

Poly(1,4-bis((E)-2-(3-dodecylthiophen-2-yl)vinyl)benzene) for Solution Processable Organic Thin Film Transistor

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New semiconducting polymer, poly[1,4-bis((E)-2-(5-bromo-3-dodecylthiophen-2-yl)vinyl)benzene], was designed, synthesized and characterized. The structure of polymer was confirmed by ¹H-NMR, IR and elemental analysis. The polymer was soluble in specific organic solvent. The weight-average molecular weights (MW) of polymer was found to be 11,000 with polydispersity of 1.82. UV-Visible absorption spectrum showed the maximum absorption at 428 nm (in solution) and 438 nm (in film). The highest occupied molecular orbital (HOMO) energy of the polymer is -5.36 eV by measuring cyclic voltammetry (CV). A solution-processed polymer thin film transistor device shows a mobility of $8.59 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, an on/off current ratio of 2.0×10^4 .

Key Words : Organic thin film transistor, Organic semiconductor, Mobility, Solution process

Introduction

Solution processable conjugated polymers have received considerable attention as a novel class of organic semiconducting materials out of uses their numerous potential applications, such as organic light emitting diodes (OLEDs), organic thin film transistor (OTFTs) and organic solar cell, owing to their remarkable electronic and optical properties and their possible application in low performance plastic circuits.¹⁻¹² OTFTs based on solution-processable organic semiconductors have been increasingly investigated for use in low-cost memory devices, large-area display devices, and flexible electronic devices.¹³⁻¹⁶ Especially, easy solution-processable polymeric semiconductors can be deposited using low-cost solution processing methods such as spin-coating, ink-jet printing, and gravure printing.

High performance in organic electronic devices requires the development of methodologies that allow precise control of the polymer electronic structure to achieve a desired band gap, and highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy levels. Considerable effort has been devoted to understand the relationship between energy levels in a polymer and OTFT performance. Among them, thiophene-based polymers have shown highest mobility with high crystalline orders on the substrate. For example, regioregular head-to-tail poly(3-hexylthiophene)s (P3HT) has mobility of $0.1 \text{ cm}^2/\text{Vs}$.⁴ However, because P3HT have relatively low ionization potential (4.98 eV),¹⁷ its TFT performances can be easily degraded by oxidative doping in air.⁸ Recently, Ackermann *et al.* reported oligothiophenes end-capped with styryl and divinylbenzene end-capped with oligothiophenes, which showed high field-

effect mobility with high stability.^{18,19} Our group also reported small fused acenes containing divinylbenzene which showed not only good mobilities but also good oxidation stability.²⁰⁻²²

In the present study, we designed and synthesized the new semiconducting polymer, poly(3-dodecylthienyl-divinylbenzene-3-dodecylthienyl) for solution processable OTFT. It is expected that the introduction of electron rich and structural rigid divinylbenzene can increase interchain stacking, lead to increased mobility. And the long alkyl groups substituted thienyl ring can increase the solubility of polymer for solution process.

Experiment

Materials. 3-Bromothiophene, 1-bromododecane, *N*-bromosuccinimide (NBS), *n*-butyllithium, 2-isopropoxy-3,3,4,4-tetramethyl-1,3,2-dioxaborolane, 1,3-bis(diphenylphosphinopropane)-dichloronickel, *N,N*-dimethylformamide (DMF), sodium hydride, and tetrakis(triphenylphosphine)-palladium (0) were purchased from Aldrich and xylenebis(triphenyl-phosphonium bromide) was purchased from Alfa.

Measurements. The ¹H-NMR and ¹³C-NMR spectra were recorded using a Bruker AM-200 spectrometer. FT-IR spectra were measured on a Bomem Michelson series FT-IR spectrometer. The melting points were determined with an Electrothermal Mode 1307 digital analyzer. The thermal analysis were performed on a TA TGA 2100 thermogravimetric analyzer in a nitrogen atmosphere at a rate of 20 °C/min. Differential scanning calorimeter (DSC) was conducted under nitrogen on a TA instrument 2100 DSC. The sample was heated at 20 °C/min from 30 °C to 250 °C. UV-vis absorption

