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Synthesis and characterization of fluorine–thiophene-based π-conjugated polymers using coupling reaction

Jang Yong Lee [a], Yoon Jung Kwon [b], Je-Wan Woo [c], Doo Kyung Moon [a,*]

[a] *Department of Materials Chemistry and Engineering, Konkuk University, Seoul 143-701, Republic of Korea*
[b] *Department of Textile Engineering, College of Engineering, Konkuk University, Seoul 143-701, Republic of Korea*
[c] *Major in Industrial Chemistry, College of Natural Sciences, Sangmyung University, Seoul 110-743, Republic of Korea*

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Abstract

A solution processible fluorine–thiophene-based copolymers, namely poly[2,7-bis(4-octyl-2-thienyl)-9,9-dioctylfluorene-co-alt-5,5′-(2,2′-bithiophene)] (**P1**), poly[2,7-bis(3-octyl-2-thienyl)-9,9-dioctylfluorene-co-alt-5,5′-(2,2′-bithiophene)] (**P2**), poly[2,7-bis(3,3′-dioctyl-5,5′-bithien-2yl)-9,9′-dioctylfluorene-co-alt-5,5′-(2,2′-bithiophene)] (**P3**) were synthesized using Suzuki and Stille coupling reaction. The polymers showed weight loss starting around 400 °C indicative of good thermal stability. UV–vis properties and photoluminescence (PL) properties were investigated in toluene. **P1**, **P2** and **P3** exhibited the absorption maximum at 450, 428 and 435 nm and their PL spectrum peaked at 587, 559 and 560 nm, respectively. And all polymers, **P1**, **P2** and **P3**, showed electroluminescence (EL) spectrum peaked at 592, 595 and 607 nm in the range of orange red. The polymers were electrochemically active in oxidation regions. **P3** especially showed high oxidation stabilities in 1.17 V vs. Ag/Ag$^+$. And **P1** and **P3** showed higher crystallinity than **P2**, because they have a repeated unit of 3,3‴-dialkyl-quaterthiophene.

Keywords: Conjugated polymers; Light-emitting diodes (LED); Luminescence

1. Introduction

Recently, for semiconductor and conjugated polymer, many researches are being conducted in the application field of organic light-emitting diode (OLED) [1–8], organic thin film transistor (OTFT) [9,10], photovoltaic cell [11–13], and drive circuit of large area [14–16]. Thiophene-based poly(3-alkylthiophene) can be raised as a material having attracted attention in these sectors for last several decades [17,18]. But, since its oxidation stability is weak due to moisture or oxygen in air, researches to supplement its weakness are continued and materials utilizing fluorene have been studied much recently. Polyfluorene, which is a polymer of fluorene, is a blue light-emitting element, and it attracts attention in the field of organic EL. Moreover, polymer that forms copolymer with thiophene has wide band gap and excellent oxidation stability, and it attracts attention as an organic semiconductor material for OTFT [19,20]. In particular, studies are being conducted, which is attempted to enhance oxidation stability by introducing conjugated units between alkylthiophene of structurally head-to-head (HH) type and then shortening conjugation length as a whole [21]. It was reported actually in many researches that copolymer of fluorene and thiophene exhibits excellent thermal properties, oxidation stability and EL characteristics. It was also reported that mutually different light-emitting properties are exhibited depending upon the substitution location of alkyl radical of thiophene that forms copolymer with fluorene [7]. But, change of structural properties was not reported.

In this study, new π-conjugated copolymer was synthesized using the Suzuki coupling reaction and the Stille coupling reaction with fluorene having excellent oxidation stability and alkylthiophene having excellent electrical properties. Poly[2,7-bis(4-octyl-2-thienyl)-9,9-dioctylfluorene-co-alt-5,5′-(2,2′-bithiophene)](**P1**), poly[2,7-bis(3-octyl-2-thienyl)-9,9-dioctylfluorene-co-alt-5,5′-(2,2′-bithiophene)] (**P2**) and poly[2,7-bis(3,3′-dioctyl-5,5′-bithien-2yl)-9,9′-dioctylfluorene-co-alt-5,5′-(2,2′-bithiophene)] (**P3**) of synthesized copolymer was shown in Fig. 1. In the obtained copolymer it was confirmed by means of ^{1}H NMR and FT-IR that the polymer was synthesized successfully. Moreover, according to the result of XRD, the

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* Corresponding author. Tel.: +82 2 450 3498; fax: +82 2 450 3498.
E-mail address: dkmoon@konkuk.ac.kr (D.K. Moon).

