Synthesis and Thin-Film Transistor Performance of Fluorene-based Copolymers Containing Thiophene Moieties Having Different Position of Alkyl Side Chain

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ABSTRACT

We have synthesized fluorene-based copolymers (PF-HT-TT-TH and PF-TH-TT-HT) containing thiophene moieties having different position of alkyl side chain via the palladium-catalyzed Suzuki coupling reaction. The number-average molecular weight ($M_n$)s of PF-HT-TT-TH and PF-TH-TT-HT were respectively found to be 11,800 and 22,300. These polymers dissolve in common organic solvents such as chloroform, chlorobenzene and toluene, etc. The PL emission peak of a film of PF-TH-TT-HT is clearly red-shifted with respect to PF-HT-TT-TH, due to the repulsion of alkyl side chains in the between fluorene and thiophene moieties. Through studies of X-ray diffraction (XRD), we could access molecular alignment. The thermal properties of these polymers were measured by TGA and DSC, and electrical properties were studied by cyclic voltammetry (CV). They exhibited different field-effect transistor (FET) properties depending on their positions of alkyl side chains. The PF-TH-TT-HT having little repulsion showed better field-effect transistor performance than that of PF-HT-TT-TH.

Keywords: field-effect transistor

1 INTRODUCTION

Organic field-effect transistors (FETs) can be used in low cost memories, smart cards, and the driving circuits of large-area display devices. To minimize manufacturing costs, the FET fabrication process should ideally include solution-based methods. The use of soluble polymeric semiconductors has made possible the development of active-matrix multipixel displays using solution-based technology. The design and synthesis of organic semiconductors with a high charge carrier mobility and good stability has become a focus of research into organic electronic materials. Fluorene-based copolymers have recently attracted significant attention as promising materials for polymer FET.1,2 Fluorene-based copolymer have better stability than thiophene-based polymers because of their rigid structures and lower HOMO levels, as well as good film-forming and hole-transporting properties. In this paper, we report the synthesis and field-effect transistor performance of fluorene-based copolymers containing thiophene moieties having different position of alkyl side chain.

2 EXPERIMENTAL AND RESULTS

2.1 Materials.

Scheme 1: Structure and synthetic route of the polymers.

All starting materials were purchased from Aldrich Chemical Co. All reactions were performed under nitrogen atmosphere.

Chemical structures and synthetic routes of PF-TH-TT-HT and PF-HT-TT-TH were showed Scheme 1. Two fluorene-based copolymers containing thiophene moieties having different position of alkyl side chain were synthesized by Suzuki coupling reaction. An important difference between two polymers is a position of alkyl side chains attached to thiophene units.

2.2 Results and discussion
The number-average molecular weight ($M_n$) of the synthesized polymers, PF-TH-TT-HT and PF-HT-TT-TH, were 22,300 (PDI = 1.8) and 11,800 (PDI = 1.7), respectively. Table 1 shows physical properties of these polymers.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$M_w$</th>
<th>$M_n$</th>
<th>$T_{3d}$</th>
<th>$T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-TH-TT-HT</td>
<td>39,000</td>
<td>22,300</td>
<td>407 °C</td>
<td>128 °C</td>
</tr>
<tr>
<td>PF-HT-TT-TH</td>
<td>19,500</td>
<td>11,800</td>
<td>387 °C</td>
<td>109 °C</td>
</tr>
</tbody>
</table>

Table 1. Physical properties of the polymers

The thermal stabilities of the polymers above 380 °C were evaluated by means of thermo gravimetric analysis (TGA) under nitrogen atmosphere. Thermally induced phase transition behaviors of the polymers were investigated with differential scanning calorimetric (DSC). As shown in Figure 1, the glass transition temperatures of PF-TH-TT-HT and PF-HT-TT-TH were ca. 128 and 109 °C, respectively, comparable with those of poly(9,9'-dialkylfluorene)s that usually range from about 60 to 100 °C. PF-TH-TT-HT had a higher $T_g$ than PF-HT-TT-TH because alkyl chains of the PF-TH-TT-HT were well ordered due to the less repulsion of alkyl chains between fluorene and thiophene moieties.

