CHAPTER 1

INTRODUCTION

There is an increasing research interest in the relatively new field of conjugated polymer materials. In industrial chemistry, the area of polymerization using organized assemblies such as micelles and microemulsions is becoming an important means. Hitherto, these self-assembly techniques have been employed in organic-inorganic composites. ‘Self-assembled structures’ as ‘templates’ are also being used not only for the synthesis of inorganic materials but also for organic species. Hence, organized media can be a promising route to synthesize conjugated polymer structures. Interest in conjugated polymer synthesis has followed from the first report by MacDiarmid et al. (1971) [1] that polymers having conjugated bonds exhibit conductive behaviour. Since then, the attraction of conducting polymers to the electrical/electronic applications included the ease and low cost of their synthesis and fabrication as compared to conventional semiconductors and metals. But most of the earlier conducting polymers have been amorphous materials exhibiting low conductivities. In fact, completely crystalline ‘conductive’ polymers free of structural defects and irregularities remain a challenge even today and hence a prime target for researchers to improve the structural properties [2]. Thus structural characteristics of organic conducting polymers have demanded more attention in the light of ever-increasing application areas. In this context, it is essential to know how structural evolution takes place in conjugated polymer materials.

Although improvement of solidstate properties through high quality materials is a general goal of materials science, the best quality conjugated polymer materials are obtained by the right choice of synthetic methods. For example, electronic/electrical conductivity of polyaniline (PANI)
depends on the nature and extent of intrinsic/extrinsic (undoped/doped) structural perfection of the polymer. Higher conductivity or “metallic” behaviour of PANI which is more popularly known as conducting polymer is obtained by a doping process. How the undoped (intrinsic) PANI is nonconducting and doped (extrinsic) PANI is conducting? Looking at the existing mechanism of electrical conductivity in PANI, the simplistic observation is that the undoped PANI is amorphous or disordered, and doped PANI is crystalline or ordered; and the electrical conductivity of the doped PANI is related to the enhanced structural order promoted by the dopant ions. Higher the structural order, higher is the electrical conductivity. In other words, the PANI structure exhibits conductivity only when it is more ordered as a conjugated molecule. The conjugated conformation is essentially a long rigid planar structure, and the conjugated polymers (intrinsically electronically highly conductive polymers) are fundamentally self-organizing (ordered) system. Hence on doping, the stiff conjugated chains self-consistently force the dopant counter-ions to go into channels or molecular planes beforming long-range ordered (crystalline) structure. It is due only to their self-organization of the molecules with the charged dopant ions that are spatially removed from the quasi-one-dimensional conduction path, and hence resistive back-scattering arising out of disorder never arises. The situation is somewhat analogous to artificially layered semiconductors wherein the high mobility carriers are confined to layers spatially separated from the alternate layers containing the dopant ions. This effect is further enhanced for conjugated conductive polymers by a combination of anisotropic structure and the quasi-one-dimensional nature of the charge-transport [3].

However, doping has a saturation level beyond which the conductivity drops due to higher concentration (>50%) of dopant ions. The fact is that the excessive dopant ions become disordered charge impurities making so ineffective in scattering the conduction electrons. And, in high quality or highly ordered or molecular chain-aligned materials, the number of
charged counterion impurities are very much less and hence resistive back-scattering from them is essentially negligible. Whether it is the scattering of conduction electron in the charge-transport process or the uniform (coherent) x-ray scattering by the electron clouds, the long-range order and/or anisotropic structure is the main feature of the conjugated polymers. That is where low-, high-, or semi-conductivity of conducting polymers can be gauged at once by their amorphous, crystalline (long-range ordered/anisotropic) or semicrystalline structural characteristics using x-ray diffraction. In this way, higher crystalline order gives rise to higher charge-transport (or other chemical and physicochemical) characteristics of the polymer materials. Thus, highly ordered conjugated polymers are the ones having highly organized intrinsic characteristics. On this basis, the strive for improvement in polymer materials’ quality through enhanced structural order enables the exploration of the intrinsic charge-transport properties. It is only with the knowledge of these intrinsic characteristics, the fundamental mechanism of charge-transport process can be understood in detail in this class of conductive conjugated polymer materials.

The exact structural feature that differentiates conducting polymers from conjugated polymers is conjugation length and chain alignment of the molecules. In amorphous precursor polymers like PANI, the disordered domains exhibit low conductivity of a few S.cm$^{-1}$ dominated by localization and hopping (jumping) of electrons, while the conjugated conductive polymers including crystalline PANI having significant chain-extension and chain-alignment become metals indicating conductivities of several thousands of S.cm$^{-1}$ due to delocalized carriers. That is, when the conjugation length is sufficiently large, the conductivity reaches the maximum intrinsic level and the electronic mean free path is determined by phonon scattering from the least deviations from the regular periodic atomic spacings called crystal lattice planes (due to thermal motion of the atoms about their ideal equilibrium configuration). To avoid localization inherent to one-dimensional systems,
and to possibly improve inter-chain charge transfer promoting enhanced intrinsic conductivity, the single crystal lattice configuration or single phase order is preferred since in well-ordered/crystalline conductive polymers (with molecular chains having precise phase order), the interchain diffusion is a coherent process [4] promoting better charge-transport characteristics. Hence, conductivities more than even the best conventional metals can be achieved in conjugated (conductive) polymers if methods can be developed to synthesize oriented or anisotopic structures having higher conjugation length (higher molecular weight) and a high degree of chain perfection [5]. Thus, research to synthesize, understand, improve and stabilize the conjugated polymer structures is essential in the modern era of science and technology. It is the intent of the present thesis to study some details of molecular, crystalline and morphological features of the conjugated polymer structures.

1.0 Conjugated Polymers

Polymers are molecules that contain many atoms, typically of thousands to million. Most synthetic polymers are organic, containing carbon as an essential element along the chains. Conjugated polymers possess alternate covalent single- and (π-conjugation) double- bonds along the main backbone chains. As in metals and semiconductors wherein electrical conductivity arises from the delocalized electrons of the system, the π-conjugation of the polymer backbone having delocalized electronic states is the reason for its charge-transport characteristics. Chemical structures of such simple π-conjugated polymers, polyacetylene (PA), polyaniline (PANI), poly(paraphenylene) (PPP), polythiophene (PTh) and polypyrrole (PPy) are given in Scheme I and their π-conjugated molecular structural forms in Scheme II.

