined as $DR = \frac{A_{\text{parallel}}}{A_{\text{perpendicular}}}$, where $A_{\text{parallel}}$ is the maximum absorbance of polarized light parallel to the alignment direction and $A_{\text{perpendicular}}$ is the maximum absorbance of polarized light perpendicular to the alignment direction, was calculated at 573 nm. The calculated DR of 4.8 under optimum conditions gives a clear evidence of the uniaxially aligned polymer chains. In addition to the DR value reflecting the absorbance intensity difference depending on the polarized light, it is worth mentioning that the absorption maximum is red-shifted by 5 nm for CP1-P, when films are prepared by the FTM compared to that of the film by spin-casting (Figures 2a and S1). The absorption of longer wavelength together with much stronger main peak (565–575 nm) intensity compared to the second peak (520–530 nm) can be attributed to enhanced intermolecular packing because of the alignment.19,22

Figure 2. (a) Polarized UV–vis absorption spectra of the CP1-P film from the solution in CF with 3 vol % DCB. The inset represents the directions of linear polarizer (black lines) and polymer chain alignment (red arrow), respectively. (b) DR (the bar graph) and order parameter ($S$, the blue solid sphere) as a function of CF-DCB blend ratios. The error bars represent the standard deviation. All films were formed by FTM on the subphase liquid of ethylene glycol–glycerol blend (1:1 v/v).

Figure 3. (a) Schematic illustration of the FTM film formation mechanism by CP1-P solution in CF and CF/DCB (97:3 v/v), respectively. (b) Optical microscopy images of a highly concentrated (top, ~200 mg/mL) and a diluted (bottom, <50 mg/mL) CP1-P solution under a crossed polarizer. The white scale bars represent 10 μm.
solvent composition. Complete alignment should exhibit $S = 1$ and no preferential orientation corresponds to $S = 0$. The optimum blending ratio of hydrophilic liquid was found to be 1:1 (ethylene glycol/glycerol v/v). When the amount of glycerol is smaller than ethylene glycol, the spreading speed of the polymer droplet was too fast so that the resulted film tended to be torn apart before it solidified into a uniformly aligned thin film. On the other hand, when the mixture contained more glycerol than ethylene glycol, the solution dried even before the polymer droplet formed a thin film. This is because the high viscosity of glycerol hampers the mobility of the polymer on it. In case of solvent composition to prepare polymer solutions, we compared four different conditions; CF only and CF containing small amounts of the high BP solvent 1,2-dichlorobenzene (DCB) with different volume ratios (CF/DCB 99:1, 97:3, and 95:5). The use of a high BP solvent is one common approach to improve device performance by providing enough time for self-assembly of CPs. However, it has been described that the FTM polymer films from a high BP solvent tend to have a random macromolecular arrangement unlike the films from a low BP solvent because the choice of solvent affects the balance between the solvent evaporation and the spreading speeds in the process. Instead, we used only a small volume of the high BP solvent as an additive not as the primary solvent so that we can take advantage of relatively slower evaporation and uniform morphology without sacrificing the alignment feature of FTM. When we added 1 vol % of DCB, a slight improvement in terms of alignment was noticed, whereas when 5 vol % was added, we observed no significant alignment, which is similar to the CF-only case. A schematic illustration of the differences in the alignment during the film formation process is shown in Figure 3a. We speculated that if we had too much DCB, the polymer solution would spread out all over the surface without forming a highly concentrated region because of its high BP so that we could not induce an efficient lyotropic LC property of CP1-P. We experienced when we used 3 vol % of DCB, the solvent composition provided enough time for close packing and self-assembly of polymer chains. By having this optimum blending ratio of DCB and CF, the remaining 97 vol % of CF still allows relatively fast drying to form a highly concentrated region, resulting in lyotropic LC phase transition. Thus, the alignment can be the most efficient. The degree of alignment quantified by DR was improved by almost three times as we added the high BP solvent through the formation of a more ordered structural alignment. As anticipated, charge transport properties follow the same trend: the mobility of the device when polymer chains are parallel to the source−drain electrodes increases four times because of the high BP solvent effect during the film formation process (Figure S3).
CPs, we fabricated OTFTs in the bottom-gate and top-contact configuration. The aligned polymer films were transferred from the hydrophilic liquid surface (ethylene glycol–glycerol 1:1 blend) to the octadecyltrichlorosilane (OTS)-treated substrate by staining. The samples were then rinsed with isopropyl alcohol to remove the remaining liquid. The best charge transport performance was observed from the devices postannealed at 200 °C. The thermal gravimetric analysis shows that CP1-P is thermally stable up to 250 °C (Figure S4). In order to explore charge transport anisotropy, the source–drain electrodes were deposited in two different directions (channel angles of 0° and 90° relative to the alignment direction of polymer chains). As a control, spin-cast films were also prepared in the same device geometry (Figure S5). In comparison to the device when source–drain electrode is deposited perpendicularly (⊥), the device with parallel direction (//) is responsible for its higher hole mobilities by more than an order of magnitude from $8.73 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ ($\mu_{//}$) to $1.21 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ ($\mu_{⊥}$) (Figure 4). The primary reason for this mobility anisotropy is due to a substantial difference in charge-transport pathways, which are determined by the orientation of the polymer chain alignment relative to the source–drain electrodes direction. In other words, in a parallel device, a charge carrier can travel mainly along the polymer chains, whereas it should move by hopping through π–π stacks in a perpendicular device.26 As anticipated, the devices prepared by spin-coating, which have no anisotropic orientation, showed their mobility values ($\mu_{iso}$) between $\mu_{∥}$ and $\mu_{⊥}$ of the device with aligned CP1-P. Additionally, the effect of side chain removal followed by solvent rinsing on the device performance was investigated. Although a ~1.3-fold decrease in mobility was observed upon the side chain cleavage and rinsing process, the device still exhibited superior hole transporting property over randomly oriented devices. This suggests that the alignment feature has been only slightly disturbed after exposure to UV and organic solvent (CF). The maximum mobility values for each condition with an average mobility, on/off ratio, and threshold voltage are summarized in Table 1. Even though the overall trend matches well with the result predicted by an anisotropic orientation, the difference between the spin-coated film and the aligned film was relatively small compared to our previous data. A plausible explanation for this result is that bulky aromatic rings in the side chains are likely to hinder more efficient alignment and close packing during the film formation process.27 As discussed above in the optical property analysis, when the polarized light is perpendicular to the alignment direction, the absorbance is not zero, indicating less-effective polymer alignment.

