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Diketopyrrolopyrrole-Based π-Conjugated Copolymer Containing β-Unsubstituted Quintetthiophene Unit: A Promising Material Exhibiting High Hole-Mobility for Organic Thin-Film Transistors

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Ⓢ *Supporting Information*

ABSTRACT: A new diketopyrrolopyrrole-based π-conjugated copolymer (PDPP5T) with high molecular weight has been synthesized by Stille coupling polymerization of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo-[3,4-c]-pyrrole-1,4(2H,5H)-dione with α,α′-bis(trimethylstannyl)-ter-thiophene. Its hole mobility without thermal annealing reaches 1.08 cm² V⁻¹ s⁻¹, and a higher hole mobility of 3.46 cm² V⁻¹ s⁻¹ is obtained annealed at 200 °C directly in an air atmosphere. This indicates that introducing a longer β-unsubstituted quinquethiophene (5T) unit into the main-chain of DPP-oligothiophene copolymer produces much pronounced p-type behavior and also reduces the steric hindrance of the bulk side-chain groups, which is favorable to enhance the molecular ordering capability at low temperatures and improve the organic thin-film transistors (OTFT) performances. This work demonstrates that PDPP5T is a promising material that can be applied to the cost-effective and large-scale production of OTFTs.

KEYWORDS: *donor−acceptor copolymer, organic thin-film transistors, hole mobility*

PDPP5T (R = 2-octyl-1-dodecyl)
μ max = 3.46 cm² V⁻¹s⁻¹
(Annealing at 200 °C in air atmosphere)
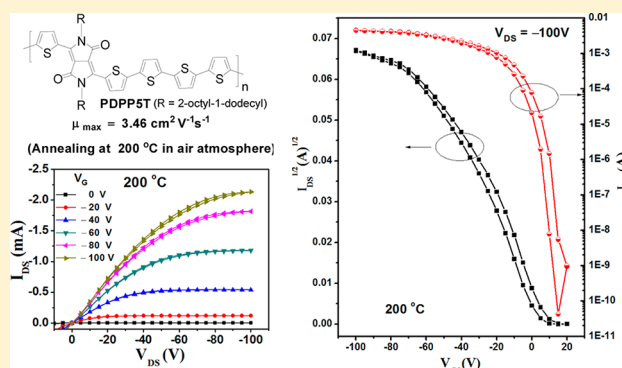
■ INTRODUCTION

Over the past decade, conjugated small organic molecules and main-chain polymers for organic thin-film transistors (OTFTs) have attracted considerable attention due to their easily modification of structure, solution processability, and cheap device fabrication such as printing technique.[1−10] Thanks to the significant efforts of scientists, great achievements for polymer-based OTFTs have been acquired in recent years. Some polymer-based OTFTs show high mobility over 1.0 cm² V⁻¹ s⁻¹.[11−22] It has been found that the introduction of a strong electron-accepting and electron-donating unit into donor−acceptor (D−A) copolymer can greatly enhance the charge transport mobility and efficiently improve the OTFT perform-ances of the devices due to strong donor−acceptor interaction between the nearest neighboring intermolecular overlapping and ordered π−π close packing of the polymer chains.[8,11,19] However, most of these polymers need thermal annealing at high temperature in vacuum or in inert atmosphere to improve the molecular ordered-organization of the polymeric main chain in the thin films. Obviously such inefficient fabricating processes are unfavorable for the large-scale production of OTFT devices at low cost. Therefore, to meet the demand of

the industrial application, design and synthesis of high mobility OTFT polymers without annealing or annealed directly in an air atmosphere is a great challenge.

