

Preparation and Characterization of Aqueous Dispersions of Poly(3,4-ethylenedithiathiophene-co-3,4-ethylenedioxythiophene)/Poly(styrene sulfonate) and Their Conducting Films

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ABSTRACT: The chemical oxidative copolymerization of 3,4-ethylenedithiathiophene (EDTT) with 3,4-ethylenedioxythiophene (EDOT) and 2'-hydroxymethyl-3,4-ethylenedioxythiophene in a poly(styrene sulfonic acid) aqueous solution was successfully carried out to form stable, dark blue colloidal dispersions in water. Coating these dispersions onto polypropylene substrates led to the formation of free-standing copolymer films. The mechanical, electrical, and thermoelectrical properties of these films were investigated; the films showed superior properties in comparison with those of poly(3,4-ethylenedithiathiophene) (PEDTT)/poly(styrene sulfonate) (PSS). The copolymer film based on EDTT and EDOT achieved a high electrical conductivity ($8.2 \times 10^{-2} \text{ S cm}^{-1}$) at 298 K; this could be improved about 10 times through the addition of dimethyl sulfoxide (DMSO) or DMSO/isopropyl alcohol into the polymer dispersion with almost constant Seebeck coefficients of about $9 \mu\text{V K}^{-1}$. On the contrary, these additives had almost no effect on the conductivity of PEDTT/PSS. The structure and morphology of the polymer films were studied by X-ray diffraction and SEM analyses. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1717–1725, 2013

KEYWORDS: conducting polymers; copolymers; films; polyelectrolytes; thermal properties

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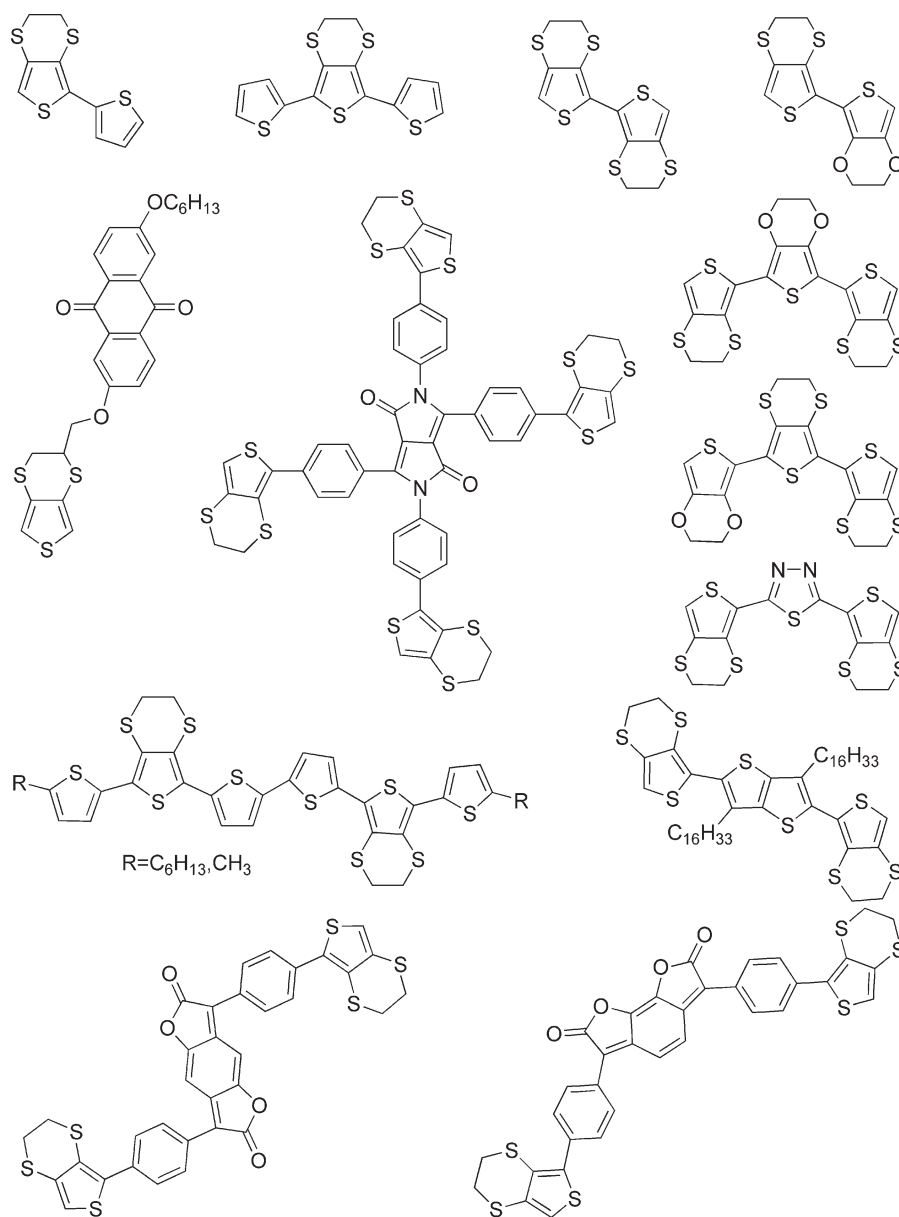
INTRODUCTION

Poly(3,4-ethylenedioxythiophene) (PEDOT), probably the most successful and extensively explored conducting polymers, has been widely used in organic electronics because of its interesting properties, such as its high conductivity, excellent environmental stability, and high transparency in the doped state.^{1–3} Benefiting from its good processing properties together with its excellent film-forming ability, PEDOT/poly(styrene sulfonate) (PSS), an aqueous dispersion, has attracted much attention among the PEDOT family, and it has been used in a number of commercial applications, including antistatic coatings, electrode materials, rechargeable batteries, printed circuit boards, and optoelectronics.^{1–3}

