Preface

Past decade has witnessed the demanding research of conducting polymers as well as their nanocomposites as potential materials for large area fabrication of various devices such as batteries, capacitors, biosensors, chemical sensors, energy harvesting devices and supercapacitors. In addition to above devices, organic polymer based electronic devices such as FETs and OLEDs in particular have attracted major scientific attention. The major grounds for their preference over inorganic counterparts are their stupendous architectural flexibility, light weight, potentially low cost, environmental stability, thin film processibility and flexible device fabrication. In organic polymers, the chemical structure (functionality and side chain) and molecular interactions (interchain and intrachain) are the inherent properties that can be tuned (ordered) for their molecular self-assembly and chain alignment through different ordering techniques. Variety of ordering techniques both at synthesis and at post-synthesis (film formation) levels have been developed to modify and tune the assembly (ordering) of these conducting polymers in order to embrace and interface them into thin film particularly for large area based electronic applications. At synthesis level, polymeric assembly has been enhanced either by employing synthetic procedures that yield regioregular structures or by incorporating conducting nanomaterials that can template the polymerization. Such developments are highly desirable as they could potentially provide the long range ordered array of polymer π-backbone chain leading to enhancement in device performances.

The emphasis of the present work is on the polymer assembly and its chain alignment during synthesis steps and its ordered film formation at post synthesis level. Preorganised polymer and its composites formed have been then ordered through an excellent nanostructure assembly technique "Langmuir-Blodgett or Langmuir-

Schaefer". This technique offers precise control over the molecular level ordering (via non-covalent interactions) at air-water interface. Multiple reports have been published utilizing this technique, but most of them are for ampiphilic (containing hydrophobic alkyl chain and hydrophilic part) molecules and polymers. If any non-ampiphilic conducting polymer is explored for its ordering at air-water interface, it is usually mixed with surfactants (insulator) to facilitate their spreading onto water subphase thus compromising with their electrical properties. Therefore, in this work Langmuir technique has been standardized for ordering of non-ampiphilic polymers and its composites for various technological applications including large area organic electronics.

Polyindole (PIn) and its derivatives possess excellent electroactivity, environment stability, excellent thermal stability, easy degradation, etc. Among various π-conjugated polymers, particularly this polymer group attracted our attention due to its lost significance in the electronic industry despite of above mentioned properties. This is probably due to its poor solution prcessability for film formation and low conductivity as compared to other organic polymers. These problem statements have been addressed for the first time successfully in this work by forming orederd polymer thin films and incorporating conducting nanomaterials in polymer matrix and ordering them through Langmuir technique. Nanomaterials such as MoS_2 nanosheets and silver nanoparticles have been synthesized and utilized for composite formation. Their self organizing properties together with Langmuir technique have been explored for obtaining ordered films of PIn.

The whole work has been presented in the form of seven chapters. The introductory chapter **Chapter–1**, outlines briefly on the significance of ordering of conducting polymers at all levels of hierarchy. Various ordering techniques employed at

synthesis level and post synthesis level has been discussed here. The chapter also describes about interfacial strategies (L/L, G/L viz. Langmuir technique) for polymer ordering at molecular level. This chapter further details about the previous works and advances in the Langmuir technique and various parameters for its standardization. **Chapter–2** presents a brief description about the material synthesis, sample preparation and characterization techniques viz. UV-Vis, FT-IR, Raman, TGA, SEM, TEM (SAED), AFM, phase imaging, and charge transport parameters. **Chapter–3** illustrates the air-water interface assisted assembly of unsubstituted PIn via Langmuir Blodgett system. Surface pressure vs. area isotherm obtained for PIn was justified via AFM and SEM characterization prior to deposition of films. This study presents interaction property of PIn over water surface, attainment of stable and large area thin films and layer dependent charge transport with improvement in device performance. In this series, **chapter-4** highlights the liquid-liquid interface assisted morphology controlled synthesis of poly(5-aminoindole), 5-APIn and its Langmuir assisted assembly at air-water interface. Large area, ordered and compact film of 5-APIn was obtained via Langmuir-Schaefer method and validated through SEM and AFM and investigayted for its charge transport property. **Chapter–5** explores air-water interface for homogenous dispersion of MoS_2 nanosheets forming larger interface with higher surface to mass ratio on the PIn matrix assisted by Langmuir Technique. The results were validated by TEM and AFM results. These ordered films exhibited significant enhancement in electrical properties of the polymer. **Chapter-6** details about the utilization of liquid/liquid interface for obtaining uniform size AgNPs and their decoration in PIn matrix at air-water interface via Langmuir technique. Non-covalent interaction between them was the driving force for uniform distribution and assembly and enhancement in charge transport property. **Chapter 7** compiles a chapter wise summary of the work.

Introduction & Literature Survey

1.1   Introduction

Conductive polymers (CPs) are considered as a class of organic semiconducting materials possessing unique optical and electrical properties similar to those of inorganic counterparts. CPs in various applications have gained significant attention due to their tunable electrical conductivity, economically favorable synthesis approach, light weight, high mechanical durability and ease in their material processing [1,2]. Past decade has witnessed the demanding research of CPs as well as their nanocomposites as potential materials for large area fabrication of various semiconductor devices such as battery, capacitor, biosensor, EMI shielding, antistatic agent, chemical sensor, energy harvesting and supercapacitors (as displayed in Figure 1.1) [1-7]. With regard to organic polymer based electronic devices such as organic field effect transistors (OFET) and organic light emitting diodes (OLED), modification in the structural design of the polymer conjugated backbone is a demanding research area. In view of this, side-chain substitution, and augmenting the layer (film) properties (such as uniformity and thickness) has upraised the potential of these materials to standards (mobilities~0.1 $cm^2V^{-1}s^{-1}$) comparable to that of inorganic counterparts (amorphous silicon). Figure 1.2 (i) shows the chemical repeat units (in pristine form) of various types of CPs such as polyacetylene (PA), polyaniline (PAN), polypyrole (PPy), polythiophene (PT) and polyindole (PIn). However, for an extensive application of these organic polymer based devices, there are some important features of semiconducting polymer layer that are prerequisite to be considered. They are environmental stability, material costs and production, ecological friendliness and most important of all, ordering of π-conjugated