



CHAPTER II

LITERATURE SURVEY

2.1 Polydiphenylamine

Athaware and Kulkarni (2000) studied polyaniline and its substituted derivatives as sensor for aliphatic alcohols. They polymerized polyaniline and its substituted derivatives by a chemical oxidative polymerization and made pellets of the polymers by applying a pressure of 7 ton using Pye-Unicam system. The performance of the polymers as sensors was tested by subjecting these polymer pellets to saturated alcohol vapors in a closed vessel. The result showed that polymer sensors were suitable for short chain alcohols: when the polymers were exposed to methanol and ethanol environmental. The conductivity increased, because of their short chains and their polarity with high dielectric constant. But the conductivity decreased in butanol and heptanol environments, because of their longer chain lengths and non-polarity.

Wang *et al.* (2001) synthesized and characterized poly(ethylene glycol) (PEG)-grafted polyaniline (PAni). PEG-grafted PAni copolymers were prepared by incorporating a chlorine end-capped methoxy PEG (mPEGCl) of molecular weight of about 2000 onto the leucoemeraldine form of PAni via N-alkylation. They studied the electrical conductivity of PEG-grafted PAni. The mPEG-grafted-PAni copolymers exhibited enhanced solubility in common organic solvents such as dimethyl sulfoxide (DMSO), toluene (CHCl₃), tetrahydrofuran (THF), dichloromethane (CH₂Cl₂), and N-methylpyrrolidone (NMP). The electrical conductivity of the mPEG-grafted-PAni copolymer film decreased by a factor of 5 at the mPEG graft concentration of 0.05.

Hua and Ruckenstein (2003) synthesized polydiphenylamine (PDPA) grafted with poly (ethylene oxide) (PEO) through a graft onto process. There were grafted copolymers with various PEO chain lengths (200, 350 and 750) and were obtained by substituting the tosylates and group of tosylate PEO with an amine-functionalized PDPA. The graft copolymers became water-soluble when molecular weight (M_n) of grafted PEO was above 750. Furthermore, these copolymers were

oxidized in aqueous acidic solution in the presence of air (3 N HCl solution) to generate a polaron (diphenylbenzidine radical cation) or a bipolaron (diphenylbenzidine dication). Its electrical conductivity was 0.37 Scm⁻¹. The conductivity decreased with increasing PEO side chain length because of the volumetric dilute effect of the nonconductive PEO side chains as well as the increasing torsional effect.

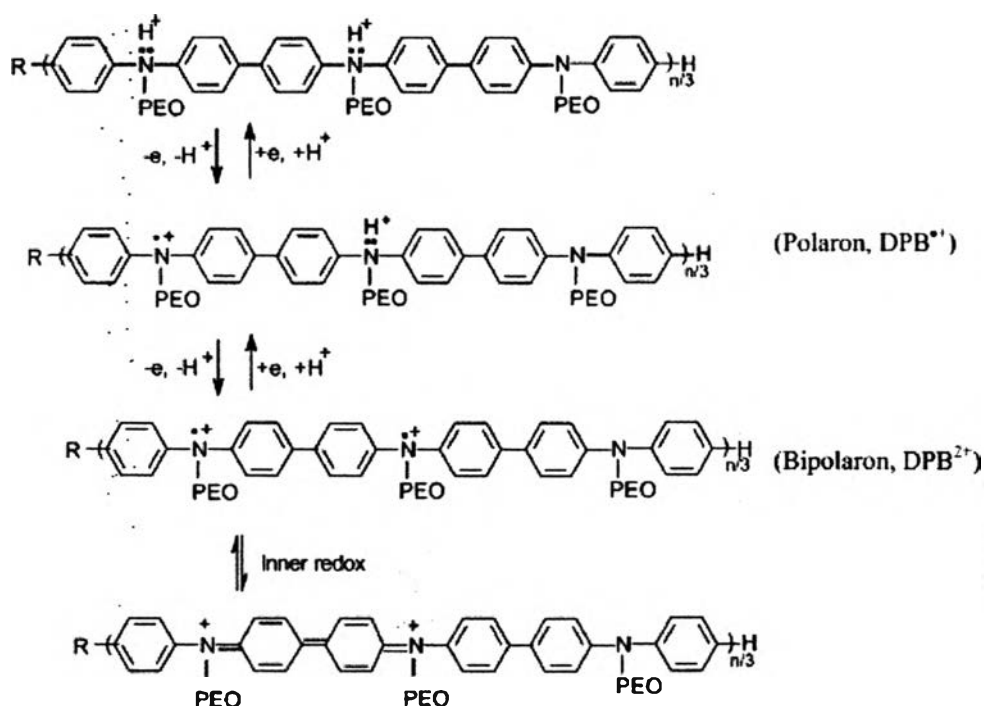


Figure 2.1 Reduction by hydrazine and oxidation in air in the presence of an aqueous acidic solution (Hua *et al.*, 2003).

