Systematic Study on Chemical Oxidative and Solid-State Polymerization of Poly(3,4-ethylenedithiathiophene)

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ABSTRACT: Systematic research on the synthesis, chemical oxidative polymerization of 3,4-ethylenedithiathiophene (EDTT) in the presence of surfactants or not, and solid-state polymerization of 2,5-dibromo-3,4-ethylenedithiathiophene (DBEDTT) and 2,5diiodo-3,4-ethylenedithiathiophene (DIEDTT) under solventless and oxidant-free conditions has been investigated. Effects of oxidants (Fe³⁺ salts, persulfate salts, peroxides, and Ce⁴⁺ salts), solvents (H₂O, CH₃CN/H₂O, and CH₃CN), surfactants, and so forth on polymerization reactions and properties of poly(3,4-ethylenedithiathiophene) (PEDTT) were discussed. Characterizations indicated that FeCl₃ was more suitable oxidant for oxidative polymerization of EDTT, while CH₃CN was a better solvent to form PEDTT powders with higher yields and electrical conductivities. Dispersing these powders in aqueous polystyrene sulfonic acid (PSSH) solution showed better stability and film-forming property than sodium dodecylsulfate and sodium dodecyl benzene sulfonate.

INTRODUCTION Conducting polymers, since their initial discovery in 1977, have won fast-growing attention for their applications in transparent conductive coatings, solid electrolyte capacitors, antistatic coatings, electroluminescent lamps, organic light emitting diodes (OLEDs), organic solar cells (OSCs), electrochromic materials, organic field-effect transistors (OFETs), printed wiring boards, and so on.^{1,2} However, in the early stage, typical conducting polymers such as polyanilines, polypyrroles, polythiophenes exhibited low solubility and poor processability. Therefore, a great deal of efforts have been focused on the modification of their chemical structures, in order to alter their electronic structures and improve their electrical properties, environmental stability, and processability.² A breakthrough progress has been achieved in the preparation of poly(3,4-ethylenedioxythiophene) (PEDOT), which was developed from polythiophene (as shown in Scheme 1).² It not only benefits smaller steric hindrance, lower oxidation potential, and higher stability, but also overcomes lower electrical conductivities of polyalkylthiophenes and polyalkoxythiophenes.^{2,3} In 1990, the first

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Oxidative polymerization of EDTT in aqueous PSSH solutions formed the solution processable PEDTT dispersions with good storing stability and film-forming performance. Solvent treatment showed indistinctive effect on electrical conductivity of free-standing PEDTT films. As-formed PEDTT synthesized from solid-state polymerization showed similar electrical conductivity, poorer stability, but better thermoelectric property than oxidative polymerization. Contrastingly, PEDTT synthesized from DIEDTT showed higher electrical conductivity (0.18 S cm⁻¹) than DBEDTT which showed better thermoelectric property with higher power factor value (6.7 \times 10⁻⁹ W m⁻¹ K⁻²). © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 1967–1978, 2012

KEYWORDS: analogs of PEDOT; chemical oxidative polymerization; conducting polymers; poly(3,4-ethylenedithiathiophene); solid-state polymerization

processable PEDOT product, poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS, Scheme 1), a dark-blue aqueous dispersion, was marked by Bayer AG.²⁻⁴ By coating or printing this dispersion, highly stable, conducting, transparent, mechanically durable, and insoluble films can be formed and their properties can be adjusted by adding various formulation components or processing conditions.^{2,3,5} To date, PEDOT/PSS has been the most successfully commercialized polythiophene. Based on it, conducting polymers enclosed PEDOT attract more and more attention because of their wide commercial applications,⁶⁻¹¹ for example, as antistatic coating materials, as transparent anodes and buffer layers in OSCs, as hole-injection layers in OLEDs, as electrodes, and active layers in OFETs.² In the past twenty years, vast amount of work has been carried out on the design and polymerization of EDOT analogs with novel structure and the properties of the resulting polymers.^{2,3}

Up to now, the family of EDOT analogs includes (1) ring-size variations, 3,4-methylenedioxythiophene (MDOT), 3,4-propylenedioxythiophene (PDOT), and 3,4-butylenedioxythiophene



SCHEME 1 Structural evolution from polyacetylene to PEDOT and PEDOT/PSS.