Although polymer science and engineering have traditionally been concerned with the synthesis and characterization of chain molecules
<table>
<thead>
<tr>
<th>POLYMER</th>
<th>REPEAT UNIT</th>
<th>CHEMICAL STRUCTURE</th>
<th>MATERIAL SYSTEM</th>
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<td>CH₂</td>
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<td>(PTH)</td>
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<td>POLYPYRROLE</td>
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<td>(PPY)</td>
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<tr>
<td>POLYPARAPHENYLENE</td>
<td>C₆H₄-C₂H₂n</td>
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<td>VINYLENE</td>
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<td>(PPV)</td>
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</table>

Scheme 1. Chemical structures of simple conjugated polymers.
Scheme II  The chemical conformation of the most important polymers having conjugated bond characteristics (alternate single- and double-bonds, and as well as alternate-facing or rotation of the rings)
constructed by means of covalent bonds, and over the last decade, there has been a revolution in much broader applications of the role of non-covalent interactions such as electrostatic and hydrogen bonding in the synthesis of polymeric materials. In this context, polymerization in monolayers, bilayers and liquid-crystalline regions have become the main areas of investigation. Though non-covalent bonds are significantly weaker than the covalent bonds, hydrogen bonding/electrostatic interactions exhibit better directional character; and therefore are useful in controlling the size and shape of the macromolecular arrangements. Intensive studies of molecular reorganizations in materials chemistry are giving new strategies for the assembly of large-scale structures [5A].

Along with the synthesis, identification of structures for specific materials behaviour is necessary for effective industrial development and applications in materials science. In this respect, molecular characterization is critical to the understanding of conjugated polymer structures. The existing and new polymeric materials must be characterized to understand how the structure determines their behaviour for such informations might answer fundamental questions and enable many industrial applications in the field of chemical, electrochemical, electronic, optoelectronic and optical sciences. Details of the solidstate structural characteristics of the conjugated polymers have become essential as the need to understand particularly the complicated structures of semicrystalline polymers in terms of morphology and crystallinity.

Crystallinity reinforces and stiffens an otherwise compliant amorphous polymer when oriented in thin films; even semicrystalline polymers can exhibit outstanding chemical, physical and physicochemical behaviours [5B]. The structure and behavioural characteristics of the crystal-amorphous interface and their dependence on the molecular conformations need more attention. A better understanding of chain topology such as entanglements
and the chains inter-connecting crystallites at the crystallite boundaries. Its change with crystallization conditions, and its influence on the thin film and bulk properties is thus a subject that warrants detailed studies. In this context, the study has been motivated by interests in (i) the initial organization of the monomer as a strategy for controlling polymer structure, and (ii) the use of polymerization methods to induce, stabilize, or to have the characteristics of ordered and anisotropic structures that are useful for effective and new conjugated polymer applications. In what follows, application areas which demand such fundamental investigations are listed and discussed.

1.1 Conjugated Polymer Applications

The initial promise of conducting polymers was a conductivity like copper combined with a processibility like polyethylene (PE). A vital part of the early development of plastics was the evolution of methods of polymerization to reliable high molecular weight products. Structure and mechanical properties are very sensitive to molecular weight and to a small fraction of branches or cross-links. Polyacetylene (PA) is made by a method which is analogous to the commencial polyolefins and has been shown to be a high molecular weight linear polymer. Most of the other candidates studied earlier including polythiophenes, polypyrroles and polyphenylenes have structures which are uncertain as to both molecular weight and chain-defects. Coupling reactants were particularly ineffective for producing high molecular weight products, and many aromatic polymers produced by those methods were often like more than oligomeric organic “glasses”. Hence, producing good polymers has been very demanding since then. The conducting properties have not been proved to be very sensitive to the molecular weight and structure, but many of the properties during the use of these polymers have been very dependent only on the chain microstructure or morphology.
In addition, intractability of the conducting polymers made characterization difficult, and this in turn slowed the development of better polymers. The precursor routes were very attractive because they provided intermediate polymers which were properly characterized. A precursor polypyrrole or polythiophene greatly enhanced the ability to understand the structure of the polymers produced electrochemically.

Regarding the polymer crystalline structure, it is then believed to be not very dependent on molecular weight or chain microstructure [5B]. However, the ratio of crystal-to-amorphous content is later “somewhat” understood to be very sensitive to chain regularity. On the other hand, a few percent of copolymer units or of interruption to tacticity of polymer molecule can eliminate the crystallinity, for example in vinyl polymer. These results have led to a two-phase model for the structure of crystalline-amorphous polymer after a long hard-fought battle through 1940’s and 1950’s. While this is established for flexible chain polymers, it has not been clear till 1970’s whether that model also applies to stiff-chains like the conducting polymers.

In 1970’s methods for the production of highly conducting oriented-PAs were developed and then demonstrated in 1980’s that their conductivities were caused by chain-chain hopping of the charge carriers. Later, the observed values of conductivity of doped polymers of PA, PPP, PPY, and PTh have been observed to be PA = PPP ≈ PPY > PTh, reflecting the chain-packing effects. How the conductivities of highly oriented polymers might compare with other isotropic or small chain polymers is an interesting question to ask. The production of high levels of orientation and perfection in other polymers has become a high research priority for the elucidation of the origin of the special properties of the oriented-PAs produced in silicone or liquid-crystal solvents [5C]. If such materials become available, much more sensitivity of conductivity to molecular weight and structural regularity can
then be realized! Thus, conducting polymers have become a prime point of many applications of structurally more sensitive conductive (conjugated) polymer materials.

Of the large number of possible applications of conductive conjugated polymers, the most promising and the first significant one can be mentioned in rechargeable batteries. The systems being developed during 1980's were hoped to be somewhat better than lead-acid batteries in terms of their pure laboratory performance (but can be developed far better as of today).

