A Role of Side-Chain Regiochemistry of Thienylene–Vinylene–Thienylene (TVT) in the Transistor Performance of Isomeric Polymers

So-Huei Kang, ‡ Hae Rang Lee, ‡ Gitish K. Dutta, † Junghoon Lee, † Joon Hak Oh, ‡ and Changduk Yang ‡

†Department of Energy Engineering, School of Energy and Chemical Engineering, Perovtronics Research Center, Low Dimensional Carbon Materials Center, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulju-gun, Ulsan 44919, South Korea
‡Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), 77 Cheongam-ro, Pohang, Gyeongbuk 37673, South Korea

ABSTRACT: The π-extended \((E)-2-(2-((\text{thiophen}-2-\text{yl})-\text{vinyl})\text{thiophene})\) (TVT)-based polymers are an interesting class of semiconducting polymers because of their excellent mobilities and unique film microstructures. Despite these properties, the effect of the side-chain regiochemistry of TVT skeletons on the intrinsic properties of these polymers remains unclear. To investigate this, in this study, hexyl-substituted TVT subunits with a “tail in (TI)” or “tail out (TO)” regiosymmetrical arrangement were first introduced into diketo-pyrrolopyrrole (DPP)-based copolymer main chains to afford “isomeric” polymers PI and PO, respectively. By combining optical spectroscopy, atomic force microscopy (AFM), and grazing incidence X-ray diffraction (GIXD) data, we quantitatively characterized the aggregation, crystallization, and backbone orientation of both polymer films, which were then correlated to the charge-carrier mobilities. The PI film exhibited a bimodal packing motif comprising a mixture of edge-on and face-on orientations, which was beneficial for three-dimensional (3D) charge transport and resulted in a hole mobility 2-fold larger than that in the PO film \((\mu_h = 1.69 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\). This comparative study substantiates the important role of the regiochemistry of TVT in developing high-performance semiconducting polymers.

INTRODUCTION

Organic field-effect transistors (OFETs) based on π-conjugated polymers have attracted substantial scientific interest in the quest for “plastic electronics” such as flexible and low-cost E-papers, smart cards, radio-frequency identification tags, and displays. In the past decade, extensive studies in materials design have boosted the OFET mobilities, exceeding those of amorphous silicon. It has long been believed that an outstanding OFET performance originates from highly ordered structures with optimally oriented and π-stacked domains. A π-extended \((E)-2-(2-((\text{thiophen}-2-\text{yl})-\text{vinyl})\text{thiophene})\) (TVT) moiety has proven to be a promising building block for facilitating significant long-range ordered structures into the polymer backbone because of the rotational freedom between consecutive thiophenes and the strong π−π interactions exerted by the thiophene units. Currently, several TVT-based semiconducting polymers optimized for either p-channel or n-channel OFET operation exhibit the highest charge-carrier mobilities reported to date. The representative materials in this category include donor–acceptor copolymers, incorporating diketo-pyrrolopyrrole (DPP)–TVT, isoindigo (IIG)–TVT, or naphthalene diimide (NDI)–TVT moieties.

On the other hand, several recent studies have indicated that a change of side chains (e.g., tuning the chain length and type, polarity, and branching point) on the polymer backbones has a significant impact on molecular packing and thin-film morphology and therefore on the device performance. Despite these various advances in side-chain engineering, no attention has yet been given to the effects of side-chain regiochemistry for TVT-based frameworks. It should be of great interest to determine whether the side-chain regiochemistry in TVT-based polymers has a strong influence on the physical, morphological, and electronic properties, as has been observed in regioregular poly(3-hexylthiophene) (rr-P3HT), often referred to as the fruit fly of semiconducting polymers.

Received: November 12, 2016
Revised: January 6, 2017
Published: January 24, 2017
To this end, we designed hexyl-substituted TVT subunits with a “tail in (TI)” or “tail out (TO)” regiosymmetrical arrangement, wherein TI and TO refer to the hexyl chain configuration on the thiophene moieties relative to the vinylene linkages, as shown in Figure 1. We chose DPP with siloxane side chains as a counterpart comonomer because of its successful utilization in conjugated polymers as well as excellent charge-carrier mobility and ambient stability, as demonstrated by our previous studies.5,30,31 In this study, two new TVT-based “isomeric” polymers, PI and PO, were synthesized via copolymerization of each hexyl-substituted TVT monomeric unit with DPP. A comparison of the properties of the two PI and PO copolymers allows us to systematically investigate the influence of TVT regiochemistry on relevant optical and electrochemical properties, molecular ordering and orientation, and macroscopic charge-carrier transport characteristics.

