

# Electrically Conductive Poly(3,4-ethylenedioxythiophene)–Polystyrene Sulfonic Acid/Polyacrylonitrile Composite Fibers Prepared by Wet Spinning

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**ABSTRACT:** Composite conductive fibers based on poly(3,4-ethylenedioxythiophene) (PEDOT)–polystyrene sulfonic acid (PSS) blended with polyacrylonitrile (PAN) were prepared via a conventional wet-spinning process. The influences of the PEDOT–PSS content on the electrical conductivity, thermal stability, and mechanical properties of the composite fibers were investigated. The fibers with 1.83 wt % PEDOT–PSS showed a conductivity of 5.0 S/cm. The breaking strength of the fibers was in the range 0.36–0.60 cN/dtex. The thermal stability of the PEDOT–PSS/PAN composite fibers was similar to but slightly lower than that of the pure PAN. The X-ray diffraction results revealed that both the pure PAN and PEDOT–PSS/PAN composite fibers were amorphous in phase, and the crystallization of the latter was lower than that of the former. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 370–374, 2013

**KEYWORDS:** blends; conducting polymers; fibers; synthesis and processing

Received 20 September 2012; accepted 11 February 2013; published online 16 March 2013

**DOI:** 10.1002/app.39174

## INTRODUCTION

Conductive fibers based on conducting polymers have been investigated from both fundamental and technological points of view to understand their electrical and mechanical properties and practical uses for electromagnetic interference shielding, conducting textiles, and organic electronics.<sup>1–3</sup> It was reported that conductive polyaniline-dodecyl benzene sulfonic acid/polyacrylonitrile (PANI-DBSA/PAN) fibers could be obtained with a wet-spinning process from a solution of dodecyl benzene sulfonic acid doped PANI and PAN prepared in dimethylformamide. The conductivity of the fibers containing 7 wt % PANI-DBSA reached  $10^{-3}$  S/cm, and the tensile strength of the fibers was in the range 2.5–3.5 cN/dtex.<sup>4</sup> Foroughi et al.<sup>5</sup> prepared polypyrrole fibers by wet spinning; the ultimate tensile strength, elastic modulus, and elongation at break of these fibers were 25 MPa, 1.5 GPa, and 2%, respectively, with an electronic conductivity of about 3 S/cm. Among the conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(4-styrenesulfonate) (PSS), one of the most commercially successful conductive polymers, has attracted wide attention because of its excellent characteristics in its conductive state; these include a low band gap ( $E_g \approx 1.6$  eV), superior electrochemical and thermal stabilities, and high transparency, which provide it with

various potential applications for electronics, especially for organic or plastic electronic and optical devices.<sup>6–9</sup> Okuzaki and Ishihara<sup>10</sup> fabricated PEDOT–PSS conducting microfibers by a wet-spinning technique. The electrical conductivity of the as-spun microfibers was on the order of  $10^{-1}$  S/cm. The Young's modulus, tensile strength, and elongation at break of the resulting microfibers were  $1.1 \pm 0.3$  GPa,  $17.2 \pm 5.1$  MPa, and  $4.3 \pm 2.3\%$ , respectively. However, because it was confined by its viscosity, it was difficult to spin the pure PEDOT–PSS solution into continuous longer fibers.

In this study, to explore a simple, safe, and industrially viable technique for spinning PEDOT–PSS, a self-made PEDOT–PSS solution was blended with PAN. Then, a traditional wet-spinning process was carried out, and finally, PEDOT–PSS/PAN composite conductive fibers with excellent electrical conductivity and good mechanical performance were obtained.

