

CHAPTER II

LITERATURE

2.1 Synthesis

MacDiarmid *et al.* (1985) reported that polyaniline could be synthesized in various forms both chemically and electrochemically in aqueous media. The quinoid-benzinoid diimine form, an insulator, was doped in a dilute aqueous protonic acid to obtain the metallic regime. This represented a new type of p-doping phenomenon in a conducting polymer. The non-conductive and conductive forms are stable in the presence of air and/or water. The doping process could be reversed by treatment with aqueous alkali.

Huang *et al.* (1986) reported that the emeraldine base form of polyaniline (PANI) could be synthesized electrochemically as a film exhibiting a well-defined fibrillar morphology closely resembling that of polyacetylene. Cyclic voltammograms of chemically synthesized and electrochemically synthesized PANI were identical. The emeraldine salt form of PANI had a symmetrical conjugated structure having an extensive charge delocalization.

Cao *et al.* (1989) reported the chemical polymerization of aniline in aqueous solution, and studied the effect of synthesis parameters such as pH, reactive concentration of reactants, polymerization temperature, and time etc. They found that the reactive yield was not sensitive to most variables; on the contrary, the inherent viscosity of the polymer, measured in solution of concentrated sulfuric acid, was strongly dependent on the synthesis parameters.

Fong *et al.* (1995) studied the polymerization of aniline using mixed oxidizers. They reported that potentiometric and calorimetric measurements on aniline polymerized by persulfate revealed an induction period, which may be

decreased or eliminated by the addition of ceric (Ce^{IV}) ion. The addition of the second oxidizer appeared to promote nucleation. The molecular weight and electrical conductivity of the resulting polyaniline were also measured. Substantial shortening of the reaction time and improvement of polymer conductivity might be realized with the addition of 0.1-1% Ce^{IV} co-oxidizer in the standard polymerization technique.

MacDiarmid *et al.* (1996) described the synthesis of PANI oligomer and chiral PANI film, the use of PANI in light-emitting devices, the effect of substrate surface on properties of PANI, PPy, and the application of soluble PPy in solution for volatile organic compounds.

Stejskal *et al.* (1996) found that the oxidative polymerization of aniline gave rise to polyaniline, which existed in a variety of forms, differing in electrical conductivity and in colour. They also proposed a scheme of interrelated structures, which accounted for all the spectroscopic and conductometric observation together with a set of equation summarizing the chemical transformation.

2.2 Doping

MacDiarmid *et al.* (1987) reported that the analytically pure base form of polyaniline was converted from an insulator to a conductor by treatment with 1M aqueous HCl to form a corresponding salt, the emeraldine hydrochloride. This involved a new type of doping of conductive polymer in which the number of electrons associated with the polymer underwent no change during the protonic acid doping process. The metallic emeraldine chloride was believed to be a delocalized poly(semiquinone radical cation) having a polaron conduction band, with most of the positive charge residing on the nitrogen atoms.

Cao *et al.* (1992) reported that the counter ion could induce processibility of the resulting PANI complex when using a suitable

functionalized protonic acid to protonate PANI. Their result demonstrated the feasibility of processing, in the conducting form, polyaniline and a variety of polyblend made from PANI. The resulting conductive polymer materials could be melt-processed or processed from a solution to enable the fabrication of thin films, sheets, fibers, transparent conductive films, bulk ports, etc. These materials exhibited relatively high levels of electrical conductivity, while maintaining excellent mechanical properties.

Taka *et al.* (1994) discovered a processable and conductive polyaniline complexes including functionalized sulfonic acids that were an important discovery in the field of conjugated polymers. The conductivity, electronic and crystalline structure properties of polyaniline protonated with dodecylbenzenesulfonic acid were proportional to the molar concentration of the acid. The protonation led to a layer structure as evident in X-ray diffraction pattern and the crystallinity degree was a function of the acid concentration similar to an increase in the conductivity. The electronic structure measured by UV-Vis spectroscopy showed an increase in the polaron concentration as acid concentration increased.