Notably, we found that the relative crystallinity of the lamellar packing and the crystallite orientation distribution can be greatly affected by the regiochemistry of the TVT blocks along the polymer backbones, thereby resulting in a marked effect on OFET performances. For example, the solution-processed OFETs of PI show a high hole mobility of up to 1.69 cm² V⁻¹ s⁻¹, which is approximately twice that of PO under the optimized conditions. Our systematic study demonstrates that this distinct difference in hole mobility originates from the large difference in their intergranular connectivity and molecular packing motifs, which highlights the importance of the side-chain regiochemistry in TVT-based polymers.

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthetic routes of all intermediates and TVT-based polymers (PI and PO) are shown in Figure 1. First, the compounds 2-formyl-3-hexylthiophene (1) and 2-formyl-4-hexylthiophene (4) were synthesized using different formylation methods to obtain position selectivity according to the procedure reported in the literature.32,33 A McMurry-type reduction coupling was performed using the respective aldehydes and a low-valent titanium reagent (TiCl₄/Zn) to afford the key intermediates (E)-1,2-bis(3-hexylthiophen-2-yl)ethene (2) and (E)-1,2-bis(4-hexylthiophen-2-yl)ethene (5), respectively. Finally, each TVT-based compound was converted into the corresponding bis-stannylated monomer (3 and 6) via lithiation and subsequent treatment with trimethyl tin chloride. The palladium-catalyzed Stille copolymerization of monomers 3 and 6 with a dibrominated monomer, 3,6-di(2-bromothen-5-yl)-2,5-bis[6-(1,1,3,5,5,5,7-heptamethyltrisiloxan-3-yl)butyl]pyrrolo[3,4-c]-pyrrole-1,4-dione, afforded the target copolymers PI and PO.
respectively. Both the copolymers are readily soluble in common organic solvents, including chloroform, chlorobenzene, and dichlorobenzene, at room temperature. The synthetic details and complete characterizations of these copolymers are provided in the Experimental Section of the Supporting Information. The number-average molecular weights (\(M_n\)) of PI and PO were determined to be 10.3 and 10.1 kDa, with polydispersity indices (PDI) of 3.76 and 2.54, respectively, as estimated via a high-temperature gel permeation chromatography (HT-GPC) at 120 °C with 1,2,4-trichlorobenzene as an eluent. The calculated degree of polymerization for both polymers was approximately 8. Note that the similar \(M_n\) and PDI values can minimize possible interference from \(M_n\) and PDI variations.

Theoretical Calculations and Optical and Electrochemical Properties. To predict the polymer structural conformations and \(\pi\)-electronic structures, a density functional theory (DFT) calculation for the dimeric units of PI and PO was performed using a Gaussian B3LYP/6-31G base with the Gaussian 09 program. The estimated frontier molecular orbitals and the optimized geometry of the dimers are shown in Figure 2. For both copolymers, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were well-delocalized over the polymer backbones, and the calculated HOMO and LUMO levels of each isomeric dimer were \(-4.59\) and \(-2.85\) eV for PI and \(-4.54\) and \(-2.86\) eV for PO, respectively.

Another interesting feature in the side view of the structures is that the backbone coplanarity correlates with the regiopositioning of the side chains in the TVT subunit (Figure 3). For example, the intratorsion angles (\(\theta_1\)) between two thiophene units within the TVT subunits for PI and PO are 23.3° and 1.0°, respectively, and both the structures exhibit similar intermonomeric torsion angles (\(\theta_2\)) between the DPP and TVT blocks. Additionally, the neighboring oligothiophene rings within the PI backbone cross toward the left and right of each other, whereas for PO, they are mutually twisted in the same direction, thereby implying a certain coil-like polymer conformation. In addition, using the DFT calculation, we also obtained the energy levels and molecular geometry of the dimer of the unsubstituted parent polymer consisting of DPP and unsubstituted TVT. As shown in Figures S7 and S8, the unsubstituted parent polymer showed deeper-lying HOMO/LUMO levels with better planar conjugated backbone compared to both the substituted copolymers.

Figure 4 shows the optical absorption spectra and cyclic voltammograms of PI and PO, and the relevant data are summarized in Table 1. Both the copolymers present dual-absorption bands covering the whole visible to near-infrared range; a less intense \(\pi\rightarrow\pi^*\) band was observed in the shorter-wavelength region, and a strong intramolecular charge-transfer (ICT) band was observed in the longer-wavelength region.