## EXPERIMENTAL

### Materials

3,4-Ethylenedioxythiophene ( $\geq 99.5\%$ ) was purchased from Suzhou Yacoo Chemical Reagent Corp., Suzhou, China. Polystyrene sulfonic acid (PSS, chemically pure) was provided by Shanghai Jiachen Chemical Co., Ltd., Shanghai China. Ferric trichloride

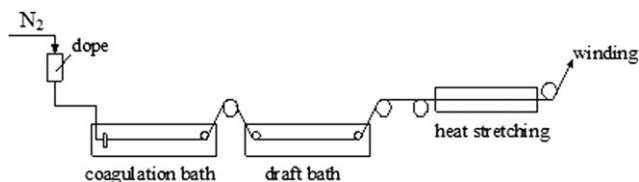


Figure 1. Schematic diagram of the wet-spinning process.

(FeCl<sub>3</sub>, analytical reagent) was purchased from Xi Long Chemical Co., Ltd., Beijing China. Sodium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>; analytical reagent) was provided by Tianjin Da Mao Chemical Reagent Factory, Tianjin China. PAN (weight-average molecular weight = 50,000 ± 5000) was purchased from China's Oil Daqing Lianhua Co., Heilongjiang China. Sodium thiocyanate (NaSCN) was purchased from Beijing Chemical Works, Beijing China. All reagents were used as received without further purification.

### Preparation of PEDOT-PSS

In this study, we prepared PEDOT-PSS dispersions by chemical oxidative polymerization. The specific process was as follows. First, 0.15 g of 3,4-ethylenedioxythiophene was blended with 0.41 g of PSS. Second, 7 mL of water was added to the mixture and stirred for 15 min. We then added a solution of 0.38 g Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> dissolving in 6 mL of water into the mixture. Third, 0.45 mL of FeCl<sub>3</sub> solution (1 mol/L) was diluted with 7 mL of water and was then added dropwise to the previous solution. Last, the mixture was stirred for 24 h at room temperature. The obtained mixture was called PEDOT-PSS and was used in the following experiment.

### Preparation of the Spinning Solution

A given amount of deionized water (0, 20, 40, 60, or 80 mL) was added to a 20-mL PEDOT-PSS dispersion, and then, 20,

40, 60, 80, or 100 g of NaSCN, respectively, was added to the previous corresponding mixture. In the next step, a certain amount of PAN powder (6.0, 11.9, 17.9, 23.9, or 29.9 g) was added to the PEDOT-PSS mixture to make it into a 13% PAN spin dope, which included 1.83, 0.92, 0.62, 0.47, or 0.38 wt % PEDOT-PSS, respectively. To prepare the pure PAN dope, 60 g of NaSCN was added to 60 g of deionized water; then, 17.9 g of PAN powder was added to the mixture. Ultimately, the dissolved solutions were placed in a vacuum-drying oven at 45°C for 2 days to degas. The dopes obtained in this way were called the PEDOT-PSS/PAN mixture.

### Preparation of the Composite Conductive Fibers

The PEDOT-PSS/PAN fibers were fabricated through a wet-spinning technique with a multihole spinneret (18 holes, diameter = 0.2 mm). Figure 1 gives the schematic diagram of the wet-spinning process used in this study. To extrude the dope from the reservoir into the spinneret, nitrogen gas was used to provide the required pressure. The coagulation bath was filled with NaSCN solution with a concentration of 10 wt %. The temperature of the coagulation bath was maintained at 0–5°C and controlled by ice. The draft bath was filled with NaSCN solution with a concentration of 4 wt %. The temperature of the draft bath was maintained at 50°C and was controlled by a potential transformer. The resulting microfibers were then placed on a hot plate (160°C) and underwent continuously winding. All of the samples in this study had a total draw ratio of 4.

### Characterization

A scanning electron microscope (JSM-6360LV, the Japanese electronics company, Japan) was used to collect electron micrographs of the pure PAN fibers and the PEDOT-PSS/PAN fibers. The imaging conditions were 10.0 kV and work distance = 29 mm. The structure of the fibers was analyzed by a Nexus 670

