

Synthesis of Soluble Polythiophene Partially Containing 3,4-Ethylenedioxythiophene and 3-Hexylthiophene by Polycondensation

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Abstract

A novel poly(quinquethiophene) partially containing 3,4-ethylenedioxythiophene (EDOT) and 3-hexylthiophene, poly(3,3''''-dihexyl-3',4',3''',4''''-diethylenedioxy-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene), was synthesized by three types of polycondensations. Among them, direct C-H coupling reaction gave the polymer with the highest molecular weight. The resulting polymer was soluble in common organic solvents. Absorption and fluorescence spectra of the polymer showed a remarkable red-shift compared with the corresponding monomer due to the expansion of effective π -conjugation length.

Keywords

Polycondensation, Polythiophene, Ethylenedioxythiophene, Alkylthiophene, Solubility

1. Introduction

Since the late 1970s, π -conjugated polymers have attracted a great deal of attention from many researchers, especially in the field of plastic electronics [1]-[5]. Among them, polythiophenes have been well investigated as the most significant class of π -conjugated polymers. Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most popular polythiophene derivatives and has excellent properties such as stability of the oxidized state, moderate band-gap energy, low oxidation potential, and optical transparency in the visible spectral region [5]-[11]. These properties result from the synergistic associations of the strong donor effect of the ethylenedioxy groups

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with the propensity of 3,4-ethylenedioxythiophene (EDOT) to develop noncovalent intramolecular S-O interaction [12]-[17]. This S-O interaction, on the other hand, leads to a rigid polymer backbone to reduce the solubility in solvents. Thus, PEDOT obtained by electrochemical oxidation of EDOT is insoluble in common organic solvents.

Until now, several types of polythiophenes partially containing EDOT have been synthesized and successfully applied to electrochromic devices because of the stable nature of the oxidized state [18]-[24]. However, there are few reports on the characterization of these polymers and their charge transport properties. Recently, we have synthesized a polythiophene partially containing EDOT unit in the repeat unit, poly(3',4'-ethylenedioxy-2,2':5',2''-terthiophene) (**polyTET**), by electrolytic polymerization of the EDOT-containing terthiophene, 3',4'-ethylenedioxy-2,2':5',2''-terthiophene (**TET**) (**Scheme 1**) [25]. The resulting polymer was found to be soluble in dimethylsulfoxide (DMSO), tetrahydrofuran (THF) and dimethylformamide (DMF), and could be characterized by ¹H NMR and mass spectroscopies, and gel permeation chromatography (GPC). The electrical conductivities of **polyTET** were measured as a function of oxidation levels, and the highest conductivity was found to be comparable to that of polythiophene obtained by the electrolytic polymerization of unsubstituted thiophene. However, the molecular weight of the polymer was not so high because the cationic species formed by electrochemical oxidation were stable and could not be polymerized, and the film-forming property was very poor.

Poly(arylene)s including polythiophenes have been synthesized not only by electrolytic polymerizations [26], but also by chemically oxidative polymerizations [27] [28] and organometallic polycondensations [29]. Since the polycondensations afford the polymers with well-controlled bonding between monomeric units, many types of polycondensations have been developed.

In this paper, three types of polycondensations using (1) Suzuki, (2) Stille, and (3) direct C-H coupling reactions were investigated to obtain a novel EDOT-containing polythiophene, poly(3,3''''-dihexyl-3',4',3''',4''''-diethylenedioxy-2,2':5',2''':5''',2''''':5''''',2''''''-quinquethiophene) (**polyHE5T**) (**Figure 1**).

2. Experimental

2.1. Materials and Instrumentation

n-Hexane, toluene, THF, dimethylacetamide (DMAc), dichloromethane, diethyl ether, acetic acid (AcOH), and acetonitrile were purified by conventional methods and used immediately after purification. All reagents and organic solvents were purchased from Tokyo Chemical Industry, Wako Pure Chemical Industries, Sigma-Aldrich, Kanto Chemical, and Nacalai Tesque and were used without further purification. 2-Bromo-3-hexylthiophene was synthesized from 3-bromothiophene according to the literature [30] [31]. *N*-Bromosuccinimide (NBS) was purified by recrystallization from benzene and dried under vacuum.

