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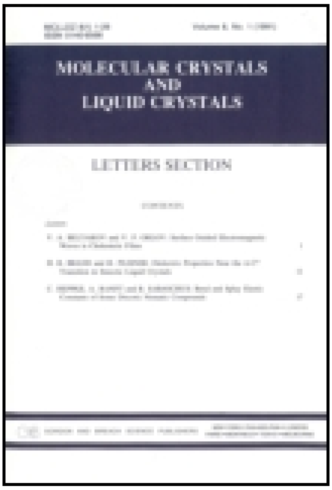

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Annealing-Free High-Mobility Diketopyrrolopyrrole-Benzodithiophene Copolymer for Organic Thin Film Transistors

Dae Hee Lee[a], Jicheol Shin[a], Tae Wan Lee[a], Min Ju Cho[a] & Dong Hoon Choi[a]

[a] Department of Chemistry, Research Institute for Natural Sciences, Korea University, Seoul, Republic of Korea

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Annealing-Free High-Mobility Diketopyrrolopyrrole-Benzodithiophene Copolymer for Organic Thin Film Transistors

DAE HEE LEE, JICHEOL SHIN, TAE WAN LEE, MIN JU CHO, AND DONG HOON CHOI*

Department of Chemistry, Research Institute for Natural Sciences, Korea University, Seoul, Republic of Korea

Diketopyrrolopyrrole (DPP)-based conjugated polymer (P(DPP-BDT)) containing benzodithiophene (BDT) was successfully synthesized via *Stille coupling reaction. The synthesized polymer shows good solubility in common organic solvents and good self-film-forming properties. The electrical properties of the polymer were evaluated in organic thin film transistors (OTFTs). The TFT made of pristine P(DPP-BDT) film exhibits good carrier mobility of 0.38∼0.40 cm^2 V^{-1} s^{-1} ($I_{on/off} = 10^6$, $V_{th} = -9$ V), which is close to the mobility of TFT made of the thermally annealed film.*

Keywords Conjugated polymer; benzodithiophene; diketopyrrolopyrrole; semiconductor; mobility; organic thin film transistor

Introduction

In the past, a number of promising π-conjugated polymers have been developed for obtaining high-performance organic thin film transistors (OTFTs) with high carrier mobilities. The development of high-performance solution-processable semiconducting materials is therefore an important research goal in the future flexible display and soft electronics. The TFT devices made from conjugated polymers have been fabricated mostly by using solution process such as conventional low-cost spin-coating or drop-casting techniques [1, 2].

Recently, π-conjugated polymers composed of donor (D) and acceptor (A) units in the repeating group have been highlighted to have an excellent carrier mobility, which is attributed to strong intermolecular interaction between the polymer chains [3]. In D-A conjugated polymers, proper selection of donor and side chain moieties are expected to govern the degree of crystallinity and chain orientation on the desired substrate.

Among many donor moieties, the fused benzo[1,2-*b*:4,5-*b*′]-dithiophene (BDT) structure inherently showed rigid and flat π-conjugated molecular frameworks. However, the D-A polymers bearing BDT unit have been less reported for application of OTFTs compared to others such as thienothiophene (TT) and dithienothiophene (DTT) [4–6]. Therefore, BDT–based monomer with reactive groups can be employed to constitute the structure of D-A conjugated polymer for highly efficient TFTs.

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*Address correspondence to Dong Hoon Choi, Department of Chemistry, Research Institute for Natural Sciences, Korea University, Seoul 136-701, South Korea. E-mail: dhchoi8803@korea.ac.kr

In this study, we demonstrate the synthesis and application of a new conjugated polymer, P(DPP-BDT) containing diketopyrrolopyrrole (DPP) and BDT moieties to OTFTs. DPP has been frequently employed as an acceptor building unit for high-performance semiconducting polymers, because it is a strong symmetric acceptor having a fused ring to impose coplanarity and to promote high crystallinity and uniform orientation of the polymer chains. Evidently, DPP-based conjugated copolymers are extensively considered as great potential materials for OTFTs [7, 8]. The solubility of P(DPP-BDT) was substantially improved by introducing a 2-octyldodecyl group at the *N*-position of DPP unit. To investigate the effect of the thermal annealing of thin film on its TFT performance, the films were treated under various thermal conditions. The hole mobilities of TFT devices reach about 0.4 $cm^2\ V^{-1}\ s^{-1}$ in the pristine film, which is similar to those of the devices made from thermally annealed films. It was well supported by the results of atomic force microscopy (AFM) in terms of surface morphology of thin films.