1.1.1 Conductive Conjugated Polymer Batteries

MacDiarmid's group has put a great deal of effort into rechargeable batteries using polyacetylene (PA) which is the first candidate of the conductive conjugated polymer systems [5]. The essential issues with respect to a practical rechargeable battery are the energy density, the power density, spontaneous discharge rate, fractional charge recoverable (reversibility) and the lifetime. Based on this and on the basis of the weight of the electrode alone, the claimed energy density was 47Wh. Kg\(^{-1}\) and the power density was 3.2 kW. kg\(^{-1}\). This result is purely due to the structural criteria; that is, high surface area is due to the fibrillar (crystalline) structure, and thus showed the capability of high power density. More specifically, in the PA (trans-(CH)\(_2\))\(_n\)/Li\(^+\) cell, the slow diffusion of Li ions within the PA fibrils limit the discharge rate of the cell and hence the battery performance.

However, PA showed instability when doped (>10% of oxidising dopants such as perchlorate) due to a loss of conjugation lengths during cyclic charging and discharging. Also self-discharge was a serious problem with 50% of the charge being lost in 5 hours, attributed to reactions between the dopant and polyacetylene. In PPP/Li batteries (using pressed
powder pellets of PPP), Li gives rather a low voltage of 0.9 V dropping to 0.4 V during discharge. Hexafluoroarsenate-doped PPP/Li gives 4.4 V but its stability was improved with electrodes of electropolymerized PPP. In PPy/Li batteries, the initial voltage of 3.5 V dropped to 2.5 V during discharge. During the first few cycles, this dropped to 30% as the Li took up the water; the self-discharge rates were 1% per day. An important factor in limiting the energy density was the need for enough electrolyte to solvate all the extra ions produced during discharge. In higher repeat-unit molecular weight polymers other than PA, the reduced energy density is possibly due to the cause of doping again. For example, in PPy-electrolyte-PPy battery, the n-doped PPy is unstable. Of course, this was avoided later by using PPy-polyanion electrode, where the charge and discharge depend upon small cations moving into and out of the electrode. A PTh-PTh battery has also been achieved. PANI has been studied as a potential battery cathode, for use with an aqueous electrode. A variety of conductive conjugated polymers can be used as potential electrodes, according to a review by Shacklette et al [6], but the question of electrolye stability has to be solved. Conductive polymer rechargeable batteries can potentially compete [7-21] with the existing batteries, but not vastly superior yet for commercial replacement.

Also, the conductive conjugated polymers should be sufficiently stable for critical applications since all applications of conducting polymers depend on the structural stability of the polymer materials. For example, the instability of the polymers to oxygen in doped polymers is due to the result of charge-transfer complex that has a low activation energy for reversible oxidation. Oxygen diffuses rapidly into the PA-like polymers which therefore can only be stabilized by pre-reaction with another dopant or by processing to eliminate structural imperfections. The processes which can contribute to the instability are: (i) the reaction of the main chain with oxygen leading to irreversible loss of conjugation and conductivity, (ii) reaction of the main chain
with its counter-ion, again leading to an irreversible loss of conjugation and conductivity; (iii) reaction with oxygen or counter-ions at hetero-atoms without loss of conjugation but with modification of the electronic structure of the polymer, and (iv) reversible or partly reversible undoping reactions of the conjugated system. However, other polymers like PThs are more stable to oxygen particularly when doped, since lower Fermi level (due to ordered lattice) prevents polymer interaction with oxygen. Also, these materials are not very moisture-stable in the doped state. The whole range of earlier conducting polymers were commonly unstable in the accelerated tests of conductivity decay [5B,5C,15]. From these reports, it is envisaged that the carbenium ion structures that are required to permit conduction in conjugated polymers must be compatible with the presence of oxygen and water, and the only practical route towards conducting polymers having environmental stabilities is certainly to seek ordered structures whose bandgap is intrinsically small enough to allow thermal excitation without the need for doping.

1.1.2 Catalysis

There is a strong interest in the use of modified conducting polymers as catalytic electrodes. Noufi [22] and Bard et al [23] have included RuO₂ and phthalocyanines in polypyrrole to catalyse photo-oxidation of water and reduction of O₂ to H₂O₂ respectively. Incorporation of a sulfonated cobalt porphyrin as an anion in PPy is claimed to give good activity for oxygen reduction [24]. Polythiophene with incorporated silver and platinum particles has been used to catalyse the reduction of H⁺ [25]. The silver, at 80% of the polymer aggregated on the polymer fibres enhanced the conductivity, while the Pt located near the film surface was found responsible for the catalytic activity. The catalytic activity was 80% higher than for a Au-Ag-Pt electrode wherein platinum and other active particles have been incorporated into
polypyrrole composition by dispersing the particles of polyvinylchloride and then electropolymerizing pyrrole in the PVC matrix [26].

1.1.3 Sensors

Considering their sensitivity to oxidation and to doping gases, it would seem natural to use conducting polymers as chemical sensors. Polyacetylene (PA) for instance readily doped by oxygen induces a large increase in conductivity than many ceramic gas sensors where conductivity changes occur often in rather poorly characterized surface layers. Higher operating temperatures, degradation of conducting polymers, and slow diffusional processes limiting response times are some of the drawbacks. For example, a PPy sensor for NO₂ and NH₃ has been made by electropolymerization of pyrrole onto a pattern of interdigitated electrodes [26A]. On exposure to 0.1% NH₃, the conductivity changed by 2.5% but the response time was greater than 15 minutes. It is thus necessary to sense a rate of change of conductivity or to develop a more open morphology which would respond faster.

