



CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Materials Used for the Study on the Investigation of Color Change of Electropun Fibers

The poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) used in this study was synthesized according to the procedure described in literature by Neef et al. (Neef, 2000) The used solvent was 1,2-dichloroethane (DCE; Carlo Erba, Italy) and pyridinium formate (PF), a volatile organic salt. PF was prepared by reacting of pyridine (Carlo Erba, Italy) and formic acid (Merck, England) in an equimolar quantity.

3.1.2 Materials Used for the study on the Electrospinning of Conductive Polymers

The poly(ethylhexyloxy-octyloxy-p-phenylene ethylene) (EHO-OPPE)EHO-OPPE ($M_n \approx 1.4 \times 10^4$ Da) and poly(2,7-(9,9-bis(2-ethylhexyl)fluorene)) (BEH-PF) ($M_n \approx 3.2 \times 10^4$ Da) were synthesized following a procedure described by Scherf et al. (Scherf, 2002) and Weder et al. (Weder, 1996), respectively. Polystyrene (PS) ($M_w \approx 3.0 \times 10^5$ Da; pellet form) was a general purpose grade from Dow Chemicals (USA). The solvents used were DCE (Lab-Scan (Asia), Thailand] and chloroform (CF; Carlo Erba, Italy). PF was also prepared by reacting pyridine [Lab-Scan (Asia), Thailand] and formic acid (Merck, England) in an equimolar quantity.

3.2 Equipment

3.2.1 Equipment for Electrospinning Process

- High voltage power supply from Gamma High Voltage Research Inc. (Ormond Beach, Florida), model ES30P DC was used to generate positive DC voltage
- Plastic syringe with volume size of 5 mL was served as a container for polymer solutions.
- Stainless steel needle with gauge number 20 (or the inner diameter of 0.91 mm) was used as the electrode to conduct the electrical from power supply to the solutions.
- An aluminum foil wrapped around a rigid plastic sheet was used as the collector plate.
- A Kd Scientific syringe pump was used to control the feed rate of the polymer solution at about $1 \text{ mL}\cdot\text{h}^{-1}$.
- Specialty coating systems model P6700 used for spin coating.

3.2.2 Equipment for Characterizations

- A JEOL JSM 5410LV scanning electron microscope (SEM) was used to study morphological appearances.
- A Thermo-Nicolet Nexus 670 Fourier-transform infrared (FT-IR) spectroscope was used to characterize chemical functional groups.
- A Bruker Advance-AC400 proton-nuclear magnetic resonance spectroscopy (^1H NMR), operating at 400 MHz, was used to study the chemical structure.
- A Hewlett Packard-8254A diode array UV-Vis spectrophotometer was used for an absorption study.
- A Perkin-Elmer LS50 luminescence spectrometer and was used for an emission study.

3.3 Methodology

3.3.1 Study on the Investigation of Color Change of Electropun Fibers

Fresh solutions of MEH-PPV (0.001, 0.005 and 0.01% w/v) were prepared by dissolving measured amounts of the polymer powder in DCE. Different concentrations (0.1 and 10 vol.-%) of PF, prepared by mixing pyridine and formic acid in an equimolar quantity, were then added into the system. The mixed solutions were sealed in vials and left in darkness at ambient conditions. Absorption and photoemission spectra of the solutions were recorded as a function of time until no noticeable change was observed. The absorption spectra were measured using a Hewlett-Packard 8254A diode array UV-vis spectrophotometer. Quartz cuvettes with thicknesses of 2 mm or 10 mm, depending on the polymer concentration, were used. The emission spectra were measured using a Perkin-Elmer LS50 luminescence spectrometer. An inner filter effect was minimized by using a 2 mm-thick quartz cuvette in all measurements. Any structural change of MEH-PPV was investigated by a Bruker Avance-AC400 proton-nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$), operating at 400 MHz, and a Thermo-Nicolet Nexus 670 Fourier-transform infrared spectrometer (FT-IR). Samples for these measurements were prepared by evaporating the solvent at 130 °C for 1 h. Only small amount of the solvent remained after this procedure. The samples were subsequently dried at 80 °C in a vacuum oven for 12 h. Solutions of MEH-PPV in DCE and PF in DCE were also subjected to the same drying procedure. These were used as control samples.

