

A Study of Polyaniline – A Unique Conjugated Polymer

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Abstract - Conducting polymers, in particular, have found use in solar cells, organic light emitting diodes, and sensors thanks to their electrochemical characteristics. Among the conducting polymers, polyaniline has drawn a lot of interest. Extensive study with the polymer in either its unmodified or functionalized form has been conducted. The fundamental reason for this is how simple it is to chemically or electrochemically synthesise polyaniline, as well as its derivatives, composites, and co-polymers with other materials. The process for creating polyaniline and its This brief article discusses polyaniline, a favoured conducting polymer, its many forms, electrochemical synthesis, the creation of polymer conducting films, and polyaniline's ability to conduct electricity.

Keyword - polyaniline, Conducting polymers

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INTRODUCTION

Polyaniline (PANI) stands out among conducting polymers because it has the potential for more widespread applications than other polymers, making it a topic of intense research interest across the globe right now. Additionally, it is in a class of its own because of its amine-imine structural properties in its polymer backbone and its doping and conductivity being protonation-dependent. Polyaniline is the oldest conducting/ semiconducting polymer reported. Aniline black has been used as a dye since early 19th century. The first successful attempt to study aniline black was however made by Fritsch in 1840. Numerous approaches had since been developed to understand conduction in this compound, but the possible interpretations obtained, so far, have been controversial. The current phase of research on semiconducting polymers has commenced since 1980, when various eminent workers seriously involved themselves to solve many of the unsolved & controversial problems encountered during their various studies conducted on polyaniline. Nevertheless the searchers in this field have not yet succeeded to unravel all different phenomena, such as mechanism of polymerization, role of doped ions, protons & redox mechanism etc. The existing models thus need to be elaborated to explain the observed experimental results.[1]

The academic community and the chemical and electronic industries throughout the globe have conducted extensive research and development on conductive polymers during the last two decades. New possibilities are emerging for polymeric materials thanks to their application in high-value industrial and consumer goods.[2]

Although polyaniline has been known for years, its electronic uses have been established only recently. The structure and properties of this polymer have been widely studied and its feasibility as solid state devices for use as sensors, optoelectronic devices, energy storage devices, metallization of printed circuit boards, radiation shielding materials has been established. Polyaniline is prepared by various methods and is normally used as powder or pellet form. The nanocrystalline thin films of polyaniline have been proved to be suitable for fabrication of electronic devices.

POLYANILINE - A PREFERRED CONDUCTING POLYMER

Among all conducting polymers polyaniline has a special representation due to:

1. Controlled electrical conductivity by non-redox doping of protonic acids.
2. Easy synthesis.
3. Environmental stability.

It has been a primary goal of conductive polymer technology development to bring together the mechanical and processability qualities of commodity bulk polymers with the electrical and optical capabilities of these new materials. Producing new goods with qualities that are difficult or impossible to obtain with current materials is now conceivable thanks to the development of novel conductive materials with great application potential as alternatives. Some polyaniline-based compounds

can be processed in both a solution and a melt. They have obvious advantages over regular polymers that are made conductive by the use of additives (carbon blacks, metal particles and flakes, metal fibers, carbon fibres etc.).[3]

Polyaniline offers low-cost options for the creation of transparent and coloured thin films and coatings, finely regulated electrical conductivity via protonic acids across a broad range, and improved phase compatibility and, consequently, blend ability with bulk polymers.

Experimentalists have been interested in the field of polyaniline both due to its ease of synthesis and processability. Recent progress of this class of organic semiconducting materials has resulted in distinct improvement in processability. It has been experimentally shown that polyaniline can be vacuum evaporated upon glass plates. Besides this, ordered mono and multi molecular layers of polyaniline have been fabricated using vacuum coating unit. Semiconducting polyaniline thin film prepared by vacuum deposition has been found to exhibit electrical and optical non-linearity. The electrical conduction in polyaniline thin film is field dependent. The low field conduction follows Schottky and Poole-Frenkel type of mechanism.[4]

Good environmental stability of polyaniline in its doped and undoped states along with its ease of processability has led to a large number of its applications. The increasing interest of scientific community in this challenging and technologically important conducting polymer has resulted in the publication of more than 1500 papers in the last decade. Such a widespread interest of researchers in polyaniline has been linked with the numerous possible applications on one hand while on the other hand to the fact that aniline is a very cheap product, its synthesis is facile, yield is very high and polyaniline synthesized is environmentally much stable.

