Chapter-1

Introduction to Conducting Polymers, Various Applications and Different Synthesis Methods for Conducting Polymer Nanostructures

Jayanta Hazarika

Department of Physics, Tezpur University
Napaam, 784028 Assam India
E-mail: jhazarika2012@gmail.com

This chapter highlights about the exciting and emerging field of conducting polymers with an emphasis on different nanostructures of conducting polymers. The chapter deals with the historical background and potential applications of conducting polymers. The mechanism of electrical transport in conducting polymers and various synthesis methods for preparation of conducting polymer nanostructures as functional materials have been discussed.

1. INTRODUCTION

The discovery of polymers has given a new dimension in the present era. In general, polymers are known as a class of heat sensitive, flexible,

electrically insulating amorphous materials. The polymers either natural or synthetic are large macromolecules comprising of small building blocks or repeating units connected by each other by covalent bonds. The polymers are generally known for their insulating properties because of the covalent bond present in the saturated carbon compounds [1]. After the discovery of polyacetylene as a highly conductive organic material in the year of 1977 [2], a class of materials called the conjugated polymers or intrinsically conducting polymers (ICPs) could be differentiate from the rest of the polymers. The path breaking discovery of conducting polymers was celebrated in the form of Nobel Prize in chemistry to A. G. MacDiarmid, A. J. Heeger and H. Shirakawa in the year of 2000. Conducting polymers are also known as "conjugated polymers" because of their ability to conduct electricity due to the presence of alternate single and double bonds along their backbone structures [3]. The special conjugation in the chain of conducting polymers enables to some of the π-electrons to be delocalized. The delocalized π-electrons can move throughout the whole system and become the charge carriers to make the polymer conductive. This type of polymers can be transformed into a conductive state when electrons are removed from the backbone resulting in cations or added to the backbone resulting as anions. The anions and cations behave as charge carriers which jump from one site to the other site under the influence of electric filed resulting increasing in electrical conductivity [4]. During the last few decades the conducting polymers have attracted an overwhelming interest around the world due to their considerable potential applications in scientific and industrial areas. Because of the broad range of electrical

conductivities and vast uses in number of electronics and optoelectronics applications, conducting polymers can replace the conventionally used metallic conductors. Different types of conductive polymers such as polypyrrole (PPy), polyaniline (PAni), Polythiophene (PTh) and poly(3, 4-ethylenedioxythiophene) (PEDOT) etc. have been studied extensively with a broad range of electrical conductivities i.e. from 10^{-10} to 10^5 S/cm [5]. Fig. 1 depicts the chemical structures of some of the mostly studied conducting polymers. The comparison of conductivity values of conducting polymers with some common metallic and semiconducting materials are shown in Fig. 2.
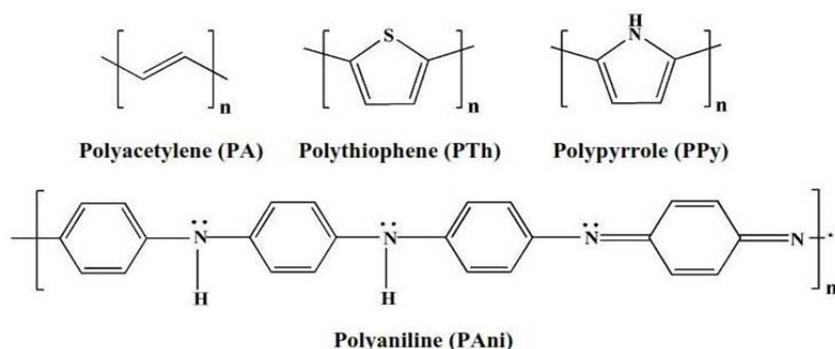
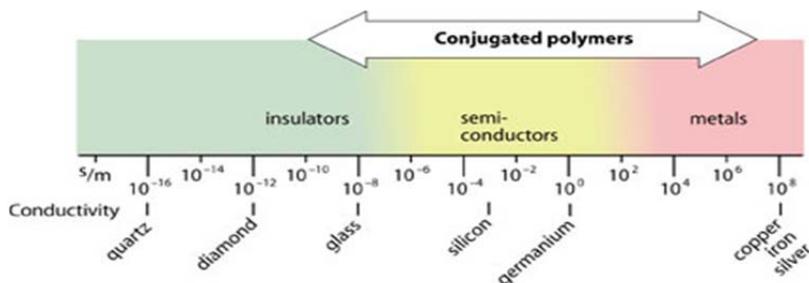**Fig. 1: Chemical structure of some mostly studied conducting polymers.**

Fig. 2: Diagram showing range of conductivity for various materials including conducting polymers.

2. APPLICATIONS OF CONDUCTING POLYMERS

Fig. 3: Different applications of conducting polymers as smart window, solar cell, actuator, organic light emitting diodes and organic thin film transistor.

Conducting polymers are functional materials which can be used as organic conductors taking the advantages of excellent mechanical strength and light weight. The potential applications of various conducting polymers include in sensors (including gas and bio sensors), actuators, super capacitors, polymeric rechargeable batteries, electro-chromic windows and displays, functional membrane, drug and bio molecule release, corrosion protection, light emitting devices, photovoltaic applications etc. [6-9] The above Fig. 3 shows pictorial diagrams of different applications of conducting polymers.

2.1. Field effect transistor

The field effect transistors (FETs) are also called the unipolar transistor to contrast their single carrier type operation with the dual-carrier-type operation of bipolar junction transistors (BJT). An organic field-effect

transistor (OFET) is a field effect transistor that uses an organic semiconductor such as conducting polymers in its channel. These devices have been fabricated to realize low-cost, large area electronic products. Xue et al. [10] developed two field effect transistors by both spin-coating and ink-jet-printing methods using conducting polypyrrole (PPy) as semiconducting materials. The spin-coated transistor showed better device performance than that of the ink-jet-printed transistor. Covington et al. [11] fabricated polymer FET for gas sensor applications. Ashizawa et al. [12] developed the fabrication of a metal-insulator-semiconductor field effect transistor (MISFET) using poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) as an active channel by the multiple line patterning which is one of the most simple, rapid and inexpensive method capable of making patterns of conducting polymers, insulators and metals using a standard laser printer. The MISFET operated both in the depletion and enhancement modes in response to positive and negative gate voltages, respectively, where the gate current was crucial to the performance of the device. Liu et al. [13] fabricated an all-polymer field-effect transistor (FET) using an ink-jet printing technique. Poly(3, 4-ethylenedioxythiophene) works as the source/drain/gate electrode material because of its good conductivity. Polypyrrole acts as the semiconducting layer and Poly(vinyl pyrrolidone); an insulating polymer with a dielectric constant of 60 operates as the dielectric layer.