Table 1. OTFT Performance of CP1-P

| Side chains | $\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$) | $V_{th}$ (V) | $I_{on}/I_{off}$ |
|-------------|-----------------|-------------|-----------------|
| Spin-coated (annealed at 200 °C) | before cleavage | $2.56 \times 10^{-3}$ | $-24.3$ | $10^{-5}$ |
| FTM-perpendicular | before cleavage | $8.73 \times 10^{-4}$ | $-31.7$ | $10^{-4}$ |
| (annealed at 200 °C) | cleavage | $9.58 \times 10^{-4}$ | $-30.5$ | $10^{-4}$ |
| FTM-parallel | before cleavage | $1.21 \times 10^{-3}$ | $-30.6$ | $10^{-3}$ |
| (annealed at 200 °C) | cleavage | $1.36 \times 10^{-1}$ |
| FTM-parallel | after cleavage | $3.94 \times 10^{-3}$ | $-22.2$ | $10^{-3}$ |

$\mu$ is the carrier mobility, $V_{th}$ is the threshold voltage, and $I_{on}/I_{off}$ is the on/off current ratio. All active layer processing by FTM was done in air. Mobility values were measured under a nitrogen atmosphere. The maximum values are listed in parentheses.

**CONCLUSIONS**

We report a lyotropic LC CP with photocleavable side chains and their uniaxial alignment via the FTM. The lyotropic LC behavior leads to the uniaxial orientation of polymer chains and the photolabile side chains render solvent resistance of the polymer and multilayer fabrication capability. The optical and electrical anisotropies achieved by the floating film transfer have been explored through optical spectra and field effect transistors. The effect of solvent composition and subphase liquid composition on the polymer alignment was systematically investigated. The small amount of high BP solvent as an additive, which was added into the polymer solution prior to the film formation process, largely enhances the polymer alignment by providing ample time for close packing and self-assembly of the polymer. The average charge-carrier mobility anisotropy ($\mu_{//}/\mu_{⊥}$) in the optimized condition was found to be 13.86, emphasizing the importance of controlling solvent composition to maximize the degree of alignment. The hole mobility of CP1-P after the side chain cleavage decreased from $1.21 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ to $9.34 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, but was still significantly larger than the devices having perpendicular ($8.73 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$) or spin-cast random orientation ($2.56 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$) before cleavage. This indicates that the alignment has been preserved during the process of rinsing.
with CF, which is a good solvent for CP1-P. Our results demonstrate that rod-like LC CPs having photocleavable side chains are promising for various flexible organic electronics as highly aligned and solvent-resistant semiconducting materials. Rational functionalization on the carboxylic acid, which was obtained as the result of side chain cleavage, will enable wider range of applications for organic electronics such as potentiometric sensors.

