

Synthesis and characterization of soluble poly(3,4-phenylenedioxythiophene)



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ABSTRACT

Asymmetric 2,5-dibromo-3,4-phenylenedioxythiophenes having a branched alkyl side chain at the phenylene part are polymerized by Yamamoto (Y) and Grignard metathesis (GRIM) methods to give several soluble poly(3,4-phenylenedioxythiophene)s. Poly{1,4-[4-(2-hexylundecyl) phenylene]dioxothiophene-2,5-diyl} synthesized by GRIM (**PPTa-G**) exhibits a narrower band gap about 1.85 eV, higher absorption coefficient, and shorter π -stacking distance about 3.9 Å than those of the polymer synthesized by Y method (**PPTa-Y**). Introducing a fluorine substituent at the phenylene part of **PPTa-Y** deepens the energy level of a highest occupied molecular orbital of the polymer 0.17 eV. Thin film of **PPTa-G** shows hole mobility of $2.52 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ determined by performance of the organic field-effect transistor in a preliminary experiment.

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1. Introduction

A variety of conducting and conjugated polymers have been developed [1] and attempted to be applied to various organic devices such as organic light emitting diodes (OLEDs) [2–5], organic field effect transistors (OFETs) [6–10], and organic photovoltaic cells (OPVs) [11–14]. It has been recognized that poly(3,4-ethylenedioxythiophene) (PEDOT) is a representative conducting polymer for reasons of excellent properties such as high electrical conductivity with narrow band gap and good environmental stability [15–17]. However, the low solubility of PEDOT has limited its practical usage in various industrial applications because common organic devices are usually fabricated by a spin-coating method using polymer solutions. A successful solution was development of PEDOT-polystyrenesulfonic acid, an aqueous solution of doped PEDOT, which is widely used as hole injection/transport material for anode interlayer in OLEDs [2–5]. On the other hand, introducing a long alkyl side chain into the out-of-plane ethylene bridge of PEDOT could improve the solubility but simultaneously caused steric hindrance, which resulted in enlargement of a π -stacking distance between the polymer backbones and lowering of carrier mobility [18]. In 2004, Roquet et al. have reported that poly(3,4-phenylenedioxythiophene) (PPheDOT) ($R_1, R_2 = H$) [18,19] has a planar structure by replacing the

ethylene bridge of PEDOT with phenylene (Fig. 1). Owing to the well developed planar conjugated polymer structure, PPheDOT was expected to be not only an alternative to PEDOT but also an electron donating polymer to be used in OFETs and OPVs, if the solubility was adequately good to be made organic devices. In 2007, Grenier et al. have synthesized PPheDOT-(C₁₂)₂ [20] that has two dodecyl side chains at 4,5-positions of phenylene, but it was poor soluble in common organic solvents due to high molecular association property. Considering these historical results, first of all the low solubility of PPheDOT must be improved to be used in organic devices.

It is thought that introducing an asymmetric substituent to the symmetrical structural unit of PPheDOT is an appropriate strategy for synthesis of the soluble polymers. The asymmetrical substitution generally increases amorphous nature and lowers phase transition temperatures of polymers. The structural irregularity might cause deterioration of carriers' transportability, whereas usage of asymmetric units for constructing narrow band gap polymers has succeeded in improving not only solubility but also their organic device performances [21,22].

In this paper, the synthesis and fundamental properties of soluble PheDOT based polymers have been reported. Introduction of a long and branched chain, 2-heptylundecyl group, at 4-position of the phenylene moiety was effective to produce several soluble PPheDOT analogs, whereas introduction of a linear decyl chain or a branched 2-ethylhexyl chain was not enough to solubilize resultant polymers. Furthermore, a fluorine substituent is

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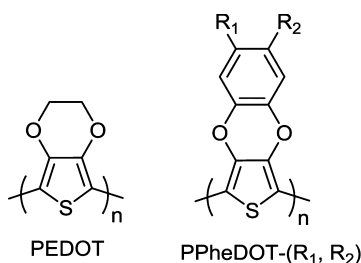


Fig. 1. Structures of PEDOT and PPhDOT analogs.

introduced at phenylene in addition to the branched alkyl chain to control electron donating /accepting property.

2. Experimental

2.1. Materials

All the chemicals were purchased from Kanto Chemical Co., Inc., Tokyo Chemical Industry Co., Ltd., Nacalai Tesque Inc., or Sigma–Aldrich Co., LLC., and were used without further purification unless stated. Dichloromethane was refluxed over calcium hydride and distilled. Toluene and THF were refluxed over sodium and distilled. *N,N*-Dimethyl formamide (DMF) was distilled under reduced pressure. *p*-Toluenesulfonic acid was purified according to a common method. Column chromatography was performed on a silica gel (Kanto Chemical, 60 N spherical, neutral).

2.2. Synthesis

Monomers **6a** and **6b** were synthesized from **1** and corresponding veratrole derivatives according to Scheme 1. All compounds (**1**, **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **5a**, **5b**, **6a**, and **6b**) were synthesized by modified methods reported previously (see Supporting information) [20,23–26]. Poly{1,4-[4-(2-hexylundecyl)phenylene]dioxothiophene-2,5-diyl} (**PPTa**) and poly{1,4-[4-(2-hexylundecyl)phenylene]dioxothiophene-2,6-diyl} (**PPTb**) were synthesized from corresponding monomer **6** by different polymerization methods, Yamamoto polycondensation (-Y) [23] and Grignard metathesis GRIM (-G) [24,25], respectively.

