CHAPTER II
LITERATURE REVIEW

2.1 Conductive Polymers

Conductive or conducting polymers are a special class of organic materials which can behave like a semiconductor. The discovery of these polymers led Alan Heeger, Hideki Shirakawa and Alan G. MacDiarmid to the Nobel Prize in Chemistry 2000. In general, the intrinsic nature of conductive polymers mainly arises from their architectures constituting of alternating single and double/triple bonds along the main chain, therefore, in some instances, they are called conjugated polymers. (Feast, 1996; Kumar, 1998)

The appropriate arrangement of π-orbitals in the backbone could provide a convenient pathway for π-electrons to delocalize over the entire molecule. However, this ideal situation is never realized because of the flexibility and defects in polymeric chains. The delocalization of π-electron is normally confined within some distances, called conjugation length. Various chromophores with different conjugation length exist in one conjugated chain. (Sumpter, 2005) Therefore, its electronic properties (i.e., photoconductivity and electrical conductivity) and optical properties (i.e., absorption and emission) are dictated by the distribution of chromophores in the system, according to the difference in energy levels between the highest occupied molecular orbital (HOMO) or valence band and the lowest unoccupied molecular orbital (LUMO) or conduction band. (Kertesz, 2005)

Because of interesting properties of conductive polymers such as photoconductivity (Davidenko, 2006), high electrical conductivity after doping (Saxena, 2003), high luminescence efficiency in both electro- and photoluminescene (Weder, 1996; Ding, 2004), they have been developed for various applications, such as transistors (Xu, 2004), organic light-emitting diodes (OLED) (Huang, 2007), solar cells (Ahn, 2003), and sensor (McQuade, 2000), etc.

Recently, nanowires and nanofibers of conductive polymers are widely interest, especially, the materials produced from electrospinning. They are being fundamentally studied and applied in small scaled application such as

nanocomposites, electronic and optoelectronic devices. (Pinto, 2006; Chae, 2007; Briseno, 2008; Rojas, 2008; Granato, 2009) The principle of electrospinning and the electrospinning of various kinds of conductive polymers will be described below, respectively.

2.2 Electrospinning

Electrospinning is a fiber spinning technique that produces polymer fibers of nanometer to micrometer range in diameters by using electrical charge to form a mat of fine fibers. This technique combines characteristics of both the commercial electrospray technique and the commercial spinning of fibers. In general, the general electrospinning setup consists of a spinneret with a metallic needle, a syringe pump, a high-voltage power supply, and a grounded collector. The polymer solutions or polymer melts are placed into a container that has a small size needle and this liquid is driven to the needle tip by a syringe pump, forming a droplet at the tip. When a voltage is applied to the needle produced a high electric field between a needle and a grounded collecting screen, the droplet is first stretched into a structure called the Taylor cone (Taylor, 1969). If the viscosity of the polymer solutions or polymer melts is sufficiently high, varicose breakup does not occur (if it does, droplets are electrosprayed). When the electric field reaches a critical value at which the repulsive electric force overcomes surface tension at the surface of polymer solutions or polymer melts, a charged jet forms. As the jet travels in air, the jet is then elongated and whipped continuously by electrostatic repulsion as well as solvent evaporates until it is deposited on the grounded collector resulting in the fabrication of uniform fibers with nanometer-scale diameters. (Doshi, 1995).

The formation of fibers from this spinning process can be divided into two parts:

2.2.1 The Initiation of the Jet

Before the electric field is applied to the polymer solutions, and when the capillary tube are in a vertical position and carries a drop at the tip of nozzle, the

relation between the surface tension and the height of the column of liquid under equilibrium conditions is given by

$$2\gamma(1/R + 1/r) = \rho gh \qquad (1)$$

where γ is the surface tension of the liquid of density ρ, h is the height of the column of liquid above the lowest surface of the drop, R is the radius of curvature of the liquid at the upper liquid surface and r is the radius of curvature of the liquid at the lower surface of the liquid (Michelson, 1990).

Consider a droplet of polymer solutions that is applied to a high electric field. Charges that flow onto liquid surface repel each other. The repulsion forces are opposed to the forces from surface tension. The polymer droplet becomes unstable when the charge distributed on the surface overcomes the surface tension. The conditions that are necessary for a charged surface to become unstable are described by considering the equilibrium equation,

$$V_* = (4 \ \pi r\gamma)^{1/2} \qquad (2)$$

where V_* is the critical potential, r is the droplet radius, and γ is the surface tension of the solutions (Koombhongse, 2001). For the droplets subjects to a higher potential, $V > V_*$, the droplet elongates into a cone-like shape that was described mathematically by Taylor and often referred to as a Taylor cone (Taylor, 1969).