Thus, in contrast to polymers like polypyrrole, polythiophene and polyethylene- vinylene etc., polyaniline is becoming the subject of much more interest for physicists, chemists & material scientists.

DIFFERENT FORMS OF POLYANILINE

Polyaniline is a unique material amongst the conjugated organic polymers showing a number of oxidation states and it refers to a class of polymers comprising of a large number of oxidized and reduced repeat units. These can be considered as being derived from a polymer having a generalized composition.

The different forms of PANI according to γ -value. Their structures The conductivity of all the three form of PANI is around 10^{-5} S/cm. It is possible to form the matching salt by protonating all or some of the nitrogen atoms in any of these species. It is the

polymeric base's oxidation state and the surrounding pH that determine how much protonation occurs. Poly emeraldine salt is the base's protonated state. When compared to the conductivity of standard metal (10^3 S/cm), this is green and far less conductive (10^{-5} S/cm). Due to the rigidity of the chains and the interchain interaction, PANI is insoluble in most solvents. An effective way for increasing PANI's solubility in typical organic solvents is the N-alkylation technique using leuco emeraldine base, which involves the addition of a viable alkyl chain to the PANI structure.

Chemical Synthesis

Using potassium persulfate ($K_2S_2O_8$) in aqueous HCl (1M) as an oxidant at ice temperature, polyaniline was produced by oxidative polymerization of doubly distilled aniline dissolved in aqueous HCl (1M). The aniline (0.2 mol) and potassium persulphate (0.2 mol) were both dissolved in 1 litre of 1M HCl aqueous solution (1M). The aniline solution was cooled to room temperature, and the oxidant solution was added slowly while being stirred continuously. After one hour of stirring in a water bath, the reaction mixture was chilled overnight in the fridge, where the PANI precipitate was washed with 1M HCl until the filtrate was colourless and then with double-distilled water until it was acid free. Using soxhalation with acetone, polyaniline was reduced to a powder and the low molecular weight oligomers were removed. Polyaniline (ES form) was dried in an oven at 60 °C for 48 hours and then kept in a desiccator.

Electrochemical Synthesis

Various potentiodynamic techniques, such as cyclic voltammetry and cycloamperometry, as well as galvanostatic techniques, may be employed for electrochemical synthesis. A three-electrode setup is optimal for achieving synthesis with any of these methods. A working electrode, counter electrode, and reference electrode make up this system. Depositing conducting polymers, platinum, stainless steel, gold, indium tin oxide (ITO) glass has been used effectively as working electrodes; in many situations, the polymers deposited on the electrode surface may be peeled off into their self-stand states.[5]

PROTONATION IN POLYANILINE

The emeraldine (0.5) oxidation state of polyaniline exhibits the highest level of conductivity upon protonation on reaching its value to 15 S/cm with 50% protonation. The protonation occurs when polyaniline reacts with protionic acid such as HCl.

The Cl^- of HCl acts as the counter ion, which is not the part of polymer backbone but facilitates charge transport. PANI structure. The shortened form of 2.3 (A) occurs in its entirety. Quinoid and benzenoid structural units make up the bulk of PANI chains (Scheme A). To clarify, the protonated PANI is only electrically conductive for

$y = 1/2$ (Benzenoid: Quinoid = 3: 1), and this is not the case for all doped PANI. Doping with protonic acid is shown in Scheme.