Recently, diketopyrrolopyrrole (DPP)-based D−A copoly-mers have gained much attention for their promising application in OTFTs.[13−17,21,23−36] The strong electron-deficiency of DPP unit endows the D−A copolymer ambipolar (hole and electron) transport properties and the strong intermolecular interaction.[21,25,28,34,35] For example, some diketopyyrrolopyrrole-oligothiophene copolymer exhibited the excellent hole-transport property with high hole mobility annealing at suitable temperature (PDPP3T, μ = 1.73 cm² V⁻¹ s⁻¹;[34] PDPP4T, μ = 0.97[14] or 1.04[17] cm² V⁻¹ s⁻¹). Compared with the OTFT performances of some diketopyyr-rolopyrrole-oligothiophene coploymers (PDPPNT, N = 2,[32] 3,[24,33−35] and 4[14,17]), the introduction of a longer β-unsubstituted oligothiophene unit (such as 3T and 4T) as the electron-donating unit not only adequately offset the

excessive electron-accepting effect of DPP, but it also slightly weakens the main-chain interaction, which is favorable to enhance the molecular ordering capability of the polymer at lower temperature and efficiently improve the hole mobility of the OTFTs. Thus, it exhibited high mobility of 0.89 cm^2 V^{-1} s^{-1} even without thermal annealing for PDPP4T.[14,17]

In order to further enhance the mobility of the OTFTs and also to better understand the correlation of the molecular structure and OTFT performance, we synthesize a new conjugated main-chain copolymer, diketopyrrolopyrrole-quin-tetthiophene copolymer (PDPP5T) with much high molecular weight and low polydispersity, which contains a DPP group and a β-unsubstituted quintetthiophene (5T) in the repeating unit. We expect that the introduction of more thiophene group into diketopyrrolopyrrole-oligothiophene copolymer can extend the conjugation length of donor blocks and make the p-type behavior of the polymer more pronounced that will lead to the enhancement of the hole mobility of the OTFT device. On the other hand, introducing the 5T unit into DPP-based copolymer can increase the distance of two bulk side-chain groups in the DPP unit and diminish their intermolecular steric hindrance, which is favorable for $\pi-\pi$ stacking to form a well-ordered lamellar structure and enhance the OTFT mobility. As expected, the OTFT performance of the PDPP5T-based devices is greatly improved. The hole mobility reaches 1.08 cm^2 V^{-1} s^{-1} without thermal annealing, and a much higher hole mobility of 3.46 cm^2 V^{-1} s^{-1} is obtained annealed at 200 °C even in an air atmosphere. Here we present the synthesis, photophysical and electrochemical properties, and the OTFT performances of PDPP5T.

■ EXPERIMENTAL SECTION

Materials. All the chemicals are purchased from Aldrich. Toluene was distilled from K−Na alloy under an atmosphere of argon, and other chemicals were used without further purification. 3,6-Bis-(5-bromo-thiophen-2-yl)-N,N′-bis(2-octyldodecyl)-1,4-dixo-pyrrolo[3,4-c]-pyrrole (**1**) and α,α'-bis(trimethylstannyl)-terthiophene (**2**) were synthesized according to previous reports.[13,37]

Synthesis. *Synthesis of PDPP5T.* Compound **1** (158 mg, 0.154 mmol), compound **2** (88.8 mg, 0.154 mmol), and Pd(PPh$_3$)$_4$ (9 mg, 5 mol %) were added into a flask. Then it was subjected to five successive cycle of vacuum followed by refilling with argon, and 10 mL of anhydrous toluene was added via a syringe. The polymerization was carried out at 90 °C for 60 h under the protection of argon atmosphere. Afterward, 0.5 mL of bromobenzene was added to the mixture to react with the residual trimethylstannyl end group. The mixture was kept stirring at 90 °C for 8 h. Then it was cooled to ambient temperature and dropped into methanol. The raw product was filtered off and subjected to subsequently Soxhlet extraction with acetone, methanol, hexane, chloroform, and finally chlorobenzene. The chlorobenzene fraction was collected, concentrated, and precipitated from methanol. The product was collected as dark green solid in a yield of 52%. M_w/M_n (GPC) = 84 600/44 000. Anal. Calcd for C$_{66}$H$_{92}$N$_2$O$_2$S$_5$, C 71.69, H 8.39, N 2.53; found, C 71.87, H 8.43, N 2.45.

