

## Effects of Solvents on the Morphology and Conductivity of Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) Nanofibers

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**ABSTRACT:** In this study, the effect of solvents on the morphology and conductivity of poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) nanofibers is investigated. Conductive PEDOT:PSS nanofibers are electrospun by dissolving a fiber-forming polymer, polyvinyl alcohol, in an aqueous dispersion of PEDOT:PSS. The conductivity of PEDOT:PSS nanofibers is enhanced 15-fold by addition of DMSO and almost 30-fold by addition of ethylene glycol to the spinning dopes. This improvement is attributed to the change in the conformation of the PEDOT chains from the coiled benzoid to the extended coil quinoid structure as confirmed by Raman spectroscopy, X-ray diffraction, and differential scanning calorimetry. Scanning electron microscopy images show that less beady and more uniform fiber morphology could be obtained by incorporation of ethylene glycol in the spinning dopes.

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### INTRODUCTION

Electrically conductive polymers have both the physical and chemical properties of organic polymers as well as the electrical properties of metals. PEDOT:PSS, a conducting polymer, attracts special attention because it has electrochemical, thermal, and oxidative stability. Owing to these excellent properties, PEDOT:PSS has broad applications in areas of flexible electrodes, nanocomposites, electrochromical displays, and transistors.<sup>1–4</sup> Recently, there has been an increased interest in PEDOT for biomedical applications due to its good oxidative stability.<sup>5</sup> However, when compared with other conducting polymers, PEDOT:PSS shows lower conductivity, generally  $<1 \text{ S cm}^{-1}$  for thin films.<sup>6</sup>

Incorporation of some organic solvents, such as ethylene glycol (EG), poly(ethylene glycol) (PEG), dimethyl sulfoxide (DMSO), or sorbitol, in an aqueous dispersion of PEDOT:PSS, results in an improvement of the conductivity of PEDOT:PSS thin films.<sup>6–13</sup> Several theories for the mechanism by which the conductivity is increased have been presented, such as conformational change in PEDOT structure, removal of insulating PSS 'shell', and decrease in Coulomb interaction between PEDOT and PSS chains. Ashiwaza et al. observed enhancement in the conductivity of PEDOT:PSS thin films after adding various amounts of ethylene glycol and suggested that the added solvent reduced the effective energy barrier for hopping charge carriers between localized states.<sup>6</sup> Kim et al. observed an increase in

conductivity after adding DMSO, DMF, or THF to the aqueous dispersion of PEDOT:PSS.<sup>13</sup> They noted that polar organic solvents with high dielectric constants induce a screening effect between positively charged PEDOT chains and negatively charged PSS chains by reducing the Coulomb interaction between them. Jönsson et al. demonstrated that conductivity was enhanced by adding sorbitol and, -*N*-methylpyrrolidone in PEDOT:PSS aqueous dispersion.<sup>12</sup> They concluded that solvents wash away the excessive nonconductive PSS 'shell' which surrounds the PEDOT:PSS grains and increases the PEDOT-to-PSS molar ratio. Ouyang et al. proposed that ethylene glycol treatment induces a conformational change of the PEDOT chain from coil to extended coil or linear structure and suggested that the new linear or extended coil structure would improve conductivity through increased interaction between the PEDOT chains.<sup>7</sup>

In addition to films, the effects of solvents on the conductivity of PEDOT microfibers have also been investigated. Okuzaki et al. fabricated highly conductive PEDOT:PSS microfibers by wet spinning followed by dip treatment in ethylene glycol. They explained the mechanism of conductivity improvement as removal of the insulating PSS layer from the surface of the PEDOT:PSS grains. They found that dip treatments in ethylene glycol increased not only electrical properties, but also mechanical properties of fibers. This enhancement of mechanical properties was attributed to the molecular change in PEDOT molecules from the amorphous state to the crystalline state.<sup>14</sup>

Most research with regard to solvent effects on PEDOT:PSS has been conducted with thin films prepared by casting or spin coating, or with micro fibers produced by wet spinning. Solvent effects on PEDOT:PSS in the nanofibrous form have not been investigated. Therefore, this study utilizes the conductive properties of PEDOT:PSS in the form of high surface area nanofibers and seeks to investigate the effect of solvents. Conducting PEDOT:PSS nanofibers are potential candidates for use in highly sensitive, real-time electrically based sensors for radiation detection<sup>15</sup> and as nanomaterials for biosensor applications in solution-processable microfluidic devices<sup>16</sup> due to their extremely large surface-to-volume ratio, 3D structure, hydrophilicity, and small diameters of about 150 nm. Both thin films and wet-spun micro fibers have some limitations for these applications. Thin films cannot provide 3D structure or large surface area to volume ratio, and wet-spun PEDOT:PSS micro-fibers have a large fiber diameter of around 5  $\mu\text{m}$  reducing the surface to volume ratio as compared to nanofibers.<sup>17</sup>

Investigation of the solvent effects on electrospun PEDOT:PSS nanofibers is more challenging with a greater parameter space than film and microfiber studies, because the properties of added solvents also play an important role on electrospun nanofiber morphology. There are several electrospinning parameters that may be influenced by adding organic solvents. The optimum combination of solution, experimental parameters and the appropriate solvent selection has to be determined to produce ultrathin and greater conducting fibers from solution.

