

CHAPTER II

LITERATURE SURVEY

2.1 Light-Emitting Diodes Based on Polymer

The discovery by Friend *et al.* (1990) at Cambridge, the conjugated polymers were capable of emitting light under small D.C. potential, had created enormous interest in the use of conjugated polymers in light emitting displays devices. They also demonstrated that PPV, prepared by way of a solution-processable precursor, can be used as the active element in a large-area light-emitting diode.

Lenz *et al.* (1988) had prepared two new types of *p*-xylene bis-sulfonium chloride monomers were prepared from cycloalkylene sulfides. The polymerization characteristics of these monomers to form poly(*p*-xylene sulfonium chlorides), and the thermal elimination reactions of their polymers to poly(*p*-phenylene vinylene), were compared with those of two monomers prepared from dialkyl sulfides. The cycloalkylene sulfonium chloride monomer polymerized to higher yields and to higher molecular weight polymers, which showed more efficient elimination reactions.

A comparative analysis of the electronic structures of poly(acetylene), poly(*p*-phenylene), and poly(*p*-phenylene vinylene) has been described in the literature (Friend *et al.*, 1993). In a broad sense, poly(*p*-phenylene vinylene) can be thought of as being a regular copolymer of poly(acetylene) and poly(*p*-phenylene), its bandgap, ionization potential, and electron affinity assuming values which were intermediate between those of poly(acetylene) and poly(*p*-phenylene).

Greenham *et al.* (1993) studied the use of combined methoxy and cyano substituent to increase significantly the electron affinity value, a feature which results in improved efficiency of electron injection contacts with aluminum. In addition, the synthesis of the most studied dialkoxy-PPV, MEH-PPV, was shown by Heeger *et al.* (1993). The branched side chain had a favorable effect on the solubility of the polymer, the polymer dissolves easily in solvents such as tetrahydrofuran, chloroform, or xylene.

Dai *et al.* (1999) used a Gilch or sulfonium precursor route to prepare 2,5-substituted PPV derivatives with methoxy-terminated oligo (ethylene oxide) side chains and demonstrated the influence of the side chain length on optoelectronic properties.

The characteristics of light-emitting diodes based upon MEH-PPV were determined by tunneling of both the holes and the electrons through interface barriers caused by the band offset can control the useful operating voltage of the device as well as its efficiency (Parker *et al.*, 1994). A model was developed and clearly explained the device characteristics of a wide range of diodes based on MEH-PPV. The turn-on voltage for an ideal device was shown to be equal to the band gap, 2.1 eV for MEH-PPV, and was slightly lower at 1.8 eV for an indium-tin oxide/MEH-PPV/Ca device.

Light-emitting diodes made with MEH-PPV using indium tin oxide (ITO) as anode and calcium as cathode had been examined as they were aged during operation in a dry inert atmosphere (Scott *et al.*, 1996). Two primary modes of degradation were identified. First, oxidation of the polymer led to the formation of aromatic aldehyde, i.e., carbonyl which quenched the fluorescence. The concomitant chain scission resulted in reduced carrier mobility. ITO was identified as a likely source of oxygen. The second process involved the formation of localized electrical shorts which did not necessarily cause immediate complete failure because they can be isolated by self-induced melting of the surrounding cathode metal.

Copolymers presenting an attractive solution to this problem can be much more versatile than homopolymers and may even be chemically tuned to provide a range of materials with considerably improved EL properties. Carter *et al.* (1997) had developed modified PPV to improve its performance in organic electroluminescent devices. Light emitting polymer devices based on the converted PPV copolymer, which consisted of conjugated PPV segments and non-conjugated α -acetyloxy-*p*-xylylene units, had continuous operating lifetimes of more than 7,000 hours at room temperature and over 1,100 hours at 80°C. In both cases of room and elevated temperature operation there were no apparent indications of an intrinsic degradation of the device performance and device failure was due to local hot spots.

Devices showed efficient emission at high brightness, low drive voltage and good operating stability.

Another approach to raising the efficiency of PPV was the effect of conversion conditions on the device characteristics of PPV light-emitting diodes (Zhang *et al.*, 1993). Both electroluminescence and photoluminescence intensities decreased with increasing and gave an efficiency, about two orders of magnitude more efficient than from similar devices prepared from fully converted PPV. The results of constant current stress measurements suggested that the partially conjugated PPV diode was relatively stable at room temperature.

PPV has been prepared successfully from *p*-xylylenebis (triphenylphosphoniumbromide) in acetonitrile solution via an electroreduction polymerization (Chang *et al.*, 1996). *P*-xylylenebis (triphenylphosphonium bromide) also acted as an electrolyte in the solution. The resultant electropolymerized PPV film was transparent and dense, and had considerable adhesion to an indium-tin oxide (ITO) electrode. The electropolymerized PPV showed a blue shifted both in the ultraviolet-visible absorption spectrum and photoluminescence, compared with the PPV prerepared from a *p*-xylylenebis(tetrahydrothiopheniumchloride) precursor route, indicating that it has a shorter π -conjugation chain length. The Al/electropolymerized PPV/ITO light-emitting diode emitted green light with an emission maximum at 530 nm. Annealing the electroluminescence device in a high vacuum oven at 160°C for 3 h significantly enhanced the electroluminescence performance as a result of improvement of the interfacial contact between PPV and the Al metal electrode.