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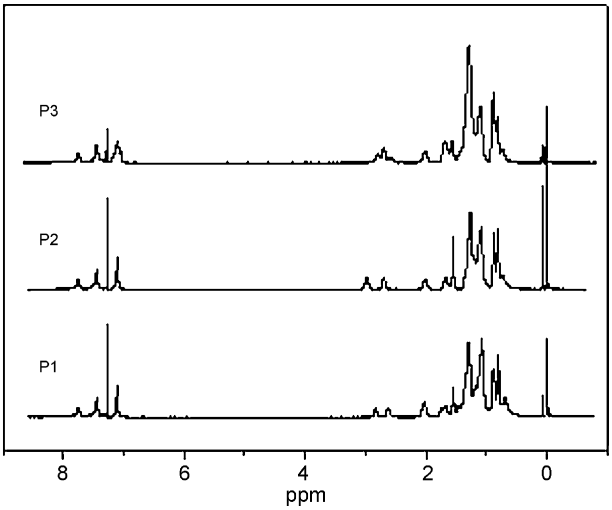


Fig. 1. ^{1}H NMR spectra of **P1**, **P2** and **P3**.

obtained copolymer exhibited mutually different crystal structures depending upon the coupling location of alkyl radical of alkylthiophene. Optical characteristics were reviewed with the measurement by UV–vis spectroscopy and photoluminescence (PL). Basic device was fabricated to confirm an application possibility of OLED into light-emitting material, and its light-emitting properties were investigated.

2. Experimental

2.1. Materials

All reagents and chemicals were purchased from Aldrich. Chloroform was dried over $CaCl_2$ and THF, toluene were dried over sodium. Other reagents and chemicals were used as received. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9′-dioctylfluorene (**2**), 2-(4-octyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**), 2-Bromo-3-octylthiophene (**4**) and 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (**5**) were prepared as described in the literatures [22–27].

2.2. Instruments

^{1}H NMR spectra were recorded at 400 MHz on a Bruker AMX400 spectrometer, using the resonances of the solvent as an internal reference. Chemical shift (δ) are reported in ppm downfield from TMS. UV–vis spectrometer were recorded on a Agilent 8453 UV–visible spectroscopy system. Photoluminescence (PL) spectra were measured using a Hitachi F-4500 spectrophotometer. The molecular weight of polymers was measured by GPC method, and polystyrene was used as a standard. TGA measurement was performed on a PerkinElmer TGA-7. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with Pt plate as working electrode, counter electrode, and Ag/Ag^+ electrode as reference electrode, in a 0.1-mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution.

2.3. Synthesis

2.3.1. 2,7-Bis(4-octyl-2-thienyl)-9,9-dioctylfluorene: *M6*

To a solution of 9,9′-dioctyl-2,7-dibromofluorene (5.5 g, 10 mmol) and 2-(4-octyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.5 g, 20 mmol) in toluene (100 mL) was added tetrakis(triphenylphosphine) palladium (0) (5 mol%). After stirred approximately for 10 min, degassed aqueous 2 M K_2CO_3 solution (50 mL) and several drops of Aliquot 336 were added. The reaction mixture was stirred at 85–90 °C for 12 h and then was poured into a 1-M HCl solution. CH_2Cl_2 (100 mL) was added to extract the product from the aqueous layer, and the combined organic layers were washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, and the solvent was removed by rotary evaporation, and the residue was purified by column chromatography to provide 7.2 g (93%) of the title product as a yellowish green liquid. ^{1}H NMR ($CDCl_3$): δ = 7.70 (d, 2H), 7.41 (d, 2H), 7.39 (s, 2H), 7.02 (s, 2H), 6.92 (s, 2H), 2.68 (t, 4H), 2.53 (t, 4H), 1.62 (m, 4H), 1.24 (m, 20H), 1.18 (m, 4H), 1.05 (m, 20H), 0.86 (t, 6H), 0.80 (t, 6H).

2.3.2. 2,7-Bis(3-octyl-2-thienyl)-9,9-dioctylfluorene: *M7*

To a solution of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9′-dioctylfluorene (5.5 g, 10 mmol) and 2-bromo-3-octylthiophene (5.5 g, 20 mmol) in toluene (100 mL) was added tetrakis(triphenylphosphine) palladium (0) (5 mol%). The following reaction was followed to react under the conditions given for the synthesis of **6**. The compound was purified by column chromatography to provide 7.17 g (92%) of the title product as a yellowish green liquid. ^{1}H NMR ($CDCl_3$): δ = 7.70 (d, 2H), 7.41 (d, 2H), 7.39 (s, 2H), 7.24 (d, 2H), 7.00 (d, 2H), 2.68 (t, 4H), 2.00 (t, 4H), 1.53 (m, 4H), 1.24 (m, 20H)1.18 (m, 4H), 1.05 (m, 20H), 0.86 (t, 6H),0.80 (t, 6H).

2.3.3. 2,7-Bis(5-bromo-4-octylthien-2-yl)-9,9-dioctylfluorene: *M9*

To a solution 2,7-bis(4-octylthien-2yl)-9,9-dioctylfluorene (7.2 g, 9.3 mmol) in $CHCl_3$ was added of *N*-bromosuccinimide (3.48 g, 19.5 mmol) was added in portions over 40 min to a solution. The reaction mixture was stirred at 40–45 °C for 24 h. The reaction mixture was poured onto ice water and extracted several times with CH_2Cl_2. The combined organic layers were washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, and the solvent was removed by rotary evaporation, and the residue was purified by column chromatography to provide 6.97 g (80%) of the title product as a yellowish green liquid. ^{1}H NMR ($CDCl_3$): δ = 7.70 (d, 2H), 7.49 (d, 2H), 7.43 (s, 2H), 7.05 (s, 2H), 2.63 (t, 4H), 1.94 (t, 4H), 1.58 (m, 4H), 1.24 (m, 20H), 1.18 (m, 4H), 1.05 (m, 20H), 0.86 (t, 6H), 0.80 (t, 6H).

