

Synthesis of n-type semiconducting polymer consisting of benzodipyrrolidone and thieno-[3,4-*c*]-pyrrole-4,6-dione via C-H direct arylation

Zhi An Wang ^a, Junpei Kuwabara ^a, Akito Ichige ^a, Takeshi Yasuda ^b, and Takaki Kanbara ^{a*}

^a Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8573, Japan

^b Research Center for Functional Materials, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

*Corresponding author. Tel.: +81-29-853-5066, fax: +81-29-853-4490,

E-mail address: kanbara@ims.tsukuba.ac.jp

Abstract

Direct arylation polycondensation of 3,7-bis(4-bromophenyl)-1,5-bis(2-octyldodecyl)benzo[1,2-*b*:4,5-*b'*]dipyrrole-2,6(1*H*,5*H*)-dione with 5-(2-ethylhexyl)-thieno-[3,4-*c*]-pyrrole-4,6-dione gave the corresponding benzodipyrrolidone-based conjugated polymer with a molecular weight of 147,000 in 92% yield. The optical and thermal properties of the polymer were evaluated. The polymer showed n-type semiconducting behavior in organic field-effect transistors with an electron mobility of $1.3 \pm 0.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Keywords: Conjugated polymers; benzodipyrrolidone; polycondensation; direct arylation; n-type semiconducting material

1. Introduction

Polycondensation via direct C-H arylation has been recognized as an effective method for the practical synthesis of π -conjugated polymers because the reaction process eliminates the prior preparation of organometallic reagents and the treatment of metal-containing byproducts [1]. Recently, several groups have attempted to utilize this reaction for the synthesis of π -conjugated polymers for use as semiconducting materials for optoelectronic devices such as organic photovoltaic cells (OPVs) [2,3], organic field effect transistors (OFETs) [3,4], and light emitting diodes [5]. Among these π -conjugated polymers, copolymers containing naphthalene diimide serve as n-type semiconducting materials in OFETs [4b,d,e, 6].

In the context of n-type semiconducting polymers, the benzo[1,2-*b*:4,5-*b'*]dipyrrole-2,6(1*H*,5*H*)-dione unit, also known as benzodipyrrolidone (BDP), has attracted attention owing to its excellent electron-accepting property and planar conjugated lactam structure, resulting in a lowered LUMO level and improved thermal stabilities of its π -conjugated polymers [7]. BDP-based polymers thus serve as n-type semiconducting materials and/or as donor-acceptor low bandgap polymers for the fabrication of OFETs and OPVs. Such polymers have been synthesized by the Suzuki-Miyaura and Migita-Kosugi-Stille cross-coupling polycondensation reactions. Owing to the high potential of BDP-based polymers, we have examined direct arylation polycondensation of 3,7-bis(4-bromophenyl)-1,5-bis(2-octyldodecyl)benzo[1,2-*b*:4,5-*b'*]dipyrrole-2,6(1*H*,5*H*)-dione (Br₂-BDP) with 5-(2-ethylhexyl)-thieno-[3, 4*c*]-pyrrole-4,6-dione (TPD). TPD is an appropriate choice of coupling partner for BDP because TPD possesses good reactivity toward direct arylation polycondensation and serves as an electron-accepting unit in the π -conjugated polymers [2a,b, 8]. We herein report the synthesis of a π -conjugated BDP-TPD polymer via direct arylation polycondensation, and also describe the physical properties and semiconducting behavior of the polymer.

2. Experimental

2.1. Materials

p-Phenylenediamine, 4-bromo-DL-mandelic acid, 2-octyldodecanol, Pd(OAc)₂, Cs₂CO₃, pivalic acid (PivOH), tricyclohexylphosphonium tetrafluoroborate (PCy₃-HBF₄), and other chemicals were received from commercial suppliers and used without further purification. Anhydrous toluene was purchased from Kanto chemical and used as a dry solvent. Br₂-BDP [7] and TPD [9] were prepared with references to procedures reported in the literatures.