Poly(3,4-ethylenedithiathiophene) (PEDTT), as one of the most studied PEDOT analogues, has unique electrical and optical properties and potential applications in the fabrication of rechargeable batteries, sensors, photovoltaic devices, electrochromic devices, polymer-fullerene devices, and so on.^{3,4–23} In the past 20 years, the electrochemical homopolymerization of com-

pounds containing 3,4-ethylenedithiathiophene (EDTT) units, as listed in Scheme 1, has been studied in detail.^{6,9–11,16,18,20,22} Other methods, such as chemical oxidative and solid-state homopolymerization and, recently, Stille coupling, have also been reported.^{4,7,23–26} However, PEDTT and its derivatives achieved from these methods are usually powders. Consequently, they are difficult to process into thin films via solution or melting. Recently, our group reported a solution-processable aqueous colloidal dispersion of PEDTT/PSS.²⁶ However, it also had disadvantages, such as a relatively low electrical conductivity (σ) and poor thermoelectricity of the as-formed PEDTT/PSS films; these disadvantages have limited its applications in some certain practical fields.²⁶ Therefore, it is necessary to further improve these properties.

It is well known that the preparation of copolymers from mixtures of 3,4-ethylenedioxythiophene (EDOT) with other heterocyclic monomers has successfully progressed by direct chemical or electrochemical polymerization.^{1,3,27} Generally speaking, the physical and chemical properties of these copolymers are usually intermediate between those of the constituent homopolymers.



Scheme 1. Compounds containing EDTT moieties.^{6,9–11,16,18,20}

However, there have been no reports on the copolymerization of EDTT with other compounds and also no reports on chemical oxidative copolymerization to form copolymer dispersions in water. For these reasons, the aim of our research was to produce novel copolymer films from aqueous copolymer dispersions from the chemical oxidative polymerization of mixtures of EDTT and EDOT or its derivatives in the presence of a water-soluble polyelectrolyte, poly(styrene sulfonic acid) (PSSH), to modify the electrical properties of the PEDTT/PSS films.

In this study, 2'-hydroxymethyl-3,4-ethylenedioxythiophene (EDOT-MeOH) was selected as a polar derivative of EDOT because it could improve the poor aqueous solubility and lower the onset oxidation potential of EDOT through the introduction of hydroxyl groups.^{3,28} Second, it also benefited its facile derivatization and was an important synthon in the functionalization

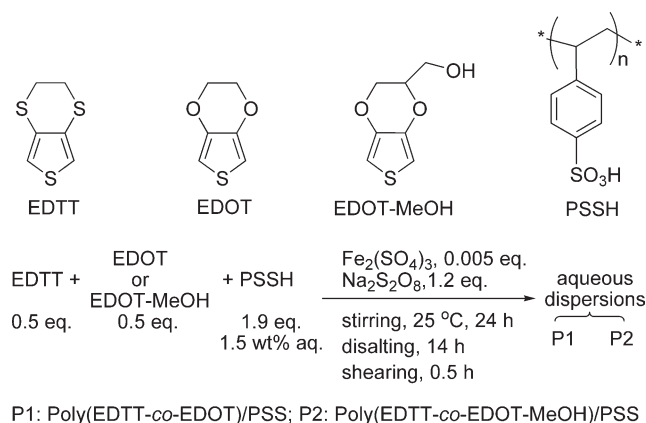
of EDOT with moieties in side chains.³ Third, poly(2'-hydroxymethyl-3,4-ethylenedioxythiophene) (PEDOT-MeOH) was of particular interest because it possesses several advantages, such as a similar conductivity and a better water solubility and biocompatibility, over PEDOT.³

If EDTT and EDOT or EDOT-MeOH could be copolymerized successfully, these novel copolymers with intermediate properties could open lots of applications for PEDTT in organic films. Therefore, in this study, the copolymerization was investigated, as shown in Scheme 2.

EXPERIMENTAL

Materials

We synthesized EDTT, EDOT, and EDOT-MeOH from 3,4-dibromothiophene and corresponding diols following our



Scheme 2. Chemical structures of the monomers and PSSH and preparation of aqueous polymer dispersions via chemical oxidative copolymerization.

previous work^{26,29} and distilled them under reduced pressure before use. PSSH (weight-average molecular weight = 75,000; 30 wt % aqueous) was a product of Alfa Aesar (United States) and was used as received. A strongly basic anion-exchange resin (201 \times 7, batch number F20101009) and a strongly acidic cation-exchange resin (001 \times 7, batch number F20101009) were purchased from China National Medicine Group Shanghai Chemical Reagent Co. (Shanghai, China). Other chemicals and reagents (analytical grade, >98%) were all purchased commercially from Beijing East Longshun Chemical Plant (Beijing, China) and were used directly without any further treatment.

Oxidative Copolymerization Experiments

EDTT (1.758 mmol) and EDOT (1.758 mmol) or EDOT-MeOH (1.758 mmol) were added to 86.169 g of PSSH aqueous solutions (1.5 wt %), and these mixtures were stirred vigorously for 20 min in a 25 $^\circ\text{C}$ water bath under nitrogen. Upon the addition of $\text{Fe}_2(\text{SO}_4)_3$ (0.01758 mmol) and $\text{Na}_2\text{S}_2\text{O}_8$ (4.219 mmol) in turn, these mixtures were stirred for 24 h at 25 $^\circ\text{C}$ and subjected to desalting as follows. The as-prepared mixtures were diluted with twice their 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 filtrates were treated with a strongly acidic cation-exchange resin (001 \times 7) in the same way. The final filtrates were condensed to a solid content of around 1.5 wt %. After treatment with a high-shear dispersing emulsifier for 1 h, this method finally gave two aqueous polymer dispersions, poly(3,4-ethylenedithiathiothiophene-co-3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (P1) and poly(3,4-ethylenedithiathiothiophene-co-2'-hydroxymethyl-3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (P2).