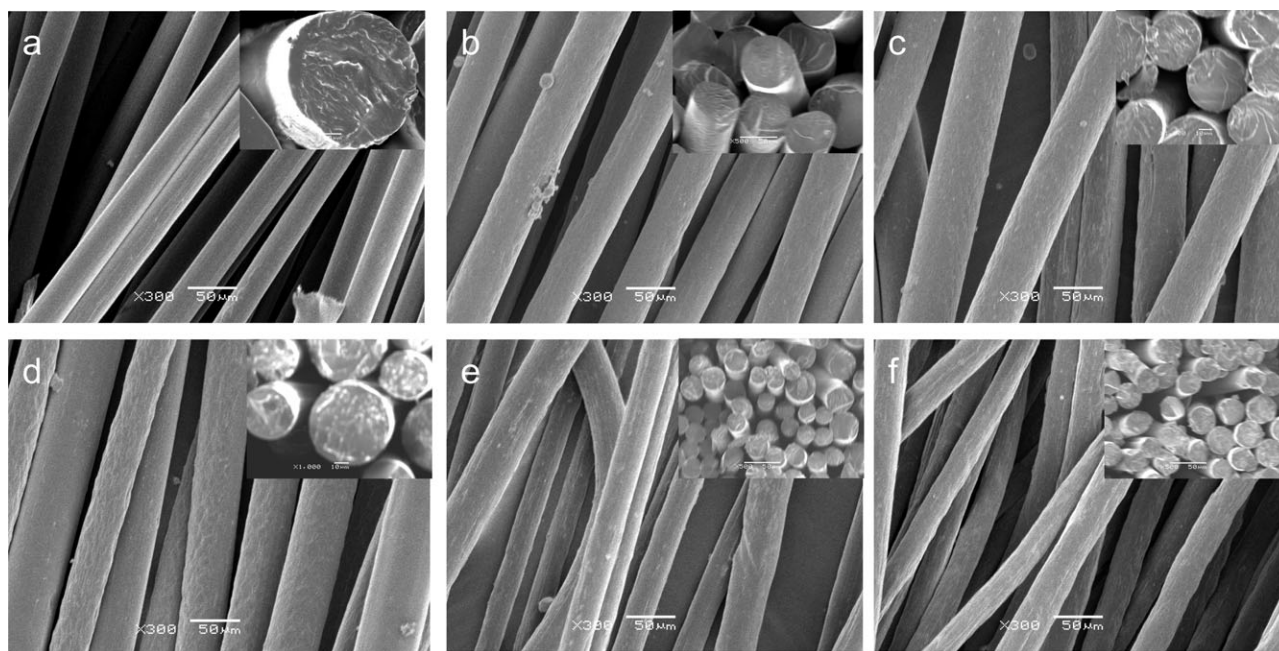


Figure 2. SEM images of the pure PAN and PEDOT-PSS/PAN composite conductive fibers with different PEDOT-PSS contents: (a) 0, (b) 0.38, (c) 0.47, (d) 0.62, (e) 0.92, and (f) 1.83 wt %.

Fourier transform infrared (FTIR, Nicolet company, America) spectroscope. The thermostability was observed by a TG6300 (SHI company, Japan) instrument operating at a heating rate of 10°C/min under a nitrogen atmosphere. The temperature range was 20–800°C. X-ray diffraction (XRD) patterns of powder samples were recorded with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 50 mA with a Rigaku wide-angle goniometer, Japan RIGAKU company, Japan. The data were collected in the range  $6^\circ < 2\theta < 36^\circ$ . The mechanical properties of the fibers were measured by a YG004N electronic single-fiber tensile strength tester, Nantong Dahong experimental instrument company, China. The electrical conductivities of the samples were measured by a four-probe conductivity meter (Keithley 6221+2182A, Keithley Instruments Inc., America). The diameters of the fibers were obtained via scanning electron microscopy (SEM) images. The conductivities were calculated by the following formula:

$$\delta = IL/V_S \quad (1)$$

where  $\delta$  is the conductivity (S/cm),  $I$  is the constant current through the two outer electrodes,  $V$  is the variational potential through the two inner electrodes,  $L$  is the distance of the two inner electrodes, and  $S$  is the area of the fiber section.

