Synthesis of functionalizable derivatives of 3,4-ethylenedioxythiophene and their solid-state polymerizations

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ABSTRACT: Four polythiophenes based on poly(3,4-ethylenedioxythiophene) (PEDOT) framework have been successfully prepared by the facile thermal activated solid-state polymerization (SSP) process from their corresponding dibromothiophene derivatives, which were efficiently obtained using our improved methodology. Rates of polymerizations of these precursors were varied and most of the processes were incomplete under the reaction condition chosen for the synthesis. Raising the reaction temperature of the SSP further advanced the polymerization progress and improved the conductive properties of the polymer. The polymer of 3,4-ethylenedioxythiophene-methanol (EDTM) and its two related derivatives with functionalizable groups were prepared for the first time by the SSP method. The process and these new SSP-derived polymers could help solving the fabrication difficulty and expand the scope of their applications. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42233.

INTRODUCTION

Conjugated polymers have become the major focus in material science and continued to attract attentions of researchers, apparently because of their wide range of potential applications including capacitors, antistatic coatings, electrochromic devices, organic light emitting diodes, solar cells, transistors, energy storage, and sensors.[1–8] Among most reports in this field, polythiophene and especially poly(3,4-ethylenedioxythiophene) (PEDOT) stands out as one of the most studied and important materials due mainly to its exceptional stability, excellent conjugated properties, and ease of synthetic access.[3] The polymer still suffers from its insolubility that limits processing possibilities. This fabrication problem could be indirectly resolved by the discovery of spontaneous topochemical solid-state polymerization (SSP) of dihalogenated derivatives of 3,4-ethylenedioxythiophene (EDOT).[9,10] Apart from the general advantages of being environmentally friendly, economical, and convenient, this unique method provides PEDOT in high yield with superior conductive properties under catalyst, reagent, and solvent-free conditions. Heating the prefabricated solid monomers would sidestep the solubility problems and provide the desired polymers in the readily processed forms.

Many examples of dihalogenated thiophene derivatives have been reported to successfully undergo SSP to yield their corresponding polymers such as various dioxythiophenes, dithiathiophenes, and dioxyselenophenes.[11–17] Nevertheless, this fascinating procedure still found some limitations. Not all dioxythiophene monomers could be polymerized by this process and almost all successful examples are symmetrical molecules with relatively inert side chains that hinder possible postprocessing of the resulting polymers and restrict further developments from specific interactions and modifications on the polymer chains. Although many dioxythiophenes derivatives with functionalizable groups have appeared, they were not tested for possibilities to be polymerized under SSP condition.[18–21] This prompted us to begin our explorations on this aspect to expand the versatility of the intriguing polymerization method. In this report, we present some of our early successes on the synthesis of novel thiophene monomers and their subsequent SSP procedures. Improvements on the properties of the obtained polymers were also revealed and discussed.

EXPERIMENTAL

General Information

^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury 400 or Bruker Avance 400 spectrometers, operated at 400 MHz for ^{1}H and 100 MHz for ^{13}C nuclei. FTIR spectra were recorded on a Nicolet 6700 spectrometer. UV–visible spectra of solid samples were obtained using reflectance mode on Shimadzu UV-2550

Additional Supporting Information may be found in the online version of this article.

spectrophotometer. Surface conductivity values were measured by four-point probe technique using KEITHLEY Semiconductor Characterization System 4200. Surface morphologies of the polymers were analyzed by JEOL scanning electron microscope JEM-2100. Low-resolution mass spectra were determined on Waters Micromass Quatto micro API ESCi, or on Bruker Daltonik GmbH matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) Microflex mass spectrometer. High-resolution mass spectra were recorded on Bruker Daltonik GmbH micrOTOF-Q II 10335. X-ray diffraction data were collected on a Bruker X8 APEXII KAPPA CCD diffractometer. Melting points were determined on a Stuart Scientific Melting Point SMP10. All reagents and solvents were used as purchased or distilled prior to use.