In 2006, Orlov studied the chemical oxidative polymerization of diphenylamine via three mechanisms: (1) Polymerization in a solution of sulfuric acid, a 0.1 solution of diphenylamine in 5 M sulfuric acid (H₂SO₄) and 0.125 M solution of ammonium persulphate (NH₄)₂S₂O₈ in 5 M sulfuric acid (1/4 based on the total volume) were prepared. (2) Polymerization in a H₂SO₄-tert-butanol mixture, a 0.2 M solution of diphenylamine in a mixture of 4 M H₂SO₄ and tert-butanol (equal volumes) and 0.25 M solution of (NH₄)₂S₂O₈ in the same solvent (1/4 based on the

total volume) were prepared. (3) Interfacial polymerization, 0.2 M solution of diphenylamine in toluene and a 0.25 M solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in the same volume of a 1 M solution of HCl were prepared. In order to start polymerization, solution of monomer and oxidizer were first cooled to $-2-0\text{ }^\circ\text{C}$ and mixed momentarily at a certain time interval, the reaction mixture was precipitated into either a 5-fold excess of ice water (polymerization in H_2SO_4 and the H_2SO_4 -*tert*-butanol mixture) or a 5-fold excess of isopropyl alcohol cooled to $-2-0^\circ\text{C}$ (the interfacial polymerization), filtered, and washed many times with distilled water until the reaction was neutral. For polymerization in solution of H_2SO_4 , the kinetic curves did not exhibit the S-shaped pattern as the typical kinetic curve polymerization of aniline, slow rate of polymerization, low molecular weight, and short induction time. But in the interfacial polymerization, the kinetic curve exhibited the S-shaped and had higher molecular weight. Hence, it is expected to use the interfacial polymerization for preparation of polydiphenylamine.

Hua *et al.* (2005) investigated the pH response of a hyperbranched sulfonated polydiphenylamine. In the dedoped state, at pH values above 7, the particle size decreased slightly with increasing pH and the aggregates of the polymeric particles had almost a uniform diameter around 40 nm. However, at lower pH values (<5), the external HCl doping became dominant and the aggregates acquired smaller sizes of about 120 nm.

Sathiyarayanan *et al.* (2006) used polydiphenylamine (PDPA) in vinyl coating for a corrosion protection of steel in 3% sodium chloride (NaCl) solution. PDPA was prepared by chemical oxidative method of diphenylamine in ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and hydrochloric acid (HCl) medium. The synthesized PDPA was blended with a vinyl resin at 0.5% concentration. PDPA was found to offer a higher corrosion protection at the vinyl resin concentration more than 3%. From the FT-IR spectra of PDPA is shown in Figure 2.2.

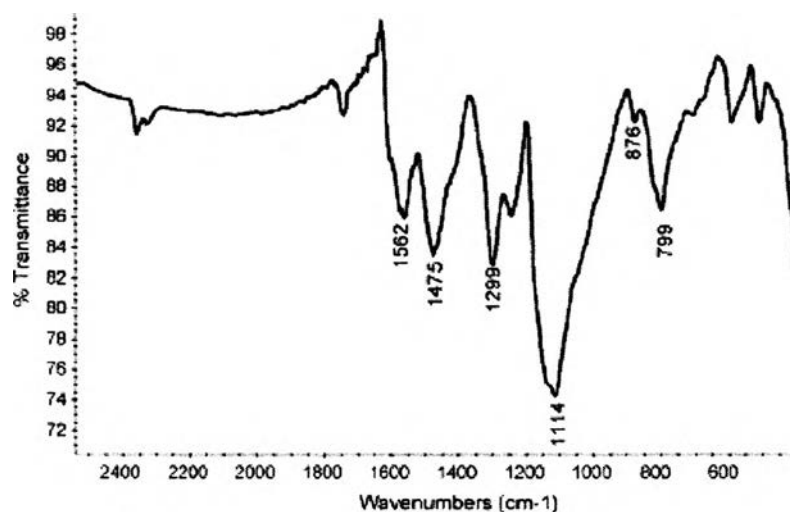


Figure 2.2 FT-IR spectrum of polydiphenylamine (PDPA) (Sathiyarayanan *et al.*, 2006).