1.1.4 Electrochromic devices

Yoshine et al [27,28] and Gazard [29] have described electrochromic devices which exploit the colour change in PPy or PTh films on doping. These films can switch in 0.2s at a voltage of ±1.4V, and will operate for 5 x 10⁵ cycles. This is comparable with tungstic oxide devices, and also faster switching occurs at higher potentials but at the cost of more rapid degradation of the film structure. The switching time is limited by the diffusion rate in the film depending upon the structure.
1.1.5(a) Electronic devices

The attraction of semiconducting polymers is the potential for promoting large sheets of cheap photovoltaic cells or transistors. This is only viable if the properties are comparable with those of Si; and the possible advantage has been partly removed by the development of good amorphous Si films. The two stumbling blocks towards harnessing polymer semiconducting properties are their structural instability and the low carrier mobilities. Hence, the polymers should be more stable and have higher intrinsic conductivities to make electronic devices. This can be achieved with highly oriented conjugated polymers. That is, higher carrier mobilities can be obtained with a greater extent of intra-chain conduction due to the removal of structural defects. The use of precursor polymer films and their derivative films are not desirable for manufacturing such devices [30]. Instead, epitaxial films having smooth and defined morphology obtained by electrochemical approach are more preferable. It has been found that the fibrillar morphology is not well-suited for producing good junctions [5C].

1.1.5(b) Optoelectronic Devices

Optoelectronic characteristics of the polymers are harnessed in electroluminescent devices. In case of organic molecules, electrons and holes are constrained by electrostatic interaction to form a localized excitation, an exciton. In many conductive conjugated polymers having higher crystallinity, there is evidence that the excitonic states occur, and that injected electrons and holes can recombine and relax by emitting a photon [31]. Such electroluminescence (EL) is the basis of light emitting diodes (LEDs) having semiconductive polymers as active materials. Electronically conductive conjugated polymers can be used as shielding materials [32], against electromagnetic interference. A p-n heterojunction type device has been fabricated on the basis [33,34] of the junctions formed between two polymer layers. The coating of metal particles having conductive polymers are
protected from oxidation and have improved processibility [35,36]. An electrical memory device can be constructed using chemically synthesized conductive conjugated polymers [9]. Also oligomers such as conjugated sexithiophene (6T) and other oligothiophenes are reported [31] to be ideal photochromic materials for efficient and ultrafast incoherent-to-coherent optical converters [32]. Recent reports [37,38] on polyaniline microstructures for LEDs (obtained through electrochemical approach) are notably impressive. The conductive conjugated polymers such as PThs are also becoming more promising materials for optoelectronic devices.

1.1.6 Electrochemical Applications

Conducting polymers represent an interesting class of materials for use in electrochemical capacitors owing to the combination of high capacitive energy density and low material costs; and further research may lead to successful supercapacitors and to even ultracapacitors. Studies of the effects of electrochemical growth conditions on the morphology of films of PANI by Rubinstein et al. [39-41] reveal long-range order as a result of (electrochemical) film annealing. This consists in a temporary application of cathodic bias during film growth process (at a constant current) brings about a preferential mode of morphology, useful for the classification of the effects of undoping-doping cycles applied to conducting polymer membranes to achieve optimized gas-separation characteristics. The electrochemical studies of morphological changes during charge/discharge cycling are also interesting. There is already a great interest in conjugated polymers for harnessing their selectivity for use in gas-separation membranes. Martin et al. [42] have prepared such membranes based on PPy, while Anderson et al. [43] and others [44] have developed PANI-based membranes that exhibit remarkable selectivity ratios. A recent evidence [45] is the chemical oxidation of aniline at the liquid/liquid interface of two immiscible solvents resulting in the growth of an electroactive polymer membrane that shows redox behaviour similar to conventionally electrodeposited PANI. Ion transport membranes based on
conjugated polymers are also reported [46]; that is, the transport of cations (Na+, K+ and Ca2+) through substituted polypyrrole membrane is demonstrated. Again, the importance of structural aspects in terms of morphology is stressed in all these reports [42-46] and recently by Arbizzani et al [47].

The synthesis of substituted conjugated polymers such as PThs, polypyrroles and PANIs have led to the proliferation of this important class of polymers for advanced applications. In particular, PTh derivatives exhibit interesting electrochemical behavior that can be used for the fabrication of modified electrodes [48]. Some of the most recent applications include bichromic devices [49] and biosensors [50], supercapacitors [51], circularly polarized electroluminescent active layers [52], light emitting electrochemical cell [53] and other new applications [54,55]. Modulation of the function of enzyme immobilized in a conjugated polymer by electrochemical means [56] is also possible. Organic synthetic strategies for the construction of nano-architecture [57] have been reported. The best review articles [58-61] on the conjugated conductive polymers have already been made available including the latest one by Higgins in 1997 [58]. Several reviews have appeared in literature covering various stages of development in conducting polymer research [58-61].

The synthetic revolution from flexible-chain (nonconductive) polymers to rigid-chain (conductive) polymers is now passing on to the next stage of synthesizing anisotropic rigid-chain polymers to occupy many more fields of applications. Following the history of conducting polymer structures in terms of chain structure and morphology and solid state physics of tackling the transport of electrons in disordered and ordered polymer systems during pre-1990 years, the crystalline structural study of conjugated polymer materials follows naturally likehow crystalline characteristics are the natural consequence of orderly organization of polymer chains. Thus the catalytic
manipulation of chemical design criteria can surely lead to the synthesis and manifestation of structural aspects of highly ordered and organized conjugated systems. This is indeed achieved through a right choice of the synthetic method and its conditions.

1.2 Structural Aspects of Conjugated Polymers

Viewing from the foregoing details of conducting polymer applications, it becomes evident that the major focus of conjugated polymer structures is on molecular, crystalline and microstructural aspects. Although the fundamental behaviour (including low bandgap [62]) of the polymers is determined by their molecular structure, thin film and bulk properties, they are controlled by the organized arrangement of the molecules. In polycrystalline polymers, it is the organized arrangement of the molecules (rather than their constituent atoms of the molecule) that leads to diverse behaviours. The molecules may organize either (i) into a highly ordered crystalline one, or (ii) into a rather "loose" noncrystalline structure. The crystalline and noncrystalline contributions make up the building blocks in crystalline/ semicrystalline polymers. The semicrystalline polymers have different ratios of crystalline and noncrystalline domains. And crystalline and noncrystalline domains are composed of the same polymeric molecule but are different due to the molecular order. The molecular order determines the polymeric material behaviour. For example, the characteristics along the molecular axis will be different from those across the molecular axis. This fundamental feature is the basis of anisotropic conjugated polymer structures. Thus, structural regularity is dependent on the molecular order and is characterized as the specific molecular conformation, extent of conjugation, organized (crystalline) structure of the polymer chains and polycrystalline texture [63]. The nature and extent of molecular order in conjugated polymers are important because many of the synthetic design/theoretical
treatments are aimed at fully crystalline materials, while experimental [64] samples are invariably semicrystalline.

