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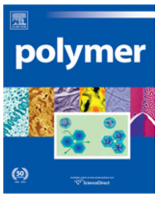

Preparation of the thermally stable conducting polymer PEDOT – Sulfonated poly(imide)

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ABSTRACT

We describe the template polymerization of EDOT with sulfonated poly(amic acid) (SPAA), resulting in a stable conducting polymer aqueous dispersion, PEDOT-SPAA, with particle size *ca.* 63 nm. In films of PEDOT-SPAA, the sulfonated poly(amic acid) template undergoes imidization within 10 min at temperatures greater than 150 °C, resulting in PEDOT-sulfonated poly(imide) (PEDOT-SPI) with 10-fold conductivity enhancement. This material is highly thermally stable as compared to PEDOT-PSS. Thermal stability is necessary for many processing applications of conducting polymers, including annealing for OPVs and melt-processing of polycarbonate for device encasement. Isothermal TGA experiments were run at 300 °C for PEDOT-PSS and PEDOT-SPAA and we found that PEDOT-SPAA had a smaller slope for degradation. Annealing of films at 300 °C for 10 min caused the conductivity of PEDOT-PSS films to be unmeasurable ($<1 \times 10^{-5}$ S/cm), while those of PEDOT-SPAA increased 6-fold. Secondary doping of the PEDOT-SPAA system with additives commonly used for PEDOT-PSS was also investigated.

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1. Introduction

Conducting polymers such as polypyrroles, polythiophenes, polyanilines, and poly(para-phenylene-vinylenes) have attracted much attention due to their light weight [1], high conductivities, electrochromic properties [2], and use in a wide variety of applications such as organic light emitting diodes (OLEDs) [3], organic photovoltaic devices (OPVs) [4], capacitors [5], and sensors [6]. Poly(3,4-ethylenedioxythiophene) (PEDOT) is among the most popular conducting polymers, having achieved commercialization in the form of a colloidal dispersion in water, PEDOT-PSS. It has shown good conductivities, ranging from 10^{-2} to 10^{-5} S/cm for OLED grade [7]. However, PEDOT alone is an insoluble polymer in common solvents. This issue was solved by template polymerization with a polyanion, poly(styrene sulfonic acid) (PSSA). PSSA is a charge-balancing dopant during polymerization in water which allows for the formation of a colloidal dispersion of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonic acid) or PEDOT-PSS [8,9]. This material has achieved popularity for applications due to its many advantageous properties, such as high stability in the p-doped form [10], high conductivity [11], good film formation [12], and excellent transparency in the doped state [13]. PEDOT-PSS dispersed in water can easily be spin-coated (among other methods) [14], resulting in transparent films that have relatively high electrical conductivity (0.05–10 S/cm) [10]. PEDOT-PSS has been used as a transparent electrode for electrochromic devices as well as a hole-injection layer for solar cells [15–17].

However, the thermal stability of PEDOT-PSS has hindered its use for high-temperature processing or applications. It is stable up to 200 °C [18], however annealing beyond this temperature causes a marked decrease in conductivity [19]. Electrochemically prepared PEDOT is stable up to 300 °C, based on our own TGA measurements. It is therefore possible that the use of a new template may allow for higher thermal stability of the conducting polymer. It is not likely that devices using PEDOT-PSS will ever be subjected to operating temperatures approaching these degradation limits [20], yet a variety of processing steps may easily exceed them. For example, annealing with secondary dopants or additives is a common practice, but again, above 200 °C (or for prolonged periods at 180 °C), conductivity will suffer instead of improve. Melt-processing of polycarbonate to create ballistic-type coatings (temperatures *ca.* 220 °C) might be a viable processing step for an electrochromic device or a photovoltaic, as well. This would also create problems for PEDOT-PSS, being above the desired thermal range for the

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polymer. With these obstacles in mind, a different template was conceived for the preparation of PEDOT-based conductors.