Monomer Syntheses

Synthesis of (±)-4a,5,6,7,8,8a-Hexahydrobenzo[e]thieno[3,4-b][1,4]dioxine (1). 3,4-Dimethoxythiophene (0.144 g, 1 mmol) was mixed with (±) trans-1,2-cyclohexanediol (0.233 g, 2 mmol) and *p*-toluenesulfonic acid (PTSA, 0.020 g, 0.1 mmol) in 10 mL dry toluene.[22] The mixture was stirred at 100°C under nitrogen atmosphere for 72 h. It was then washed by saturated NaHCO$_3$ and extracted twice with ethyl acetate. The combined organic layer was concentrated and the crude product was purified by column chromatography eluted with hexane/dichloromethane (3:2). Compound **1** was obtained as white solid crystal in 0.197 g (86% yield, with 8% of the starting material recovered), mp 142–143°C (lit. mp 144–146°C)[22]; ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 6.30 (s, 2H; 2Ar–H), 3.78–3.68 (m, 2H; 2CH), 2.20–1.24 (m, 8H; 4CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 142.4, 99.0, 77.1, 30.1, 23.8; IR (KBr, cm^{-1}): 2947, 1471, 1402, 1026.

Synthesis of (±)-1,3-dibromo-4a,5,6,7,8,8a-hexahydrobenzo[e]thieno[3,4-b][1,4]dioxine (DB1). Compound **1** (0.098 g, 0.5 mmol) was dissolved in 5 mL chloroform and slowly added *N*-bromosuccinimide (NBS, 0.223 g, 1.25 mmol) and stirred at room temperature for 1–2 min. The reaction was quenched by adding saturated NaHCO$_3$ (10 mL) and extracted twice with dichloromethane (2 × 10 mL). The combined organic layer was concentrated and the crude product was purified by column chromatography eluted with hexane/dichloromethane (3:2). Compound **DB1** was obtained as white solid in 0.166 g (94% yield). The product had been recrystallized from ethanol solution for further analysis by X-ray crystallography, mp 127–128°C; ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 3.81–3.65 (m, 2H; 2CH), 2.28–1.17 (m, 8H; 4CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 140.4, 84.8, 77.7, 29.9, 23.7; HRMS (ESI, m/z): Calcd for C$_{10}$H$_{10}$Br$_2$O$_2$SNa [M+Na]$^+$: 374.8666; found 374.8671. IR (neat, cm^{-1}): 2941, 1505, 1404, 1065; Elemental analysis: Anal Calcd. for C$_{10}$H$_{10}$O$_2$Br$_2$S: C, 34.92; H, 2.85%; Found: C, 34.78; H, 2.83%.

Synthesis of (5,7-dibromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methanol (DBEDTM). 3,4-Ethylenedioxythiophene-methanol (EDTM, 0.086 g, 0.5 mmol) was dissolved in 5 mL chloroform and added NBS (0.223 g, 1.25 mmol) and stirred the mixture for 1 min.[23] The reaction was quenched by adding saturated NaHCO$_3$ (10 mL) and extracted twice with dichloro-

methane (2 × 10 mL). The collected organic layer was concentrated and purified by column chromatography eluted with ethyl acetate/hexane (1:1). The product was obtained as clear liquid in 0.137 g (83%yield), ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 4.41–3.66 (m, 5H; CH$_2$CHCH$_2$), 1.99 (s, 1H; OH); ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 139.6, 139.3, 85.3, 74.9, 66.4, 61.3. HRMS (ESI, m/z): Calcd for C$_7$H$_7$Br$_2$O$_3$S [M+H]$^+$: 328.8483; found 328.8487.