2.2. Sensors

Conducting polymers have wide range of applications as sensors. There are different types of sensors that use conducting polymers such as polyaniline, polypyrrole, polythiophine etc. as the active layers. Bai et al. [14] reviewed the fabrication of gas sensors using different conducting polymers such as polyaniline (PAni), polypyrrole (PPy), and poly(3, 4-ethylenedioxythiophene) (PEDOT) as the active layers. The conducting polymer films were prepared using different fabrication methods such as the electrochemical deposition, dip coating, spin coating etc. Shrivas et al. [15] studied the toxic gas sensing property by PAni thin film for ammonia gas. One dimensional conducting polymer nanofibers are promising materials due to their chemical doping specificities, large surface areas, high electrical conductivity, light weights, low cost, easy processing and scalable productions. The nanofibrillar morphology significantly improves the performance of conducting polymers in applications such as biosensors [16] and chemical sensors [17]. S. Virji et al. [18] developed PAni nanofibers gas sensor and compared them to the conventional PAni sensors. The higher surface area, porosity and small diameters enhanced the diffusion of molecules and dopants into the PAni nanofibers and hence the PAni nanofibers showed enhanced sensing compared to the conventional thin films. The basic requirement for a chemical or biological sensor is to convert a molecular binding event into a measurable signal. Conducting polymers are attractive for sensor applications because of their ability to directly convert the binding event into an electrical signal. Additionally the conducting polymers can be modified chemically with functional groups for

specific recognition and detection of different analytes. Because of these unique properties, many groups have applied conducting polymers into the chemical and biosensors applications [19, 20]. Forzani et al. [21] presented different chemical sensor applications based on nanoscale functionalized conducting polymer junction arrays.

2.3. Shielding of electromagnetic interference

In recent years, electromagnetic interference (EMI) problem or electromagnetic pollution has received wide attention because of the malfunctioning of the electronic equipments from the radiations generated from the source or emanating from other electronic equipments. The research on the last past decades has established the ability of polymer composites made with electrically conducting polymers to be suitable as a shield against the electromagnetic interference [22, 23]. Koul et al. [24] studied the electromagnetic interference shielding effectiveness of conducting PAni-ABS composites at 101 GHz. The shielding effectiveness of the composites increases with the increase in the loading levels of the conducting polymer doped with hybrid dopants. Kim et al. [25] fabricated intrinsically conducting polymer (ICP)/PET textile composites by chemical and electrochemical polymerization approach and investigated the effects of the chemical or electrochemical polymerization conditions on the properties of resulting composites, such as electrical conductivity and electromagnetic interference shielding effectiveness (EMI SE). ICPs are new alternative candidates for EMI shielding applications because of their corrosion

resistance, lightweight, ease of processing and tunable electrical conductivities.

2.4. Polymer light-emitting diodes

Conjugated polymers show the semiconducting behavior due to the presence of delocalized π-electron along the polymer chain. The π-bonding and π^*-antibonding form the delocalized valence and conduction wave functions, which support the mobile charge carriers. The electroluminescence from conducting polymers was first reported using poly(phenylene vinylene) (PPV) as the single semiconductor layer between aluminium electrodes [26]. In this structure, the indium-tin oxide (ITO) layer behaves as a transparent electrode and allows the light generated within the diode to leave the device. The LED operation can be obtained with sufficient biased to achieve injection of positive and negative charge carriers from opposite electrodes. The capture of oppositely charged carriers within the region of the polymer layer can then result in photon emission. Such type of LED can be fabricated by solution processing of the semiconducting polymer onto the ITO-coated glass such that the film thickness is no more than typically of 100 nm.

2.5. Solar cells

Polymer solar cells are a type of organic solar cell which produces electricity from sunlight using polymers. In general, solar cells are made from the refined, highly purified silicon crystal. However, the high cost and complex production process of silicon solar cell has increased interest in alternative photovoltaic technologies. As compared to silicon-based solar

cells, the conducting polymer solar cells have the advantages of their lightweight, disposable, inexpensive to fabricate, flexible, customizable on the molecular level and have lower potential for negative environmental impact.

2.6. Artificial muscles

The use of conducting polymers as artificial muscles was first demonstrated by Baughman and co-workers in 1990 [27]. The conducting polymer artificial muscles use the dimensional changes resulting from electrochemical ion insertion, possibly along with associated solvating species. Since both the electrodes can comprise conducting polymers, they can be used as artificial muscles. Depending upon the conducting polymer/electrolyte system used, the initial state and the rate of potential change used for actuation, electron insertion into one electrode can be accompanied by a volume increase as cations are inserted or a volume decrease as anions are removed. Hara et al. [28] reported on the artificial muscles based on polypyrrole actuators with large strain and stress. In another previous study, Otero et al. [29] reported on the construction and electrochemomechanical characterization of the polypyrrole artificial muscles.

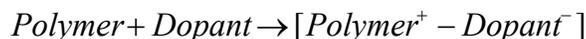## 3. DOPING IN CONDUCTING POLYMERS

The concept of doping is the unique, central, underlying and unifying theme which distinguishes conducting polymers from all other types of polymers [30, 31]. In general the intrinsic conducting polymers exhibit poor electrical

conductivity ($\sim 10^{-12}$ S/cm) in their intrinsic states and behave as insulator. The intrinsic conducting polymers need to be treated with a suitable oxidizing or reducing agent to increase their electrical conductivity to the metallic or semiconducting regime. This phenomenon is termed as "doping". In general, doping can be regarded as the insertion or injection of electrons and doping in conducting polymers results in dramatic changes in electrical, optical, magnetic and structural properties of the polymeric system. Upon doping the electrical conductivity of iodine doped polyacetylene (PA) can be increased by 9-13 orders of magnitude [30]. Doping of conducting polymers is usually quantitative and the carrier concentration is directly proportional to the dopant concentration and doping in conducting polymers involves the random dispersion or aggregation of dopants in molar concentration in the disordered structure [32]. Doping of conducting polymers leads to the formation of conjugation defects viz. solitons, polarons or bipolarons in the polymer chains. The X-ray diffraction study on iodine doped polyacetylene showed that the C-C bond length in polyacetylene chain increased with donor doping while the C-C length decreased with the acceptor doping. The presence of localized electronic states of energies less than the band gap arising from changes in the local bond order, including the formation of soliton, polaron or bipolarons have led to the possibility of new types of charge conduction present in these polymer systems. Table 1 show the charge and spin characteristics of these defects.
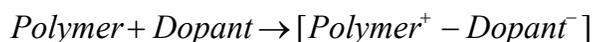
Table 1: Typical properties of solitons, polarons and bipolarons.

