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An Amorphous Polythiophene as a Binder Material for Organic Thin-Film Transistor Channel Applications

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Blending of crystalline low molecular-weight organic semiconductors, e.g., 6,13-bis (triisopropylsilylethynyl)pentacene (TIPS-Pentacene), and binder polymers has recently been known to be an effective way to achieve high performance organic thin-film transistors (OTFTs). However, only limited number of examples has been reported as binder materials for OTFT applications, e.g., poly(triarylamine), poly(α-methylstyrene), and etc. In this work, an amorphous polythiophene derivative, poly(3-(2-ethylhexyl)thiophene) (P3EHT), was prepared by introducing 2-ethylhexyl group as a side-chain to the polythiophene. The P3EHT was synthesized by Grignard metathesis (GRIM) polymerization to give a molecular weight (Mn) of 4,100 (PDI = 3.4), and it was readily soluble in common organic solvents, such as chloroform, tetrahydrofuran, toluene, and etc. An amorphous nature of the P3EHT was confirmed from differential scanning calorimetry (DSC) and ultraviolet-visible spectroscopy results. A mobility of $2.5 \times 10^{-4}\,cm^2/Vs$*, an on/off ratio of* 0.57×10^3 *and a threshold voltage of 1.6 V have been obtained with OTFTs using a P3EHT/TIPS-Pentacene blend.*

Keywords Binder; GRIM polymerization; organic semiconductor; OTFT; thiophene

Introduction

Solution-processable transistors open a new possibility to future electronics, because the manufacturing cost can be lowered and large-area fabrication becomes possible with solution processing or printing. Among the various kinds of technologies related with solution-processable transistors, organic thin-film transistors (OTFTs) have attracted much research interest during the past decades [1]. At the initial stage of soluble OTFT research, thiophene-based π-conjugated polymers have been widely used as *p*-type semiconductors due to their high charge carrier mobility [2,3]. Recently, another approach utilizing crystalline low molecular-weight organic semiconductors, such as TIPS-Pentacene and its derivatives, has also proved its possibility [4]. Moreover, improved performance and uniformity of the device has

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Address correspondence to Changjin Lee, Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Sinseongno 19, Yuseong-gu, Daejeon 305-600, Korea. Tel.: 82-42-860-7208; Fax: 82-42-860-7200; E-mail: cjlee@krict.re.kr been reported by blending such small molecules with binder polymers [5]. However, only limited number of examples has been reported as binder materials for OTFT applications, e.g., poly(triarylamine) (PTAA) [5,6], poly(α-methylstyrene) (PAMS) [5–7], polystyrene (PS) [8], poly(4-vinylbiphenyl) (PVBP) [6], and etc.

In this work, we prepared and applied an amorphous polythiophene as a binder polymer for a crystalline low molecular-weight organic semiconductor, e.g., TIPS-Pentacene. The good crystallinity of the well-known P3HT comes from its planar molecular structure along the main-chain and the side-chain. We therefore introduced 2-ethylhexyl group to the 3-position of thiophene resulting in bulky and non-planar structure, and synthesized poly(3-(2-ethylhexyl)thiophene) (P3EHT) which is different in its side-chain compared with the most known polymer semiconductor, P3HT. The physical, optical and electrochemical properties of the P3EHT were revealed using differential scanning calorimetry (DSC), UV-Vis absorption spectroscopy and cyclic voltammetry. OTFT device characteristics using a blend of P3EHT and TIPS-Pentacene were also investigated.

Experiments

Instrumentation and Characterization

The NMR spectra were recorded at room temperature using a Bruker 300 NMR spectrometer. The molecular weight and the molecular weight distribution (relative to polystyrene standards) of the polymers were obtained by gel permeation chromatography (GPC) using Shodex GPC columns with a chloroform eluent. DSC was conducted using METTLER TOLEDO DSC1. Absorption spectra were measured using a SHIMADZU UV-2550 UV-Visible Spectrophotometer. Cyclic voltammetric measurements were performed on a BAS 100 voltammetric system with a three-electrode cell in a solution of 0.10 M tetrabutylammonium hexafluorophosphate in acetonitrile at a scanning rate of 50 mVs^{-1}. An Ag/Ag^+ electrode (0.01 M $AgNO_3$ in acetonitrile) was used as a reference electrode, and platinum wires were used as a counter electrode and a working electrode. Current-voltage characteristics of the OTFT device were measured using Agilent 4155C semiconductor parameter analyzer.