(BDOT);^{12,13} (2) sulfur analogs, 3,4-methylenedithiathiophene (MDTT), 3,4-ethylenedithiathiophene (EDTT), EDTT-R (R = Br, CH₂OH etc.), 3,4-propylenedithiathiophene (PDTT), and thieno[3,4-b]-1,4-oxathiane (EOTT);¹⁴⁻¹⁸ (3) selenium analogs, 3,4-ethylenedioxyselenophene (EDOS), 3,4-propylenedioxyselenophene (PDOS), PEDOS-R₂ (R₂ = C_nH_{2n+1} , n = 4, 6, 10), 3,4ethylenedithioselenophene (EDTS), seleno[3,4-b]-1,4-oxathiane (EOTS), and 3,4-ethylenediselenathiophene (EDST);^{19–25} (4) nitrous analogs, 3,4-methylenedioxypyrrole (MDOPy), 3,4-ethylenedioxypyrrole (EDOPy), 3,4-propylenedioxypyrrole (PDOPy), 3,4-butylenedioxypyrrole (BDOPy), 3,4-methylenedithiopyrrole (MDTPy), and 3,4-ethylenedithiopyrrole (EDTPy); $^{26-29}$ (5) phosphorous analog, 3,4-ethylenedithiaphosphole (EDPP);³⁰ (6) oxygenic analogs, 3,4-ethylendithiafurane (EDTF), 3,4-ethylenedioxyfuran (EDOF), and 3,4-dihydro-2H-thieno[3,4-b]pyran (EDTP);^{31–33} (7) telluric analog, 3,4-ethylenedioxytellurophene (EDOTe) as a predicted structure based on 3,4dimethoxytellurophene (DMOTe).³⁴ Structures of the above are summarized in Scheme 2.

Among them, EDTT, as the all-sulfur analog of EDOT, shows some unique properties.^{15,35-39} For example, EDTT has a lower oxidation potential compared to EDOT, and there is a better electronic interaction between polymer chains through intermolecular S."S attractions in PEDTT than PEDOT.^{15,35,39,40} Nowadays, PEDTT and its derivatives have found possible applications as the electron donor materials in photovoltaic devices,^{35,37,38,41–44} and as the cathode active materials for rechargeable lithium batteries with better cathode capacity than PEDOT.⁴⁵ More recently, electrosynthesized PEDTT materials were introduced into organic electronic display field and sensors owing to their electrochromic and electrochemical catalytic properties.^{21,46-48} However, since firstly reported by Kanitzidis and coworkers in 1995,15 much of the research associated with EDTT has entailed the incorporation of it with other conjugated structures or introduced other functional groups into its structure, 16,17,35,37,38,41,42,46 and most polymers relating to PEDTT were prepared by electrochemical polymerization. Inconsistent with its significance to actual applications, chemical oxidative polymerization of EDTT and its derivatives was barely reported and characterization of corresponding polymers has been not adequate.

Therefore, systematical investigation of chemical oxidative polymerization of EDTT is very necessary.

In this article, chemical oxidative polymerization of EDTT by different oxidants, with different kinds of sulfonate surfactants or no, was discussed in detail. Solid-state polymerization of 2,5-dibromo-/diiodo-EDTT under solventless and oxidant-free conditions was also studied carefully for comparison. The effect of factors such as oxidants, solvents, surfactants, additives, reaction temperatures, etc. on electrical conductivity, processability, stability, and other properties of corresponding polymers were investigated.

EXPERIMENTAL

Materials

3,4-Dibromothiophene (Shanghai Bangcheng Chemical Co., China), 1,2-ethanedithiol (Shanghai Zhuorui Chemical Co., China), and ethylene glycol (EG; Beijing East Longshun Chemical Plant, China) were all analytical grade (98+%) and distilled under reduced pressure prior to use. Chloroform (99+%; Beijing East Longshun Chemical Plant) and acetonitrile (99+%; Tianjin Bodi Chemicals Co., China) were purified by distillation with calcium hydride under a nitrogen atmosphere before use. Toluene (98+%; Beijing East Longshun Chemical Plant) was washed with concentrated sulfuric acid and saturated sodium bicarbonate in sequence, and then distilled under reduced pressure before use. Methanol (99+%; Tianjin Bodi Chemicals Co.) was distilled from magnesium powder in the presence of catalytic amount of iodine under a dry argon flow. N-bromosuccinimide (NBS, 99%), N-iodosuccinimide (NIS, 99%), polystyrene sulfonic acid (PSSH, $M_w = 75,000$; 30 wt % aq.), and polystyrene sulfonate sodium salt (PSSNa, $M_{\rm w} = 70,000$) were products of Alfa Aesar and used as received. Strongly basic anionexchange resin (201 \times 7, batch number F20080403) and strongly acid cation-exchange resin (001 \times 7, batch number F20090303) were purchased from China National Medicine Group Shanghai Chemical Reagent Company. Other chemicals and reagents were all purchased commercially in analytical grade (98+%) from Beijing East Longshun Chemical Plant (China) and used directly without any further treatment.



