



# Thermoelectric properties of polythiophenes partially substituted by ethylenedioxy groups

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## ABSTRACT

In order to investigate the relationship between thermoelectric properties and chemical structures of conducting polymers, electrochemically-doped polythiophenes partially substituted by ethylenedioxy groups have been synthesized and their thermoelectric properties were measured. Two types of monomers consisting of 3,4-ethylenedioxythiophene (EDOT) and 3-hexylthiophene (HT) with different mole fractions of EDOT have been synthesized. The electrolytic polymerization of these monomers in propylene carbonate solutions containing sulfonated poly( $\beta$ -hydroxyether) (S-PHE) as an electrolyte gave smooth and lustrous free-standing films. The electrical conductivities and Seebeck coefficients of the polymer films doped with S-PHE were increased with the increase in the temperature or the decrease in the current density during the electrolytic polymerization. By the comparison of thermoelectric properties of S-PHE doped polymer films, it was revealed that the thermoelectric performances were strongly affected by the mole fractions of EDOT in the copolymers.

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## 1. Introduction

Thermoelectric (TE) devices based on the Seebeck effect are able to harvest electricity from waste heat generated from households, chemical plants, or even human bodies by utilizing the diffusion of charge carriers induced by the temperature gradient [1–3]. The performance of a TE material is represented by their dimensionless figure-of-merit ( $ZT$ ) or by the power factor ( $PF$ ) defined, respectively, by  $ZT = \sigma S^2 T / \kappa$  and  $PF = \sigma S^2$ , where  $\sigma$  is the electrical conductivity,  $S$  is the Seebeck coefficient,  $T$  is the absolute temperature, and the  $\kappa$  is the thermal conductivity. Until quite recently, a number of studies have been devoted to the development of TE devices based on inorganic materials, such as Bi-Te, Co-Sb, Bi-Pb, Sn-Te alloys, and transition metal oxides [4–11]. However, the inorganic TE materials are generally expensive, rare, heavy, brittle, poorly flexible, and relatively difficult to process, and thus impeding their widespread use. In addition, some inorganic TE materials are highly toxic, which is not suitable for practical use. Compared to the inorganic TE materials, conducting polymers are recently attracting attention as promising candidates because of low cost of fabrication, abundance of raw

materials, flexibility, and solution processability over large areas [12–15]. Furthermore, organic compounds have relatively low  $\kappa$  values, which are beneficial for obtaining high  $ZT$  values. Since the early work on the thermoelectric properties of polyaniline doped with camphorsulfonic acid was reported by Toshima et al., in 1999 [16], several types of conducting polymers such as polyaniline [17–20], polypyrrole [21–24], polyphenylenevinylene [25,26], polythiophene [27–29], and its derivatives including poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) [30–34] have also been investigated. Among them, the PEDOT:PSS has been well-studied because its water-dispersion solution is commercially available and the film can be easily obtained from the solution [35,36]. In most cases, these polymers, however, are obtained either by the electrochemical or chemical oxidative polymerization of the commercially available monomers or by the purchase from the commercial sources. In order to improve the performances of the organic TE materials, it is necessary to survey the performances of conducting polymers having various chemical structures.

In order to investigate the relationship between the chemical structure of conducting polymers and their thermoelectric properties, we have synthesized the free-standing films of novel electrochemically-doped polythiophenes partially containing ethylenedioxy groups with different mole fractions (Fig. 1), and

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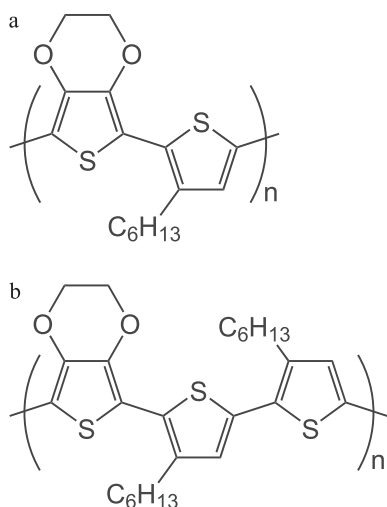


Fig. 1. Chemical structures of (a) PE1HT and (b) PE2HT.

investigated the thermoelectric properties of their films prepared by the optimized polymerization conditions in relation to their chemical structures.

## 2. Experimental

### 2.1. Materials

Poly( $\beta$ -hydroxyether) (PHE) ( $M_w = 50,000$ ,  $M_w/M_n = 2.7$ ) and propylene carbonate (PC) were purchased from Sigma-Aldrich, while 3,4-ethylenedioxythiophene (EDOT), sulfur trioxide pyridine ( $\text{PySO}_3$ ), and tetrabutylammonium hydroxide ( $\text{Bu}_4\text{NOH}$ ) (40% in water) were obtained from Tokyo Chemical Industry. PC and EDOT were distilled under reduced pressure and stored in a Schlenk tube filled with dry argon gas. *N*-Bromosuccinimide (NBS) was purchased from Nacalai Tesque, purified by recrystallization from benzene, and dried under vacuum. Sulfonated PHE (S-PHE) was prepared according to Scheme 1 as described previously [37]. The degree of sulfonation ratio was estimated to be almost 100% by  $^1\text{H}$  NMR. 2-Tributylstannyl-3,4-ethylenedioxythiophene [38], 3-hexylthiophene (HT) [39], 2-bromo-3-hexylthiophene (Br1HT) [40], and 3,4'-dihexyl-2,2'-bithiophene (2HT) [41] were synthesized according to the literature. All the other reagents were used as received without further purification.