Defect	Spin	Charge	
Soliton	1/2	neutral	0
Soliton	0	charged	+ e or - e
Polaron	1/2	charged	+ e or - e
Bipolaron	0	charged	+ 2e or - 2e

The resultant conductivity in conducting polymers depend on many factors, viz. nature and concentration of dopant, homogeneity of doping, carrier mobility, crystallinity and morphology of the polymer. In general, n-type doping is achieved with an electron acceptor and p-type doping is conducted with an electron donor. The dopants are either strong oxidizing or reducing agents and on doping, either positive or negative charges are created in conducting polymers.

$$Polymer + Dopant \rightarrow [Polymer^+ - Dopant^-]$$

(Acceptor)   Charge transfer complex

$$Polymer + Dopant \rightarrow [Polymer^+ - Dopant^-]$$

(Donor)   Charge transfer complex

Fig. 4: Action of a dopant on polymer.

3.1. Different types of doping

The doping of conducting polymers can be done by the following methods:

✓ *Redox doping*

Redox doping is the most common method of doping and is also known as oxidative doping which is accomplished by removing π-electrons from the conjugated polymers. The conducting polymers such as PAni, PPy, PTh etc.

undergo p- and/or n- redox doping by chemical and /or electrochemical processes during which the number of electrons associated with the conducting polymer backbone changes.

✓ *Non redox doping*

This type of doping differs from the redox doping is that the number of electrons associated with the polymer backbone does not change during the doping process. The energy levels are rearranged during doping process. The emeraldine base form of polyaniline (PAni) was the first example of doping of a conjugated polymer to a highly conducting regime by this process to produce an environmentally stable polysemiquinone radical cation. This was accomplished by the treating emeraldine base with aqueous protonic acids and conductivity increased by nine to ten orders of magnitude [33, 34].

✓ *Photo doping*

When the polymers are exposed to radiation of energy greater than the band gap energy, the electrons are promoted across the band gap and polymer undergoes "photo-doping".

3.2. Doping techniques

Doping in polymers can be done by following ways,

- Gaseous doping
- Solution doping
- Electrochemical doping
- Self doping
- Radiation induced doping

- Ion exchange doping

In gaseous doping process, the conducting polymers are exposed to the vapour of the dopant under vacuum. The level of doping can easily be controlled by controlling the temperature, vacuum and the time of exposure. Solution doping involves the use of a solvent in which all the products of doping are soluble and the polymer is treated with the dopant solution. In the electrochemical doping process, the simultaneous polymerization and doping occurs. In this method only ionic type dopants are used as the electrolyte in polar solvents.
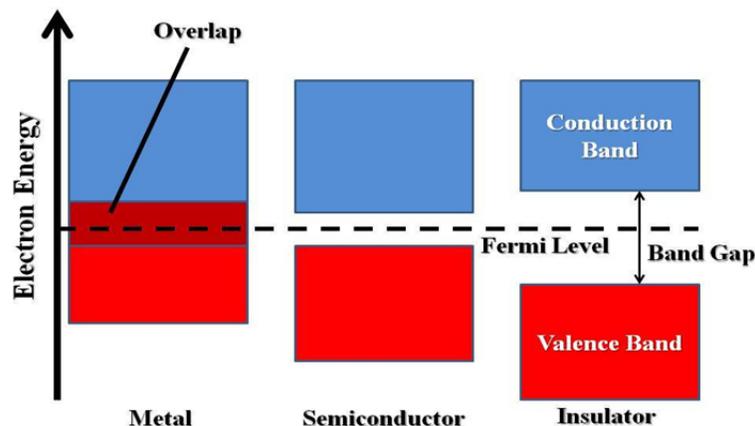
4. CONDUCTION MECHANISM IN CONDUCTING POLYMERS

Fig. 5: Energy level diagrams for metal, semiconductor and insulator.

The conducting polymers are a special class of organic semiconductors and hence the electrical properties of conducting polymers can be explained in a simple and straightforward way called the HOMO (Highest occupied molecular orbital)-LUMO (Lowest unoccupied molecular orbital) theory

[35]. Although the conducting polymers possess a relatively large number of delocalized π-electrons, a fairly large energy gap exists between the valence band and conduction band (greater than 1 eV). Thus the conducting polymers are considered as semiconductors and hence must be doped (i.e. altering the number of π-electrons) in order to render electrical conductivity. The basic requirement for a polymer to become conductive is that there should be overlapping of molecular orbitals to allow the formation of delocalized molecular wave functions. This electronic delocalization provides the highway for charge carriers and the overall conducting properties depend on two components, namely (i) intrachain mobility which corresponds to the charge transfer along the polymer backbone chain and (ii) interchain mobility which involves the hopping and tunnelling of the charge carriers from a bond to neighboring bonds [36].
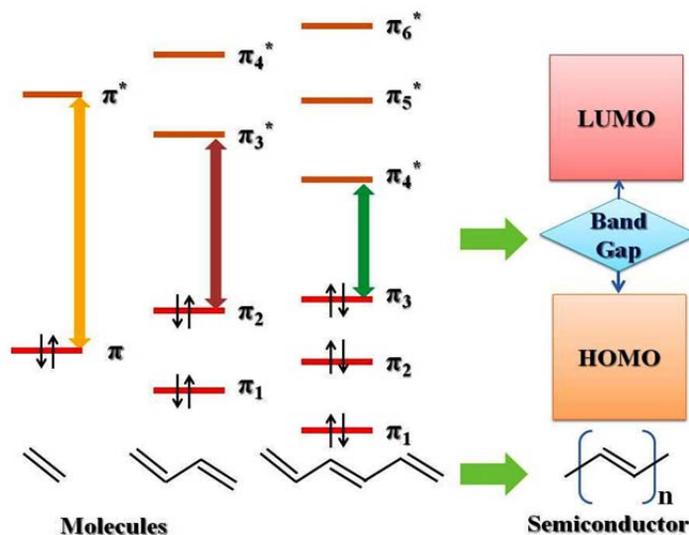
Fig. 6: HOMO-LUMO theory in organic semiconductor polymers.

