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Electrokinetic separation of co-solutes into bimodal fibers by electrospinning

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Composite and chemically/physically distinct fibers of sodium poly[2-(3-thienyl)-ethoxy-4-butylsulfonate] (PTEBS) and polyethylene oxide (PEO) were formed by electrospinning from a homogeneous aqueous solution containing PTEBS and PEO co-solutes. Composite nanofibers of diameter of ~ 60 nm were electrospun from an aqueous solution. The addition of ammonium hydroxide (NH_4OH) to the water solution resulted in “bimodal” electrospun fibers consisting of distinct large diameter white PEO fiber segments and small diameter black PTEBS fiber segments. The optical absorption spectrum of the composite PTEBS/PEO nanofibers did not exhibit the characteristic peak around 460 nm, which is present in the bulk spectrum. © 2008 American Institute of Physics. [DOI: 10.1063/1.2894512]

In electrospinning, a high voltage is applied to a polymer solution to produce very small fibers with diameters in the range from a few nanometers to several microns using electrostatic rather than mechanical forces.¹⁻³ Polymer and polymer composite fibers have been electrospun from a wide variety of polymer/solvent systems and in numerous morphologies including ribbons, porous fibers, hollow or coaxial fibers, and beaded structures.⁴⁻⁹ However, it has proven challenging to electrospin conjugated, semiconducting polymers due to their rigid structure, low molecular weight, and/or limited solubility.^{1,10} To solve this problem, conjugated polymers are often combined in solution with more readily “spinnable” polymers or spun using newly developed side-by-side and coaxial techniques.^{1-3,10-16} Using these methods, composite fibers such as poly(phenylene vinylene) (PPV)/poly(vinylpyrrolidone),¹⁰ polyaniline (PANI)/poly(ethylene oxide) (PEO),^{14,15} PANI/polystyrene,¹⁵ PEO/poly(aniline sulfonic acid),¹⁶ poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV)/poly(3-Hexylthiophene),¹² and MEH-PPV/poly(9,9-dioctylfluorene)¹² have been produced and typically consist of a mat of composite fibers with a relatively narrow size distribution.

While electrospun mats exhibiting varying and even bimodal size distributions have been produced,⁷⁻⁹ chemically and physically distinct fibers have not been previously electrospun from a single homogeneous solution. Gupta and Wilkes reported “bicomponent” fibers of poly(vinyl chloride)/segmented polyurethane and poly(vinyl chloride)/poly(vinylidene fluoride), but the bicomponent fibers were produced from two different polymer solutions using side-by-side technology.¹³

Sodium poly[2-(3-thienyl)-ethoxy-4-butylsulfonate] (PTEBS) is a water-soluble thiophene polymer semiconductor, which has been used as an electron donor to prepare environmentally friendly water-soluble polymer thin film solar cells.¹⁷ In this paper, PTEBS was combined in an aqueous solution with PEO and then electrospun into fibers in order

to study its electrospinning properties and the effect of fiber diameter on optoelectrical properties.

PTEBS solutions were prepared both with and without ammonium hydroxide (NH_4OH). Both solutions were dissolved in de-ionized water at a concentration of 1.5%. The PTEBS solution without NH_4OH was then magnetically stirred for 14 days. For the PTEBS solution with NH_4OH , 20 mg of NH_4OH was added per 1 ml of PTEBS solution immediately after the de-ionized water was mixed with PTEBS. Because the NH_4OH accelerates the dissolution, the PTEBS solution with NH_4OH was magnetically stirred for only 3 days. The PEO with a molecular weight of 2 000 000 g/mol was then added to these two PTEBS solutions at a concentration of 20 mg per 15 mg PTEBS and stirred for one day.

Following the preparation, both solutions were electrospun using a high voltage dc power source (Spellman CZE 1000R).^{16,18} The infusion rate of the solution was controlled using a Harvard Apparatus PHD 2000 syringe pump. The electrospun fibers were collected on a substrate mounted on a rotating hexagonal drum with a speed of ~ 1725 rotations/min. All of the fibers were electrospun at an infusion rate of 1 $\mu\text{l}/\text{min}$ and with a needle tip to a substrate distance of 10 cm. The electrospinning voltage was set at a value slightly above that required to get stable jet: 4.5 kV for the solution without NH_4OH and 6.5 kV for the solution with NH_4OH . The morphology was characterized using an optical microscope (Olympus BX60) and transmission electron microscopy (TEM) (Jeol JEM-1230). The absorption spectra were measured with UV/vis spectrometer (Perkin Elmer Lambda 40). A high speed video camera (Photron FASTCAM-PCI R2) was used to observe the formation of the Taylor cone and jet.

