

CHAPTER II

LITERATURE REVIEW

2.1 Poly(para-phenylene-vinylene) and Oligo(phenylene vinylene)

Conjugated polymers now provide a class of processible, film-forming semiconductors and metals. The development of the semiconductor physics of these materials by using them as the active components in a range of semiconductor devices. Polymer light-emitting diodes show particular promise, and recent developments in color range (red, green, and blue), efficiency (above 20 lumen/W for green emitters), and operating lifetime are discussed. Progress on their application to displays, with integration with active-matrix TFT drive, and with patterned deposition using inkjet printing techniques is also reviewed. The role played by interfaces between electrode and semiconducting polymer is also discussed (Friend *et al.*, 2001).

Sharma *et al.* (2006) reported that PPV is normally synthesized by two methods: precursor route and direct solution polymerization for organic soluble polymers. Among the methods investigated, the precursor route is very simple and can normally result in polymers with high molecular weights and high structural regularity. In precursor route, a commercially available monomer (p-xylylenebis) is polymerized with a NaOH base to yield a sulphonium salt polyelectrolyte precursor polymer. The precursor polymer is converted to standard PPV by heat treatment in vacuum at temperatures of typically 220°C. In a typical experiment, 5.6 ml of ice-cold, N₂-purged dry-methanolic NaOH solution (0.57 gm in 5.6 ml of methanol) was added in a slow stream to an ice-cold, N₂-purged dry-methanolic solution of the p-xylylenebis (tetrahydrothiophenium chloride) monomer (4 gm in 30 ml of methanol). The resulting mixture was stirred for 2 h at room temperature under inert atmosphere; the polymer that precipitated out was isolated, washed with methanol, filtered and redissolved in THF. The THF solution was then filtered concentrated and the polymer precipitated from methanol. The process of dissolution and reprecipitation was repeated four times to get rid of low molecular weight acidic

impurities. The polymer was then dried at 65 °C in vacuum for 1 h and at 220 °C for an additional 5 h. The PPV polymer then obtained was suspended in various solvents (toluene, Triton X-100) for absorption and emission measurements.

Cirpan *et al.* (2003) suggested that PPV was also obtained chemically in order to investigate the effect of the synthetic method on the structure and electrical conductivity. The characterization of the polymers was carried out by means of fourier transform infrared spectrometer (FTIR), differential scanning calorimetry (DSC) and thermal gravimetry analysis (TGA) techniques. The doping effect on the conductivity of the PPV was investigated by using different agents such as H₂SO₄, I₂ and metallic Na. It was concluded from the results of spectroscopical investigations that trans-vinylene units are formed on the backbones of polymers obtained by both chemical and electrochemical methods. Thermal analysis data confirmed that the thermal elimination of diethyl sulfide from the polymers obtained by electrochemical and chemical methods are almost complete, and therefore, the resultant product is PPV. It was evident from the TGA results that the polymer obtained chemically had a thermal stability higher than the electrochemically prepared polymer. Although the polymers obtained were insoluble and insulating, they were successfully converted into conducting polymers with the maximum conductivity of 10⁻³ S/cm by doping in solution or in vapor.

Akcelrud (2003) suggested that one of the most important soluble precursor routes to PPV was developed by Wessling and co-workers in the 1960s based upon aqueous solvent synthesis of poly(p-xylylene-a-dialkylsulfonium halides) from a,a-bis(dialkyl sulfonium salts), followed by thermolytic formation of the final conjugated polymer. The charged sulfonium groups solubilize the polymer and are removed during the conversion step. Molecular weights for the polyelectrolyte are in the 10,000 to 1,000,000 range, which may be precipitated or dialyzed to give typical yields of about 20% high molecular fraction. The mechanism is believed to proceed according to a chain growth polymerization via the in situ generation of the monomer based on the facts that high molecular weight is formed very quickly, within the first minutes of the reaction and also that various radical inhibitors limit or prevent formation of long polyelectrolyte chains. However, the initiation process was not unequivocally identified

Nowadays, many researches try to improve the application of PPV then they use the classical method blending, grafting, and mixing with other materials. For example Joseph *et al.* (1988) found that blends of poly(p-phenylene vinylene) (PPV), with other polymers were made by film-casting from an aqueous mixture of the water-soluble sulfonium salt precursor to PPV and the second polymer. The rates of chemical doping, using AsF and of electrochemical doping, using perchlorate counter ion, of the PPV component are strongly influenced by the nature of the added macromolecule. In all cases studied the blends appear to be phase separated under all conditions. The most versatile blend was with poly (ethylene oxide) (PEO), which could be heated to 225°C without degradation and which yielded the highest electrical conductivity when doped. The utility of blends was demonstrated using freestanding PPV/PEO blend samples as rechargeable battery electrodes.