For comparison, the chemical homopolymerization of the monomers (EDTT, EDOT, and EDOT-MeOH) with an amount of 3.516 mmol was also carried out in the previous oxidative systems; this led to aqueous dispersions of PEDTT/PSS, PEDOT/PSS, and PEDOT-MeOH/PSS, respectively. All of the dispersions could be cast onto polypropylene (PP) film substrates to form free-standing polymer films after they were dried at 60 $^\circ\text{C}$ for 12 h.

Polymer Dispersion Treatment with Organic Solvents

Pristine polymer dispersions were mixed with dimethyl sulfoxide (DMSO; 5 wt %) or DMSO (5 wt %) mixed with isopropyl alcohol (IPA; 30 wt %). These mixtures were stirred for 24 h at 25 $^\circ\text{C}$, treated with ultrasonic vibration for 5 min, and then cast onto PP film substrates. After they were dried at 60 $^\circ\text{C}$ *in vacuo* (38 mmHg) for 24 h, free-standing polymer films were formed.

Characterization

The pH values of the polymer dispersions were tested by a pen-like pH meter (CT-6022, Shanghai Rentong Meter CO., Ltd., Shanghai, China). The viscosities were measured by a digital viscometer (NDJ-5S, Shanghai Hengping Meter Co., Ltd., Shanghai, China). A thickness gauge (CH-1-S/ST, Shanghai Liuling Meter Co., Ltd., Shanghai, China) was used to measure the thicknesses of the free-standing films. The temperature dependence of both σ and the Seebeck coefficient (S) were determined with a standard four-probe technique by a measurement unit of the 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 the sample with a conductive carbon paint (colloidal graphite in IPA, 20% solids) at room temperature. Thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) experiments were performed with a Pyris Diamond thermogravimetry/differential thermal analyzer (PerkinElmer, United States) under a nitrogen stream from 293.15 to 1073.15 K at a constant heating rate of 10 K/min. X-ray diffraction (XRD) investigations were performed on a Bruker D8 Advance X-ray diffractometer (Germany) with the Cu K α radiation method (40 kV, 40 mA). A cold field emission scanning electron microscope (S-4300 N, Hitachi, Japan) was used to analyze the surface morphologies of the polymer films.

RESULTS AND DISCUSSION

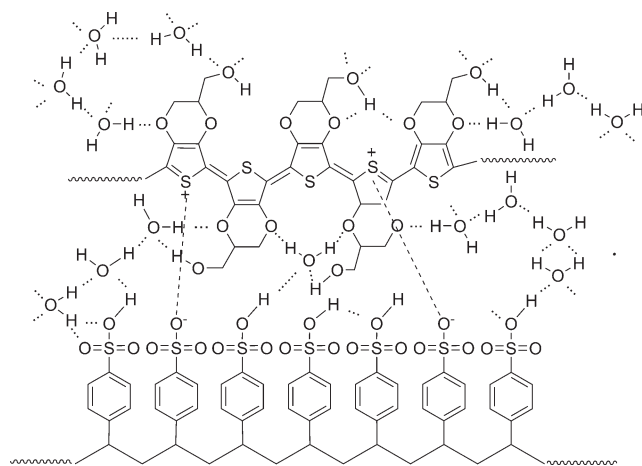
Chemical Oxidative Copolymerization

The basic physical properties of the five polymer dispersions are listed in Table I. It can be seen that except for the light brown PEDTT/PSS dispersion, the others containing the PEDOT backbone units were all dark blue. The solid contents of the five dispersions were all controlled at about 1.5 wt %, with much higher concentrations forming deposits easily during conventional storage periods. However, the viscosities showed large differences between each other. Generally, the polymerization involving

Table I. Physical Properties of the Aqueous Polymer Dispersions

Sample	Color	Solid content (wt %)	Viscosity (mPa s) ^a	pH ^a
PEDOT/PSS	Dark blue	1.56	23.7	1.41
PEDOT-MeOH/PSS	Dark blue	1.37	53.2	0.82
PEDTT/PSS	Light brown	1.39	1.8	0.55
P1	Dark blue	1.72	17.7	0.97
P2	Dark blue	1.73	2.1	0.78

^aThese data were measured at 18 $^\circ\text{C}$.



Scheme 3. Possible hydrogen-bond networks and crosslinking structures in an aqueous dispersion of PEDOT-MeOH/PSS.

EDTT, especially homopolymerization, finally achieved dispersions with much lower viscosities than that based on EDOT and EDOT-MeOH (Table I). One reason may be the strong S...S steric interactions resulting from the electronegativity of sulfur atoms in the PEDTT molecular chains; this increased the repulsion between molecules in the PEDTT/PSS composites.^{8,21} Another quite important reason was the existence of intramolecular and intermolecular hydrogen bonds O—H...O between the positively charged hydrogen atoms and the negatively charged oxygen atoms, which occurred widely among EDOT, EDOT-MeOH, H₂O, and the sulfonic acid groups of PSSH.