### 2.2. Synthesis of monomers

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

### 2.3. 3,4-Ethylenedioxy-3'-hexyl-2,2'-bithiophene (E1HT)

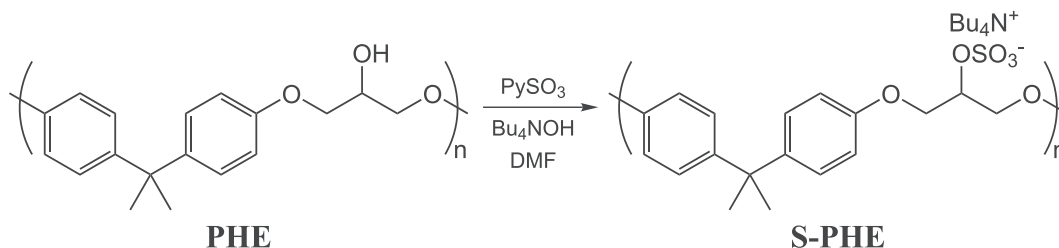
To a solution of EDOT (0.87 g, 8.1 mmol) in THF (20 mL) at  $-78^\circ\text{C}$  was added 5.0 mL (8.1 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) by syringe. The mixture was stirred at  $-78^\circ\text{C}$  for 1 h. Tri(*n*-butyl)tin chloride (2.5 mL, 9.1 mmol) was added to the solution. The resulting mixture solution was stirred at  $-78^\circ\text{C}$  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 filtered solution was added to a solution of tetrakis(triphenylphosphine)palladium (0.61 g, 0.53 mmol) and Br1HT (1.6 mL, 3.5 mmol) in toluene (30 mL). The solution was stirred at  $80^\circ\text{C}$  for 8 h. The mixture was poured into sat. aq.  $\text{Na}_2\text{CO}_3$  and extracted with dichloromethane. The extract was then successively washed with water. After being dried over anhydrous  $\text{Na}_2\text{SO}_4$ , the solvent was evaporated and the crude product was purified by column chromatography on silica gel with a mixed solvent of *n*-hexane and toluene ( $v/v = 1/2$ ) as an eluent to afford a yellow liquid (1.6 g, 5.2 mmol). Yield: 65%.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{CO}$ ,  $\delta$ , ppm): 0.86 (t,  $J = 6.92$  Hz, 3H,  $\text{CH}_3$ ), 1.24–1.36 (m, 6H, thienyl- $(\text{CH}_2)_2(\text{CH}_2)_3\text{CH}_3$ ), 1.59 (tt,  $J = 7.73$ , 7.73 Hz, 2H, thienyl- $\text{CH}_2\text{CH}_2$ ), 2.68 (t,  $J = 7.73$  Hz, 2H, thienyl- $\text{CH}_2$ ), 4.23–4.31 (m, 4H,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 6.51 (s, 1H, EDOT- $\text{H}$ ), 6.99 (d,  $J = 5.24$  Hz, 1H, thienyl- $\text{H}$ ), 7.38 (d,  $J = 5.24$  Hz, 1H, thienyl- $\text{H}$ ).  $^{13}\text{C}$  NMR (125 MHz,  $(\text{CD}_3)_2\text{CO}$ ,  $\delta$ , ppm): 14.19, 23.07, 29.69, 29.69, 31.07, 32.16, 65.03, 65.37, 99.31, 110.15, 125.41, 127.97, 129.86, 139.15, 141.29, 142.49. HRMS (GC/ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{20}\text{O}_2\text{S}_2$  ( $\text{M}^+$ ) 308.09047, found 308.09032.

### 2.4. 5'-Bromo-3,4'-dihexyl-2,2'-bithiophene (Br2HT)

To a chloroform/acetic acid (20 mL/10 mL) solution of 2HT (0.60 g, 1.8 mmol), NBS (0.31 g, 1.8 mmol) was slowly added in the dark at  $0^\circ\text{C}$ . The reaction mixture was stirred in the dark at room temperature for 2.5 h. Water and chloroform were added to the solution, and the organic phase was extracted and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated, and the residue was purified by column chromatography on silica gel with *n*-hexane as an eluent to afford a yellow viscous liquid (0.61 g, 1.5 mmol). Yield: 82%.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{CO}$ ,  $\delta$ , ppm): 0.82–0.94 (br, 6H,  $\text{CH}_3$ ), 1.24–1.44 (br, 12H, thienyl- $(\text{CH}_2)_2(\text{CH}_2)_3\text{CH}_3$ ), 1.56–1.70 (br, 4H, thienyl- $\text{CH}_2\text{CH}_2$ ), 2.60 (t,  $J = 7.54$  Hz, 2H, thienyl- $\text{CH}_2$ ), 2.74 (t,  $J = 7.54$  Hz, 2H, thienyl- $\text{CH}_2$ ), 6.97 (s, 1H, thienyl- $\text{H}$ ), 7.03 (d,  $J = 4.69$  Hz, 1H, thienyl- $\text{H}$ ), 7.39 (d,  $J = 4.69$  Hz, 1H, thienyl- $\text{H}$ ). HRMS (GC/ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{29}\text{Br}_1\text{S}_2$  ( $\text{M}^+$ ) 412.08864, found 412.08940.

### 2.5. 3,4-Ethylenedioxy-3',3''-dihexyl-2,2':5',2''-terthiophene (E2HT)

E2HT was prepared according to the same procedure as described for E1HT by using Br2HT instead of Br1HT as a starting material.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{CO}$ ,  $\delta$ , ppm): 0.87 (t,  $J = 6.85$  Hz,



Scheme 1. Synthesis of sulfonated PHE (S-PHE).

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