As the potential is increased, which obtain the maximum instability of the liquid surface, a jet of liquid ejected from the tip of the cone. Taylor (1969) showed that the critical voltage V_c (expressed in kilovolts) at which the maximum instability develops is given by

$$V_c^2 = 4H^2/L^2 (\ln 2L/R - 1.5)(0.117\pi R\gamma) \qquad (3)$$

where H is the distance between the electrodes, L and R are the length and radius of the capillary, respectively, and γ is the surface tension.

2.2.2 The Continuous Flow of the Jet

The mechanism of the appearance of a stable electrospinning jet is evidently established by the observation of the jet formation through the high speed electronic camera which recorded up to 2000 frames per second with a time resolution of approximately 0.0125 ms (Reneker, 2000).

There are two kinds of electrical forces that act on the jet: the external field that tries to pull the jet toward collector and the self-repulsion between the charges carried by adjacent segments of the jet that try to push each other apart. The self-repulsion can also cause different types instability such as bending instability and splitting instability.

In bending instability, or whipping instability, the jet rotates in a conical region, whose vertex is the end of the straight jet. The other end of the jet, which is highly stretched, and reduced in diameter, is deposited on the collector as a result of the fast whipping motions (Shin, 2001).

After some time, segment of a loop suddenly developed a new bending instability, but at a smaller scale than the first. Each cycle of bending instability can be described in three steps (Reneker, 2000).

Step (1) A smooth segment that was straight or slightly curved suddenly developed an array of bends.

Step (2) The segment of the jet in each bend elongated and the array of bends became a series of spiraling loops with growing diameters.

Step (3) As the perimeter of the loops increased, the cross-sectional diameter of the jet forming the loop grew smaller; the conditions for step (1) were established on a smaller scale, and the next cycle of bending instability began.

The schematic drawing of the electrospinning process is shown in Figure 2.1.
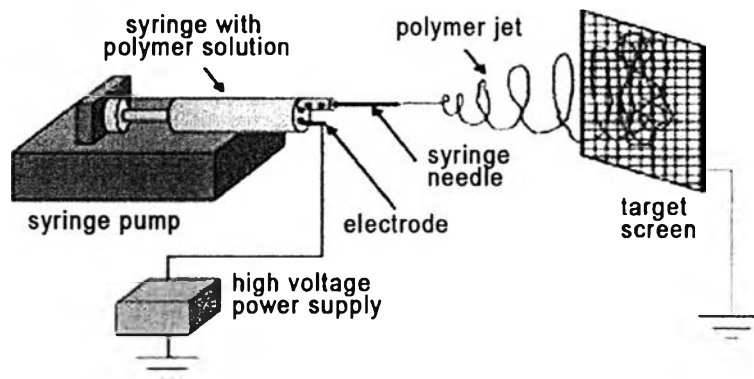
Figure 2.1 The general setup of electrospinning process

The other instability of the charged jet is the splitting instability. It occurs when the charge density of the charged jet increases as the solvent evaporates. The charged jet can reduce its charge per unit surface area by ejecting a smaller jet from the surface of the primary jet, or by splitting apart to form two smaller jets (Koombhongse, 2001).

2.3 Electrospinning of Conductive Polymers

There are a few conductive polymers which were fabricated into a fiber form by electrospinning because of the limitations of suitable molecular weight and solvents. Studies of the properties of electrospun conductive polymers have been divided into two ways which are electrical and optical properties. For here, the optical properties of various based conductive polymer derivatives such as poly(p-phenylene vinylene)s (PPVs), poly(fluorene)s (PFs), and poly(p-phenylene ethynylene)s (PPEs) in either binary blends (i.e., one conductive polymer with an inert polymer, and two conductive polymers) and ternary blend (i.e., two conductive polymers with an inert polymer) will be shown below.

