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ACS Appl. Mater. Interfaces, **Just Accepted Manuscript** • DOI: 10.1021/acsami.8b01196 • Publication Date (Web): 23 Mar 2018

Downloaded from <http://pubs.acs.org> on April 4, 2018

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Pronounced Side Chain Effects in Triple Bond-Conjugated Polymers Containing Naphthalene Diimides for n-Channel Organic Field-Effect Transistors

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ABSTRACT:

Three triple bond-conjugated naphthalene diimide (NDI) copolymers, poly[[N,N'-bis(2-R₁)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-[(2,5-bis(2-R₂)-1,4-phenylene)bis(ethyn-2,1-diyl)] (PNDIR₁-R₂), were synthesized via Sonogashira coupling polymerization with varying alkyl side chains at the nitrogen-atoms of the imide ring and 2,5-positions of the 1,4-diethynylbenzene moiety. Considering their identical polymer backbone structures, the side chains were found to have a strong influence on the surface morphology/nanostructure, thus playing a critical role in charge-transporting properties of the three NDI-based copolymers. Among the polymers, the one with an octyldodecyl (OD) chain at the nitrogen-atoms of imide ring and hexadecyloxy (HO) chain at the 2,5-positions of 1,4-diethynylbenzene, P(NDIOD-HO), exhibited the highest electron mobility of 0.016 cm²V⁻¹s⁻¹, as compared to NDI-based copolymers with an ethylhexyl (EH) chain at the 2,5-positions of 1,4-diethynylbenzene. The enhanced charge mobility in the P(NDIOD-HO) layers is attributed to the well-aligned nanofiber-like surface morphology and highly ordered packing structure with a dominant edge-on orientation, thus enabling efficient in-plane charge transport. Our results on the molecular structure-charge transport property relationship in these materials may provide an insight into novel design of n-type conjugated polymers for applications in the organic electronics of the future.

KEYWORDS: side chain engineering, triple bond-conjugated, naphthalene diimide, field-effect transistor, chain orientation

1. INTRODUCTION

Impressive progress in development of solution-processable n-type conjugated polymers has been achieved over the past three decades for their potential applications in flexible organic electronics such as field-effect transistors, solar cells, and memory devices.¹⁻⁶ A variety of n-type polymers with high electron mobilities have been reported by introducing electron-deficient moieties such as benzothiadiazole (BT), isoindigo (IID), diketopyrrolopyrrole (DPP), as well as naphthalene diimide and perylene diimide (NDI and PDI).⁷⁻¹⁹ Among those electron-deficient units, in particular, NDI moieties have proved to be the most promising building block due to their high thermal and photochemical stability, low-lying lowest unoccupied molecular orbital (LUMO) energy level, and coplanar structure, leading to strong intermolecular interaction.²⁰⁻²²

Correlations between device performance and structure of NDI-based copolymers have been extensively investigated by incorporating the NDI unit into a series of thiophene-based, selenophene-based, and fluorene-based linkers.^{11, 19, 23-32} In addition, side chain engineering especially at the nitrogen-atoms of the imide ring with linear or branched alkyl chains, hybrid siloxane chains, and semifluoroalkyl side chains, etc., is a key strategy to control their solubilities, nanostructures, and self-assembly capabilities.³³⁻³⁵ Appropriate selections of bridging groups (linkers) and side chains can influence the charge-transporting properties in NDI-based copolymers, and thus device performance. Very recently, the copolymer comprising NDI-bithiophene (T2), demonstrated the remarkable electron mobility of $6.4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with high performance uniformity by employing bar-coating deposition technique and polymer/polymer solar cells consisting of P(NDI2OD-T2) as an electron-acceptor reached a power conversion efficiency of 8.27 %.³⁶⁻³⁷ Moreover, NDI-thienylene-vinylene-thienylene (TVT) with semifluoroalkyl side chains (PNDIF-TVT) exhibited a high electron

mobility of $6.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ because of the side chain-induced strong self-organization.³⁸