Synthesis of 3,4-Dimethoxythiophene

Sodium (14.220 g, 618.3 mmol) was added into a 500-mL three-necked round bottom flask which fitted with a reflux condenser under an atmosphere of nitrogen. Methanol (150 mL) was added dropwise and stirred until sodium dissolves completely. 3,4-Dibromothiophene (30.630 g, 126.6 mmol), KI (0.205 g, 1.237 mmol), and CuO (9.840 g, 123.7 mmol) were added and then the mixture was refluxed at 97 °C for 48 h. After that, another 0.205 g (1.237 mmol) of KI and 10 mL of 30% sodium methoxide/methanol solution was added. The mixture was refluxed for 12 h and another 10 mL of 30% sodium methoxide/methanol solution was added and stirred for another 12 h. Thin-layer chromatography (TLC) was used to detect the completion of the reaction. After most of the solvent was distilled out at the same temperature, the mixture was cooled, filtered, diluted with water, and extracted with ether. The collected organic layer was dried over anhydrous MgSO₄, filtered, and the solvent was removed on a rotary evaporator to afford a yellow-brown oil liquid. The crude compound was purified by silica gel column chromatography using petroleum ether as the eluent to give about 17.50 g (121.5 mmol) of product as colorless oil. Yield: 96%. $R_{\rm f}$: 0.05 (silca gel, petroleum ether; the by-product 3-bromo-4-methoxythiophene: 0.28, 3,4-dibromothiophene: 0.71). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 3.86 (s, 6H), 6.20 (s, 2H).

Synthesis of EDTT

A mixture of 3,4-dimethoxythiophene (16.400 g, 113.9 mmol), *p*-toluenesulfonic acid (0.824 g, 4.784 mmol), 1,2-ethanedithiol (43.100 g, 457.5 mmol), and toluene (100 mL) was stirred under nitrogen atmosphere for 48 h at 90 °C. The reaction was monitored by TLC. Later, another 43.100 g (457.5 mmol) 1,2-ethanedithiol and 0.824 g (4.784 mmol) *p*-toluenesulfonic acid was added and stirred for another 24 h at the same temperature. After that, the mixture was allowed to cool to room temperature, removed toluene under reduced pressure, extracted with ether, and then washed with 5% NaOH solution and water. The collected organic phase was dried over anhydrous MgSO₄, filtered, and





SCHEME 3 Synthesis of EDTT and EDOT. pTSA = p-toluene-sulfonic acid.

concentrated in vacuum. The crude product was purified by means of silica gel column chromatography using petroleum ether as the eluent to afford a colorless liquid (19.050 g). Yield: 90%. $R_{\rm f}$: 0.31 (silca gel, petroleum ether). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 3.23 (s, 4H), 6.98 (s, 2H).

Synthesis of 2,5-Dibromo-3,4-ethylenedithiathiophene

2,5-Dibromo-3,4-ethylenedithiathiophene (DBEDTT) crystal was prepared by straightforward bromination of EDTT with NBS in 58% yield as described in Scheme 3 according to the literature.²¹

Synthesis of 2,5-Diiodo-3,4-ethylenedithiathiophene

To a solution of EDTT (1.743 g, 10 mmol) in CHCl₃ (40 mL) and glacial acetic acid (AcOH, 20 mL) at 0 °C, NIS (4.837 g, 21.50 mmol) was added slowly under nitrogen atmosphere. After stirring at 0 °C for 15 min, the solution was further stirred at room temperature for 24 h. The resulting mixture was diluted with 100 mL deionized water and extracted with CHCl₃ (50 mL \times 3). The organic phase was neutralized with 10% NaHCO₃ solution, washed with deionized water, dried with anhydrous MgSO₄, and concentrated. The crude product was isolated by column chromatography (silica gel; hexane/CHCl₃: 5/1, v/v) to give a light brown solid. It was recrystallized from ethanol to produce 1.747 g of light tawny crystals. Yield: 41%. $R_{\rm f}$: 0.31 (silca gel; hexanes/CHCl₃: 5/1, v/v). m.p.: 130.0 °C. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 3.22 (s, 4 H).

Chemical Oxidative Polymerization of EDTT

EDTT (4.673 g, 26.811 mmol) was dropped into 154 mL CH₃CN solution of FeCl₃ (9.992 g, 61.600 mmol), and the mixture was stirred vigorously for 72 h in 25 °C water-bath. A dark-green powder was filtered, washed successively with CH₃CN and acetone. After drying at 60 °C for 18 h, an amount of 2.845 g PEDTT product was obtained in the doped form. Moreover, a brown neutral PEDTT powder [0.821 g, Fig. 1(right)] was obtained by treating the dark-green powder [1.005 g, Fig. 1(left)] with hydrazine hydrate (5 mL) and H₂O (100 mL) for 48 h, and was filtered, washed with water, and dried at 60 °C for 24 h.