2.2. General measurements and characterization

NMR spectra were recorded on Bruker AVANCE-600 and AVANCE-400 NMR spectrometers. Gel permeation chromatography (GPC) measurements were carried out using a SHIMADZU prominence GPC system equipped with polystyrene gel columns, using CHCl₃ as an eluent after calibration with polystyrene standards at 40 °C. Ultraviolet visible absorption spectra of the spin coated thin films were recorded on a JASCO V-630 spectrophotometer. The HOMO energy level was estimated by photoelectron yield spectroscopy (PYS) using a Riken Keiki AC-3 spectrometer. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN Elemental Analyzer. X-ray diffraction patterns were recorded at 298 K on a Rigaku model Multi-Flex X-ray diffractometer with a CuK α radiation source. The thermal properties were measured on an EXSTAR TG/DTA6300 instrument.

The surface morphology of the BDP-TPD film was observed using an atomic force microscopy (AFM) (Hitachi High-Tech Science 5100N). Thermogravimetric (TG) analysis was carried out using a Seiko Instruments Inc. TG/DTA7300 systems. All the manipulations for the reactions were carried out under a nitrogen atmosphere using a glove box or standard Schlenk technique.

2.3. Synthesis

A mixture of Pd(OAc)₂ (0.89 mg, 0.0040 mmol), PCy₃·HBF₄ (1.47 mg, 0.0040 mmol), PivOH (6.9 μL, 0.060 mmol), Cs₂CO₃ (130 mg, 0.40 mmol), Br₂-BDP (211 mg, 0.20 mmol), and TPD (53 mg, 0.20 mmol) was stirred in anhydrous toluene (1.0 mL) for 24 h at 100 °C under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into methanol and the precipitate was separated by filtration and washed with an aqueous solution of ethylenediaminetetraacetic acid disodium salt (pH = 8), 0.1 M HCl solution, distilled water, methanol, and hexane. The precipitate was dissolved in CHCl₃ and the solution was filtered through a plug of Celite to remove insoluble material. A reprecipitation from CHCl₃/methanol gave a polymeric product as a purple black solid. The product was purified by Soxhlet extraction with toluene and then finally collected with CHCl₃ to give BDP-TPD polymer in 92% yield. $M_n = 147,000$, $M_w/M_n = 2.65$. ¹H NMR (600 MHz, 353K, C₂D₂Cl₄): δ 8.33 (s, 4H), 7.93 (s, 4H), 6.48 (s, 2H), 3.60 (s, 6H), 1.91 (s, 3H), 1.54 (s, 4H), 1.50-1.20 (m, 72H), 1.05-0.95 (m, 6H), 0.88 (m, 12H). ¹³C{¹H} NMR (100MHz, 353K, C₂D₂Cl₄): δ 162.8, 151.0, 144.6, 144.0, 134.9, 131.4, 129.9, 128.3, 126.2, 120.2, 118.5, 44.2, 37.1, 31.9, 31.7, 30.7, 29.8, 29.5, 29.4, 29.1, 28.6, 26.6, 24.1, 22.9, 22.5, 13.9, 10.5. Anal. Calcd. for C₇₈H₁₁₁N₃O₄S : C, 78.50; H, 9.62; N, 3.61. Found: C, 78.08; H, 9.46; N, 3.68.

2.4. Fabrication and characterization of OFET

To estimate the electron mobility of the polymer, OFETs with a top-contact geometry were fabricated and characterized as follows. A glass/Au gate electrode/Parylene-C insulator substrate was prepared according to the previously reported methods [10]. The BDP-TPD polymer was spin-coated from *o*-dichlorobenzene solution onto the Parylene-C layer and the coated substrate was dried for 10 min at 110 °C in a N₂-filled glove box. Ag (40 nm) source-drain electrodes were thermally evaporated onto the substrates through shadow masks. The channel length and width were fixed at 75 μm and 5 mm, respectively. The OFET measurements were conducted using a Keithley 2636A System Source Meter. In OFETs measurements, five devices were characterized to obtain an average value with the standard deviation. OFETs consisting of glass/Au gate electrode/Parylene-C insulator/BDP-TPD polymer/Au source-drain electrodes were also fabricated for estimating the p-type semiconducting characteristics.