Polymerization

To a solution of 2,5-dibromo-3-(2-ethylhexyl)thiophene **1** (3 g, 8.47 mmol) in anhydrous tetrahydrofuran was added methylmagnesium bromide solution (1.0 M in THF, 7.62 mL, 7.62 mmol) dropwisely while refluxing. Ni(dppp)Cl_2 (0.046 g, 0.08 mmol) was added in one portion after 1 hour. The solution was further refluxed for two hours, and then the reaction mixture was dropped into 900 mL of methanol to precipitate the polymer. Then the precipitated dark brown solid was filtered and subjected to sequential Soxhlet extraction with methanol to remove low molecular weight fraction of the material. The yield of P3EHT by this procedure was 19.9%. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 6.94 (s, 2H), 2.73 (br d, 2H), 1.69 (br s, 1H), 1.29 (br m, 8H), 0.88 (br t, 6H).

The same procedure was applied for P3HT synthesis.

OTFT Device Fabrication

Predefined substrates with gold source/drain electrodes were carefully cleaned by methanol, isopropyl alcohol and deionized water, and then further cleaned by

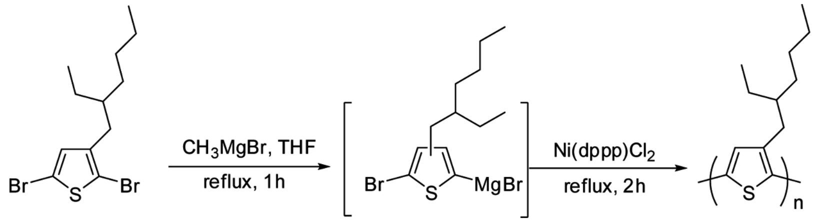
UV/ozone treatment. The organic semiconductor solution (1:1 blend of P3EHT: TIPS-Pentacene in toluene) was spin-coated at 500 rpm for 30 seconds, and the film was dried at 100°C for 30 minutes. A diluted solution of CTL-809 M (from Asahi Glass Co., LTD) was spin-coated onto the organic semiconductor layer at 900 rpm for 30 seconds to give a gate dielectric layer of CYTOP. The CYTOP gate dielectric layer was dried in a vacuum oven at 90°C for 1 hour. A gate electrode was vacuum-deposited from gold to finalize the device fabrication.

Results and Discussion

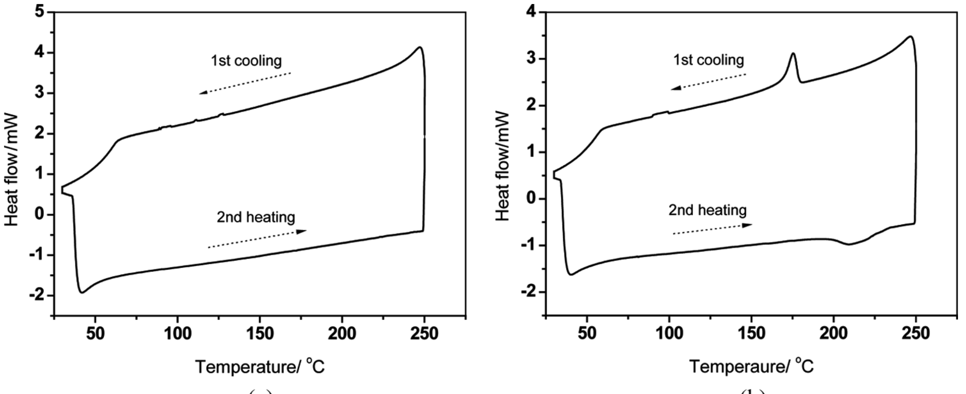
For monomer synthesis, 2-ethylhexyl side-chain was introduced to the 3-position of thiophene by Kumada coupling reaction between 3-bromothiophene and 2-ethylhexylmagnesium bromide. Following bromination with N-bromosuccinimide (NBS), 2,5-dibromo-3-(2-ethylhexyl)thiophene was obtained. The polymerization was carried out according to a GRIM polymerization method to yield P3EHT (Scheme 1) [9]. P3HT was also synthesized by the same procedure for comparison. The number-average molecular weight (Mn) of P3EHT and P3HT were 4,100 (PDI = 3.4) and 4,600 (PDI = 2.3), respectively. Both of the polymers were readily soluble in common organic solvents, such as chloroform, tetrahydrofuran, toluene, and etc.