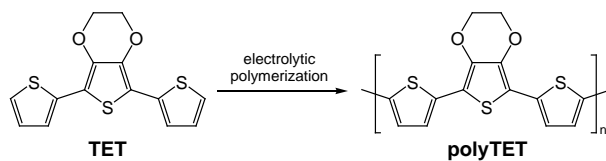
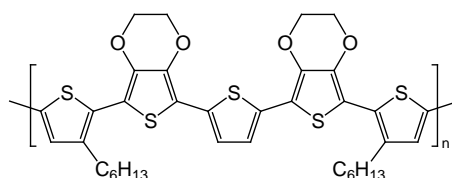
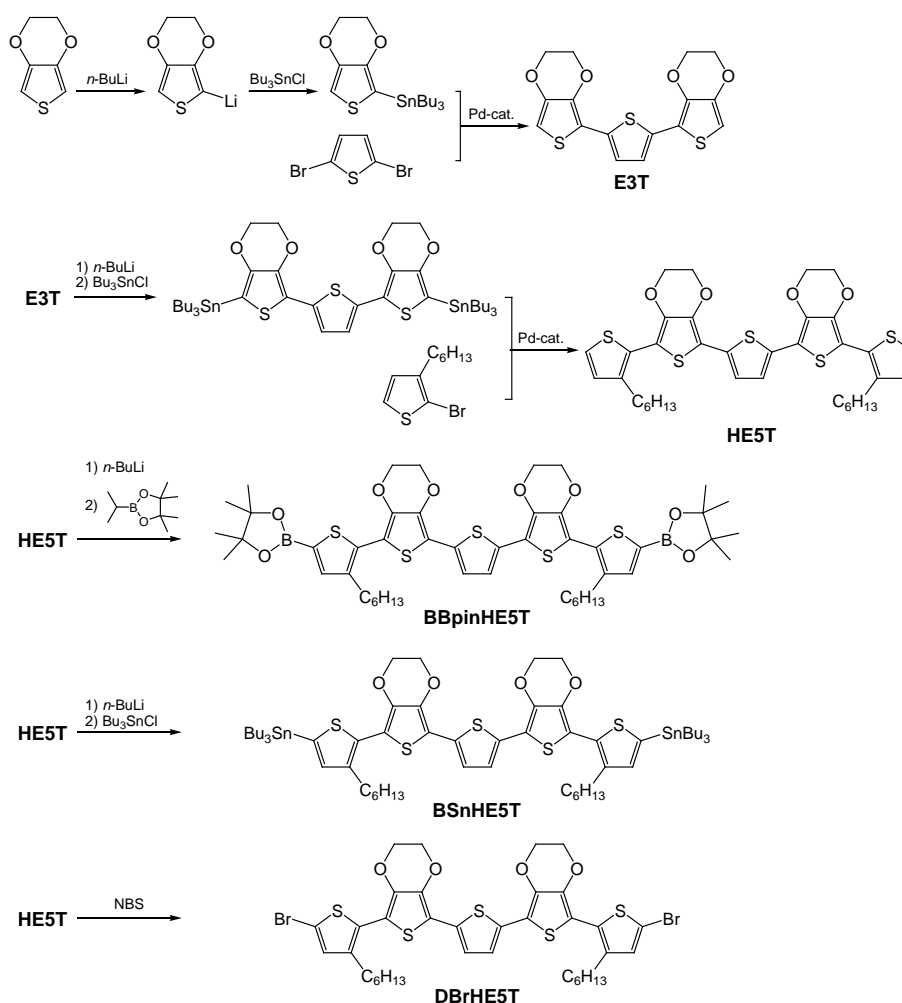
¹H NMR spectra were recorded by a 500 MHz spectrometer (Varian Inc., NMR System 500). IR spectra were taken on a Perkin Elmer Spectrum One FT-IR spectrophotometer by ATR method. Molecular weights of the resulting polymers were analyzed by a GPC coupled with an UV detector (Shimadzu Corp., SPD-10A). Combination of Shodex KF-801 (30 cm, exclusion limit: $M_n = 1.5 \times 10^3$, polystyrene) KF-802 (30 cm, exclusion limit: $M_n = 5.0 \times 10^3$, polystyrene) and KF-803L (30 cm, exclusion limit: $M_n = 7.0 \times 10^4$, polystyrene) columns (linear calibration down to $M_n = 100$) were used for molecular weight analysis with THF (1.0 dm³·min⁻¹) as an eluent. Measurements of mass spectroscopy and the elemental analysis were made using a High Performance Gas Chromatograph—Time-of-Flight Mass Spectrometer (JEOL, JMS-T100GCV (Accu TOFGCV 4G)) and an Elemental Analyzer (PerkinElmer, 2400 Series II CHNS/O), respectively. UV-vis absorption and fluorescence spectra were measured by a Shimadzu UV-3150 spectrophotometer and a Hitachi F-4500 spectrophotometer, respectively. Fluorescence quantum yields (Φ) were determined by a Hamamatsu C9920-01 equipped with CCD by using a calibrated integrating sphere system.