Synthesis of (2,3-Dihydrothieno[3,4-b][1,4]dioxin-2-yl)methyl 4′-methylbenzenesulfonate (2). EDTM (0.086 g, 0.5 mmol) and *p*-toluenesulfonyl chloride (0.191 g, 1.0 mmol) was dissolved in 2 mL of dry dichloromethane, added triethylamine (0.2 mL, 1.4 mmol), and stirred for 2 days under nitrogen atmosphere at room temperature. The reaction was quenched and washed by adding 5% H$_2$SO$_4$, followed by saturated NaHCO$_3$. After purifying the separated organic layer by column chromatography using ethyl acetate and hexane (1:4) as eluent, the product **2** was obtained as white solid in 0.130 g (80% yield), ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.80 (d, J = 7.9 Hz, 2H; 2Ar–H), 7.36 (d, J = 7.9 Hz, 2H; 2Ar–H), 6.29 (m, 2H; 2Ar–H), 4.40–3.98 (m, 5H; CH$_2$CHCH$_2$), 2.46 (s, 3H; CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 145.3, 141.0, 140.4, 132.5, 130.0, 128.0, 100.2, 100.2, 70.8, 66.9, 65.0, 21.6.

Synthesis of (5,7-Dibromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methyl 4′-methylbenzene sulfonate (DB2). Compound **2** (0.131 g, 0.4 mmol) was reacted with NBS (0.178 g, 1 mmol) following the same procedure as the synthesis of DBEDTM above. The crude mixture was purified by column chromatography using ethyl acetate. The product **DB2** was obtained as white solid in 0.174 g (90.4% yield), ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.81 (d, J = 8.3 Hz, 2H; 2Ar–H), 7.37 (d, J = 8.1 Hz, 2H; 2Ar–H), 4.46–4.05 (m, 5H; CH$_2$CHCH$_2$), 2.46 (s, 3H; CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 145.5, 139.0, 138.5, 132.2, 130.1, 128.0, 86.1, 71.3, 66.3, 65.3, 21.7; HRMS (ESI, m/z): Calcd for C$_{14}$H$_{12}$Br$_2$O$_5$S$_2$Na [M+Na]$^+$: 504.8391; found 504.8374.

Synthesis of (2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methyl 2'-chloroacetate (3). EDTM (0.086 g, 0.5 mmol) and K$_2$CO$_3$ (0.207 g, 1.5 mmol) was mixed with 5 mL dry dichloromethane. The mixture was added N,N′-dimethylaminopyridine (DMAP) (0.012 g, 0.1 mmol) and chloroacetyl chloride (0.16 mL, 2 mmol). The reaction was stirred at room temperature under nitrogen atmosphere for 24 h. The mixture was then added to saturated NaHCO$_3$ and extracted twice by dichloromethane. The combined organic layer was purified by column chromatography using ethyl acetate/hexane (1:1). The product **3** was obtained as clear liquid in 0.124 g (quantitative yield), ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 6.29 (m, 2H; 2Ar–H), 4.39–3.96 (m, 7H, CH$_2$CHCH$_2$, CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 167.0, 141.1, 140.8, 100.3, 100.2, 71.1, 65.3, 63.8, 40.5.

Synthesis of (5,7-Dibromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methyl 2'-chloroacetate (DB3). Compound **3** (0.124 g, 0.5 mmol) was reacted with NBS (0.178 g, 1 mmol) following the same procedure as the synthesis of DBEDTM above. The crude mixture was purified by column chromatography using ethyl acetate. The product **DB3** was obtained as white solid in
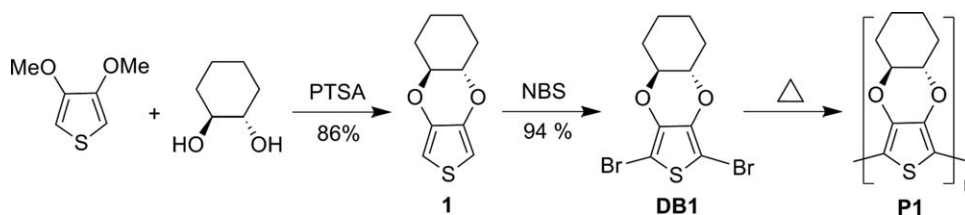
Scheme 1. Synthesis of compound **1** and its subsequent bromination and polymerization.