studies were carried out using Perkin Elmer LAMBDA-900 UV/VIS/IR spectrophotometer. The photoluminescence spectra were measured on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. Molecular weight and polydispersity of the polymer was determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (waters high-pressure GPC assembly Model M515 pump, u-Styragel columns of HR4, HR4E, HR5E, with 500 and 100 Å, refractive index detectors, solvent CHCl₃). Cyclic-voltammetry (CV) was performed on an EG and G Parc model 273 Å potentiostat/galvanostat system. The polymer films were coated on a square Pt electrode (0.50 cm²) by dipping the electrode into the corresponding solvents and then drying in air. A Pt wire was used as the counter electrode, and an Ag/AgNO₃ (0.1 M) electrode was used as the reference electrode.

Fabrication of the OFET Device. Top contacted OFETs were fabricated on a common gate of highly n-doped silicon with a 300 nm thick thermally grown SiO₂ dielectric layer. Octadecyltrichlorosilane monolayer was treated in toluene solution for 2 h. Films of organic semiconductor were obtained using chlorobenzene solvent. Gold source and drain electrodes were evaporated on the top of semiconductor for the thickness of 100 nm. For all measurements, we used channel length (L) of 100 μm and channel width (W) of 2000 μm. The electrical characteristics of the fabricated FETs were measured in air using both Keithley 2400 and 236 source/measure units. Field-effect mobility were extracted in the saturation regime from the slope of the source-drain current.

3-Dodecylthiophene. This was synthesized according to the literature²¹ with yield of 70%. bp = 104 °C/1 mmHg. ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.26 (s, 1H), 6.95 (m, 2H), 2.65 (t, 2H), 1.63-1.67 (m, 2H), 1.30-1.34 (m, 18H), 0.92 (t, 3H).

2,5-Dibromo-3-didodecylthiophene. *N*-Bromosuccinimide (14 g, 79.2 mmol) was added to the solution of compound 1 (10 g, 39.6 mmol) in tetrahydrofuran (250 mL) at 0 °C. The reaction mixture was stirred for 24 h and poured into water. After extracted with methylene chloride, the organic phase was separated and dried over magnesium sulfate. The product was obtained after a column chromatography using hexane as eluent. Yield: 12 g (74%). FTIR (KBr, cm⁻¹): 2852-2952 (aliphatic CH₂), ¹H NMR (300 MHz, CDCl₃, ppm) δ 6.77 (1H, s), 2.50 (t, 2H), 1.53 (m, 2H), 1.27 (m, 18H), 0.88 (t, 3H).

5-Bromo-3-dodecylthiophene-2-carbaldehyde. Compound 2 (5 g, 12.1 mmol) was mixed with dry THF (150 mL). *n*-Butyllithium (4.8 mL, 2.5 M in hexane, 12.1 mmol) dropwise was added to this mixture at -78 °C under nitrogen. After the addition was finished, the mixture was stirred for another 1 h, and anhydrous *N,N*-dimethylformamide (0.98 g, 13.4 mmol) was added into solution. The mixture was slowly warming to room temperature overnight and poured into 2 N HCl. The organic layer was extracted with ethyl acetate and dried over MgSO₄. The product was purified by

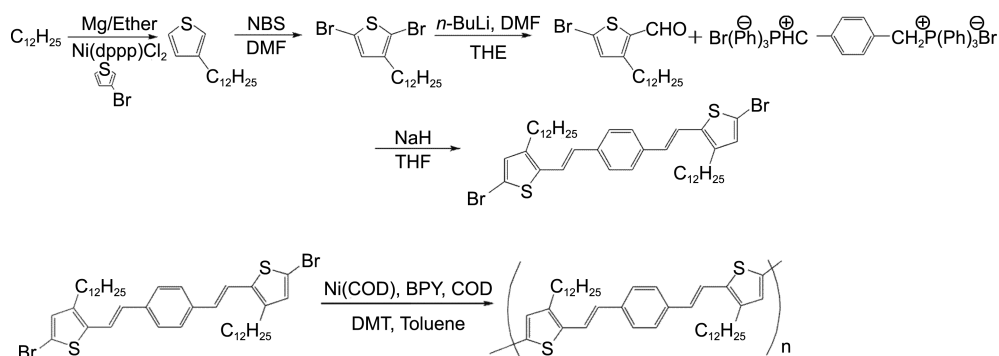
column chromatography using hexane and ethyl acetate. Yield: 2.71 g (62%). FTIR (KBr, cm⁻¹): 2852-2959 (aliphatic CH₂), 1747 (C=O), ¹H NMR (300 MHz, CDCl₃, ppm) δ 9.73 (s, 1H), 7.45 (s, 1H), 2.57 (t, 2H), 1.57-1.62 (m, 2H), 1.08-1.31 (m, 18H), 0.66-0.89 (t, 3H).