2.2. Monomer Synthesis

The synthetic routes of the monomers are shown in **Scheme 2** and the detailed synthetic processes are described below.

2.2.1. Synthesis of 3,4,3''',4''''-Diethylenedioxy-2,2':5',2''-terthiophene (**E3T**)

To a solution of 3,4-ethylenedioxythiophene (2.8 g, 20 mmol) in THF (60 mL) at -78°C was added 15 mL (24 mmol) of *n*-butyllithium (1.65 M in *n*-hexane) by syringe. The mixture was stirred at -78°C for 30 min.

Scheme 1. Synthesis of **polyTET** by electrolytic polymerization.Figure 1. Chemical structure of **polyHE5T**.

Scheme 2. Synthetic route of monomers.

Tri(*n*-butyl)tin chloride (5.7 g, 18 mmol) was added to the solution, and the resulting mixture was stirred at -78°C for 30 min, warmed to room temperature, and stirred further for 3 h. The solvent was removed *via* rotary evaporation, and *n*-hexane was added to the residue. The soluble fraction was extracted by filtration. The filtrated solution was added to a solution of tetrakis(triphenylphosphine)palladium (720 mg, 0.6 mmol) and 2,5-dibromothiophene (1.8 g, 7.6 mmol) in DMF (50 mL). The solution was stirred at 100°C for 12 h. The mixture

was poured into sat.aq. NH_4Cl (400 mL) and extracted with dichloromethane. The extract was then successively washed with water. After being dried over anhydrous Na_2SO_4 , the solvent was evaporated, and the residue was purified by column chromatography on silica gel with a mixed solvent of *n*-hexane and ethyl acetate ($v/v = 3/2$) to afford a yellow solid (2.7 g, 7.3 mmol). Yield: 96%. $^1\text{H NMR}$ (500 MHz, CDCl_3 , δ , ppm): 4.23 - 4.37 (m, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 6.21 (s, 2H, thienyl-*H*), 7.12 (s, 2H, thienyl-*H*). FTIR (ATR, ν , cm^{-1}): 3113, 3103, 3067, 2979, 2924, 2871, 1530, 1481, 1434, 1362, 1329, 1165, 1137, 1071, 1053, 1017, 968, 905, 881, 802, 710, 678. Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{O}_4\text{S}_3$: C, 52.73; H, 3.32; S, 26.39. Found: C, 53.11; H, 3.30; S, 25.53. HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{12}\text{O}_4\text{S}_3$ 363.9898 (M^+), found 363.9890(M^+).

2.2.2. Synthesis of 3,3''''-Dihexyl-3',4',3''',4''''-diethylenedioxy-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene (HE5T)

To a solution of **E3T** (1.5 g, 4.0 mmol) in THF (40 mL) at -78°C was added 2.7 mL (4.4 mmol) of *n*-butyllithium (1.65 M in *n*-hexane) by syringe. The mixture was stirred at -78°C for 30 min. Tri(*n*-butyl)tin chloride (1.4 g, 4.3 mmol) was added to the solution, and the resulting mixture was stirred at -78°C for 30 min, warmed to room temperature, and stirred further for 1 h. The solvent was removed *via* rotary evaporation, and *n*-hexane was added to the residue. The soluble fraction was extracted by filtration. The filtrated solution was added to a solution of tetrakis(triphenylphosphine)palladium (200 mg, 0.17 mmol) and 2-bromo-3-hexylthiophene (1.8 g, 7.2 mmol) in DMF (40 mL). The solution was stirred at 100°C for 12 h. The mixture was poured into sat.aq. NH_4Cl (400 mL) and extracted with dichloromethane. The extract was then successively washed with water. After drying over anhydrous Na_2SO_4 , the solvent was evaporated, and the residue was purified by column chromatography on silica gel with a mixed solvent of *n*-hexane and dichloromethane ($v/v = 2/3$) to afford a dark red solid (1.6 g, 2.3 mmol). Yield: 58%. $^1\text{H NMR}$ (500 MHz, acetone- d_6 , δ , ppm): 0.88 (t, $J = 7.03$ Hz, 6H, CH_3), 1.25 - 1.42 (m, 12H, $(\text{CH}_2)_3\text{CH}_3$), 1.60 - 1.68 (m, 4H, thienyl- CH_2CH_2), 2.76 (t, $J = 7.77$ Hz, 4H, thienyl- CH_2), 4.38 - 4.51 (m, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 7.02 (d, $J = 5.22$ Hz, 2H, thienyl-*H*), 7.23 (s, 2H, thienyl-*H*), 7.43 (d, $J = 5.22$ Hz, 2H, thienyl-*H*). FTIR (ATR, ν , cm^{-1}): 3097, 3077, 3061, 2953, 2924, 2868, 2854, 1527, 1491, 1438, 1360, 1322, 1096, 1081, 1062, 1013, 959, 914, 874, 830, 782, 689, 650, 478. Anal. Calcd for $\text{C}_{36}\text{H}_{40}\text{O}_4\text{S}_5$: C, 62.03; H, 5.78; S, 23.00. Found: C, 61.88; H, 5.58; S, 22.67. HRMS (EI) m/z calcd for $\text{C}_{36}\text{H}_{40}\text{O}_4\text{S}_5$ 696.1530 (M^+), found 696.1539 (M^+).

