Chapter 2

Scope and Objective
2.1. Preamble

The conducting polymer field is interdisciplinary incorporating unique challenges, difficulties and opportunities. The macromolecular structural modification can lead to reduce the band gaps of conduction and valence band and hence increases the intrinsic conductivity of conducting polymers. With this all round development in the basic aspects of conductivity, stability, processability, and mechanical strength, the conducting polymers are now at the threshold of revolutionary technology of electronic materials.

Ever since the discovery of the phenomenon of conductivity in conjugated polymers by the three material stalwarts in 1977, there has been a tremendous growth in research activity and publications on conducting polymers. Flourishing as a novel type of materials they possess a great scope of application in diversified fields like electronics, electrical storage devices, capacitors, sensors, smart materials and in other fields such as drug carriers, heart valve etc. A few of the potential applications have already been materialised and commercialised, for instance, the Li coin-type cells, chemical and biological sensors, electromagnetic interference shielding. Though the essential requirement for all these applications is the conductivity, other characteristics, especially of material and polymer origin are crucial and decide the efficiency, durability and cost factor of the specific application/device of the conducting polymer.

In this respect, polyaniline has emerged as a promising material outweighing others, owing to its unique physico-chemical characteristics, environmental stability,
easy synthesis and the cheap price of aniline monomer. Hence polyaniline has secured a focus point from many researchers of conducting polymers.

2.2. *Polyaniline—Unique in its class and choice for the present work*

Polyaniline, one of the conjugated conducting polymers, but a prominent one in its class has unique molecular characteristics and hence it has a wide spectrum of applications. The chief characteristics which make polyaniline distinct are:

i) The presence of amine-imine nitrogen moieties.

ii) Protonation-dependent doping and conductivity without change in total number of conduction electrons.

The chemically flexible amine-imine N groups of polyaniline and the corresponding alteration in its physico-chemical properties such as redox state, colour, structure and the charge carrier, hold the key for its entire applications. Though many of its material characteristics are favourable for technological applications, certain chemical properties, notably its processability, poor solubility in common organic solvents, plasticity and long term stability with retention of conductivity still pose problems and do not fructify their potential applications. Hence much research effort is needed to further improve its characteristics with tailor-made properties so as to suit the end applications. To find remedies to these problems is the task of the present attempt.

2.3. *Objective and work plan*

The objective of the present work is very clear. Improvement in material and polymer characteristics of the versatile conducting polymer polyaniline by chemical means in order to fetch more practical applications is the goal and objective.
As one can see from the literature, currently different methods are adopted to accomplish the same. In the present work, it is aimed to fulfill the same in three different approaches. They are:

1) Formation of organic-inorganic hybrid materials.
2) Polymer blend formation.
3) Incorporation of functional organic dopants in polyaniline.

2. 4. Chemical method for first two approaches

The first two approaches are performed in the chemical polymerisation of aniline in the \textit{in-situ} condition with PDS as oxidant in aqueous $\text{H}_2\text{SO}_4$. An electrochemical method may not be feasible as the redox process of inorganic/polymeric dopant at the electrode may be detrimental to it.

Water-soluble inorganic metal complexes bearing negative charge are novel candidates for dopants. In the present case, metal oxalate complexes of $\text{Cr(III)}$, $\text{Fe(III)}$, $\text{Mn(III)}$, $\text{Co(III)}$ and $\text{Al(III)}$ are to be synthesised and incorporated into polyaniline during \textit{in-situ} polymerisation of aniline. Since the complexes have water solubility and characteristics entirely different from conventional inorganic dopants of mineral acids, the resulting organic-inorganic hybrid materials have a good chance to possess new properties.

Polymer blend formation involving polyaniline and other non-conducting polymer is an already existing technique and has been utilised with PVC, PVA, PMA, PMMA, etc. Yet the involvement of water-soluble polymer with enriched properties through complexation with other species is not so far thought of and hence illustrates a new approach. The two water soluble polymers PVA and PVP as such or in their
complexed form with Cu(II) ion and I\textsubscript{2} respectively are employed in blend preparation with polyaniline and the emerging materials are characterised and investigated.

2.5. Third approach by electrochemical way

Electrochemical method of polymerisation is more advantageous than chemical method in the sense that in the former both polymerisation and doping occur simultaneously and the electrodeposited polymer is devoid of any impurity and possesses regularly arranged polymer chain structure. The only essential condition is that the dopant should not undergo any redox reaction at the electrode. Keeping in mind this advantage, the third approach is attempted in electrochemical way.

Analogous compounds of naphthalenesulphonic acids are employed as functional organic dopants. The presence of —SO\textsubscript{3}H group imparts water solubility and the large planar naphthalene moiety with \pi-electron cloud may facilitate an electron-level interaction with polyaniline and may thereby tune its electric properties. This is to be confirmed by a comparison with the influences of catechol and naphthalenesulphonic acids on polyaniline, under the varying influences of two protonic acid media H\textsubscript{2}SO\textsubscript{4} and HClO\textsubscript{4}. The effect of substituents on the dopant role of naphthalene sulphonic acids is also to be examined.

Investigation on the characteristics of different polyaniline materials is made in different angles, i.e., chemical (chemical analysis, doping, de-doping, redoping, etc.), structural (XRD, FTIR, UV-VIS, EPR) thermal (TGA), electrical (conductivity with temperature variation) and electrochemical (CV) characterisations are performed