0.148 g (72.8% yield), ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 4.46–4.02 (m, 7H; CH$_2$CHCH$_2$, CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 166.9, 139.1, 138.8, 86.1, 86.0, 71.5, 65.6, 63.2, 40.5; HRMS (ESI, m/z): Calcd for C$_9$H$_7$Br$_2$ClO$_4$SNa [M+Na]$^+$: 426.8018; found 426.8050.

Solid-State Polymerization (SSP)

General Procedure. Brominated monomer (0.5 mmol) was placed in a flask and heated at 80°C for 24 h. During this period, the solid precursor turned into dark blue solid polymer. The resulted product was washed by dichloromethane to remove the nonpolymerized monomer and dried in a dessicator overnight to afford the corresponding bromine-doped solid polymer, which was insoluble in all common solvents. The weights of the polymers obtained by SSP all exceeded 100% due to the extra weight from doped bromine concomitantly release during the reaction.[9,10]

Following the general SSP procedure above, compound **DB1** (0.177 g, 0.5 mmol) was turned into insoluble polymer **P1** in 0.135 g, IR (neat, cm^{-1}): 1431, 1102; UV (solid): λ_{max} 499.5 nm. Similarly, **DBEDTM** (0.165 g, 0.5 mmol) was turned into insoluble **PEDTM** in 0.122 g, IR (neat, cm^{-1}): 3425, 1502, 1135; UV (solid): λ_{max} 653 nm. Compound **DB2** (0.242 g, 0.5 mmol) was turned into insoluble polymer **P2** in 0.183 g, IR (neat, cm^{-1}): 1485, 1290, 1125; UV (solid): λ_{max} 549.5 nm. Compound **DB3** (0.203 g, 0.5 mmol) was turned into insoluble polymer **P3** in 0.146 g, IR (neat, cm^{-1}): 1735, 1481, 1134; UV (solid): λ_{max} 540 nm.

Since the SSP process may not be completed under the condition above, compound **DB1** was subjected to another SSP at higher temperature of 120°C for 24 h. The general procedure afterward was then followed to yield **P2**. The polymer has the same properties as what prepared at lower temperature except that the λ_{max} of its UV–Visible absorption spectrum was higher at 714 nm.

Single-Crystal X-ray Analysis

X-ray diffraction data of **DB1** were collected at 296(2) K on a Bruker X8 APEXII KAPPA CCD diffractometer operating at 50 kV, 30 mA, producing an intense monochromatic MoKα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using SHELXS-97 and refined using full-matrix least squares on F^2 with SHELXL-97.[24] Crystal data, final R-values, and selected refinement details are given in Supporting Information, Table S1 in the accompanied Supplementary Material Section. Crystal data of **DB1** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1041905) and can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

We began our investigations by exploring the synthesis of dibromo derivatives of EDOT. Although the usual method using NBS in a medium containing acetic acid could provide the desired product, we noticed some impurities developed as the reaction progressed.[9,10,25] Preliminary GC-MS analysis of quenched samples collected during the reaction suggested that the bromination completed early within a few minutes and the dibromo product slowly lost one or two bromine atoms in the prolonged reaction. It is clear that EDOT is sufficiently reactive toward bromination and the product could be hydrodebrominated in acidic medium at long reaction time. Consequently, we eliminated the acid co-solvent from the process and shortened the reaction time to only 1–2 min. The desired dibromo derivative was conveniently obtained in excellent yield and pure enough for later use in SSP and characterizations. We had applied this success on the synthesis of other new derivatives, particularly compound **1**, the cyclohexane analog of EDOT (Scheme 1).