The major functions of the hydrogen bonds are listed as follows. First, they could enhance the attractive forces between the EDOT monomers with water molecules and, therefore, facilitate their aqueous solubility. This could have led to better efficiency of the oxidative polymerization and higher molecular weights of the polymers; this may explain why PEDOT-based polymers are often hardly soluble and why PEDOT/PSS dispersions often result in the formation of nonredispersable deposits after drying in comparison to PEDTT/PSS.²⁶ However, this also makes the polymer films sensitive to humidity levels in the atmosphere and influences their environmental stability. Second, as an example shown in Scheme 3, the hydrogen-bond networks

make π -conjugated polymers form crosslinking structures with O—H bond containing units, such as water molecules and PSSH. Therefore, this can cause an increase in the viscosities of the aqueous dispersions of PEDOT-based polymers.

Particularly, the presence of hydroxymethyl in polymer chains further enhanced such phenomena (Scheme 3); thus, the PEDOT-MeOH/PSS dispersions had the highest viscosity. This character, which could improve the adhesion strength of the PEDOT-MeOH coatings with the substrate surfaces, with its intrinsic solution processability and facile functionalization properties, unquestionably, could be very useful for the preparation of high-performance PEDOT-MeOH/PSS modified electrodes in extremely efficient biosensors.³

It should be pointed out that the copolymerization of EDTT and EDOT-MeOH led to a dispersion with a very low value of 2.1 mPa s, close to that of PEDTT/PSS. We speculated that the EDTT units occupied the larger portion of the π -conjugated chains than EDOT-MeOH in the P2 dispersion. This was proven by later electrical conductive measurements; that is, P2 and PEDTT/PSS showed similar conductivity. Moreover, the hydrogen-bonding donation (acidity) and acceptance (basicity) changes in the water, together with various solid contents, made the pH values differ from each other.

Application of the Aqueous Dispersions in Achieving the Conducting Films

Figure 1 shows the photographs of the free-standing polymer films obtained by the casting of five polymer dispersions and their corresponding DMSO/IPA second-doped samples onto PP film substrates. In contrast to the polymer film achieved from the aqueous PSSH solution (1.5 wt %), which was viscous and dense because of the aggregation of PSSH chains during the drying process, these polymer films were thin and flexible and could be easily cut into various forms (with the PEDOT-MeOH/PSS, P1, and P2 films used as examples, as shown in Figures 2 and 3). Moreover, the PEDOT/PSS, PEDOT-MeOH/PSS, and copolymers showed much better mechanical performances.

Thermal Stability of the Polymer Films

To investigate the thermal stability of the polymer films, we carried out TGA experiments, and these results are demonstrated in Figure 3. The heat-degradation behaviors of these polymer

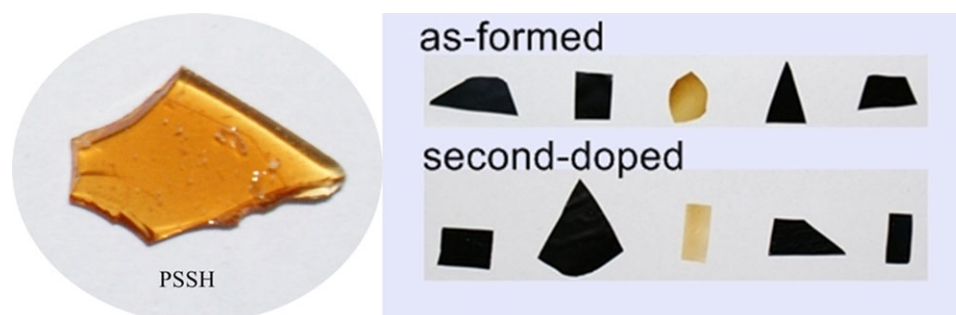


Figure 1. Photographs of the PSS, as-formed, and DMSO/IPA second-doped free-standing polymer films deposited on PP substrates. PEDOT/PSS, PEDOT-MeOH/PSS, PEDTT/PSS, P1, and P2 are lined up from left to right. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

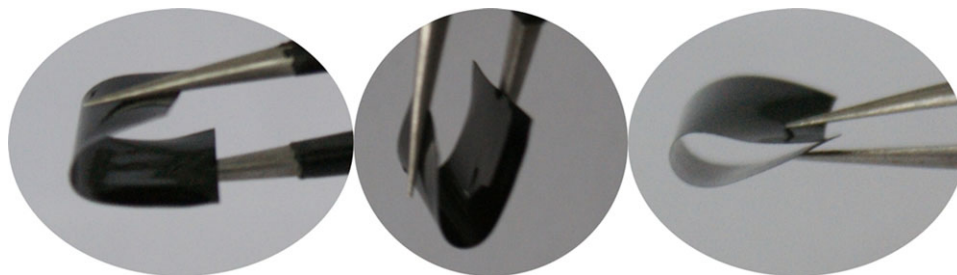


Figure 2. Photographs of the as-formed free-standing PEDOT-MeOH/PSS (left), P1 (center), and P2 (right) films deposited on the PP substrates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

films were similar; that is, they could be divided into three stages. From 298 to 533 K, they went through a mass loss of 15–20%, and the maximum degradation rate occurred at 333 K according to the DTG curves, mainly because of the loss of some water or moisture, dust, impurities, and dopant ions in the polymers. From 523 to 683 K, they produced serious weight losses of 30–35%, and these were caused by the degradation of the oligomers. In this temperature range, two rapid degradations occurred, first, the maximum near 570 and, next, at 640 K, as observed in the DTG curves; this was caused by the breakage and degradation of the polymer chains of different molecular weights. Later, polycationic chain with higher molecular weights and part of the PSS polyanion chains began degrading with increasing temperature. When the temperature reached 1073 K, except in PEDOT-MeOH/PSS, other polymers went through slow degradation and finally remained steady at about 40% of their weights; this revealed the decomposition of the skeletal polymer main-chain structures. For PEDOT-MeOH/PSS, only 25% of its weight remained and tended to decrease continuously; this might have been due to the proportion of its structural units of PEDOT⁺-MeOH polycations and PSS⁻ polyanions in accordance with its relatively high viscosity and the lower molecular weight of the polycations. The previous results suggest that the obtained polymer films, no matter whether they were from copolymerization or homopolymerization, all exhibited good thermal stability and could meet the needs of many applications.