The film morphology of both polymers was examined with AFM. Films were prepared by dissolving 10 mg/mL of polymer in toluene and then spin coating at 1500 rpm on SiO$_2$ wafers. To evaporate solvent, the films were annealed for 30 min at 110 °C. Figure 2 shows the morphologies of the polymers. We could not find large grain size at two polymers, but there is apparent difference between two polymers. The morphology of PF-TH-TT-HT is smoother than that of PF-HT-TT-TH. Maybe, this difference will have influence on field-effect transistor properties because when gold was deposited as source and drain electrode, a degree of penetration of gold into the semiconductor layer was little for smoother surface. Figure 3 exhibits XRD patterns of the polymers. To evaluate the crystallinity of polymers, PF-TH-TT-HT and PF-HT-TT-TH, XRD measurements were taken of drop cast films onto a quartz glass substrate. PF-HT-TT-TH polymer, exhibited diffraction peak at $2\theta = 8.06^\circ$, corresponding to an inter chain d-spacing of 10.95 Å. A next peak at $2\theta = 19.59^\circ$ corresponds to a $\pi$-$\pi$ stacking distance of 4.52 Å. This $\pi$-$\pi$ stacking distance falls in the region observed in PF-TH-TT-HT (4.35 Å). However, the inter chain spacing between the individual polymer chains is higher than that observed in PF-HT-TT-TH. This increased spacing could be due to the interaction of between alkyl chains of fluorene and thiophene, which could force the alkyl chains to adopt a more vertical orientation.

The UV-vis absorption and PL properties of these polymers in solution and film states were investigated, and
summarized in Table 2. Figure 4 and 5 show the normalized UV-visible absorption and photoluminescence (PL) emission spectra of PF-TH-TT-HT and PF-HT-TT-TH. Both the absorption and emission peaks of two copolymers, PF-TH-TT-HT is clearly red-shifted compared to those of PF-HT-TT-TH. This spectral shift could be understood in terms of the more planar conformation of the backbone and a smaller band gap in the case of thiophene rings. The most prominent vibrational progression of an electronic absorption or emission band is often associated with a vibration whose equilibrium position is most greatly changed by the radiative electronic transition. Both the polymers showed two most probable transitions. The UV absorption maxima of PF-TH-TT-HT appeared at 435 nm, and that of PF-HT-TT-TH was at 427 nm. In PL, the emission spectra of two polymer solutions showed typical vibronically structured band comprising a maximum, a shoulder, and a tail. The PL emission maxima of PF-TH-TT-HT appeared at 519 nm, and that of PF-HT-TT-TH is at 501 nm. This result indicates that the 3-substituted hexylthiophene have more expanded effective conjugated length than 4-substituted hexylthiophene.

The UV-vis. absorption and PL emission spectra of PF-TH-TT-HT and PF-HT-TT-TH as films are shown in Figure 5. Both absorption and emission maximum of film state became red-shifted compared to those of solution state because of the increased intermolecular interaction between neighboring molecules in film state. Especially, compared with the shift of the PL emission maximum from PF-HT-TT-HT to PF-HT-TT-TH (from 501 nm to 519 nm) in solution, the shift in film states (from 523 nm to 573 nm) is much larger. This result indicates that the π-conjugation length of PF-TH-TT-HT is much longer than that of PF-HT-TT-TH in film states.

<table>
<thead>
<tr>
<th>polymer</th>
<th>solution λ_{max} (nm)</th>
<th>film λ_{max} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>absorption</td>
<td>emission</td>
</tr>
<tr>
<td>PF-TH-TT-HT</td>
<td>435</td>
<td>519</td>
</tr>
<tr>
<td>PF-HT-TT-TH</td>
<td>427</td>
<td>501</td>
</tr>
</tbody>
</table>

Table 2. UV–vis. absorption and PL emission spectral data of PF-TH-TT-HT and PF-HT-TT-TH in chloroform and as films.