2.3.4. 2,7-Bis(5-bromo-3-octylthien-2-yl)-9,9-dioctylfluorene: *M10*

2,7-Bis(3-octylthien-2yl)-9,9-dioctylfluorene (7.17 g, 9.2 mmol) and NBS (3.48 g, 19.5 mmol) in 50 mL $CHCl_3$ were allowed to react under the conditions given for the synthesis of **9**. After the usual workup, the compound was purified by column chromatography to provide 7.2 g (78%) of the title product as a yellowish green liquid. ^{1}H NMR ($CDCl_3$): $\delta = 7.70$ (d, 2H), 7.37 (d, 2H), 7.35 (s, 2H), 6.94 (s, 2H), 2.63 (t, 4H), 1.94 (t, 4H), 1.58 (m, 4H), 1.24 (m, 20H), 1.18 (m, 4H), 1.05 (m, 20H), 0.86 (t, 6H), 0.80 (t, 6H).

2.3.5. 2,7-Bis(3,3′-dioctyl-5,5′-bithien-2yl)-9,9-dioctylfluorene: ***M8***

To a solution of 2,7-bis(5-bromo-3-octylthien-2yl)-9,9-dioctylfluorene (1.87 g, 2 mmol) and 2-(4-octyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.29 g, 4 mmol) in toluene (20 mL) was added tetrakis(triphenylphosphine) palladium (0) (5 mol%). The following reaction was followed to react under the conditions given for the synthesis of **6**. The compound was purified by column chromatography to provide 2.13 g (91%) of the title product as a yellowish green liquid. ^{1}H NMR ($CDCl_3$): $\delta = 7.72$ (d, 2H), 7.42 (d, 2H), 7.39 (s, 2H), 7.05 (s, 2H), 7.02 (s, 2H), 6.79 (s, 2H), 2.63 (t, 4H), 2.54 (t, 4H), 1.64 (m, 4H), 1.24 (m, 20H), 1.18 (m, 4H), 1.05 (m, 20H), 0.86 (t, 6H), 0.80 (t, 6H).

2.3.6. 2,7-Bis(2′-bromo-3,3′-octyl-5,5′-bithien-2yl)-9,9-dioctylfluorene: ***M11***

2,7-Bis(3,3′-dioctyl-5,5′-bithien-2yl)-9,9-dioctylfluorene (2.13 g, 1.82 mmol) and NBS (0.68 g, 3.82 mmol) in 15 mL $CHCl_3$ were allowed to react under the conditions given for the synthesis of **9**. After the usual workup, the compound was purified by column chromatography to provide 2.12 g (87%) of the title product as a yellowish green liquid. ^{1}H NMR ($CDCl_3$): $\delta = 7.73$ (d, 2H), 7.43 (d, 2H), 7.39 (s, 2H), 6.99 (s, 2H), 6.87 (s, 2H), 2.63 (t, 4H), 2.54 (t, 4H), 1.64 (m, 4H), 1.24 (m, 20H), 1.18 (m, 4H), 1.05 (m, 20H), 0.86 (t, 6H), 0.80 (t, 6H).

2.4. General procedure of polymerization through the Stille reaction

To a mixture of $Pd(PPh_3)Cl_2$(1.0 mol-%), 5,5′-bis(trimethylstannyl)-2,2′-bithiophene and **9–11**, respectively, was added a degassed mixture of toluene (|monomer| = 0.25 M) and 2 M K_2CO_3 aqueous solution (3:2 in volume). The mixture was vigorously stirred at 85–90 °C for 48 h under the nitrogen. After the mixture was cooled to room temperature, it was poured into the methanol. A powder was obtained by filtration was reprecipitated with methanol several times. The polymer was further purified by washing methanol and acetone, respectively, in a Soxhlet apparatus for 24 h and dried under reduced pressure at 50 °C.

2.4.1. Poly[2,7-bis(4-octyl-2-thienyl)-9,9-dioctylfluorene-co-alt-5,5′-(2,2′-bithiophene)]: ***P1***

Red solid 0.3 g (63.7%). ^{1}H NMR ($CDCl_3$): $\delta = 7.70$ (d, 2H), 7.58 (d, 2H), 7.54 (s, 2H), 7.25 (s, 2H), 7.10 (d, 2H), 7.05 (d, 2H), 2.63 (t, 4H), 1.94 (t, 4H), 1.58 (m, 4H), 1.24 (m, 20H), 1.18 (m, 4H), 1.05 (m, 20H), 0.86 (t, 6H), 0.80 (t, 6H).

2.4.2. Poly[2,7-bis(3-octyl-2-thienyl)-9,9-dioctylfluorene-co-alt-5,5′-(2,2′-bithiophene)]: ***P2***

Red solid 0.36 g (76.5%). ^{1}H NMR ($CDCl_3$): $\delta = 7.70$ (d, 2H), 7.49 (d, 2H), 7.43 (s, 2H), 7.25 (s, 2H), 7.10 (d, 2H), 7.05 (d, 2H), 2.63 (t, 4H), 1.94 (t, 4H), 1.58 (m, 4H), 1.24 (m, 20H), 1.18 (m, 4H), 1.05 (m, 20H), 0.86 (t, 6H), 0.80 (t, 6H).