1,4-Bis((*E*)-2-(5-bromo-3-dodecylthiophen-2-yl)vinyl)benzene. 0.2 g (8.3 mmol) sodium hydride was added to the solution of xylenebis(triphenyl-phosphonium bromide) (2.98 g, 3.7 mmol) in THF (100 mL). The mixture was stirred at room temperature for 3 h and compound 3 (3 g, 8.3 mmol) was added into solution. After the mixture was refluxed for 24 h, it was poured into water and extracted with chloroform following drying with MgSO₄. The solvent was removed *via* rotary evaporation, and the residue was purified by column chromatography (25% CHCl₃ in hexane as eluent). The monomer was recrystallized by ethanol. Yield: 0.93 g (32%). MS (EI) *m/z* 788 (M⁺). FTIR (KBr, cm⁻¹): 3000 (aromatic C-H), 2846-2916 (aliphatic CH₂), 1030 (aromatic C-Br) ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.39 (s, 4H), 7.25-7.10 (d, 2H), 6.78-6.72 (d, 2H), 6.74 (s, 2H), 2.53-2.48 (t, 4H), 1.57-1.54 (m, 4H), 1.30-1.11 (m, 36H), 0.90-0.85 (m, 6H). ¹³C-NMR (300 MHz, CDCl₃, ppm): 142.7, 142.3, 136.2, 127.8, 127.0, 126.6, 121.3, 108.1, 77.4, 76.9, 76.5, 31.9, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.1, 22.6, 14.0 Anal. Calcd. for C₄₂H₆₀Br₂S₂: C, 63.96%; H, 7.62% Found: C, 63.90%; H, 7.59%.