2.2.1. Synthesis of PPTa-Y

Into a mixture of nickelbis(cyclooctadiene) ($\text{Ni}(\text{cod})_2$) (92.5 mg, 0.34 mmol), 2,2'-bipyridine (bpy) (53 mg, 0.34 mmol) and

1,5-cyclooctadiene (cod) (33.3 mg, 0.31 mmol) in 0.79 ml dry DMF under argon in a Schlenk flask stirred for 30 min at room temperature, was added a solution of **6a** (0.1 g, 0.17 mmol) in dry THF (0.79 ml), which was heated at 80 °C for 3 days. Polymeric products were precipitated from MeOH containing aqueous HCl. The collected polymer was redissolved in CHCl_3 and was purified by reprecipitations from MeOH containing aqueous NH_3 and from acetone in sequence, affording **PPTa-Y** as a dark purple solid (69 mg, 91% yield).

^1H NMR(400 MHz, CDCl_3 , δ) 0.86 (br, 6H, CH_3), 1.25 (br, 29H, CH_2 , CH), 2.46 (br, 2H, CH_2), 6.91 (br, 3H, Ar); FTIR (KBr): ν = 2958 (m), 2923 (s), 2852 (s), 1599 (w), 1505 (m), 1452 (s), 1267 (s), 1206 (m), 1108 (m), 967 (w), 927 (w), 805 (m); Anal. Calcd. for $\text{C}_{28}\text{H}_{42}\text{O}_2\text{S}$: C 75.97, H 9.56; Found: C 74.61, H 8.58.

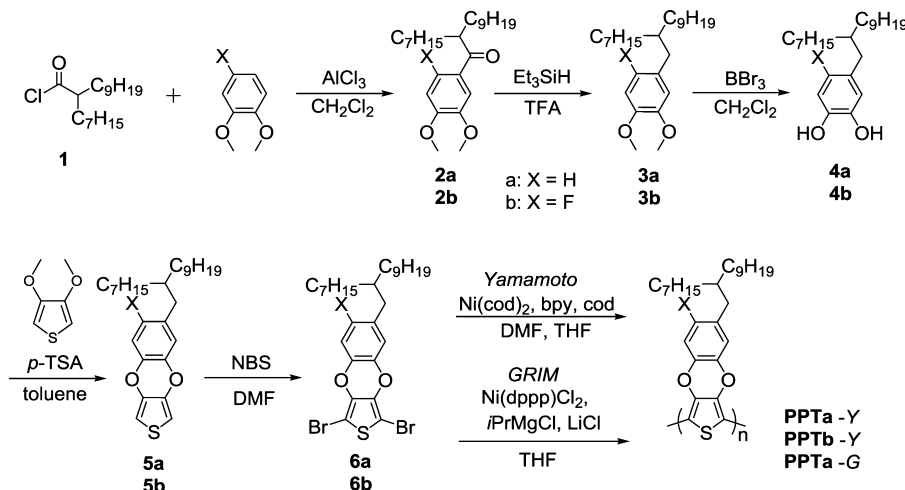
2.2.2. Synthesis of PPTb-Y

PPTb-Y was synthesized from **6b** by the same procedure for synthesis of **PPTa-Y**. The product was obtained as a purple black solid (81% yield); ^1H NMR (400 MHz, CDCl_3 , δ) 0.86 (br, 6H, CH_3), 1.25 (br, 29H, CH_2 , CH), 2.45 (br, 2H, CH_2), 6.76 (br, 2H, Ar); FTIR (KBr): ν = 2957(m), 2924 (s), 2853 (s), 1636 (w), 1608 (w), 1507 (s), 1453 (s), 1313 (m), 1261 (m), 1206 (m), 1153 (m), 1091 (m), 946 (m), 873 (m), 801 (m); Anal. Calcd. for $\text{C}_{28}\text{H}_{42}\text{O}_2\text{S}$: C 73.00, H 8.97; Found: C 67.78, H 7.96.

2.2.3. Synthesis of PPTa-G

Into a solution of **6a** (0.17 mg, 0.28 mmol) in dry THF under argon in a Schlenk flask, were added LiCl (11 mg, 0.28 mmol) and *i*PrMgCl (2.0 M in THF, 138 ml) successively after cooling at 0 °C. After reacting for 30 min, [1,3-bis(diphenylphosphino)propane]dichloro-nickel(II) ($\text{Ni}(\text{dppp})\text{Cl}_2$) was added. Resulting solution was stirred at 0 °C until color of the solution changed from red to dark blue, which was reacted overnight at room temperature. Polymeric products were precipitated from MeOH containing aqueous HCl. The collected polymer was redissolved in CHCl_3 and was purified by reprecipitation from MeOH containing aqueous NH_3 and from acetone in sequence, affording **PPTa-G** as a film (52 mg, 43% yield).

^1H NMR (400 MHz, CDCl_3 , δ /ppm) 0.86 (br, 6H, CH_3), 1.24 (br, 29H, CH_2 , CH), 2.43 (d, 2H, CH_2), 6.90 (m, 3H, Ar); FTIR (KBr) ν = 3035 (w), 2923 (s), 2852 (s), 1599 (m), 1505 (s), 1448 (s), 1267 (s), 1205 (m), 1109 (m), 967 (m), 928 (m), 811 (m); Anal. Calcd. for $\text{C}_{28}\text{H}_{42}\text{O}_2\text{S}$: C 75.97, H 9.56; Found: C 74.39, H 8.83.



Scheme 1. Pathway for the synthesis of the polymers.

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