Faure and coworkers found the first sulfonated five-membered ring polyimides from 4,4′-oxydiphthalic anhydride (O-DPDA), which were practically tested in fuel cell systems [21]. A major application of condensation polyimides is as thin films in electronics packaging, wire insulation, and gas separator membranes [22]. It is well-known that polyimides have found wide applications in many industrial fields due to their excellent thermal stability [23], high mechanical strength [24], good film forming ability, and superior chemical resistance [25]. They have also been used as dielectric materials for circuitry applications [26]. The creation of a conducting polymer–polyimide complex, using the precursor poly(amic acid) as a new template, represents a significant step towards the development of highly conductive and highly thermally stable polymeric systems. Further, such a composite should exhibit better adhesion to a polyimide dielectric material, particularly upon heat treatment.

Some applications for which these conducting polymer dispersions are suitable require high conductivity, as well. Conductivity in polymer systems has previously been improved by so-called secondary doping [27]. The addition of a dopant such as glycerol [11,28,29], sorbitol [10,11,30], or a mixture of sorbitol, *N*-methylpyrrolidone (NMP), and isopropanol, dimethyl sulfoxide (DMSO) [31], *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF) to improve conductivity have been investigated. The morphological changes induced by the presence of the dopants are important factors in the increased conductivity for doped films. The addition of a polar solvent, such as dimethyl sulfoxide (DMSO) to PEDOT-PSS was found to increase the conductivity by a factor of 100, attributed to the screening effect. Furthermore, Winter et al. [32] found that sustained heating at 150 °C causes irreversible structural changes in the PEDOT main chain and further shows that electrical properties of conducting polymers are strongly dependent on film morphology and chemical and physical structure. These properties are in turn affected by the annealing temperature.

Herein, the use of a sulfonated poly(amic acid) for the template polymerization of PEDOT is accomplished, resulting in a stable colloidal dispersion in water, PEDOT-SPAA, shown in Scheme 1. The dispersions obtained are comparable to PEDOT-PSS in terms of particle size, film forming properties, and, most importantly, conductivity. This system, PEDOT-SPAA, undergoes a conversion to the poly(imide) form (PEDOT-SPI) upon heating (Scheme 1), confirmed by FTIR measurements [33]. The innovativeness of this work is that unlike templates formerly used for PEDOT, this template undergoes a chemical transformation in the annealing process that can have an effect on the resulting morphology of the films. Imidization causes a 10-fold increase in conductivity for the films, without secondary dopants. These films exhibited higher thermal stability without the loss of conductivity (up to 300 °C). Poly(3,4-ethylenedioxythiophene)-sulfonated poly(imide) films can resist higher temperatures than PEDOT-PSS and still maintain their conductivity.

2. Experimental

2.1. Materials

4,4′-Diaminodiphenyl ether (4,4′-ODA), 4,4′-oxydiphthalic anhydride (O-DPDA), triethylamine (Et_3N), m-cresol, fuming sulfuric acid (SO_3, 20%), poly(styrene sulfonic acid) (18 wt.% in water), iron (III) p-toluene sulfonate hexahydrate, 3,4-ethylenedioxythiophene (EDOT), lithium trifluoromethane sulfonate, and *N,N*-dimethylformamide (DMF) were purchased from Sigma–Aldrich. EDOT was distilled before use. Concentrated sulfuric acid (95%), sodium hydroxide (NaOH), hydrochloric acid (HCl), and acetone were purchased from Fisher Scientific and were used as received. Surfynol® 2502 surfactant was purchased from Air Products, Inc. D-Sorbitol 97% and ion-exchange resin DOWEX 50WX8 50–100 mesh were purchased from Acros Organics. Dialysis tubes (Molecular weight cut off [MWCO] = 3.5 to 5 kDa) were purchased from Spectrum Laboratories Inc.

