

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 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) 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), polypyrrole (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

backbone of polymer chains. Chain ordering in case of polymers is associated with their assembly into supramolecular structures via non-covalent (secondary) interactions at all

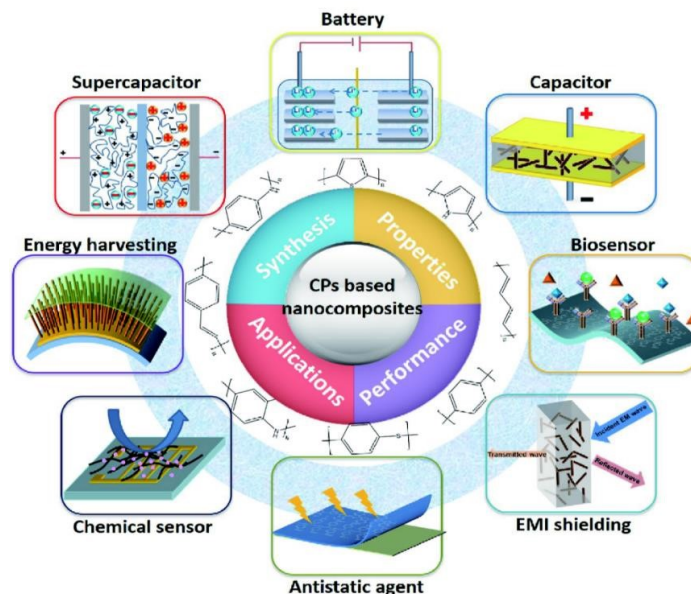


Figure 1.1 Large area based application of CPs and its composites [2].

levels of hierarchy. Variety of techniques both at synthesis and at post-synthesis (film formation) levels have been developed to tune the assembly (ordering) of these CPs to embrace and interface them into thin film particularly for large area based electronic applications. Such developments are highly desirable in various application fields such as optoelectronics, transparent displays, field effect transistors (FETs), electrochromics, supercapacitors, sensors, batteries, etc. as they could potentially provide the long range ordered array of polymer backbone leading to enhancement in device performance.

1.2 Historical background and conduction mechanism of (π -conjugated) CP

The major breakthrough in the field of CPs was in the year 1977 when doping of PA with Iodine (strong oxidising agent) enhanced its conductivity with seven orders of

magnitude: from 10^{-9} - 10^{-2} to 10^2 - 10^3 Scm^{-1} [3,4]. In the late 1980s, PA conductivity was reported around that of copper metal. These significant findings were pioneered by A. J. Heeger, A. G. MacDiarmid, H. Shirakawa for which they were awarded noble prize in chemistry, in the year 2000 [5]. CPs in their undoped (pristine) form are known for their basic electronic feature, the π -conjugated system. This system is formed by the overlap of carbon p_z orbitals containing alternating single and multiple (double) bonds, sometimes heteroatom in conjugation (in case of PAN, PIn, PPy, PT), in which π electrons delocalize along the entire backbone of the polymer chain. Figure 1.2 (ii) displays a comparison between the conductivities of PA, PAN and PPy in their undoped (pristine) and doped forms. The significant enhancement of nearly 10 orders of magnitude in their conductivities upon doping have been reported in the past few decades [1,2,6]. Actually doping in case of conjugated polymers is a just redox reaction through which pristine polymer is oxidised or reduced to its polymeric cation or anion, forming an ionic complex with reduced or oxidised form of the dopant. In such alternating single (σ) and double (π) bonded carbon atoms, there is possibility of Peierls instability (i.e. coupling amid electronic and elastic properties), due to which the π -band is divided into π bonding orbital (filled) forming lowest unoccupied molecular orbital (LUMO) band and π^* anti-bonding orbital (empty) forming highest occupied molecular orbital (HOMO) band with a gap (E_g) in the electronic excitation spectrum [6,7]. This band like energy distribution into LUMO and HOMO resemble valence band and conduction band like that in traditional inorganic semiconductors. Delocalization of these π electrons does not impart sufficient conductivity to these polymers, so in their pristine state they behave as insulating materials. These polymers when doped with

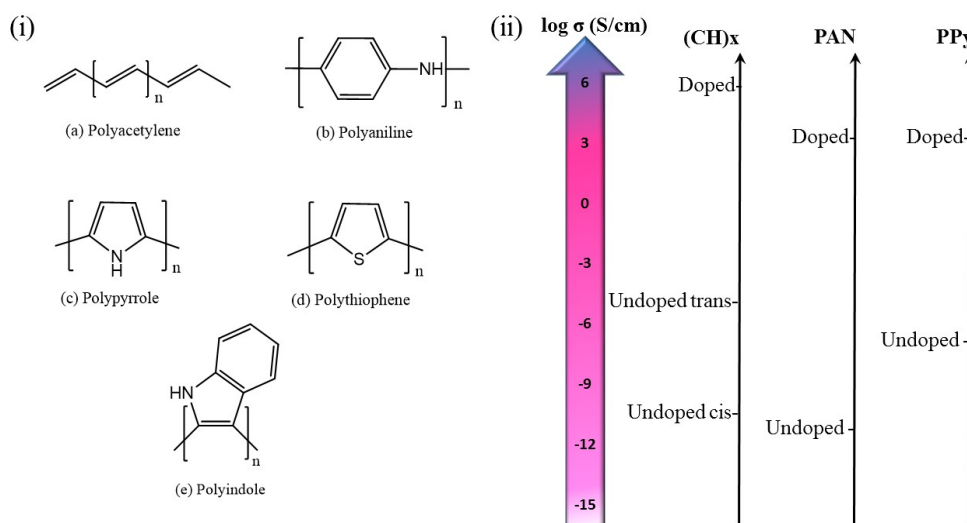


Figure 1.2 (i) Chemical structure of CPs, (ii) conductivity comparison of undoped (pristine) and doped polymers [7].

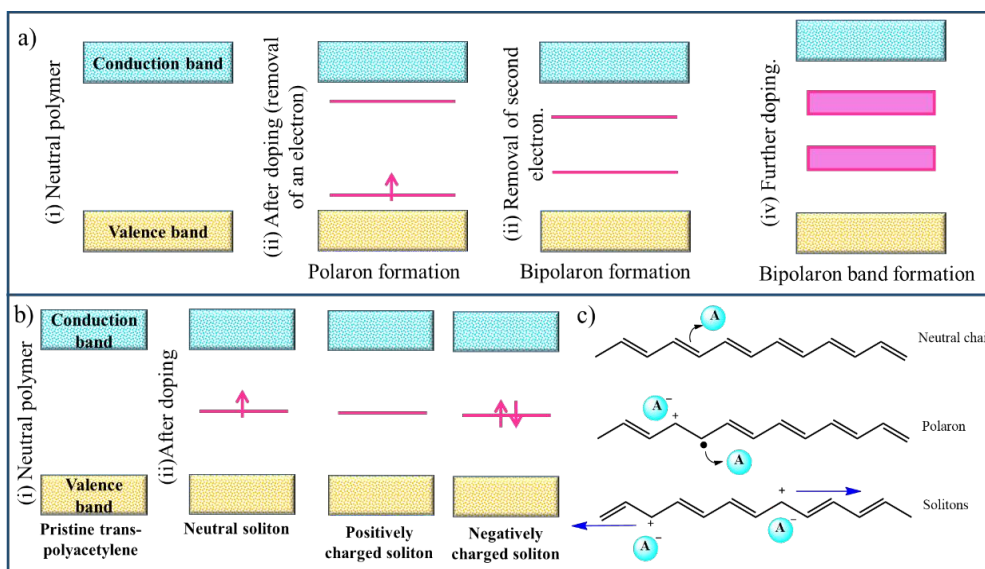


Figure 1.3 (a) Generation of polaron, bipolaron and bipolaron bands as a result of doping level in various CPs (b) Formation of neutral, positive and negatively charged soliton, (c) formation of two charged solitons on a chain of trans-PA [6].

