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Ultrafine Electrospun Conducting Polymer Blend Fibers and Their Photoluminescence Properties

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Summary: Ultrafine poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene-vinylene) (MEH-PPV)/polyvinylpyrrolidone (PVP) blend fibers with the average diameters ranging from 625 nm to 1.46 μm were prepared by electrospinning of polymer blend solutions in the mixed solvent of chlorobenzene and methanol. The average diameter of fibers was found to decrease with initial increase in the applied electrical potential and composition of MEH-PPV, reach a minimum value at an intermediate value, and increase with further increase in the applied electrical potential and composition of MEH-PPV, while it was found to decrease with increasing collection distance. PVP was easily removed from MEH-PPV/PVP fibers by the Soxhlet extraction, and after the removal of PVP at high composition of MEH-PPV, pure MEH-PPV fibers were obtained as a ribbon-like structure aligned with wrinkled surface in fiber direction. The increase in MEH-PPV composition and the removal of PVP from as-spun MEH-PPV/PVP fibers resulted in a significant blue-shift in UV-Vis absorption peak and red-shift in PL peak.

Keywords: conducting polymers; electrospinning; fibers; MEH-PPV; photoluminescence

Introduction

The 1-direction characteristic-ultrafine fibers have been interested recently because when the diameters of polymeric materials are shrunk to sub-micrometers or nanometers, there appear to be several specific characteristics such as improved mechanical performance, very large surface area to volume ratio, and flexibility in surface functionalities.[1] Among various fibers processing technique, electrospinning has become one of the simple technique that uses electrostatic forces to produce polymeric, ceramics, and composite continuous ultrafine fibers with diameters ranging from microns down to a few nanometers.[2,3]

Recently, conjugated or conducting polymers are being exploited in many applications because of a combination of specific properties from optical and electronic points of views with easy processing.[4,5] Some of those applications are organic electronics including photovoltaic cells,[6] light emitting diodes,[7] and thin film transistors.[8] From various forms of conducting polymers; nanowires, nanofibers, and nanotubes are growing broad interest in nanoelectronic and nanophotonic device applications.[9] Conducting polymer nanowires and nanofibers have been prepared by various methods, such as self-assembly,[10] polymerization in nanoporous templates,[11] dip-pen nano-lithography,[12] and electrospinning.[8,13,14] For electrospinning, because of the limitations on molecular weight and solvents suitable for electrospinning, only a few conducting polymers such as derivatives of polythiophene, polyaniline, and poly(*p*-phenylene vinylene) (PPV) have been electrospun. From such of those conducting polymers, PPV and one of its derivatives, poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene-vinylene) (MEH-PPV), have been much interested to

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fabricated into ultrafine fibers because of their non-linear optical properties, electroluminescence, photoluminescence, and high electrical conductivity upon doping.

Madhugiri *et al.* have reported firstly the electrospinning of neat MEH-PPV and MEH-PPV/silica composite fibers with average diameters of 200 and 700–800 nm, respectively, in 2003.[14] Those obtained fiber mats showed the formation of many beads on fibers which was called that leaf-like structures. For the increase in the uniformity of fibers, the successful fabrications of electrospun MEH-PPV fibers in its blends with polystyrene (PS) from the blend solutions have also been reported.[13,15] However, this type of blending is not suitable for some applications which require only conducting polymers because PS can not be easily removed out from the blends due to PS and MEH-PPV can be dissolved in the quite same solvents. In recent years, electrospinning of the blends of MEH-PPV and polyvinylpyrrolidone (PVP) from non-compatible solutions using a coaxial two-capillary spinneret[8,16] and instead of polymers, electrospinning of the blends of PPV precursor/PVP follow by the polymerization[17,18] have been reported to successfully generate uniform nanofibers. The extraction of PVP out from the electrospun fibers in those techniques can be carried out easily, but the design of spinneret for the first case and the post thermal conversion of PPV precursor to PPV for the later one are quite complicated.