Experimental Section

All reagents were purchased from Sigma-Aldrich Co. and used as-received, unless stated otherwise. The reagent-grade solvents used in this study were dried using standard distillation methods. The monomers, 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (**1**) and 1,1′-benzo[1,2-*b*:4,5-*b*′]dithiophene-2,6-diylbis[1,1,1-trimethylstannane] (**2**) were prepared using published procedures [4].

Poly(3-(5-(benzo[1,2-b:4,5-b’]dithiophen-2-yl)thiophen-2-yl)-2,5-bis(2-octyldodecyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione) P(DPP-BDT) (3):

An oven-dried, magnetic-stirred, 50-mL round-bottom flask (RBF) was charged with a solution of **1** (0.54 g, 0.53 mmol), **2** (0.28 g, 0.53 mmol), and tetrakis(triphenylphosphine) palladium(0) (0.035 g, 0.03 mmol). The mixture was heated at 90°C for 72 h. The dark green solution was cooled down to room temperature. The polymer was precipitated in methanol : H_2O (10:1 v/v) solution. The crude polymer was collected by filtration and then purified by Soxhlet extraction with acetone, hexane, and chloroform, successively. The final product was obtained by precipitation into methanol. The product was then dried under vacuum for 1 day to get the polymer, **3**, as a dark green solid with 82% yield (M_n = 44 kDa, polydispersity (PDI) = 5.1).

^{1}H NMR ($CDCl_3$, 300MHz), δ (ppm): 8.95 (broad, 4H), 7.60 (broad, 4H), 3.92 (broad, 4H), 1.26 (broad, 63H), 0.88 (broad, 15H), Anal. Calcd. for $C_{64}H_{92}N_2O_2S_4$: C, 73.55; H, 8.98; N, 2.60; S, 11.90; found: C, 73.31; H, 8.69; N, 2.80; S, 12.25.

Instrumentation

X-ray diffraction (XRD) measurements were recorded with a Rigaku D/MAX Ultima III using nickel-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) over a range of $2^\circ < 2\theta < 40^\circ$ and X’celerator detector operating at 40 kV and 30 mA. The samples was prepared by drop casting the solution on *n*-octyltrichlorosilane (OTS)-treated silicon wafers.

In order to study absorption behavior, the polymer film was fabricated on quartz substrates as follows. The solution (1 wt%) in chloroform was filtered through an acrodisc syringe filter (Millipore 0.2 μm) and subsequently spin-cast on the quartz glass. The films

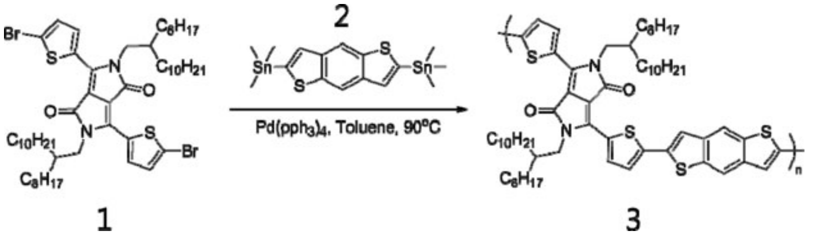

Figure 1. Synthetic procedure for the polymer, P(DPP-BDT) **3**.

were dried overnight at 70°C for 24 hours under vacuum. Absorption spectra of samples in film and solution states (chloroform, conc. 1 × 10^{-5} mole/L) were obtained using a UV-VIS spectrometer (HP 8453, photodiode array type) in the wavelength range of 190-1100 nm.

Fabrication of OTFTs

For the characterization of TFT performance, bottom gate top contact device geometry was employed. On the heavily n-doped Si/SiO_2 substrate the spin-coated films (thickness ~ 40–50 nm) were prepared with chloroform as a solvent. Surface modification was carried out with OTS to make hydrophobic dielectric surface. Source and drain electrodes were then thermally evaporated (100 nm) through shadow mask with the channel width and length of 1500 μm and 100 μm, respectively. We followed the fabrication and measurement methods reported in our previous literature [9].