2.4.3. Poly[2,7-bis(3,3′-dioctyl-5,5′-bithien-2yl)-9,9′-dioctylfluorene-co-alt-5,5′-(2,2′-bithiophene)]: ***P3***

Red solid 0.35 g (53%). ^{1}H NMR ($CDCl_3$): $\delta = 7.74$ (d, 2H), 7.43 (d, 2H), 7.39 (s, 2H), 7.10 (s, 2H), 7.05 (s, 2H), 6.99 (d, 2H), 6.87 (d, 2H), 2.63 (t, 4H), 2.54 (t, 4H), 1.64 (m, 4H), 1.24 (m, 20H), 1.18 (m, 4H), 1.05 (m, 20H), 0.86 (t, 6H), 0.80 (t, 6H).

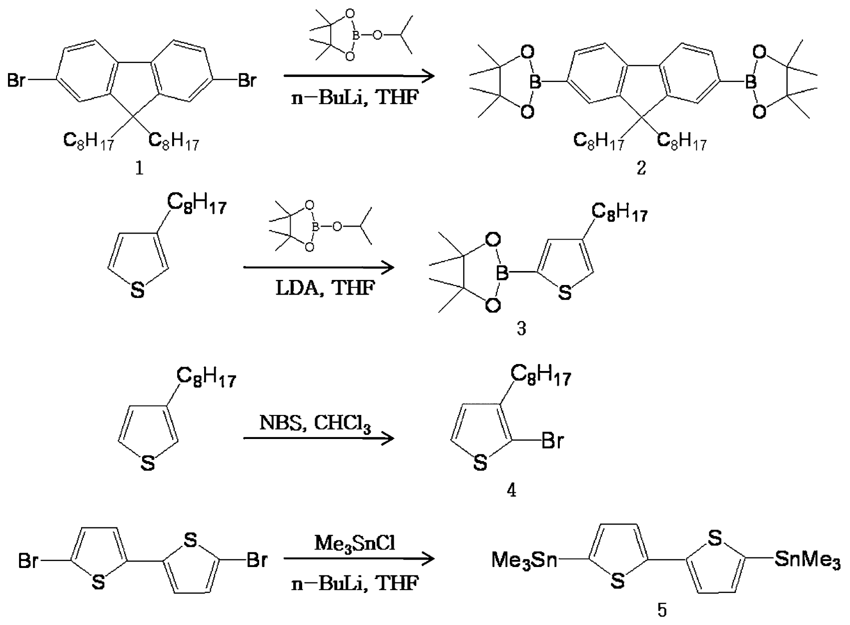
2.5. Device fabrication and characterization

An LED was fabricated on prepatterned indium tin oxide (ITO) with a sheet resistance of 10–20 $\Omega/\square$. The substrate was ultrasonically cleaned with acetone, detergent, deionized water, and isopropyl alcohol. An oxygen plasma treatment was performed for 10 min as the final step of the substrate cleaning, to improve the contact angle just before film coating. Onto ITO glass, a layer of polyethylenedioxythiophene–polystyrene sulfonic acid (PEDOT–PSS) film was spin-coated from its aqueous dispersion (Baytron P 4083, Bayer AG.) for 30 s at the speed of 4000 rpm, aiming to improve the hole injection and to prevent the possibility of leakage. The PEDOT–PSS film was dried at 80 °C for 2 h in a vacuum oven. The solution of copolymers in toluene was prepared in a nitrogen-filled dry box and spin-coated on top of the ITO/PEDOT–PSS surface for 40 s at the speed of 1000 rpm. A thin layer of lithium (20 Å) as an electron injection cathode and the subsequent 200-nm thick aluminum protection layers were then thermally deposited by vacuum evaporation. The cathode area defines the active area of the device. The EL layer spin-coating process and the device performance tests were carried out in air conditions. Luminance was calibrated with a PR-670 SpectraScan Spectrophotometer (Photo Research) after the encapsulation of devices with UV-curing epoxy and thin cover metal can.