Crystallization of polymers is a difficult and complex process, since polymer molecules are long chains which inherently entangle each other. However, a single chain can fold upon itself to form a locally ordered structure known as lamellae which is the starting point of the growth of ordered morphology. The chain arrangements in single crystal and noncrystalline region model of a semicrystalline polymer is a two-phase system [Fig. 2.2.1 in Chapter 2] of distinct crystalline and amorphous regions. The amorphous region is characterized in an x-ray diffraction pattern by its diffuse "halo" as differentiated from the discrete Bragg reflections [sharp peaks] of the crystalline regions. The crystalline regions are identified by crystal structural characteristics. The crystal lattice details of semicrystalline conjugated polymers cited in earlier reports are summarized in Table 1.1. The morphology corresponding to crystalline polymers appears as sharp microstructures like lamella, globules, needles, plates, tubules and flakes. Higher the degree of crystallinity, more defined is the morphology of conjugated polymers. One among them is the spherulite morphology.

Depending on the nature of crystal nucleation, the crystalline regions are organized into supermolecular structures called spherulites. This crystalline component in the semicrystalline matrix must have a definite arrangement inside the spherulite. It is known from the morphology of conventional polymers that the spherulites are birefringent structures that can range in size from about 1 μm to 1 mm in diameter, depending on the nucleation density. They are not seen in ordinary light but can be examined as Maltese Cross in thin section between crossed polarizers using an optical microscope. As such, this is the simple illustration of birefringence so far observed only in melt-grown [65] polymers. This spherulitic morphology
### Table 1.1: A summary of crystal lattice details of (semicrystalline) conjugated polymers [98-110].

<table>
<thead>
<tr>
<th>Conjugated Polymer</th>
<th>Crystal lattice &amp; its Dimensions</th>
<th>Reference</th>
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<tbody>
<tr>
<td>1 Polyacetylene (PA)</td>
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</table>
| (i) trans - PA | Monoclinic  
  a=0.418, b=0.734, c=0.245nm,  
  β=90.5°, \( V_o = 0.0752 \text{nm}^3 \),  
  \( \rho_o = 1160 \text{ kg m}^{-3} \) | [98-101] |
| (ii) Cis - PA | Orthorhombic  
  a=0.761, b=0.447, c=0.439nm,  
  \( V_o = 0.149 \text{nm}^3 \), \( \rho_o = 1050 \text{ kg m}^{-3} \) | [98] |
| 2 Polypyrrole (PPy) | Monoclinic  
  chain axis, c=0 341nm | [106] |
| 3 Polyaniline (PANI) |  |  |
| (i) Emeraldine base - I | Orthorhombic  
  a=0.765, b=0.575, c=1.022nm,  
  \( V_o = 0.450 \text{nm}^3 \) | [102,103] & [105,108] |
| (ii) Emeraldine Salt - I | Orthorhombic  
  a=0.702, b=0.847, c=1.047nm,  
  \( V_o = 0.623 \text{nm}^3 \) | [102,108] |
| (iii) Emeraldine Salt - I | Pseudo-orthorhombic  
  a=0.430, b=0.590, c=0.960nm,  
  \( V_o = 0.244\text{nm}^3 \) | [103] |
| 4 Poly(paraphenylene (PPP) |  |  |
| (i) I Form | Orthorhombic  
  a=0.781, b=0.553, c=0.420nm,  
  \( V_o = 0.181 \text{nm}^3 \), \( \rho_o = 1390 \text{ kg m}^{-3} \) | [107] |
| (ii) II Form | Monoclinic  
  a=0.787, b=0.517, c=0.432nm,  
  β = 105.7°, \( V_o = 0.169 \text{nm}^3 \) | [104,109] |
| 5 Polythiophene (PTh) |  |  |
| (i) I Form | Orthorhombic  
  a=0.780, b=0.555, c=0.808nm,  
  \( V_o = 0.350 \text{nm}^3 \), \( \rho_o = 1500 \text{ kg m}^{-3} \) | [110] |
| (ii) II Form | Monoclinic  
  a=0.783, b=0.555, c=0.830nm,  
  \( V_o = 0.361 \text{nm}^3 \), \( \rho_o = 1600 \text{ kg m}^{-3} \) | [110] |
illustrates an example of an ordered morphological structure of crystalline conjugated polymers.

Generally, how do morphology, crystalline and molecular structures correlate conjugated polymer characteristics, as they are inter-related? What are the means of achieving highly ordered conjugated polymer structures? Higher the structural order, better are the polymer properties like higher conductivities. High degree of crystalline order and anisotropic layer structures can be achieved by controlling the polymer molecular architecture through a right choice of synthetic method. One such method is based on organized assemblies [66-68] like micelles and microemulsions.