electron donating (n-type) and electron accepting (p-type) dopants, can be transformed into conducting with increasing doping levels. As a result of Peierls distortion in polymer (1D) chains, doped charges are stored in energy levels or states such as solitons, polarons and bipolarons, which ascribe to charge and their surrounding lattice distortion. Figure 1.3 (a) shows the generation of polaron, bipolaron and bipolaron bands as a result of doping level in various CPs. In case of doping, on removal of an electron from polymer backbone, polaron ($\frac{1}{2}$ spin) is formed, then on removal of second electron with increment in doping, both polarons formed recombine to form spinless bipolarons. With further enhancement in doping levels, the bipolaron levels overlap and eventually form continuous bands.

PA with a degenerated ground state has slightly different conduction mechanism. As shown in Figure 1.3 (b), soliton exists as charge carriers which are created due to the solitary wave defect. In pristine trans-PA, neutral soliton (unpaired π -electron or radical) exists which leads to appearance of localized electron states at the middle of band gap which is half occupied (neutral soliton) and empty in case of charged soliton (positively and negatively charged). Figure 1.3 (c) displays the formation of two charged solitons on a chain of trans-PA. As a result of the degeneracy, the two charges forming in trans-PA can readily separate [6,7].

PA though remains the most crystalline conductive polymer till date. However, its easy oxidation in air, sensitive to humidity and requirement to be doped externally diminishes its applicability for ambient device testing. For these reasons, it was necessary to focus on the polymers that can be doped during synthesis and are stable in

air. Some, heteroatom containing polymers like PPy, PT, PAN were synthesized and their conductivities were found to be 10^4 Scm^{-1} after they were ordered via any suitable method of film formation technique [1,2,6,7]. These polymer films without competing with inorganic counterparts, are being utilized in flexible and large area based devices. CPs are intrinsically amorphous in nature, so their assembly or ordering from their isotropic melt (solution state) to their solid (film) state is very essential to be utilized in these large area based devices.

1.3 Conducting polymer composites

Nano science field has blossomed due to development of various nanomaterials in various application areas due to their structural features. The advent of polymer nanocomposite formation particularly the incorporation of inorganic nanomaterials as conducting fillers has attracted research attention due to their improved properties and forthcoming applications in the aerospace, construction based, automotive and electronic industries [6-8]. In this regard, composite formation of CPs and conducting nanomaterials have recently exhibited reasonably high electrical charge transport properties, often exceeding the analogous results when measured alone for pristine semiconducting polymer layers (film). As the significant fold enhancement in the device performance could be obtained even for a minute concentration of the conducting filler added into semiconducting polymer matrix, these nanomaterials (filler) enhance the charge transport properties as well as uniformity of the large area film of the polymer. These nanomaterials actually enhance the performance of the active semiconducting polymer layer by enhancing the polymer crystallinity (ordering)

[6-8]. They act as in-situ template for ordering (π - π stacking) of polymeric chains during film formation. This property elicits intense research on various potential nanomaterials that can multiply polymer performance. Amongst the majority of inorganic nanomaterials developed, 2D nanomaterials particularly transition metal dichalcogenides (TMDs) and transition metal nanoparticles (NPs) have been described here with their rewards [9-15].

1.3.1. Modified polymers with 2D TMD nanomaterials

Layered materials are an unexploited foundation of 2D systems that possess distinctive material properties such as excellent electronic properties along with high specific surface areas which are prerequisite for sensing, energy storage, catalysis, and large area display electronic device applications [9,10]. Although graphene is the most renowned layered material, TMDs and other 2D compounds have also emerged their importance. However, the scarcity of simple procedures for their exfoliation into mono or few stacked layers has hindered the progress of these 2D materials. Among TMDs, molybdenum disulfide (MoS_2) displays highest conductivity but associated with the scalability cost issues to a major extent [9]. Till date there are various reported synthetic procedures for MoS_2 nanosheet morphology such as micromechanical exfoliation, liquid phase exfoliation, physical vapor deposition, chemical vapor deposition, chemical solution process, etc. that require severe experimental conditions [9-12]. To overcome this, hydrothermal route that is a solution-based process yields MoS_2 nanosheet morphology in mild conditions with best control and maximum exfoliation in the liquid phase. The details of its synthesis are discussed in chapter 2. There are plenty

reports available on composite formation of CPs with MoS₂, for instance, Kanatzidis et al. have reported encapsulation of polyaniline in MoS₂ resulting in enhanced charge transport properties [16]. Recently, Tang et al. have utilized MoS₂ nanosheets as template for oxidative polymerization of pyrrole (Py) for supercapacitor application [17]. These reports clearly demonstrate the increasing interest towards MoS₂ nanosheets polymer composite. In this regard, we have employed another N-containing polymer i.e. polyindole (PIn) in which MoS₂ nanosheets are dispersed uniformly via Langmuir-Blodgett (LB) utilized for the first time [18]. This is discussed in detail in chapter 5.

1.3.2. Modified polymers with transition metal based NPs

Due to their integration of the physicochemical characteristics of organic polymers with the electrical characteristics of metal NPs, CPs have attracted a significant amount of attention in the recent decade [13-15]. Noble metal-based conducting fillers possess intrinsically high electrical conductivity. Various morphologies of NPs obtained under different wet chemical synthetic conditions is one of the most important factor that affects the conductivity of the polymer composite through percolation networks [19-21]. Moreover, these NPs can be transferred from aqueous to organic solvents and vice-versa according to the polymer dispersed phase [19,22,23]. This can subsequently facilitate their solution-based processing for electrodes and device fabrication. Recently, metal NPs like gold (Au), silver (Ag), etc. incorporated in polymer matrix have been widely studied for potential applications in fuel cells, batteries, capacitors, photovoltaic, electro catalysis, bio-sensing, and anti-corrosion coatings because of their unique properties at nano level [8]. Development of ordered nanostructure of polymer

composite materials effortlessly by sustainable ordering methods is being primarily focused [19-27]. NPs when incorporated into CP matrix, their assembly and molecular packing (π - π stacking) via controlled ordering technique such as Langmuir-Blodgett method have drastically improved, thus leading to augmented charge transport properties via charge transfer interaction [8]. NPs, especially Au and Ag, possess unusual properties in the mesoscopic assembly that differ largely from their isolated and the bulk phase [28-32]. The molar extinction coefficient of Ag-NPs is far greater (100 fold) than that of the Au-NPs, in spite of the fact that, in comparison to Au, Ag-NPs are slightly susceptible to chemical degradation and surface oxidation in aqueous medium. This advantageous property of Ag-NPs has been explored for nanohybrid formation with CPs in many reports [8,30-32].