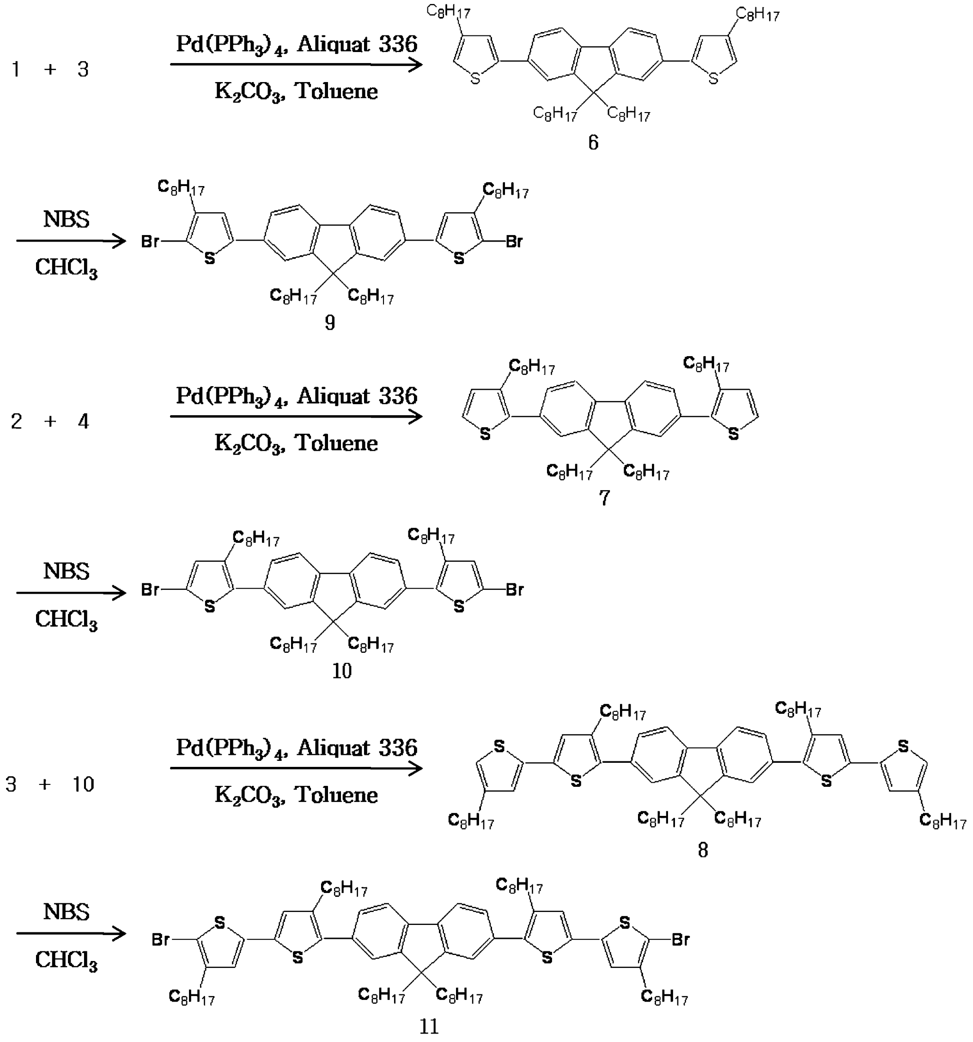
3. Results and discussion

In Scheme 1, the synthesis route of the monomer, which is for synthesizing co-monomer of thiophene and fluorene having been confirmed with ^{1}H NMR, and 5,5′-bis(trimethylstannyl)-2,2′-bithiophene was exhibited.

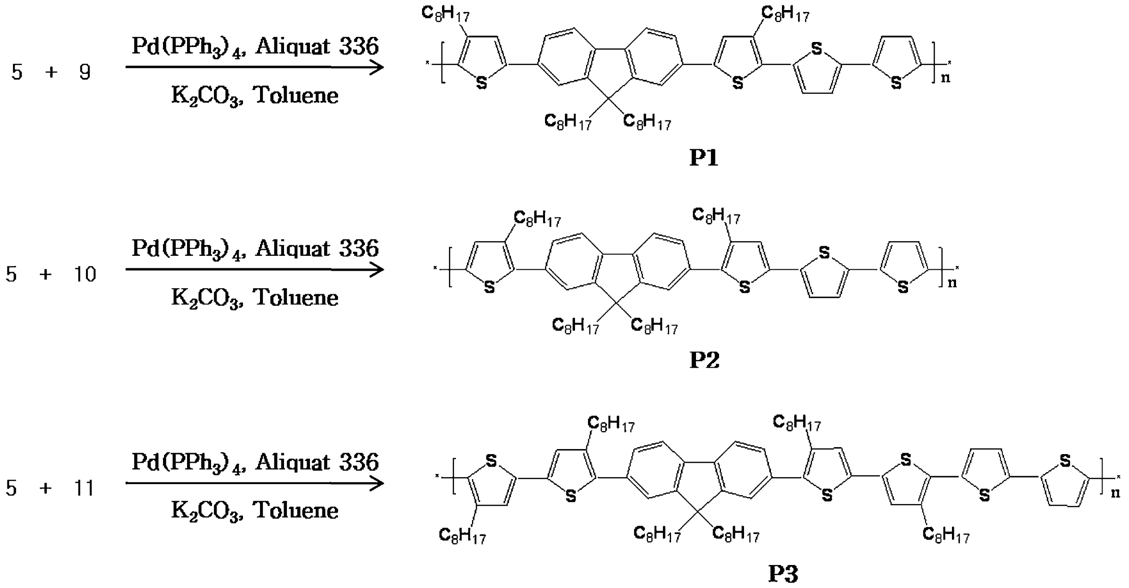
Scheme 2 shows the synthesis route of the monomers for polymerization. After each monomer is synthesized through the Suzuki coupling reaction with the monomer shown in Scheme 1, brome radical was introduced into its both ends in order to use it in the Stille reaction. In the synthesis of **M6**, it could be confirmed by means of ^{1}H NMR that the peak of doublet, doublet, singlet, doublet, and doublet was exhibited respectively in 7.70, 7.39, 7.35, 7.23, and 6.99 ppm. In the monomer **9** in which Br radical was introduced, it could be confirmed that proton of 6.92 ppm disappeared in **6**. In **7** it could be confirmed



Scheme 1. Synthesis of monomers.