3. Results and discussion

3.1. Synthesis and characterization

The polycondensation of Br₂-BDP with TPD via direct arylation was conducted under the optimal conditions described in a previous report [8f]. The polycondensation reaction afforded the corresponding BDP-TPD polymer with a molecular weight of 147,000 in 92% yield (Scheme 1). Owing to the introduction of long alkyl chains, the obtained polymer exhibits good solubility in CHCl₃, 1,1,2,2-tetrachloroethane, and *o*-dichlorobenzene.

<Scheme 1>

The chemical structure of the BDP-TPD polymer was characterized by NMR spectroscopy and elemental analysis. As shown in Figure 1, each ^1H NMR signal can be assigned to the repeating unit; the integral ratios of the signals agree with the assignments and are consistent with the alternating structure of the polymer. The signal of the terminal C-H moiety of the TPD unit at 7.01 ppm was scarcely observed in the ^1H NMR spectrum because of its high molecular weight, and other minor signals assigned to the structural defects were not observed. All $^{13}\text{C}\{^1\text{H}\}$ signals were also assigned to the carbons in the recurring unit (Figure S1, Supplementary data).

<Figure 1>

3.2. Physical and chemical properties

The UV-vis absorption spectra of the BDP-TPD polymer and the reference polymer (F-TPD, Scheme 2) [8f] are shown in Figure 2. Owing to the presence of the BDP unit, the polymer exhibits absorption in the long wavelength region, with the λ_{max} at 592 nm in the film state. The film-state absorption of the BDP-TPD polymer is in the same range as when in solution, indicating weak π - π stacking interchain interaction due to the steric hindrance of the branched alkyl chains. The absorption onset of the polymer film reaches 704 nm, indicating the optical bandgap ($E_{\text{g}}^{\text{opt}}$) of 1.76 eV. The HOMO energy level of the polymer was determined to be -5.98 eV by photoelectron yield spectroscopy. The LUMO energy level was estimated to be -4.22 eV ($E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}$). The LUMO energy level was considerably lower than that of the F-TPD polymer (-3.64 eV) and in almost the same range as those of the related π -conjugated BDP-based polymers [7]. These results suggest that the steric hindrance between BDP and TPD moieties would be a minor effect.

<Scheme 2>

<Figure 2>

X-ray diffraction analysis of the BDP-TPD polymer film shows no sharp diffraction pattern, which is indicative of an amorphous polymer. The AFM image of the BDP-TPD polymer film shows a flat surface with a root-mean-square (RMS) roughness of 0.67 nm, which is also characteristic of an amorphous polymer (Figures S2 and 3, Supplementary data). The amorphous morphology is likely associated with the presence of the bulky side chains. The TG analysis under an argon atmosphere determined the 5% weight-loss temperature ($T_{\text{d}5}$) of the polymer to be 405 °C (Figure S4, Supplementary data).

3.3. OFET behavior

Since the BDP-TPD polymer has a small $E_{\text{g}}^{\text{opt}}$ and low LUMO levels, the electron carrier mobility of the polymer was evaluated in top-contact OFETs. The results of the measurements are shown in Figure 3. The OFET showed the n-type semiconducting behavior of the polymer with a field effect electron mobility (μ_{e}) of $1.3 \pm 0.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a threshold voltage (V_{th}) of $10.2 \pm 1.4 \text{ V}$, and a current on/off ratio of $2.6 \pm 1.0 \times 10^{-3}$. Since F-TPD did not show n-type semiconducting behavior in similar OFET devices, the introduction of the BDP unit into the

polymer resulted in the n-type semiconducting characteristics. The μ_e value is comparable or somewhat lower than that of previously reported BDP-based polymers [7], presumably due to the presence of bulky side chains. The BDP-TPD polymer did not show p-type semiconducting behavior in OFETs (glass/Au gate electrode/Parylene-C insulator/polymer/Au source-drain electrodes).