In the present contribution, electrospinning of MEH-PPV in its blends with PVP, an easily spinnable and easily extractable polymer, in mixed solvent of chlorobenzene and methanol was carried out to study the effect of applied electrical potential, collection distance, and MEH-PPV composition. Ultraviolet-visible (UV-Vis) absorption and fluorescence (photoluminescence, PL) characteristics of electrospun MEH-PPV/PVP fibers at various blend compositions and MEH-PPV fibers after the removal of PVP were also investigated and compared.

Experimental Part

MEH-PPV ($M_n \approx 40{,}000$–$70{,}000$, $M_w/M_n \approx 5$) and PVP ($M_w = 1{,}300{,}000$) powders were purchased from Aldrich. The solvent used was the mixture of chlorobenzene and methanol (Wako, Japan).

Solutions of MEH-PPV were prepared in the mixed solvent of chlorobenzene and methanol [85:15 (% (v/v))] under vigorously stirring. The obtained solutions were sonicated for 10 min and heat to 40 °C to exceed the dissolubility of MEH-PPV. A controlled amount of PVP was added into MEH-PPV solutions with vigorously stirring. For the solution concentration; in order to study the effects of applied electrical potential and collection distance, the concentration of MEH-PPV and PVP was fixed at 1:3 [% (w/v)]. In order to study the effects of MEH-PPV composition, the concentration of MEH-PPV was varied in the range of 0.1 to 2.5% (w/v), while, concentration of PVP was fixed at 6% (w/v).

As-prepared solutions were electrospun by loading each of them in a 3-ml plastic syringe. The nozzle was a blunt-end stainless-steel gauge 22 needle. The collector was a sheet of aluminum foil on a plastic plate. A Gamma High Voltage Research power supply was used to charge the solution across an electrode in solution and the collector (positive emitting and grounding electrode, respectively). In the typical procedure, as-prepared solutions were electrospun under an applied electrical potential of 15 kV over a fixed collection distance of 15 cm at room temperature. The solution feed rate was controlled by means of Kd Scientific syringe pump at 1 $\mathrm{mL \cdot h^{-1}}$. The collection time were fixed for all experiments at 1 min. For the removal of PVP from as-spun MEH-PPV/PVP fibers, the Soxhlet extraction was carried out. Methanol was used as a solvent at the extraction temperature of 75 °C. The extraction time was fixed at 12 hr. The samples were then dried overnight at 60 °C in a vacuum oven. The morphological appearance of the as-spun fiber mats was investigated by a JEOL JSM-6500FE scanning electron microscope (SEM), operating at an acceleration voltage of 10 kV. UV-Vis spectra were measured by a Shimadzu UV-2450 UV-Vis spectrophotometer, while PL spectra were investigated by a Jasco FP-777 spectrofluorometer with the excited light in the wavelength of 385 nm.

Results and Discussion

Electrospinning of MEH-PPV/PVP Blends

For the selection of solvent, MEH-PPV and PVP can be dissolved in different kinds of solvents because of the functionality differences. The solubility of MEH-PPV in chlorobenzene and PVP in methanol is very well, while the opposite matching is hopeless. However, electrospinning of ultrafine fibers from PVP solutions in the mixed solvent of chlorobenzene and methanol was found to be successfully. Therefore, the mixture of chlorobenzene and methanol was chosen as the solvent for electrospinning of MEH-PPV/PVP solutions. Among various solutions investigated, MEH-PPV/PVP solution in chlorobenzene/methanol with a composition ratio of 85/15 (v/v) was chosen for recent study because the solubility of MEH-PPV in this solution was better than those of other solutions and smooth resulting fibers were obtained after electrospinning of this solution.