1.3 Microemulsion Approach - Surfactant Aggregates

Template-directed reactions which model DNA replication have received a great deal of attention and have generally involved the irreversible coupling of activated constituents to form complimentary products. In an effort to better define essential features of the DNA polymerization reaction, Goodwin and Lynn [69] have developed a template-directed reaction wherein substrate-template association directs product formation. Also, biopolymers such as polynucleotides, polypeptides, and polysaccharides can take the helical structure which is very important in the occurrence of biological function. The formation of similar helical structures has recently been reported [70] with assemblies of some native and artificial amphiphiles. While in inorganics, following the first reported synthesis of inorganic mesoporous materials using ionic surfactants as template molecules by Beck et al [71,72], surfactant-modified synthesis has been used to form a variety of mesoporous materials [73,74]. Such materials could find application in catalysis, membrane and separation technology, and molecular engineering.
Recently, templating of the silica microstructures from an ordered liquid-crystalline mesophase is reported [75] using a high concentration (>>cmc) of non-ionic surfactants. Also hydrophobically modified water-soluble polymers have become the subject of extensive research because of their use as aqueous viscosity modifiers in oil recovery and latex paint systems. For example, a hydrophobic monomer (ethylphenylacylamide) has been prepared by free radical copolymerization using an aqueous micellar process; the use of a surfactant enables good solubilization of the hydrophobe first in polymer synthesis and second in the control of the copolymer microstructure. Addition of surfactant to the copolymer solutions allows control of the hydrophobic interaction, apart from its being used as thickening agents for copolymer solutions. The aqueous solution copolymer properties strongly depend on the amount of surfactant used in the synthesis, as characterized by the difference in the copolymer microstructure, depending on block distribution of the hydrophobic units [76].

Surfactants as amphiphiles are used as bilayers to produce relevant structural features required for chemical engineering applications such as for membrane formation [77]. These surfactant bilayers are often composed of amphiphiles with two aliphatic chains. Some reports have also shown that bilayers are formed from single-tailed amphiphiles when two different types, one cationic and one anionic are mixed. Presumably, ion-pairing between the components simulates the "double-tailed condition". However, Menger et al [77] have recently reported that bilayer structures can be prepared with a pure unmixed amphiphile having only one aliphatic chain, useful to the structural requirements for membrane formation also. And the field of structural evolution of polymer materials using surfactant chemistry is steadily growing with different forms including micelles and microemulsions as organized media.
Thus, self-organization of molecules into a highly ordered architecture continues to draw increasing attention for a wide range of scientific interests. Polymerization of organic monomers in an environment of ordered situation is one such method wherein polymers of unique structures can be obtained. Microemulsion as an organized medium can be employed for the synthesis of ordered polymer structures as exemplified in the following discussion:

The main function of (micellar or) microemulsion media is due mainly to surfactant. And the most important characteristics of surfactants as organic detergents are (i) to increase the solubility of oil in water and (ii) to act as counterions to promote structural ordering in solid state. According to polymer science reports, for example, pyrrole (a hydrocarbon monomer as oil) is sufficiently soluble in water to be polymerizable from aqueous solutions of suitable electrolyte; with the use of surfactants, a much wider range of counterions is accessible as reported by Warren and Anderson [78] and Qian et al [79,80]. Of particular interest is the possibility of including very large counter-ions. Warren et al [81,82] have used aqueous solutions of detergent to prepare polypyrroles having counter-ions derived form N-alkyl sulfates, sulfonates, phosphates and phosphonates. The products are interesting in the sense that packing requirements of the large counter-ions impose some local structural ordering on the polypyrrole chains [83]. This idea can be extended to polymeric counter-ions and for example, polymers with counter-ions derived form poly (vinyl sulfate) [84] and poly (p-styrene sulfonate) [85] have been described. One perceived advantage in these cases is that the counter-ions are immobilized [30]. However anionic-, cationic-, and neutral surfactants can be used in microemulsions to nucleate and organize the polymerized molecules to arrive at ordered structures during the polymerization reaction.
Microemulsion \[86\] is (thermodynamically) a stable liquid or solution consisting of a surfactant, water and oil. It is macroscopically homogeneous and the solution is structured on a nanoscopic scale [1-100 nm] into polar and apolar nanodomains separated by a surfactant-rich film. It depends on the conditions that oil-in-water (o/w) or water-in-oil (w/o) or bicontinuous microemulsion results. The o/w microemulsions are conductive, having oil droplets covered by surfactant and (or co-surfactant) monolayers in a continuous phase of water. W/o microemulsions are not conductive because oil is the continuous phase surrounding the bound-water droplets during surfactant coat. In a bicontinuous microemulsion, both oil and water are continuous throughout the system; surfactant residues in monolayers are along an extended oil-water interfacial network; and these fluids are conductive because one of the continuous phases is water. The structure of a bicontinuous microemulsion is seen as a highly inter-twined network of oil and water [Fig.1.3.1(c)]. The structures of o/w and w/o microemulsions can also be best undestood from Fig.1.3.1(a,b) \[87\]. Conductive o/w microemulsion can be used for electrochemical studies because their conductivities approach those of homogeneous aqueous electrolyte solutions \[87\].

How do microemulsions function as media? Does the surfactant help to obtain ordered conjugated polymer structures? The microemulsion droplets can be considered as microreactors where certain chemical reactions take place inside the small domain of the droplet. In this way, suitable control of the size of the droplets regulates the growth process for polymer (or particle) formulation \[88,89\]. The radius of a nanometer-sized microemulsion droplet is controlled by the water-pool ratio, \( w_o = [H_2O]/[\text{surfactant}] \) and has a typical dimension of 1-15 nm \[90\]. Hence, a suitable microemulsion medium can be selectively chosen based on the structural details of surfactants and their aggregates, and the aggregation phenomena.
Figure 131 Model structures of microemulsions (a) oil-in-water (o/w), (b) water-in-oil (w/o). Circles denote head groups and curved lines represent hydrocarbon tails. Molecules having solid circle head groups in (a) are cosurfactants. (c) Representation of the network structure of a bicontinuous microemulsion (Inset shows orientation of surfactant molecules along a portion of water conduit) [87].
are often of central importance to the function of self-organizing molecules such as conjugated polymers.

Surfactants, commonly called as organic detergents are amphiphilic molecules having distinct hydrophobic (water rejecting) and hydrophilic (water liking) regions. Depending on the chemical structure of their polar head groups, surfactants can be neutral, cationic or anionic. The apolar moiety can be of differing lengths of certain unsaturated bond(s), and/or consists of one, two or more chains. (Functional groups can also be incorporated into surfactant molecules [91]). The surfactants as amphiphilic molecules associate in aqueous solution and interface to form different aggregate structures [92]. The hydrocarbon chains (usually called 'tail') are hydrophobic, and the polar ends (or “head” groups) are hydrophilic so that the hydrophobic interaction induces the molecules to associate the polar heads to the aqueous phase. [Surfactant molecule as the mediator self-aligns to align other molecules of the medium through polar-to-polar and apolar-to-apolar interactions to have a homogenously organized assembly that helps to achieve highly ordered structures or homogeneous systems in general].