## EXPERIMENTAL SECTION

### Materials

All reagents were acquired from commercial suppliers [Aldrich or Tokyo Chemical Industry Co., Ltd. (TCI)] and used without any further purification. \((\text{2,5-Difluoro-1,4-phenylene)}\)\text{bis(}thiophene-5,2-diyl)\text{bis(trimethylstannane)}\) was prepared according to the reported procedures. The synthetic procedure used to prepare the monomer with cleavable side chains is shown in Scheme 1, and the details are presented in the Supporting Information. Molecular weights were determined by gel permeation chromatography (GPC) in CF against polystyrene standards using a Waters 515 HPLC Pump equipped with a Waters 2410 refractive index detector and three Waters styragel columns (flow rate: 1.0 mL/min). NMR spectra were recorded using a Bruker Ultrashield 400 MHz or Bruker AVANCE 600 MHz spectrometers in CDCl₃ at 298 K. Absorption spectra were measured using a Cary 50 Bio UV–vis spectrophotometer (Varian). UV light irradiation was performed using a 365 nm LED lamp with a power density of 25 mW cm⁻². AFM images were recorded on an Asylum Research MFP-3D stand-alone AFM in the tapping mode with a Cantabro ULTRA probe (spring constant 40 N/m and radius of curvature of 8 nm). Out-of-plane XRD patterns were collected using a Rigaku Ultima III diffractometer system with graphite monochromatized Cu Kα radiation \((\lambda = 1.5406 \text{ Å})\) at 48 kV and 40 mA.

### Multilayer Film Formation

Multilayer films were prepared with repetitive spin-casting, followed by UV irradiation and rinsing with CF, for each of the first two layers. The photocleavage of side chains gave good solvent resistance to the resulting film. The subsequent spin-casting on top of the insoluble first (second) layer produced the second (third) layer.

### Device Fabrication and Characterization

Top-contact, bottom-gate thin film transistors were fabricated on heavily n-doped silicon wafers with a 300 nm thick thermally grown SiO₂ as the gate dielectric (capacitance 10 nF cm⁻²). The substrates were cleaned by sonication in detergent and deionized water, acetone, and isopropyl alcohol, followed by a UV–ozone treatment for 20 min. The surface of the cleaned silicon substrates was treated with 0.1 M OTS in toluene at 60 ℃ for 30 min followed by rinsing with toluene and isopropyl alcohol. The polymer film was prepared either by spin-casting at 1000 rpm under a nitrogen environment or by FTM under ambient conditions, from 0.4 wt % solution in CF and 0.3 wt % solution in CF containing 0–5 vol % DCB, respectively. Subsequently, the devices made by FTM were annealed at 80 ℃ for 3 min to remove any residual solvent. Au source–drain electrodes were deposited by thermal evaporation through a shadow mask \((L = 100 \text{ μm}, W = 500 \text{ μm})\). Electrical characterization was carried out under nitrogen atmosphere using an Agilent 4145C precision semiconductor parameter analyzer. The mobilities were extracted according to the equation of \(I_{DS} = \mu C_{i} (W/2L) (V_{G} – V_{th})^{2}\), where \(I_{DS}\) is the drain current, \(\mu\) is the mobility in saturation regime, \(C_{i}\) is the gate dielectric capacitance per unit area, \(W\) and \(L\) are the channel width and length, respectively, \(V_{G}\) is the gate voltage, and \(V_{th}\) is the threshold voltage.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02205.

Details on polymer synthesis, DRs of FTM films, UV–vis spectra, XRD profiles, TGA curves of CP1-P, and electronic properties and AFM images of OTFT devices (PDF).

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The manuscript was written by D. S. Yang and revised by J. Kim through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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