Summary and future work

This thesis describes the large area ordering of polymer and it's composite at air-water interface aided by molecular level ordering technique, Langmuir (LB/LS) technique. This technique was employed for assembly of non-alkyl chain containing (unsubstituted) PIn and its derivative 5-APIn without addition of any surfactant. Langmuir technique enables the study of interactions between the molecules using the Langmuir Pressure-Area isotherm over water surface. In addition, PIn composites with conducting nanomaterials such as MoS_2 nanosheets and AgNPs were also assembled at air-water interface. In this work, Langmuir technique was further standardized and explored for their uniform distribution in polymer matrix and their thin film preparations over appropriate substrate for various characterizations and device application as Schottky diode. Prior to assembly via interfacial Langmuir technique, polymer and its composites were synthesized and assembled via chemical route, electrochemical route and at liquid-liquid interface. Liquid-liquid interface technique is having potential not only for ordering but a controlled morphology was achieved at the interface either during polymerization and by using surfactant for size sorting of nanomaterials developed in one phase to another phase. This approach was utilized for 5-APIn synthesis to obtain morphology controlled bulk yield and uniform size sorting of AgNPs. The use of air-water interface in Langmuir method for uniform distribution and assembly of nanomaterials in PIn matrix forming nanohybrid and annealing out the traps by very slow compression of the film has proved to be expedient in three ways. First, possession of self-organization property of the nanomaterials used here acted as a template for preorganization of polymers prior to fabrication, facilitating their ordering via Langmuir. Second, MoS_2 and AgNPs both contributed in charge transport property enhancement of the nanohybrid Langmuir films formed. Third, successive slow compression of the Langmuir layer enabled sufficient time for relaxation and filing up the spaces (traps) of the nanohybrid and thus resulting in its increased ordering and crystallinity (π-π stacking and the interlayer stacking of backbones). Enhancement in increased conjugation length and ordering of Langmuir films has been confirmed by UV-vis and Raman spectroscopy. Large area uniformity and structural study were assured via SEM, AFM topography, phase imaging KPFM and TEM (and SAED pattern). The charge transport properties have been explored in sandwiched configuration of device Al/Langmuir film/ITO Schottky diode. Chapter wise summary of this work is as follows:

Chapter 1 deals with the Introduction and literature survey about the significance of ordering of CPs at all levels of hierarchy. Various ordering techniques employed at two important levels i.e. at synthesis level and post synthesis level very much influence the performance of the large area based electronic devices has been discussed here. The chapter also describes an outline on interfacial strategies (L/L, G/L viz. Langmuir technique) for polymer ordering at molecular level. Interfacial assembly is the simplest, most straight forward and pragmatic. This chapter further details about the previous works and advances in the Langmuir technique and its various parameters for further standardization of this technique. Thorough literature has been searched on PIn family and its composites for its lost significance in large area device fabrication due to its related solution processability issues and others. An attempt has been done to make an up–to–date survey of the literature related to CPs and its ordering via solution processable Langmuir technique.

Chapter 2 deals with the experiment procedures done for this thesis and details of the various characterization techniques utilized in this work.

Chapter 3 deals with the air-liquid interface assisted assembly of PIn via LB system. We have successfully fabricated PIn films over various substrates exploring its self-organizing property in order to obtain its ordered, uniform and compact film. We reasonably justified the isotherm obtained for PIn via AFM and SEM characterization and validated 30 mN/m SP as the optimum point for deposition of uniform LB films. Thus, our study presents interaction property of unsubstituted PIn over water surface, attainment of stable and large area thin films and layer dependent charge transport with improvement in device performance.

Chapter 4 describes liquid-liquid interface morphology controlled and biphasic synthesis of 5-APIn and its Langmuir assisted assembly at air-water interface. This template-free technique provided ample of time without disturbance for polymer to acquire its non-uniform globular morphology and porous structure (monitored via SEM). No external phase transfer agents in case of polymerization and no extra ion impurities with finite side reactions (and by products). Further, we have successfully obtained a large area, ordered, compact film of 5-APIn via LS method validated through SEM and AFM. Charge transport property investigation reveals its scope for application in further large area based flexible electronic devices.

Chapter 5 explores air-liquid interface for homogenous dispersion of MoS_2 nanosheets in PIn matrix assisted by Langmuir Technique. Non-covalent interactions between MoS_2 nanosheet and nitrogen atom of the indole unit was the driving force of exfoliation in aqueous medium and assembly at the air-water interface. These preassembled structures were tailored using the Langmuir technique for large area uniform distribution of MoS_2 nanosheets. This was validated by TEM and AFM results. MoS_2 nanosheets formed larger interface with higher surface to mass ratio on the PIn matrix in a Langmuir trough leading to stable and uniform film. Furthermore, this simple approach for homogeneous distribution of uniformly sized MoS_2 nanosheets in the PIn matrix exhibited significant enhancement in electrical properties of the polymer. We hope that this work will encourage the usage of the Langmuir technique for obtaining homogeneously dispersed nanomaterials in other polymer matrices too.

Chapter 6 details about the utilization of liquid/liquid interface for obtaining uniform size AgNPs and their uniform decoration in PIn matrix at air-water interface via Langmuir technique. This liquid-liquid interface approach is a facile, low cost and quick method for attaining solution-processed AgNPs in organic phase triggered by DDAB serving as PTA and stabilizer both thus eradicating the use of two separate reagents. We hope, this quick and robust approach towards obtaining a size-sorted assembly of NPs may content the laboratory prototyping desire and its potential towards bio-sensing and electronics application. Further, these NPs facilitated the ordering of PIn at air-water interface. Non-covalent interaction between them was the driving force for uniform distribution and assembly. Furthermore, this simple approach for homogeneous distribution of uniformly sized AgNP in the PIn matrix can be explored for electrical properties of the polymer.

Future work

- The issues related with CPs are their low stability and mobility as compared to their inorganic counterparts. In this work, it has been justified (also in literature) that proper orientation and ordering of polymers at synthesis and post synthesis level cause enhancement in charge transport property as well as stability of polymer thin film based devices. The Langmuir technique has been explored extensively and presented here as a model technique to obtain ordered, oriented and thin films for fabrication and characterization of high performance devices. Therefore, these may be explored for other devices such as FETs in future.

- This thesis employs only water subphase for floating film formation of polymer and their composites formed at air-water interface and its isotherm investigation. So, it also urges to explore film formation behaviour of these materials over other liquid surfaces in future using this Langmuir technique which may provide some interesting observations.

- The prepared Langmuir films having potentially high surface areas and highly ordered, offered a remarkable opportunity for nanocomposite to self-assemble and disperse themselves at the air-water interface. So, inorder to achieve commercial success, it is important to further research on various conducting fillers for other devices applications and such as FET, solar cells, etc. which may have future scope of the presented scheme in this thesis.