1.4 Assembling/ordering techniques for polymer and its composites

1.4.1 Electronic device structure and assembling/ordering of the semiconducting layer

A simple electronic device structure typically consists of a multilayer structure where each layer in the stack is formed by a separate film forming methodology. To start with, the bottom most layer indium tin oxide (ITO) covered glass substrate is a transparent anode with high electrical conductivity. Second layer is the semiconducting polymer layer and third top most layer is the metal (usually aluminium) cathode layer. The layer of interest here is the semiconducting polymer layer that shows variation in charge transport properties when assembled or fabricated via different solution processable film forming techniques. At present, a level has been attained at which an initial product application of organic CPs can be considered [1,2,6-8]. In particular, CPs

deposited by highly controllable deposition method remain the best performers due to their specific molecular electronic properties and their well-ordered films. However, there have been substantial improvements in solution processed CPs and their mobilities at present are only few orders (~1 or 2) behind than those of their vapour deposited films [1,2,6-8,33,34]. These solution processing techniques are associated with cost advantage as they eliminate the use of expensive as well as time consuming vacuum chambers. It is evident that till date there are so many developed solution processable film forming and ordering techniques, however few of them have paved their way into the long range ordered and large area based electronics world [34]. Three reasons can be accounted for this. First, techniques such as spin coating, drop casting, doctor blading, etc. demand material in large quantities. Second, probability of obtaining highly ordered and same quality (uniformity and thickness) of film each time decreases and third, most techniques developed in laboratory trials are unsuitable for large scale uniform film production. All these factors led to exploration of more facile techniques that may overcome the above issues.

Before discussing various kinds of film forming techniques, it is of utmost importance to understand the orientation of the polymer chains in order to exploit their intrinsic charge transport properties and anisotropy associated with them. During the device manufacture, it must be kept in mind that there should be minimum leakage current and maximum current efficiency. This can only be accomplished when there is reduction in parasitic current pathways which in turn can be achieved by proper orientation and alignment of the polymer chains with enhanced molecular interactions. At molecular level, charge transport interactions within crystalline domains are

operational at two levels i.e. at intrachain and interchain levels. Intrachain charge transport is mainly influenced by the extent of conjugation i.e. more the planarity and lesser the chemical defects in polymer backbone, higher is its regioregularity and thus efficient π -orbital overlapping leading to enhanced conjugation [35]. Whereas, interchain charge transport (charge hopping) relies remarkably on the π - π stacking between adjacent polymeric chain segments.

To understand the significance of ordering on the device performance, most improvements of ordering the polymer chains have been carried out through materials that represent the state-of-the-art such as poly (3-hexylthiophene) (P3HT). One of the pioneer works on P3HT as solution processable (alkyl chain enhances solubility) semiconducting active layer demonstrated mobilities in the range of 10^{-5} - 10^{-4} when spin casted on substrate [36]. Later in the year 1992-93, research group led by R. D. McCullough designed a regioselective synthesis method to control the regioregularity of P3HT [37,38]. In simple terms, regioregularity in a polymer occurs when it contains only head-to-tail (H-T; 2,5') couplings, whereas those contain head-to-head (H-H; 2, 2' coupling) or tail-to-tail (T-T; 5,5' coupling) are denoted as regiorandom (rr). Regioregular (RR) P3HT polymer backbone displays more planarity and better conjugation extent due to negligible steric interference from the side group (alkyl chains) adjacent to each other. While, rr-P3HTs possess randomly twisted polymer backbones due to the steric hindrance arising from neighbouring alkyl chains interactions. The mobility of RR-P3HT drop casted on substrate was reported as $0.045 \text{ cm}^2/\text{Vs}$ which was comparatively higher than the rr-P3HT [39]. Later RR-P3HT was spin coated on substrates by Sirringhaus et al. and observed that there was enhancement

in the mobility to 0.05- 0.1 cm^2/Vs [40]. Pandey et al. have shown the mobility enhancement of P3HT from 10^{-5} (rr) to 10^{-2} (RR) cm^2/Vs by adopting the appropriate ordering technique [41]. However drop casting, spin coating, printing and other solution casting techniques are perhaps the most promoted, user friendly processing techniques at industrial level for fabricating soluble polymeric semiconductors, the LB technique has also been investigated for the film formation of P3HT based FETs [42]. The charge carrier mobility observed for rr-P3HT LB films was very low (10^{-7} - 10^{-4} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) whereas maximum mobility for RR-P3HT was obtained as $0.02 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. These results demonstrate a remarkable difference in mobility indicating the significance of polymer ordering during synthesis as well as the film forming technique adopted to fabricate the active layer. Overall, if the polymer is randomly organised i.e. in disordered state, then device performance is poor. Whereas, when the same polymer is ordered via suitable ordering technique, π - π stacking of the chains is facilitated that leads to better connectivity and better performance.

Research group led by Brinkmann have intensively investigated the orientation of P3HT and its morphology via transmission electron microscopy (TEM) adopting directional epitaxial crystallization method [35]. In this this approach, they have used a crystallisable aromatic solvent, 1,3,5-trichlorobenzene (TCB), in which the polymer was dissolved and spread onto PTFE that guided the orientation of TCB on crystallization. Schematic shown in Figure 1.4 (a) demonstrates the semicrystalline nature of oriented P3HT (backbones shown in blocks) with alternating crystalline zones separated by interlamellar amorphous zones. Same result is shown in Figure 1.4 (b) TEM micrograph in which fringes revealing film crystallinity (encircled in red) are

separated by amorphous zones. In reports by Jimison and coworkers, the charge transport anisotropy in these oriented P3HT films was explored and found that charge mobility in the direction (parallel) of the polymeric chains was around $\mu_{\parallel} > 10^{-2}$ cm^2/Vs , however mobility observed in the perpendicular direction to the polymer chains produced $\mu_{\perp} < 10^{-3}$ cm^2/Vs [43]. The reason of this anisotropy was ascribed to the presence of grain boundaries among fiber-like domains. These reports clearly demonstrate that the orientation of CPs remains a critical issue for better device performance that needs more attention particularly in thin films plastic electronics.

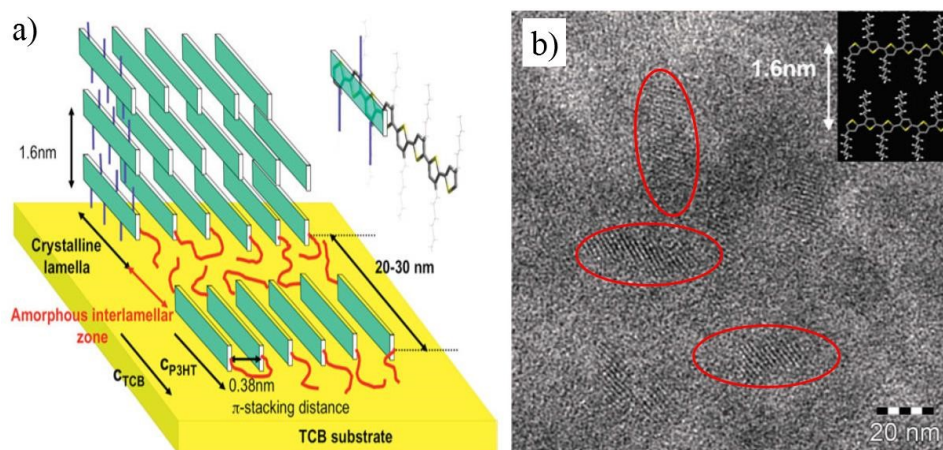


Figure 1.4 (a) Schematic representation of the semi-crystalline structure of P3HT (b) High resolution (HR)-TEM micrograph showing the packing of P3HT chains, (inset: SAED pattern) [35].