The electrochemical properties of the polymers were investigated to characterize and compare the electronic properties of the polymers by cyclic voltametric (CV). The cyclic voltamograms of the polymers, PF-TH-TT-HT and PF-HT-TT-TH, measured in a solution of 0.10 M tetrabutylammonium tetrafluoroborate (n-Bu4NBF4) dissolved in acetonitrile at scan rate of 50 mV/s are shown in Figure 6 and all the calculated electrochemical data of them are listed in Table 3. In the anodic scan, the onset of oxidation of PF-TH-TT-HT and PF-HT-TT-TH occurs at 0.59 V and 0.65 V, which correspond to $E_{\text{HOMO}}$ of −5.28 eV and −5.33 eV, respectively. As shown optical properties, for PF-HT-TT-TH polymer, reduced delocalization along the backbone results in a lowering of the polymer highest occupied molecular orbital level. The optical band gaps of PF-TH-TT-HT and PF-HT-TT-TH were 2.33 eV and 2.47 eV, indicative of grass-green and yellowish green light-emitting, respectively. These band gaps give rise to analogous tendency with optical ones (2.33 eV for PF-TH-TT-HT and 2.47 eV for PF-HT-TT-TH) calculated from assumption that $E_{\text{LUMO}}$ is given by the difference between $E_{\text{HOMO}}$ and the optical gap taken as the absorption onset. The actual redox behaviors are more accordance to the energy levels achieved electrochemically. An incorporation of electron-rich thiophene moiety into polymer backbone lead to higher HOMO and lower LUMO energy levels than polyfluorene homopolymer of −5.80 and −2.12 eV, respectively.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$E_{\text{HOMO}}$</th>
<th>$E_{\text{LUMO}}$</th>
<th>$E_{\text{gap}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-TH-TT-HT</td>
<td>-5.28</td>
<td>-2.95</td>
<td>2.33</td>
</tr>
<tr>
<td>PF-HT-TT-TH</td>
<td>-5.33</td>
<td>-2.86</td>
<td>2.47</td>
</tr>
</tbody>
</table>

Table 3. Electrochemical properties and energy levels of the polymers.

The thin-film transistors of PF-TH-TT-HT and PF-HT-TT-TH showed $p$-channel FET characteristics.
gate electrode is biased positively, they operate in the depletion mode, and the channel region is depleted of carriers resulting in high channel resistance (off state). When the gate electrode is biased negatively, they operate in the accumulation mode and a large concentration of carriers is accumulated in the transistor channel, resulting in low channel resistance (on state). Figure 7 shows the output and transfer characteristics of the polymers based OTFT. The field-effect mobility was calculated in the saturation regime using the following equation,

\[ I_{DS} = \frac{W}{2L} \mu C_i (V_G - V_T)^2 \]

Where \( I_{DS} \) is the drain-source current in saturated region, \( W \) and \( L \) are the channel width and length, respectively, \( \mu \) is field-effect mobility, \( C_i \) is the capacitance per unit area of the insulation layer, and \( V_G \) and \( V_T \) are the gate voltage and the threshold voltage, respectively.

A solution-processed PF-TH-TT-HT FET device was found to exhibit a hole mobility of \( 1.05 \times 10^{-4} \text{cm}^2/\text{Vs} \) and a low threshold voltage of \(-4 \text{V} \) without the use of any alignment technique; this mobility is 3 times higher than the mobility of PF-HT-TT-HT \((3.68 \times 10^{-5} \text{cm}^2/\text{Vs})\) under the same conditions. The higher performance of PF-TH-TT-HT indicates that this polymer have better molecular architecture than PF-HT-TT-HT. The bigger repulsion of between alkyl-side chains of PF-HT-TT-HT results in lower crystallinity and a less ordered morphology. The fluorene-based copolymers prepared in the present work showed significantly low-off-currents (e.g., \(5.4 \times 10^{-12} \) for PF-TH-TT-HT), which can be attributed to the stable (more negative) HOMO energy levels in these polymers (e.g., -5.28 eV for PF-TH-TT-HT). Similar correlations between off-current and HOMO energy have been reported for thiophene-phenylene and thiophene-thiazole semiconductors. We could regard this higher mobility of PF-TH-TT-HT as the result of close molecular packing and well-defined orientation of lower repulsion of the alkyl-side chains. Also, the HOMO level raised by the strong electron donating ability contribute to hole injection for high performance in field effect transistor.

3 SUMMARY

We have successfully synthesized fluorene-based copolymers (PF-TH-TT-HT and PF-HT-TT-TT) containing thiophene moieties having different position of alkyl side chain via the palladium-catalyzed Suzuki coupling reaction. The thermal properties and chain alignment behavior of these polymers were demonstrated with DSC, AFM, and XRD analysis. Because PF-TH-TT-HT polymer have less repulsion between alkyl-side chains of fluorene and thiophene moieties, PF-TH-TT-HT have expended conjugation length, enhanced molecular ordering. So, PF-TH-TT-HT FET devices exhibited improved mobility \((1.05 \times 10^{-4} \text{cm}^2/\text{Vs})\), which is 3 times higher than the mobility of PF-HT-TT-TT devices. The present findings on the relationship between the alkyl-side chain positions and their thermal, optical, and electrical properties provide useful guidelines for the molecular design of high mobility conjugated polymers for OTFT applications.

REFERENCES