3.3.2 Study on the Electrospinning of Conductive Polymers

3.3.2.1 *Electrospinning of EHO-OPPE*

Solutions of 8.5% (w/v) PS/EHO-OPPE in DCE or CF (the compositional weight ratio between PS and EHO-OPPE being 7.5:1) with or without the addition of 8 vol.-% PF were prepared by combining all compounds and stirring at room temperature for 5 min. A solution of 8.5% (w/v) PS in DCE was prepared in similar fashion and was used as a reference. E-spinning of the as-prepared solutions was carried out under an electrical potential of between 7.5 and 20 kV. The

collection distance and the collection time were fixed at 10 cm and 1 min, respectively. Each of the freshly-prepared spinning solutions was placed in a 5 mL plastic syringe, the open end of which was connected to a blunt 20 gauge stainless steel hypodermic needle (outer diameter = 0.91 mm), which was used as the nozzle. An aluminum foil wrapped around a rigid plastic sheet was used as the collector plate. The emitting electrode of positive polarity from a Gamma High-Voltage Research ES30P DC power supply (Florida, USA) was connected to the needle, while the grounding electrode was connected to the collector plate. The feed rate of the solution was controlled by means of a Kd Scientific syringe pump at $1 \text{ mL}\cdot\text{h}^{-1}$. Where applicable, the e-spun fibers were annealed for between 5 min and 1 h at 110°C , which is above the glass transition temperature (T_g) of PS. To note that films of the PS/EHO-OPPE blends were produced by either spin coating or solution casting from solutions comprising $8\text{-}10 \text{ mg}\cdot\text{mL}^{-1}$ of the polymer blend. Spin coating was done on a Specialty Coating Systems model P6700 with spinning speeds of 1,500-2,000 rpm to achieve a final thickness of $0.5\text{-}1 \mu\text{m}$. Solution casting was done on glass slides and resulted films of a final thickness of $1\text{-}3 \mu\text{m}$. The morphological appearance of the e-spun fibers was examined by a JEOL JSM-5410LV scanning electron microscope (SEM). The average bead diameters and the number of beads per unit area (i.e., the bead density) of the electrospayed beads or the e-spun beaded fibers were calculated from measurements of SEM images at $\times 500$ magnification. Diameters of the e-spun fibers, where applicable, were determined from SEM images at $\times 1,000$ magnification, with the average value being calculated from at least 50 measurements (for each spinning condition). For beaded fibers, only the diameters of the fiber segments between beads were measured. A Thermo-Nicolet Nexus 670 Fourier-transform infrared (FT-IR) spectroscope was used to characterize the as-received PS pellets, the as-synthesized EHO-OPPE, and some of the e-spun PS/EHO-OPPE products. Optical absorption and photoluminescence emission spectra of the PS/EHO-OPPE solutions in DCE and CF with or without PF addition, the corresponding pristine and annealed e-spun fibers, spin-coated films, and solution-cast films were measured by a Hewlett Packard-8254A diode array UV-vis spectrophotometer (UV-vis) and a Perkin-Elmer LS50 luminescence spectrometer

(PL). For the solution measurements, a 1 mm thick quartz cuvette was used in order to reduce the self-absorption effect, allowing the detection of photon emission from front surface. For PL experiments, samples were excited at 400 nm.

3.3.2.2 *Electrospinning of BEH-PF*

Blend solutions of 8.5% (w/v) PS/BEH-PF in CF (the compositional weight ratio between PS and BEH-PF being 7.5:1) with or without the addition of 8% (v/v) PF were prepared and carried out for e-spinning under an applied electrical potential, ranging between 7.5 and 20 kV. Both the collection distance and the collection time were fixed at 10 cm and 1 min, respectively. Each of the as-prepared solutions was placed in a 5 ml plastic syringe, the open end of which was connected to a blunt-ended stainless steel gauge 20 needle (the outside diameter = 0.91 mm), used as the nozzle. An aluminum sheet wrapped around a hard plastic sheet used as a backing plate was used as the collector plate. The emitting electrode of positive polarity from a Gamma High-Voltage Research ES30P DC power supply (Florida, USA) was connected to the needle, while the grounding electrode was connected to the collector plate. The feed rate of the solution was controlled by means of a Kd Scientific syringe pump at 1 ml/h. To note that the spin coating and solution casting methods were used to prepare the films of that PS/BEH-PF blend solution in CF. In details, the spin coating was done on a glass slide by Specialty Coating Systems model P6700 with the spinning speed of 1000 rpm to get a final thickness of 0.5-1 μm . Solution casting was also done on a glass slide and the resulted thickness is about 1-2 μm . Morphological appearance of the as-spun products was examined by a JEOL JSM-5410LV scanning electron microscope (SEM). Diameters of the e-spun fibers were measured directly from SEM images of 1,000 \times magnification, with the average value being calculated from at least 50 measurements (for each spinning condition). The average bead diameters and the number of beads per unit area (i.e., the bead density) on the e-spun beaded fibers were calculated from measurements on SEM images of 500 \times magnification. A Thermo-Nicolet Nexus 670 Fourier-transformed infrared spectroscope (FT-IR) was used to characterize the as-received PS pellets, the as-synthesized BEH-PF, and some

of the e-spun products. Lastly, absorption spectra and photoluminescence emission spectra of the PS/BEH-PF solutions in CF with or without PF addition, the corresponding e-spun products, spin-coated and solution- cast films were measured by a Hewlett Packard-8254A diode array UV-VIS spectrophotometer (UV-Vis) and Perkin- Elmer LS50 luminescence spectrometer (PL), respectively. Each sample was excited at 350 nm prior to measurement for PL measurement.