Figures 1(a) and 1(b) show the typical morphology of the electrospun fibers made from the PTEBS/PEO solution without and with NH_4OH . The PTEBS/PEO fibers prepared without NH_4OH show a unimodal morphology, where all the fibers have almost the same diameter and color [Fig. 1(a)]. By contrast, the fibers made from the PTEBS/PEO solution with NH_4OH produced two different kinds of fibers in a bimodal morphology: large diameter white fibers and small

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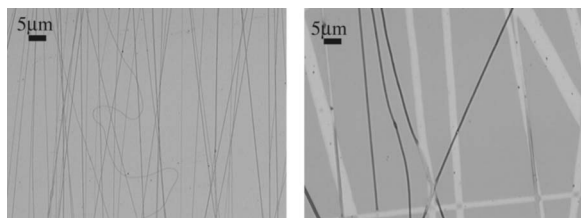


FIG. 1. Microscope photo of the electrospun PTEBS/PEO fibers: (a) The unimodal PTEBS/PEO nanofibers without NH_4OH . (b) The bimodal PTEBS/PEO fibers with NH_4OH .

diameter black fibers. Regardless of the infusion rate, the electrospinning voltage, and the distance between the needle and the substrate, and even if PEO with different molecular weights (400k, 1M, and 2M) were used, the fibers made from PTEBS/PEO solution with NH_4OH always produced a bimodal distribution.

Figure 2 shows TEM images of the unimodal and bimodal fibers. The insets are the highest definition TEM images. The diameter of the unimodal fibers [Fig. 2(a)] is around 60 nm. The highest definition TEM image reveals a composite morphology consisting of tiny irregular dark domains embedded in a white fiber.

For the bimodal fibers [Fig. 2(b)], the diameter of the small fibers is about 200 nm, while the diameter of the large fibers is more than 1 μm . The high definition TEM image of the small fibers is still very dark under the same contrast and brightness. It has been shown that the presence of sulfur in a polymer can result in a darker contrast under TEM.¹² PTEBS contains sulfur and, therefore, the TEM images of the bimodal fibers suggest that the small black fibers contain more PTEBS in comparison to the large white fibers.

PEO is also soluble in chloroform,¹⁹ whereas PTEBS is not. This was confirmed by spinning PEO fibers and then annealing them at 80 °C in a chloroform atmosphere. The pure PEO fibers were completely dry-washed away. By contrast, a thin film of PTEBS showed no change under the same conditions. In order to verify that the small fibers contain more PTEBS, the bimodal fibers were annealed at 80 °C in chloroform atmosphere. As shown in Fig. 3, the large white fibers disappeared after annealing for 20 h, while the small black fibers were left intact on the glass substrate. These results are consistent with the TEM observations and confirm that the small and large diameter fibers are chemically, as well as physically, distinct.

A high speed charge coupled device camera was used to observe the Taylor cone during the electrospinning process.

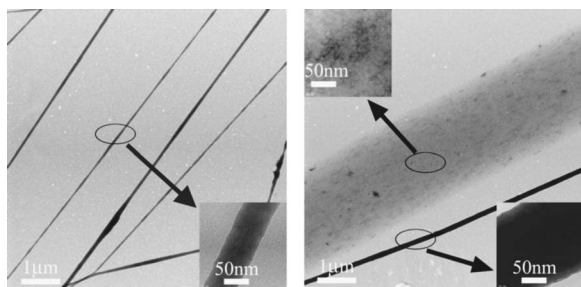


FIG. 2. TEM images of the unimodal and bimodal fibers. (a) Unimodal (the inset is the highest definition TEM image). (b) Bimodal (the top left inset is the highest definition TEM image of the big fiber, the bottom right inset is the highest definition TEM image of the small fiber).