In this study, PEDOT:PSS nanofibers were obtained by electrospinning an aqueous dispersion of PEDOT:PSS with polyvinyl alcohol (PVA) as a carrier. PVA is selected as a fiber-forming polymer due to its water solubility and biocompatibility. Several different solvents, including DMF, DMSO, THF, EG, PEG were used as secondary solvents to investigate their effects on fiber morphology. Those producing the best results (EG and DMSO) were then investigated further to examine their impact on the conductivity of PEDOT:PSS nanofibers. 5 wt % was selected as an optimum solvent concentration because no significant improvement in nanofiber morphology was noted with a lower concentration (2.5 wt %). At higher concentrations excess solvent did not evaporate completely during electrospinning, producing solvent droplets on the nanofibrous mat.

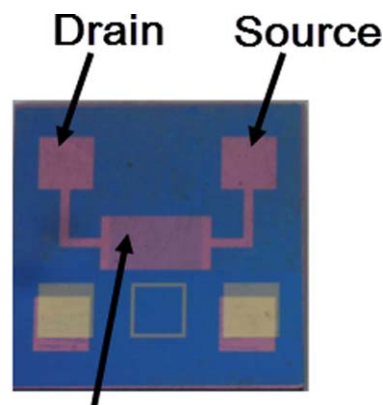
## EXPERIMENTAL

### Materials

An aqueous dispersion of PEDOT:PSS (Heraeus PH 1000, 1.3 wt %), PVA ( $M_w \sim 78,000$ , Polysciences) and nonionic surfactant Triton X-100 were used. DMSO (99.9%, Fisher Chemical), DMF (Fluka), THF (Mallinckrodt Chemicals), PEG ( $M_n \sim 400$ , Sigma Aldrich) and EG (Macron Chemicals) were used as solvents. All materials were used as received without any purification.

### Electrospinning

First, 4 wt % PVA was added to the aqueous dispersion of PEDOT:PSS and stirred on a hot plate by magnetic stirrer at 95°C for 3–4 h. Then 5 wt % solvent and 0.5 wt % Triton X were added to the solution and thoroughly vortexed for 2 min



## Finger-shaped electrodes

**Figure 1.** A two-point probe silicon-gold transistor with PEDOT:PSS nanofibers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

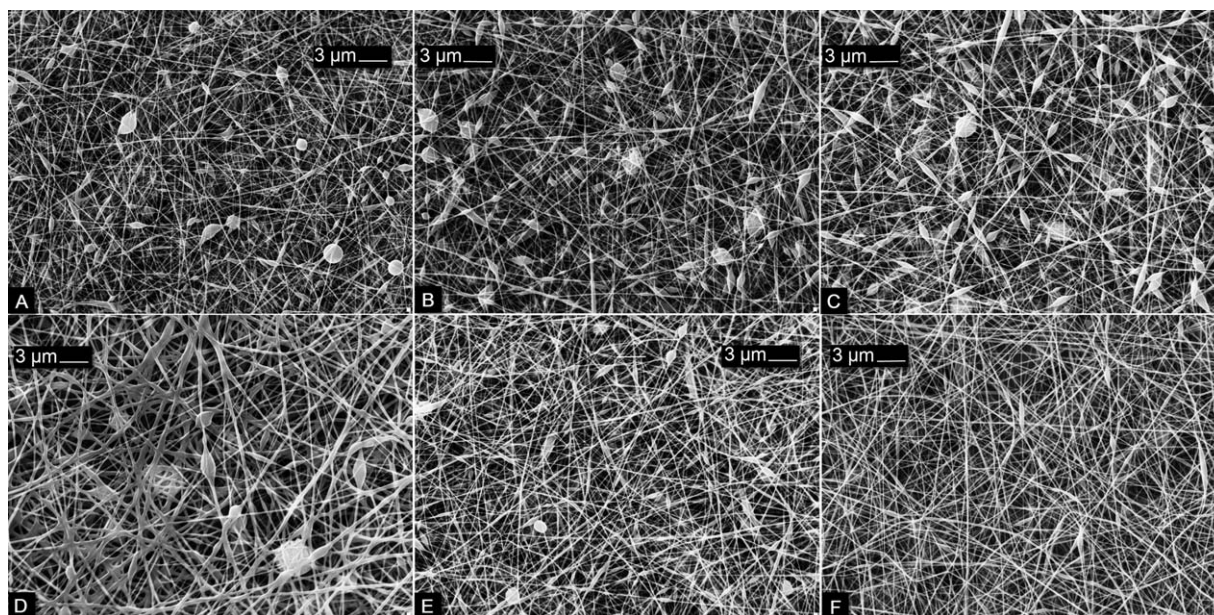
to make a homogenous spinning dope. PEDOT:PSS nanofibers were obtained without addition of secondary solvents and used as control samples to investigate the effect of the solvent on nanofibers. The polymer solutions were electrospun at room temperature using an applied voltage of 15 kV and a feed rate of 0.54 mL h<sup>-1</sup>. The distance between the spinneret and the aluminum collector was 11 cm.