1.4.2 Self-assembly of polymers

CPs are basically the π -conjugated structures inscribed with various functionalities that promotes internal, weak but specific non-covalent interactions (e.g. H-bonding, hydrophobic, π - π interactions) among themselves to form organized hierarchical architecture. Initially in the solution state (isotropic melt) as shown in

Figure 1.5, polymer chain or backbone (represented as block) are randomly oriented, isolated from one another and do not crystallize. Gradually, the polymer chains start organizing or assembling themselves into smaller regions of high order more clearly defined as molecular self-assembly [44,45]. Molecular self-assembly is the “Spontaneous association of molecules under equilibrium conditions into stable, structurally well-defined aggregates joined by non-covalent bonds” as defined by Whitesides [45]. Later, if external stimuli (ordering technique) is provided to these crystallites, they arrange themselves into long range of order. These forced assembly or externally guided techniques are in order employed at synthesis and post synthesis level that are discussed in section 1.4.4.

Ordering of polymers at interfaces has different features to those observed in bulk, as the interface confines the self-assembly process in 2D space and is responsible for anisotropy observed in optical and electrical properties [46]. In this regard, we have employed ordering of polymers at three interfaces like liquid/liquid, liquid/solid and gas/liquid interfaces. Liquid/ liquid interface between two immiscible solvents is utilized at the synthesis level for interfacial polymerization and phase transfer of various nanomaterials from aqueous to organic polymer solutions [47-51].

He et al. demonstrated the synthesis of AgNPs via liquid-liquid (water-chloroform) interfacial method in which 2D ordered superlattices were formed as shown in TEM image (Figure 1.6) [52]. Liquid/solid interface deals with the utilization of templates such as metal surface, 2D materials (TMDs), nanoparticles, etc. present in solution guiding the growth of ordered array of polymers onto them [16,17]. These kind of

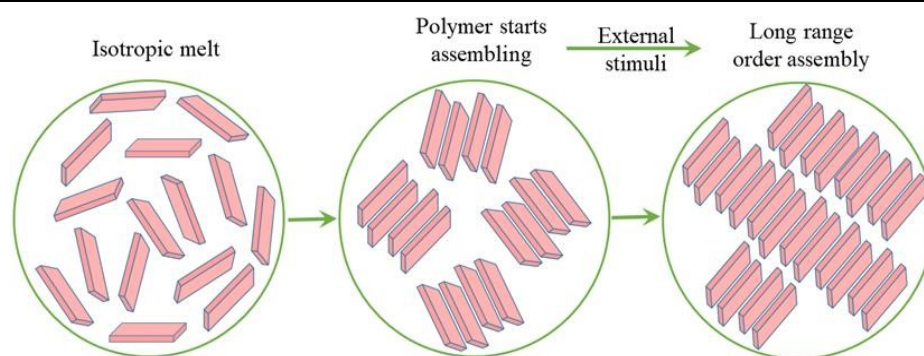


Figure 1.5 Arrangement of polymer backbone from solution (bulk) to ordered array.

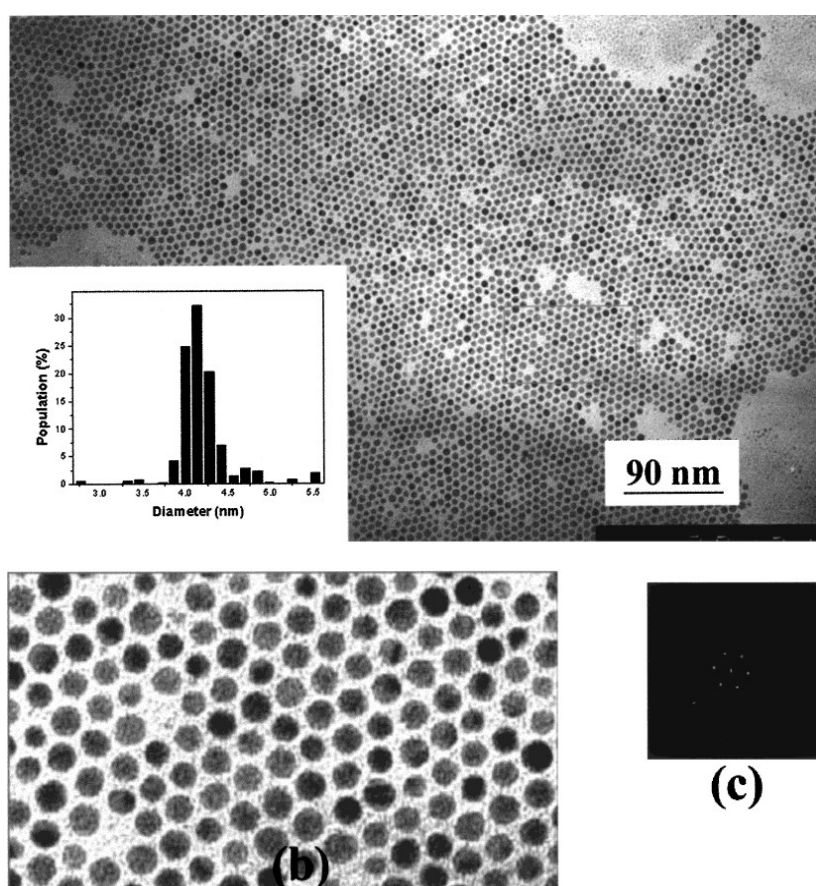


Figure 1.6 (a) TEM image of AgNP superlattice, histogram (PSD=4.1±0.23 nm) (b) HR-TEM (interparticle distance=1.51 nm) (c) 2-D Fourier transform spectrum of (b) [52].

interfaces have been discussed in detail in chapter 5. The third one which is gas/liquid interface is usually employed post synthesis for ordering and film formation of the polymer and its composites. Best example is the LB technique that employs air-water interface to assemble various materials providing their large ordered area film [53,54].

1.4.3 Assembling techniques at synthesis level

Polymer assembly techniques at synthesis level includes simple bottom-up, and cost-effective synthetic approaches such as chemical, template, electrochemical and interfacial polymerization each having its own advantages and some drawback [8,34,45,47,49,50,51]. Chemical method of polymerization yields long chain polymer in bulk with problem of removal of extra ion impurity after synthesis, low crystallinity of polymers with minimum possibility of their self-assembly [2,6-8]. Second technique is the template based technique that yields array of aligned polymeric chains with better possibility of self-assembly and crystallinity. Removal of template post-synthesis is a problematic job. Next method is the electrochemical method that offers potentially controlled and crystalline polymer with better possibility of self-assembly. Low yield and loss in redox activity (i.e. over potential) after deposition on electrodes after polymerization are the drawbacks related to this method. Interfacial synthesis is the morphology-controlled synthesis at interface of two immiscible solvents that yields uniform morphology with maximum possibility of self-assembly [6,44]. The only issue related with it is low yield in comparison to chemical method.