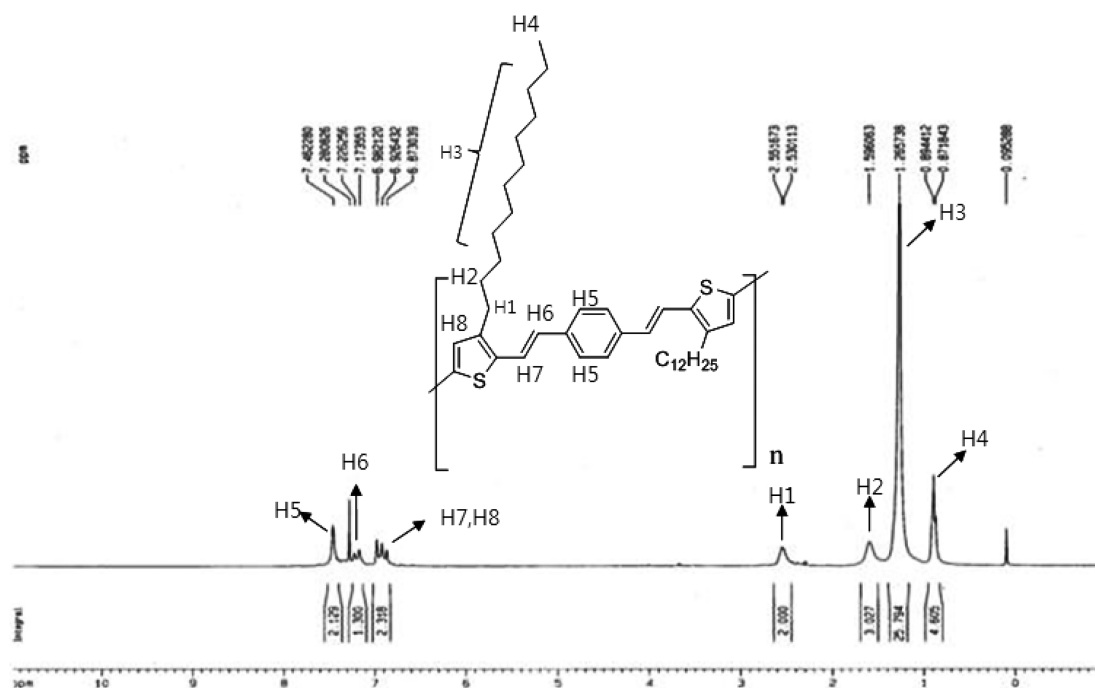
Poly[1,4-bis((*E*)-2-(5-bromo-3-dodecylthiophen-2-yl)vinyl)benzene] (PTVB). A mixture of bis(1,5-cyclooctadiene) nickel(0) (Ni(COD)₂, 0.52 g, 1.89 mmol), 2,2-bipyridine (0.29 g, 1.89 mmol), and 1,5-cyclooctadiene (0.20 g, 1.89 mmol) in anhydrous DMF (10 mL) was stirred at 80 °C for 30 min. 1,4-Bis((*E*)-2-(5-bromo-3-dodecylthiophen-2-yl)vinyl)benzene (0.5 g, 0.63 mmol) in toluene (50 mL) was added in one portion. The reaction mixture was stirred at 80 °C for 48 h. After cooled to room temperature, the mixture was precipitated into methanol. The polymer was purified by, column chromatography using toluene as eluent, the polymer was precipitated and purified by soxhlet extraction (methanol, toluene). Yield: 40%, red solid. ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.39 (s, 4H), 7.10-7.05 (d, 2H), 6.78-6.73 (d, 2H), 6.75 (s, 2H), 2.53-2.48 (t, 4H), 1.57-1.54 (m, 4H), 1.30-1.26 (m, 36H), 0.89-0.85 (m, 6H). Elemental Anal. Calc. for C₄₂H₆₀S₂: C, 80.19%; H, 9.61%, Found: C, 80.11%; H, 9.52%.

Results and Discussion

The synthetic routes to the monomer and polymer are outlined in Scheme 1. The new monomer, 1,4-bis((*E*)-2-(5-bromo-3-dodecylthiophen-2-yl)vinyl)benzene, was prepared with a Wittig reaction of xylenebis(triphenyl-phosphonium bromide) and 5-bromo-3-dodecylthiophene-2-carbaldehyde. 5-Bromo-3-dodecylthiophene-2-carbaldehyde was obtained by selective formylation on the 2-position of 2,5-dibromo-3-didodecylthiophene. The polymerization was carried out using a nickel-catalyzed Yamamoto coupling reaction for 48 h. After 48 h, end-capping was carried out with bromobenz-



Scheme 1. Synthetic route of the monomer and polymer.

Figure 1. ^1H NMR of PTVB in CDCl_3 .

ene. The structure of the synthesized polymer was characterized with ^1H -NMR, IR and elemental analysis. Figure 1 shows the ^1H NMR of the obtained polymer. The signals at around 0.9-2.5 and 6.8-7.4 ppm are assigned to the protons connected to the dodecyl groups in the thiophene unit and those connected to the aromatic rings and vinyl, respectively. The area ratio was 50:10, indicating that the polymer has a structure as outlined in Scheme 1. In the IR spectrum, the aromatic C-Br stretching is found to disappear at 1030 cm^{-1} .

The polymer exhibited solubility in specific organic solvents such as chloroform and chlorobenzene. The limited solubility is a result of the strong intermolecular interaction, which is due to by the incorporation of the rigid thiophenylene vinylene phenylene units. The molecular weight and polydispersity index of the polymer were determined with gel permeation chromatography (GPC) using polystyrene as the standard. The weight average molecular weight (MW) of the polymer was found to be 11000 with polydispersity of 1.82 (Table 1).