Synthesis of PDPP5T-Low. PDPP5T-Low was prepared under the same conditions as above by terminating the polymerization after 48 h. The raw product was filtered off and subsequently subjected to Soxhlet extractions with acetone, methanol, and hexane to remove the impurities and oligomers. Finally, the polymer was obtained by Soxhlet extraction with chloroform. The chloroform fraction was collected, concentrated, and precipitated from methanol. Yield: 89%. M_w/M_n (GPC) = 54 300/27 800. Anal. Calcd for C$_{66}$H$_{92}$N$_2$O$_2$S$_5$, C 71.69, H 8.39, N 2.53; found, C 72.15, H 8.54, N 2.36. ^{1}H NMR (CDCl$_3$, 300 MHz, δ ppm): 8.93 (broad, 4H), 6.92 (broad, 6H), 3.93 (broad, 4H), 1.22 (broad, 63 H), 0.85 (broad, 15 H).

Instrumentation. Elemental analysis of carbon, hydrogen, and nitrogen was performed on a Vario EL III microanalyzer. Molecular weight and distribution of polymer were determined by a gel permeation chromatograph (GPC) method using polystyrene as a standard, which was measured on PL-GPC220 of Polymer Laboratories Ltd. equipped with a IR5 infrared detector using 1,2,4-trichlorobenzene as an eluent at a column temperature of 150 °C (for PDPP5T) or performed on an Agilent 1100 series HPLC system equipped with a G1326A refractive index detector using THF as an eluent at a column temperature of 25 °C (for PDPP5T-Low). Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were, respectively, performed on a NETZSCH STA 449C and a Perkin-Elmer Pyris 1. Absorption spectra were taken on a Shimadzu UV-2500 spectrophotometer. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with a Pt disk coated with the polymer film, a Pt plate, and an Ag/AgCl electrode as the working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) acetonitrile solution under an argon atmosphere at a scan rate of 100 mV/s. The potential of reference electrode was calibrated using the ferrocene/ferrocenium redox couple (Fc/Fc$^+$), which has a known reduction potential of −4.8 eV. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels are calculated by the equations of HOMO = −(E^{ox} + 4.8 eV) and LUMO = −(E^{red} + 4.8 eV), where E^{ox} and E^{red} are the onset potential for oxidation and reduction, respectively. X-ray diffraction patterns of thin films were obtained with a Rigaku-D/max-2500 X-ray diffractometer. Atomic force microscopy (AFM) experiments were performed on a Nanoscope V AFM (Digital Instruments) under ambient conditions.

Fabrication and Characterization of Thin-Film Transistors. Bottom-gate and top-contact TFT test devices with PDPP5T and PDDP5T-Low as the semiconductor were prepared in silicon wafer in ambient conditions without special precautions. The device was fabricated on n$^+$-doped silicon wafer with a 300 nm thermal silicon dioxide. The n$^+$-Si layer was used as the gate electrode, and the silicon oxide layer served as the gate dielectric. The dielectrics have been modified by octadecyltrichloro-silane (OTS). Then, the semiconductor layers were deposited on the top of the OTS-modified SiO$_2$ surface by spin-coating solutions (PDPP5T 2 mg/mL, in o-dichlorobenzene; PDPP5T-Low 10 mg/mL, in chloroform) at 2000 rpm for 60 s at room temperature. These thin films were annealed at 80, 120, 160, and 200 °C in air atmosphere, respectively. Channel length (L) and channel width (W) of the devices were 80 and 8800 μm, respectively. The OTFTs were then characterized using a Keithley 4200 semiconductor characterization system in air. The carrier mobility was calculated according to equation in the saturation regime from the gate sweep:

$$I_{DS} = C_i(W/2L)(V_G - V_T)^2$$

where I_{DS} is the drain current, μ is the carrier mobility, C_i is the capacitance per unit area of the gate dielectric layer, W and L are, respectively, the semiconductor channel width and length, and V_G and V_T are gate voltage and threshold voltage, respectively.