1.4.4 Polymer assembly and ordering at post synthesis level

In the previous section 1.4.1, significance of ordering after polymerization has been

discussed with reference to published reports. Here in this section, before indulging into detailed explanations of individual solution processable film forming techniques, it is must to understand the significant role of the substrate in orientation of the polymer layer [34,35,53,54]. Prior to film formation, polymer is dissolved in an organic volatile solvent so that it can evaporate on the substrate following its pattern leaving the film behind. Based on this, substrates utilized for film formation can be divided into two types: hard (static) and soft (mobile) substrates. Hard (static) substrates are generally associated with the techniques like drop casting, spin coating, doctor blading, spray coating, etc. in which the polymer solution is spread/deposited directly onto hard substrates like ITO, glass, quartz, etc. and then allowed to dry. Whereas, another classification is soft substrate in which the polymer solution is first spread on liquid surface, allowed to dry forming a film over it and then lifted onto hard substrates. In both these procedures, polymer orients itself according to the nature and orientation of the substrate. The former methods are no doubt user friendly but they involve loss of material and mostly result in non-uniform film thickness. So, the latter approach of utilizing soft substrates first and then transferring on hard substrates gives ample of time to polymer molecules to open and assemble themselves via non-covalent interactions. These methods utilize interfacial surface tension facilitating the polymer film orientation. Some of the techniques that work on this principle are LB or Langmuir-Schaefer (LS) and floating film transfer method (FFTM) [18,28,29,42,53-58].

1.4.4.1 Air-water interface based LB method

Polymer solution drop casted on the liquid surface floats at air-water interface forming a

film that is called Langmuir film. The film whether lifted vertically or horizontally onto substrate got its name as LB or LS deposition process. LB system first developed by I. Langmuir and K. Blodgett (awarded noble prize in 1932) offers molecular level ordering and formation of large area and uniform thickness (nm to μm) films [53,58]. This technique based on air-water interface assembly of polymer monitors its film layer uniformity and thickness precisely with the help of Wilhemy plate (sensor) fitted to a balance. The plate senses the differential surface tension. Before going into its working principle, terminologies related to it are must to be understood. They are as follows:

1.4.4.1.1 Terminologies

Amphiphiles: Amphiphiles are chemical compounds that possess both hydrophobic (water repelling) and hydrophilic (water loving) parts and generally insoluble in water. The hydrophobic group is usually a large hydrocarbon chain $(-\text{CH}_2)_n$ with $n > 4$ and hydrophilic group is a positive, negative or neutral (zwitterionic) charged moiety such as anionic carboxylates (RCO_2^-), cationic amines (NH_3^+), neutral phospholipids, enzymes, etc.

Langmuir monolayer: A Langmuir monolayer is defined as a one-molecule thick layer of an organic material (insoluble) spread onto water subphase that are extensively studied prior to deposition of LB (or LS) films on solid substrates.

Gibbs monolayer: Gibbs monolayer is different from Langmuir monolayer only in terms of partially solubility of the amphiphile and rest is structurally similar in both cases. In Langmuir monolayers, molecules are trapped (suspended) at the air-water

interface. Whereas, in Gibbs monolayer molecules jumps in and out of the water subphase mostly in the case of the surfactants and proteins.

Surface tension: Surface tension (γ) is a unique property of liquids that arises due to unequal cohesive forces between molecules on or near the surface. This unbalanced force tends to contract the water surface resembling a stretched elastic membrane.

Surface Pressure: Surface pressure, SP (π) is defined as the difference between the γ of ultraclean air-water interface and the material (impurity) organic material spread onto it. In other words, it describes the change in γ of water on addition of any at the interface. $\pi = \gamma_0 - \gamma_f$, where γ_0 and γ_f are the initial and final surface tension of the water surface.

LB film deposition on substrate: An LB film consists of one or many monolayers of an organic material (amphiphile) floating on water subphase, deposited on a solid substrate by vertical dipping (and lifting) the substrate in the water subphase. Molecular orientation on the film transferred over solid substrate may vary as per its nature i.e. hydrophilic or hydrophobic. Based on this, there are three types of film structures (i.e. Z, Y and X-type) shown in Figure 1.7 (a-c) that are formed on vertical dipping of the substrate.

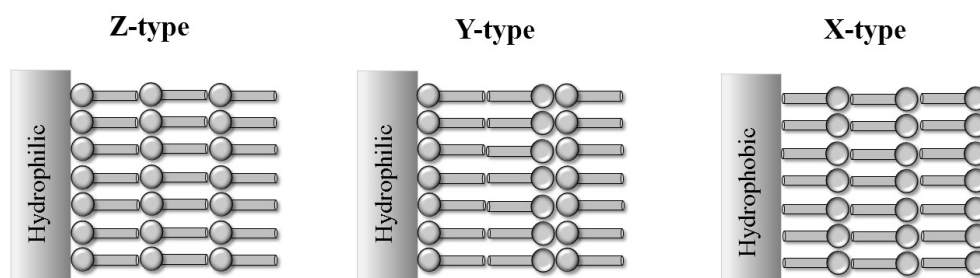


Figure 1.7 Deposition type on hydrophilic and hydrophobic substrates for transfer of Langmuir monolayers: (a) Z-type, (e) Y-type, (f) X-type.

The substrate (must be hydrophobic in nature) when stamped horizontally on the water surface, it touches the monolayer and when moved horizontally upwards, it lifts the monolayer along with it. This is Schaefer style of deposition and the film is termed as LS film [53,54].

Transfer ratio: The Langmuir films being transferred onto the substrates is monitored by another term called transfer ratio (t_r) which is defined as ratio of decrease in area (A_m) of monolayer during deposition to the area (A_s) of substrate to be covered. So, $t_r = A_m / A_s$ and $t_r = 1$ for ideal case.

1.4.4.1.2 Langmuir floating film pressure (π)–area (A) isotherm studies

For monolayer film deposition in the Langmuir method, it is very crucial to understand its formation mechanism. Figure 1.8 describes the mechanism of solvent spreading phenomenon at the air-water interface in Langmuir technique that leads to monolayer formation. For step 1, when the material (polymer) is dispersed in low surface energy solvent (hydrophobic organic solvent), it spreads easily on high surface energy solvent (water) due to surface tension gradient ($\Delta\gamma$) developed at the interface. This phenomenon is known as the Marangoni effect [60,61]. As shown in 1C, spreading speed of hydrophobic solvent is defined by a term spreading coefficient (S) that is equal to $\gamma_1 - \gamma_2 - \gamma_{12}$ (γ_1 and γ_2 denote surface tensions of water (1) and sample dispersed in hydrophobic solvent (2); γ_{12} is the surface tension at the interface of both 1 and 2). If this quantity (S) comes out to be positive then the solvent spreads uniformly forming a material monolayer on the water subphase, else the solvent remains in stagnated form. Hence solvent (2) selected for material dissolution is of key attention that is chloroform

in this entire work. Then values of S is found to be 12.9 mN/m (γ_1 (water) = 72 mN/m , γ_2 (chloroform) = 27.5 mN/m and γ_{12} = 31.6 mN/m) which justifies chloroform as an appropriate solvent for dispersing the sample. Solvent spreading phenomena is accompanied by simultaneous solvent dissolution (step 1 B) thus leaving the material suspended at the interface. Thus step 1, is the phase when material orients itself with simultaneous solvent evaporation and dissolution. It is the pivotal step that makes this air-water interface technique supreme over other solution processing methods. Other steps (2-4) include barrier compression to a certain optimum pressure (validated from isotherm) at a very slow rate, then after vertical deposition or horizontal stamping of the substrate to be coated [53,54]. A gap of around 30 min is encouraged between step 2 and 3 as it allows the molecules to rearrange themselves at the interface.