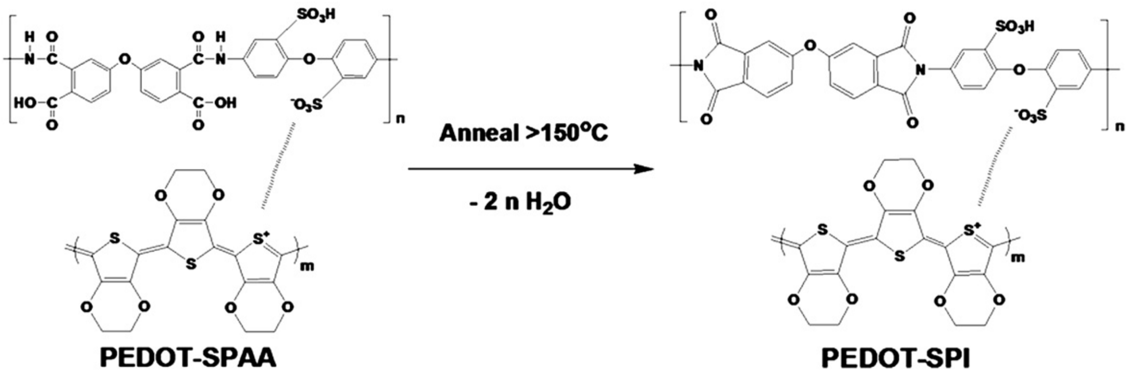
2.2. Preparation of monomer and poly(amic acid) (SPAA)

2.2.1. Synthesis of 4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (4,4′-ODADS)

To a 100 mL three-neck flask with a stirring device was added 2.00 g (10.0 mmol) of 4,4′-diaminodiphenyl ether (4,4′-ODA). The flask was cooled in an ice bath, and then 1.7 mL of concentrated (95%) sulfuric acid was slowly added with stirring. After 4,4′-ODA was completely dissolved, 10.5 mL of fuming (SO_3 20%) sulfuric acid was slowly added to the flask. The reaction mixture was stirred at 0 °C for 2 h and then slowly heated to 80 °C and kept at this temperature for an additional 3 h. After cooling to room temperature, the slurry solution mixture was carefully poured onto 20 g of crushed ice. The resulting white precipitate was filtered off and then redissolved in a sodium hydroxide solution. The basic solution was filtered, and the filtrate was acidified with concentrated hydrochloric acid. The solid was filtered off, washed with water and methanol successively, and dried at 80 °C in vacuum oven overnight [34].

2.2.2. Synthesis of sulfonated poly(amic acid) (SPAA)

To a 100 mL three-neck flask with N_2 inlet and outlet was added 0.5467 g (1.5171 mmol) of 4,4′-ODADS, 6 mL of m-cresol, and 0.3617 g (3.5745 mmol) of triethylamine. After 4,4′-ODADS was



Scheme 1. Representation of water-dispersible PEDOT-SPAA undergoing conversion to the thermally stable PEDOT-SPI.

completely dissolved, 0.4706 g (1.5171 mmol) of O-DPDA was added and then stirred at room temperature for 24 h. When the reaction was complete, the reaction mixture was decanted into acetone (75 mL), filtered, washed with acetone (25 mL, 2 times), and dried at 50 °C in a vacuum oven overnight (0.8511 g, 83.66% yield).

2.2.3. Purification

The sulfonated poly(amic acid) was purified via dialysis tube. SPAA dissolved in water was loaded inside the dialysis tube and soaked in DI water for 24 h, changing the water twice (2 times at 12 h each).

2.2.4. Ion exchange

The purified SPAA salt form was changed to SPAA acid form with an ion exchange resin of strong acid type DOWEX 50WX8 (cation exchange). The SPAA salt form was stirred in DI water with the ion exchange resin (H^+) for 1 h to convert it to the free acid form (SO_3H); it was centrifuged and filtered in a crucible filter (pH *ca.* 1), and then dried at 50 °C in vacuum oven overnight. Elemental analysis of sulfonated poly(amic acid) (SPAA) was (Theoretical/Found); %C (50.152/49.411), %H (2.705/4.190), %N (4.177/4.763), %S (9.564/7.871). Molecular weight and molecular weight distributions of SPAA were $M_n = 20{,}769$, $M_w = 35{,}502$, PDI = 1.71.