Nishino *et al.* (1995) studied EL from blends of poly(3-hexylthiophene) (P3HT) and poly(N-vinylcarbazole) (PVK). The light-violet color emission was observed (a mixture of blue and red). Since P3HT and PVK were soluble in common organic solvents, LEDs can be fabricated by spin-coating films of the polymer blends from solution without subsequent processing or heat treatment. Calcium and ITO were used as the electron-injection and hole-injection electrodes, respectively. The EL quantum efficiency was enhanced by blending, with an optimized value of 0.2% photons/electron in blend films with about 2 wt % P3HT; i.e. greater than in pure

PVK by approximately a factor of four and greater than in pure P3HT by more than two orders of magnitude.

Organic light-emitting diodes based on blends of PPV derivative and naphthylimine-gallium complex had been fabricated by spin-coating method (Xu *et al.*, 2000). Blue emission and blue-green variation depending on the ratio of the PPV derivative to the complex and the applied voltage had been observed. The investigation on PL and EL properties demonstrated that the improvement of the luminescent efficiency was related to the injection balance between holes and electrons, and the color variation was attributed to the variation of the recombination zone.

2.2 Polymer-Clay Nanocomposites

Kojima *et al.* (1993) have successfully prepared a nylon 6-clay hybrid in one-pot synthesis by polymerization of ϵ -caprolactam, phosphoric acid, and 6-aminocaproic acid in the presence of natural sodium-montmorillonite. The tensile strength, modulus, and heat deflection temperature of the composites increased with increase clay content. The results were closed to the conventional preparation method as reported by Usuki *et al.* (1993).

Yano *et al.* (1993) prepared flexible polyimide-clay hybrids using a solution casting method. The organophilic-clay was uniformly dispersed in a polyimide film. The hybrids or nanocomposites material exhibited excellent gas barrier properties and a lower thermal expansion coefficient compared to an untreated polymer.

Usuki *et al.* (1993) and Okada *et al.* (1995) prepared nylon 6-clay nanocomposites by in-situ polymerization of ϵ -caprolactam in organophilic-clay. The natural sodium-montmorillonite was cation exchanged with various ω -amino acid and concentrated hydrochloric acid. Transmission Electron Micrograph (TEM) revealed that the silicate layers produced a fine dispersion in polymer matrix. A slight addition of 2% weight of clay in nylon showed twofold improvement in tensile modulus as compared to an untreated nylon 6. The timing belt cover which was

produced from this nanocomposites exhibited good rigidity with an excellent thermal stability.

Improvements in color tunability and environmental stability had been made by light-emitting composites. Dai *et al.* (1999) intercalated certain conjugated polymers (EO₃-PPV) into clay nanoparticles (Bentone 34). The PL emission showed that the maximum wavelength continuously increased with polymer content to a limiting value of 610 nm, characteristic of EO₃-PPV, at 20% wt., then remained unchanged despite further intercalation. The features could be attributed to an intercalation-induced conformational transition from compact coil to expanded coil, which should lead to an increase in the effective conjugation length, and hence a concomitant decreased in the bandgap energy.

Oriakhi *et al.* (1999) studied on a layered nanocomposites of poly(*p*-phenylene vinylene) (PPV) with montmorillonite clay which was prepared at ambient temperature by incorporation of poly(xylylenedimethylsulfonium) (PXDMS) into the montmorillonite galleries, followed by the base-mediated elimination of dimethylsulfide. Powder X-ray diffraction on the intermediate and final product show gallery expansions of 5.5 and 4.6 Å, respectively, indicating the nanoscale ordering of polymer and montmorillonite layers. Thermogravimetric analyses of the products indicates the loss of approximately 75% of the sulfonium groups by reaction with base. Luminescence measurements show a shift in emission peak intensities indicating the conversion of PXDMS to PPV within the montmorillonite galleries.

Light-emitting devices based on environmentally stable polymer/layered silicate nanocomposites were fabricated by blending MEH-PPV with organo-clay (C6A) (Kim *et al.*, 2001). The ratio of MEH-PPV/ organo-clay was regulated from 5/1 (w/w) to 1/1 (w/w). The light-emitting device of 1/1 (w/w) blend gave the highest quantum efficiency which was enhanced 100 times compared with the pure MEH-PPV layer device.

Park *et al.* (2002) reported that polymer-rich/clay-rich phase-separated, polymer-layered silicate nanocomposites were prepared through a solution blending of poly(xylylidene tetrahydrothiophenium chloride) with two kinds of layered silicates. By spin-coating, thin film of each phase were obtained, followed by

thermal elimination of tetrahydrothiophene and hydrochloric acid to final poly(*p*-phenylene vinylene)/layered silicate nanocomposites. At ambient conditions, the PPV films were easily photodegraded due to the oxygen diffused in. PPV/layered silicate nanocomposites showed improved environmental stability against photodegradation under an air ambient condition. Additionally, optical absorption and photoluminescence measurements demonstrate that the thin films of clay-rich phase were much less photodegraded than those polymer-rich and PPV reference.