Scheme 2. Synthesis of monomers for polymerization.



Scheme 3. Synthetic scheme of polymers (**P1**, **P2** and **P3**).

that the peak of doublet, doublet, singlet, singlet, and singlet was exhibited and synthesized respectively in 7.70, 7.41, 7.39, 7.24, and 7.00 ppm. In the monomer **10** obtained through its bromination, it could be confirmed that brome radical was introduced successfully while doublet peak disappeared in 7.24 ppm of **7** and doublet peak was changed into singlet peak in 7.00 ppm. Moreover, it could be confirmed in **8** that the peak of doublet, doublet, singlet, singlet, singlet, and singlet appeared respectively in 7.72, 7.42, 7.39, 7.05, 7.02, and 6.79 ppm in an aromatic domain. In the monomer **11** obtained through its bromination, it could be confirmed that brome radical was introduced considering that singlet peak disappeared in 7.02 ppm.

The route to synthesize conjugated copolymers (**P1**, **P2** and **P3**) by using the Stille coupling reaction was shown in Scheme 3. Synthesized polymers (**P1**, **P2** and **P3**) were dissolved well in general non-polar organic solvents such as chloroform, THF, toluene, and xylene, but those were not dissolved well in organic solvents such as NMP, DMF, and DMSO.

The structures of the obtained copolymers were confirmed with ^{1}H NMR. In Fig. 1, the results of ^{1}H NMR for **P1**, **P2** and **P3** were shown. The obtained polymers exhibited a broad peak of doublet, doublet, singlet, singlet, doublet, and doublet respectively in 7.70, 7.58, 7.54, 7.25, 7.10, and 7.05 ppm.

The yield of polymer and the result of molecular weight measured with the gel permeation chromatography (GPC) were shown in Table 1. **P1**, **P2** and **P3** were obtained respectively in the yield of 64%, 77% and 53%. The molecular weight of **P2** obtained in a relatively high yield exhibited a high value comparing with molecular weights of **P1** and **P3**. The distribution of molecular weight also appeared to be wide ($M_w/M_n = 3.1$). It is a result obtained due to more advanced polymerization since octyl radical, which is a substitution radical of thiophene derivative making a coupling reaction with 5,5′-bis(trimethylstannyl)-2,2′-bithiophene and substituted in the No. 3 location, has a smaller three-dimensional barrier upon polymerization comparing with the monomer substituted in the No. 4 location.

In the XRD result for polymer powder shown in Fig. 2, **P2** of high molecular weight exhibited an amorphous structure, and **P1** and **P3** exhibited peaks indicating inter-molecular regularity near $2\theta = 8$ and at $2\theta = 20$. It is because **P1** and **P3** polymers have a repetition unit (3,3‴-dioctyl-quaterthiophene) having a shape in which bithiophene is located between head-to-head (HH) 3-alkylthiophene showing a high regularity. It is a result similar to one appeared in poly(3,3′-dioctyl-quaterthiophene) that does not have a fluorene repetition unit [22]. Regularity shown as it is the case with **P1** and **P3** means stacking to be made well between molecules. It can be explained that intermolecular crystallinity, which is a requirement of organic semiconductor for OTFT, depends also upon substitution locations of functional radicals.

Table 1
Molecular weights, PDI, and yields of polymers prepared by Stille coupling reaction, spectrum data and calculated energy levels.

Copolymers	M_n	M_W	PDI	Polymer yield (%)	λ_{max} (nm)			HOMO (eV)	LUMO (eV)	ΔE (eV)
					UV absorption	PL emission	EL emission			
P1	12,693	14,677	1.16	64	450	587	592,645	−53	−3.16	2.14
P2	31,503	97,474	3.1	77	428	559	595,640	−537	−3.09	2.28
P3	17,582	24,251	138	53	435	560	607	−5.24	−3.0	2.24

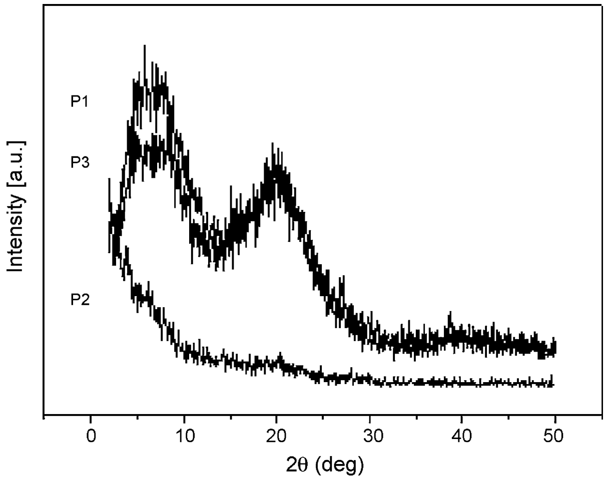


Fig. 2. XRD patterns of **P1**, **P2** and **P3** powder.