Compared to the development of high-performance NDI-based copolymers, NDI-based copolymers with triple bond-linkers have not been investigated in sufficient detail, considering their possible advantages, such as high air stability, long effective conjugation through the polymer chain direction and alleviated steric hindrance.³⁹⁻⁴⁵ Additionally, triple bond-conjugated polymers can be synthesized by Sonogashira coupling, which circumvents issues related to the highly toxic organo-tin compounds required for Stille coupling and in situ degradation of monomers in Suzuki coupling.³⁹⁻⁴⁰

The three NDI-based copolymers with 1,4-diethynylbenzene linkers described herein have been previously reported, but their electron mobility was low ($10^{-4} - 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and their structure-device performance relationship was not fully examined.⁴³ Therefore, we investigated the correlation between the electrical characteristics and nanostructure/surface morphology of the triple bond-conjugated NDI-based copolymers with different alkyl side chains at the nitrogen-atoms of the imide ring and at the 2,5-positions of the 1,4-diethynylbenzene bridging group. The alkyl side chains at the nitrogen-atoms of the imide ring and 2,5-positions of the 1,4-diethynylbenzene linker were found to have a critical impact on the polymer chain ordering as well as surface morphology, leading to the charge transport properties of the resulting transistors.

2. EXPERIMENTAL SECTION

2.1. Synthesis of P(NDIO-EH) Polymer. All chemicals were purchased from Sigma-Aldrich and were used as received without further purification unless stated otherwise. The synthesis of P(NDIO-EH) is described below.

Synthesis of N,N'-bis(octyl)-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide)

(**NDIO**). 2,6-dibromo-1,4,5,8-naphthalenetetracarboxylic acid dianhydride was synthesized according to a literature reported procedure.⁴³ 2.00 g (4.8 mmol) of crude 2,6-dibromo-1,4,5,8-naphthalenetetracarboxylic acid dianhydride was added to 200 mL of glacial acetic acid. The reaction mixture was heated to 130 °C for 1 h under nitrogen atmosphere to give a yellow solution. 2.35 g (19.2 mmol) of N-octylamine was added to the reaction mixture via syringe. The reaction mixture was heated at 130 °C for 1h to yield a dark brown colored solution, and then cooled down to room temperature. The red-brownish solid was filtered and washed with 200 mL of distilled water twice and 500 mL of methanol, and then air-dried. 1.42 g (2.26 mmol, 47% yield) of yellow/salmon-colored solid product was obtained by silica gel column chromatography using dichloromethane as the eluent. ¹H NMR (CDCl₃, 300 MHz), δ (ppm): 9.00 (s, 2H), 4.15 (m, 4H), 2.25 (m, 4H), 1.36 (m, 20H), 0.93 (m, 6H).

Synthesis of poly[[N,N'-bis(2-octyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-[(2,5-bis(2-ethyl-hexyl)-1,4-phenylene)bis(ethyn-2,1-diyl)] (P(NDIO-EH)).

0.38 g (0.586 mmol) of NDIO was added to a Schlenk flask containing a stirring bar. 0.205 g (0.586 mmol) of 1,4-bis(2-ethylhexyl)-2,5-diethynylbenzene (EH) was dissolved in 5 mL of toluene and then added to a Schlenk vessel via syringe under nitrogen atmosphere. Additional 5 mL of anhydrous toluene and 10 mL of diisopropyl amine were added via syringe. 29 mg (0.0410 mmol) of PdCl₂(PPh₃)₂ and 7.8 mg (0.0410 mmol) of copper(I) iodide were added to the reaction mixture. The reaction mixture was pump-filled with nitrogen three times, stirred for 15 min at room temperature, and then heated at 80 °C for 3 d. The reaction mixture was cooled down to room temperature and was added dropwise to 300 mL of methanol, and then the resulting solid was filtered. The blackish solid product was purified by Soxhlet extraction with methanol, acetone, hexane, and chloroform. The chloroform extracts were precipitated into methanol and dried in a vacuum oven. 400 mg (0.462 mmol, 79% yield) of **P(NDIO-**

EH) polymer was obtained. GPC (after Soxhlet) in CHCl_3 : weight-average molecular weight (M_w) = 7.5 kDa; polydispersity index (PDI) = 1.56. ^1H NMR (CDCl_3 , 500 MHz, δ (ppm)): 8.83 (br, 2H), 7.60 (br, 2H), 4.23 (br, 4H), 3.04 (br, 4H), 1.79-0.89 (br, 60H) (see Figure S1).