Results and Discussion

We outlined the synthetic route of new p-type DPP-based semiconducting conjugated polymer, P(DPP-BDT) **3**. (see Figure 1) As a solubilizing group and crystallization promoting moiety, 2-octyldodecyl group was substituted in the *N*-position of DPP unit. Stille coupling reaction of the monomers **1** and **2** yielded the conjugated polymer **3** in a high yield of 82 %. The polymer, **3** shows good solubility in common solvents such as chloroform, dichloromethane, toluene, THF, and chlorobenzene (up to 10 mg mL^{-1}) owing to long alkyl side chains in DPP units..

The number-average molecular weight (M_n) of the polymer was determined gel permeation chromatography (GPC) using a polystyrene standard and found to be 44 kDa ($M_w/M_n = 5.1$).

Figure 2 shows the UV-Vis absorption spectra of the polymer both in solution and in film samples. The absorption maximum wavelength was observed at 730 nm and 751 nm in the solution and film, respectively. The solution spectrum showed a broad absorbance, extending from 500 nm to 900 nm; it is attributed to the $\pi - \pi$ transition as well as intramolecular charge transfer (ICT) between the DPP and BDT moieties [10, 11]. The absorption spectral behaviors indicate that DPP/BDT-containing repeating groups are highly interactive mutually, forming self-assembled molecular domains through strong electronic coupling both in solution and film states. The optical bandgap of P(DPP-BDT) was determined from the absorption onset in the film state, which was 1.36 eV.

Cyclic voltammetry measurement was performed on a thin film to determine the oxidation potential (E_{ox}^{onset}). In a film state, the HOMO level of P(DPP-BDT) was calculated

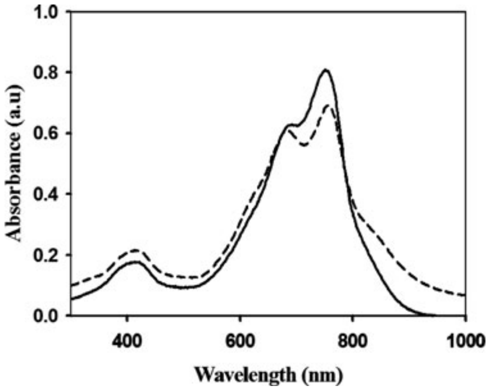

Figure 2. Optical absorption spectra of P(DPP-BDT). *Solid line: solution, Dashed line: film.

from the onset oxidation potential ($E_{ox}^{onset} = 0.94$ V) to be −5.36 eV; the LUMO level was determined to be −4.00 eV by using the optical bandgap ($E_g^{opt} = 1.36$ eV, $\lambda_{cut\text{-}off} =$ 910 nm).

From the XRD patterns presented in Fig. 3, the crystalline nature of P(DPP-BDT) was found to be evident and the variation of the diffraction pattern indicates the formation of well-grown polycrystallites in the spin-coated film on OTS-treated SiO_2/Si substrate. As was shown in the diffractogram of the as-spun film (Fig. 3 (I)) there is a clear diffraction peak arising from the lamella spacing, $d_{(100)}$; when annealing the sample at 120°C∼250°C, we could observe the 2nd-order diffraction peaks. Two highly resolved diffraction peaks were observed at $2\theta = 4.78°$ and 9.31°, which indicates that the polymer chains exhibit well-organized intermolecular lamella stacking, resulting in the enhanced crystallinity with the annealing temperature. The interlayer distance in lamellar crystalline structure of the film was determined to be $d_{(100)}$ ∼18.50 Å, which is well consistent with the spacing reported in the literatures [12, 13].

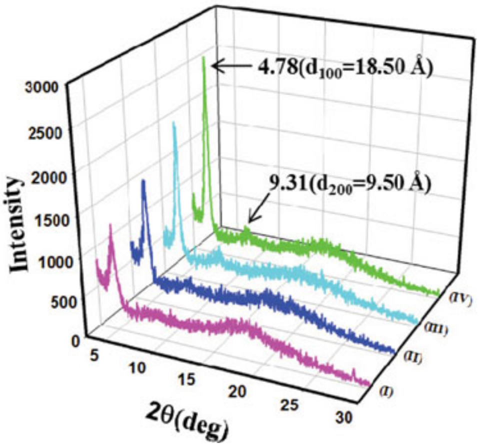

Figure 3. X-ray diffraction (XRD) patterns of P(DPP-BDT). as-spun film (I), thermally annealed films at 120°C (II), 180°C (III), and 250°C (IV).