■ RESULTS AND DISCUSSION

Scheme 1 shows the synthetic route of diketopyrrolopyrrole-quintetthiophene copolymer (PDPP5T). The polymer was prepared by Stille coupling polymerization of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo-[3,4-c]-pyrrole-1,4(2H, 5H)-dione (**1**) with α,α'-bis(trimethylstannyl)-terthiophene (**2**) in toluene at 90 °C for 60 h and was purified by precipitation into methanol followed by Soxhlet extraction with acetone, methanol, and hexane to remove small molecular and with chloroform to remove oligomers and even low molecular weight polymer. Finally, the high-molecular-weight sample of PDPP5T was obtained by Soxhlet extraction with chlorobenzene. It shows poor solubility in some common

Scheme 1. Synthetic Route for PDPP5T

PDPP5T
(R = 2-octyl-1-dodecyl)
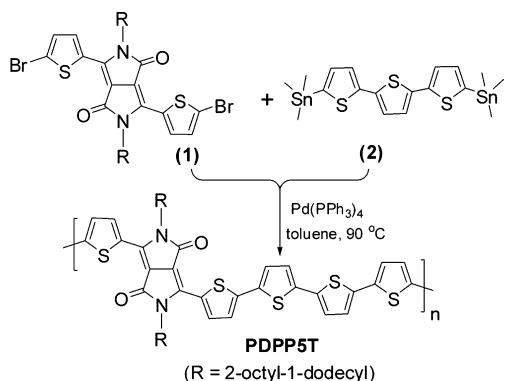
solvents such as tetrahydrofuran (THF), chloroform, and toluene due to high molecular weight. However, at a high temperature it can be soluble in chlorobenzene, dichlorobenzene, and trichlorobenzene, etc. The molecular weight and polydispersity index (PDI) were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. M_n and M_w of PDPP5T were measured at 150 °C using 1,2,4-trichlorobenzene as an eluent to be 44 000 and 84 600 (Figure S1 in the Supporting Information).

Thermal analysis of PDPP5T shows a clear endothermic peak at about 317 °C in the differential scanning calorimetry (DSC) profile during the first heating scan (see Figure S2 in the Supporting Information), which refers to the melting of the polymeric backbone. The melting of the side chains was not observed, which means that the crystallization of the polymeric main-chains is predominant during the molecular packing as compared to the long side chains. In the second heating scan, the appearance of a slightly lower melting temperature is due to partial degradation at high temperature, which is confirmed by the thermogravimetric analysis (TGA) as shown in Figure S3 in the Supporting Information. In addition, the decomposition temperature is over 400 °C, indicating that the polymer shows much high thermostability.

The UV−vis−NIR absorption spectrum of PDPP5T was measured in *o*-dichlorobenzene heated at about 100 °C and in the thin-film as shown in Figure 1. It can be seen that PDPP5T exhibits two well-defined peaks either in *o*-dichlorobenzene or in thin film, which implies that PDPP5T has an ordered structure both in solution and in the film. The optical band gap of PDPP5T is 1.32 eV estimated from the onset absorption
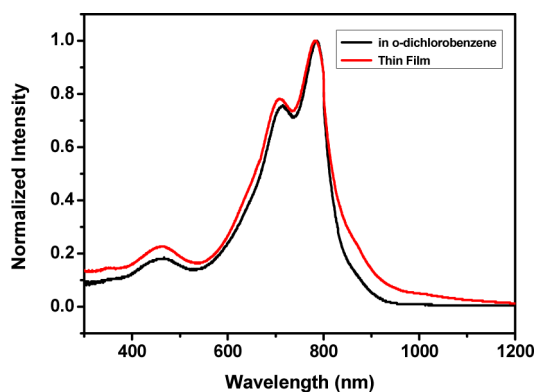

Figure 1. UV−vis−NIR absorption spectra of PDPP5T in *o*-dichlorobenzene and in thin film.

(∼941 nm) of the polymer in thin film, which is slightly larger than that of PDPP4T (1.20 eV).[14] However, the optical band gap is still small, suggesting that the intermolecular interactions are relatively strong in favor of the mobility.

The electrochemical properties of PDPP5T thin film were characterized with cyclic voltammetry (CV) (shown in Figure 2). The HOMO level and the LUMO level of PDPP5T are
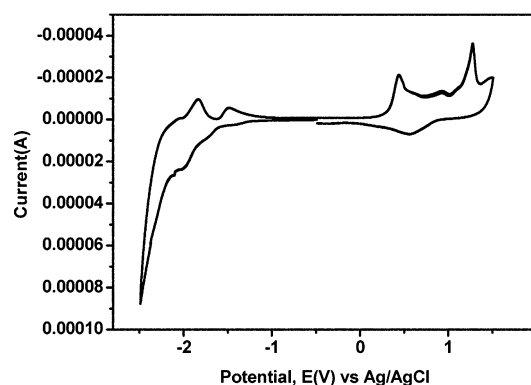