The thermal stability of the polymer was evaluated by

Table 1. Physical properties of the polymer

Polymer	Yield (%)	M_n^a	M_w^a	PDI	T_d ($^{\circ}\text{C}$) ^b
PTVB	40	6000	11000	1.82	334

^aDetermined by GPC, relative to polystyrene standards. ^bTemperature resulting in 5% weight loss based on initial weight.

thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere (Figure 2). The polymer showed 5% weight loss at a temperature of $334\text{ }^{\circ}\text{C}$. The glass transition temperature (T_g) was found to be $140\text{ }^{\circ}\text{C}$.

The electrochemical behavior of the polymer was investigated by cyclic voltammetry (CV). The CV was performed in a solution of Bu_4NClO_4 (0.1 M) in acetonitrile at a scan rate of 50 mV/s at room temperature under the protection of nitrogen. A platinum electrode was coated with a thin polymer film and was used as the working electrode. A Pt wire was used as the counter electrode. The measurements were calibrated using ferrocene (4.8 eV below the vacuum

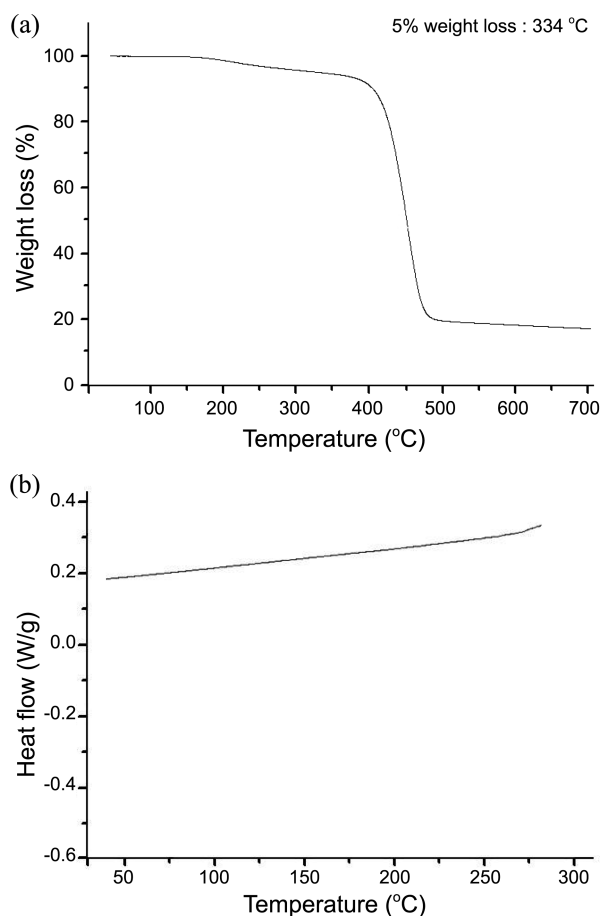


Figure 2. (a) TGA and (b) DSC thermograms of PTVB.

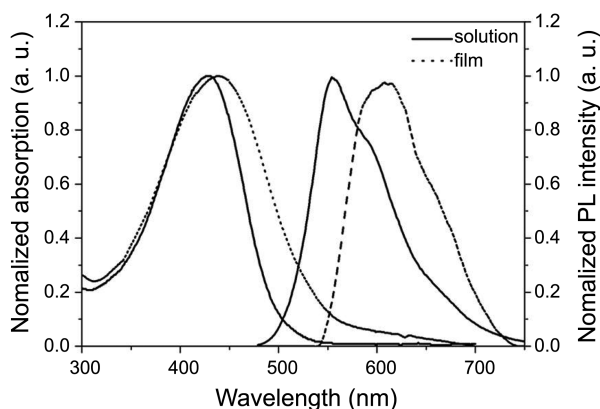


Figure 3. UV-vis absorption spectra and fluorescence spectra of a solution (10^{-6} M chloroform) and film for PTVB.

level) as the standard. The onset of the oxidation potential of the polymer was at 0.56 V. HOMO and LUMO levels were calculated according to an formula ($E_{\text{HOMO}} = E_{\text{OX}} + 4.8$ eV and $E_{\text{HOMO}} = E_{\text{LUMO}} + \text{Band gap eV}$).⁴ The HOMO-LUMO band gap was estimated to be 2.26 eV from the absorption edge of 550 nm. The HOMO and LUMO levels of the polymer were -5.36 eV and -3.1 eV, respectively. From the results, it is suggested that the obtained polymer will have oxidative stability due to deep HOMO level compared with that of regio-regular poly(3-alkylthiophene).¹⁶