In order to study the effects of applied electrical potential and collection distance on the morphological appearances and fiber diameters of as-spun fibers, MEH-PPV/PVP solutions [1:3 (% (w/v))] in chlorobenzene/methanol [85:15 (% (v/v))] were prepared and spun. The obtained results were shown in Figures 1(a), 1(b), 2, and 3. Figure 1(a) shows the diameters of the fibers obtained at various applied electrical potentials in the range of 5–30 kV. Evidently, the average diameter of the as-spun MEH-PPV/PVP fibers as well as their variation was generally found to decrease (from ~1.2 μm for diameter) with initial increase in the applied electrical potential from 5 kV, reach a minimum value (diameter was ~625 nm) at 20 kV, and increase with further increase in the applied electrical potential (e.g. diameter was ~1.24 μm at 30 kV). The increase in the applied electrical potential should cause the increase in number of charges carried within a jet, hence an increase in both the electrostatic and the Coulombic repulsion forces.[19] Therefore, it should be recognized that the observed decrease in the fiber diameters with initial increase in the applied electrical potential could be the effect from the contribution of the increase in the Coulombic repulsion force, while the observed increase in the fiber diameters with further increase in the applied electrical potential could be the effect from the contribution of the increase in the electrostatic force as following reasons. The increased Coulombic repulsion force which increased stretching force exerting on the jet segment should cause the fiber diameters to decrease, while the increased electrostatic force which increased in both of the speed of the jet segment and the mass flow rate should cause the diameters of the as-spun fibers to increase, affected on the onset for the bending instability to occur closer to the screen collector.[20] Figure 2 shows SEM images illustrating the morphology of the as-spun fibers from the electrospinning under various applied electrical potentials. It was obviously observed that increasing the applied electrical potential caused the number of the as-spun fibers per unit area to increase to a maximum value and then decrease after further increase in applied electrical potential. It is also due to the distribution between the Coulombic repulsion force and electrostatic forces.

For the effects of collection distance, Figure 3 shows selected SEM images illustrating the morphology of the as-spun fibers from 1:3 [% (w/v)] MEH-PPV/PVP solution collected at various collection distances in the range of 5–25 cm while the summarized average diameters were shown in Figure 1(b). Evidently, at the too close collection distance (e.g. 5 cm), large diameter-crooked fibers with some fibers

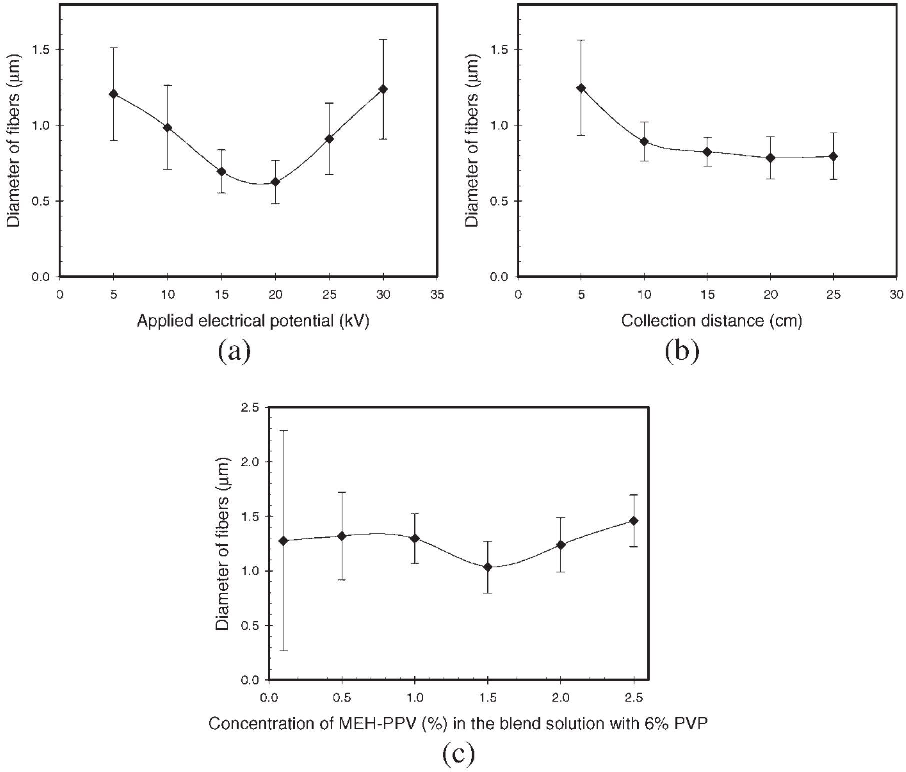

Figure 1.
Dependence of the diameter of as-spun fibers on various processing parameters; including (a) applied electrical potential, (b) collection distance, and (c) concentration of MEH-PPV. When a parameter was varied, all other parameters were fixed as following, concentration of MEH-PPV was 1% (w/v), concentrations of PVP were 3% (w/v) for (a) and (b), and 6% (w/v) for (c), applied electric potential was 15 kV, collection distance was 15 cm, and feeding flow rate was 1 ml · h^{-1}.