The transport behavior in conducting polymers depends on the type of charge carriers and band structure. The conduction mechanism and charge carriers' behavior can be explained using the concept of polarons and bipolarons. A radical cation that is partially delocalized over some polymer segment is called a polaron (spin ½) that stabilizes itself by polarizing the medium around it. When the electron is removed from the top of the valence band, a hole (or radical cation) is generated that does not delocalize completely. Due to partial delocalization over several monomeric units, they form deformed structure. The energy level associated with this radical cation represents a destabilized bonding orbital having higher energy as compared to the valence band energy. If now another electron is removed from the already oxidized polymer containing polaron, two phenomena can happen: this removing electron can come from either a different segment of polymer chain generating another independent polaron, or from the first polaron level (removal of unpaired electron) to create a dication called the bipolaron. In particular, low doping level results polarons wherein the higher doping level produces bipolarons. As compared to the polaron, bipolaron is doubly charged but spin less. Both the polarons and bipolarons are mobile and can move along the polymer chain by rearrangement of double and single bonds in the conjugated system. If the polymer is highly doped, many bipolarons are formed as a result of which their energies can start overlapping at the edges, which creates narrow bipolaron bands in the band gap. The energy difference between the top of the valence band and bottom of the conduction band is called the band gap energy of the material.

The conducting polymers either have a zero band gap or a very low band gap. The band gap controls the electronic and optical properties of conducting polymers. A reduction in optical band gap energy leads to a higher conductivity in conducting polymers and hence attempts have been made to reduce the band gap energy in such polymers by using the various methods.

5. POLYPYRROLE AS A PROMISING CONDUCTING POLYMER

Polypyrrole (PPy) is one of the most widely studied intrinsic conducting polymers among the family of conducting polymers in different areas of science and technology. PPy can be obtained from the polymerization of pyrrole (Py) monomer. The most common methods applied to synthesis PPy are chemical oxidative polymerization with doping, electrochemical polymerization, plasma polymerization and the organic synthesis. The general mechanism of oxidative polymerization of pyrrole (Py) monomer can be explained in the following way as shown in Fig. 7.
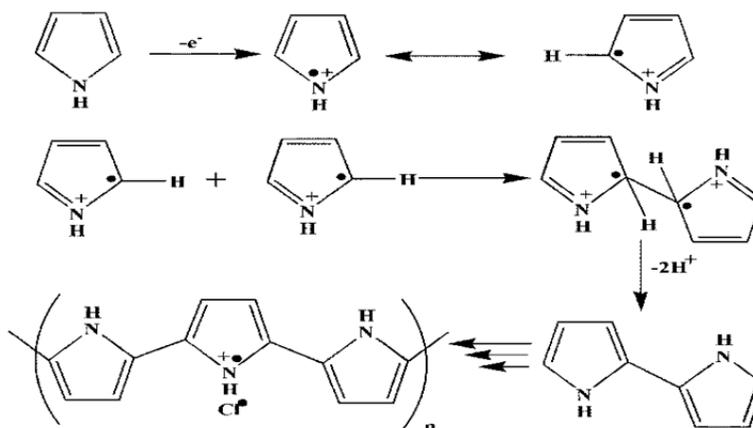
Fig. 7: Chemical oxidative polymerization and doping process in pyrrole.

Cationic free radical forms after the loss of an electron from the monomer
structure which is followed by the coupling of active resonance structures in
different positions during the reaction (oxidation of monomer, radical-
radical coupling). These coupled structures finally form polypyrrole chain
at the end of the polymerization reaction (deprotonation, re-aromatization
and chain propagation). The traditional π-conjugated structure of
polypyrrole usually is not enough to possess significant conductivity on its
own [37]. The electrical conductivity of this polymer can remarkably be
change from insulating to metallic level through the process of doping [37].
That is why the partial charge extraction (doping) process is needed and can
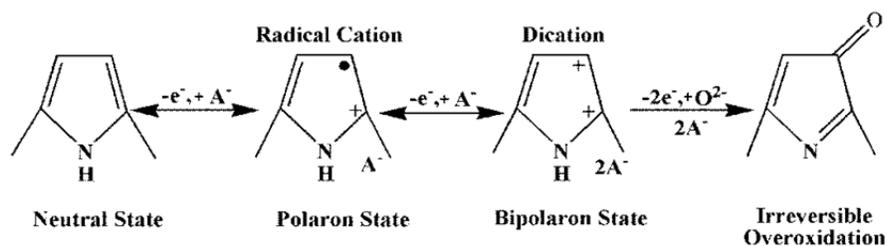be explained for this polymer in the following way as depicts in Fig. 8.

Fig. 8: Oxidation states of pyrrole.

Initially an electron is removed from the polymer backbone by yielding a
radical and a spin less positive charge [38]. The newly formed cation and
the radical are coupled to each other by local resonance. During coupling
the quinoid-like sequential rings are also formed and utilized to provide
higher energy of distortion than the remaining part of the chain. In general,
the lattice distortion extends to four pyrrole rings (charged sites) and when
they coupled with a radical, this structure is called polaron. Further

oxidation of this polaron yields a new spineless defect called the bipolaron having lower energy than that of the two distinct polarons. At higher doping level, polarons are eventually replaced by bipolarons. For the higher doping level in PPy, it is suggested that the upper and lower bipolaron merge to the valence and conduction bands respectively to produce partially filled bands and provide metal like conductivity for the final polymer [37]. Having the conductivity values between 10-50 S/cm, PPy has been used extensively in different types of applications such as electrodes for rechargeable batteries and supercapacitor, electromagnetic shielding materials, electro-chromic devices and membranes, actuators, corrosion protecting materials and fuel-cell membranes [39]. Because of the unique and tunable physico-chemical and conductivity properties along with the better environmental stability, biocompatibility and higher surface area for various applications, the PPy nanostructures have become a great prominence throughout the different studies [40, 41].
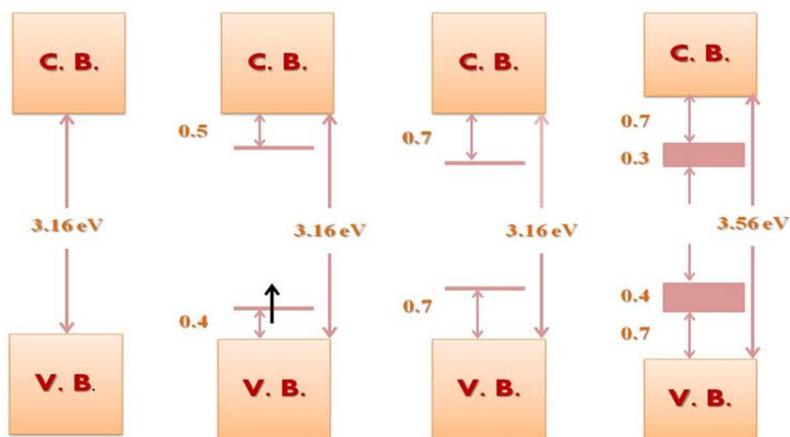