## RESULTS AND DISCUSSION

### Morphology of the PEDOT–PSS/PAN Fibers

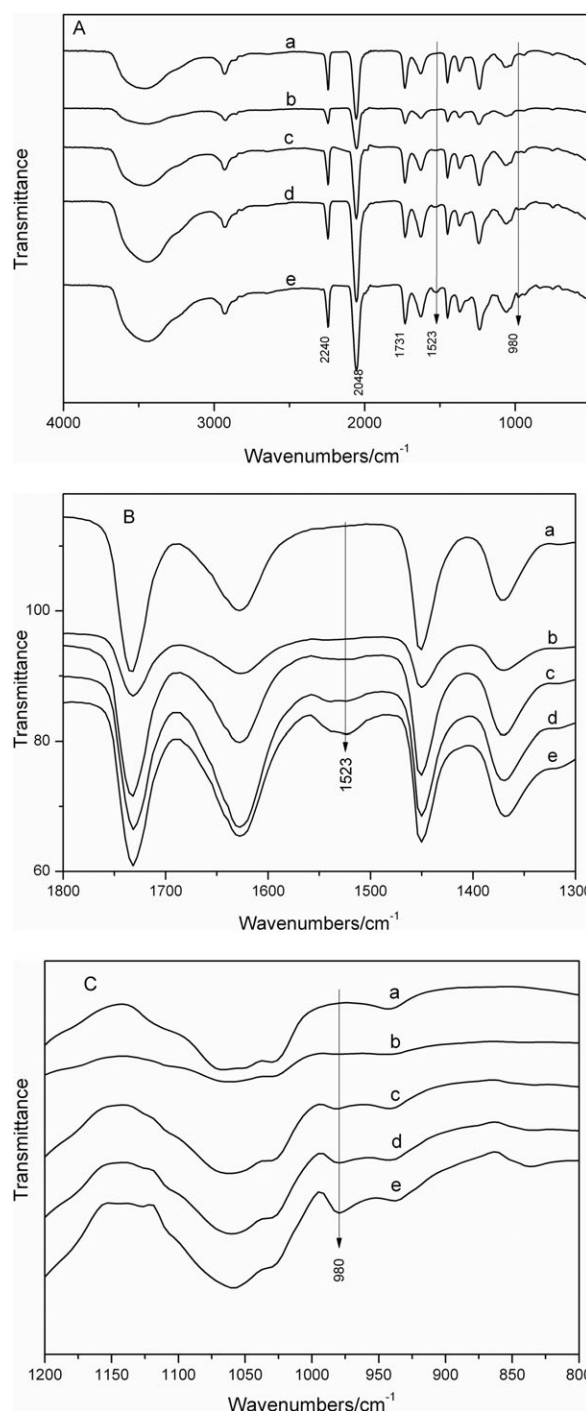
The SEM images of the PEDOT–PSS/PAN composite conductive fibers are displayed in Figure 2. As shown in Figure 2, the diameter of all of the fibers was about 30–60  $\mu\text{m}$ , and the intersecting surfaces of all of the fibers were circular. Also, the surface of the pure fibers was smoother [Figure 2(a)] than that of the PEDOT–PSS/PAN composite conductive fibers [Figure 2(b–f)]. As the content of PEDOT–PSS increased, the surfaces of the composite conductive fibers were increasingly rougher as a result of the addition of the PEDOT–PSS. This may have been due to the increasing viscosity.

### FTIR Analysis of the PEDOT–PSS/PAN Fibers

From FTIR spectra (Figure 3), we observed that all of the spectra of the pure PAN and PEDOT–PSS/PAN composite fibers were similar to each other. The FTIR spectrum of the pure PAN fiber [Figure 3(a)] showed several characteristic bands, such as those at 2243  $\text{cm}^{-1}$  for  $-\text{CN}$  stretching and 1731  $\text{cm}^{-1}$  for  $-\text{CO}$  stretching.<sup>11</sup> The absorption band at 2048  $\text{cm}^{-1}$  was attributed to  $-\text{SCN}$ . In the spectra of the PEDOT–PSS/PAN composite fibers, the newly arisen absorption bands at 1523 and 980  $\text{cm}^{-1}$  were assigned to the benzenoid rings of PSS and the  $-\text{C}-\text{S}-\text{C}-$  deformation vibration of PEDOT,<sup>12</sup> respectively. It was proven that the PEDOT–PSS was present in the PEDOT–PSS/PAN fibers.