2.3.1 One Conductive Polymer in Solution and Binary Blend

2.3.1.1 Poly(p-phenylene vinylene) Based Polymers

A study on fabrication of electrospun poly(p-phenylene vinylene) (PPV) fiber yarns by electrospinning of poly(*p*-xylenetetrahydrothiophenium chloride), a soluble precursor, was firstly reported in 2006. (Okuzaki, 2006) PPV nanofibers with average diameters of 653 nm were fabricated by electrospinning PPV precursor solution in solvent mixtures of ethanol and water at the weight ratio of 70/30 (w/w). (Zhang, 2007) However, the conductivity of the PPV precursor in solution was the most important factor influencing formation of the electrospun PPV fibers. The morphology and distribution of diameter of electrospun PPV fibers can be better controlled by blend PPV precursor solution with poly(vinylalcohol) (PVA) aqueous solution. (Zhang, 2007) Moreover, the color of florescence could be also successfully tuned from yellow-green to blue by varying the content of PVA.

Blends of poly(vinyl pyrrolidone) (PVP) and PPV polyelectrolyte precursor with different composition ratio in ethanol were prepared in order to fabricate arrays of well aligned PPV nanofibers. (Xin, 2008) PPV/PVP nanofiber arrays were successfully fabricated by electrospinning PPV/PVP mixed solution and subsequent thermal conversion. With the increasing of PVP content, the degree of alignment of PPV/PVP nanofibers increased due to the viscosity and conductivity of the electrospinning solution decreased.

Recently, core-sheath structure fibers with PPV as the sheath and easily spinnable polymers (i.e., PS and PVA) as the core were prepared by co-electrospinning. (Xin, 2008) The resulting nanofibers with uniform morphologies exhibited outstanding emission properties due to the interaction between core and sheath materials which were potentially interesting for various applications such as micro- and nanodevices and systems. Recenlty, there was a first report of the incorporation of ZnO nanocrystallites in PPV nanofibers. (Jiang, 2008) The ZnO nanocrystallites/PPV composite nanofibers showed a high photoluminescence (PL) quantum efficiency. It seemed to suggest that the ban structure of the ZnO nanocrystallites/PPV composite nanofibers should be responsible for the observed results because it was in favor of photoexciton generation and radiation of PPV.

Moreover, other PPV derivatives were also studied by electrospinning such as poly(2-methoxy-5- octoxy)-1,4-phenylene vinylene)-alt-1,4-(phenylene vinylene) (PMO-PPV) (Tan, 2008), especially, poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) as described then.

Neat electrospun MEH-PPV fibers were firstly reported in 2003. (Madhugiri, 2003) Typically the resulting fibers were approximately 200 nm in diameter with many beads on the fibers, which were referred to a leaf-like structure, while some parts showed ribbon-like structure. SBA-15, which is one such class of surfactant templated mesoporous material, was also firstly mixed with MEH-PPV in order to produce electrospun composite fibers. The electrospun MEH-PPV/SBA-15 composite fibers with average diameters of 700-800 nm showed a blue shift in their emission when compared with the neat MEH-PPV fibers.

Because of low electrospinnability and complication of the electrospinning of neat MEH-PPV, after that, polymers with easy spinnability were blended with MEH-PPV in order to get more ultra fine fibers.

Blend solutions of MEH-PPV and polystyrene (PS) in chloroform (CF), 1,2-dichloroethane (DCE), and tetrahydrofuran (THF) were successfully produced ultra fine electrospun PS/MEH-PPV fibers with average diameter of 0.3 to 5.11 μm. (Wutticharoenmongkol, 2005) Moreover, the electrospinnability of PS/MEHPPV solution in chloroform was achieved by addition of an organic salt, pyridinium formate (PF), or by addition of a minor solvent with a high dielectric constant value. The electrospun PS/MEH-PPV fibers exhibit a red shift in comparison with their blend solutions.

In 2007, a study on the color change from orange to yellow of the PS/MEH-PPV solution in DCE after 30 days of PF addition and its corresponding electrospun fibers was reported. A partial decomposition of the MEH side groups from MEH-PPV chains was responsible for the observed yellow emission color. (Chuangchote, 2007)

Ultrafine poly(vinyl pyrrolidone) (PVP)/MEH-PPV composite fibers which were prepared by electrospinning of PVP/MEH-PPV blend solutions in solvent mixtures of DCE and chlorobenzene were firstly reported. (Zhao, 2007) Electrospun PVP/MEH-PPV fibers showed a significant blue shift, a stronger

intensity of fluorescence and a higher surface photovoltage (SPV) when compared with the MEH-PPV solution and bulk.