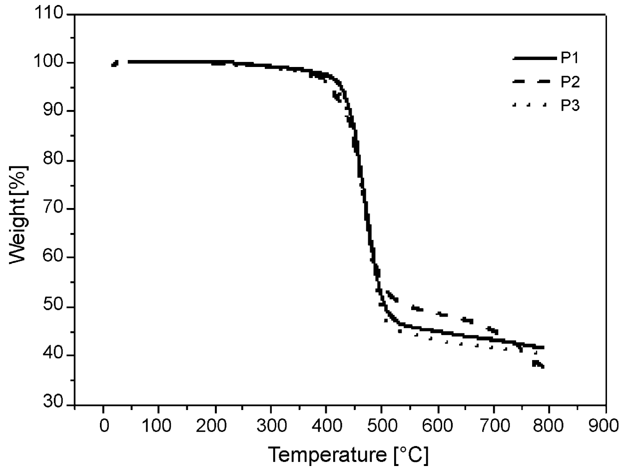


Fig. 3. Thermograms of **P1**, **P2** and **P3** measured in a nitrogen atmosphere.

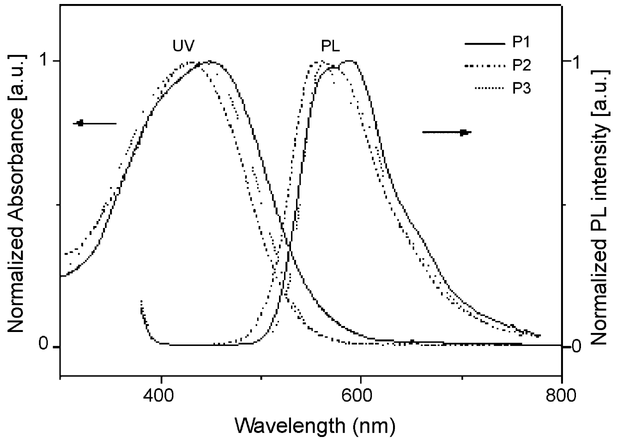


Fig. 5. UV–vis and photoluminescence spectra of **P1**, **P2** and **P3** in toluene.

In Figs. 3 and 4, the results of thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) indicating thermal properties of the synthesized polymers were shown. Each polymer exhibited excellent thermal stability indicating T_d above 400 °C **P1** and **P2** exhibited T_g respectively at 87 and 76 °C, but **P3** was not clear. It is considered that it was caused by structural change due to bithiophene of TT (tail-to-tail) structure having a high-energy barrier.

UV and PL spectra were shown in Fig. 5. **P1**, **P2**, and **P3** exhibited peak UV absorption respectively in 450, 428 and 435 nm, and also showed a strong PL spectrum peak respectively in 587, 559 and 560 nm. These are quite close to the absorption onset. Accordingly, very little energy is lost during inter- or intra-molecular reorganization and relaxation processes in the excited state. The UV and PL characteristics of the obtained polymers were shifted into the side of longer wavelength than the UV (λ_{max} = 401 nm) and PL (λ_{max} = 482 nm) spectrum peak of poly[2,7-(9,9-dihexyl-fluorene)-co-alt-5,5′-(4,4′-didecyl-2,2′-bithiophene)] already announced [7]. It is considered that it was caused by longer conjugation length due to the introduction of thiophene and bithiophene into the existing structure.

The EL spectrum of the synthesized polymer were shown in Fig. 6. The device vapor-deposited ITO as anode over the glass substrate, and then it was washed using ultrasonic wave and UV ozone before its use, and also its surface was reformed. PEDOT/PSS was spin-coated over there for 30 s at 4000 rpm

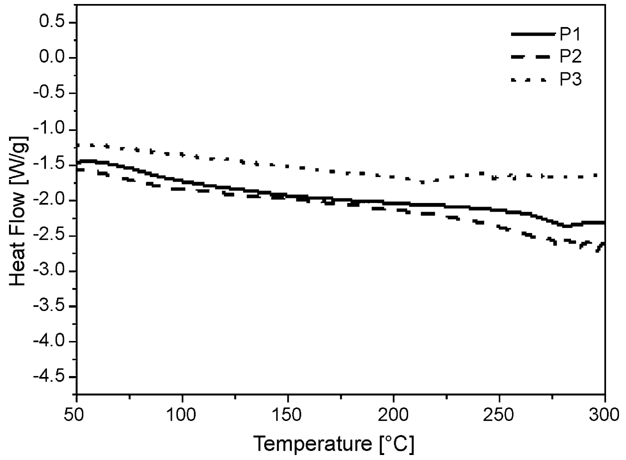


Fig. 4. DSC traces of **P1**, **P2** and **P3** measured in a nitrogen atmosphere.