Figure 2. Cyclic voltammogram of a PDPP5T film on a platinum electrode and tested in Bu_4NPF_6/CH_3CN solution (scan rate, 100 mV s^{-1}).

calculated from the onset oxidation potential (∼0.32 V) and the onset reduction potential (∼−1.28 V) to be −5.12 eV and −3.55 eV, respectively. Compared with PDPP4T, the HOMO energy of PDPP5T more closely approaches the gold electrodes (−5.0 eV), which may facilitate charge injection and increase the field-effect hole mobility.[38]

OTFTs (bottom-gate and top-contact) based on PDPP5T have also been investigated in this paper. The thin films of PDPP5T were spin-coated onto octadecyltrichlorosilane (OTS) treated SiO_2 (300 nm)/n^{+2}-Si substrate from a *o*-dichlorobenzene solution and annealed at 80, 120, 160, and 200 °C, respectively, with a hot plate in air atmosphere. The corresponding hole mobility and current on-to-off ratio (I_{on}/I_{off}) at different annealing temperatures are summarized in Table 1.

Table 1. OTFT Properties of As-Spun PDPP5T at Different Annealing Temperatures

annealing T (°C)	μ (cm^2 V^{-1} s^{-1})	$I_{on}/I_{off}{}^a$	V_{th} (V)
25	0.95−1.08	10^5	1−10
80	1.20−1.46	10^5	−2−10
120	1.68−1.98	10^6	3−12
160	2.09−2.31	10^7	2−12
200	2.80−3.46	10^8	−10−5

$^a I_{on}/I_{off}$ refers to the corresponding on-to-off ratio at the maximum hole mobility.

The output and transfer curves of OTFT devices containing PDPP5T thin film without thermal annealing and annealed at 200 °C are illustrated in Figure 3. The hole mobility of PDPP5T-based OTFT device without annealing reaches 1.08 cm^2 V^{-1} s^{-1} ($I_{on}/I_{off} = 10^5$). To the best of our knowledge, it is one of the highest results of reported OTFTs based on polymeric semiconductors without annealing. With a rise of annealing temperature, the hole mobility tends to increase, implying that the crystallinity of the PDPP5T film and ordered
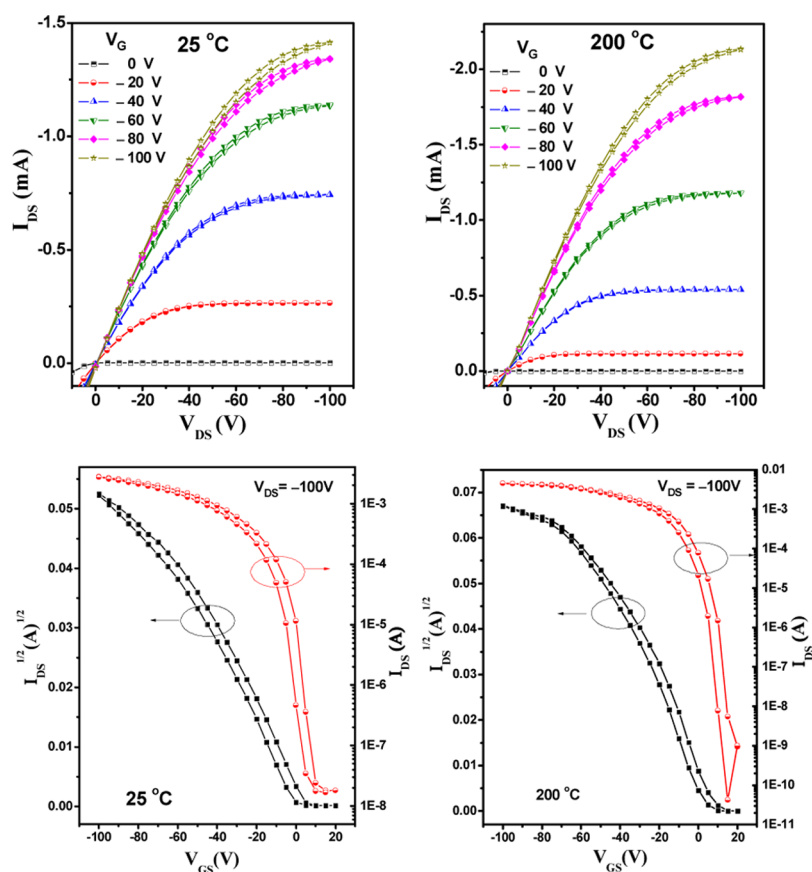
Figure 3. Output and transfer characteristics of OTFTs with a PDPP5T thin film without annealing and with an annealing temperature of 200 °C.