2.2.3. Synthesis of 2,5''''-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,3''''-dihexyl-3',4',3''',4''''-diethylenedioxy-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene (BBpinHE5T)

To a solution of **HE5T** (0.48 g, 0.69 mmol) in THF (7 mL) at -78°C was added 0.8 mL (2.1 mmol) of *n*-butyllithium (2.6 M in *n*-hexane) by syringe. The mixture was stirred at -7°C for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.32 g, 1.7 mmol) was added to the solution, and the resulting mixture was stirred at -78°C for 90 min, warmed to room temperature, and stirred further for 90 min. The solvent was removed *via* rotary evaporation, and *n*-hexane was added to the residue. The mixture was poured into sat.aq. NH_4Cl (400 mL) and extracted with dichloromethane. The extract was then successively washed with water. After being dried over anhydrous Na_2SO_4 , the solvent was evaporated, and the residue was purified by preparative GPC to afford a dark red and viscous liquid (90 mg, 0.11 mmol). Yield: 16%. $^1\text{H NMR}$ (500 MHz, acetone- d_6 , δ , ppm): 0.89 (t, $J = 6.91$ Hz, 6H, CH_3), 1.30 - 1.44 (m, 12H, $(\text{CH}_2)_3\text{CH}_3$), 1.33 (s, 24H, $\text{C}(\text{CH}_3)_2$), 1.64 - 1.71 (m, 4H, thienyl- CH_2CH_2), 2.76 - 2.80 (m, 4H, thienyl- CH_2), 4.42 - 4.52 (m, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 7.26 (s, 2H, thienyl-*H*), 7.43 (s, 2H, thienyl-*H*).

2.2.4. Synthesis of 2,5''''-Bis(tributylstannyl)-3,3''''-dihexyl-3',4',3''',4''''-diethylenedioxy-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene (BSnHE5T)

To a solution of **HE5T** (80 mg, 0.11 mmol) in THF (3 mL) at -78°C was added 0.14 mL (0.23 mmol) of *n*-butyllithium (1.65 M in *n*-hexane) by syringe. The mixture was stirred at -78°C for 1 h. Tri(*n*-butyl) tin chloride (72 mg, 0.22 mmol) was added to the solution, and the resulting mixture was stirred at -78°C for 2.5 h, warmed to room temperature, and stirred further for 1 h. The solvent was removed *via* rotary evaporation, and *n*-hexane was added to the residue. The soluble fraction was extracted by filtration and the solvent was removed *in vacuo*. Because **BSnHE5T** is unstable, it was used for polymerization without purification. $^1\text{H NMR}$ (500 MHz, acetone- d_6 , δ , ppm): 0.90 (t, $J = 7.34$ Hz, 18H, $\text{Sn}(\text{CH}_2)_3\text{CH}_3$), 0.91 (t, $J = 7.34$ Hz, 6H, thienyl- $(\text{CH}_2)_5\text{CH}_3$), 1.17 (t with fine coupling, $J = 8.10$ Hz, 12H, SnCH_2), 1.30 - 1.42 (m, 24H, thienyl- $(\text{CH}_2)_2(\text{CH}_2)_3\text{CH}_3$ and

Sn(CH₂)₂CH₂CH₃), 1.60 - 1.71 (m, 16H, thienyl-CH₂CH₂ and SnCH₂CH₂), 2.80 (t, *J* = 7.71, 4H, thienyl-CH₂), 4.37-4.49 (m, 8H, OCH₂CH₂O), 7.09 (s, 2H, thienyl-*H*), 7.22 (s, 2H, thienyl-*H*).