Following above oxidative polymerization route, other oxidants such as $(NH_4)_2S_2O_8$, H_2O_2/Fe^{2+} , $Ce(SO_4)_2$, and $(NH_4)_2Ce(NO_3)_6$ were used to replace FeCl₃ and other solvents such as H_2O and CH_3CN/H_2O (1/1, v/v) were used to replace CH_3CN .

Dispersion of Oxidatively Polymerized PEDTT in PSSH

Above PEDTT (doped) powder (0.500 g) was added into 100.455 g PSSH aqueous solution (1.5 wt %), underwent a high speed shear process at 25 °C for 1 h and then treated with homogenizer. Dispersion (Sample 1) was obtained with pH of 0.91 and viscosity of 1.9 mPa s. Following the same treatment, neutral PEDTT powder was transferred to a dispersion (Sample 2) with pH of 0.93 and viscosity of 0.7 mPa s. Other anionic surfactants such as sodium dodecylsulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), and PSSNa were also used to replace PSSH.

Oxidative Polymerization of EDTT in Aqueous PSSH Solutions

EDTT (0.614 g, 3.523 mmol) was added into 86.169 g PSSH aqueous solution (1.5 wt%) and the mixture was stirred vigorously for 20 min in 25 °C water-bath under nitrogen. Upon addition of FeCl₃ (0.742 g, 4.574 mmol), EDTT polymerized immediately, leading to a cream mixture. This mixture was stirred for 24 h at 25 °C and subjected to desalting as follows. The as-prepared mixture was diluted with twice its volume of deionized water, and stirred for 7 h at 25 $^\circ\text{C}$ in the presence of granulated strongly basic anion-exchange resins (201 \times 7). Then, the ion-exchange resins were filtered off, and the filtrate was treated with strong acid cationexchange resin (001 \times 7) in the same way. The final filtrate was condensed to the solid content of 2.1 wt %. Following treatment with homogenizer, it finally gave an aqueous PEDTT/PSS dispersion (Sample 3) with pH of 0.55 and viscosity of 1.7 mPa s.

Other oxidants such as $Fe(NO_3)_3 \cdot 9H_2O$, H_2O_2/Fe^{2+} , $Na_2S_2O_8$, and $Na_2S_2O_8/Fe^{3+}$ were also used to replace $FeCl_3$.

Treat PEDTT Dispersions with Organic Solvents

PEDTT dispersions (Sample 3) were mixed with various amount of dimethyl sulfoxide (DMSO) (0 wt %, 5 wt %, 10 wt %, 15wt %, 20 wt %, and 25 wt %). These mixtures were stirred for 24 h at 25 °C, treated by using ultrasonic vibration for 5 min, and then cast onto polypropylene (PP) film substrate. After drying at 80 °C in vacuum (38 mmHg) until constant weight, free-standing PEDTT films were formed.



FIGURE 1 Photographs of as formed (doped) and neutral PEDTT powders formed by chemical oxidative polymerization of EDTT with FeCl₃ in CH₃CN.



SCHEME 4 Chemical oxidative and solid-state polymerization of EDTT. AcOH = glacial acetic acid.

Other organic solvents such as EG, dimethyl formamide (DMF), *N*-methyl-2-pyrrolidone (NMP), and acetone were also used to replace DMSO.

Solid-State Polymerization of DBEDTT and DIEDTT

DBEDTT (2.494 g, 7.508 mmol) and 2,5-diiodo-3,4-ethylenedithiathiophene (DIEDTT) (3.194 g, 7.496 mmol) were added into two 50-mL round flasks, respectively. After heating at 40 °C (for DBEDTT) and 110 °C (for DIEDTT) for 7 days under room conditions (T = 30 °C, RH = 36%), corresponding PEDTT solids (SSP-DBEDTT and SSP-DIEDTT) were formed, as shown in Scheme 4.

Characterization

¹H NMR spectra were recorded on a Bruker AV 400 NMR spectrometer and CDCl₃ was used as the solvent. UV-vis spectra were measured with a Perkin-Elmer Lambda 900 UV-vis-near-infrared spectrophotometer. The pH values of PEDTT dispersions were tested by a pen-like pH meter (CT-6022, Shanghai Rentong Meter Co.). The viscosities were measured by a digital viscometer (NDJ-5S, Shanghai Hengping Meter Co.). The temperature dependence of both electrical conductivity (σ) and Seebeck coefficient (S) were determined by using the standard four-probe technique by measurement unit of thermoelectric properties coupled with a liquid nitrogen container for pressed pellets or free-standing films at temperatures from room temperature to 100-150 K. Cu (99.9%) wires as electrodes and the thermocouples were bound to a sample with conductive carbon paint (colloidal graphite in isopropanol-20% solids) at room temperature. PEDTT pellets were compressed for the measurements under a pressure of 15 MPa. Thickness Gauge