Compound **1** in both racemic and enantiomeric forms had been prepared through acid catalyzed transetherifications, which were then subjected to electrooxidative polymerizations.[22] The compound represents one of the closest relatives to EDOT, in which its corresponding polymer could behave similarly to PEDOT with potentially better processing property due to larger hydrocarbon portion. In our attempts to expand the scope of SSP, we successfully prepared the racemic form of **1** from trans-etherification of 3,4-dimethoxythiophene with (trans)-1,2-cyclohexanediol. The product was then brominated by NBS to obtain the precursor **DB1** in excellent yield. Heating the solid crystals of **DB1** under SSP condition gave the corresponding dark blue polymer **P1** similar to what observed for PEDOT. Although the process seemed to be more sluggish than that of DBEDOT since the crystals of **DB1** turned blue after heating for over 10 h. Unfortunately, the resulted polymer was also insoluble in all common solvents, which precluded its full structural characterizations. X-ray analysis of the single-crystal structure of **DB1** revealed that the Br···Br distances between adjacent molecules were approximately 4.2 Å, which are much larger than the double van der Waals radius of bromine (3.7 Å) (Figure 1). The result becomes another evidence confirming that the interhalogen distance is not the critical factor to induce the SSP of these dibromothiophene derivatives.[11,13]

Surface morphologies of the monomer **DB1** and polymer **P1** were compared to follow the transformation process during the SSP. Figure 2(a) displays the smooth surface of **DB1** in the typical crystal form. The polymer **P1**, however, had become
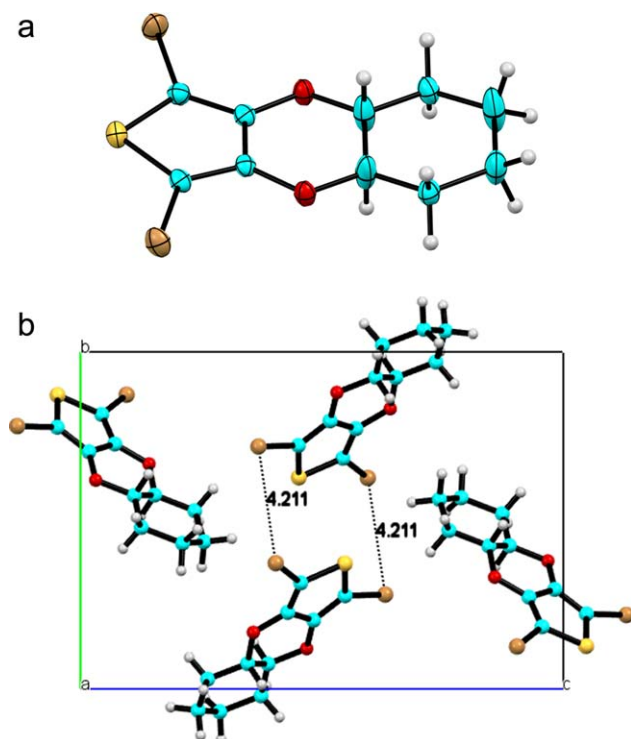
Figure 1. Single-crystal X-ray structure of **DB1**: (a) ORTEP plot (20% probability level); (b) packing diagram showing Br⋯Br intermolecular distances. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2. SEM images of (a) the crystal of **DB1**; (b) SSP-**P1** (heated at 120°C).

relatively disordered [Figure 2(b)]. It was assumed that the crystalline surface was destroyed during the SSP due probably to evaporation of the excess bromine byproduct mostly released from the surface layer.

For comparison, solution of **1** was also oxidatively polymerized using the typical FeCl₃ polymerization procedure.[26] The IR spectra of **1** and **P1** from oxidative polymerization and from SSP are shown in Figure 3. The spectra of the polymers from two polymerization methods are quite similar and carry most of the expected signals such as aliphatic C—C stretching and C=C bands of thiophene ring.

MALDI-TOF MS was used to determine the molecular weight of **P1**. With 2,5-dihydroxybenzoic acid (DHB) as the matrix, the MS spectrum shows the presence of mass signals close to 15 monomer units (theoretical value = 2916). Using α-cyano-4-hydroxycinnamic acid (CCA) as the matrix revealed the mass differences between each signal probably fragmented from the molecular ion corresponding to the molecular weight of the monomer unit (m/z = 194) (Figure 4). Although the results may not give the accurate information on the molecular weight of the polymer, they confirmed the expected polymeric structure of the obtained products.