Electrical Conductive and Thermoelectric Properties of the Polymer Films

Thermoelectric materials can turn heat into electricity and could, therefore, be a good option for power production from waste heat and natural heat sources.^{30,31} PEDOT and PEDOT/PSS have been developed as quite attractive thermoelectric materials and have achieved a growing amount of academic interest.^{30–32} σ and S are two important parameters in characterizing thermoelectric properties. A good thermoelectric material must possess a combination of a high σ and high S . For conducting polymers, S decreases when σ increases. Therefore, it is necessary to balance them, improving σ without weakening the S .³⁰ In this work, the values of σ and S of the polymer films, as listed in Table II, were measured under room conditions (298 K and 60% RH) with a standard four-probe method with or without a second doping treatment with DMSO or DMSO/IPA. The results reveal that the σ sequence of the as-formed films from

high to low was PEDOT/PSS (6.8 S cm^{-1}) > P1 ($8.2 \times 10^{-2} \text{ S cm}^{-1}$) > PEDOT-MeOH/PSS ($2.4 \times 10^{-2} \text{ S cm}^{-1}$) > P2 ($4.6 \times 10^{-4} \text{ S cm}^{-1}$) > PEDTT/PSS ($1.5 \times 10^{-4} \text{ S cm}^{-1}$); that is, the copolymerization of EDTT with EDOT or EDOT-MeOH improved the conducting properties of the PEDTT homopolymer. In other words, polymers containing EDOT structural units had higher electrical conductivities, and the introduction of hydroxymethyl groups to the PEDOT chains influenced the carrier transmission to some extent through hydrogen bonding.

As a result of its quite low conductivity, PEDTT/PSS did not show logical and stable S values. Through copolymerization