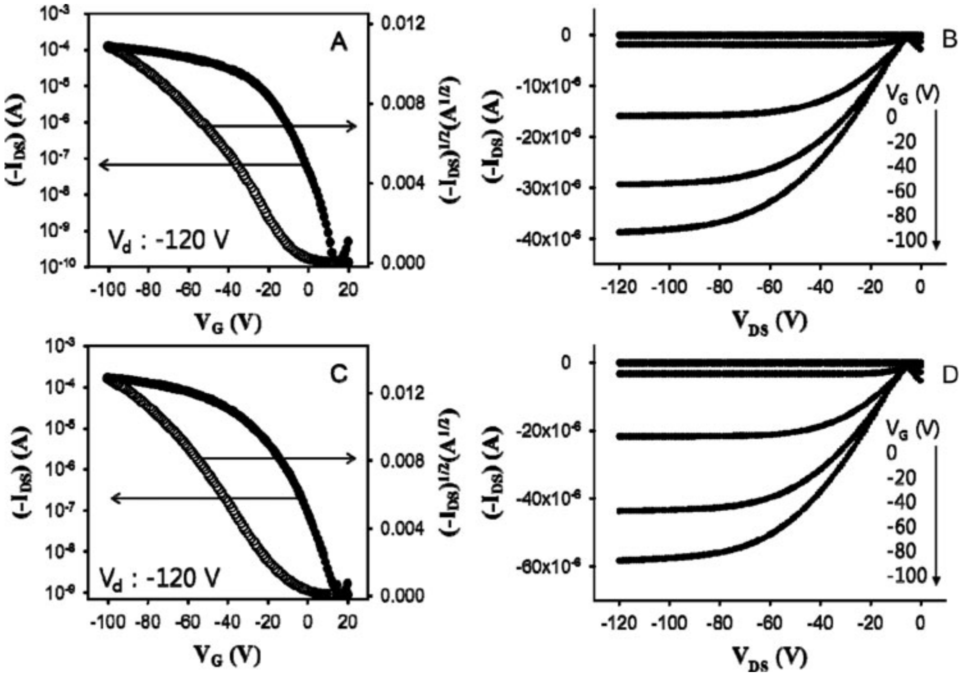

Figure 4. Transfer (A) and output (B) curves of the OTFT device fabricated with pristine P(DPP-BDT) film. Transfer (C) and output (D) curves of the TFT device fabricated with thermally annealed P(DPP-BDT) film (T_{ann}. = 250°C, for 10 min).

In order to investigate the semiconducting properties of P(DPP-BDT), we fabricated OTFT devices and characterize their performances. Top-contact OTFT devices were fabricated using gold source and drain electrodes that were thermally evaporated using the conventional method. A 50–65 nm thin film of the semiconductor was deposited on OTS-SiO_2/Si by spin-coating a 1 wt% solution of the polymer in chloroform. After spin-coating the polymer solution onto the insulator surface, gold was deposited *via* thermal evaporation.

The output characteristics showed very good saturation behaviors and clear saturation currents that were quadratic to the gate bias (see Fig. 4). The saturated field-effect mobilities, μ_{FET} can be calculated from the amplification characteristics, by using the classical equations describing FETs [14, 15].

According to the results shown in Fig. 4, the hole mobility of the pristine film of P(DPP-BDT) was measured to be 0.38~0.40 cm^2 V^{-1} s^{-1} ($I_{\mathrm{on/off}} = 10^6$, $V_{\mathrm{th}} = -9$ V). When annealing the film at 250°C for 10 min., the mobility value was also measured to be 0.38 cm^2 V^{-1} s^{-1} maintaining a high on-off current ratio of 10^5 ($I_{\mathrm{on/off}} = 10^5$, $V_{\mathrm{th}} = -10$ V).

Although the crystallinity was enhanced with the annealing temperature as can be seen in Fig. 3, the device performances between pristine film and thermally annealed film did not show significant difference. In order to verify the reason, AFM was employed to observe the morphologies of the film surfaces before and after thermal annealing.