<Figure 3>

4. Conclusion

A π -conjugated BDP-TPD polymer could be synthesized by direct arylation polycondensation. Owing to the electron-accepting BDT and TPD units, the obtained polymer served as an n-type semiconducting material. Since direct arylation polycondensation addresses the atom- and step-economical protocols better than conventional synthetic methods, this simple process should provide improved access to various semiconducting materials in organic optoelectronic devices.

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Appendix A. Supplementary data

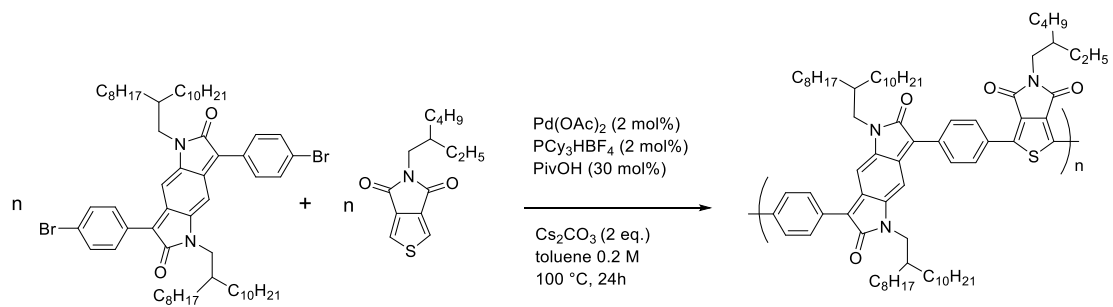
Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.synthmet.2016>.

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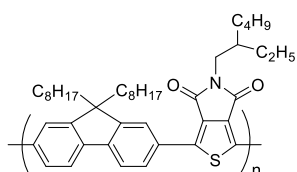
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Scheme 1. Synthesis of BDP-TPD polymer.



Scheme 2. The chemical structure of F-TPD polymer.

Captions of figures

Figure 1. ^1H NMR spectrum of BDP-TPD polymer (600 MHz, 353K, $\text{C}_2\text{D}_2\text{Cl}_4$).

Figure 2. UV-vis absorption spectra of BDP-TPD (solid line) and F-TPD (dash line) polymers (a) in chloroform solution (1×10^{-5} M) and (b) in thin film states.

Figure 3. Typical (a) output and (b) transfer characteristics (measured at drain voltage of 100 V) of the top-contact OFET for BDP-TPD polymer film spin-coated from *o*-DCB solution and annealed for 10 min at 110 °C.