After that, ultrafine PVP/MEH-PPV composite fibers with the average diameters ranging from 43 nm to 1.7 μm were prepared by electrospinning of blended polymer solutions in mixed solvent of chlorobenzene and methanol. (Chuangchote, 2008) After the removal PVP by Soxhlet extraction, pure MEH-PPV fibers were obtained as a ribbon-like structure aligned with wrinkled surface in fiber direction. Both PVP/MEH-PPV and MEH-PPV fibers showed relatively higher crystallinity, higher conjugation length, and there was a remarkable blue shift of photoluminescence peak when compared with their solution cast films. Moreover, the increase in MEH-PPV composition and the removal of PVP from as-spun MEH-PPV/PVP fibers which resulted in a significant blue shift in UV-Vis absorption peak and red shift in PL peak (Chuangchote, 2008).

The study of optical properties of nanofibers spun from polyethylene oxide (PEO) which was blended with MEH-PPV at different compositions was recently report. (Zhu, 2009) Confocal microscopic studies of a single MEH-PPV/PEO electrospun nanofiber indicated that the fluorescence spectra of the nanofiber did not show any polarization dependence which the aggregation of MEH-PPV in an inert matrix should be responsible for the observed results.

2.3.1.2 Poly(fluorene) Based Polymers

Electrospun fibers with average diameters of 250-750 nm were successfully prepared through the binary blends of polyfluorene derivative/poly(methyl methacrylate) (PMMA). (Kuo, 2007) The studied based poly(fluorene) polymer were poly(9,9-dioctylfluoreny-2,7-diyl) (PFO), poly[2,7-(9,9-dihexylfluorene)-alt-5,8-quinoxaline] (PFQ), poly[2,7-(9,9-dihexylfluorene)-alt-4,7-(2,1,3-benzothiadiazole)] (PFBT), and poly[2,7-(9,9-dihexylfluorene)-alt-5,7-(thieno[3,4-b]pyrazine)] (PFTP). The uncontinuous fiber like structure was obtained at the low PFO/PMMA blend ratio but became a core-shell structure at a high PFO blend ratio. The PFO aggregation domain in the electrospun fibers was much smaller than that in the spin-coated films and led to higher photoluminescence efficiency.

Moreover, the full color light-emitting electrospun nanofibers could be produced from the binary blends of poly(fluorene) derivative/PMMA.

2.3.1.3 Poly(p- phenylene ethynylene) Based Polymers

The electrospinning of polyester side-chain grafted poly(arylene ethynylene)s (PEPAE) containing benzene and thiadiazole units were reported in 2007. (Wang, 2007) Side chain length, polymer concentration and solvent determined the type of nanostructure (nanofibers or microspheres) formed. For example, Polyester side-chain substituted poly(p-phenylene ethynylene)s (PPEs) 5, 11, and 12 could be electrospun to give nonwoven, nanofibrous morphologies while dioctyl-PPE 6 showed microspheres. When a polyester substituted PPEs was electrospun into liquid nitrogen, nanoporous or sponge like morphology was only observed.

2.3.2 Two Conductive Polymers in Binary Blend

An electrospinning with a coaxial two-capillary spinneret of binary blends of conductive polymers which were MEH-PPV with regioregular poly(3-hexylthiophene) (PHT) and MEH-PPV with poly(9,9-dioctylfluorene) (PFO) were studied. (Babel, 2005) The phase-separated domains in MEH-PPV/PHT nanofibers (30-50 nm) are much smaller as compared to blend thin films (100-150 nm), and efficient energy transfer was observed in these blend nanofibers. The MEH-PPV/PFO blend nanofibers had cocontinuous or core-shell structures, and significant energy transfer was absent in these blend nanofibers as compared to bulk thin films. Field-effect transistors based on MEH-PPV/PHT blend nanofibers showed exponential dependence of hole mobility on blend composition. The electrospun nanofibers of binary blends of conjugated polymers have tunable, composition-dependent, optical, and electronic properties that can be exploited in field-effect transistors.

2.3.3 Two Conductive Polymers in Ternary Blend

Full color light-emitting electrospun nanofibers were successfully prepared through the ternary blends in chloroform of poly(9,9-dioctylfluoreny-2,7-diyl) (PFO)/MEH-PPV/ poly(methyl methacrylate) (PMMA) using a single capillary spinneret. (Chen, 2009) The emission colors of the PFO/MEH-PPV/PMMA blend ES fibers changed from blue, white, yellowish-green, greenish-yellow, orange, to yellow, as the MEH-PPV composition increased. The polymer domain sizes of the ES fibers were much smaller than those of the spin-coated films and led to different emitting colors and enhanced luminescence efficiency.