### Nanofiber Conductivity

To measure nanofibrous mat conductivity, nanofibers were electrospun on glass slides. Conductance was measured using a two-point probe method. The current corresponding to the applied voltage was measured. Before measuring the conductance, the fiber samples were conditioned in desiccator for 24 h. Each sample was measured ten times in different directions. Average values are reported. To measure one nanofiber conductivity, PEDOT:PSS nanofibers were spun onto a two-point electrode substrate (Figure 1) of an interdigitated microelectrode array (IDMA) consisting of 75 pairs of electrode fingers, each 15 mm wide and spaced by 5 mm and 5 mm long. The electrodes were made with 35 nm Au on top of a 5 nm thick adhesion layer. As a voltage sweep ( $-0.5$  to  $0.5$  V) was applied to a sample at a sweeping rate of  $100$  mV s<sup>-1</sup>, the conductance of nanofibers was measured using a two-probe method in accordance with ASTM 4496-04 by an Keithley 2400 Source Meter and the conductivity was calculated.

### Characterizations

Morphology of the PEDOT:PSS nanofibers was examined by scanning electron microscopy (SEM) (Leica 440). Fibers were collected onto aluminum foil and Au-Pd coated for 30 s prior to examination. The average fiber diameter was calculated from SEM images, measuring up to 50 fibers per sample. PEDOT:PSS distribution in final fiber composition was characterized using electron probe micro analyzer (EPMA) (JEOL 8900). Both energy dispersive X-ray (EDS) and wavelength dispersive energy spectroscopy (WDS) were used to collect characteristic  $K\alpha$  X-ray emission of sulfur atoms in PEDOT:PSS molecules. To



**Figure 2.** SEM images of (a) PEDOT:PSS nanofibers and nanofibers electrospun from spinning dope with 5 wt % of (b) DMF, (c) THF, (d) PEG, (e) DMSO, and (f) EG.

understand the mechanism for the increase in conductivity, the PEDOT:PSS fibers were probed using a Renishaw InVia Confocal Raman microscope and a 785 nm laser source. The XPS measurements were carried out with a Surface Science Instrument SSX-100 on PEDOT:PSS nanofibers. Differential scanning calorimetry (DSC, Model Q2000, TA Instrument, New Castle, DE) was used to analyze the glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), enthalpy of fusion ( $\Delta H_f$ ), and crystallinity of PEDOT:PSS nanofibers. All DSC analyses were performed under a nitrogen atmosphere by keeping the flow rate of 50 mL min<sup>-1</sup>, between 0 and 300°C and at a scanning rate of 5°C min<sup>-1</sup>. X-ray diffraction (XRD) patterns of the electrospinning fibers were recorded with a Scintag X-ray diffractometer, operating in theta–theta geometry using  $Cu K\alpha$  radiation at 40 kv and 40 mA in the  $2\theta$  range of 9–36. Thermogravimetric analysis (TGA Model Q500, TA Instrument, New Castle, DE) was used to analyze the thermal properties of all specimens. All TGA tests were performed under a nitrogen atmosphere by keeping the flow rate of 60 mL min<sup>-1</sup>, between 0 and 300°C and at a scanning rate of 10°C min<sup>-1</sup>.