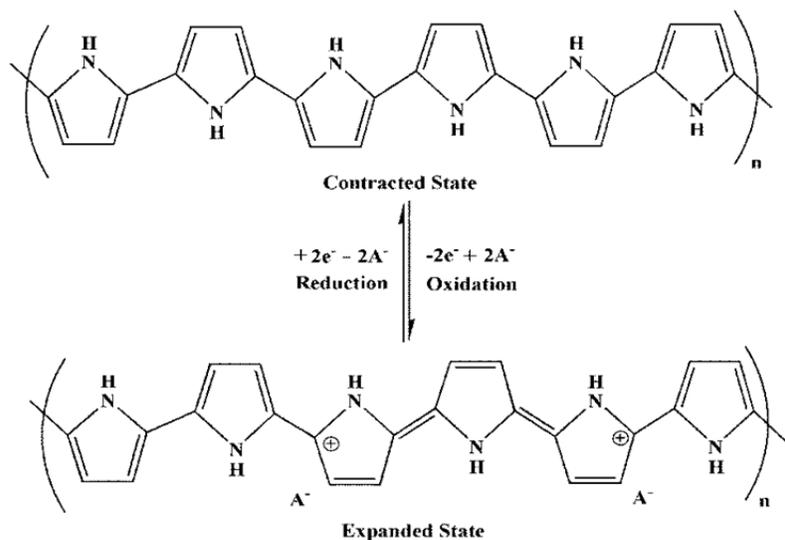**Fig. 9: Electronic energy diagrams for (a) neutral, (b) polaron (c) bipolaron and (d) fully doped polypyrrole.**

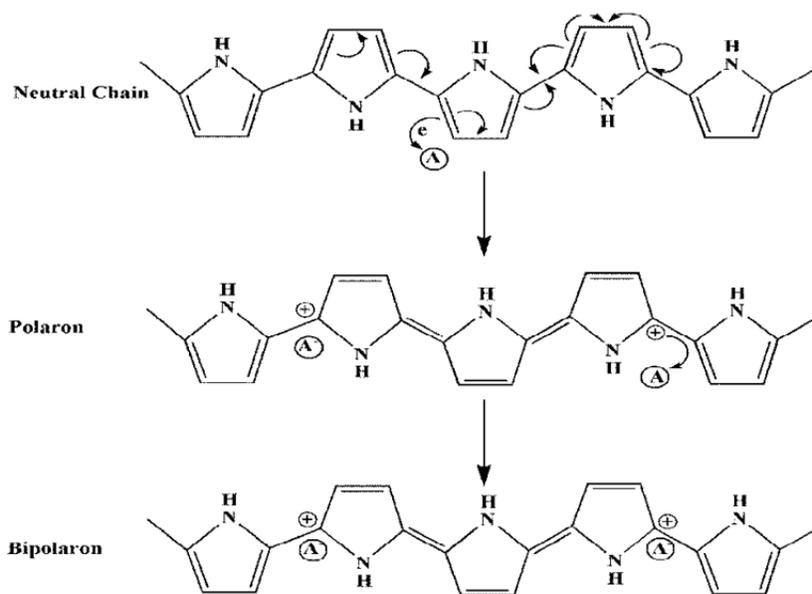**Fig. 10: Reduced (top) and oxidized (bottom) states of polypyrrole.**

**Fig. 11: Conduction mechanism for the oxidative
polymerization of polypyrrole.**

6. CONDUCTING POLYMER NANOSTRUCTURES

In the last few decades, nanostructured materials have attracted tremendous interest amongst the scientific community because of their peculiar and fascinating properties, as well as their unique applications as compared to their bulk counterparts. The nanostructured materials can lead to superior physical and chemical properties with molecular and supramolecular structures. The widespread interest in nanostructured materials mainly originates from their different properties such as the optical, electrical, mechanical and chemical performance that are usually different from those of the bulk materials. The improvement in the physico-chemical properties of nanostructured materials originated from the quantum chemical effects including quantum confinement and finite size effect as well as their nano-sized effect. Recently, nanostructured conducting polymers have received special attention in the area of nanoscience and nanotechnology because of their highly π-conjugated polymeric chains and metal like conductivity meaning that they can be regarded not only as molecular wires but also for the basic unit for the formation of nanodevices [42]. In addition, special characteristics of conducting polymer nanostructures are result from their size (1-100 nm) and large surface area; hence the electrical properties of conducting polymers are expected to be different from that of their bulk counterparts. The high performance of conducting polymer nanostructures is expected because of their nano-dimension: high conductivity, large surface area and light weight. Different conducting polymer nanostructures such as nanoparticles, nanotubes, nanofibers, nanorods, nanoneedles,

nanocapsules etc. show improved physico-chemical properties as compared to their bulk polymers.

7. SYNTHESIS METHODS FOR CONDUCTING POLYMER NANOSTRUCTURES

The synthesis method is one of the most fundamental and important object for developing conducting polymer nanostructures. A variety of synthesis methods have been developed for the fabrication of conducting polymer nanomaterials. Among the various synthesis strategies, the template approach (including hard and soft template), interfacial polymerization, self-assembly, micro-emulsion polymerization, rapid mixing polymerization, seeding polymerization, etc. have been widely employed to synthesize conducting polymer nanostructures and their composite nanostructures. The most widely used synthesis methods have been discussed in the following subsections in details.

7.1. Template guided method

Template method is a powerful and promising method for the synthesis of conducting polymer nanostructures. In general, the template method is classified by soft and hard templates. Soft template method relies on the molecular self-assembly to form nanostructures, while the hard template method needs existing nanostructure as template by physical or chemical interactions.

7.1.1. Soft-template method
Soft template also called the template free or self-assembly method is a relatively simple, cheap and powerful approach for synthesizing conducting

polymer nanostructures. By now, the surfactant, colloidal particles, structure directing molecules have served as "soft templates" and various soft template methods have been developed that includes template-free method [43, 44], rapid mixing method [45], dilute polymerization [46], reverse emulsion polymerization [47], ultrasonic irradiation [48], and radiolytic synthesis [49]. The soft-template methods are based on the self-assembly mechanisms due to hydrogen bonding, π-π stacking, Van-der Waals forces and electrostatic interactions as driving forces. The disadvantage of the soft-template method is poor control of the morphology, orientation and diameter of the conducting polymer nanostructures. The self-assembled surfactants form the micelles which act as soft templates to form conducting polymer nanostructures as shown in Fig. 12.
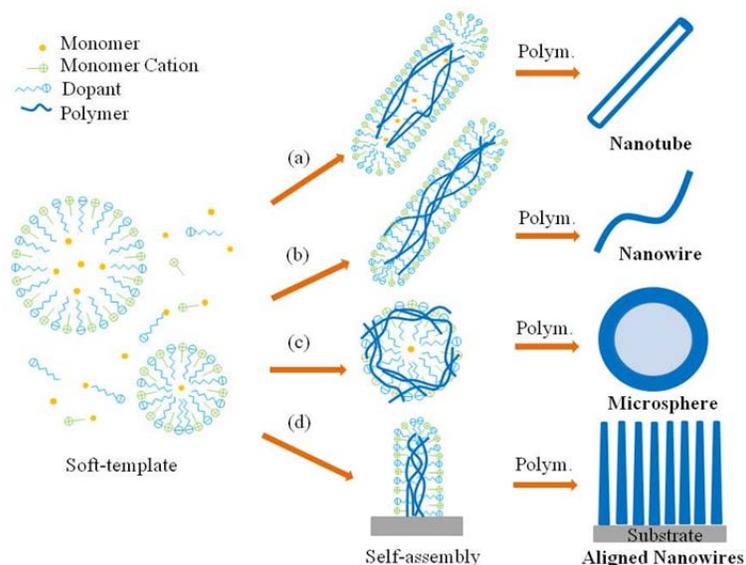