Figure 1 shows the DSC thermograms of the two polymers, P3EHT and P3HT. DSC measurements were performed to examine the crystallinity of the polymers. Due to its planar structure, P3HT is known to be crystalline, and DSC thermogram also showed reversible melting (endothermal) and crystallization (exothermal) peaks during heating and cooling scans. In contrast, no peak was observed for P3EHT, thus implying the amorphous characteristic of P3EHT. The UV-Vis absorption spectroscopy also supports this. Figure 2 shows the absorption spectra of each of the two polymers in solution state and in film state. P3EHT showed an absorption peak with λ_{max} at 433 nm in solution, and λ_{max} at 443 nm in film ($\triangle\lambda_{max} = 10$ nm). In the case of P3HT, much larger shift of λ_{max} was observed from solution to film ($\triangle\lambda_{max} =$ 63 nm). P3HT showed an absorption peak with λ_{max} at 443 nm in solution, and λ_{max} 506 nm in film. The degree of red-shift of absorption maximum from solution to film is known to be a criterion for estimating polymers' chain ordering and alignment [10]. The relatively small shift of λ_{max} for P3EHT means that P3EHT has little tendency to ordering and crystallization, while P3HT has a strong tendency to ordering and crystallization. From these results including DSC and UV-Vis absorption spectroscopy, it is apparent that P3EHT which has branched alkyl side-chains is a kind of amorphous polymers.

In addition to the characterization of the amorphous property of P3EHT, we also carried out absorption measurements of the 1:1 ratio of polymer/TIPS-Pentacene



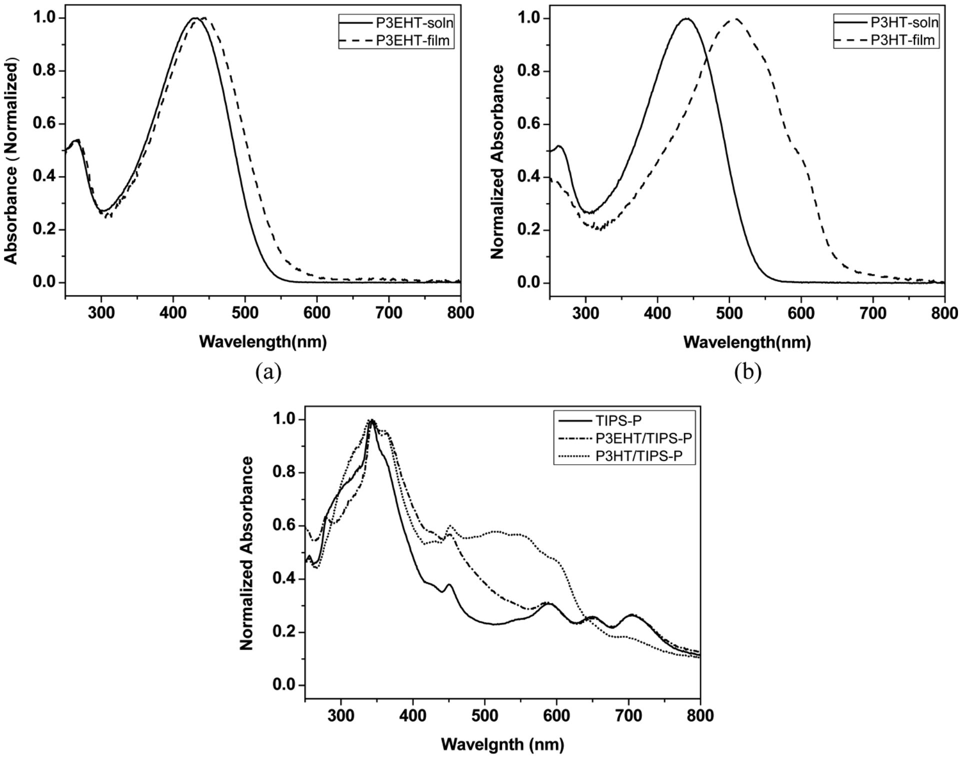
Scheme 1. Synthesis of P3EHT.