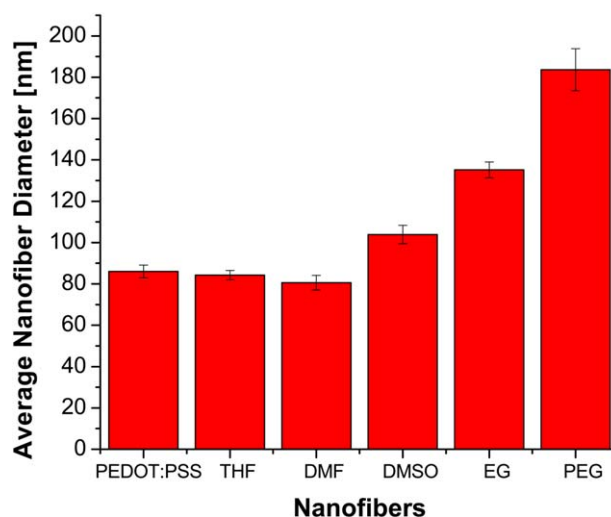
## RESULTS AND DISCUSSION

### Fiber Morphology and PEDOT:PSS Distribution in Nanofibrous Mat

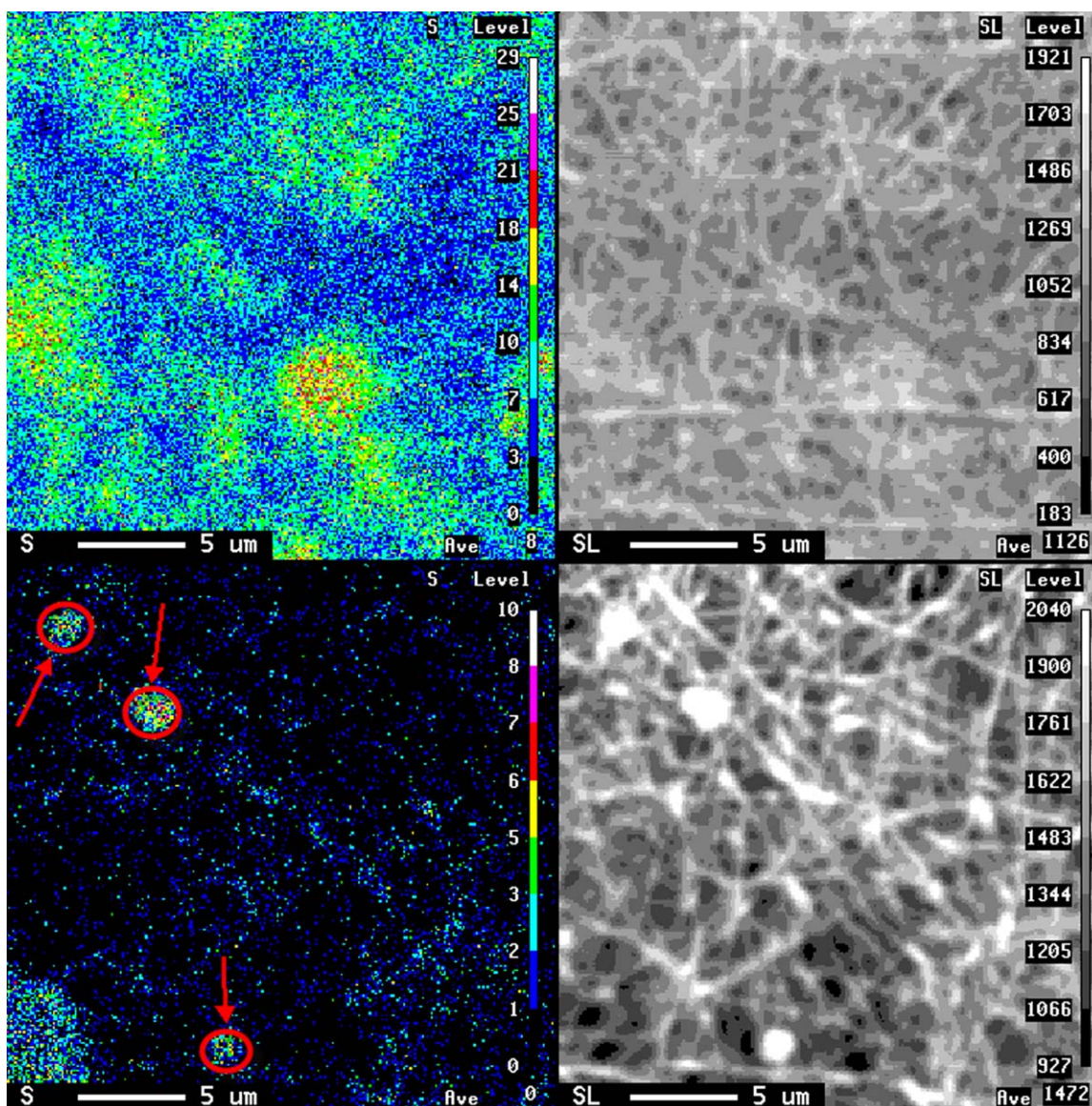
SEM images of PEDOT:PSS nanofibers are shown in Figure 2. The average diameters of PEDOT:PSS calculated with ImageJ<sup>TM</sup> are shown in Figure 3. PEDOT:PSS nanofibers, and the nanofibers electrospun from solutions with 5 wt % DMF and THF, showed beads. The average fiber diameters between the beads were statistically equal. Addition of 5 wt % DMF or 5 wt % THF did not affect the resulting fiber structure. Nanofibers electrospun from solutions with 5 wt % PEG exhibited branched fiber morphology, and had higher average nanofiber diameter when compared with other fibers. Owing to its high molecular

weight, PEG does not evaporate during electrospinning. Although some fibers were formed, electrospay also occurred. For this reason, PEG is not suitable for integration into this electrospinning system. Conversely, it was found that the number of beads decreased significantly and the average fiber diameter increased when fibers were electrospun from solutions with 5 wt % EG or DMSO. The most uniform fiber morphology was obtained by adding 5 wt % EG to the solution.