2.2.5. Synthesis of 2,5''''-Dibromo-3,3''''-dihexyl-3',4',3''',4''''-diethylenedioxy-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene (DBrHE5T)

To a CHCl₃/AcOH (50 mL/50mL) solution of HE5T (0.40 g, 0.58 mmol), a CHCl₃/AcOH (50 mL/50 mL) solution of NBS (0.21 g, 1.2 mmol) was slowly added in the dark at 0°C. The reaction mixture was stirred in the dark at room temperature for 6 h. The mixture solution was poured into water, and extracted two times with CHCl₃ (200 mL each). The combined organic extracts were washed with aq. Na₂CO₃ and water, and dried over anhydrous Na₂SO₄. The solvent was evaporated, and the residue was purified by column chromatography on silica gel with a mixed solvent of *n*-hexane and dichloromethane (*v/v* = 1/1) to afford an orange powder (0.23 g, 0.27 mmol). Yield: 47%. ¹H NMR (500 MHz, acetone-*d*₆, δ , ppm): 0.88 (t, *J* = 7.09 Hz, 6H, CH₃), 1.27 - 1.43 (m, 12H, (CH₂)₃CH₃), 1.60 - 1.67 (m, 4H, thienyl-CH₂CH₂), 2.75 (t, *J* = 7.77 Hz, 4H, thienyl-CH₂), 4.42 - 4.51 (m, 8H, OCH₂CH₂O), 7.08 (s, 2H, thienyl-*H*), 7.25 (s, 2H, thienyl-*H*). FTIR (ATR, ν , cm⁻¹): 3096, 3057, 2952, 2925, 2869, 2855, 1510, 1487, 1450, 1359, 1322, 1091, 1013, 956, 834, 780, 470. Anal. Calcd for C₃₆H₃₈Br₂O₄S₅: C, 50.58; H, 4.48; S, 18.76. Found: C, 50.50; H, 4.39; S, 18.68. HRMS (EI) *m/z* calcd for C₃₆H₃₈Br₂O₄S₅ 851.9740 (M⁺), found 851.9723 (M⁺).

2.3. Polymer Synthesis

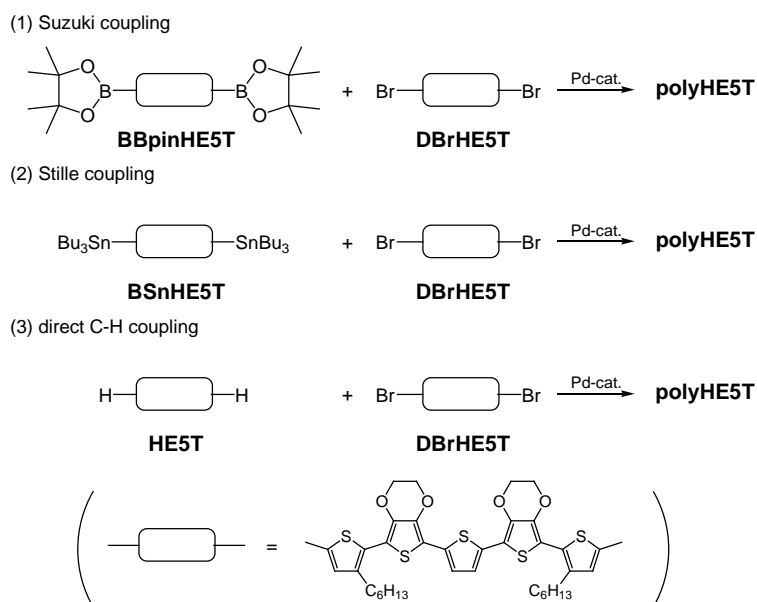
PolyHE5T was synthesized by three types of polycondensation reactions shown in Scheme 3 and the detailed synthetic processes are described below.

2.3.1. Polycondensation Using Suzuki Coupling

BBpinHE5T (90 mg, 0.11 mmol), DBrHE5T (98 mg, 0.11 mmol), tetrakis(triphenylphosphine)palladium (7 mg, 6 μ mol), potassium carbonate (48 mg, 0.35 mmol), and water (0.6 mL) were dissolved in dry THF (3 mL). The reaction mixture was stirred at 100°C for 24 h. After it was cooled to room temperature, the mixture was poured into water. The precipitate was washed with methanol.