appeared to fuse to one another at touching points were obtained, indicating incomplete drying of the jet prior to the deposition on the collector. At such a short distance, the electrostatic field strength was high caused the rapid deposition of each charged jet but the path trajectory of the jet was short, which could lead to uneven

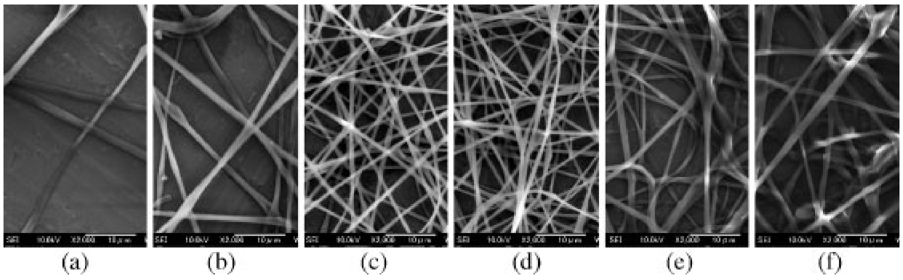

Figure 2.
SEM images (scale bar = 10 μm) of the as-spun fibers from MEH-PPV/PVP blend solutions [MEH-PPV:PVP = 1:3 (% (w/v))] in the mixed solvent of chlorobenzene and methanol [85:15 (% (v/v))] at various applied electrical potentials of 5 to 30 kV [5 kV increment for (a) to (f), respectively] over the collection distance of 15 cm. The feed flow rate was 1 ml · h^{-1}.

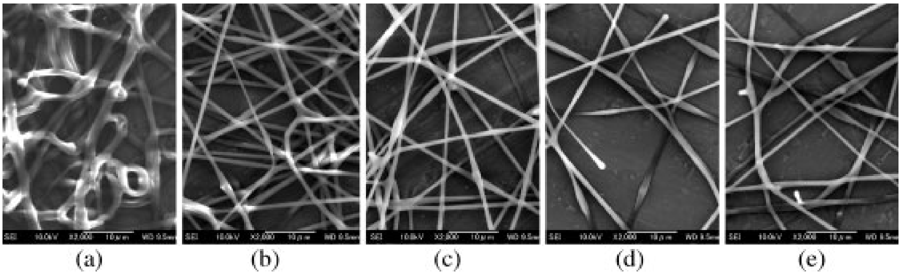

Figure 3.
SEM images (scale bar = 10 μm) of the as-spun fibers from MEH-PPV/PVP blend solutions [MEH-PPV:PVP = 1:3 (% (w/v))] in the mixed solvent of chlorobenzene and methanol [85:15 (% (v/v))] at applied electrical potentials of 15 kV over various collection distances of 5 to25 cm [5 cm increment for (a) to (e), respectively]. The feed flow rate was 1 ml · h^{-1}.

stretching of the jet. Further increase in the collection distance resulted in the formation of smoother fibers, indicating that the jet was stretched enough prior to the deposition on the collector. Furthermore, it is evident that the number of fibers per unit area was found to decrease with increasing collection distance, due to increase in the diameter of the as-spun fiber mat with increasing collection distance that come from the increase in movements during instability. Figure 1(b) shows that the average diameter of the as-spun PVA fibers decreased very rapidly from about 1.25 μm at the collection distance of 5 cm to about 894 nm at the collection distance of 10 cm and reach a plateau value of about 780–820 nm when the collection distance was equal to or greater than 15 cm. The decrease in the electrostatic field strength with increasing collection distance as a result of the increase in the total path trajectory of the jet that allowed uniform stretching of the jet during its flight to the screen collector should be a reason for this observation. Interestingly, in some instances, small-branched fibers that extruded from larger fibers were observed [see Figures 3(d) and 3(e)]. This is conceivable because at the speeds that the jet is traveling, it is not completely solidified once leaving the spinneret due to the boiling point of methanol and chlorobenzene are quite high (64.7 and 131.7, respectively). As the jet travels further into the electric field, it is exposed to stronger field strengths. It is possible that a side jet can be created from the charged jet leading to smaller diameter fibers. These phenomena caused the relative smaller average fiber diameters and larger variation at further increase in collection distance greater than 15 cm.