The differences between fiber morphologies after adding DMF, DMSO, THF, and EG, could not be explained by changes in typical electrospinning variables. Spinning conditions including feed rate, applied voltage, ambient humidity, and collection distance were held constant throughout all experiments. Solution



**Figure 3.** Nanofiber diameters. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



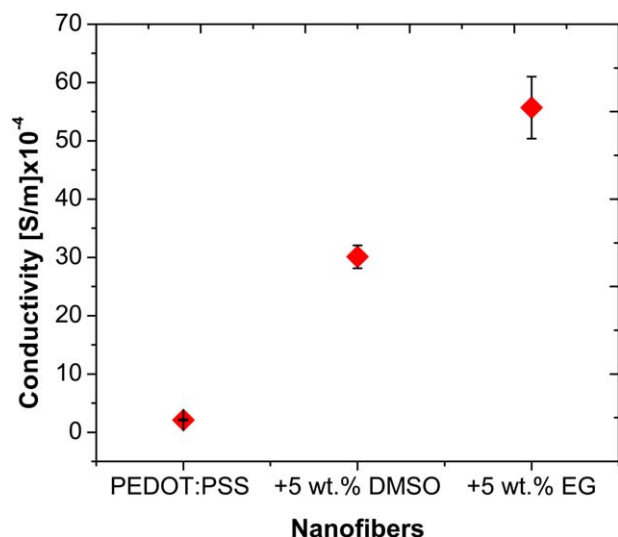
**Figure 4.** Comparison of the sulfur map of PEDOT:PSS nanofibrous mat electrospun spinning dopes with EG (top) and DMF (bottom), the color bars on the side of the left images indicates the sulfur concentration from lowest (black) to highest (white). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

variables including solution conductivity and viscosity were measured before and after the addition of these solvents. No significant difference in viscosity ( $0.5 \text{ Pa s}$  at shear rate of  $27.09 \text{ s}^{-1}$ , shear stress of  $54.87 \text{ Pa}$ ) was observed. The solution conductivity of samples was high reflecting the high conductivity of PEDOT:PSS, and exceeded the measurement limit of the conductivity meter. The addition of solvents did not decrease the solution conductivity measurably.

Although no changes in bulk properties of the spinning dope were observed, the added solvents may have had an effect on the spinnability of the solution by, as Ouyang stated, changing the conformation of PEDOT from a coil form to an extended coil form. The differences in the fiber morphologies, with decreasing bead formation on the addition of DMSO and EG, may also correlate with this mechanism. A polymer with a

linear/extended chain conformation is more easily electrospun than a polymer with a random coil conformation.<sup>18</sup> The change in conformation from coil to extended coil may increase the spinnability and improve fiber morphology. DMSO and EG may have greater effect on extending the PEDOT chain and increasing the spinnability of PEDOT:PSS to result in more homogenous fibers.

To see the effect of solvents on the distribution of PEDOT:PSS within the nanofibers, nanofiber mats were examined using EPMA. Since the sulfur atoms in this system are attributable solely to the PEDOT:PSS, distribution of PEDOT:PSS on the nanofiber mat could be mapped. Two samples which showed different fiber morphology (beady and uniform) were selected to elicit PEDOT:PSS distribution. Figure 4 shows PEDOT:PSS distribution in PEDOT:PSS nanofiber mats electrospun from



**Figure 5.** Room temperature conductivity of nanofibers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

spinning dopes containing EG, and spinning dopes containing DMF. The increased number of blue and green spots and their homogenous distribution in the PEDOT:PSS nanofiber mat electrospun from spinning dopes with EG confirmed the dispersion of PEDOT:PSS evenly throughout the mat. On the other hand, several large bright spots on the EPMA map of the PEDOT:PSS nanofiber mat electrospun from spinning dopes with DMF indicated the heterogeneous distribution of PEDOT:PSS. These results confirmed that when spinnability of dopes was low, PEDOT:PSS concentrated within beads. Conversely, the PEDOT distribution in nanofiber was continuous when spinnability and overall fiber uniformity were improved. Previous studies have shown that DMSO and EG treated PEDOT:PSS films also have higher conductivity than DMF and THF treated films.<sup>13</sup> For further investigation, EG and DMSO were selected as solvents because they had more uniform fibers and more evenly distributed PEDOT:PSS in the system than THF, DMF, or PEG.

### Electrical Conductivity

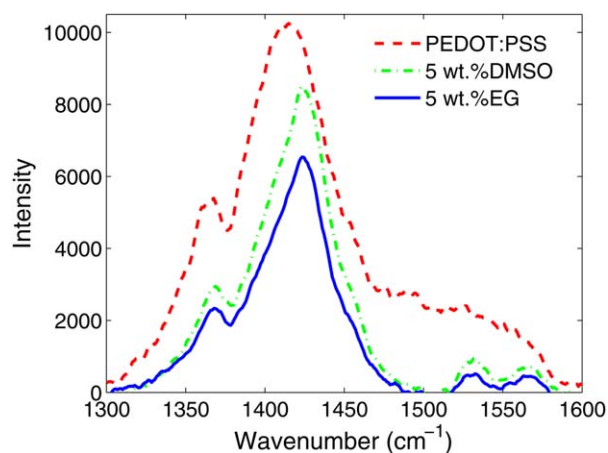
The room temperature conductivity of PEDOT:PSS nanofibers and nanofibers electrospun from spinning dopes with EG and DMSO are shown in Figure 5. PEDOT:PSS nanofibers with no addition of EG or DMSO have very low conductivity. However, there is a significant increase in conductivity when 5 wt % EG or DMSO is added to the solution before electrospinning. The conductivity of PEDOT:PSS fibers is enhanced by almost 30-fold when EG is added to the spinning dopes and by 15-fold when DMSO is added to the spinning dopes. It is evident that EG is the optimum solvent to improve both conductivity and morphology of PEDOT:PSS nanofibers. It is difficult to compare nanofiber conductivity results with PEDOT:PSS microfibers and thin films due to of pores in the fiber mats and nonhomogeneous structure of the fiber mats. To compare the conductivity results between microfibers and thin films, finger-shaped electrodes were used and conductivity of individual nanofiber was