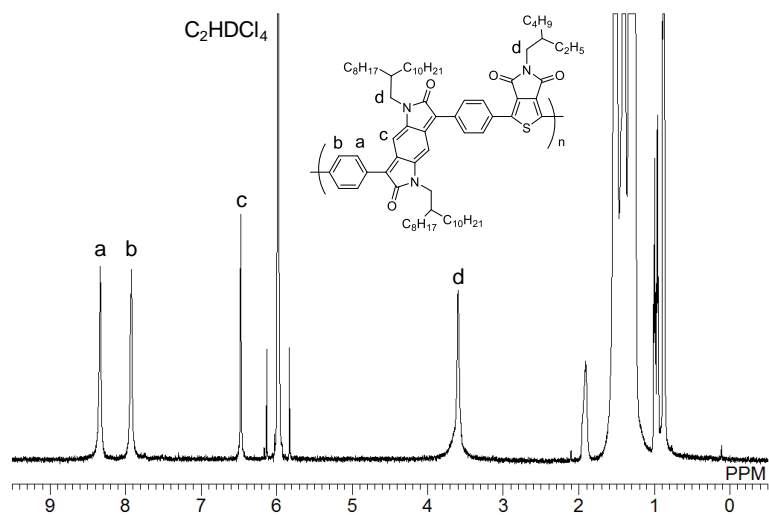


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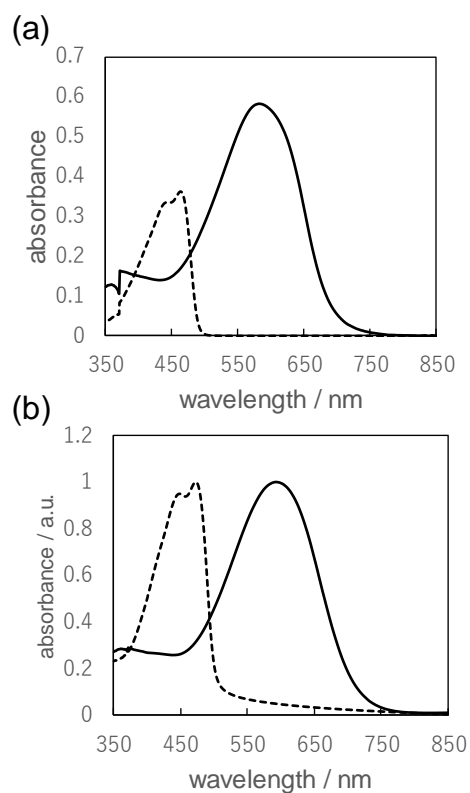


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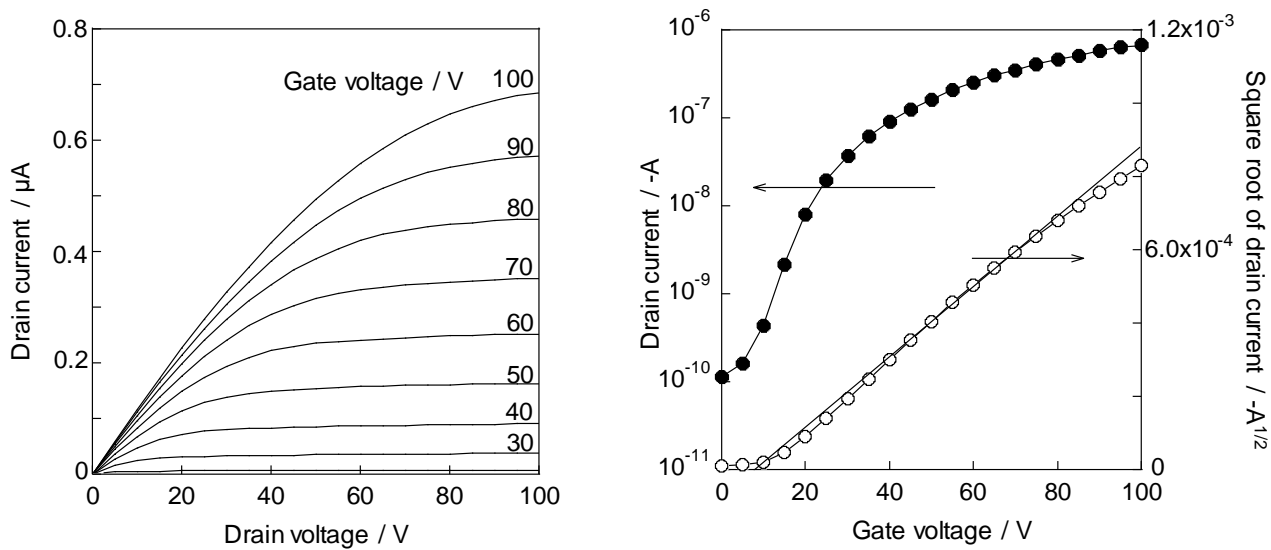


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