2.2. Transistor Fabrication and Characterization. P(NDIO-EH) solution was prepared using chloroform and P(NDIOD-EH) and P(NDIOD-HO) solutions were dissolved in chlorobenzene at a solid concentration of 5 mg/mL and were vigorously stirred at 50 °C overnight. P(NDIOD-EH) and P(NDIOD-HO) were used as prepared for the previously reported study.⁴³ The fluoropolymer dielectric, CYTOP, was used as received from Asahi Glass. The glass substrates were cleaned in an ultrasonic bath for 20 min in acetone and isopropyl alcohol, and subsequently dried with nitrogen flow.⁴⁶ Al (~5 nm) and Au (~30 nm) were sequentially thermally evaporated onto glass substrates using shadow masks to form source-drain (S-D) electrodes with 1000 and 30 μm channel width and length, respectively (note that the thin Al layer was used as an adhesion layer between Au and glass substrates).⁴⁷ NDI-based copolymers (~20 nm) were spin-coated at 1500 rpm for 30 s on glass substrates with Al/Au electrodes, and subsequently annealed at 120 °C for 15 min. Next, CYTOP (~900 nm) as gate dielectrics was spun on the NDI-based copolymers at 2000 rpm for 60 s and annealed at 60 °C for 3 h. Aluminum (~60 nm) as gate electrodes were deposited by thermal evaporation using shadow masks.

2.3. Measurements. The film thickness was measured using a Tencor Alpha Step 200 profilometer. UV-visible absorption spectra of the thin films were recorded using a PerkinElmer Lambda 750 UV/Vis/NIR spectrophotometer. The ionization potentials of

polymers were obtained using a Riken-Keiki AC2 photoelectron spectrometer with a UV light source (UV intensity = 10 nW under an anode bias voltage of 3000 V, measurement range: from 3.8 to 6.2 eV by increasing 0.05 eV). The transistor characteristics were measured inside a nitrogen-filled glove box using a 2-channel Agilent B2986 system. The operational stability of devices was obtained in air on a Keithley 4200 SCS and Microtech Cascade probe station. Atomic force microscope (AFM) measurement was performed on a Bruker Nanoscope V Multimode 8 to study the surface morphology of the thin films and a synchrotron-radiation grazing incidence X-ray diffraction (GIXD) measurement (X-ray wavelength (λ)= 1.2435 Å, incidence angle = 0.14°, 3C, SAXS I beamline, Pohang Accelerator Laboratory) was carried out to investigate the nanostructure of thin films.

3. RESULTS AND DISCUSSION

As shown in Figure 1a, a series of triple bond-conjugated NDI-based copolymers, denoted as P(NDIR₁-R₂), was prepared by Sonogashira coupling of N,N'-bis(2-R₁)-naphthalene-1,4,5,8-bis(dicarboximide) and 1,4-bis(2-R₂)-2,5-diethynylbenzene. The differences among the three P(NDI-R₁-R₂) polymers were the alkyl chains (R₁= n-octyl (O) or octyldodecyl (OD)) at the nitrogen-atoms of the imide rings and alkyl chains (R₂= ethylhexyl (EH) or hexadecyloxy (HO)) at the 2,5-positions of the 1,4-diethynylbenzene moiety (see Figure 1b). A systematic study of the electrical characteristics of P(NDI-R₁-R₂) polymers was carried out by fabricating top-gate/bottom-contact transistors (see Figure 1c).