### XRD Patterns of the PEDOT–PSS/PAN Fibers

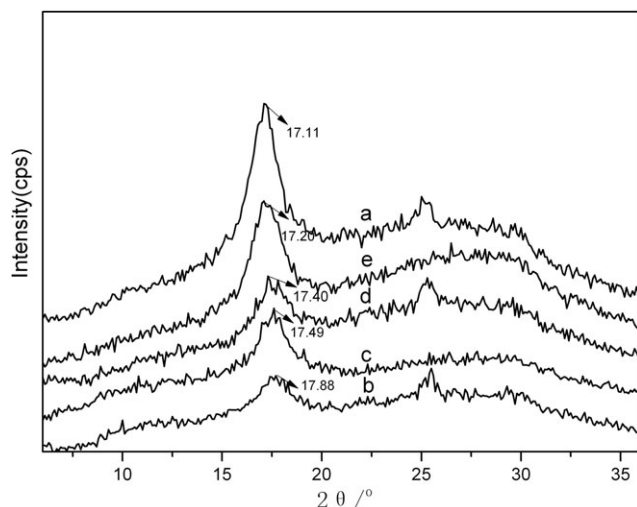
Figure 4 shows the XRD diffraction patterns of different fibers. Obviously, the strongest diffraction peak from the PAN fiber occurred around  $2\theta = 17.11^\circ$  [Figure 4(a)]; this could be indexed to the (100) plane of a hexagonal structure.<sup>12</sup> The broad diffraction peaks centered at  $25.1^\circ$  indicated that the crystallization of the pure PAN fibers was in the amorphous phase. Also, the crystallization of the PEDOT–PSS/PAN composite fibers was similar to that of the pure PAN fibers but lower.



**Figure 3.** FTIR curves of the pure PAN and PEDOT–PSS/PAN composite conductive fibers with different PEDOT–PSS contents: (a) 0, (b) 0.47, (c) 0.62, (d) 0.92, and (e) 1.83 wt %.

Also, with increasing PEDOT–PSS content, the peak of the (100) plane appeared to gradually blueshift from 17.88 to 17.20. At the same time, the crystallizations of the PEDOT–PSS/PAN composite fibers increased as the content of PEDOT–PSS increased. For all of the PEDOT–PSS/PAN composite fibers, the crystallization of the fibers with the PEDOT–PSS of content up to 1.83 wt % was the best.