lamellar structure of $\pi-\pi$ close-packing for PDPP5T main-chain are significantly improved at higher temperatures. Especially, with an annealing temperature of 200 °C, a high hole mobility of 3.46 cm^2 V^{-1} s^{-1} ($I_{on}/I_{off} = 10^8$) is acquired. It is worth mentioning that the thin film of PDPP5T was annealed in air atmosphere, and the device of OTFTs were fabricated and tested in ambient air and light without special precautions. So PDPP5T is a promising material that can make the cost-effective and large-scale production of OTFTs into a practical application.

In order to in-depth study the excellent OTFT performances of PDPP5T the thin-film microstructures and topographies were investigated by X-ray diffraction (XRD), grazing incident X-ray diffraction (GIXRD), and AFM. Figure 4 shows XRD patterns of the polymer thin film. Before the sample was annealed, only a distinct diffraction peak at $2\theta = 4.66°$ can be observed, corresponding to a d spacing of 18.95 Å. As the annealing temperature increases from 25 to 200 °C, the XRD pattern at $2\theta = 4.66°$ becomes much stronger and sharper. In addition, another two peaks are also obviously intensified, indicating that more significant crystallization and the better molecular ordering occurs at higher annealing temperature.

To get more exact molecular packing information, the grazing incident X-ray scattering diffraction (GIXRD) was measured on the polymer thin film annealed at 200 °C (Figure 5). Two diffraction peaks (100 and 200) were observed in the out-of-plane GIXRD (Figure 5a), which is almost the same as the above XRD patterns. In the in-plane pattern (Figure 5b), a diffraction peak (010) at $2\theta = 24.3°$ is observed, which can be assigned to the $\pi-\pi$ stacking distance of 3.65 Å in PDPP5T thin film. The distance is smaller than that (3.76 Å) of
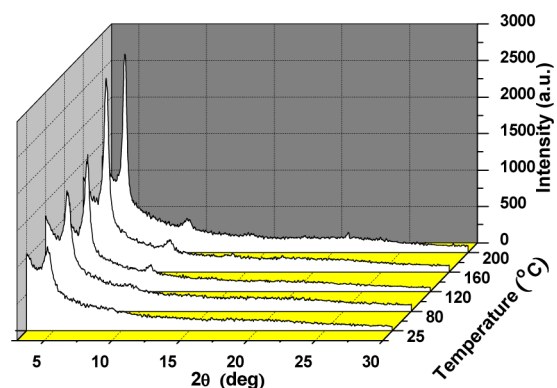

Figure 4. X-ray diffraction (XRD) patterns of a PDPP5T thin film without annealing and annealed at 80, 120, 160, and 200 °C, respectively.

PDPP4T[14] and even smaller than that (3.71 Å) of PDBT-*co*-TT,[13] indicating the occurrence of a more strong interchain $\pi-\pi$ interaction. Since the incorporation of the 5T unit (with more thiophene groups) into the DPP-based copolymer can increase the distance of two bulk side-chain groups in the DPP unit and diminish the interchain steric hindrance, it is more favorable for $\pi-\pi$ stacking to form well-ordered lamellar structure with an edge-on orientation. Thus, it greatly enhances the OTFT mobility.