(a) (b)

Figure 1. DSC thermograms of P3EHT (a) and P3HT (b).

blend films (Figure 2c). Because the polymers will be utilized in the form of blend film with TIPS-Pentacene for OTFT applications, investigation of those blend films is important. The absorption spectrum of the TIPS-Pentacene film without any binder is also shown in Figure 2c. All of the three spectra were normalized with



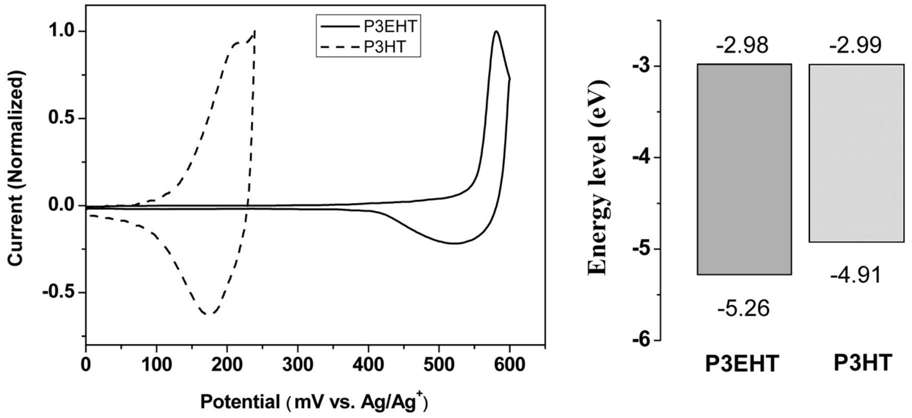
(a) (b)

(c)

Figure 2. UV-Vis absorption spectra of P3EHT (a), P3HT (b), and polymer/TIPS-Pentacene blend film (c).

respect to the highest peak around 343 nm, which originates from the TIPS-Pentacene. Other peaks at 450, 588, 650, and 705 nm also originate from TIPS-Pentacene not P3EHT nor P3HT. The spectrum of the P3EHT-based blend film coincides well with that of the TIPS-Pentacene film in the long wavelength region (>550 nm), and this implies that the thin-film structure of the TIPS-Pentacene is maintained inside the blend film based on amorphous P3EHT. However, the difference is clearly observed for the P3HT-based blend film. The broad absorption around 500 nm mainly comes from P3HT film, but what is noteworthy is that the peak intensity at 705 nm is relatively low compared with that of the TIPS-Pentacene or P3EHT-based blend film. We therefore infer that the thin-film structure of the TIPS-Pentacene has changed by blending with crystalline P3HT.

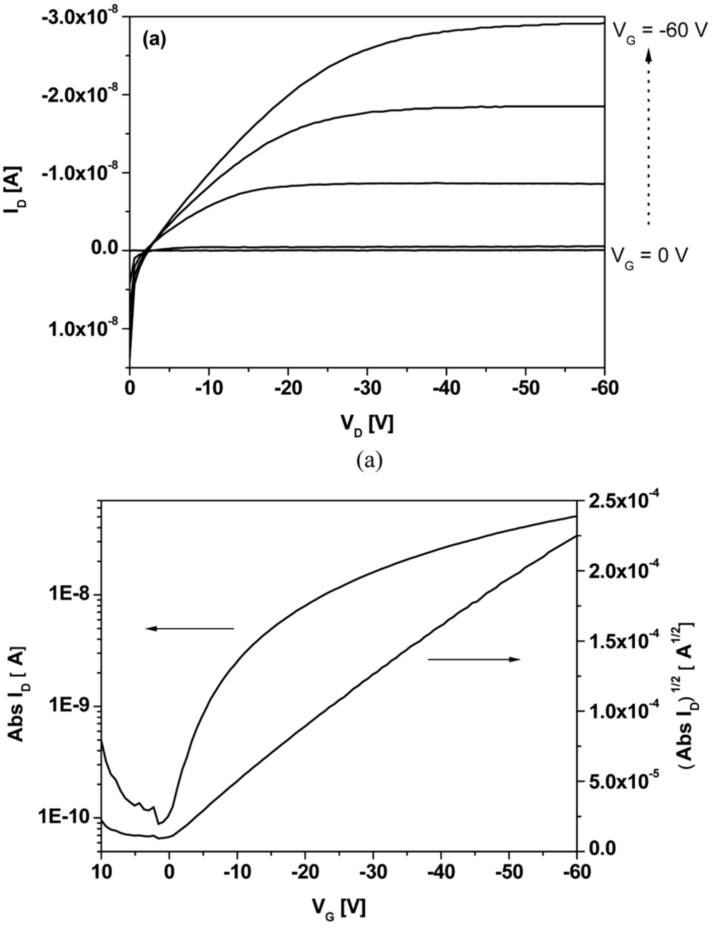
The electronic properties of the binder polymer as well as the amorphous characteristics are also very important for OTFT applications, because charges pass through the polymers during operation. Figure 3a shows the cyclic voltammogram of P3EHT and P3HT during oxidative scan. The half-wave oxidation potential ($E_{ox,1/2}$) of P3EHT was 551 mV, while P3HT was 196 mV vs. Ag/Ag$^+$. Although not displayed in Figure 3a, the first half-wave oxidation potential ($E_{ox,1/2}$) of ferrocene was measured to be 87 mV in our experiment. So the HOMO (highest occupied molecular orbital) energy level of P3EHT was estimated to be −5.26 eV from its $E_{ox,1/2}$ by regarding $E_{ox,1/2}$ of ferrocene as −4.80 eV [11]. The HOMO level of P3HT was also estimated to be −4.91 eV in the same manner. The optical band-gap was estimated from the onset position of the absorption spectrum, and P3EHT and P3HT showed 2.28 and 1.92 eV, respectively. The energy level diagram of the two polymers is depicted in Figure 3b, and it was found that the LUMO (Lowest Unoccupied Molecular Orbital) energy levels of the two polymers are almost the same. This means that the increase of band-gap from P3HT to P3EHT was mainly affected by the HOMO energy levels rather than the LUMO energy levels. The relatively low HOMO energy level of P3EHT originates from reduced π-conjugation of polythiophene main-chain due to the branched alkyl side-chain. But the value is within a range of other hole-transporting materials [12], so P3EHT can also be used as a hole-transporting polymer for *p*-type OTFT applications.