calculated. The most conductive nanofibers, spun from solution with 5 wt % EG, was selected for individual nanofiber conductivity measurement. The conductance of nanofibers, on the finger-shaped electrodes was measured as 3.8E-04 S which was equivalent to the resistance of 2.63 k $\Omega$ . The nanofiber conductivity could be calculated using the known variables (fiber diameter: 135 nm, distance between electrodes: 5  $\mu$ m). The number of fibers on the 75 pairs of electrodes was around 10, as determined using an optical microscope. Therefore, the PEDOT:PSS nanofibers had an electrical conductivity on the order of 180 S m<sup>-1</sup>. Nanofiber conductivity is close to the conductivity of untreated films and microfibers, but it is less than solvent treated films and microfibers due to the presence of nonconductive PVA in nanofibers.

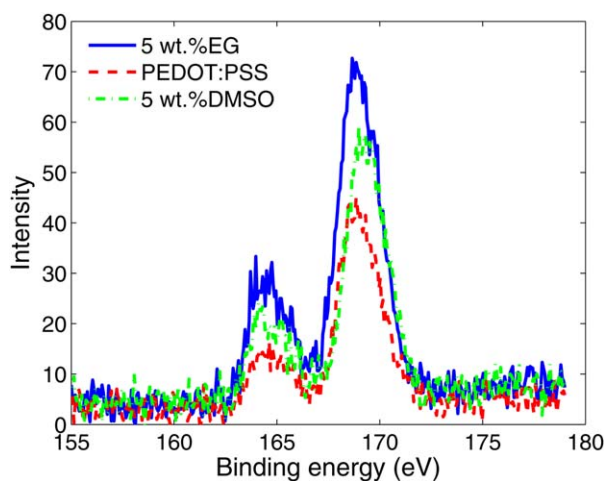
### Raman Spectroscopy and Molecular Structure

To understand the mechanism for the relationship between PEDOT chain conformation, fiber morphology and conductivity enhancement, the nanofibers, electrospun with and without addition of EG and DMSO, were studied by Raman spectroscopy. The Raman spectra of PEDOT:PSS nanofibers, is shown in Figure 6. A blue shift by 8 cm<sup>-1</sup> (centered at 1415 cm<sup>-1</sup> for PEDOT:PSS nanofibers), narrower band width and disappearance of the shoulder between 1450–1500 cm<sup>-1</sup> were observed for nanofibers electrospun from spinning dope with 5 wt % EG and DMSO. The blue shift was also reported in doped samples, and it was explained by the change in PEDOT from neutral state to oxidized state.<sup>19</sup> To elucidate whether a change in PEDOT state had occurred, curve fitting analysis was performed, but no correlation was found indicating a change between neutral and oxidized state. On the other hand, disappearance of the shoulder and narrower band width were also reported for solvent-treated PEDOT films due to the transformation of resonant structures for PEDOT from benzoid to quinoid, however a red shift instead of blue shift was observed in that study.<sup>20</sup>

Benzoid is the favored structure in the coil formation and low conductivity form of PEDOT, whereas the quinoid is the favored structure in the linear or extended coil formation and high conductivity form of PEDOT. The benzoid structure includes two conjugated  $\pi$ -electrons on the C $_{\alpha}$ =C $_{\beta}$  bond and