2.3.2. Polycondensation Using Stille Coupling

B₃SnHE5T (130 mg, 0.10 mmol), DBrHE5T (85 mg, 0.10 mmol), and tetrakis(triphenylphosphine)palladium (12 mg, 10 μ mol) were dissolved in dry DMF (5 mL). The reaction mixture was stirred at 80°C for 10 h. After it



Scheme 3. Three types of polycondensations studied in this work.

was cooled to room temperature, the mixture was poured into water. The mixture was poured into sat.aq. NH_4Cl and extracted with CHCl_3 . The extract was then successively washed with water.

2.3.3. Polycondensation Using Direct C-H Coupling

HEST (30 mg, 43 μmol), **DBrHEST** (37 mg, 43 μmol), bis(dibenzylideneacetone)palladium (1.3 mg, 2.3 μmol), tris (*o*-methoxyphenyl)phosphine (0.75 mg, 2.1 μmol), pivalic acid (6.6 mg, 65 μmol), and cesium carbonate (28 mg, 86 μmol) were dissolved in dry THF (0.5 mL). The reaction mixture was stirred at 100°C for 24 h. After it was cooled to room temperature, the mixture was poured into water. The precipitate was washed with methanol and dissolved in CHCl_3 . The solution was mixed with an aqueous solution of sodium diethyldithiocarbamate to remove the soluble palladium derivatives, and the mixture was stirred for 3 h at room temperature. The organic phase was washed with diluted hydrochloric acid and water, and dried over anhydrous Na_2SO_4 . The residue was purified by reprecipitation to afford a black solid. ^1H NMR (500 MHz, THF-d_8 , δ , ppm): 0.87 - 0.97 (br, 6H, CH_3), 1.25 - 1.50 (br, 12H, $(\text{CH}_2)_3\text{CH}_3$), 1.60 - 1.68 (br, 4H, thienyl- CH_2CH_2), 2.72 - 2.87 (br, 4H, thienyl- CH_2), 4.26 - 4.48 (br, 8H, $\text{OCH}_2\text{CH}_2\text{O}$), 6.90 - 7.38 (br, 4H, thienyl-*H*). FTIR (ATR, ν , cm^{-1}): 3061, 2951, 2922, 2866, 2853, 1482, 1435, 1359, 1084, 1014, 956, 927, 887, 876, 787, 690, 488.

3. Results and Discussion

3.1. Synthesis of Monomers

Scheme 2 shows a synthetic route of **HEST** and **DBrHEST**. **E3T** was synthesized by Stille coupling between 2,5-dibromothiophene and 2-(tributylstannyl)-3,4-ethylenedioxythiophene prepared from EDOT, and its yield was 96%. 2,5"-Bis (tributylstannyl)-substituted **E3T** was synthesized and coupled with 2-bromo-3-hexylthiophene to give **HEST** with reasonable yield. Bromination of **HEST** with NBS gave **DBrHEST**, but its yield was not so high (47%). The plausible reason of the low yield is that **HEST** or **DBrHEST** will decomposed by Br_2 formed during the reaction [32].

3.2. Polycondensation Methods

To choose the polycondensation method which gives **polyHEST** with the highest molecular weight, three types of polycondensations using (1) Suzuki, (2) Stille, and (3) direct C-H coupling reactions were investigated (**Scheme 3**).

Figure 2 shows GPC curves of as-prepared polymers obtained by three types of polycondensations. Four peaks were observed at 23.4, 21.0, 19.8, and 19.0 min, whose retention times were ascribed to the molecular weights of monomer, dimer, trimer, and tetramer of **HEST** unit. A broad shoulder peak due to component of higher molecular weight of **polyHEST** was also observed from 16 to 19 min. The intensity of the shoulder peak of a polymer prepared by direct C-H coupling was much stronger than those of polymers prepared by Suzuki and Stille coupling reactions. In the case of direct C-H coupling, the threshold value of retention time (RT_{th}), where GPC curve raise up, was 16 min corresponding to the molecular weight (MW) of 63,000 (polystyrene standard). On the other hand, RT_{th} s in the case of Suzuki and Stille couplings were 16.9 min ($MW = 22,000$) and 16.7 min ($MW = 28,000$), respectively. These results suggest that the molecular weight of **polyHEST** prepared by direct C-H coupling is higher than those of Suzuki and Stille couplings. In the case of Suzuki and Stille couplings, bis(dioxaborolanyl)- and/or bis(trialkylstannyl)-substituted **HESTs** (**BBpinHEST** and **BSnHEST** in **Scheme 3**, respectively) were synthesized from **HEST** as monomers, and coupled with **DBrHEST** in stoichiometric amount. Since the stabilities of these bifunctional **HESTs** were low, their purifications were difficult. This is the reason why the molecular weights of polymers synthesized by Suzuki and Stille coupling reactions were lower than that of the polymer synthesized by direct C-H coupling reaction.