The absorption profiles of PI were red-shifted in both solution and the solid state relative to those of PO; this in turn resulted in a smaller optical band gap (\(E_g^{opt}\)) being estimated from the absorption onset in PI films (1.30 eV) in comparison to PO (1.37 eV). Nevertheless, upon going from solution to the solid state, the main absorption peak of PI was slightly blue-shifted, whereas for PO, a large red-shift occurred toward longer wavelengths, together with pronounced vibronic shoulders at approximately 802 nm. We propose that this behavior involves different types of aggregates that are formed by these two different regiosymmetrical copolymers. For example, the PI film adopts a cofacial structure with H-aggregation, whereas in the PO film, an end-to-end formation leads to J-aggregation. This implies that PI is favorable for

Figure 2. Optimized geometries of the dimers by DFT calculation and the charge density isosurfaces for HOMO and LUMO levels.

Figure 3. Side views of the optimized geometries of the dimers.
interchain interactions, while PO predominantly involves intrachain interactions. Additionally, considering the fact that the ratio of the intensity of the 0–0 vibrational transition relative to the 0–1 transition increases as a result of a decrease in the Coulombic coupling, this can also support the theory that PI has stronger interchain coupling than PO.

The HOMO and LUMO energy levels were determined via cyclic voltammetry (CV) (Figure 4b). It can be clearly observed that PI shows deeper-lying HOMO and LUMO levels than PO (\(E_{\text{HOMO}}/E_{\text{LUMO}} = -5.2/-3.5\) and \(-5.1/-3.3\) for PI and PO, respectively); the same trend was observed in the computational study mentioned above. This indicates that a conformational change in the alkyl side chains in TVT has a strong effect on the energy levels of the resulting polymers, as indicated by previous observations of rr-P3HT chemistry.

Thin-Film Microstructural Analyses. The effects of side-chain regiochemistry on the microstructure of TVT-based isometric copolymer films were investigated using tapping-mode atomic force microscopy (AFM) and grazing incidence X-ray diffraction (GIXD) analyses. The copolymer films were drop-cast from a 3 mg mL\(^{-1}\) solution onto an \(n\)-octadecyltrimethoxysilane (OTS)-modified substrate. Figure 5 shows the representative AFM images of solution-processed copolymer films. Both the films exhibited small granular structures without thermal treatment. A relatively low surface roughness of \(\sim 1.3\) nm was obtained for PI, whereas PO exhibited a considerably agglomerated surface with a high roughness of \(\sim 4.9\) nm. After thermal annealing at 220 °C, the PI film exhibited highly developed fibrillar networks with an average thickness of 63 nm resulting from the reorganization of polymeric chains, which would be beneficial for efficient charge transport in OFETs. However, the PO film lacked the interconnected nanofibrillar networks and still exhibited high roughness, with a significant height difference of at least 20 nm after thermal treatment. This result implies a difficulty in charge-carrier transport resulting from poor intergranular connectivity in FO. As predicted from the DFT calculation results, these significant crystalline morphological differences can be attributed to the significantly disturbed intermolecular interactions caused by the distortion along the backbone of PO; the thermal energy required to change the molecular arrangement in this case will be much higher than that required in the case of PI. Furthermore, the large discrepancy in the surface energies (\(\sim 10.3\) mJ m\(^{-2}\)) of the PO polymer film and the OTS-modified substrate might result in the formation of structures more agglomerated than that between the PI polymer film and its OTS-modified substrate (\(\sim 7.6\) mJ m\(^{-2}\), Table S1).

The optimal two-dimensional (2D) GIXD images and the corresponding diffractogram profiles of the PI and PO films are shown in Figure 6 (see Figure S9 for as-cast films). PI exhibited highly ordered (h00) Bragg peaks in both in-plane and out-of-plane directions, whereas PO exhibited peaks only in the \(q_x\) direction. In both the as-cast and annealed films, the PI films showed shorter lamellar layer distances than the PO films (see Table S2) presumably because of the better \(\pi\)-backbone planarity of PI, which would facilitate well-ordered lamellar stacking. The enhanced lamellar stacking behavior can be estimated from the smaller crystalline distortion parameter value, a criterion of stacking orderliness: 3.55% for PI and 3.92% for PO, as shown in Figure S10. Note that PI exhibited a strong \(\pi-\pi\) interaction in the out-of-plane direction, indicated by an outstanding peak at \(q_z \sim 1.7\) Å\(^{-1}\). This fact can be combined with the bimodal crystalline nature of PI to validate the adoption of a three-dimensional (3D) charge conduction channel with enhanced charge transport in PI films. In contrast, PO did not exhibit a discernible (010) peak in the out-of-plane direction and only showed a (010) peak in the in-plane direction, thereby indicating the formation of a conduction pathway only through the in-plane direction (2D charge transport). Our morphological study revealed that PI polymer films with beneficial granular microstructures and bimodal molecular packing have more favorable microstructures for charge transport than PO polymer films.