Figure 1

We first investigated the UV-visible absorption spectra of NDI-based copolymers in solid state and solution, which are significantly influenced by the side chains attached to backbone (see Figure 2a and S2a). The NDI-based copolymers exhibited two distinctive absorption bands in the high- (350 – 450 nm) and low-energy (500 – 750 nm) regions, which was equivalent to a π - π^* transition and intramolecular charge transfer (ICT), respectively. Interestingly, despite the identical optical band gaps ($E_g \approx 2.0$ eV) of the P(NDIO-EH) and P(NDIOD-EH) polymer thin films, the P(NDIOD-EH) thin film showed a more distinct ICT peak than the P(NDIO-EH) thin film, which was ascribed to its distinct intermolecular interactions. More importantly, P(NDIOD-HO) thin films exhibited a pronounced absorption in the deep red and/or near-infrared region (< 750 nm), corresponding to an E_g of ~ 1.6 eV. The red-shifted (ca. 100 nm) absorption for the P(NDIOD-HO) thin film can be primarily ascribed to the increased ICT character due to the presence of an electron-rich dialkoxy side chain. We found the marginal change in the absorption spectra of as-spun and annealed thin films, indicative of the chain aggregation during spin-coating (see Figure S2b). As can be seen from Figure 2b, photoelectron yield spectra (PEYS) of the three polymer thin films were obtained to evaluate their highest occupied molecular orbital (HOMO) energy levels. Deep HOMO energy levels of -5.8 eV and -6.1 eV were determined for P(NDIO-EH) and P(NDIOD-EH) thin films, respectively, whereas P(NDIOD-HO) exhibited a lower HOMO energy level of -5.7 eV owing to the presence of electron-donating dialkoxy side chains. Finally, the LUMOs of P(NDIO-EH), P(NDIOD-EH), and P(NDIOD-HO) were obtained as -3.8 , -4.1 , and -4.1 eV, respectively (note that the LUMO energy levels were calculated from the optical band gap energy and the HOMO energy levels). Regarding the charge injection barrier between the Al/Au electrode and HOMO/LUMO energy levels ($\Delta E_{\text{Al/Au-HOMO}} = \text{ca. } 1.0 - 1.4$ eV and $\Delta E_{\text{Al/Au-LUMO}} = \text{ca. } 0.6 - 0.9$ eV), electron injection was more favorable than

hole injection (see Figure 2c). Overall, these results show that the optical and electronic properties are significantly influenced by the side chains at the nitrogen-atoms of the imide rings and 2,5-positions of 1,4-diethynylbenzene; thus, we can expect that the device performance would be influenced by different side chains.

Figure 2

As prepared transistors exhibited n-type behaviour with clear drain-source current - drain voltage (I_D - V_D , output curves) and I_D versus gate voltage (V_G) transfer characteristics (Figure 3a). Importantly, all polymers exhibit minimal operating hysteresis implying the absence of significant electron trapping and/or mobile ion accumulation at the gate insulator/semiconductor interface. Notably, I_D at V_D and V_G of 100 V for P(NDIOD-EH) and P(NDIOD-HO) polymers with octyldodecyl (OD) chains at the nitrogen-atoms of the imide ring was much higher than that for P(NDIO-EH) with an n-octyl (O) chain at the nitrogen-atoms of the imide ring (Figure 3b). In addition, a relatively high threshold voltage (V_{TH}) for the P(NDIO-EH) device (V_{TH} = ca. 42.8 V) was found, whereas the P(NDIOD-EH) and P(NDIOD-HO) devices showed relatively low V_{TH} values of ca. 31.3 and 30.7 V, respectively (Figure S3). The relatively better device performance in terms of V_{TH} and μ_e for the P(NDIOD-EH) and P(NDIOD-HO) polymers, can be ascribed to the relatively low electron injection barrier from the S-D electrodes to the LUMO energy levels of P(NDIOD-EH) and P(NDIOD-HO) as compared to that of P(NDIO-EH) ($\Delta E_{Al/Au-LUMO}$ = ca. 0.6 eV for P(NDIOD-EH) and P(NDIOD-HO) polymers and $\Delta E_{Al/Au-LUMO}$ = ca. 0.9 eV for P(NDIO-EH) polymer). Importantly, the P(NDIOD-HO) transistor exhibited the highest electron mobility (μ_e) of $0.016 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, whereas the P(NDIO-EH) and P(NDIOD-EH) devices showed