Levon *et al.* (1995) reported that doping of PANI had been achieved by introducing the dopant molecules into the solid, undoped PANI without the use of a auxiliary solvent. Complex formation in the solid phase resulted in the formation of a soluble and processable conducting complex. The doping process was similar to the oxidation of on emeraldine base with traditional protonic acid doping as observed by UV and IR spectroscopies.

MacDiaramid *et al.* (1995) discovered a new concept in conductive polymers, which was called a secondary doping. They explained that a primary dopant for a conductive polymer was a substance which drastically changed the electronic, optical, magnetic, and ion structural properties of the polymer and was usually accompanied by a large increase in conductivity. A secondary dopant was an apparently inert substance which, when applied to a

primary-doped polymer, induced further changes in the above properties including a further increase in conductivity.

Fu *et al.* (1997) studied the protonation of polyaniline with light sulfonated polystyrene in polar solvents such as dimethyl sulfoxide (DMSO) and N-methyl pyrrolidone (NMP). The UV-Vis spectroscopy results showed that quinoid units and semiquinoid units were in equilibrium and were dependent on the sulfonic acid concentration. The protonation of polyaniline was retarded in NMP compared with DMSO due to prevalent hydrogen bonding.

Geng *et al.* (1997) studied polyaniline doped with macromolecular acid. Polyaniline was doped with sulfonated PS, PPO and PEEK. The properties of doped polyanilines depended on the processing method and the structure of the backbone of the macromolecule acids.

Sertova *et al.* (1998) reported about a novel photoinduced protonation of PANI(EB)/PVC with HCl as donor. PVC blended with the base of PANI (Emeraldine base) formed a polymer composite. The protonation of EB occurred through HCl diffusion. The UV was used to induce protonation of the polymer chain. The PANI(EB)/PVC composite turned to green color after a UV exposure.

2.3 Characterization

Wan *et al.* (1992) studied an influence of the protonation state on the conductivity at room temperature. They reported that all results obtained are in agreement with the model of the conducting island, which a metallic island is due to polaron formed by protonation process separated by insulating medium.

Wan (1992) studied absorption spectra of a thin film of polyaniline on a slide glass coated by a spin coater. The absorption spectra were measured as a function of the protonation state of polyaniline, the concentration of solution of polyaniline in NMP, and the drying temperature. The absorbance value of

the 950 nm peak and the ratio of the absorbance value at 950 nm to that of the 630 nm peak increased with an increase in the protonation state of polyaniline. This was consistent with the observation of varying the conductivity with the protonation state.

Palaniappan *et al.* (1994) reported that five different PANI salts had been prepared by a chemical polymerization of aniline in aqueous solution of different acids. Thermal stability of chemically synthesized PANI salts had been studied by thermal analysis. PANI salts underwent a three-step weight-loss process in the heating cycle. The thermal stability of PANI salts depended on the concentration used and the polymers were apparently stable up to 250 °C.

Chan *et al.* (1994) described a highly conductive PANI with thermal stability superior to that of PANI doped with hydrochloric acid (PANI-HCl); the former had been prepared by postsynthesis treatment of PANI base with three different phosphonic acids, R-PA, where R= butyl(BU), decyl(Dc), and benzyl(Bn). Isothermal study showed the vastly superior thermal stabilities of PANI-RPA to those of PANI-HCl. Thermogravimetric analysis demonstrated that condensation reaction above 150 °C caused a loss of the electrical conductivity.

Avlyanov *et al.* (1995) investigated the reduced viscosity of mixtures of polyaniline (emeraldine base, EB) and d,l-camphorsulfonic acid (HCSA) in solutions of m-cresol or chloroform (or the mixtures of these solvents). Viscosity measurements as a function of (a) m-cresol content in the mixed solvent for a fully protonated $\text{EBH}^+/\text{CSA}^-$ polymer, and (b) the protonation level of EB by increasing amount of HCSA in m-cresol, indicated that the fully protonated polymer adopted a maximized expanded molecular conformation in a good solvent such as m-cresol.

Zheng *et al.* (1995) reported that the molecular conformation of doped PANI was strongly affected by its protonation level in pure acid

solution. In a strong acid, both the imine and amine nitrogen atoms of PANI were protonated, resulting in an expanded coil molecular conformation. While in weak acid, only the most basic imine nitrogen atoms were protonated resulting in a compact coil conformation.