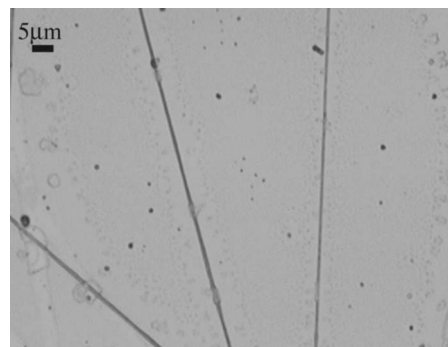


FIG. 3. Microscope photo of bimodal PTEBS/PEO fibers taken after annealing at 80 °C in chloroform atmosphere. The large white fibers have disappeared.

We observed that only one Taylor cone was formed and only one jet emerged from the tip of the Taylor cone in both the unimodal and bimodal cases. When NH_4OH was replaced with NaOH , bimodal fibers were also obtained. Therefore, we believe that the formation of bimodal fibers of chemically distinct polymers may be related to the presence of OH^- radicals in the electrospinning solution. We also found that the conductivity of a pure PTEBS thin film was increased by about one order of magnitude when made from a solution containing NH_4OH . The higher electrical conductivity indicates that more PTEBS molecules were ionized when using NH_4OH . The negatively charged PTEBS ions, unlike PEO, should move against the direction of the electric field. We believe that the different polarity and electrophoretic mobility of PTEBS and PEO lead to separation within the cone-jet region and the formation of chemically distinct fiber segments. The electric fields employed in the electrospinning process are comparable to the fields used in electrokinetic processes such as gel electrophoresis, but to our knowledge electrokinetic chemical separation has not been previously reported in electrospinning.

Figure 4 shows the absorption spectra of the unimodal PTEBS/PEO nanofibers. In order to eliminate the influence of the absorption of the substrate in the UV region, quartz slides were used as substrates to collect the electrospun fibers. Moreover, a quartz slide was used as the reference for the absorption measurement. The absorption spectrum was significantly changed when the structure changed from thin film to nanofibers. Unlike the spin coated thin films of pure PTEBS and PTEBS/PEO, the absorption spectrum of the

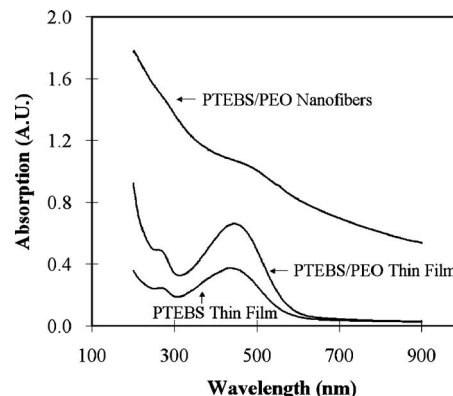


FIG. 4. Absorption spectra of a pure PTEBS thin film, a PTEBS/PEO thin film, and unimodal PTEBS/PEO nanofibers.

unimodal PTEBS/PEO fibers does not have an obvious peak around 460 nm.

The observed difference in the optical absorption spectra of the 60 nm composite fibers may be produced by the nanoscale PTEBS domains disorderly embedded in PEO [Fig. 2(a)]. The nanoscale PTEBS domains (with a band gap of 2.0 eV) are embedded within the transparent wide band gap PEO forming an assembly of organic quantum dots. It is well established that the optical properties of semiconducting quantum dots can be different from the optical properties of bulk material, and the PTEBS/PEO composite nanofibers appear to have unique optical characteristics in comparison to their bulk or thin film counterparts.

The optical absorption of the larger bimodal PTEBS/PEO fibers was almost the same as that of a spin coated PTEBS/PEO composite thin film (not shown in this paper). We believe that this is due to the much larger (200 nm and 1 μm) diameters of the bimodal fibers, which are too large to produce any optical changes in the polymers.

In conclusion, electrospinning from an aqueous PTEBS/PEO solution without NH_4OH resulted in the formation of a mat of composite nanofibers with relatively uniform size distribution and an optical absorption spectrum different from that of the bulk material. Electrospinning from an aqueous PTEBS/PEO solution with NH_4OH resulted in the formation of a mat of chemically and physically distinct fibers; large diameter white (PEO) fibers and small diameter black (PTEBS) fibers. Microscope photos taken after annealing at 80 °C in chloroform atmosphere and TEM images revealed that the small black fibers contained primarily PTEBS and the large white fibers contained primarily PEO. Electrokinetic separation of co-solutes in an electrospinning process represents a new approach for the formation of advanced nanostructured materials.

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