2.3. Template polymerization of EDOT and poly(styrenesulfonic acid) (PEDOT-PSS)

To a 25 mL one neck flask, 51.12 mg (0.36 mmol) of EDOT and 0.697 g of 18 wt.% PSSA aqueous solution were added. To this suspension 257.53 mg of iron (III) p-toluene sulfonate hexahydrate was added. The total mass of all the reactants was adjusted to 10 g by adding an appropriate amount of de-ionized water. The reaction mixture was stirred vigorously for 24 h at room temperature leading to a dark blue dispersion, purified according to literature procedure [35,36].

2.4. Template polymerization of EDOT and sulfonated poly(amic acid) (PEDOT-SPAA)

To a 25 mL one neck flask, 21.30 mg (0.15 mmol) of EDOT and 0.200 g of SPAA were added. To this suspension 103.2 mg of iron (III) p-toluene sulfonate hexahydrate was added. The total mass of all the reactants was adjusted to 10 g by adding appropriate amount of de-ionized water. The reaction mixture was stirred vigorously for 7 days at room temperature leading to a dark blue dispersion, purified according to literature procedure [35,36].

2.5. Preparation of PEDOT-PSS and PEDOT-SPAA films

Films were prepared by spin coating, for 60 s at 3000 rpm, PEDOT-PSS, PEDOT-SPAA and doped PEDOT-SPAA onto glass slides at room temperature. The films were annealed at 180 °C for 10 or 90 min, and 300 °C for 10 min for improving conductivities with thermal treatment. Separate films of each material were evaluated for conductivity at room temperature after annealing. PEDOT-SPAA films were also prepared with 5 wt.% of D-sorbitol, 0.1 wt.% DMF, 0.1 wt.% Surfynol® 2502, and with all three components.

2.6. Measurements

Fourier transform infrared spectroscopy (FTIR) was performed using a MAGNA-IR560. Spectra was taken on ground powder in a KBr matrix with a scanning range of 500–4000 cm^{-1}, 64 scans at a resolution of 4 cm^{-1}. Thermogravimetric Analysis (TGA) was performed by a Perkin–Elmer TGA 7 series analysis system at a heating rate of 20 °C/min under air at a flow rate of 60 mL/min. Gel Permeation Chromatography (GPC) was done using a millipore model 150-C GPC system; DMAC was used as the mobile phase. The results were calibrated by standards of poly(methyl methacrylate). Nuclear Magnetic Resonance (NMR) ^1H NMR spectra were recorded on a Bruker DMX-500 NMR Spectrometer. Elemental analysis was performed using a Vario Micro Elementar CHNS system. The PEDOT-PSS and PEDOT-SPAA particles were imaged using JEOL 2010 Fas and Philips EM420 transmission electron microscope. Conductivities were measured using a four-line collinear array utilizing a Keithley Instruments 224 constant current source and a 2700 Multimeter. The polymer was coated on the glass substrate having four gold coated leads on the surface across the entire width of the polymer and 0.25 cm apart from each other. The current was applied across the outer leads and voltage was measured across the inner leads.

3. Results and discussion

3.1. Monomer synthesis and polymerization

4,4′-Diaminodiphenyl ether-2,2′-disulfonic acid (4,4′-ODADS) was synthesized by direct sulfonation of the 4,4′-diaminodiphenyl ether (4,4′-ODA). Fuming sulfuric acid was used as a sulfonating agent. First, 4,4′-ODA was reacted with concentrated sulfuric acid (H_2SO_4) to form the sulfuric acid salt of 4,4′-ODA. Second, SO_3 in fuming sulfuric acid reacted with 4,4′-ODA at 80 °C. The monomer structure was confirmed by ^1H NMR and FTIR. The FTIR spectrum shows absorptions at a) 1031.8 and b) 1088.3 cm^{-1} for the sulfonic acid group, and at c) 3481.7 cm^{-1} assigned to NH_2 of the diamime. The sulfonation primarily occurred at the meta position.