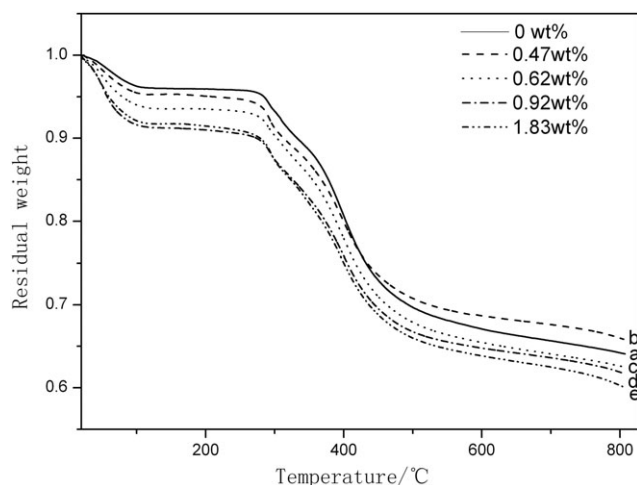




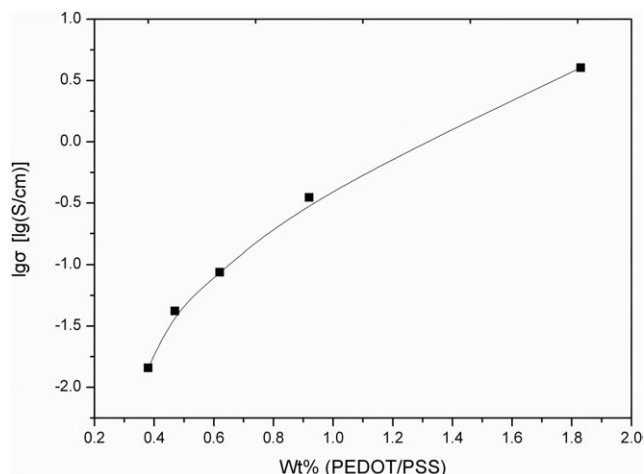
**Figure 4.** XRD patterns of the pure PAN and PEDOT–PSS/PAN composite conductive fibers with different PEDOT–PSS contents: (a) 0, (b) 0.47, (c) 0.62, (d) 0.92, and (e) 1.83 wt %.

### Thermal Performance Analysis of the PEDOT–PSS/PAN Fibers

The thermal stability of the PEDOT–PSS/PAN composite fibers was studied by thermogravimetry, which is an important method for detecting the degradation behavior of fibers. As shown in Figure 5, the thermograms were similar to each other for both the pure PAN fibers (solid line) and the PEDOT–PSS/PAN composite fibers (broken lines). The first weight loss of 5–10 wt % at 20–110°C was attributed to the elimination of absorbed moisture,<sup>13</sup> and the second one at 280–500°C<sup>14</sup> represented the degradation of the PAN molecular chains. The final amount of residual carbon was from 60 to 66%. As shown in Figure 5, the thermal stability of the PEDOT–PSS/PAN composite conductive fibers was similar to that of the pure PAN fibers but was slightly lower.



**Figure 5.** Thermogravimetric diagrams of the pure PAN and PEDOT–PSS/PAN composite conductive fibers with different PEDOT–PSS contents: (a) 0, (b) 0.47, (c) 0.62, (d) 0.92, and (e) 1.83 wt %.



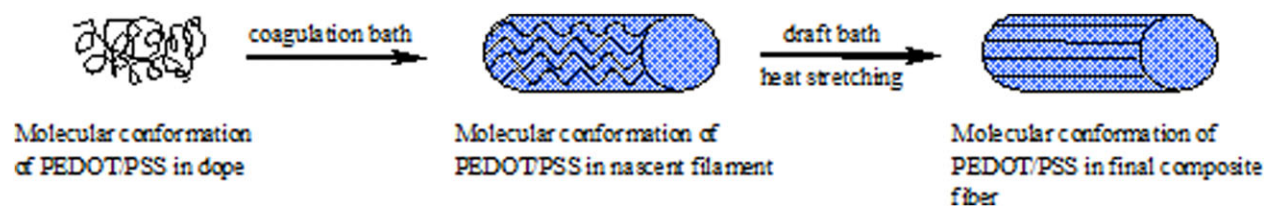
**Figure 6.** Relation of the content of PEDOT–PSS and the conductivity ( $\sigma$ ) of the PEDOT–PSS/PAN composite fibers.

### Conductivity of the PEDOT–PSS/PAN Fibers

Figure 6 gives the relationship of the content of PEDOT–PSS to the conductivity of the PEDOT–PSS/PAN composite fibers. As shown in Figure 6, the conductivity of the PEDOT–PSS/PAN composite fibers increased as the content of PEDOT–PSS increased. The highest value of conductivity was up to 5.0 S/cm when the PEDOT–PSS content was 1.83 wt %. This could be attributed to the conductive mechanism of the conductive fibers. As a matter of fact, many factors, including the doped extent of PEDOT, the dispersion and distribution of PEDOT in the polymer matrix, and the measuring technique influenced the conductivity of the blends.<sup>15</sup> In this case, as the content of PEDOT–PSS increased, the effective conductive paths of the conductive fibers also increased, and this made the conductivity rise.