We next extended the scope of the research to other derivatives that carry functionalizable groups. The versatile EDTM was naturally chosen due to its extensive studies and availability of *o*-derivatized analogs. Disappointedly, the dibromo derivative DBEDTM is liquid at room temperature and it seems unable to
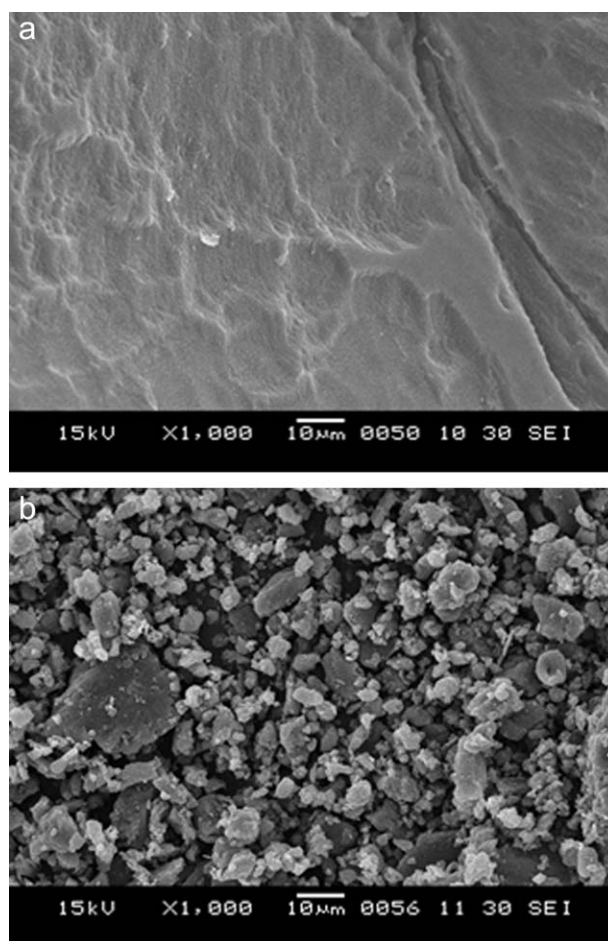
be polymerized under SSP. Nevertheless, we noticed that the solution of the compound changed color while being concentrated at high temperature. Thus, we decided to heat the liquid sample of DBEDTM under the usual SSP procedure and found that the dark blue insoluble solid polymer PEDTM was obtained. The result was believed to be the first report of
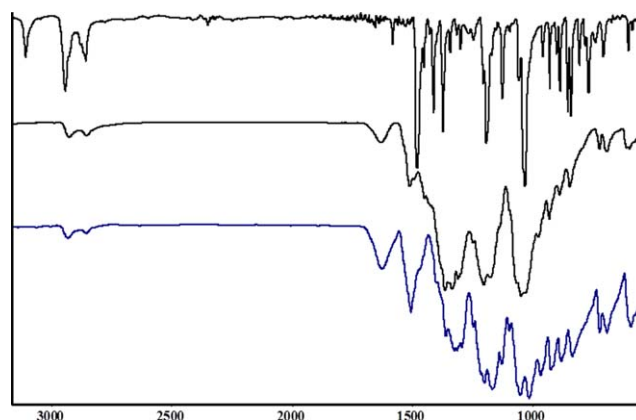