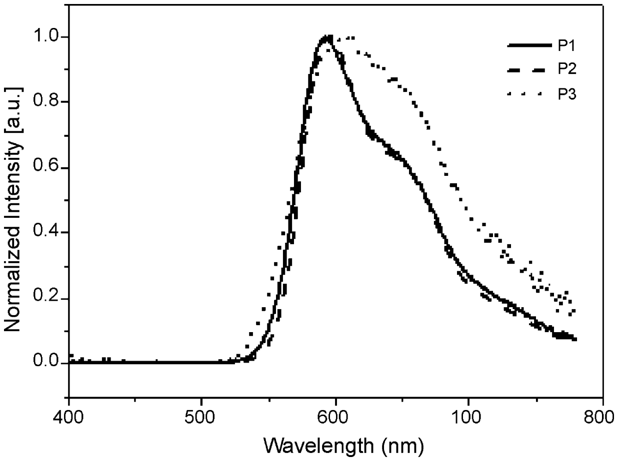


Fig. 6. Electroluminescence (EL) spectra of **P1**, **P2** and **P3**.

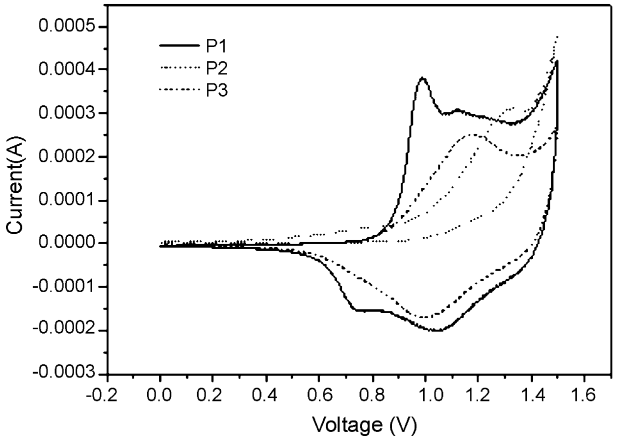


Fig. 7. Cyclo voltammograms of films of **P1**, **P2** and **P3** on Pt plates in an CH_3CN solution of Bu_4NPF_6 with a sweep range 0–1.5 V vs. Ag/Ag^+.

with vacuum transportation layer, and then polymer of light-emitting material was spin-coated for 40 s at the speed of 1000 rpm. LiF (20 Å):Al (2000 Å) was vapor-deposited as cathode by using the thermal evaporator. Finally it was encapsulated using the metal can within the glove box to prevent oxidation by moisture and oxygen. As a result of EL measured with the device fabricated like this, peak light-emitting wavelengths of **P1**, **P2**, and **P3** are respectively 592 nm and a shoulder peak at 645, 595 nm and a shoulder peak at 640, 607 nm, and it could be confirmed that those emit light in an orange-red domain.

Electrochemical behavior of polymers confirmed using the cyclic voltametry (CV) was shown in Fig. 7. As **P1** exhibited p-doping peak near 1 V (vs. Ag/Ag^+) and **P3** exhibited p-doping peak near 1.17 V (vs. Ag/Ag^+), it could be seen that those exhibited very stable oxidation stability. It is considered that such difference was caused by energy barrier increased due to TT (tail-to-tail) alkylthiophene of **P3**. But **P2** showed an unclear CV curve due to unstable electrochemical behavior. p-Doping peak of **P2** is not exhibited although p-doping peak of **P2** is exhibited on 1.3 V. It is considered that oxidation stability of **P2**, which is turned out to be without crystallinity, is relatively low.

4. Conclusion

The polymers based on fluorene and alkylthiophene was synthesized successfully using the Stille coupling reaction. The monomers to synthesize them were obtained using the Suzuki coupling reaction, and their structures were confirmed with the ^1H NMR and FT-IR. The obtained polymers showed excellent thermal properties exhibiting mass reduction within 5% up to 400 °C, and **P1**, **P2** showed T_g respectively at 87 and 76 °C, but **P3** was not clear. As a result of XRD analysis, **P1** and **P3** exhibited higher degree of crystallinity and regularity comparing with **P2**. It is considered that it is caused by repetition units of 3,3′-dialkyl-quaterthiophene, of which high regularity was confirmed already. It indicates that **P1** and **P3** have a potentiality to be used as a material for OTFTs.Furthermore, as a result of cyclic voltametry, **P3** exhibited oxidation peak at 1.17 V, and thereby it was confirmed to have also excellent oxidation stability. **P1**, **P2**, and **P3** exhibited peak UV absorption respectively at 450, 428 and 435 nm. As a result of dissolving them into toluene and then irradiating UV-ray of 365 nm, PL phenomenon could be confirmed in all of them, and their light-emitting wavelengths were respectively 587, 559, and 560 nm. In the PL light-emitting wavelength of these polymers, the distribution of light-emitting wavelength appeared to be narrow centered on the peak light-emitting wavelength. As a result of fabricating a device and then measuring EL (electro-luminescence), all of **P1**, **P2**, and **P3** exhibited light-emitting wavelength of 592, 595 and 607 nm in the orange-red domain.

In this result, it is expected that these materials can be applied into organic semiconductor for OTFT or organic photovoltaic cell as well as light-emitting polymer for OLED in future, and also performance improvement following the introduction location of the polymer's substitution radical is expected.

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