In the sensing process of conducting polymer based sensors, doping and undoping play crucial roles. The amount of electrons in the underlying chemical bonding mechanism is not altered throughout these activities, making them non-redox. This reaction yields polarons, which are cation radicals. It's possible that they will find a compatible partner in the transition phase.

The polarons and bipolarons are mobile and under the influence of electric field can move along the polymer chain from one chain to another chain and from one granule to another granule, exactly in the manner electrons do in inorganics. The polarons and bipolarons move along the chain through the rearrangement of double and single bonds.[6]

CREATING POLYMER CONDUCTING FILMS

The sensor's active layer is its beating heart. In order to accommodate a wide range of sensing materials and geometries, a number of methods have been devised for creating conducting polymer films. It is possible to deposit conductive polymer films using the following techniques:

1. Electrochemical depositing

Electrochemical deposition is the most efficient method for depositing conducting polymer films. When deposited on microelectrodes with a predetermined pattern, the film's thickness may be controlled by varying the current through the electrochemical cell. The deposition process cannot occur without a conductive substrate.

- **Dip-coating.**

Substrates that are dipped into solutions used for chemical polymerization will have some of the polymer deposited onto their surfaces. This procedure is performed on various substrates, with the film thickness typically being managed by the duration of the dipping process. An other method that is conceptually similar employs alternating dips of a substrate into the monomer and oxidant solutions. The monomer that has been adsorbed on the substrate's surface will undergo polymerization there.

- **Spin-coating**

Films may be easily prepared using the spin-coating technique with soluble conductive polymers. The conducting polymer solution is applied to a revolving substrate. Due to solvent evaporation, a thin layer is produced. The film's thickness may be adjusted by repeating the aforementioned procedure. The solution concentration and the substrate's rotating rate both play significant roles in controlling the final film thickness. The approach described here may be used to coat conducting polymers onto either conducting or insulating surfaces.[7]

- **The method of Langmuir and Bloodgett (LB)**

The LB technique is widely used to create a polymer and surfactant thin film. The LB method entails depositing a polymer and then a monomer, and finally polymerizing the mixture on the substrate.

- **This self-assembly method is called "layer-by-layer" (LBL)**

A substrate is submerged in a polymeric anion solution and a polymeric cation solution in alternating cycles to produce a composite film (layer by layer) comprising the two polymeric electrolytes. Coating a polymer with a polymeric anion is made feasible by the positive charge on the backbone of doped conducting polymers like PANI. If the LBL pattern is repeated often enough, a thicker film will form.

- **Thermal evaporation**

To use this technique, heating conducting polymer in a vacuum causes it to evaporate, and the deposited polymer may then conduct electricity. The time it takes for the solvent to evaporate establishes the film's thickness.

- **Vapour deposition polymerization**

The two processes of this technique are the creation of an oxidant film and its subsequent immersion in a monomer vapour. The film is polymerized as the monomer diffuses into it. Not only is this method helpful for making a single-polymer conducting film, but it may also be used to create composite films that have many distinct conducting polymers..

- **Drop-coating**

Drop drying refers to the process of applying and drying a polymer solution to a substrate by dropping and reacting with solutions of monomer and oxidant. The technology behind this is rather basic. The coating that forms, however, seldom has a consistent thickness.[8]

CONDUCTION IN POLYANILINE

In the last decade the semiconducting and metallic properties of organic π -electron systems have drawn considerable attention both from fundamental and applications point of view. Among various types of π -electron Recently, conjugated polymers have displayed broad variety of intriguing qualities in their electrical and optical properties, leading to applications such as light emitting diodes, photodiodes, electronic circuits, lasers, sensors, solar cells, etc. Many conjugated systems have been created and their physical characteristics studied since the discovery of metallic polyacetylene in 1977. Structure and morphology play important roles in the electrical characteristics of polymeric materials since they are intrinsically partly crystalline and partially amorphous. In addition, the proportion of disordered to organised

areas in conjugated macromolecules $[(-C=C-C=C-C=C-)_n]$. The scale at which a system operates, from the nanometer to the macroscopic, may change greatly depending on the circumstances in which a sample is prepared and processed. Understanding charge transport characteristics in conducting polymers has proven challenging in comparison to more traditional systems due to the intricate link between structure/morphology and electronic properties. In addition, the metal-insulator (M-I) transition in doped conducting polymers is critically influenced by disorder-induced localization. The charge transport characteristics of doped polyaniline provide an excellent example of this situation (PANI).