Figure 3. IR spectra of (a) compound **1**; (b) oxidative polymerized **P1**; and (c) SSP-**P1**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
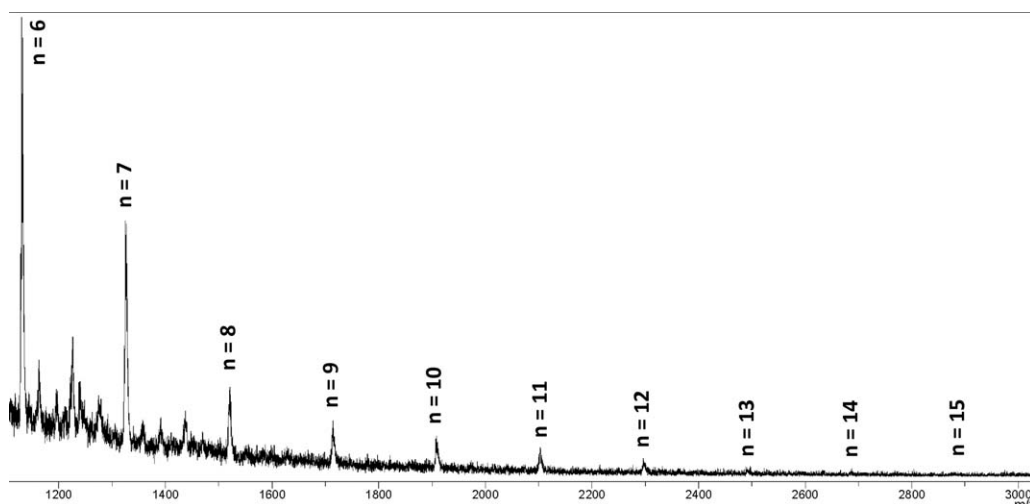
Figure 4. Expanded MALDI-TOF MS spectrum of SSP-**P1**.

thermal-activated polymerization of DBEDTM similar to SSP. The reaction was so facile that it was uncertain how, in solid or liquid state, the process took place.

The presence of the hydroxyl groups on the PEDTM added many useful properties to the family of SSP-derived conjugated polymers such as increasing polarity, hydrogen bond ability, and, in particular, functionalizability. To demonstrate this latter applicability, compounds **2** and **3** were efficiently prepared from acylations of EDTM by *p*-toluenesulfonyl chloride and chloroacetyl chloride, respectively (Scheme 2). After their brominations by NBS using the same procedure, the solid dibromo derivatives **DB2** and **DB3** were heated under SSP condition to yield the corresponding polymers **P2** and **P3**, once again, as dark blue

insoluble solid powder. While **DB2** turned blue within an hour, the SSP process of **DB3** was rather slow similar to that of **DB1**, in which the blue color of the polymer product appeared after long heating time of over 10 h. Their UV–Visible absorption spectra appeared as broad bands with the maxima in the range of 500–650 nm, covering the same area as PEDOT.[27] This result partly supported the structural similarity of their conjugated systems.

A compressed thin polymer pellet of each polymer sample was measured its surface conductivity by four-point probe technique immediately after doping by iodine vapor for 24 h. The results were shown in Table I. Although PEDOT film obtained from SSP of DBEDOT (Entry 2) showed higher value than that was obtained from oxidative polymerization by $FeCl_3$ (Entry 1), the difference margin was not as high as what has been previously reported.[9,10] The possible reason could be due to the reaction time that was limited to 24 h in our case. We observed that the solution washed from **P1** and **P3** immediately obtained from SSP processes could recover a certain amount of unreacted monomers (at least 8% of **DB1** and 5% of **DB3**). After the experiments, the conductivities of some samples were remeasured and found to continue to increase after being kept at room temperature, indicating that the SSP were incomplete and
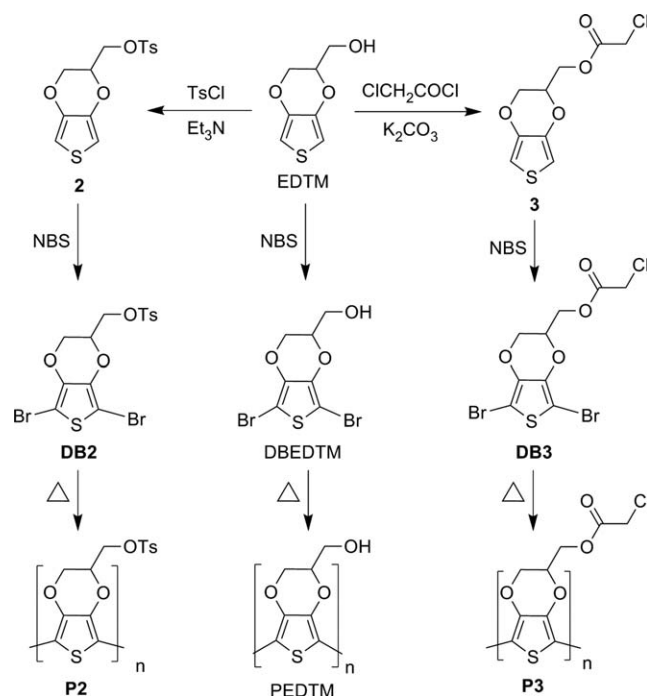
Scheme 2. Synthesis of derivatives of EDTM and their subsequent brominations and polymerizations.