At the thermodynamic equilibrium, the geometry of an amphiphile molecule in the aggregate is given by the surfactant packing parameter, \( p_o = \frac{v_o}{a l} \); where \( a \) is the (optimum) surface area occupied by the head groups when the total interfacial energy per molecule in the aggregate is a minimum; \( v_o \) is the volume of the hydrocarbon chain(s); and \( l \) is the effective length that the chains can assume. From the self-assembly model and the molecular geometry, it is possible to determine the nature, shape and size of the aggregate that the amphiphilic molecules can pack. Since surfactant structure controls system architecture, the following rules have been derived based on the choice of the surfactant packing parameter, \( p_o ( = \frac{v_o}{a l}) \).
Thus the packing parameter \( p_0 \) allows the choice of a surfactant for a desired type of organized [93] assembly from its molecular dimensions [94]

Amphiphiles that form planar bilayers must have the dimension of the surfactant packing parameter close to but less than 1 and the critical packing shape has to be cylindrical. It has experimentally been found [95] that as pH decreases or electrolyte concentration increases, the value of \( a \) decreases and hence the packing parameter \( p_0 \) becomes close to 1 indicating the formation of planar bilayers. It is also reported that as amphiphiles self-organize in water to form molecular bilayers, the hydrophobic effect [96] causes aggregation and holds the bilayers together. And small differences in bilayer packing, having no changes in medium or aggregate composition, can modulate the rate of supermolecularly modified chemical reactions. The subtle differences in the aggregate structure can give rise to significant effects, and the stereoselectivity is affected by the size of aggregates. Solute
distribution, localization, orientation and local order can also be determining factors for the rate and mechanism differences observed in the distinct aggregates. However, the molecular behavior of bilayers depend on head group packing, and in turn is a function of the aggregate diameter. Controlled change of the aggregate diameter thus allows structural changes of the bilayer with no changes in the molecular structure of the monomer and/or composition of the medium.

A literature study on surfactant aggregates is thus helpful in understanding the structural evolution of the crystalline conjugated polymers during chemical and electrochemical syntheses in microemulsion media. And electrochemical experiments in an organized medium of surfactants can control the macromolecular architecture during the polymerization reaction. Most surfactants (anionic, in particular) with long aliphatic chains/aromatic sulfonates confer cation-transport properties in conjugated PANI, PPy and PTh due to their ionic size. In addition, morphology appears to control the cation selective properties. There is an increasing trend in the study of conjugated polymer thin film synthesis from surfactant solutions. For example, a special morphology called columnar microstructures has been observed recently [97]. The advantage of the choice of electrochemical synthesis from surfactant solutions for controlling the conjugated polymer morphology has recently been reported or realized [98-110]. The electrochemical initiation of polymerization on the electrode surface is a two-dimensional process. The structural order already existing with the two-dimensional structure of the monolayers influences further organization of polymerized molecules. It is speculated that the surfactant aggregates can initiate and also form templates to organize these polymer molecules to adopt to well-defined macromolecular arrangement, higher crystalline order, smooth morphology and also anisotropic layer structure in conjugated polymers. This forms the scope of the present investigation of the structural aspects of simple conjugated polymers, PANI, PPy and PTh (including
conjugated oligothiophene, 6T), synthesized in micellar and microemulsion media.

1.4 Synthetic Approach

There is a growing trend among chemists to think about the behaviour of molecules, not only in terms of their reactivities but also their structures. The synthesis of conjugated polymers to assemble with regular molecular structures of high long-range order such as crystals, liquid-crystals, monolayers and anisotropic thin films can be obtained by rightly designing the mutual interaction of individual monomers. The ability to control the molecular structure is a powerful tool for areas of research ranging from catalysis to materials science. Molecular construction 'kits' are helping chemists to build a large number of highly organized macromolecular structures including those of conjugated polymers.

1.4.1 Electrochemical synthesis

Electrochemical synthesis has been a chosen method for forming thin films on solid electrode substrates. The simplicity and reproducibility of this method explains its growing importance. The polymer films can be synthesized readily from commercially available reagents using simple apparatus. The thickness of the films can be controlled by polymerization time/charge or the number of cycles.

The electrochemical reactions that yield conductive conjugated polymer films may be illustrated in the following hypothetical steps:

\[
\begin{align*}
\text{HMH} & \rightarrow \text{HM}^+ \text{H} + e^- \quad \text{(1)} \\
2(\text{HM}^+\text{H}) & \rightarrow \text{HM}^+\text{HMM}^+\text{H} \rightarrow \text{HMMH} + 2\text{H}^+ \quad \text{(2)} \\
n(\text{HMH}) & \rightarrow \text{HM}_n\text{H} + (2n-2)\text{H}^+ + (2n-2)e \quad \text{(3)} \\
\text{HM}_n\text{H} & \rightarrow \text{H(M}_{n})^+\text{H} + ye \quad \text{(4)}
\end{align*}
\]
In the first step (eq. 1) a monomer M is oxidized at the electrode surface, giving up an electron to form a radical cation M⁺. The second step (eq. 2) involves the coupling of two radical cations to give a dimer that can immediately split off to two protons. Steps 1 and 2 repeat continually to increase length of the growing oligomer chain. The net reaction can be represented by equation (3); (a large number or) n monomer units interact to form a polymer HMcH, releasing (2n-2) protons and an equivalent number of electrons. In the final step (eq. 4) the polymer HMcH is oxidised, releasing y electrons to form the oxidized polymer H(Mc)⁺yH. The degree of polymerization n is practically not known exactly. Most conductive conjugated polymers have a range of chain lengths that include some relatively short oligomers. It is shown experimentally that normally an n value of about 750 has been determined, equivalent to a relative atomic mass of \( \sim 10^5 \) (amu). It may be recalled that during electrochemical oxidation of an aromatic monomer into a polymer, the aromatic structure is maintained [111].