To illustrate the effect of MEH-PPV composition as well as the solution concentration, the MEH-PPV/PVP solutions in the mixed solvent of chlorobenzene and methanol at the different concentrations of MEH-PPV in the range of 0.1 to 2.5% (w/v) blended with fixed-6% (w/v) PVP were testified as shown in Figure 4 (suffix “1”). Figure 1(c) shows the average diameter of those obtained fibers. The results suggest that, at low concentration of MEH-PPV [0.1% (w/v)], there are two major sizes of as-spun MEH-PPV/PVP fibers, ~1.7 μm and 200 nm, hence the large variation in diameter as shown as the first point of a line in Figure 1 (c). After increase in composition of MEH-PPV, the diameter and its variation was generally found to decrease reach a minimum value at concentration of MEH-PPV of 1.5% (w/v), and increase with further increase in the applied electrical potential. The observed high size variation and the decrease in the fiber diameters with initial increase in the composition of MEH-PPV could be the effects from the contribution of the increase in the conductivity, while the observed increase in the

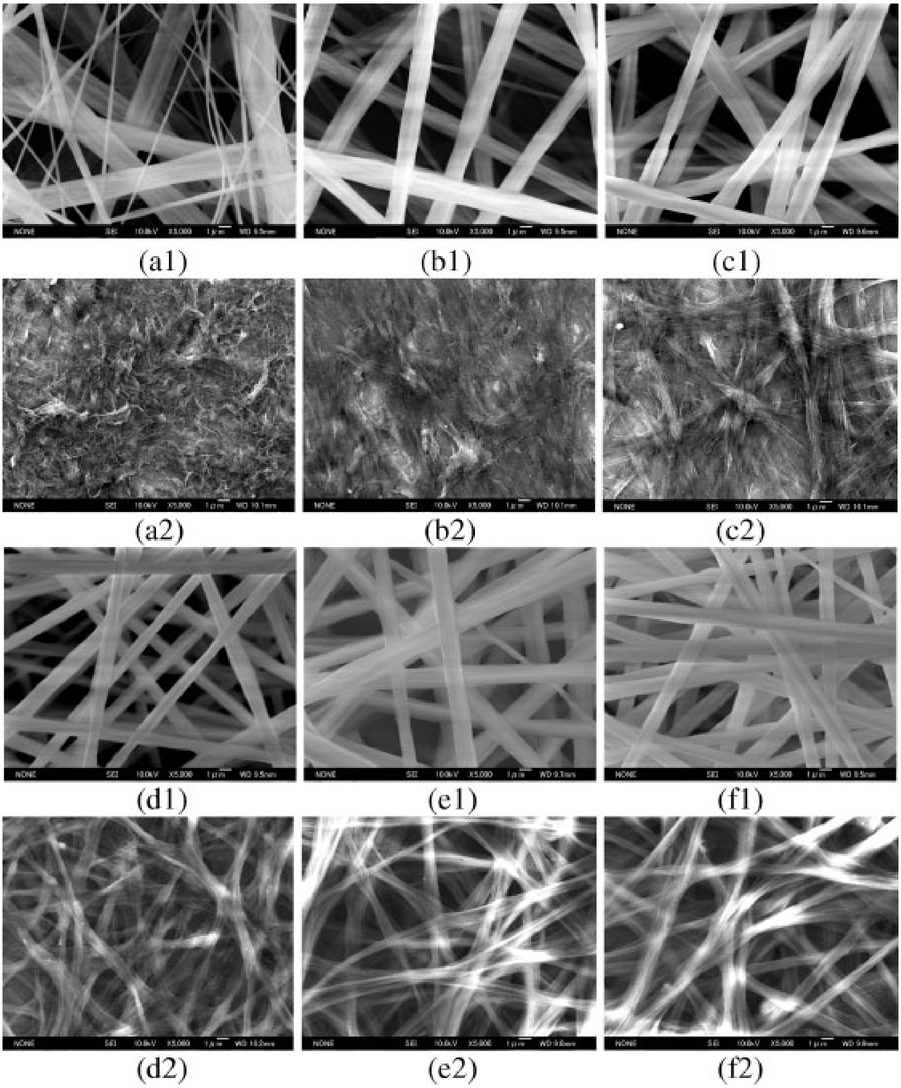

Figure 4.
SEM images (scale bar = 10 μm) of the as-spun fibers from MEH-PPV/PVP blend solutions in the mixed solvent of chlorobenzene and methanol [85:15 (% (v/v))] at blending ratios of MEH-PPV to PVP of (a) 0.1:6, (b) 0.5:6, (c) 1.0:6, (d) 1.5:6, (e) 2.0:6, and (f) 2.5:6. The concentration of MEH-PPV was fixed at 1% w/v. The condition during electrospinning was following; applied electric potential was 15 kV, collection distance was 15 cm, and feeding flow rate was 1 ml · h^{-1}. Suffixes "1" and "2" represent before and after the removal of PVP by the Soxhlet extraction, respectively.

fiber diameters with further increase in the composition of MEH-PPV could be the effects from the contribution of the increase in the viscosity and surface tension of spinning solution. The effects of composition of MEH-PPV on the blend solution have been reported and discussed already in the literature,[21] so it will not be discussed here anymore.

Removal of PVP from MEH-PPV/PVP Fibers

The Soxhlet extraction was carried out for the removal of PVP from the as-spun MEH-PPV/PVP fibers. The extraction time was fixed at 12 hr. Figure 4 (suffix "2") shows the typical SEM images of results after PVP had already been removed from MEH-PPV/PVP fibers at various compositional ratios of MEH-PPV/PVP in the range of 0.1:6 to 2.5:6. The completely extraction of PVP was confirmed by comparison of