3.3. Reaction Condition of Direct C-H Coupling

Polycondensation reactions using direct C-H coupling were carried out under various conditions. **Table 1** summarizes the reaction conditions, and **Figure 3** shows the GPC curves of as-prepared polymers obtained by these conditions.

Because $\text{PCy}_3\cdot\text{HBF}_4$ was reported as an effective ligand for Pd-catalyzed direct C-H coupling reaction of thiophene derivatives [33] [34], the catalytic system of $\text{Pd}(\text{OAc})_2$ with $\text{PCy}_3\cdot\text{HBF}_4$ was examined first (entry 1-3).

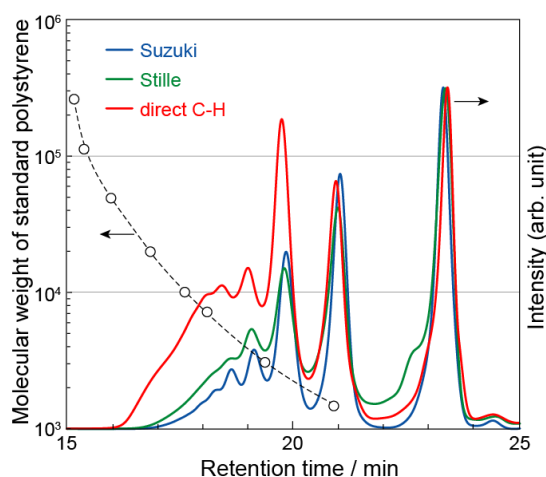


Figure 2. GPC curves of as-prepared **polyHESTs** obtained by three types of polycondensations.

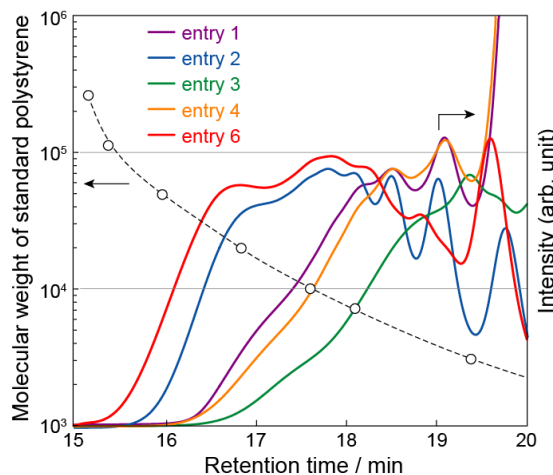


Figure 3. GPC curves of as-prepared **polyHESTs** obtained by polycondensation reactions using direct C-H coupling with different reaction conditions.

Table 1. Reaction conditions of polycondensations using direct C-H coupling^{a)}.

Entry	Pd catalyst ^{b)}	Ligand ^{c)}	Base	Solvent
1	Pd(OAc) ₂	PCy ₃ ·HBF ₄	K ₂ CO ₃	Toluene
2	Pd(OAc) ₂	PCy ₃ ·HBF ₄	K ₂ CO ₃	DMAc
3	Pd(OAc) ₂	PCy ₃ ·HBF ₄	K ₂ CO ₃	THF
4	Pd(OAc) ₂	<i>t</i> -Bu ₂ Me·HBF ₄	K ₂ CO ₃	DMAc
5	Herrman	PCy ₃ ·HBF ₄	K ₂ CO ₃	DMAc
6	Pd(<i>dba</i>) ₂	P(<i>o</i> -MeOPh) ₃	Cs ₂ CO ₃	THF

a) Reactions were carried out using palladium source (5 mol%), ligand (5 mol%), base (2.0 equiv), and pivalic acid (1.5 equiv) at 0.1 M of monomer concentration at 100 °C for 24 h; b) Pd(OAc)₂ = palladium (II) diacetate, Herrman = *trans*-bis(acetato)bis[*o*-(*di*-*o*-tolylphosphino)benzyl]dipalladium(II), Pd(*dba*)₂ = bis(dibenzylideneacetone)palladium(0); c) PCy₃·HBF₄ = tricyclohexylphosphinetetrafluoroborate, *t*-Bu₂Me·HBF₄ = di(*tert*-butyl)methylphosphinetetrafluoroborate, P(*o*-MeOPh)₃ = tris(*o*-methoxyphenyl)phosphine.