The electrodeposition of conjugated polymer films occurs in several steps [112-114]:

(a) nucleation,
(b) first monolayer,
(c) layer by layer films,
(d) anisotropy, and then
(e) granular (bulk) structure. Electrochemical deposition is essentially a two-dimensional growth process. The formation of isolated nuclei during initial stages has also been demonstrated [105].

1.4.2 Influence of electrochemical parameters

Different strategies have been reported [115,116] for obtaining highly ordered films such as (i) polymerization of crystalline monomers, (ii) epitaxial crystallization of the monomer on a single crystal substrate and subsequent polymerization, (iii) blocking of sites to prevent their participation
in coupling, and (iv) polymerization at low temperatures. The change in structural properties of conjugated polymers due to electrochemical parameters can be summarized as follows:

(a) **Applied potential** for example, high applied potential leads to cross-linking of polymer chains and / or side reaction [117].

(b) **Current density** In general, polymer film coatings formed at higher densities show “rough” surface while low current- densities build up a homogeneously compact and smooth morphological structure [118].

(c) **Electropolymerization temperature**: The current efficiency of polymerization and charge storage efficiency [119] increase when the temperature of polymerization decreases.

(d) **Monomer concentration** A decrease in monomer concentration increases [water] / [monomer] ratio, and the presence of water in the electropolymerization process leads to more nonconducting and passivated films [120]. And with low monomer concentrations, not only longer polymerization times are needed to deposit the same polymer thickness, but also poor [121] behaviours are observed.

(e) **Choice of monomer** Commonly, increase in conjugation of the monomer leads to decrease in the polymer conjugation length and hence poor behaviours. However, an exception is that polymerization of bithiophenes at lower oxidation potential and at low monomer concentration can give polymers of high yield and better structural regularity than with thiophenes [122].
(f) **Polymerization time:** The early stage of growth giving well-ordered chains is followed by less-ordered structures at later stages of polymerization [123].

(g) **Substrate:** The morphologies of several poly(heteroarylene)films synthesized galvanostatically on optically transparent indium-tin-oxide (ITO) electrodes seem to be substantially different from those of the films formed on platinum surfaces; the kind of substrate effect increase in the order Au < Ag < Cu < Al < C depending on the strength of interaction between polymer and the substrate [124].

### 1.4.3 Why Chemical / electrochemical Methods?

The plasma polymerized films of some conjugated polymers are reported [125] to have higher content of hydrogen than that in electrochemically polymerized films. Although the surface morphology of PTh films deposited from high efficiency flux density is observed [126] to be similar to that of films prepared by electrochemical methods, the later method picks up the credibility of simplicity and better control of experiments. In case of vacuum-evaporated oligomer (hexathiophene, 6T) films, favourable structural properties like high degree of orientation is achieved even with thicker deposits obtained at higher temperatures [127], but has an undesirable effect of film instability apart from the technique being multiple-step, sophisticated and highly expensive for polymers.

Most of the aromatic conjugated polymers are insoluble in organic solvents, and is a disadvantage for the industrial applications. The attempts to increase the solubility and processibility of conjugated polymers included strategies by introducing polar groups and / or long flexible side-chains in the heteroaromatic or aromatic chain yielding conjugated polymer derivatives [128]. Polymer powders in bulk quantity are commonly obtained
by chemical routes, while homogeneous films are obtained by
electropolymerization. The morphology of the as-synthesized chemically and
electrochemically obtained polymers are quite different. Electrochemical
polymerization of thiophenes at higher potentials is reported [129] to be a
suitable technique to produce smooth, flexible, electroactive, free-standing
films or thin layers of polymers, but are structurally less regular than their
chemically or low-potential means of electrochemically synthesized
counterparts. Chemical synthesis is more convenient to get polymers
because chemical oxidation by FeCl₃ gives standard quality polymers in
good yield, while electrochemically synthesized polymer film is expected to
have more compact morphology compared to that of chemically synthesized
(and layered) polymer films. Although there exists a broad contrast in
morphological features, appropriate choice of polymer structures can be had
by either chemical or electrochemical routes.

The recent trend of polymerizing the functionalized monomers
leading to the synthesis of conjugated polymers deals with the use of
intermolecular hydrogen bonds to obtain self-assembled ladder
structures[130], switching mode of doping / dedoping [131] by electrochemical
means, self-assembled copolymer structures[132] etc are the interesting
interfacial aspects of the surfactant chemistry; and hence surfactant-assisted
self-assembly reaction is considered here to provide polymerization media.
Also, the surfactant approach is broadly employed in the development of
advanced chemical materials today more than ever before [133,134]. The
microemulsion media obtained using surfactants are expected to play a
favourable role of improving the structural characteristics in a direct single-
step method. Hence this approach is employed here in the study of
synthesizing simple conjugated polymers such as PANI, PPP and PTh.
1.5 Thesis Outline

The INTRODUCTION chapter of the thesis gives the fundamental aspects and scope of the research work on conjugated polymers. Literature details pertaining to each candidate of the conjugated polymer system have been incorporated in their respective chapters while discussing the relevance of their structural aspects. The second chapter deals with the details of EXPERIMENTAL methodology employed in this study. Chapter 3 through 5 essentially concern the details of the chemical and electrochemical synthetic methods, structural analysis and morphological observations followed by the discussion of the results pertaining to PANI, PPP and PTh (including 6T) respectively. Also included is a preliminary study of electroluminescence and photoluminescence characteristics of PPP and PTh thin active layers. The CONCLUSIONS chapter summarizes the important results. The mechanism of nucleation and templating effect of surfactant is discussed in detail to understand how self-assembly by means of hydrophobic effect can help organizing the polymer macromolecules to conform to high structural order and anisotropic layer structure. The continuing and future scope of the conjugated polymer structures is also presented.