(CH-1-S/ST, Shanghai Liuling Meter Co) was used to measure the thickness of pellets and films. Melting points were recorded on a hot-coil stage melting point apparatus (XSZ-4G, Beijing Fuka Keyi Science and Technology Co.). X-ray diffraction (XRD) investigations were performed on a Bruker D8 ADVANCE X-ray diffractometer using Cu K α radiation method (40 kV, 40 mA). A Cold Field Emission Scanning Electron Microscope (S-4300 N, Hitachi) was used to analyze the surface morphologies of the polymer films.

RESULTS AND DISCUSSION

Synthesis of EDTT

Following the synthetic strategy depicted in Scheme 3, EDTT was prepared in one step by acid-catalyzed nucleophilic substitution of 3,4-dimethoxythiophene with 1,2-ethanedithiol with a yield of 90% (lit.²¹ 77%, lit.⁴⁹ 40%). It should be noted here that the precursor 3,4-dimethoxythiophene was synthesized from a commercial chemical, 3,4-dibromothiophene, with a yield of 96% (lit.⁴⁹ 81%, lit.⁵⁰ 70%). In comparison with other routes,^{15,16,22,35,51-54} this transetherification reaction can avoid complex operating procedures and strict reaction conditions. More importantly, by modifying

 $\begin{array}{l} \textbf{TABLE 1} \mbox{ Yields and Electrical Conductivities (Measured at 298 K and 60\% RH) of PEDTT from Chemical Oxidative Polymerization of EDTT by FeCl_3 in Different Solutions \\ \end{array}$

Solvent	Yield	σ (S cm ⁻¹)
H ₂ O	55%	0.11
CH ₃ CN/H ₂ O (1/1, v/v)	58%	0.14
CH ₃ CN	61%	0.19





FIGURE 2 UV-vis absorption (a) and fluorescence emission spectra (b) of doped and neutral PEDTT formed by chemical oxidative polymerization of EDTT with FeCl₃ in CH₃CN. Solvent: NMP (0.1 mg mL⁻¹).

the raw material quantity, reaction time and post-treatment as described in the Experimental part, the total yield of EDTT can rise up to 86.40%, not only a little better than that of EDOT (80.64%, lit.⁵² 39\%) when EG replaced the thiol as shown in Scheme 3, but also much higher than previous reports. $^{21,35-37,49,50}$

Effect of Oxidants and Solvents on Chemical Oxidative Polymerization of EDTT

Although electrochemical polymerization⁵⁵ and many other polymerization methods, such as in-situ polymerization,² Stille coupling reaction,^{56,57} transition metal-mediated oxidative dispersion polymerization,⁵⁸ Kumada coupling polymerization,⁵⁹ ring-opening metathesis polymerization,⁶⁰ and so forth, have been developed to prepare polythiophenes including PEDOT and its analogs, chemical oxidative polymerization is still the most important and irreplaceable way for large-scale industrial applications until now. Therefore, herein, chemical oxidative polymerization of EDTT with oxidants was performed in different solvents. The main attention was paid to achieve high conducting polymers with good yields by optimizing oxidation conditions, including solvents and oxidants. In the viewpoint of the cost, processing, and safety, water was the best choice as the solvent for oxidation polymerization. However, EDTT owns extremely low water-solubility in H₂O, which partially offsets its advantages. A possible improving strategy is adding CH₃CN, a much suitable highly polar solvent media allowing complete dissolving of EDTT. Finally, in this study, H₂O, CH₃CN, and CH₃CN/H₂O were investigated for the chemical polymerization of EDTT. For oxidants, FeCl₃, (NH₄)₂S₂O₈, H₂O₂/Fe²⁺, $Ce(SO_4)_2$, and $(NH_4)_2Ce(NO_3)_6$ were used. Among them, FeCl₃ seems the most convenient, because it is dissolved completely both in CH₃CN and in H₂O. Characterization of UV-vis, solubility, yields, electrical conductivity, and so forth, of the final polymers was carried out. The primary results of them have been enclosed in another report.⁶¹ In conclusion, EDTT oxidized with FeCl₃ led to PEDTT with the highest electrical conductivity (0.1–0.2 S cm^{-1} at 298 K, lit.¹⁵ 0.1 S cm⁻¹) and better yields (55–61%). Moreover, as listed in Table 1, a dark-green PEDTT powder with the highest conductivity of 0.19 S cm⁻¹ at 298 K and the best yield of 61% was achieved in CH₃CN. Brown neutral PEDTT powder was obtained in 81.69% yield after treating this as-prepared powder with hydrazine hydrate for 48 h (Fig. 1). Both polymers can partly dissolve in NMP (0.1 mg mL^{-1}) at room temperature. Electronic spectra and photoluminescence spectra of them in NMP display two absorption bands (410 nm



FIGURE 3 Comparison of the storing stability and dispersive performances of PEDTT dispersions Sample 1 (a), Sample 2 (b), and Sample 3 (c).