relatively low μ_e values of 0.0011 and 0.009 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. However, P(NDIOD-HO) transistors annealed at above 120 °C (150, 180, 210, and 240 °C) showed inferior device performance in terms of V_{TH} and μ_e (Figure S4 and S5) as discussed below. The operational stability for all devices in air ambient condition under constant bias (at V_{D} and $V_{\text{G}} = 60$ V over 600 s) was further investigated (see Figure S6). The normalized I_{D} of the P(NDIOD-HO) devices decayed by 8.3 % from its initial value, while the P(NDIO-EH) and P(NDIOD-EH) devices exhibited 16.6 % and 12.0 % reduction in I_{D} , respectively, reflecting that the charge-carrier trapping in the bulk or at the interface was relatively small for P(NDIOD-HO) transistor.

Figure 3

In order to clarify the effect of side chains on the thin film surface morphology, which may closely relate to the device performance, we carried out atomic force microscopy (AFM) measurements. As shown in Figure 4, the phase-mode AFM image of the P(NDIO-EH) film revealed randomly distributed nanoscale aggregates with considerably coarse domains in height-mode AFM image (root-mean-square roughness (R_{RMS}) = 3.11 nm). Nano-aggregates of the P(NDIO-EH) polymer can be attributed to the presence of linear n-octyl side chain in the NDI moiety, which was also reported for a linear n-octyl side chain on a PDI moiety.⁴⁵ In addition, the low Mw of P(NDIO-EH) could have a strong tendency to aggregate and the resulting grain boundaries between crystalline domains can reduce the charge mobility. Interestingly, on the contrary, a nanofiber-like morphology for P(NDIOD-EH) and P(NDIOD-HO) was presented in the phase-mode AFM images. In addition, relatively smooth surfaces were found in height-mode AFM images for P(NDIOD-EH) and P(NDIOD-HO) thin

films ($R_{\text{RMS}} = 0.93$ nm for P(NDIOD-EH) and $R_{\text{RMS}} = 1.27$ nm for P(NDIOD-HO)). Here it is noteworthy that the diameter and length of 15 ~ 20 nm and 50 ~ 150 nm were estimated as evident from the AFM images. Hence, the relatively better electron transport seen in P(NDIOD-EH) and P(NDIOD-HO), as compared to P(NDIO-EH), can be related to the well-aligned nanofiber-like and smooth surface morphology of the thin films.

Figure 4

The nanostructure of the three NDI-based polymers was investigated using synchrotron GIXD technique in order to account for the impact of the structural changes on the electron transport characteristics in the various materials. As shown in Figure 5a, the (100) Debye ring was clearly observed in the 2D GIXD image of the P(NDIO-EH) layer, implying the presence of randomly oriented crystallites, while noticeable (100), (001), and (010) peaks in the out-of-plane (OOP) direction and a (100) peak in the in-plane (IP) direction were measured for the P(NDIOD-EH) film, indicating the co-existence of edge-on and face-on chain stacking (note that the azimuthal angle (α), $\alpha = 0^\circ$ and $\alpha = \pm 90^\circ$, indicates the OOP and IP directions, respectively). Furthermore, the P(NDIOD-HO) film exhibited more pronounced (100) and (001) peaks in the OOP direction than those in the IP direction. Looking closely at the 1D profiles in Figure 5b, the (100) peak position of the P(NDIOD-EH) polymer thin film was noticeably shifted toward the low scattering vector (q), compared to that of P(NDIO-EH) thin film owing to the different lamellar d-spacing values of 19.04 Å ($q = 0.33$ Å⁻¹) and 22.44 Å ($q = 0.28$ Å⁻¹) for the P(NDIO-EH) and P(NDIOD-EH) polymers, respectively (here we note that q and d are defined as $q = (4\pi/\lambda) \sin(\theta) = 2\pi/d$, respectively, where d and θ are d-spacing and half of the scattering angle, respectively). On the contrary, a prominent (100) peak in the

OOP direction for the P(NDIOD-HO) thin film was observed at $0.21 \text{ \AA}^{-1}$ (d-spacing value = $29.92 \text{ \AA}$), implying a significantly improved crystallinity in the OOP direction. The pronounced edge-on orientation of the P(NDIOD-HO) polymer thin film can be crucial for promoting charge transport in the in-plane direction.