Fig. 12: Pictorial representation of soft-template synthesis of different nanostructures of conducting polymers.

Surfactant is a class of molecules that form thermodynamically stable aggregates of inherently nanoscale dimensions both in solutions and at interfaces. In equilibrium, the allowed packing of surfactant molecules into the aggregates can be described by a dimensionless parameter, referred to as the critical packing parameter (P). This critical parameter of the aggregates is controlled by the volume (V) and length (l) of the surfactant tail within the hydrophobic core of the surfactant aggregates and the effective area (a) occupied by each surfactant head group of the aggregate, which can be expressed as [50],

$$P = V/al \tag{1}$$

In general, the aggregate morphology of a surfactant in a solution is spherical, cylindrical or a flat bi-layer, depending on these parameters [50]. For a spherical micelle of radius R and aggregation number N, the total volume of the micelle can be written as

$$\frac{4}{3}\pi R^3 = NV \tag{2}$$

and the total surface area of the micelle can be written as

$$4\pi R^2 = Na \tag{3}$$

The packing criteria impose the restriction that the radius of the micelle cannot be greater than the length l of the hydrocarbon tail of the surfactant molecule.

i.e., $$R = (3V/a) \leq l \tag{4}$$

In terms of packing parameter P $(P = \frac{V}{al}) \leq \frac{1}{3}$, which means that when the packing parameter P is less than 1/3, spherical micelles are the preferred form of aggregate structure. By a similar argument, it can be easily shown that the cylindrical micelles form when the packing parameter is between 1/3 and 1/2 (i.e. $1/3 \leq P \leq 1/2$).

For a template-free method, the formation, size and morphology of the micelles as the soft-templates are greatly affected by the nature of the dopant, polymeric chain and the oxidant as well as the polymerization conditions. Different nanostructures of PPy such as wires, ribbons, sphere etc. have been synthesized by surfactants as soft templates [51]. Typical synthesis of this sort includes micro-emulsion polymerization and reversed micro-emulsion polymerization [52]. In general the micro-emulsion (oil-in-water) polymerization method is used to produce conducting polymer nanoparticles with control size. The concentration and structure of the surfactant plays the critical role for the formation of conducting polymer nanoparticles and to control their morphology [53]. The surfactants that suitable for the micro-emulsion polymerization should have alkyl chain lengths between C-6 to C-16, since the alkyl chains shorter than C-6 processes weak hydrophobic interactions, however alkyl chains longer than C-16 process a very high viscosity to form the self-assembled conducting polymer nanostructures. Moreover, the critical micelle concentration (CMC) of the surfactant plays a critical role for the formation of nanostructures.

The reversed micro-emulsion which is defined as an aggregate of surfactant molecules containing a nanometer sized aqueous pool in the oil phase is another common method for the synthesis of conducting polymer nanostructures with controlled morphology. The most commonly used surfactant to form reverse micelles is sodium bis(2-ethylhexyl) sulfosuccinate (AOT), which is an anionic surfactant with two hydrophobic tail-groups. The AOT molecules form the reverse micelles in the oil phase because of their bulky hydrophobic tail-groups compared with the hydrophilic head-groups [54]. Jang et al. [73] synthesized polypyrrole nanotubes via oxidation polymerization in sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse emulsions. PPy nanotubes with diameter 94 nm and length 2 mm were synthesized by using AOT reverse cylindrical micelles as the soft-templates. Zhang et al. [74] reported the soft template reverse emulsion polymerization of conducting poly(3,4-ethylenedioxythiophene) (PEDOT) nanotubes having diameters in the range of 50-100 nm. The soft template method owns low cost and produce large scale yields of conducting polymer nanostructures. The shortage of soft template method in energy storage devices rises from the discontinuous morphology of particles in electrode, which increases the electronic impedance in a certain extent.

7.1.2. Hard template method

Hard template method is an effective technique to synthesize aligned nanotubes and nanowires of conducting polymers with controllable diameter and length. This method is simple to handle and following steps

are followed for synthesis of nanostructures: (i) fill the nanoscale pores of a membrane with a monomer, (ii) polymerize the monomer inside the pores and (iii) remove the template in order to obtain the pure polymer. The porous membrane is the basic and most important part of the hard template method. The porous aluminium membranes (Al_2O_3) prepared by electrochemical method [55] and polycarbonate (PC) membranes prepared by a ''track-etch'' method [56] are widely used as commercial membranes. These membranes contain a wide range of a pore diameters (down to 10 nm) and with pore densities approaching 10^9 pores/cm^2 across the membrane surface [57].
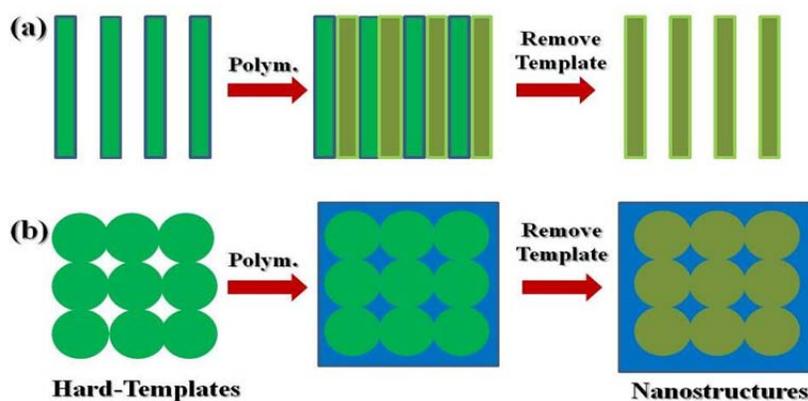

Fig. 13: Schematic of hard template synthesis of different conducting polymer nanostructures.