Electrical Characterization and the Performance of OFETs. The electrical performance of bottom-gate/top-contact OFETs was measured to elucidate the impact of side-chain regiochemistry on charge-transport properties. The experimental details of device fabrication and measurements are described in the Experimental Section of the Supporting Information. The optimal post-treatment conditions were determined by...
testing the electrical performance of OFETs based on as-prepared films and those annealed at various temperatures (Figure S11 and Table S3). Interestingly, both copolymers exhibited unipolar $p$-type field-effect behavior because the HOMO levels of both polymers are relatively well-matched to the work function (~5.1 eV) of Au electrodes. As-cast PI and

Figure 5. AFM height (top) and phase (bottom) images of drop-cast (a, b) PI and (c, d) PO films (a, c) before and (b, d) after thermal treatment. The scale bar is 500 nm.

Figure 6. 2D-GIXD images of drop-cast (a) PI and (b) PO films after thermal treatment at 220 °C. The corresponding 1D-GIXD profiles of (c) in-plane and (d) out-of-plane GIXD patterns. Pole figures for (e, f) lamellar and (g, h) $\pi-\pi$ stacking of (e, g) PI and (f, h) PO (where $\chi$ is defined as the semicircular angle between the crystallite orientation and the surface normal).

Figure 7. $I-V$ characteristics of the optimized FETs obtained from drop-cast thin films of (a, b) PI and (c, d) PO. (a, c) Transfer curves obtained at hole-enhancement operation with $V_{DS} = -100$ V and (b, d) output characteristics ($L = 50 \mu m$ and $W = 1000 \mu m$).
PO films exhibited maximum hole mobilities ($\mu_{h,max}$) of 1.28 and 0.46 cm$^2$ V$^{-1}$ s$^{-1}$, respectively. As the annealing temperature increased, the charge-carrier mobilities increased and reached the maximum values of 1.69 cm$^2$ V$^{-1}$ s$^{-1}$ for PI and 0.90 cm$^2$ V$^{-1}$ s$^{-1}$ for PO at an optimized annealing temperature of 220 °C. The corresponding transfer and output characteristics under the optimized conditions are depicted in Figure 7. The enhanced charge transport in PI with a tail-in-side-chain conformation can be attributed to the well-delocalized HOMOs and LUMOs along the relatively planar conjugated backbone and the effective intermolecular interaction with strong interchain coupling. Moreover, compared with the PO film, which had a poor intergranular connectivity and unimodal molecular packing, the PI film exhibited highly interconnected fibrillar networks and bimodal molecular packing that could form 3D charge-conduction channels; this also accounts for the facilitated charge transport in PI.

**CONCLUSION**

In summary, we prepared two new TVT-based isomeric polymers (PI and PO) by tailoring the side-chain regiochemistry on the TVT subunit. By analyzing and comparing the optical, structural, and charge-transport data for the resulting polymers, we found that different regiosymmetrical arrangements in the main backbone can play a pivotal role in governing the intrinsic properties of the polymers. For example, the PI polymer film has a strong tendency to form H-aggregates and bimodal molecular packing for 3D charge transport, whereas J-aggregation of the PO film induces a predominantly unimodal molecular packing motif. In addition, we found that side-chain regiochemistry significantly influences the grain morphology and intergranular connectivity. By controlling the side-chain conformation, we observed a large difference in OFET mobility between PI ($\mu_h = 1.69 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and PO ($\mu_h = 0.90 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) under the optimized conditions. This study demonstrates that incorporation of a TVT-TI subunit into the polymer backbone is an effective way to achieve high baseline mobility; this furthers our understanding of how the film microstructure and charge-transport characteristics are influenced by the side-chain regiochemistry of TVT.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b02447.

Detailed synthetic procedures and fabrication method, additional figures (NMR spectra of new materials, surface energy analyses, GIXD data and profiles, mobility distributions based on various temperature, transfer and output characteristics for TVT-based isomeric polymers (PI and PO)), and summary of crystallographic parameters (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: joonhoh@postech.ac.kr (J.H.O.).
*E-mail: yang@unist.ac.kr (C.Y.).

**ORCID**

Changduk Yang: 0000-0001-7452-4681

**Author Contributions**


**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2015R1A2A1A10053397, 2014K1A3A1A9066591, 2014R1A2A2A01007467) and Center for Advanced Soft Electronics under the Global Frontier Research Program (Grant 2013M3A6A5073175) of the Ministry of Science, ICT & Future Planning, Korea. The GIXD experiment at the PLS-II 3C SAXS I beamline was supported in part by MEST, POSTECH.

**REFERENCES**