Xia *et al.* (1995) reported that PANI-HCSA had a more expanded coil-like conformation in *m*-cresol, *p*-cresol, 2-chlophenol, 2-fluophenol, and 3-ethylphenol than in chloroform, NMP, DMF, and Benzyl-alcohol. They also found that the conductivity of more expanded coil-like of PANI chain was high because of higher charge carrier mobility.

Nicolan *et al.* (1997) reported that some difference in the UV-VIS-NIR light adsorption spectra of the camphorsulfonic acid-protonated PANI (CSA-PANI) solution were observed. They were related to the molecular weight (MW), aggregation state of the PANI and to the counteranion nature. High molecular weight PANI synthesized at low temperature gave a CSA-PANI film with an enhanced polaron delocalization.

Pielichowski (1997) studied kinetic analysis of the thermal decomposition of polyaniline. Typical two and three step decomposition profiles were obtained. They reported that the degradation mechanism strongly depended on the experimental conditions and structure of the polyaniline form.

Li *et al.* (1998) prepared a porous polyaniline film with high conductivity at room temperature by a new method called “doping-dedoping-redoping”. They explained that the resulting polyaniline chains still kept the expanded conformation like PANI-CSA in *m*-cresol, which might be why high room-temperature conductivity could be obtained by this new method.

Wenguang (1999) showed the thermal stability in order of PANI-H₃PO₄ > PANI-*p*-TSA > PANI-H₂SO₄ > PANI-HCl, PANI-HClO₄ > PANI-CSA. The conductivity of doped PANI films at room temperature was reduced after a thermal treatment, and it was dependent on the counterions. It was found that

the conductivity stability of PANI-p-TSA and PANI-CSA was the best below 200 °C.

Pomfret *et al.* (2000) developed a new-acid solution processing route for polyaniline (PANI) which is a one step wet-spinning process of inherently conductive PANI fibres. This was achieved from solution of PANI protonated with 2-acrylamido-2-methyl-1-propanesulfonic acid in dichloroacetic acid. As-spun fibres had Young's moduli of 40-60 MPa, ultimate tensile strengths of 20-60 MPa and electrical conductivities of 70-150 S/cm.

2.4 Application: Gas Sensor

Miasik *et al.* (1982) developed solid-state semiconductor gas sensors based on organic sensor elements. Devices based on metal phthalocyanines showed useful responses to NO₂. Lead phthalocyanine combined the highest conductivity with the maximum sensitivity to NO₂. Conducting polymers, and particularly chemically doped polypyrrole, showed responses to toxic gases at ambient temperature whereas phthalocyanine sensors had been operated at 170°C to obtain a conductance with reasonable speeds of response and recovery.

Agbor *et al.* (1995) reported that thin films of PANI have been deposited by spinning, evaporation, and the Langmuir-Blodgett technique. The films were shown to possess slightly different features and properties. The conductivity was found to depend on the gas ambient. All types of PANI films were sensitive to H₂S and NO_x.

Kukla *et al.* (1996) studied a new type of ammonium sensor with PANI as a sensitive element. The use of PANI ensured a high chemical stability of sensor in oxidizing ambients. A sensor design was based on a silicon chip custom-packed into a linear plastic cage.

Agbor *et al.* (1997) showed that PANI could be deposited onto a substrate as finely thin films. The thickness per layer was 5.5 ± 0.6 nm.

Exposing a single LB layer of PANI to NO_2 and H_2S produced increases in reflectivity and resonance angle. The effects were partly reversible, with lower detection limits of about 50 vapor part per million at room temperature.

Grummt *et al.* (1997) reported that thin layers of PANI were suitable to measure the pH in the range of 2-12 in the near infrared region. The deposition of such layers was strongly facilitated by the use of solution-processable PANI. Testing the sensor layers over a period of 300 hours and up to 500 titration cycles revealed excellent reproducibility and stability.

Dhawan *et al.* (1997) reported that the leaching of the polaronic site in the doped PANI grafted surface on exposure to NH_3 led to a characteristic change in the resistance of the polymer. The surface resistance of doped PANI changed on exposure to aqueous ammonium.