(a) (b)

Figure 3. Cyclic voltammogram (a) and energy level diagram (b) of the polymers.

To characterize the TFT performance of the polymer/TIPS-Pentacene blend, top-gate OTFT test device was fabricated. A 1:1 ratio of blend between the polymer and TIPS-Pentacene was used as a semiconducting channel, and CYTOP was used as a gate dielectric. The channel width and length was 3000 μm and 50 μm, respectively. But OTFT devices using P3HT-based blend did not operated at all, and only devices using P3EHT-based blend operated well in a *p*-type mode. Figure 4 shows the representative OTFT device characteristics of P3EHT/TIPS-Pentacene blend. Saturation behavior at high drain voltage was clearly observed in the output curve (Figure 4a). However, drain current offset is observed at low drain voltage region. This phenomenon is known to be related to gate leakage, and it can be overcome by optimization of device structure, such as patterning of the semiconductor film [13]. For the transfer characteristics measurement, gate voltage (V_G) was swept from +10 V to −60 V at constant drain voltage (V_D) of −60 V (Figure 4b). In this saturation regime, the extracted mobility of the P3EHT/TIPS-Pentacene blend device was 2.5×10^{-4} cm^2/Vs with on/off ratio of 0.57×10^3 and threshold voltage (V_T) of 1.6 V.



(a)

(b)

Figure 4. Output curve (a) and transfer curve (b) of P3EHT/TIPS-Pentacene OTFT device.

Although our OTFT device did not show the higher performance than the previously reported works [5–8], to our knowledge, this is the first example of a polythiophene derivative used as a binder polymer for TIPS-Pentacene. As a preliminary data, this result indicates that an amorphous polythiophene, P3EHT, can be successfully applied as a binder polymer for TIPS-Pentacene-based OTFT applications. From the viewpoint of materials, we believe that control of the crystallinity or amorphous characteristics of the conjugated polymer is a key to achieve high performance OTFTs. Further device optimization such as varying composition ratio, solvents, annealing conditions, device geometry, and etc. would be able to improve the OTFT characteristics.

Conclusion

In this paper, an amorphous polythiophene containing branched alkyl side-chain was prepared and applied as a binder polymer for TIPS-Pentacene-based OTFT device. Poly(3-(2-ethylhexyl)thiophene) (P3EHT) was successfully synthesized via GRIM polymerization, and its amorphous characteristic was analyzed by DSC and UV-Vis spectroscopy. Due to the branched alkyl side-chain, P3EHT showed the larger band gap and the lower HOMO energy level compared to P3HT. From the OTFT results using 1:1 blend of P3EHT/TIPS-Pentacene, the extracted mobility of the device was $2.5 \times 10^{-4}\,\mathrm{cm}^2/\mathrm{Vs}$ with an on/off ratio of 0.57×10^3 and V_T of 1.6 V. Considering this preliminary results, P3EHT is a promising binder polymer for *p*-type OTFT applications based on crystalline low molecular-weight organic semiconductors. Further characterization of the thin-film structure and optimization of the device fabrication would be expected to improve the device performance of P3EHT/TIPS-Pentacene blend.

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