Figure 6 shows the AFM height images of the PDPP5T thin film without annealing and annealed at 80, 120, 160, and 200 °C, respectively. It can be seen that the as-spun thin film without thermal annealing shows donut-like features, indicating
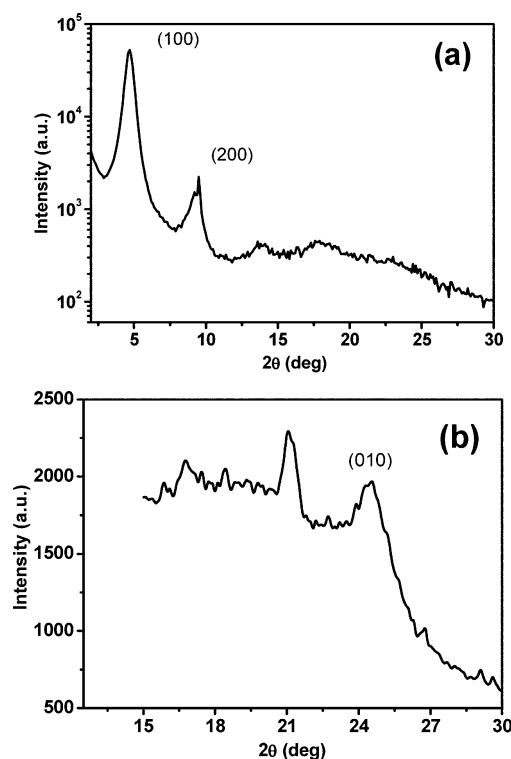
Figure 5. Grazing incident X-ray scattering patterns (out-of-plane, a; in-plane, b) of PDPP5T thin film annealed at 200 °C.

that the polymer chains have self-assembled into circular structures after spin-coating. Such nanostructures lie next to each other that facilitate the establishment of a polymer network and provide efficient charge-carrier transporting pathways. Therefore, the mobility for unannealed PDPP5T thin film reaches 1.08 cm^2 V^{-1} s^{-1}. As the annealing temperature is gradually increased to be 80, 120, 160, and 200 °C, the densely interconnected chain networks is formed and the roughness of thin film reduces, which can facilitate the charge transport.[39] Therefore, the excellent results of OTFT devices are in good accordance with XRD, GIXRD, and AFM images.

To the best of our knowledge, few π-conjugated polymers for OTFTs were obtained by Soxhlet extraction with chloroform to

remove the oligomer and low molecular-weight polymer and finally purified by Soxhlet extraction by chlorobenzene. Since the OTFT performances can be greatly affected by the molecular weight of the polymer,[14] we also synthesized a polymer with low molecular weight (PDPP5T-Low) by shortening the reaction time to 48 h. It was purified by precipitation into methanol followed by Soxhlet extraction with acetone, methanol, hexane to remove the small molecules and oligomers. Finally, the purified polymer was obtained by Soxhlet extraction with chloroform. It shows good solubility in some common solvents such as tetrahydrofuran (THF), chloroform, toluene and chlorobenzene etc. M_n and M_w of PDPP5T-low were determined to be 27 800 and 54 300, respectively, at 25 °C using THF as eluent (Figure S4 in the Supporting Information). The charge-transport properties of PDPP5T-Low were also investigated by fabricating OTFTs with bottom-gate/top-contact devices under similar measured conditions to PDPP5T. The corresponding hole mobility and current on-to-off ratio (I_{on}/I_{off}) of PDPP5T-Low at different annealing temperatures are shown in Figure S5 in the Supporting Information and summarized in Table S1 in the Supporting Information. As can be seen, PDPP5T (the polymer with high molecular weight) shows much better OTFT performances than PDPP5T-Low, suggesting that high molecular weight is much favorable for the formation of ordered packing of the polymeric interchains and can facilitate the establishment of efficient pathways for charge transport.[14,18]