Sulfonated poly(amic acid) polymerization of O-DPDA and 4,4′-ODADS was carried out in m-cresol medium in the presence of triethylamine (Et_3N). The poor solubility of 4,4′-ODADS in m-cresol was improved by the addition of Et_3N. The reaction was carried out at room temperature to prevent any imidization from occurring at this stage. The poly(amic acid) polymerization is an exothermic reaction [37]; if the reaction was carried out at a higher temperature, hydrolysis would have occurred, producing lower molecular weight and unstable polymers. The poly(amic acid)s in the salt form were converted to the free acid form (H^+) by using a strong acid ion exchange resin. The structure of poly(amic acid) in acid form was confirmed with FTIR. The broad absorption band at 3476.9 cm^{-1} is assigned to the absorbed water in the sample (the sulfonic acid groups are highly hydrophilic). The strong absorption bands around 1719.7 cm^{-1} are assigned to the symmetric imide C=O stretching, however this peak did not indicate complete imidization. Complete imidization will occur after heating at 180 °C, wherein two molecules of water will be liberated from the poly(amic acid) backbone and result in cyclization to the polyimide. The peak at 1663.3 cm^{-1} indicate the absorption bands of carbonyl group (CONH) and peak at *ca.* 2500–3500 cm^{-1} indicate the absorption bands of the carboxylic acid (COOH). The sulfonic acid groups (SO_3H) appear at 1029.0 cm^{-1}, which confirmed formation of the prepared poly(amic acid).

3.2. Conductivity

Conductivity for PEDOT-PSS and PEDOT-SPAA films was measured via the four-point probe technique. We observed a successful increase in conductivity by heat treatment at 180 °C for 10 min of the PEDOT-SPAA, resulting in PEDOT-SPI. Without the addition of dopants, conductivities for the PEDOT-SPI were found to be 10-fold greater, while those of PEDOT-PSS showed no change.

This increase is attributed to the imidization reaction which occurs at this temperature. This imidization was confirmed by FTIR measurements, as shown in Fig. 1. The conversion of the SPAA template to SPI is shown in Fig. 1 I, while the conversion of PEDOT-SPAA to PEDOT-SPI is shown in Fig. 1 II. In both cases, the peaks at 1778.6 cm^{-1} and 1718.6 cm^{-1} correspond to the imide form and the amide form, respectively. This confirmed that imidization takes place during the relatively short curing process. After heat treatment, the chain alignment in thin polymer films often changes with temperature, leading to modified morphologies. The peak at 1191.7 cm^{-1} in Fig. 1 II indicated stretching in the ethylenedioxy group in structure which is differential peak from SPI and SPAA. The other peaks at 1515, 1473, 1388, 1311 cm^{-1} indicate the C=C and C–C bonds in thiophene.

Films were also prepared and annealed for 90 min at 180 °C. It is known that films of PEDOT-PSS can be heated in air at 100 °C for up to 1000 h with no change in conductivity [13]. However, at this temperature for this time, PEDOT-PSS was reduced to 84% of its conductivity, while PEDOT-SPI films exhibited a 3-fold improvement over the PEDOT-SPAA. Annealing at 300 °C for 10 min resulted in PEDOT-PSS samples that could no longer be measured ($<1 \times 10^{-5}$ S/cm) whereas PEDOT-SPI films showed a 6-fold increase in conductivity. These conductivities are summarized in Table 1.