UV-Vis spectra from two times extraction (not shown here). After the removal of PVP, at high composition of MEH-PPV in MEH-PPV/PVP fibers (2.0:6 and 2.5:6), pure MEH-PPV fibers showed a ribbon-like structure with wrinkled surface as comparable to the literature that used a coaxial two-capillary spinneret for electrospinning of MEH-PPV and PVP solutions,[8] except that, there was an alignment of wrinkled surface in the spinning direction. These results suggest that there was a phase separation of MEH-PPV and PVP in the sub-micrometer scale during deposition of fibers. The confinement nature of electrospinning could enhance the orientation of this phase separation or also might be that of polymer chains in fiber direction.[22] In addition, the removal of PVP also resulted the decrease in diameter of fibers and thickness of fiber mats, and the enhancement of contacts parts of fiber mats. The decrease of MEH-PPV in the compositional ratio of MEH-PPV/PVP caused the reduction in the aligned-wrinkled surface and also resulted in the change form of MEH-PPV products from fiber to rough film-like form. This observation is conceivable, at low composition of MEH-PPV, high amount of PVP parts can be fused to adjacent fibers during the extraction due to the extraction solvent is methanol and extraction temperature is quite high as a result of remain MEH-PPV could not be still in fiber form.

UV-Vis Absorption and PL Characteristics

Figure 5 shows the normalized absorption (UV-Vis) spectra and summarized absorption peak from both of as-spun MEH-PPV/PVP fibers and MEH-PPV products after the removal of PVP. For the absorption spectra of MEH-PPV/PVP fibers, the increase in MEH-PPV composition resulted in the relative blue-shift in absorption peak, indicating that there were the change in chain distribution within each fibers and affected to delocalized π-conjugation and extended conformation.[23] Moreover, the absorption bands of fibers with higher MEH-PPV compositions are broadened suggesting a more inhomogeneous environment. This kind of phenomena was also reported in the case of MEH-PPV composites.[14] After the removal of PVP from MEH-PPV/PVP fibers, PVP-extracted MEH-PPV products also showed same trend of peak shift as compared to MEH-PPV/PVP fibers. However, at the same composition ratio of MEH-PPV/PVP, the absorption peak appeared at the blue-shift position and absorption band was narrower (with a shoulder) than as-spun MEH-PPV/PVP fibers indicating a more homogeneous environment of MEH-PPV after the removal of PVP.