Figure 5 and Table 1

The chain orientation distribution was obtained by extracting the peak intensity versus scattering vector (q) as a function of azimuthal angle (alpha, α) from the corresponding 2D GIXD images. Here we note that the ratio of chain orientation was determined by the ratio of the entire area to the integration area of $\alpha = -15^\circ \sim +15^\circ$ for edge-on chain stacking and $\alpha = -90^\circ \sim -75^\circ$ and $75^\circ \sim 90^\circ$ for face-on chain stacking (Figure 6a and 6b). The P(NDIO-EH) layer showed a mainly random orientation (56.7 %) rather than edge-on and/or face-on chain orientation, whereas the P(NDIOD-EH) thin film exhibited a relatively clear bimodal distribution (edge-on (44.2 %) versus face-on (23.3 %)). However, the P(NDIOD-HO) thin film predominantly exhibited an edge-on orientation (74.6 %), which was close to the unimodal orientation. Here it is noteworthy that the population of edge-on chain orientation for the P(NDIOD-HO) thin film annealed at above 120°C decreased, which is in agreement with the reduction in the field-effect mobility (see Figure S7). Given the GIXD results, the charge transport in triple-bond conjugated NDI copolymers strongly correlated with the coexistence of edge-on and face-on crystallites. As can be seen from Figure 6c, the charge transport in P(NDIO-EH) and P(NDIOD-EH) layers can be highly limited by the randomly oriented nanocrystalline domains; however, the edge-on orientation in P(NDIOD-HO) thin film can facilitate charge transport in the lateral direction.

Figure 6

4. CONCLUSIONS

In conclusion, three triple bond-conjugated n-type polymers by introducing different alkyl side chains at the nitrogen-atoms of the imide rings and 2,5-positions of 1,4-diethynylbenzene via Sonogashira coupling polymerization were synthesized. Distinct changes in the optical absorption of the three copolymers in the solid state were observed. A more pronounced ICT peak for the P(NDIOD-EH) thin film than for the P(NDIO-EH) layer was observed and the optical absorption spectrum of the P(NDIOD-HO) thin film was significantly shifted towards the deep red and/or near-infrared region as compared to P(NDIO-EH) and P(NDIOD-EH) thin films because of the pronounced ICT between the electron-deficient NDI unit and electron-rich hexadecyloxy side chain. When employed as the charge-transporting materials in thin-film transistors, all polymers showed typical electron transporting characteristics due to suitable charge injection from the S-D electrodes to the LUMO energy level of all polymers. In particular, P(NDIOD-HO) transistors exhibited a higher electron mobility value ($0.016 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) than those measured for P(NDIO-EH) and P(NDIOD-EH) polymer-based devices, indicating that the side chain on the polymer backbone has a significant influence on the charge transport. The latter observation was attributed to the different surface morphology/nanostructure of the resulting polymer thin films. Specifically, the nano-aggregated surface and randomly oriented nanocrystalline domains observed for the P(NDIO-EH) layers most likely limits charge transport. This is not the case for the P(NDIOD-EH) and P(NDIOD-HO) layers both of which exhibited well-aligned nanofiber-like surface morphologies with relatively smooth surfaces. More

importantly, a coexistence of edge-on and face-on chain stacking (bimodal orientation) was identified in the P(NDIOD-EH) layer with the P(NDIOD-HO) layers exhibiting a dominant edge-on orientation close to the unimodal orientation, thus facilitating the charge transport in the in-plane direction. Hence, it is evident that the side chains at the imide rings and the triple-bond linkers influences the thin film nanostructure as well as the optoelectronic properties, and surface morphology, thus governing the charge transport. Further enhancement of charge carrier mobility can be expected when different side chains are introduced into triple bond-conjugated polymers.

■ ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at <http://pubs.acs.org>. ^1H NMR spectrum, UV-visible absorption spectra for solutions and thin films, $I_D^{0.5}$ vs V_G curves, transistor characteristics of P(NDIOD-HO) devices annealed at above 120 °C, operational stability, and GIXD data for P(NDIOD-HO) thin films according to the annealing temperature.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENT

This work was financially supported by grants from the Korean Government (NRF_2016H1D5A1910319, NRF_2017M2A2A4A01071010, NRF_2015R1A2A2A01003743, Basic Science Research Program_2009-0093819).

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Figure 1. (a) Synthesis of P(NDI-R1-R2) polymers via Sonogashira coupling reaction. (b) Chemical structure of triple bond-conjugated NDI-based copolymers. (c) Device structure of top gate/bottom contact field-effect transistors with P(NDIR1-R2) polymers, chemical structure for gate-insulating polymer, CYTOP and film images for each polymer.

Figure 2. (a) Normalized optical density (O.D.) and (b) photoelectron yield spectra (PEYS) of triple bond-conjugated NDI-based copolymers films coated on quartz and ITO-glass substrates, respectively. (c) Flat energy band diagram for field-effect transistors with three NDI-based copolymers.

Figure 3. (a) Output and transfer curves for field-effect transistors based on three NDI-based copolymers and (b) representative output (at $V_G=100$ V) and transfer curves (at $V_D= 100$ V) for transistors based on three NDI-based copolymers.

Figure 4. Phase-mode (left) and 3D height-mode (right) AFM images ($1\ \mu\text{m} \times 1\ \mu\text{m}$): (a) P(NDIO-EH), (b) P(NDIOD-EH), and (c) P(NDIOD-HO) thin film. Note that the nano-aggregates and nanofiber-like parts are marked with circles and arrows, respectively.

Figure 5. (a) 2D GIXD images and (b) 1D profiles for P(NDIO-EH), P(NDIOD-EH), and P(NDIOD-HO) thin films annealed at 120 °C coated on silicon substrate. The main diffraction peaks for each polymer are marked inside the 2D GIXD images and 1D profiles.

Figure 6. (a) Intensity for (100) peak of each polymer as a function of azimuthal angle (α). (b) Ratio for face-on, edge-on, and other orientations (note that the ratio of chain orientation was determined by the ratio of the entire area to the integration area of $\alpha = -15^\circ \sim 15^\circ$ for edge-on chain stacking, $\alpha = -90^\circ \sim -75^\circ$ and $75^\circ \sim 90^\circ$ for face-on chain stacking, and $\alpha = -90^\circ \sim -75^\circ$ and $75^\circ \sim 90^\circ$ for other chain stacking). (c) Illustration of charge transport in random orientation (top) and edge-on orientation (bottom).

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Table 1. Summary of weight-average molecular weight (Mw), polydispersity index (PDI), energy levels, device performance parameters, and d-spacing values for the three NDI-based copolymers.

Material	Mw (kDa)	PDI	HOMO (eV)	LUMO (eV)	Eg (eV)	μ_e (cm ² V ⁻¹ s ⁻¹)	V _{TH} (V)	I _{D,ON/OFF}	d-spacing (alkyl- alkyl) (Å)	d-spacing (π - π) (Å)
P(NDIO-EH)	7.5	1.56	-5.8	-3.8	2.0	0.0011	42.8	2300	19.04	4.19
P(NDIOD-EH)	56.7	2.56	-6.1	-4.1	2.0	0.0092	31.3	38000	22.44	4.05
P(NDIOD-HO)	117	1.84	-5.7	-4.0	1.7	0.016	30.7	41000	29.92	3.81

<TOC Graphic>