Recently, several researchers reported the OTFT properties of series DPP-oligothiophene copolymers (PDPPNT, N = 2, 3, and 4). For example, DeLongchamp and co-workers[33] explored the relationship between the structure and OTFT performance of DPP-oligothiophene copolymers. In most cases, the hole mobility of PDPPNT (N = 2[32] and N = 3[24,33,34]) with nonannealing is less than 0.20 cm^2 V^{-1} s^{-1}. However, through introduction of one or more thiophene groups into PDPPNT copolymer such as PDPP4T[14,17] and PDPP5T (in this work), the hole mobility without annealing are greatly enhanced reaching to 0.89 cm^2 V^{-1} s^{-1} (PDPP4T) and 1.08 cm^2 V^{-1} s^{-1} (PDPP5T). This indicates that the longer β-unsubstituted oligothiphene unit in PDPPNT copolymer favors to form well-ordered lamellar structure that is very beneficial to the enhancement of the mobility of the OTFTs. Considering the structural characteristics of PDPPNT copolymer, the bulk side-
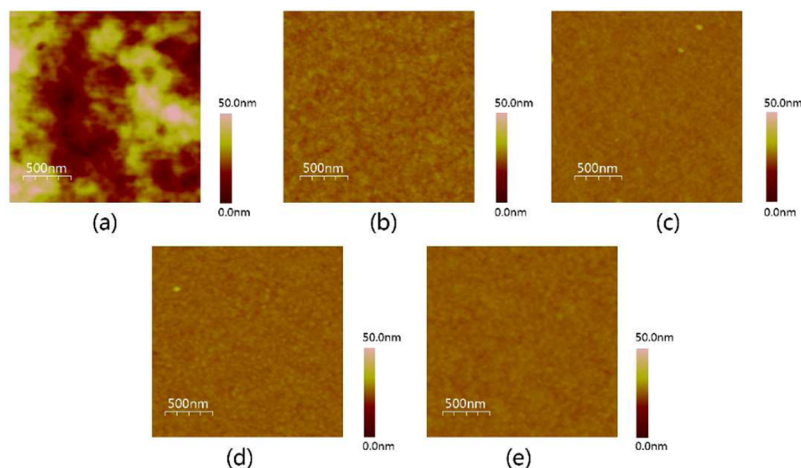

Figure 6. AFM height images of the PDPP5T thin film without annealing (a) and annealed at 80 (b), 120 (c), 160 (d), and 200 °C (e).

chain groups such as 2-octyldodecyl group in DPP unit obviously hinder the development of $\pi-\pi$ stacking for the polymeric main-chains. However, the introduction of more thiophene groups into the PDPPNT main-chain can increase the distance of two bulk side-chain groups in the DPP unit and diminish their steric hindrance. This is favorable to form a well-ordered lamellar structure of $\pi-\pi$ stacking. In addition, as a β-unsubstituted thiophene group in the oligothiophene unit is continually increased, the rigidity of polymeric main-chain of PDPPNT will be strengthened. This is unfavorable to the solubility of the copolymer in organic solvents as well as the solution processablity, which may finally affect the formation of ordered laminar structure of the PDPPNT thin film and impair the OTFTs performance. Therefore, it can be inferred that there should be a suitable long-chain oligothiophene unit for PDPPNT copolymer to adjust the OTFT performance with an optimal result that needs to be further explored in progress.

CONCLUSIONS

An alternating copolymer PDPP5T containing DPP and a quintetthiophene unit has been synthesized and characterized. The introduction of more β-unsubstituted thiophene groups into the main-chain of PDPP5T polymer not only makes the p-type behavior of the polymer more pronounced but also slightly reduces the steric hindrance of the bulk side-chain groups in the DPP unit that favors to construct a well-ordered lamellar structure of $\pi-\pi$ stacking after solution deposition and to strengthen the molecular ordering capability of the polymer at lower temperature, so it exhibits a very high hole-mobility of 1.08 cm^2 V^{-1} s^{-1} without thermal annealing. In addition, the annealing process at high temperature reduces the roughness of the thin film and increases the crystallinity of PDPP5T chains. Thus, its hole-mobility reaches 3.46 cm^2 V^{-1} s^{-1} annealed directly in an air atmosphere, which has been confirmed by the XRD and GIXRD patterns and AFM images.

In brief, PDPP5T is an encouraging OTFT material due to its excellent physical properties and excellent device performances. Easy synthesis and high mobility annealed directly in air atmosphere or even without annealing makes it become a promising material for the cost-effective production of OTFTs in a high-throughput and roll-to-roll manufacturing manner. Further structural modification for PDPPNT copolymer and device optimization for the OTFT performance is very promising and studying is still under way.

ASSOCIATED CONTENT

ⓢ Supporting Information
Additional graphs (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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