Figure 5 shows the AFM topographic images of the films made of P(DPP-BDT). They illustrates that the film surfaces displayed to have densely filled chain networks, which can support the favorable charge transport through active channels in TFTs. In particular,

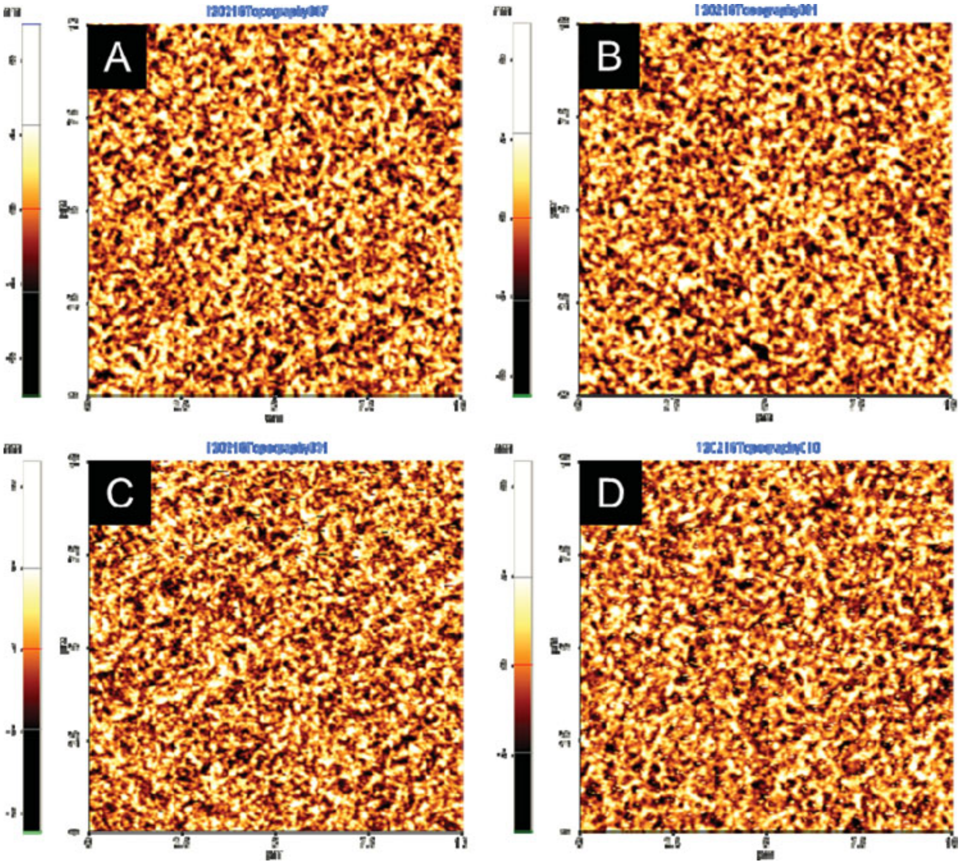

Figure 5. Tapping mode atomic force microscopy (AFM) images of thin films made of P(DPP-BDT). as-spun film (A), annealed film at 120°C (B), 180°C (C), and 250°C (D).

the surface morphology of polymer films did not change significantly even after thermal treatment.

In brief, the network structure of the polycrystallites in film state is one of the crucial factor for governing the charge transport property of an active channel in TFTs. Identity of the surface structure might support the similar charge transport properties of as-spun and thermally annealed films in TFT devices. The relationship between the network structure of film surface and the side chains tethered into DPP unit will be studied further for achieving more enhanced carrier mobility in TFTs.

Conclusions

We have successfully synthesized and characterized new DPP-based conjugated polymer bearing BDT moiety as a p-type semiconducting material. The polymer showed good film forming property and a high degree of crystallinity in the solid state. The thin-film transistor device provided a field effect mobility of 0.38~0.40 $cm^2\ V^{-1}\ s^{-1}$, together with a high current on/off ratio ($>10^5$) and a threshold voltage ($V_{th} = -10$ V). Our study unambiguously demonstrates that DPP-based conjugated polymer with planar BDT moiety can be utilized for fabricating highly efficient OTFT devices even without thermal annealing.

Acknowledgments

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