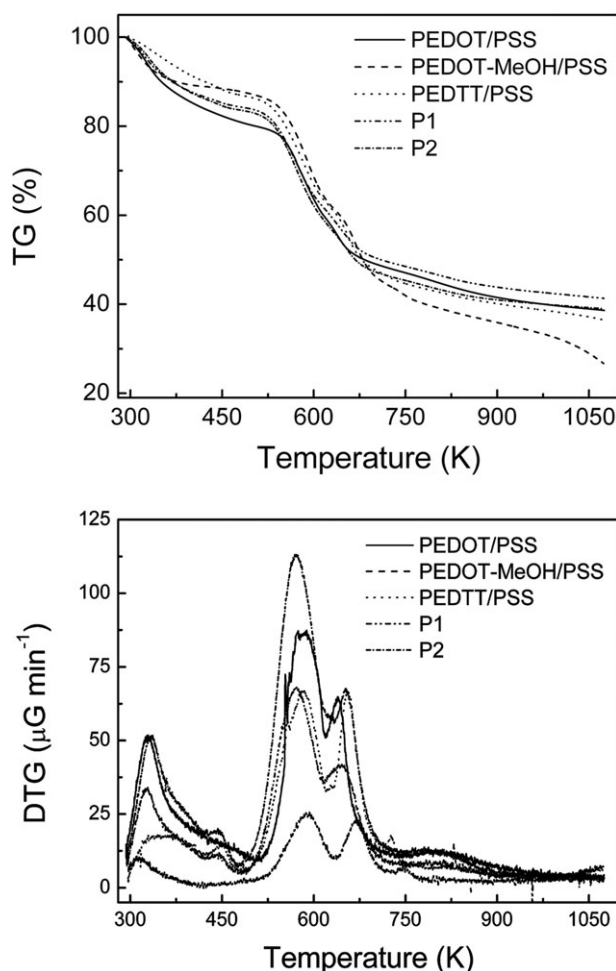
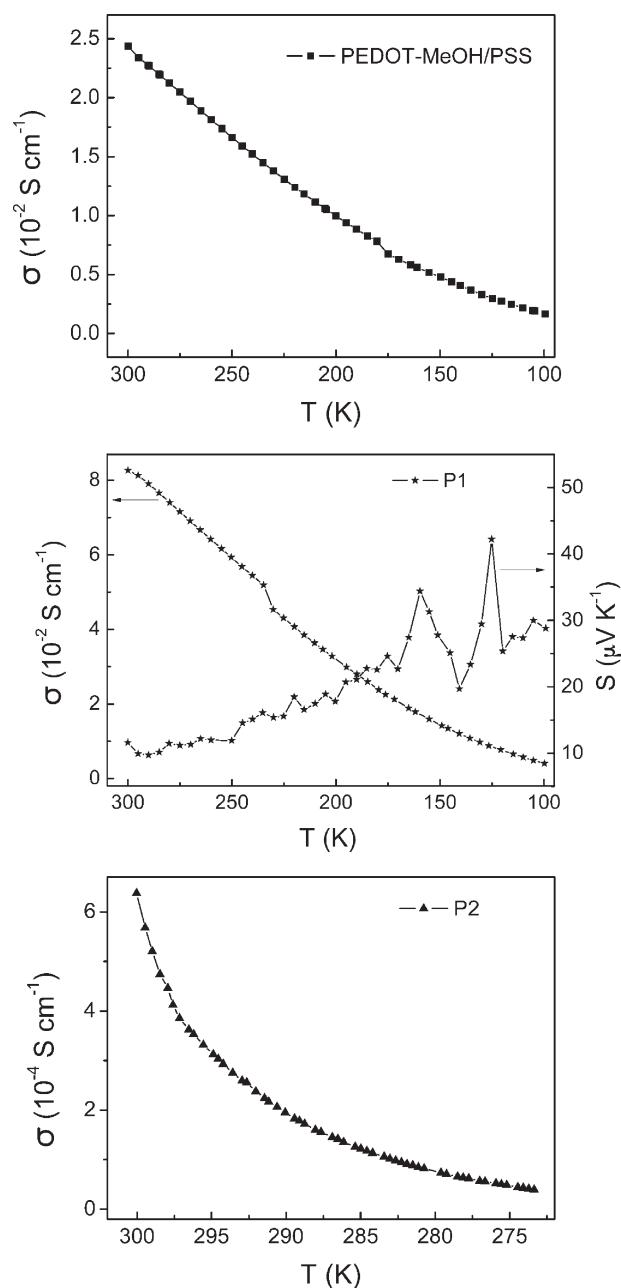
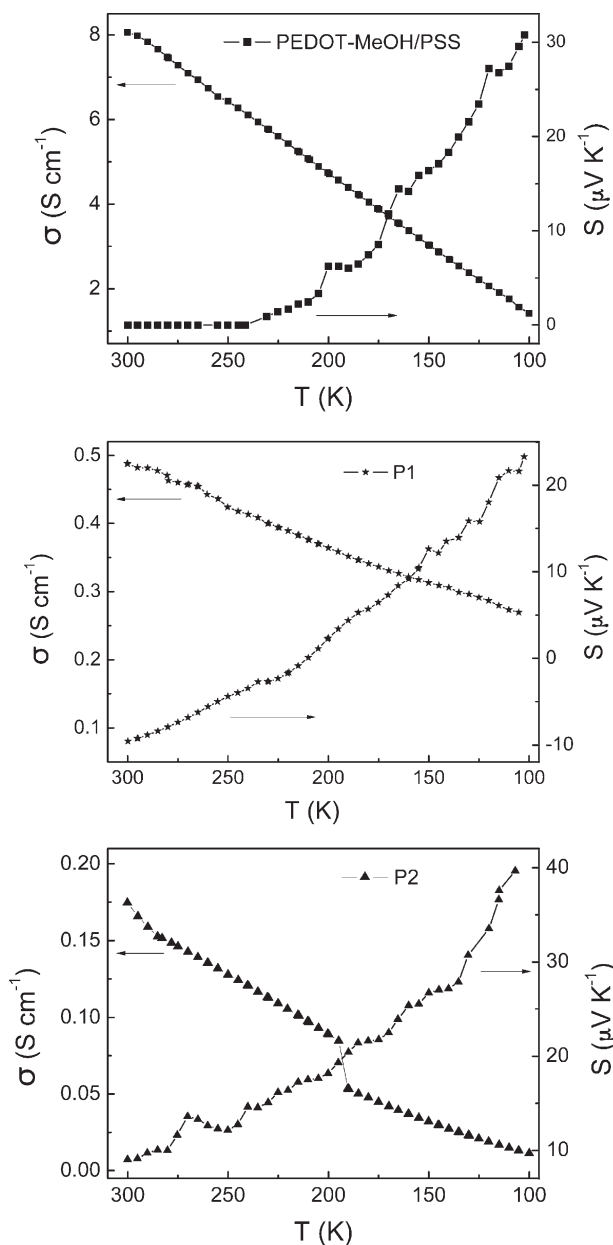


Figure 3. TG (up) and DTG curves (down) for the polymer films.

Table II. σ and S Values for the As-Formed and Second-Doped Polymer Films Measured at 298 K

Sample	None		DMSO		DMSO/IPA	
	σ (S cm ⁻¹)	S (μ V K ⁻¹)	σ (S cm ⁻¹)	S (μ V K ⁻¹)	σ (S cm ⁻¹)	S (μ V K ⁻¹)
PEDOT/PSS	6.8	5.1	69	10	70	9.9
PEDOT-MeOH/PSS	2.4×10^{-2}	4.8	8.3	4.3	8.5	4.0
PEDTT/PSS	1.5×10^{-4}	—	1.3×10^{-4}	—	1.1×10^{-4}	—
P1	8.2×10^{-2}	10	0.50	8.5	0.52	8.4
P2	4.5×10^{-4}	—	0.14	4.8	0.17	9.1

**Figure 4.** Temperature (T) dependence of σ and S for the as-formed films of PEDOT-MeOH/PSS, P1, and P2.**Figure 5.** Temperature (T) dependence of σ and S for the DMSO/IPA treated films of PEDOT-MeOH/PSS, P1, and P2.

with EDOT, P1 had a measurable value of $10 \mu\text{V K}^{-1}$, nearly twice the values of PEDOT/PSS or PEDOT-MeOH/PSS, whereas P2 did not because of its lower σ .

The temperature dependence of σ and S of PEDOT/PSS and PEDTT/PSS has been demonstrated in our previous reports.^{26,33} These results indicate that the electrical conductivities decreased as the temperature fell; this is a typical behavior of semiconducting materials. Here, we also found the same phenomena for PEDOT-MeOH/PSS and the copolymers, as depicted in Figure 4. As the temperature decreased from 300 to 100 K, σ of PEDOT-MeOH/PSS decreased gradually from 2.4×10^{-2} to $1.7 \times 10^{-3} \text{ S cm}^{-1}$, whereas that of P1 decreased from 8.3×10^{-2} to $4.1 \times 10^{-3} \text{ S cm}^{-1}$ and that of P2 decreased from 6.4×10^{-4} to below $4.0 \times 10^{-6} \text{ S cm}^{-1}$ (measured at 273 K; if it continued to decrease, the data would have been beyond the range of measurement for the instrument). With the decrease of σ , S of P1 increased from $11.6 \mu\text{V K}^{-1}$ (300 K) to $29 \mu\text{V K}^{-1}$ (100 K), and from 160 K, the data became quite unstable and corresponded to much lower conductivities.