Bjorklund *et al.* (2004) reported the effects of blending a non-conjugated polymer, polyvinyl alcohol (PVA), with the precursor polymer of poly (p-phenylene vinylene) (PPV). After thermal conversion, the PVA/PPV blends show markedly different absorption and luminescence spectra than neat PPV, even in blends containing only 1wt% PVA. These changes coincide with the disappearance of the nanocrystalline domains present in neat PPV. The temperature dependence of the fluorescence decay is not as sensitive to PVA concentration, but also disappears for blends containing more than 60% PVA. The extreme sensitivity of PPV's optical spectroscopy to small amounts of amorphous blends suggests that the ordered domains play an important role in determining its spectroscopic properties.

Yang *et al.* (1999) reported that the effect of pressure to 65 kbar has been measured on the steady-state and time-dependent emission of MEH-PPV in seven polymers. Both the shape and intensity of the emission spectra vary strongly with pressure. In all blends there is a drop in intensity over the first 20-25 kbar probably in part associated with long-range intramolecular electron transfer increased by compression. Above 30 kbar some blends show a considerable increase in intensity in the higher energy region of the spectrum. The time-dependent emission can, in general, be fit using single or multiple exponentials. However, in all but one blend the emission at high energy can be equally well fit using the Forster energy-transfer theory. Those blends that show a significant increase in intensity associated with the

higher energy emission at high pressure also show an increase in the efficiency of energy transfer. Those blends that do not show an increase in energy transfer efficiency show no increase in intensity.

Weder *et al.* (1997) had shown that gel processing and subsequent tensile deformation of blends of different PPEs and ultra-high molecular weight polyethylene leads to an outstanding orientation of the conjugated polymer guest, resulting in state of the art polarized photoluminescence and absorption of the prepared films. Maximum orientation and polarization is obtained when the conjugated guest is of high molecular weight and derivatized with sterically hindered, rather than only linear, side chains. The orientation process used appears to induce a transformation of an initially phase-separated system into an apparent molecular dispersion of the conjugated polymer guest in the PE host.

Leung *et al.* (2001) described that the synthesis of series of highly soluble PPV chains grafted poly(organophosphazene) (PPz) copolymers. The PPV chains on the average are rather short and have a distribution in the conjugation length. Surprisingly, the grafted copolymers have strong emission in the blue color range which is known to be difficult to achieve for main chain conjugated polymer. The copolymers were measured and compared. For improvement, it was shown that either a higher volume fraction for the conductive segments or a well dispersed conductive fraction in copolymer layer is required.

Yan *et al.* (2005) found that blending conjugated polymers was an efficient method to improve the properties of the films. The phase diagram of poly (9,9-dihexylfluorene) (PF) and poly (2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene) (MEHPPV) was predicted by a modified Flory-Huggins theory based on the topological method (graph theory) for the structure-property correlations. It shows that the two polymers have a strong trend to separate. Atomic/friction force microscopy (AFM/FFM) measurements show there exist microphase separations in film prepared at room temperature. After annealing at 160°C, serious phase segregations took place in both the lateral and vertical direction. The photoluminescence of the thin films was also measured by a fluorophotometer.

Quan *et al.* (2006) found that the temperature dependence of the optical properties in poly (2-methoxy-5-2'ethylhexyloxy)-p-phenylene vinylene) (MEH-

PPV) blending with 2-(4-biphenyl)-5-(4-tertbutylphenyl)-1,3,4-oxadiazole (PBD) has been investigated. The blending influence on the chain conformation and exciton energy migration in blend film is described. The PL emission from the pure and blend films are all blue shifted with increasing temperature. An addition of PBD in MEH-PPV films suppresses the relative intensity of 0-1 vibronic peaks at lower temperature. This phenomenon will not be promoted with increasing temperature-dependent migration process of singlet excitons.

Moroni *et al.* (1996) reported that the synthesis and the efficient polymerization of a PPV trimer, 4-tert-butyl-4'-(4-vinylstyryl)-trans-stilbene was prepared following two radical polymerization routes: first via a classical procedure with AIBN as initiator in toluene, leading to polymer p3PVa, and then using the TEMPO-BPO initiation method in refluxing xylene, to give p3PVb. In order to check if thermal polymerization could take place, the monomer was put in the same reaction conditions without initiator, to get p3PVc. After precipitation, p3PVa was still containing a large amount of unreacted monomer, which was very difficult to remove because the monomer and the polymer have similar solubility. The polymer was finally purified by elution over a preparative size exclusion chromatography column. For p3PVb, no monomer was detected in the product after precipitation, indicating that the conversion was much higher via the TEMPO route. Consequently, the purification problem did not show. (2,2,6,6-tetramethylpiperidin-1-xyloxy)-mediated free-radical polymerization method, the corresponding polymer was obtained in high yields, with a fair molecular weight and a small polydispersity. The presence of phenylenevinylene units in the side chains of the polymer gave rise to efficient blue fluorescence which made the material suitable for light emission applications.