The effect of secondary dopants on the PEDOT-SPAA/PEDOT-SPI system was also investigated. Films were prepared using pristine, 5 wt.% D-sorbitol, 0.1 wt.% DMF, 0.1 wt.% Surfynol® 2502, and a combination of all three dopants. Conductivity was measured at room temperature (PEDOT-SPAA) and after annealing at 180 °C and 300 °C (PEDOT-SPI). The conductivity values for this series of experiments are listed in Table 2. It was found that, upon annealing, films of PEDOT-SPI doped with D-sorbitol or DMF were observed to have a 100-fold increase in their conductivity. The values observed were comparable to commercially available PEDOT-PSS dispersions.

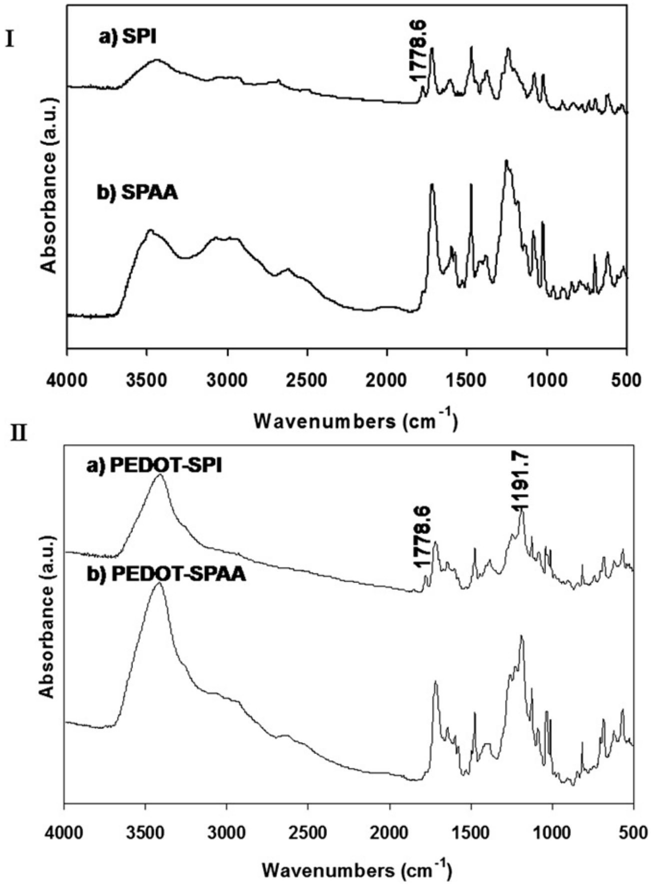


Fig. 1. (I) FTIR spectrum of a) SPI, b) SPAA. (II) FTIR spectrum of a) PEDOT-SPI, attained after annealing b) PEDOT-SPAA. In each case, the peak at 1778.6 cm^{-1} indicates imidization. The peak at 1191.7 cm^{-1} corresponds to the ethylenedioxy bonds in PEDOT [38].

Table 1
Conductivities of PEDOT-PSS (in-house) and PEDOT-SPAA. Upon annealing, PEDOT-SPAA imidizes to PEDOT-SPI.

Processing temperature		PEDOT-PSS	PEDOT-SPAA
20 °C	Conductivity (S/cm)	3.15×10^{-4}	1.12×10^{-4}
	Std. Dev.	4.03×10^{-5}	8.69×10^{-6}
180 °C (90 min)	Conductivity (S/cm)	2.65×10^{-4}	2.96×10^{-4}
	Std. Dev.	3.32×10^{-5}	5.49×10^{-6}
300 °C (10 min)	Conductivity (S/cm)	$<1 \times 10^{-5}$	6.06×10^{-4}
	Std. Dev.	$<1 \times 10^{-5}$	4.84×10^{-5}

3.3. *Thermal stability of PEDOT-PSS and PEDOT-SPAA films*

The thermal properties of PEDOT-SPAA and PEDOT-PSS, in an air atmosphere, were investigated (details in Supporting Information). Isothermal TGA analyses were run at a variety of temperatures for 5 h in order to assess the long term thermal stability of these systems. At 300 °C, the thermal stability of PEDOT-SPI was higher than that of PEDOT-PSS; the slope of degradation was more pronounced for PEDOT-PSS (Fig. 2). The overall mass loss for PEDOT-SPAA is 10.7% after heating at 300 °C for 300 min. By comparison, PEDOT-PSS lost 33.2% of its mass under the same conditions.