Second Doping of Polymer Dispersions

Until now, numerous efforts have been made to overcome the limitations of the low conductivity of conducting polymer films. Presently, researchers have observed that the conductivity of PEDOT/PSS films can be enhanced by more than 1 or 2 orders of magnitude through the addition of organic solvents, such as DMSO and IPA, to pristine PEDOT/PSS dispersions.^{34,35} The term *secondary doping* is used to define this phenomenon, and such organic solvents are called *secondary dopants*.³ However, for PEDTT/PSS, these solvents do not show the same effects.²⁶ On the contrary, DMSO treatment of PEDTT/PSS dispersions slightly decreased the electrical conductivities of the corresponding films within the same order of magnitude.²⁶

To further study the effect of DMSO and IPA treatments on conducting polymer dispersions, herein, five dispersions mixed with DMSO (5 wt %) or DMSO (5 wt %)/IPA (30 wt %) were prepared. After they were cast on a PP substrate and dried, various smooth polymer films were subsequently formed, as exhibited in Figure 2, and the results of σ measurement of these films are listed in Table II. It can be seen that after the second doping, in addition to a slight decrease in σ of PEDTT/PSS, the conductivities of the other films improved 10^1 to 10^3 times, and the effect of DMSO/IPA was a little bit better than that of the single addition of DMSO. It was clear that the influence of the additives for S was not as significant as that for the conductivity, which basically ranged from 4 to $10 \mu\text{V K}^{-1}$, and did not show a well-regulated law. However, it should be pointed out that PEDTT/PSS still could not produce an effective S because of their quite low conductivities, whereas P2 could with a significant increase in conductivity. The temperature dependence of σ and S for polymer films coated from PEDOT-MeOH/PSS, P1, and P2 mixed with the secondary dopant DMSO/IPA are indicated in Figure 5.

Although it was still unclear what factors governed these phenomena, the short conjugated chain of PEDTT, the tight attachment of PEDTT⁺ and PSS⁻ chains caused by the distortion of

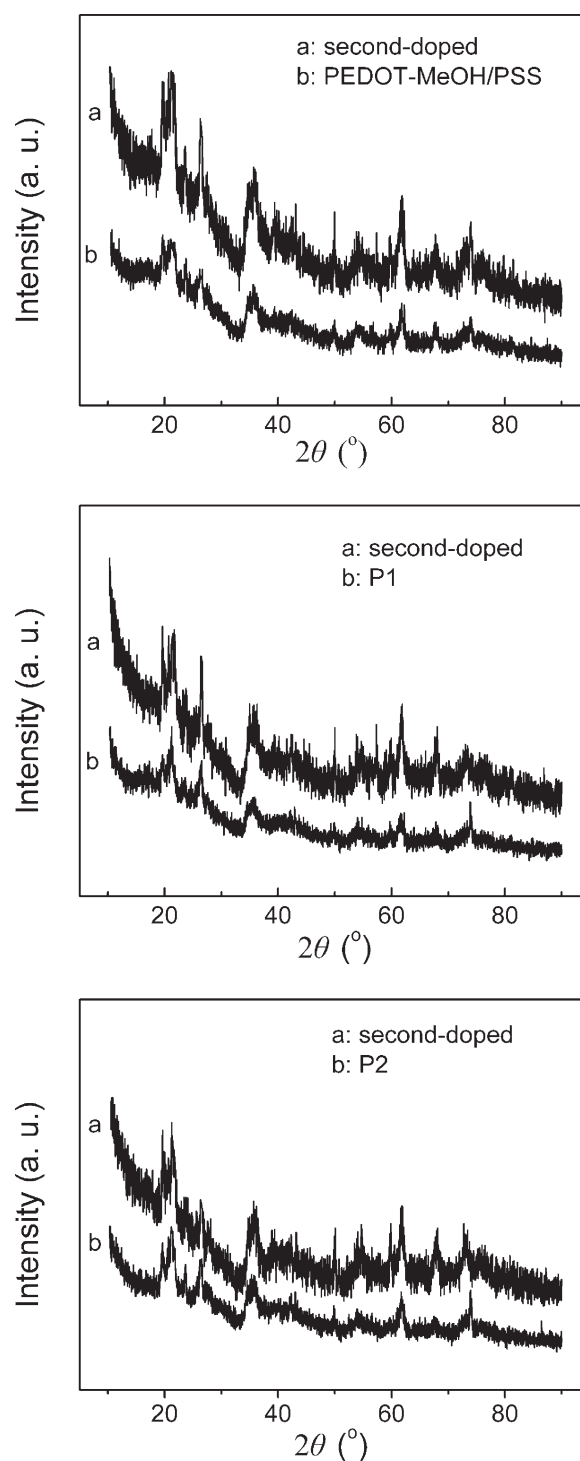


Figure 6. XRD spectra of the as-formed and corresponding DMSO/IPA second doping films of PEDOT-MeOH/PSS, P1, and P2.

the π -conjugated chains, the very weak chain ordering through S...S interactions, and the presence of hydrogen bonding may be possible reasons.^{8,21,26} For PEDOT-MeOH/PSS, P1, and P2, the XRD and SEM characteristics were investigated to explain the conductivity-enhancing phenomenon. According to the XRD analysis results in Figure 6, it can be seen that the XRD