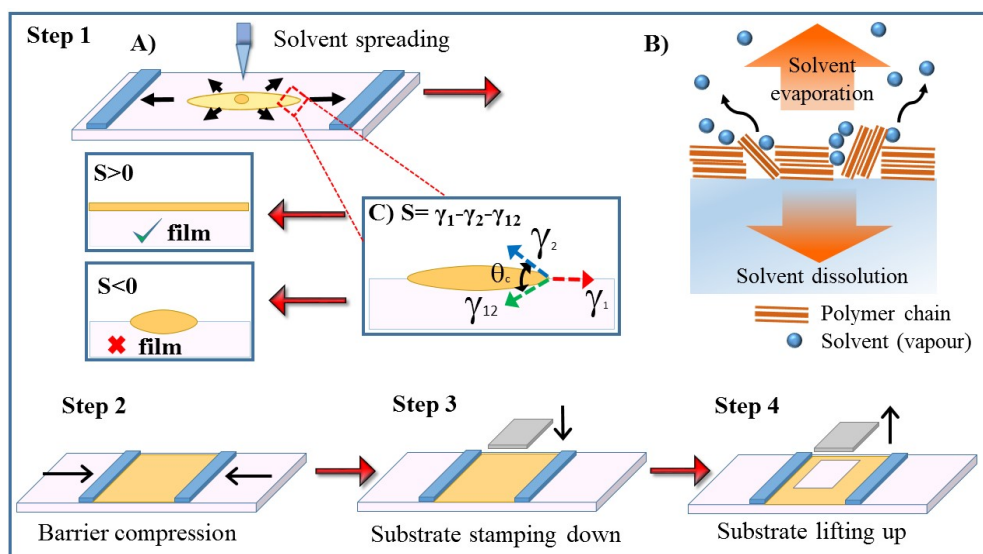


Figure 1.8 Various steps involved in Langmuir technique. Step 1: A-C) solvent spreading, Step 2: Barrier compression, Step 3: Substrate stamping (Schaefer style), Step 4: Substrate lifting.

Before going for film deposition (step 2-4), it is of utmost importance to investigate the film property via studying its pressure (π) vs. area (A) isotherm (π - A) at air-water interface. Precise control of the SP, barrier compression speed and deposition speed are very important in certifying uniform and homogenous layer deposition. Isotherm is the curve obtained between SP against area per molecule (at fixed temperature) on slowly compressing (\sim rate of 10 mm/min) the monolayer film formed at interface [53,54,58]. As the monolayer is compressed slowly, it undergoes various phase transformations (slope changes) analogous to gases, liquids and solids marked by kinks or sharp bends shown in Figure 1.9. Phase transition is recognized by monitoring the SP as a function of the area occupied by the film. On this basis, different four regions have been identified. First, at low SPs, the monolayer consisting of far apart molecules behaving like gaseous phase with negligible interaction marked as Region I. Region II denotes liquid phase in which molecules approach each other and assemble themselves. Further

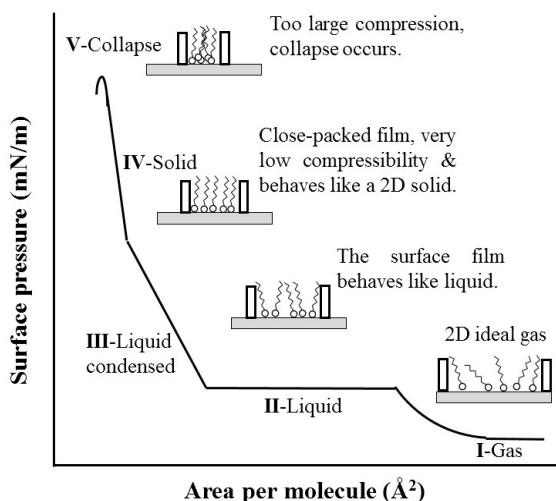


Figure 1.9 SP vs. area (π - A) isotherm depicting various monolayer phase transitions.

with increase in SP, a clear transition from liquid to liquid condensed in which molecules are just close enough forming compact arrangement in Region III. Then Region IV defines the solid phase in which monolayers just start overlapping due to excess pressure. With further increment in SP, monolayer film becomes unstable and a kink is observed with sudden decrease in pressure. A very keen observation of π -A isotherm is very important as it is the signature of molecule whose film is to be deposited. It is important to note that all these phases for a particular molecule may not be clearly defined as they strongly rely on the compression rate and temperature.

1.4.4.1.3 Stability (compression-relaxation) curve

Langmuir films deposited from single compression step on solid substrates immobilize the monolayer structures that may not be sometimes stable at the air-water interface. The stability of these films can be investigated when the film is monitored under constant area over time. Stability of the films formed is the deciding parameter for uniform film formation before its deposition, which is done by monitoring the surface pressure compression-relaxation process [29,58]. Stability curve helps to predict how stable is the film formed. If the area under curve is lesser than the other material, this denotes that former takes lesser time to come back to its original state, so it is more compressible as compared to latter which can be accounted to stronger intermolecular (non-covalent) interactions between molecules [29,53,54].

LB method is amongst the best methods which involves compression of the floating monolayer uniaxially leading to nanostructures assembly and packing over the water subphase, overcoming the drawbacks of other popular polymer processing

techniques. This technique is not only for amphiphilic molecules but also various other organic and inorganic nanomaterials have been ordered and deposited via this technique [53,54,58]. Moreover, some previous reports state that the film uniformity of non-amphiphilic polymer (stable) films formed at the air-water interface can be improved by varying the substrate nature and lifting style employing Schaefer style method [53,58,59,62]. LS method minimizes the disruptive force that may disturbing the uniformity of rigid monolayer during vertical upliftment.

1.4.4.1.4 Self-assembly at air-water interface

Self-assembly is recognised by molecular interactions (non-covalent) and their orientations that are highly controlled at air-water interface in this floating film methodology and confined in 2D spaces [54,58,62]. Consequently, polymer orientation at the interface displays different features that cannot be observed during self-assembly in the bulk phase. In the process of forming floating Langmuir monolayers of CPs (i.e. after spreading onto subphase), various secondary interactions (π - π interaction, hydrophobic, electrostatic, H-bonding, etc.) among component molecules bring them closer forming an assembled structure in the form of small nanostructured islands. This ordering is due to self-assembling properties of the material. Later the barrier compression, which is very slow enough to disturb the assembled structures, forces these nanostructured islands to assemble into large area ordered films. Finally, the Langmuir films are lifted on the solid substrates.

1.5 Electronic device applications of CPs and their composites

The electrical conductivity of organic semiconductors is one of the crucial parameters

that directly influences the performance of the final electronic devices [63-68]. In this section, we are concerned with the basic physical principles, electrical properties, and applications of the metal-semiconductor contacts and devices. It is well known that device technology mainly depends on metal-semiconductor (M-S) junctions, for which Schottky barrier height is a key electronic parameter to be understood. Schottky contact defines the junction of metal and semiconductor whose properties strongly rely on the interface of the two electrodes utilized in diode fabrication and their work function differences leading to formation of rectifying contact [66-68]. Schottky contacts are being utilized as “test vehicles” to investigate the physical and electrical parameters of the semiconductor layer for a widespread device applications. To illustrate, electrical parameters derived from a Schottky diode helps to predict the defects in the bulk as well as interfacial properties of an M-S structure. For that reason, it is crucial to get the basic concepts of the M-S interface so that improvements can be made in fabricating methods of polymer for developing Schottky contacts for device applications. Conduction in case of Schottky diode is mainly controlled by the thermionic emission of majority carriers produced by difference in work functions of the metal and semiconductor contact [6-8]. Differences in work function at M-S interface leads to classification of Schottky barrier into three types-

Type-I: Metal work function (Φ_m) is greater than semiconductor (n-type) work function (Φ_s), ($\Phi_m > \Phi_s$):