Table I. Conductivity Measurements of the Prepared PEDOT Derivatives

Entry	Polymer	Polymerization method	Reaction temperature (°C)[a]	Conductivity (S/cm)
1	PEDOT	Oxidation	30	3.62
2	PEDOT	SSP	80	5.91
3	PEDTM	SSP	80	44.50
4	**P1**	SSP	80	0.31
5	**P2**	SSP	80	19.00
6	**P3**	SSP	80	1.08
7	**P1**	SSP	120	161.0

[a] The reaction time was limited to 24 h.

still in progress. Much higher values of PEDTM and its tosylate derivative **P2** (Entries 3 and 5) suggested that SSP of these derivatives were more facile, possibly because the polar interactions among the side chains of the monomers help situate them toward suitable arrangements for effective SSP. In fact, the monomer DBEDTM was quite difficult to purify as it kept turning blue upon standing at room temperature or being concentrated from a warm solution.

Upon examining the data at first, it seemed that PEDTM and **P2** from SSP were the two best materials in this group. However, realizing that their SSP processes were much faster than any other derivatives, it is possible that they were unfairly compared at different stages of polymerizations. We then decided to repeat the SSP of **DB1** at higher temperature for the same 24 h period (Entry 7). The structural characters of the obtained **P1** from this method were quite similar to the previous one. As expected, its conductivity was raised up to a surprisingly high value. This result confirmed our hypothesis that the observed low conductivity values were obtained from materials with low degree of polymerizations. Giving more time or accelerating rate of polymerization by increasing reaction temperature would drive the process to more advanced stages toward the completion, and better conjugated polymers would be obtained.

CONCLUSION

We have successfully synthesized four dibromothiophene precursors for SSP investigations. Compound **DB1** was obtained from transetherification of 3,4-dimethoxythiophene and cyclohexanediol followed by NBS bromination using our newly developed methodology. Compounds **DB2** and **DB3** were prepared from substitutions on the hydroxyl groups of EDTM and subsequent brominations by the same method. All dibromothiophene derivatives were subjected to the facile thermal-activated SSP process to give the corresponding polythiophenes based on PEDOT framework. Rates of polymerizations of these precursors were varied and seemed to be incomplete within the reaction condition chosen for the synthesis. To verify this incompletion, the reaction temperature of the SSP of **DB1** was raised to just below its melting point, which has dramatically improved the polymerization progress and yielded better polymer **P1**, evidenced by the large increase in the conductive property. The long Br. . .Br distance between **DB1** molecules determined from the crystal structure supported the earlier observation that the halogen proximity was not the critical factor to induce SSP of dibromothiophene derivatives, though it may have some effects on rate of polymerization. PEDTM, **P2**, and **P3** were the three polymers with functionalizable groups first prepared by SSP method. The presence of these functional groups would add the possibilities of many postprocessing applications on the polymers, particularly in the field of organic electronic and photonic materials,[2,3] which were the goals of our future investigations currently pursued.

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