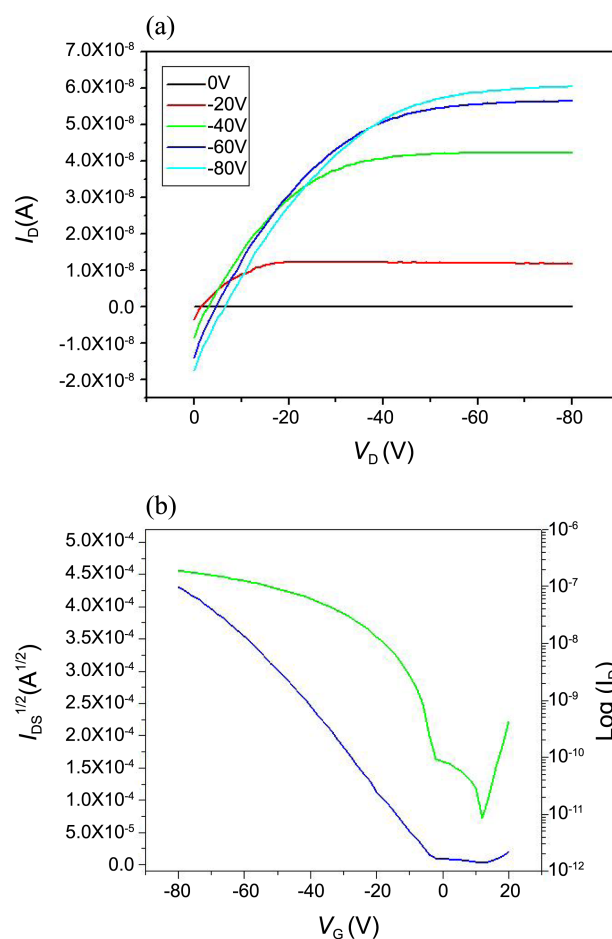


Figure 4. (a) Plot of drain current (I_D) versus drain-source voltage (V_{DS}) characteristics of the compound TFT at different gate voltage (V_G). (b) Plot I_D of V_G versus and $I_D^{1/2}$ versus V_G for a TFT prepared using PTVB as the semiconductor material.

Figure 3 shows the normalized UV-vis absorption and photoluminescence (PL) emission of a solution (chloroform) and of a spin-coating of polymeric film. While UV-vis absorption maximum appears at 428 nm in the solution, the maximum appears at 438 nm in the film. The absorption peak of the polymer in the film shows itself to be red-shifted and broader than that of the solution, which discrepancy is attributed to the planarization of the backbone and to intermolecular π stacking between polymer chains. While the PL emission in the solution is shown to take place at 595 nm, the PL emission in thin film shows at 595 nm. The PL spectra show 57 nm red shifts from solution to thin film. This shift means that the ordering interaction affects the form of the solution and the thin film of the polymer. Therefore, π -stacking in the polymer structure considerably increases from solution to film.

A semiconductor layer was deposited on ODTS-12-modified SiO_2 surface by spin-coating of the solution in chlorobenzene. The thin-film transistor was found to exhibit type p-channel FET characteristics in output and transfer curves (Figure 4(a) and 4(b)) at 100 °C annealed conditions. As can be seen in Figure 6, the FET mobility was calculated to be $8.59 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$, with current on/off ratio at 2.0×10^4

and the V_{th} at -2.3 V.

It is supposed that the low mobility of the polymer may be result of the amorphous conformation and the limited solubility of the polymer.

Conclusion

We have developed a new polymer by Ni-catalyzed Yamamoto-coupling reaction. The thermal, optical and electrochemical properties of the polymer were investigated. The polymer has a low HOMO level of -5.36 eV, indicating its good oxidation stability. The polymer thin-film transistor was found to exhibit type p-channel FET characteristics with hole mobility of $8.59 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ and on/off ratio of 2.0×10^4 . The somewhat low mobility may be the result of the amorphous nature of the polymer and its limited solubility.

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