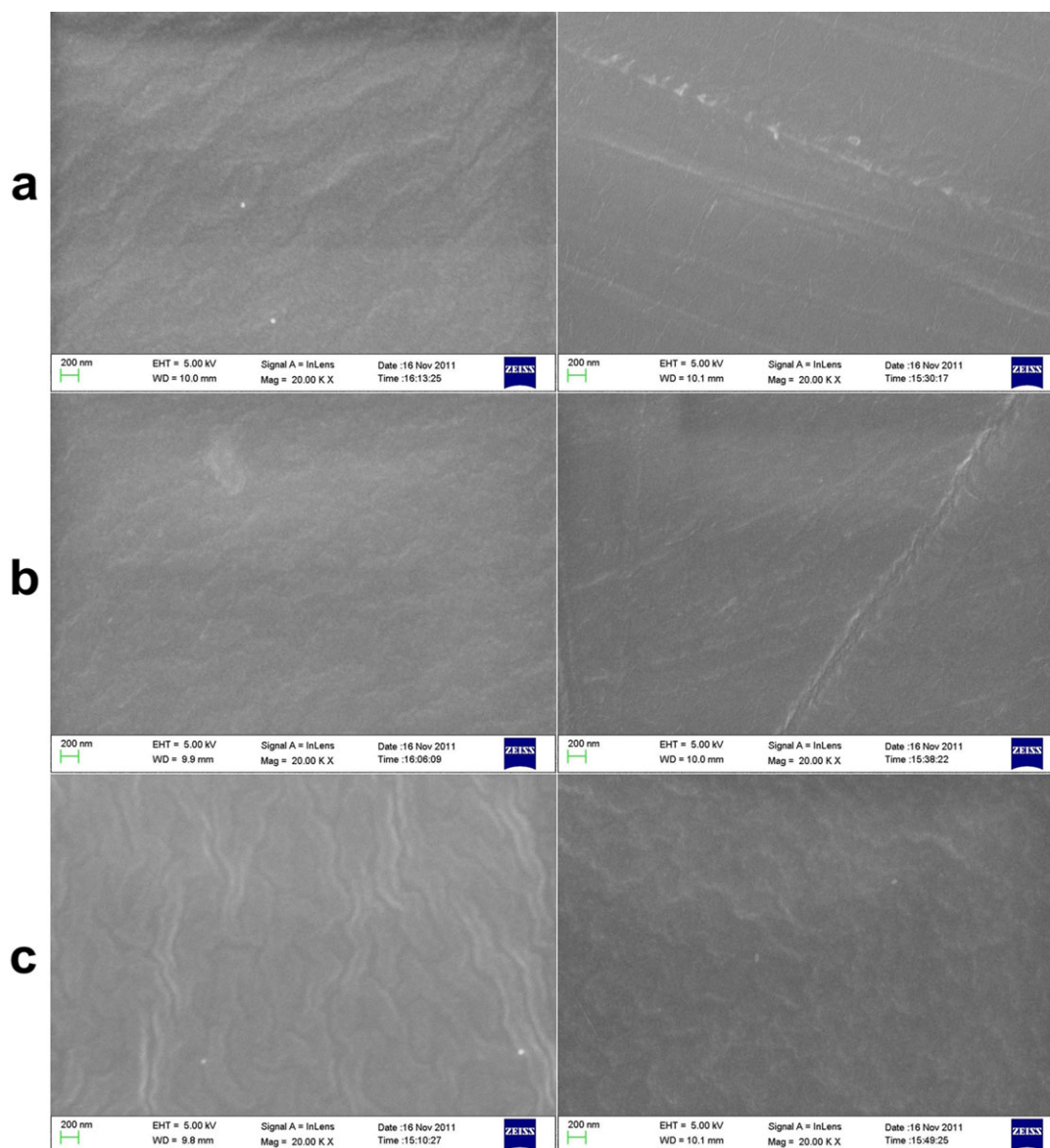


Figure 7. Micrographs ($\times 20,000\times$) of the surface of the as-formed (left) and DMSO/IPA second-doped (right) polymer films: (a) PEDOT-MeOH/PSS, (b) P1, and (c) P2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

patterns did not change after the second doping, as compared with previous research on PEDOT/PSS; that is, the structure of the polymers did not change with solvent treatment.³⁴ However, the surface morphologies of the polymers became smoother, homogeneous, and compact through solvent processing, as shown in Figure 7; this allowed the polymer chains to become stretched, which is beneficial to carrier transmission among polymer chains and results in improved conductive properties.

CONCLUSIONS

Copolymer aqueous dispersions of EDTT and EDOT or EDOT-MeOH were prepared by chemical oxidation with monomer mixtures in PSSH solutions. In comparison with the brown dispersion via the homopolymerization of EDTT, they were both

dark blue and had better film-forming properties. The corresponding free-standing copolymer films showed many advantages, such as good mechanical behavior, favorable thermal stability, high σ , and good thermoelectric properties. Moreover, DMSO or DMSO/IPA second-doping studies revealed that in contrast to that of the PEDTT homopolymer, σ of the copolymer films could be improved by 1 to 3 orders of magnitude, whereas S remained roughly stable in the meantime. In addition, polymers containing PEDTT units, whether prepared from homopolymerization or copolymerization, and PEDOT-MeOH/PSS had relatively poor electrical conductivities compared to PEDOT/PSS. Hydrogen bonding may have played an important role in determining these differences. All of these results imply the potential application of these conducting polymer/PSS films in optoelectronics, sensors, and so on.

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