FIGURE 4 Images of the free-standing films (the later was folded from the former) casting from PEDTT dispersion (Sample 3) on PP substrate.

and 333 nm for doped, 418 nm and 341nm for neutral) in the UV-visible region [Fig. 2(a)], and broad band luminescence with a peak at 569 nm [Fig. 2(b)]. These values are quite similar to Kanatzidis and coworkers' results.¹⁵

Effect of Surfactants on Dispersion of PEDTT

In order to improve the solubility of oxidatively polymerized PEDTT, a simple processing method was first introduced to prepare processable PEDTT dispersions in water, as shown in Scheme 4. Generally, PEDTT powders were dispersed into aqueous surfactant solutions through a high-speed shear treatment. For this, aforementioned PEDTT powders (doped and neutral) synthesized from oxidative polymerization of EDTT with FeCl₃ in CH₃CN, and several common sulfonate surfactants, including SDS, SDBS, PSSH, and PSSNa were used. It has been found that PEDTT dispersed in SDS and SDBS solutions was such unstable that visibly precipitated within 6 h, and no continuous and compact films can be coated on substrates from the final dispersions. Contrastingly, dispersing PEDTT in aqueous PSSH and PSSNa solutions led to relatively stable dispersions from which durable and free-standing films can be obtained on PP substrate. Therefore, PSSH and PSSNa were the better choice among surfactants. Simultaneously, in view of the unfavorable influence of inorganic metal ions in organic films, PSSH was the final choice and state of corresponding PEDTT dispersions (Sample 1 for doped and Sample 2 for neutral) are shown in Figure 3 (a1,b1). Electrical conductivity measurement of pristine PEDTT films indicated a value of 1.26 \times 10^{-2} S cm⁻¹ at 298 K for Sample 1, much higher than that of Sample 2 (2.35 \times 10⁻⁶ S cm⁻¹). The electrical conductive property of neutral PEDTT after dispersion can be attributed to PSSH. As a water-soluble polyelectrolyte, it can not only serve as good dispersant for PEDTT in water, but also function as the charge balancing counter ion or dopant to the PEDTT.⁴

Chemical Oxidative Polymerization of EDTT in Aqueous PSSH Solutions

In comparison to the aforementioned method to prepare PEDTT dispersions, chemical oxidative polymerization of EDTT with oxidants in aqueous PSSH solutions (as shown in Scheme 4) has obvious advantages. It combined the polymerization of EDTT with the dispersion of PEDTT, and finally formed PEDTT/PSS complex rather than just blends of PEDTT and PSSH. Three kinds of oxidants, including iron salts, persulfates and peroxides, were chosen. Differently from chemical oxidative polymerization forming PEDTT powders above, $Fe(NO_3)_3 \cdot 9H_2O$, $Na_2S_2O_8$, and $Na_2S_2O_8/Fe^{3+}$ were used to replace unpleasant (NH₄)₂S₂O₈,⁶¹ and more aggressive ceric-based oxidants.^{61,62} Following desalting with ion-exchange resins and homogenizing, five aqueous colloidal PEDTT/PSS dispersions with orange color (Samples 3-7 in Table 2) were obtained. These samples can maintain their steady colloidal state more than one month, while visible PEDTT deposits can be seen in Sample 1 and Sample 2 after storing for one month at room temperature. In Figure 3, images gave a vivid illustration of the better storing stability of Sample 3 in comparison with Sample 1 and Sample 2. Here, it should be pointed out that more or less PEDTT deposits as shown in Fig. 3 (a2,b2,c2), appearing after storing PEDTT dispersions [Fig. 3 (a1,b1,c1)] for one month at

TABLE 2 Comparison of	Oxidants on Elec	ctrical Conductivities
of PEDTT Films (Measu	red at 298 K and 6	30% RH)

Sample	Oxidants	σ (S cm ⁻¹)
3	FeCl ₃	2.4×10^{-3}
4	Fe(NO ₃) ₃ ·9H ₂ O	1.3×10^{-4}
5	H_2O_2/Fe^{2+}	1.0×10^{-3}
6	$Na_2S_2O_8$	4.1×10^{-4}
7	$Na_2S_2O_8/Fe^{3+}$	8.0×10^{-5}





FIGURE 5 Temperature dependence of electrical conductivity of the film casting from PEDTT dispersion (Sample 3) on PP substrate.

room temperature, can be dispersed again into water by shaking. This phenomenon is different to PEDOT/PSS, which may result in the formation of non-redispersible deposits. One reason for this is steric interaction between adjacent EDTT moieties would decrease the extent of π -conjugation through the polymer system and, thus, PEDTT presented relatively short conjugated chains in PEDTT/PSS complex.^{35,39} Coating Samples 3–7 onto PP film formed free-standing thin films, and can be cut into various shapes. A picture of cutting films (in Fig. 4) from Sample 3 was taken as an example.