When DMAc was used as a solvent, **polyHE5T** with the highest molecular weight was obtained (entry 2). It is known that $\text{PtBu}_2\text{Me}\cdot\text{HBF}_4$ was the best ligand for the polycondensation of 1,2,4,5-tetrafluorobenzene with 2,7-dibromo-9,9-dioctylfluorene [35], while this catalytic system did not promote the polycondensation reaction of 3,3',4,4'-tetramethylbithiophene and 2,7-dibromo-9,9-dioctylfluorene [36]. In our case, the use of $\text{PtBu}_2\text{Me}\cdot\text{HBF}_4$ (entry 4) did not improve the molecular weight of **polyHE5T** compared with the case of $\text{PCy}_3\cdot\text{HBF}_4$ (entry 2). Herrmann's catalyst is also known as an effective catalyst for direct C-H coupling [37]-[39], but polycondensation did not proceed in the current system (entry 5). Very recently, Ozawa *et al.* reported that the palladium complex with dibenzylideneacetone and $\text{P}(o\text{-MeOPh})_3$, in conjunction with pivalic acid and Cs_2CO_3 exhibit high catalyst performance in polycondensation [40] [41]. Using this catalytic system (entry 6), the molecular weight of **polyHE5T** was slightly improved in comparison with the catalytic system of $\text{Pd}(\text{OAc})_2$ and $\text{PCy}_3\cdot\text{HBF}_4$ (entry 2). Since the resulting polymer was found to be soluble in common organic solvents such as THF, CHCl_3 , DMF, and *o*-dichlorobenzene, the polymer could be purified by reprecipitation. GPC analysis of **polyHE5T** obtained by the reaction condition of entry 6 revealed that the molecular weight of the polymer was $M_n = 8600$, $M_w = 14,000$ and $M_w/M_n = 1.6$.

3.4. Physicochemical Properties of PolyHE5T

The normalized UV-vis absorption and fluorescence spectra of **HE5T** and **polyHE5T** in dilute THF solution are depicted in **Figure 4**, and their optical properties are summarized in **Table 2**. Both absorption and fluorescence spectra of **polyHE5T** were red-shifted compared with those of **HE5T** due to the expansion of effective π -conjugation length by the polymerization. It was also found that smooth films of **polyHE5T** were successfully obtained by spin-coating of its solution in *o*-dichlorobenzene on ITO and/or glass substrate. Using the good film-forming property, it is expected that electrochemical and electrical properties of **polyHE5T** in film state can be investigated. Their detailed properties will be discussed in the near future.

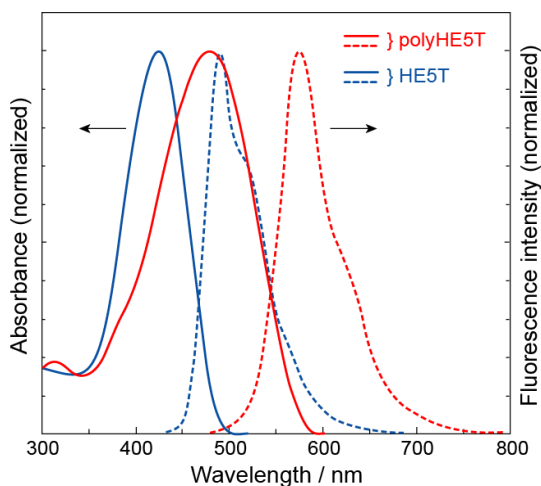


Figure 4. UV-vis absorption (solid line) and fluorescence (dashed line) spectra of **polyHE5T** (red) and **HE5T** (blue) in THF solution.

Table 2. Optical properties of **HE5T** and **polyHE5T**^{a)}.

Compound	Absorption		Fluorescence	
	$\lambda_{\text{max}}/\text{nm}$	$\log \epsilon$	$\lambda_{\text{max}}/\text{nm}$	Φ
HE5T	425	4.65	491 ^{b)}	0.20
polyHE5T	477	4.56	575 ^{c)}	0.28

a) Measured in THF solution (concentration: $10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ (absorption), $10^{-6} \text{ mol}\cdot\text{dm}^{-3}$ (fluorescence)); b) excited at 425 nm; c) excited at 477 nm.

4. Conclusion

Polythiophene containing 3,4-ethylenedioxythiophene in a repeat unit was firstly synthesized by polycondensation. Among polycondensation reactions which were tried in this study, direct C-H coupling reaction gave a polymer with the highest molecular weight. The molecular weight of the polymer was further increased by selecting the appropriate condition of catalytic system. Absorption and fluorescence spectra of the resulting polymer were red-shifted in comparison with those of the corresponding monomer reflecting that the effective π -conjugation length was expanded by the polymerization.

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