The semi-rigid intractable polymer PANI is readily made through chemical polymerization of aniline. When PANI is doped with acids ($H^+ A^-$), the insulating emeraldine base may be converted to the conducting emeraldine salt. Band structure of PANI, a semiconductor with a band gap of around 2.6 eV, is seen in Fig. In contrast to common inorganic semiconductors, it has mid-gap polaronic states. The change from insulator to metal is triggered by doping, which causes the mid-gap level to enlarge and combine with conduction/valence bands.[9]

In contrast to its low solubility in solvents like N-methyl pyrrolidone (NMP) for undoped PANI, the charged chains of this molecule become rather rigid when it is doped. Therefore, it has a low solubility in most solvents. PANI was insoluble until Cao et al. used a dopant with a surfactant counterion to dissolve it, resulting in a conductive solution. PANI's processibility was boosted by the addition of a surfactant counter ion, allowing for the production of high-quality, self-supporting films. Doped PANI's conductivity has grown from 10 S/cm to 103 S/cm as a result of this, and the material's inherent metallic characteristics have been seen for the first time. Simultaneously, it became clear that the electrical characteristics of PANI may be drastically altered by exposing the polymer chain to different combinations of surfactant counterions and solvents via molecular recognition interactions. PANI's increased process ability through the solution method has also allowed for its fabrication in a wide variety of forms, including thin films, free-standing films, fibres, etc., for use in a wide range of electronic devices. [10]

GENERAL PROPERTIES OF POLYANILINE

The emeraldine base form of polyaniline differs substantially from other polymers like polypyrrole, polythiophene etc. in several aspects, firstly, it is not charge conjugation symmetric and its Fermi level is not exactly at the center of the band gap so that the valence and conduction bands are highly asymmetric. Consequently, the energy level position of the doping induced and photo-induced absorption spectra differ substantially from those in charge-conjugation symmetric conducting polymers. Secondly, both carbon ring and nitrogen atoms are within the conjugation path forming a generalized polymer. Thus,

the emeraldine polymer differs substantially for polypyrrole and polythiophene whose hetero atoms do not contribute significantly to p-band formation. Thirdly, the emeraldine base can be converted from an insulating to conducting state ($\sigma_{dc} = 10 \text{ S/cm}$) at room temperature, if protons are added to N sites while the number of electrons in the chain are held constant.

When polyaniline is doped with protonic acids, a broad polaron band appears in a gap instead of two and a second band appears deep in the gap with a very narrow band near conduction edge. The polaron metal band has been proposed for polyaniline.

X-ray spectroscopic analysis of oligomeric polyaniline shows an angular rotation of adjacent rings relative to zigzag chains of the nitrogen atoms in accordance with theoretical predictions in polyaniline.

The electronic band structure of PANI exhibits in the intermediate and fully oxidized form, polaronic and bipolaronic defects in the band gap.

The conducting form of polyaniline is suggested to be a polaron metal where the defects are delocalized over the whole undisturbed conjugation length in semi-quinoid distortions for all the ring structure (polaron lattice). Traditionally, halogens such as chloride, iodine and bromide have been used to enhance the electrical conductivity of the emeraldine base. The charge transfer interaction with halogens results in a decrease in imine repeating unit in the case of emeraldine base.[11]

CONCLUSION

The FTIR studies indicate the vibrational frequencies of different bonds in a PANI molecule. The corresponding results for different undoped and doped forms of PANI are well presented and explained. Finally, the X-ray diffractometry data are presented and it is seen that similar crystal structure exists for all the PANI varieties whether undoped or doped type.

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