The spectrum is very much similar to that of polyaniline (Jeyaprabha *et al.*, 2006) : (i) the bands at 1562 cm⁻¹ and 1475 cm⁻¹ were assigned to the nitrogen quinone (Q) and the benzenoid ring B (ii) the band at 1299 cm⁻¹ to the C–N stretching of a secondary aromatic amine, (iii) the band at 876 cm⁻¹ to the out of plane bending of aromatic C–H, (iv) the band at 799 cm⁻¹ to the 1,4-substituted benzene, and (v) the strong band at 1114 cm⁻¹ can be related to the electronic band or the vibration band of nitrogen in quinone (Sathiyarayanan *et al.*, 2006).

In 2008, Li *et al.* synthesized a sulfonated polydiphenylamine (SPDPA) by sulfonation of neutralized polydiphenylamine (PDPA) to study water soluble properties. SPDPA could be dissolved in water as well as in polar organic solvents.

2.2 Gas Sensors Based on Conductive Polymers

Melo *et al.* (2005) used the technique of polymerization in vapor phase to obtain different composite blends of polypyrrole (PPy) and other polymers as: (i) poly(caprolactone), PCP; (ii) poly(ethylene oxide), PEO; (iii) poly(methyl-methacrylate), PMMA; (iv) poly(vinyl alcohol), PVA and (v) poly(vinyl acetate), PVAC, and tested the corresponding sensitiveness towards the volatile compounds:

methanol, ethanol, carbon tetrachloride, and benzene. These polymeric blends were obtained in the form of films deposited on ITO substrates. PMMA/PPy, PVA/PPy and PVAC/PPy blends had a substantial increase in their conductivity after exposure to the polar compounds such as methanol and ethanol. These blends show a better level of recognition of polar compounds than that of the doped PPy films.

Aniline and pyrrole were oxidized with ammonium peroxydisulfate in aqueous solutions, in the presence of equimolar quantities of hydrochloric acid. Blinova *et al.* (2007) studied the effect of oxidant-to-monomer molar ratio on the syntheses of polyaniline (PAni) and polypyrrole (PPy). The yield of polymerization increased as the oxidant-to-monomer molar ratio increased from 0.2 to 1.5. The conductivity of the polymers was only slightly dependent on this ratio. The maximum conductivity of PAni was 4.0 Scm^{-1} at the oxidant-to-monomer molar ratio 1.3, and of PPy 0.3 Scm^{-1} at the ratio 1:1.

Torsi *et al.* (2004) studied dipentoxy substituted polyterthiophene thin films as an active layer in organic thin-film-transistor device configuration, for using as alcohol sensing layers, both in a thin-film-transistor (TFT) and in a quartz crystal microbalance (QCM) configuration. The responses to 1-hexanol and ethanol molecules are very fast; extremely reversible and the best extrapolated sensitivities were as good as 0.7 ng/ppm .

2.3 Gas Sensors Based on Electrospun Nanofibers

Manesh *et al.* (2007) studied a nanofibrous sensor for ammonia gas fabricated by an electrospinning composites of poly(diphenylamine) (PDPA) with poly(methyl methacrylate) (PMMA) onto the patterned interdigit electrode. PDPA was prepared by the oxidative polymerization of diphenylamine with ammonium persulfate and doped with β -naphthalene sulfonic acid (NSA). Adequate amounts of PMMA and PDPA were dissolved in DMF/acetone mixture (7 : 3 v/v) and electrospun on the pattern encoded over an IDT electrode to obtain the sensor device. The composite electrospun membrane showed interconnected fibrous morphology. Functional groups in PDPA and the high active surface area of the fibrous membrane made the device able to detect a lower concentration of ammonia with a good

reproducibility. The composite exhibited the combination of a lower detection limit and a lower the response time.

Gopalan *et al.* (2008) studied composites of poly(vinylidene fluoride) (PVdF)–polydiphenylamine (PDPA) which were electrospun as nanofibrous membranes, PVdF–PDPA-CFM (CFM represents composite nanofibrous membrane). Polymer electrolytes were prepared by loading lithium salts into PVdF–PDPA-CFM for lithium batteries. From the field emission scanning electron microscope, the inter-fiber twisting in the PVdF-PDPA-CFM generated microcavities. These interconnected morphological features of PVdF–PDPA-CFM resulted in higher ionic conductivity, effective lithium ion transport, and good interfacial characteristics with lithium electrode.