**Figure 6.** Raman spectra of electrospun PEDOT:PSS nanofibers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

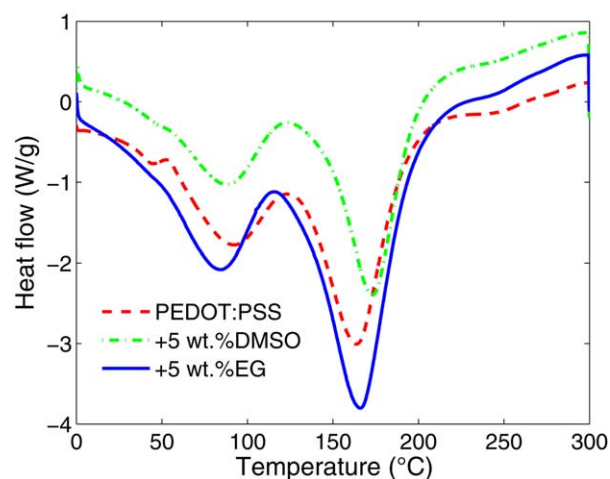


**Figure 7.** XPS (S2p) spectra of electrospun PEDOT:PSS nanofibers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the quinoid structure does not include any conjugated  $\pi$ -electrons on the  $C_{\alpha}-C_{\beta}$  bond.<sup>7</sup> Although a red shift was not observed in our Raman results, the other observations like high intensity peaks and disappearance of shoulder are similar with treated PEDOT:PSS films.<sup>20</sup> The conductivity enhancement and less beady fiber formation can only be explained by transformation of resonant structures due to the change in coil formation to extended coil formation. Extended coil/linear conformations increase inter-chain interactions among the PEDOT chains, thereby increasing the conductivity and supporting fiber formation. PEDOT:PSS nanofibers have both resonant structures, but after addition of EG or DMSO to the spinning dopes, the benzoid structure is thought to transform the quinoid. Blue shift may be observed due to the difference of PEDOT:PSS between used in this study and previous studies.

#### XPS Analysis

Raman spectroscopy is not suitable for characterization of PEDOT to PSS ratios because PSS does not give strong a Raman peak due to the nonconjugated double band. To investigate the effect of solvents on the PEDOT to PSS ratios, XPS measurement was performed, using the PEDOT:PSS nanofibers electrospun from solutions with and without 5 wt % EG or DMSO. Figure 7 shows the XPS spectra (S2p) of PEDOT:PSS nanofibers. Peaks at around 169 and 165 eV correspond to the S(2p) of PSS and PEDOT.<sup>12</sup> The peak areas of S(2p) spectra were calculated to find PEDOT to PSS ratios. The PEDOT to PSS ratios increased from 0.22 (PEDOT:PSS) to 0.25 (5 wt % DMSO) and 0.26 (5 wt % EG). Okuzaki et al. reported large increases from 0.45 to 0.86 (P grades of PEDOT:PSS) and 0.64 to 0.91 (PH grades of PEDOT:PSS) after EG dip treatment of wet-spun microfibers and explained the increase by removal of excessive PSS layer on the surface of PEDOT:PSS grains.<sup>14</sup> However, only slight increases were observed in our experiments. The insignificant increase in PEDOT to PSS ratio confirms that transformation of the resonant structure of PEDOT:PSS from benzoid to quinoid is a driving mechanism rather than removal PSS layer for conductivity improvement. The production

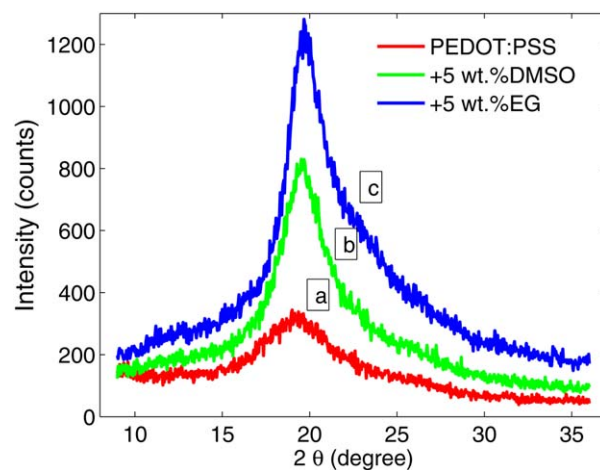


**Figure 8.** DSC thermograms of electrospun PEDOT:PSS nanofibers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

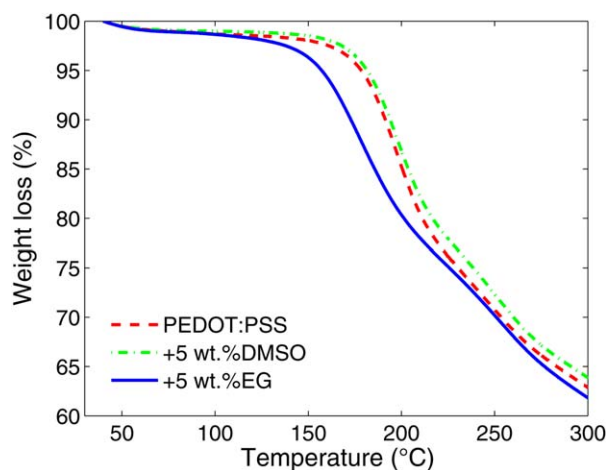
technique may also play an important role driving mechanism because unlike wet-spinning, high voltage is used to drive this nonmechanical, electrostatic spinning technique, and creates an electrical potential between a grounded target and the surface of the polymer solution droplet. When the applied electric force overcomes the surface tension of the polymer solution, a jet is produced and solvent molecules begin to evaporate rapidly.<sup>21,22</sup>

#### DSC Analysis and XRD Patterns

PEDOT:PSS nanofibers were characterized by DSC and XRD. Figure 8 shows the DSC curves of the PEDOT:PSS electrospun nanofibers. The first feature of the DSC curves indicates that the glass transition temperature ( $T_g$ ) of nanofibers. The glass transition temperature for PVA nanofibers has been seen at around 82–85°C in previous studies.<sup>23</sup> The high glass transition temperature of PEDOT:PSS nanofibers is observed at 92.3°C in our study. Adding EG or DMSO to the solution, decreased the glass transition temperature from 92.3 to 84.1 and 87.9°C,