In this method, the content of the PEDOT–PSS in the whole composite fiber was only 1.83%, but its conductivity was as high as 5.0 S/cm; this was much higher than the conductivity of the pure PEDOT–PSS fiber (0.1 S/cm) prepared by Okuzaki and Ishihara.<sup>10</sup> What was the reason for this phenomenon? In our opinion, it may have occurred because the PEDOT–PSS added to the composite fiber, although its content was low, it has formed a kind of consecutive phase in the solid fiber that was an effective conductive path of the electron conduction in the solid fiber.<sup>15</sup> The consecutive phase of conductive materials is important and will guarantee that the composite fiber realizes a high conductivity with a small amount of conductive material.

On the other hand, the high draw ratio was the other reason for the high conductivity (in this study, the draw ratio of all of the samples was 4). Figure 7 gives the sketch map of the molecular conformation of PEDOT–PSS at different stages of the wet-spinning process. As depicted, the molecular conformation of PEDOT–PSS in the dope was mixed and disorderly; when it was extruded to form the nascent filament, the PEDOT–PSS displayed a certain orientation, generating a kind of loose and consecutive conformation. Then, after the draft bath and heat stretching, the PEDOT–PSS molecules were highly oriented and formed a



**Figure 7.** Molecular conformation of PEDOT–PSS in different state of the wet-spinning process. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

consecutive and fully straight molecular conformation; this was the more effective conductive path and resulted in a higher conductivity. In another study, we have demonstrated that the conductivity of the composite conducting fiber prepared by the wet-spinning method increased with increasing of the draw ratio.<sup>16</sup>

#### Mechanical Performance of the PEDOT–PSS/PAN Fibers

The drawing strength is the most important index of fiber spinnability, and it has a close relationship with the process performance. Through testing the stress–strain curve of the pure PAN fibers and PEDOT–PSS/PAN composite fibers with different PEDOT–PSS contents, we found that for all of the samples, there existed yield points, which belonged to strong and tough materials.<sup>17</sup> The tensile test results are tabulated in Table I. As shown in Table I, the mechanical performance, including the breaking strength, elongation at break, and initial modulus of the PEDOT–PSS/PAN composite fibers were all lower than that of the pure PAN fiber. There were no obvious rules between the PEDOT–PSS content and the mechanical performance. For pure PAN, the breaking strength, elongation at break, and initial modulus were 0.60 cN/dtex, 49.91%, and 5.06 cN/dtex, respectively. When the content of PEDOT–PSS was 1.83 wt %, the breaking strength, elongation at break, and initial modulus were 0.36 cN/dtex, 36.73%, and 3.32 cN/dtex, respectively.

#### CONCLUSIONS

PEDOT–PSS/PAN composite conductive fibers were successfully prepared via a conventional wet-spinning process, which is a kind of simple, safe, and industrially viable technique. The mechanical properties and the crystallization of the obtained PEDOT–PSS/PAN conductive composite fibers were slightly lower than that of the pure PAN fibers. The fiber with 1.83 wt % PEDOT–PSS had a conductivity of 5.0 S/cm and showed good thermal stability compared to the pure PAN fibers. The

**Table I.** Mechanical Performance of the Pure PAN and PEDOT–PSS/PAN Composite Fibers

PEDOT–PSS content (wt %)	Breaking strength (cN/dtex)	Elongation at break (%)	Initial modulus (cN/dtex)
0	0.60	49.91	5.06
0.47	0.43	35.19	2.03
0.62	0.31	43.98	2.31
0.92	0.33	33.02	3.04
1.83	0.36	36.73	3.32

formation of the consecutive phase of the conductive materials and the high draw ratio during the wet-spinning process were responsible for the high conductivity of the as-spun composite conductive fibers.

#### ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the National Nature Sciences Foundation of China (contract grant number 20974005) and the Beijing Nature Sciences Foundation (contract grant number 2102017).

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