When semiconductor (n-type) comes in contact with metal, there is flow of electron from the semiconductor conduction band (CB) (at higher energy level) into metal to

align the Fermi energy levels of the two. This results in bending of CB and valence band (VB) of semiconductor at the M-S interface as shown in Figure 1.10. CB of semiconductor displays upward bending at interface due to movement of electron from

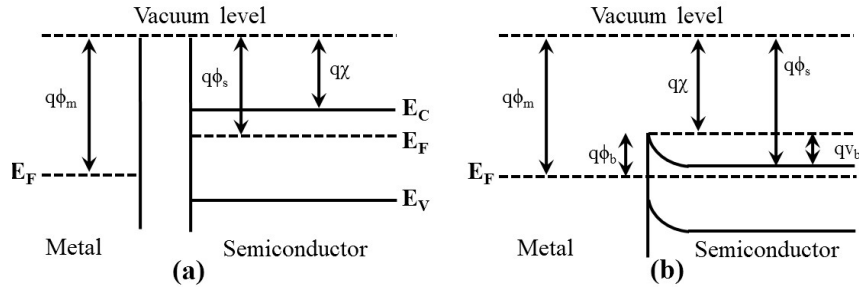


Figure 1.10 Energy level diagram of M-S (n-type) interface (a) before and (b) after the contact.

semiconductor to metal establishing thermal equilibrium, which leads to creation of depletion region. In basic terms, the work function difference is depicted by the built in potential difference (qV_{bi}) developed across the depletion region.

$$qV_{bi} = \phi_m - \phi_s \quad (1.1)$$

The barrier height ϕ_b is then defined as:

$$q\phi_b = q(\phi_m - \chi) = qV_{bi} + (E_C - E_F) \quad (1.2)$$

$$\text{Since,} \quad q\phi_s = q\chi + (E_C - E_F) \quad (1.3)$$

Type-II Semiconductor (p-type) work function (Φ_s) is greater than metal work function (Φ_m), ($\Phi_s > \Phi_m$):

In this type, when a semiconductor (p-type) comes in contact with a metal, the flow of electrons from metal to semiconductor till the Fermi levels in the two get aligned. As

the electron moves to semiconductor, it eliminates the hole from VB, thus leaving behind ionized charge of acceptor. These negative charges accumulate upto a thickness of W in the semiconductor. Whereas, the positive charge on metal is confined upto a distance of an atomic layer behaving as a surface charge. The dipole formed due to layer of charges form an electric field as shown in Figure 1.11. The barrier height ϕ_b and built in potential is then defined as:

$$q\phi_b = \chi + E_g - q\phi_m \quad (1.4)$$

$$qV_{bi} = \phi_s - \phi_m \quad (1.5)$$

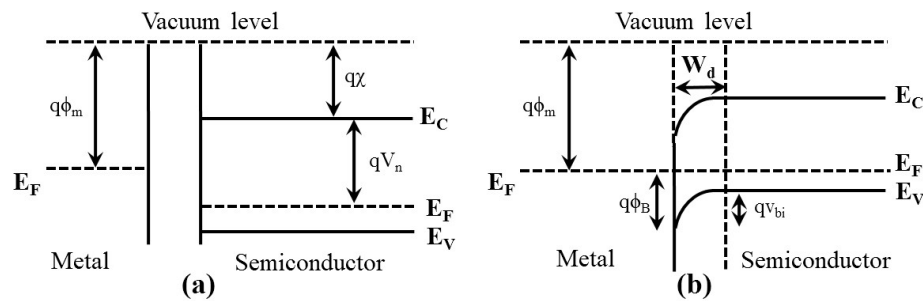


Figure 1.11 Energy level diagram of M-S (p-type) interface (a) before and (b) after the contact.

Type III: Ohmic contact- When semiconductor (n-type) $\Phi_s > \Phi_m$ and semiconductor (p-type) $\Phi_s < \Phi_m$

When a semiconductor (n-type) makes a contact with a metal such that $\Phi_s > \Phi_m$, the flow of electron occurs from metal to semiconductor till the Fermi levels get aligned in the two. Negatively charged electrons accumulate in the semiconductor region within a Debye length thickness basically as a surface charge. As a result, no depletion region is formed in the semiconductor region thus electrons flow from semiconductor to metal or

vice-versa without any barrier as displayed in Figure 1.12. Once a potential bias is applied to this structure, almost total voltage applied appears across the semiconductor (neutral). This kind of metal-semiconductor contact displaying non-rectifying behaviour is termed as ohmic contact.

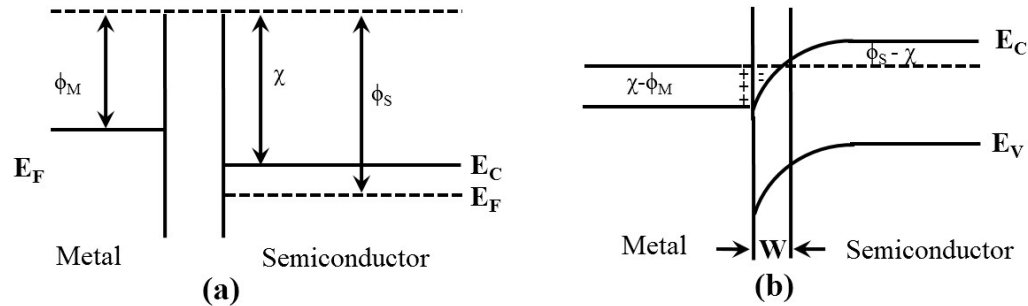


Figure 1.12 Energy level diagram of metal-semiconductor interface for ohmic behaviour (a) before and (b) after the contact.

1.5.1 Charge transport property and mechanism of Schottky diode and electrical parameters extractions from J-V characteristics

The flow of current in Schottky barrier occurs due to applied voltage or thermal effect. Charge transport mechanism across the M-S interface occurs via four main pathways. They are (1) electron transport from semiconductor into the metal across the potential barrier which is also the main process in case of moderately doped semiconductors operating at room temperature (~ 300 K), (2) charge carrier tunnelling across the potential barrier (main process for highly doped semiconductors and ohmic contact), (3) recombination of charge carrier in the depletion region, and (4) recombination of charge carrier in the neutral region, that can also be related to injection of minority charge carriers. It is well known that the electrical characteristics of Schottky diode junction

can be elucidated using standard thermionic emission-diffusion theory [18,41,63]. As per this theory, J varies with V according to the expression:

$$J = J_0 \left[\exp\left(\frac{qV}{\eta kT}\right) - 1 \right] \quad (1.6)$$

where J and J_0 denote current density flowing through the diode, reverse saturation current density; q, V, T, η , k, represent the electronic charge, applied bias voltage, absolute temperature, ideality factor, Boltzmann constant, respectively. Furthermore, J_0 is directly connected to barrier height ϕ_B as:

$$J_0 = A^* T^2 \exp\left(\frac{-q\phi_B}{kT}\right) \quad (1.7)$$

where A^* denotes effective Richardson coefficient and calculated to be $120 \text{ A cm}^{-2} \text{ K}^{-2}$, ϕ_B denotes the barrier height. Utilizing above relations, we have extracted various electrical parameters such as barrier height ϕ_B , saturation current density J_0 , and ideality factor η of the devices fabricated.