3.4. *Particle size of colloidal dispersions*

The particle size of the colloidal dispersions PEDOT-PSS and PEDOT-SPAA were investigated by TEM, as shown in Fig. 3. Fig. 3a shows the particle sizes for a sample of PEDOT-SPAA, averaging *ca.* 63 nm. Fig. 3b shows the particle sizes for PEDOT-PSS, averaging *ca.* 137 nm.

Table 2
Conductivities of secondary-doped PEDOT-SPAA at various processing temperatures. Upon annealing, PEDOT-SPAA imidizes to PEDOT-SPI.

Processing temperature		PEDOT-SPAA	DMF 0.1 wt.%
20 °C	Conductivity (S/cm)	2.04×10^{-4}	5.76×10^{-4}
	Std. Dev.	3.42×10^{-3}	6.09×10^{-5}
180 °C (10 min)	Conductivity (S/cm)	5.83×10^{-3}	8.99×10^{-2}
	Std. Dev.	1.18×10^{-3}	8.28×10^{-2}
300 °C (10 min)	Conductivity (S/cm)	6.47×10^{-4}	4.25×10^{-2}
	Std. Dev.	3.73×10^{-5}	2.03×10^{-2}

Processing temperature		Surfynol 0.1 wt.%	D-sorbitol 5 wt.%	Combination
20 °C	Conductivity (S/cm)	1.82×10^{-4}	4.22×10^{-2}	3.78×10^{-4}
	Std. Dev.	2.51×10^{-5}	5.84×10^{-3}	9.33×10^{-5}
180 °C (10 min)	Conductivity (S/cm)	3.33×10^{-4}	2.00×10^{-2}	4.34×10^{-3}
	Std. Dev.	3.59×10^{-5}	3.51×10^{-3}	8.54×10^{-4}
300 °C (10 min)	Conductivity (S/cm)	5.68×10^{-3}	6.56×10^{-3}	3.74×10^{-3}
	Std. Dev.	1.48×10^{-3}	1.50×10^{-3}	1.13×10^{-3}

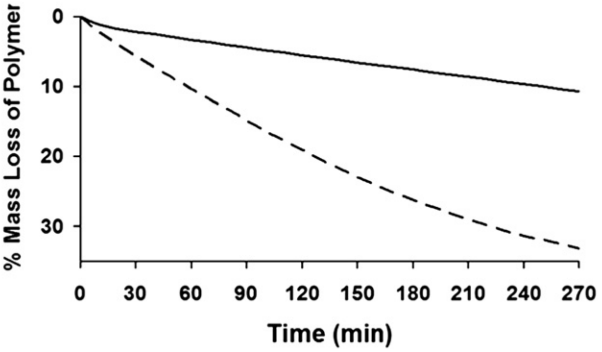


Fig. 2. Isothermal TGA at 300 °C for PEDOT-SPAA (solid line) and PEDOT-PSS (dashed line). Samples were dried for 30 min at 75 °C before mass loss measurements were taken.