PL spectra and summarized emission peaks of MEH-PPV/PVP blend fibers and PVP-extracted MEH-PPV products at various compositional ratios of MEH-PPV/PVP were shown in Figure 6. Obviously, for both of MEH-PPV/PVP fibers and PVP-extracted MEH-PPV products cases, the emission peak of higher composition of MEH-PPV showed the red-shift in position. It is well known that the peak position of PL spectra of dyes and also conducting polymers is much influenced by the distance between their molecules, in another word, that is their concentration.[21] Therefore, it is reasonable that the distance between the molecules of MEH-PPV in the MEH-PPV/PVP fibers and PVP-extracted MEH-PPV products increased with increasing in the composition of MEH-PPV. Compared with MEH-PPV/PVP fibers at the same MEH-PPV composition, PVP-extracted MEH-PPV products showed the significant red-shift in emission wavelength, indicates the insulating nature of PVP in MEH-PPV/PVP fibers and the present of PVP in fibers cause the prevention of aggregation of MEH-PPV. [14,21] MEH-PPV in

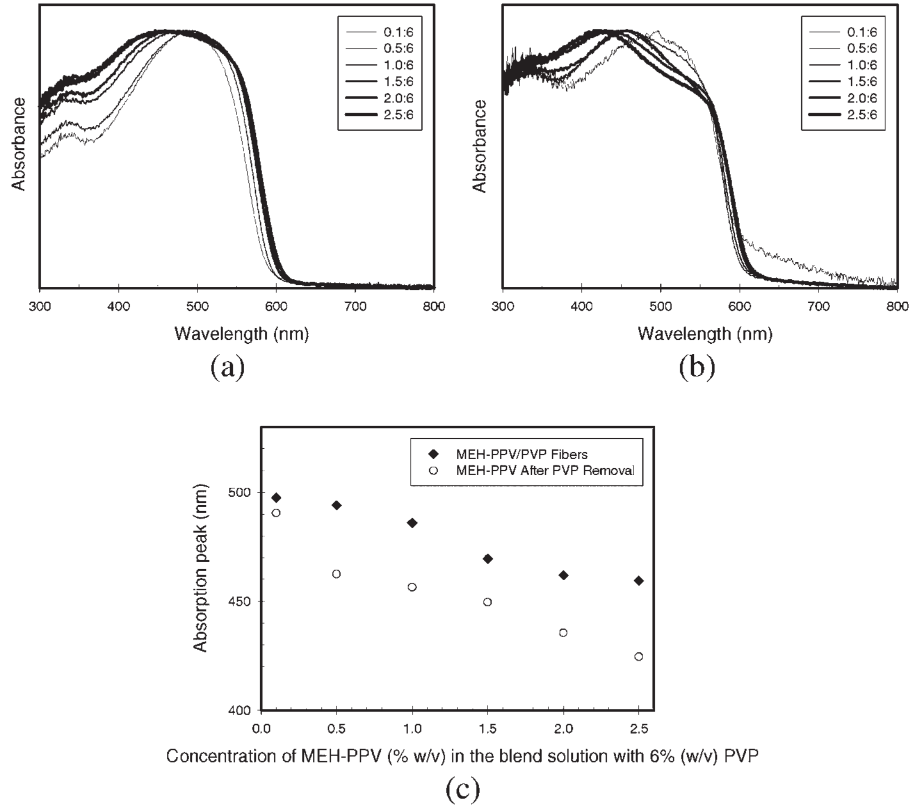

Figure 5.

Normalized UV-Vis spectra of (a) as-spun MEH-PPV/PVP fibers at various blending ratios of MEH-PPV to PVP and (b) corresponding MEH-PPV fibers (or films in some cases) after the removal of PVP from those MEH-PPV/PVP fibers; and (c) summarized absorption peak positions at various compositions of MEH-PPV in the blend solutions.

MEH-PPV/PVP fibers is less aggregated and has predominant intrachain excitations, which produce an emission at higher energy compared to that in the PVP-extracted MEH-PPV products. In the PVP-extracted MEH-PPV products where the MEH-PPV chains are closer, interchain excitations are also possible which lead to an emission at lower energy when compare to MEH-PPV/PVP fibers.