2.2 Deformation Sensor

Kinami *et al.* (2005) showed the preparation and characterization of blends of polyesters and excimer-forming, photoluminescent 1,4-bis-(R-cyano-styryl)-benzenes, which function as built-in deformation or threshold temperature sensors.

Binary blends of poly(ethylene terephthalate) (PET) or poly(ethylene terephthalate glycol) (PETG) and small amounts (0.2-2% w/w) of a series of sensor dyes were prepared by melt-processing. Subjecting appropriately processed samples to either temperatures above their glass transition or mechanical deformation can significantly change the extent of molecular aggregation of the photoluminescent guest molecules, which in turn leads to a variation of the contributions of monomer and excimer emission. Since the emission maxima associated with these transitions can differ by as much as 138 nm, this change can readily be detected by spectroscopic means and in many cases even by the unassisted eye.

As found by Crenshaw *et al.* (2003) Binary blends of linear low-density polyethylene (LLDPE) and a series of highly photoluminescent (PL) 1,4-bis(R-cyano-4-alkoxystyryl)benzenes were prepared using melt processing techniques. It was shown that the phase behavior of these blends, which comprised 0.01-3% w/w of the PL guest, could be controlled via the molecular structure of the dye, its concentration, and the processing conditions. Because of the dyes' strong tendencies to form excimers, the emission characteristics of the blends strongly depended on the extent of molecular aggregation of the PL guest molecules. Bathochromic shifts of up to 147 nm were observed when comparing the PL emission spectra of molecularly mixed blends with samples that comprise aggregates of the dyes. Phase-separated blends with apparently very small dye aggregates could be produced by rapidly quenching the samples after melt processing and subsequent plasticization with a hydrocarbon solvent. The mechanical deformation of the blends thus produced led to a pronounced change of the materials PL characteristics. When the films were stretched to a draw ratio $\lambda = (l - l_0)/l_0$ 500%, the monomer to excimer emission ratios I_M/I_E were increased by a factor of up to 10. This effect appears to bear significant potential for the use of such dyes as internal strain sensors in polymer object.

Crenshaw *et al.* (2005) reported that the molecularly mixed, glassy solutions of BCMB and PMMA or PC matrices could readily be produced via melt-processing and rapid quenching of the homogeneous melts. These blends exhibited PL characteristics that were dominated by monomer emission. Subjecting blends of sufficiently high dye concentration to temperatures above their glass transition led to

permanent and significant changes in the emission spectra of the materials due to phase separation of the polymer and the excimer-forming dye. This effect appears to bear significant potential for technological applications, such as the use of cyano-OPV/polymer blends as TTIs. It should be noted that the operating principle is fundamentally different from those employed in previous fluorescent thermometers. It is also different from the principles that were used to measure the T_g by means of fluorescent probes, and mechanisms considered useful for application in TTIs. Key advantages of the approach described here are that the transition scheme is a significant, readily detectable color change (not an intensity or PL lifetime change), the absence of reactive chemicals, the fact that no complex geometric requirements exists, and that objects of various shapes can readily be produced via conventional melt-processing techniques. The possibility to easily conceal the fluorescent sensor makes them useful for security features, which, for example may allow one to detect tempering heat treatment in delamination at temperatures.

Pucci *et al.* (2005a) found that poly(propylene) (PP) films containing different concentrations of bis(benzoxazolyl)stilbene (BBS) have been prepared by melt processing. They demonstrated that the emission characteristics of PP films depend on BBS concentration and polymer deformation. A well-defined excimer band is observed with more than 0.2 wt% of BBS, conferring to the film a green luminescence. During drawing (130 °C) the PP reorganization breaks the BBS excimer-type arrangement, leading to the blue emission of the single molecules. They have efficiently applied the photophysics of this commercial stilbene derivative to the production of powerful tools acting as an internal probe for PP deformation.

Lowe *et al.* (2002) reported that the emission color of blends of host of polymer and low-molecular photoluminescent dyes can readily be operated over a wide range by controlling the aggregation degree of the dyes. From this method showed that cyano-OPV is attractive for this purpose, since the colors of monomer (green) and excimer (orange-red) emission changed an unusually large range. They have shown the supra molecular structure, and the emission color, of LLDPE/dye blends can tuned via the composition the processing conditions, or the temperature. Most importantly, they have demonstrated that solid-state tensile deformation can

lead to substantial changes in the emission characteristics of such blends. Their technique appears to bear significant potential for technological applications, for example the use of such dyes as molecular strain sensors in polymeric objects.