Till date, nanotubes and nanowires of different conducting polymers such as polyaniline (PAni), polypyrrole (PPy) and PEDOT have been chemically or electro-chemically synthesized by this hard template approach. A range of pore sizes have been synthesized and some as small as 5 nm have been reported [58]. The polymerization takes place on the surface of the template resulting core-shell structure [59]. After removal of the template, hollow

nanocapsules or nanotubes can be obtained [60]. The advantages of the hard template method are as follows: (i) Materials nanostructures including metal, semiconductor and conducting polymers can be synthesized either chemically or electrochemically and (ii) The diameter of the nanostructures is controlled by the size of the pores or channels in the membrane, whereas the length and thickness of the nanostructures can be adjusted changing the polymerization time. That is why the hard-template method is most commonly used synthesis approach for preparation of the well controlled and highly oriented nanostructures and the diameter of the conducting polymer nanowires can be obtained as small as 3 nm [61]. On the other hand, the disadvantages of this synthesis method are summarized as follows: (i) Using a membrane as a template requires post processing to remove the template which complicates the preparation process and the post process can destroy or disorder the resulting nanostructures and (ii) The quantity of the nanostructures produced by this method is limited by size of the template membrane, which limits its applications in large-scale production.

In the hard-template method, the synthesis of conducting polymer nanostructures is carried out by either chemical or electrochemical polymerization. Chemical hard-template synthesis approach is accomplished by simply immersing a membrane in a solution of the desired monomer, dopant and oxidant, and then allowing the polymerization of monomer within the pores of the templates which served as the ''nano-reactor'' [62, 63]. However, different types of nanostructures can be

produced by controlling the polymerization time. In general, the short polymerization results the tubular nanostructures with thin walls, while long polymerization leads to thick wall tubular or even fibrillar nanostructures.

In the electrochemical synthesis method, a metal film coated on one surface of the membrane is required to carry out the polymerization of the desired polymer within the pores of the membrane [64]. Compared to the chemical hard-template method, the electrochemical hard-template approach is more complex and expensive, but this method is more controllable through changing current density, applied potential and polymerization time. On the other hand, the large mass production by the electrochemical hard-template method is impossible due to the limiting size of the membrane that used as the template.

7.1.3. Interfacial polymerization

Based on the traditional synthesis method, Kraner et al. [65] have developed a simple chemical route to synthesize conducting polymer nanostructures under ambient condition using the aqueous/organic interfacial polymerization. This method allows the oxidative polymerization of monomer only at the interface of the aqueous/organic phase. The organic phase consists of monomer droplet whereas the oxidant is in aqueous phase and the resulting product enters into the aqueous phase. Interfacial polymerization does not depend on any specific template or dopant. An important aspect of interfacial polymerization method is that it enables the addition of various surfactant molecules, either negatively or positively charged, to the organic phase or even hydrophilic surfactants to the aqueous phase. As a result, the morphological and structural characteristics of the

resulting polymer can be easily controlled according to the reaction conditions. Moreover, the high formation yields make the method easily scalable and reproducible. Haung et al. [65] successfully synthesized polyaniline nanofibers with diameter of 50 nm using the interfacial polymerization method. The interfacial polymerization method has also been applied to synthesis the nanorods of PAni, PPy and PEDOT with an average diameter of 30 nm [66, 67].

1.7.4. Electrospinning method

The electrospinning is an effective technique to fabricate conducting polymer nanofibers with diameter ranging from micrometers to 100 nm by using strong electrostatic forces [68, 69]. In this method, the polymer solution is extruded from an orifice to form a small droplet in presence of an electric field and the charged solution jets are extruded from the cone. The fluid extension occur first in uniform, and then the straight flow lines undergo vigorous whipping and/or splitting motion due to fluid instability and electrically driven bending instability. Finally, the spun fibers are deposited as a nonwoven web on a collector. Compared with other methods, electrospinning method seems to be the only method that can produce continuous long nanofibers.

8. DIFFERENT NANOSTRUCTURES OF POLYPYRROLE

Polypyrrole is one of the most promising conducting polymers because of its ease of synthesis, high electrical conductivity, reversible redox property and environmental stability. PPy can be prepared by the chemical or

electrochemical polymerization via the oxidation of pyrrole monomer [70]. In general, the chemical polymerization leads to intractable powder, whereas the electrochemical polymerization results in film deposited on the electrode. The different nanostructures of PPy have been discussed in the following subsections.

8.1. Nanoparticles

Spherical PPy nanoparticles have been fabricated by the chemical oxidation polymerization with the aid of surfactant or stabilizer in an aqueous solution. Among all, the micro-emulsion polymerization has been extensively used to synthesize conducting polymer nanoparticles. Micro-emulsion synthesis of PPy nanoparticles with diameter of several nanometers could be obtained at low temperature [71]. At low temperature, the inner space of the micelles reduces by virtue of deactivating the chain mobility of the surfactant. As the polymerization temperature increased, the size of the PPy nanoparticles grew as a result of the enhanced chain mobility of the surfactant molecules. However, the size of the PPy nanoparticles decreased with shortening the chain length of the surfactant. The micelle aggregation number, defined as the number of surfactant molecules needed to form a micelle for polymerization, becomes smaller as the chain length of surfactant molecules decreases. The reduced micelle results the formation of smaller size nanoparticle. In an another micro-emulsion polymerization approach, PPy nanoparticles were synthesized using ferric chloride ($FeCl_3$) as oxidizing agent, and dodecylbenzenesulfonic acid (DBSA) and butanol were used as a surfactant and a co-surfactant, respectively [72]. It was observed that the micro-

emulsion polymerization not only increased the yield of resulting PPy nanoparticles but also the extent of the conjugation length in the polymer as compared with solution and conventional emulsion polymerization.

Dispersion polymerization has also been widely used to synthesis PPy nanoparticles by several research groups. Zelenev et al. [73] synthesized the PPy nanoparticles with diameter of 20-60 nm by the oxidation of pyrrole monomer with sodium persulfate (oxidizing agent) and 4-ethylbenzenesulfonic acid (doping agent) in the presence of Rhodasurf TB970 (polymeric stabilizer). Recently, PPy nanoparticles with uniform diameter of 46 nm were prepared via a facile one step aqueous dispersion polymerization using poly-vinyl alcohol (PVA) as stabilizer [74]. It was observed that with increasing pyrrole concentration, the resultant PPy nanoparticles became coarser with broadening the particle size distribution. Furthermore, increase in the PVA concentration resulted in faster polymerization and smaller size PPy nanoparticles.