Effect of Solvent Treatment on Electrical Conductivity of PEDTT/PSS films

Electrical conductivity measurement of PEDTT/PSS films was taken under room conditions (298 K, 60% RH) by using the standard four-probe method. A range of values within the order of magnitude between 10^{-5} and 10^{-3} S cm⁻¹ was tested. The results (as listed in Table 2) indicated that the highest electrical conductivity value was present when FeCl₃ was used as the oxidant in polymerization reaction. The electrical conductivity also showed temperature dependence as depicted in Figure 5. It was 2.38 \times $10^{-3}~S~cm^{-1}$ at ambient temperature and decreased to 2.09 \times $10^{-3}~S~cm^{-1}$ at 100 K. To make an attempt to increase the electrical conductivity of PEDTT/PSS films, a range of organic solvents, including acetone, DMSO, EG, DMF, and NMP, were used as additives into the PEDTT/PSS dispersions. After casting on PP substrate and dried, free-standing PEDTT/PSS films were subsequently formed. Electrical conductivity measurement of these films indicated that values of PEDTT/PSS decreased with the additive concentration of organic solvents out of proportion. Values between different solvents did not show many differen-



FIGURE 6 Electrical conductivity (measured at 298 K and 75% RH) of the films versus the amount of DMSO (wt %) in the Sample 3 (a), Sample 5 (b), and Sample 7 (c, inset).

ces. Therefore, only one example is given in Figure 6. It indicated that DMSO treatment on PEDTT/PSS dispersions tended to slightly decrease the electrical conductivities of corresponding films within the same order of magnitude. Such results were quite different to PEDOT/PSS.⁴ Although it is still unclear what factors govern this phenomenon, the short conjugated chain of PEDTT, and the tight attachment of PEDTT⁺ chains and PSS⁻ through S^{...}S interaction may be one reason for it.

Synthesis and Solid-State Polymerization of DBEDTT and DIEDTT

Recently, solid-state polymerization of 2,5-dihalothiophene derivatives under solventless and catalyst-free conditions has attracted significant attention for the synthesis of highly ordered polymers and macroscopic polymer single crystals.^{14,63–65} In 2003, Skabara and coworkers demonstrated the applicability of this method for the preparation of bromine-doped PEDTT by heating the crystal of DBEDTT.¹⁴ However, no detailed synthetic information and electrical conductivity of PEDTT were given. Therefore, in this work, DBEDTT was prepared by straightforward bromination of EDTT with NBS under very mild conditions with EDTT as a starting material in 58% yield (lit.²¹ 55.8%). And, a new diiodo compound, DIEDTT, was first synthesized by iodinization with NIS in chloroform/glacial acetic acid (CHCl₃/AcOH) under ice-water bath with a yield of 41%, as illustrated in Scheme 4.

Solid-state polymerization of DBEDTT and DIEDTT was performed under room conditions by heating them at certain temperatures. Corresponding polymers, SSP-DBEDTT and

TABLE 3 Properties of DBEDTT and DIEDTT, and their Polymers After Solid-State Polymerization

Monomer	Color	Melting point	Polymerization temperature	Reaction time	Polymer	Color	Appearance
DBEDTT	White	55 °C	40 °C	7 days	SSP-DBEDTT	Greenish black	Slice
DIEDTT	Tawny	130 °C	110 °C	7 days	SSP-DIEDTT	Cyan	Powder



FIGURE 7 The release of an orange iodine vapor for SSP-DIEDTT (a) and a brown bromine vapor for SSP-DBEDTT (b) after stored at room conditions for 3 weeks.

SSP-DIEDTT, were formed and can be used for characterizations without further treatment. During the polymerization, 2,5-dibromo- and 2,5-diiodo-EDTT crystals showed distinct color change accompanied with release of brown or orange vapor due to comitant release of dibromine or diiodine which doped the polymer as they were formed. These results are listed in Table 3. Here, it should be noted that the visible color change and the presence of chromatic gas can be seen for DBEDTT after standing over one day at room temperature, while for DIEDTT over three days. By detecting the rate of color change and degassing, it indicated that solid-state polymerization can be accelerated by heating, that is, a higher polymerization temperature leads to a more rapid polymerization rate. However, if the temperatures were set to rapidly melt DBEDTT and DIEDTT as done during the melting points test, no observable change in their color is



FIGURE 8 XRD spectra of SSP-DBEDTT and SSP-DIEDTT.