**Figure 9.** XRD patterns of (a) PEDOT:PSS nanofibers and nanofibers were electrospun from spinning dope with 5 wt % of (b) DMSO, and (c) EG. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 10.** TGA thermograms of electrospun PEDOT:PSS nanofibers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

respectively, due to the plasticizing effect of the solvents. A single melting temperature is observed at 165.8°C for PEDOT:PSS nanofibers. By adding EG or DMSO to the spinning dopes, melting temperature increased from 165.8 to 167.6 and 174.0°C, respectively. The measured enthalpy value of PEDOT:PSS nanofibers is  $\Delta H = 201.4 \text{ J g}^{-1}$ . The addition of EG and DMSO to the spinning dopes increased the enthalpy  $\Delta H = 297.4 \text{ J g}^{-1}$  and  $\Delta H = 247.6 \text{ J g}^{-1}$ , respectively. The maximum enthalpy value was obtained from the PEDOT:PSS nanofibers electrospun using dopes with 5 wt % EG. The crystalline melting temperature for PVA nanofibers has been observed at 230°C and the %100 crystalline PVA enthalpy value found in literature is  $\Delta H_c = 138.6 \text{ J g}^{-1}$ .<sup>23,24</sup> Both the increasing melting temperature and the high enthalpy values observed in this research are attributed to the contribution of PEDOT:PSS and a strong association between PVA and PEDOT:PSS. This association increases as the PEDOT:PSS increasingly adopts the extended coil conformation. The increased enthalpy correlates with the improved fiber morphology, increased conductivity and PEDOT:PSS confirmation shift towards more extended chains.

The XRD patterns of various PEDOT:PSS nanofibers are shown in Figure 9. PVA has diffraction peaks at 16.0°, 19.4°, and 22.7° and, PEDOT:PSS has a diffraction peak at around 25°. Jia et al. stated that if there is no interaction or only weak interaction between components in polyblend fibers, there would be two different crystalline peaks for each component.<sup>25</sup> In our study, only one diffraction peak is seen for all nanofibers around 19.0° due to the strong interaction between PEDOT:PSS and PVA. The diffraction peak is seen at  $2\theta = 19.0^\circ$  for PEDOT:PSS nanofibers. The addition of DMSO or EG to the solution shifts the peak from 19.0° to 19.3° and 19.7°, respectively. XRD results showed that fibers with EG or DMSO have larger and sharper peaks when compared with the PEDOT:PSS nanofibers. Depression of the PVA peaks at 16.0° and 22.7°, the increase in degrees from 19.0° to 19.7°, and sharper-larger peaks indicate the formation and development of new crystalline structure.<sup>26</sup> The increased crystallinity was consistent with the change in PEDOT structure from coiled to extended coil chain conformation.

### Thermal Gravimetric Analysis

To determine whether residual solvents remain and assess influence of solvents on the thermal stability in nanofibrous mats, the fibers were analyzed with TGA. DMSO has a lower boiling temperature (189°C) and lower density ( $1.09 \text{ g mL}^{-1}$ ) when compared to the boiling temperature (195°C) and density of EG ( $1.11 \text{ g mL}^{-1}$ ). Due to these properties, DMSO may evaporate faster and result in little or no residual solvent in nanofibers when compared with EG. Figure 10 shows the TGA curves of electrospun nanofibers. The first weight loss between 30 and 120°C could be attributed to the desorption of physically adsorbed water. The second weight loss between 120 and 220°C is about the same for all samples and is due to decomposition of the doping material of PEDOT:PSS<sup>27</sup> and side chain of PVA,<sup>28</sup> however, the second weight loss starts at a lower temperature for nanofibers electrospun from spinning dope with EG. This difference may indicate the existence of the residual EG in the PEDOT:PSS nanofibrous mat. The third weight loss, which starts around 270°C, shows the degradation of PSS.<sup>27</sup> Although there is not a certain weight loss related with the solvents, DSC results showed that the glass transition temperature was decreased when solvents added to the spinning dope, small amounts of EG and DMSO may remain in nanofibers and act as a plasticizer and decrease the thermal stability of nanofibers, especially nanofibers electrospun from solution with 5 wt% EG. Due to its higher evaporation rate, DMSO did not affect the thermal stability notably when compared with EG.

### CONCLUSION

In this study, effects of different solvents on fiber morphology were investigated. Adding EG and DMSO to the spinning dopes resulted in transformation of PEDOT:PSS chains from random coil to extended coil conformation. The transformation from random coil to extended coil not only increased the conductivity by increasing the interchain interactions among the PEDOT chains, but also improved the fiber morphology and spinnability of the solution. DSC investigations indicated an increase in crystallinity after solvent addition to the solution and a strong interaction between PEDOT:PSS and PVA. XRD results showed the formation and development of a new crystalline structure when either EG or DMSO was added to the spinning dopes. The most uniform and conductive nanofibers resulted from introducing EG to the dopes.

### ACKNOWLEDGMENTS

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