Conclusion

Ultrafine MEH-PPV/PVP blend fibers with the average diameters ranging from 625 nm to 1.46 μm were fabricated by electrospinning of MEH-PPV/PVP solutions in the mixed solvent of chlorobenzene and methanol [85:15 (% (v/v))]. The average diameter of fibers was found to decrease with initial increase in the applied electrical potential and composition of MEH-PPV, reach a minimum value at an intermediate value, and increase with further increase in the applied electrical potential and composition of MEH-PPV, while it was found to decrease with increasing collection distance. After the removal of PVP at high composition of MEH-PPV, pure MEH-PPV products were obtained as a ribbon-like structure aligned with wrinkled surface in fiber direction. Unfortunately, if the composition of MEH-PPV is too low, it could not still in fiber form, the obtain MEH-PPV products will be changed to

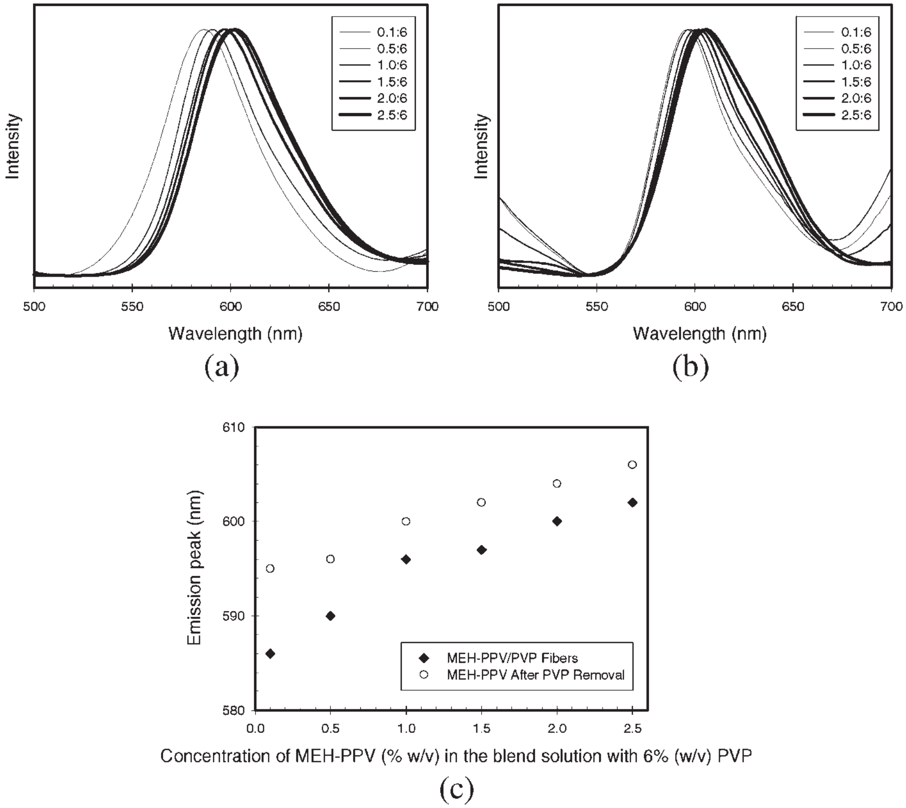

Figure 6.

Normalized PL spectra of (a) as-spun MEH-PPV/PVP fibers at various blending ratios of MEH-PPV to PVP and (b) corresponding MEH-PPV fibers (or films in some cases) after the removal of PVP from those MEH-PPV/PVP fibers; and (c) summarized emission peak positions at various compositions of MEH-PPV in the blend solutions.

film-like form after the removal of PVP. The increase in MEH-PPV composition and the removal of PVP form as-spun MEH-PPV/PVP fibers resulted in a significant blue-shift in UV-Vis absorption peak and red-shift in PL peak. Obtained structures and properties of conducting polymer fibers in this work may be widely applicable for some specific applications, such as photovoltaic cells, thin film transistors, light emitting diodes, and so on. Moreover, the study in the electrical and photoelectrical properties is necessary for further study and it is being carried out.

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