FIGURE 9 Temperature (*T*) dependence of electrical conductivity σ and Seebeck coefficient *S* (a) for SSP-DBEDTT and SSP-DIEDTT, power factor *P* (c) estimated as $P = \sigma S^2$ from the corresponding σ and *S* at a certain temperature, and electrical conductivity σ (b) after stored at room temperature for 5 months.

seen. ¹H NMR and IR characterization indicated that no polymerization reaction occurred. Therefore, the polymerization temperatures highly depend on the melting points of DBEDTT and DIEDTT. In this work, as shown in Table 3, heating temperatures about 15–20 °C below their melting points for 7 days were chosen.^{53,64} As-formed polymers SSP-DBEDTT and SSP-DIEDTT were completely insoluble in common organic solvents such as DMF, DMSO, NMP, and THF at



FIGURE 10 SEM images (50k×) of the surface of SSP-DBEDTT (left) and SSP-DIEDTT (right).

room temperature. If shortening the heating time to one day, solubility of the polymers can be improved due to relatively lower degree of polymerization.

Electrical Conductivity and Thermoelectric Property of SSP-DBEDTT and SSP-DIEDTT

According to the image in Figure 7, it can be seen that the appearance of orange iodine vapor for SSP-DIEDTT and faint brown bromine vapor for SSP-DBEDTT can be detected after stored for 3 weeks at room temperature. A reasonable explanation is, to solid-state polymerization of DBEDTT and DIEDTT, further polymerization of higher oligomers may still take place after complete transformation of all starting monomers.⁶⁴ This can be supported by the existence of crystal structures in SSP-DBEDTT and SSP-DIEDTT, as indicated by XRD spectra (Fig. 8), which may be responsible for the origin of solid-state polymerization reaction.⁶³ Electrical conductivity measurement [Fig. 9(a,b)] also confirmed the property change of PEDTT. After stored at room temperature for 5 months, electrical conductivity of these samples decreased by two orders of magnitude. The electrical conductivity of SSP-DBEDTT and SSP-DIEDTT decreased gradually with a decrease in the temperature (from 300 K to 100 K), showing a typical behavior of semiconductors. SSP-DIEDTT exhibited much higher electrical conductivities in the range between 0.2 and 0.08 S $\rm cm^{-1}$ than that of SSP-DBEDTT (between 0.013 and 1.85 \times 10⁻⁴ S cm⁻¹). This may be in virtue of a more flattened surface as pictured by scanning electron microscope (Fig. 10).

Specifically, temperature dependence of both the values of Seebeck coefficient [*S*, Fig. 9(a)] and power factor *P* [*P* = σS^2 , Fig. 9(c)] of SSP-DIEDTT and SSP-DBEDTT was described. Comparably, SSP-DBEDTT achieved much better values of Seebeck coefficient in the range from 63 to 122 μ V K⁻¹ as the temperature range from 300 to 175 K

than SSP-DIEDTT (from 9.5 to 18.9 μ V K⁻¹), and has the highest power factor value up to 6.7 \times 10⁻⁹ W m⁻¹ K⁻² at 285 K. These results are pleasant findings because they gave the first valuable, regular, and positive thermoelectrical data for PEDTT.¹⁵ Moreover, although these values within a order of 10⁻⁹ W m⁻¹ K⁻² are too low to meet the requirement for applications,⁶⁶⁻⁶⁸ solid-state polymerization still proved to be a feasible way to synthesize thermoelectric materials.

CONCLUSIONS

A series of PEDTT powders or free-standing films have been achieved via chemical oxidative polymerization of EDTT with different oxidants in H₂O, CH₃CN, CH₃CN/H₂O, and aqueous sulfonate surfactant solutions, and spontaneous polymerization of dibromo- and diiodo- EDTT in their solid form. Systematic discussions of the effect of oxidants, solvent, surfactants, and so forth, on reactions and properties of polymers were investigated. Although there are still many challenges ahead to improve electrical conductivity and thermoelectric performance of PEDTT, results of this study can be regarded as an important reference toward the synthesis of other analogs of PEDOT, including PEDTT derivatives. Research directed to achieve higher conducting PEDTT materials using chemical oxidative polymerization, solid-state polymerization, and copolymerization is in progress in our group. Related theoretical research and applications of resulting polymers as chief compositions, especially in antistatic coatings, organic electrochromic materials, anticorrosive coatings, thermoelectrical materials, and sensor materials are also ongoing.

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