1.6 Polyindole

1.6.1 Structure and properties

Indole is an aromatic nitrogen atom containing heterocyclic molecule with structure consisting of a five-membered pyrrole ring fused with six-membered benzene ring. Historically, it was first synthesized from indigo dye and oleum so got its name indole. It is an abundantly found compound in nature such as in natural jasmine oil (2.5 %), product of bacterial physiological process, key component of auxins and many alkaloids [69]. Consequently, plenty of research has been done towards the polymerization of

indole and its derivatives for various applications in areas of drug delivery, sensor applications, battery electrode, electrocatalysis, anticorrosion coatings, and electronics [69,70]. The key advantages of polyindole over other conducting polymers are its excellent photoluminescent properties, excellent electroactivity, quick switchable electrochromic activity, high thermal stability, slow degradation rate, and air stable conductivity, etc. These above said properties, if utilized along with uniform film formation, could be applicable in large area based electronic devices. Despite of possessing these above said properties, it lacks behind in its utilization for large area flexible electronic devices only due to partial solubility in common organic solvents. This issue has been addressed by adopting co-solvent methodology later discussed in the thesis.

1.6.2 Polyindole synthesis

1.6.2.1 Chemical oxidative synthesis

Polyindole can be synthesized via oxidative polymerization of an indole monomer in presence of oxidizing agent like FeCl_3 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, KIO_3 and H_2O_2 in a suitable solvent like acetonitrile (CH_3CN), chloroform (CHCl_3), ethanol ($\text{C}_2\text{H}_5\text{OH}$), methanol (CH_3OH) or water/ethanol miscible solvents [69-72]. Other parameters that play crucial role during chemical synthesis are reactant concentrations, temperature, nature of the oxidant, solvent and temperature. This method offers bulk synthesis of the polymer at low cost. Figure 1.13 displays the polymerization mechanism of indole via radical-radical mechanism. Initially a monomer is oxidized, producing a cation radical species that combines with another radical cation yielding a dimer dication. Consequently, loss

of two protons occurs to produce a neutral dimer that undergoes further oxidation steps resulting in polymer as the end product [71,72].

1.6.2.2 Electrochemical synthesis

Electrochemical methods for PIn synthesis are mainly performed in a three-electrode cell assembly systems consisting of working, counter and reference electrodes dipped in monomer solutions of CH₃CN, dichloromethane (CH₂Cl₂), ionic liquids, etc.[70,73-76].

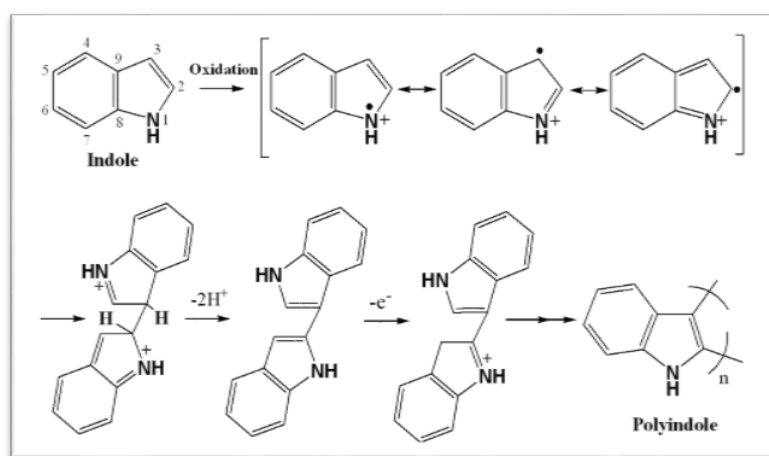


Figure 1.13 Oxidative polymerization mechanism of indole.

Though the method produces polymer in low yield but associated with the merits such as high chemical purity, redox activity, thermal stability and slow degradation rates.

1.6.2.3 Interfacial synthesis

The interfacial polymerization of PIn is carried out at the interface of two immiscible liquids (aqueous/organic solvent) where monomer is dissolved in organic phase and oxidant such as FeCl₃ and (NH₄)₂S₂O₈ is present in the aqueous phase. The monomer and oxidant react at the interface producing assembled polymer layer [51,69,77,78].

This method facilitates the morphology control of the polymer forming at the interface. Koiry et al. have reported long PIn fibers formation at the stationary aqueous/ CH_2Cl_2 interface, however, when the solution was stirred and then allowed to polymerize, they obtained spherical morphology of PIn [78]. Prakash et al group also synthesized PIn via interfacial polymerization at the interface of aqueous/dichloromethane, uniform nanorods of diameter around 500 nm and few μm long were obtained [72].

1.6.3 Composites of polyindole

There have plenty of reports that demonstrate enhancement in properties of polyindole via composite formation [79-82]. Hassanien et al. have reported the formation of PIn nanowires chemically synthesized on DNA-template with enhanced conductivity [79]. Raj et al. have demonstrated remarkable capacitive performance of cobalt oxide (Co_3O_4)-PIn composite when taken as electrode material [82]. Elango et al. have reported decoration of zinc oxide (ZnO) and AgNPs on the surface of polyindole (PIn/Ag-ZnO) for antibacterial activity. Here, PIn being easy to prepare and its long term environment stability have been focussed mainly [83].

1.6.4 Polyindole electrical properties

Previous studies on electrical properties of PIn (bulk) have reported conductivities in the range of 10^{-5} to 10^{-1} S cm^{-1} [69,71,84,85]. These wide variations are most likely due to alterations in mainly three factors (1) doping level, (2) defect density, and (3) structural factors. Incorporation of different materials (dopant) with PIn to improve its conductivity include nanomaterials (2D), metal and carbon based NPs or blending it with other polymers, etc. These act as conducting fillers and have shown significant

improvement in PIn conductivity when fabricated via appropriate ordering technique [69].

1.7 Scope of the work and objectives of the thesis

There are numerous reports available on ordering of the molecules and polymers via appropriate post synthesis fabricating techniques [53,54,58]. However, for CPs a few reports are available, among which most of them are for amphiphilic (containing hydrophobic alkyl chain and hydrophilic part) molecules and polymers. If any non-amphiphilic CP is explored for ordering at air-liquid interface, it is usually mixed with surfactants (insulator) to facilitate their spreading onto water subphase thus compromising with their electrical property [53,54]. Therefore, there is need to provide a facile technique for ordering of non-amphiphilic polymers (substituted and unsubstituted) for various technological applications including large area organic electronics. So in view of above following specific objectives are proposed for study:

- Air-water interface technique (LB) for unsubstituted PIn and 5-APIn for large area ordering.
- Characterization of ordered polymer film for its applications.

Further, air-liquid interface technique is not known extensively for ordering of nanomaterials or uniform distribution of nanomaterials in ordered polymer films to form homogenous polymer nanocomposite till this work [58]. A few techniques have been recently reported for assembly at air-water interface from our group [57,61]. However, there is a need to further standardize this process (LB) for polymer nanocomposite. In view of this, specific objectives are proposed as below:

- Air-water interface technique (Langmuir) for MoS₂-polyindole and AgNP-polyindole composite for large area ordering.
- Further, characterization of ordered polymer composite film for its applications.

Apart from these, growth and ordering of these polymers at liquid-liquid (L/L) interface is also important and recently reported for conducting polymers [69,72,77,78]. This technique is having potential not only for ordering but a controlled morphology can be achieved at the interface either during polymerization or by using surfactant for size sorting of nanomaterials developed in one phase to another phase. This is a new approach for morphology control of conducting polymers or uniform size sorting of nanomaterials. In view of this, specific objectives are proposed as below:

- Interfacial synthesis (L/L) of 5-APIn with controlled morphology.
- Size sorting of AgNPs at L/L interface.