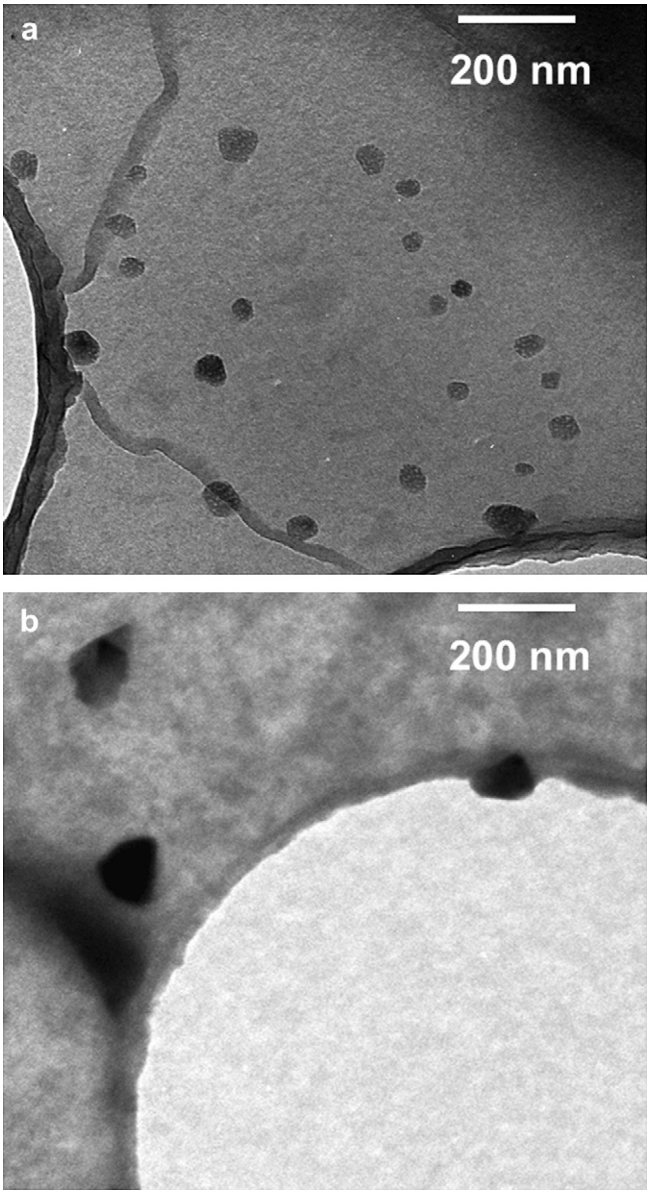


Fig. 3. Transmission electron micrographs of a) PEDOT-SPAA and b) PEDOT-PSS dispersions in water.

4. Conclusion

The use of a sulfonated poly(amic acid) for the template polymerization of PEDOT was accomplished, resulting in PEDOT-SPAA. This offers an alternative route for the preparation of PEDOT while using a template which can be chemically changed to a poly(imide) that imparts greater thermal stability to the system. By polymerizing 3,4-ethylenedioxythiophene (EDOT) in the presence of a sulfonated poly(amic acid) in water, a stable colloidal dispersion was prepared. Thermal treatment of this material at 180 °C (forming PEDOT-SPI) was shown to boost conductivities, even without the addition of dopants (10-fold increase). The use of D-sorbitol, DMF, and a surfynol to increase the properties of the dispersion resulted in conductivities which more closely match those of in-house prepared PEDOT-PSS. The thermal stability of PEDOT-SPAA (and the corresponding PEDOT-SPI) was a large improvement over PEDOT-PSS. PEDOT-SPI displayed an increase in conductivity at 300 °C while PEDOT-PSS dropped below the measurable limit ($<1 \times 10^{-5}$ S/cm). The dopants used were those commonly associated with PEDOT-PSS, however these materials (particularly alcohols, sugars, and low-boiling solvents) are not amenable to high temperature applications. We are currently investigating the use of more appropriate small-molecule additives that can withstand the high temperatures used and more favorably associate with the amic acid and imide backbones. This conductive dispersion is a promising step towards highly conductive *and* highly thermally stable materials. Its use in applications or processing steps which require temperatures greater than 180 °C would relieve the property losses observed in PEDOT-PSS at these temperatures.

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Appendix. Supporting information

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2010.01.048.

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