8.2. Hollow nanospheres

Hollow nanospheres of PPy have been obtained using various template approaches [75]. PPy-chitosan hollow nanosphere of core diameter of 20±3 nm and shell thickness of 15±4 nm have been successfully fabricated using AgCl nanoparticles as sacrificial core at 2 °C [76]. The chitosan stabilized the AgCl nanoparticle and prevented the aggregation of PPy nanospheres during the synthetic process. Additionally, PPy hollow nanospheres were stable in acidic aqueous media and insoluble in basic media due to the presence of chitosan in the shell part. In recent studies, PPy hollow

nanospheres have been fabricated using core-shell nanomaterials composed of an identical polymer [76].

8.3. Nanofibers

A bulk synthesis of PPy nanofibers with diameter ranging from 60 nm to 90 nm was carried out using the nanofiber seeds as a template. V_2O_5 nanofibers with diameter of 15 nm treated by chemical method with pyrrole monomer were used as reactive seed templates. Yang et al. [77] synthesized the high yield PPy nanofibers using the reactive template approach. The reactive template of $FeCl_3$ and methyl orange (MO) guided the formation of uniform PPy nanofibers. Chronakis et al. [78] reported the synthesis of PPy nanofibers with average diameter in the range about 70-300 nm by the electrospinning method. The resulting PPy nanofibers exhibited well defined morphology and physical stability. Moreover, Feng et al. [79] reported the synthesis of PPy micro/nanofibers via the self-assembly method in presence of $FeCl_3$ as oxidant.

8.4. Nanotubes

In general, PPy nanotubes have been mainly synthesized by the hard template method [80, 81]. PPy nanotubes with highly uniform surface and controlled morphology were fabricated by one-step VDP using AAO membrane. Recently, a reliable synthesis method called the soft template was developed for synthesizing PPy nanotubes against the hard template synthesis. Jang et al. [47] reported the synthesis of PPy nanotubes with average diameter of 95 nm and length more than 5 μm using the reverse micro-emulsion polymerization method. The PPy nanotubes have exhibited

higher electrical conductivity of 30.4 Scm^{-1}. Yang et al. [82] reported the facial fabrication of functional PPy nanotubes via the reactive self degrade template method with outer and inner diameters of 70 and 50 nm, respectively.

9. CONCLUSIONS

The present chapter concludes that conducting polymers can be used as organic conductors and can replace the traditional metallic conductors due to their high electrical conductivity, flexibility, low cost, light weight etc. Conducting polymers cover wide range of applications such as in sensors, dugs delivery devices, actuators, artificial muscles, supercapacitors, electrochromic displays and windows etc. The nanostructured conducting polymers exhibit improved physico-chemical properties over their bulk counterparts due to their high aspect ratio and quantum confinement effect. The conducting polymer nanostructures can be synthesized using different synthesis methods such as template synthesis (soft and hard), interfacial polymerization, electrospinning method, radiolytic method etc. The morphology of the nanostructures is different as per application and henforth the desired nanostructure can be synthesized using the standard synthesis method. Among the family of conducting polymers, polyaniline (PAni), polypyrrole (PPy), polythiophne (PTh) etc. and their various nanostructures such as nanoparticles, nanotubes nanorods, nanofibers, nanoneedles etc. are mostly studied owing to their high electrical conductivity (comparable to the metallic conductivity), ease of synthesis, biocompatibility, solubility and light weight. Moreover, the one

dimensional conducting polymer nanostructures can be used as molecular wires in futuristic nanodevices.

REFERENCES

[1]   Kivelson, S., & Heeger, A.J. *Synth. Met.* **22**(4)*,* 371-384, 1988.

[2]   Shirakawa, H., Louis, E.J., MacDiarmid, A.G., Chiang, C.K. & Heeger, A.J. *J. Chem. Soc., Chem. Commun.* (16), 578-580, 1977.

[3]   Batchelder, D.N. *Contemp. Phys.* **29**(1), 3-31, 1988.

[4]   Kaake, L.G., Barbara, P.F. & Zhu, X.Y. *J. Phys. Chem. Lett.,* 1(3) 628-635, 2010.

[5]   Long, Y.Z., Li, M.M., Gu, C., Wan, M., Duvail, J.L., Liu, Z., & Fan, Z. *Prog. Polym. Sci.* **36**(10), 1415-1442*,* 2011.

[6]   Jeon, S.S., Kim, C., Ko, J. & Im S.S., *J. Mater. Chem.,* **21,** 8146-8151, 2011.

[7]   Abdelhamid, M.E., O'Mullaneb, A.P. &   Snook G.A. *RSC Adv.,* **5,** 11611-11626, 2015.

[8]   Kaur, G., Adhikari, R., Cass, P., Bown, M. & Gunatillake, P. *RSC Adv.,* **5,** 37553-37567, 2015.

[9]   Xia, C., Chen, W., Wang, X., Hedhili, M.N., Wei, N. & Alshareef, H.N. **5**(8), 1401805, 2015.

[10] Xue, F., Su, Y., & Varahramyan, K. *MRS Conference Symposium* **814**, 2004.

[11] Covington, J.A., Gardner, J.W., Bartlett, P.N., & Toh, C.S. *IEE Proceedings-Circuits Devices and Systems* **151**(4) 326-334, 2004.

[12] Ashizawa, S., Shinohara, Y., Shindo, H., Watanabe, Y., & Okuzaki, H. *Synth. Met.* **153**(1-3), 41-44, 2005.

[13] Liu, Y., Varahramyan, K., & Cui, T. *Macromol. Rapid Commun.* **26**(24), 1955-1959, 2005.

[14] Bai, H. & Shi, G. *Sensors* **7**(3), 267-307, 2007.

[15] Shrivas, A.G., Bavane, R.G., & Mahajan, A.M. *International Workshop on Physics of Semiconductor Devices,* 621-623, 2007.

[16] Palod, P.A. & Singh, V. *Sens. Actuator B-Chem.,* **209,** 85-93, 2015.

[17] Wu, D.Q., Wu, L.L., Cui, H.C., Zhanga, H.N. & Yua, J.Y. *J. Mater. Chem. B,* **4,** 1520-1527, 2016.

[18] Virji, S., Huang, J., Kaner, R.B. & Weiller B.H. *Nano Lett.* **4**(3), 491-496, 2004.

[19] Byshkin, M.S., Buonocore, F., Matteo, A.D. & Milano, G. *Sens. Actuator B-Chem.,* **211,** 42-51, 2015.

[20] Aydemir, N., Malmström, J. & Travas-Sejdic, J. *Phys. Chem. Chem. Phys.,* **18,** 8264-8277, 2016.

[21] Forzani, E.S., Zhang, H.Q., Nagahara, L.A., Amlani, I., Tsui, R., & Tao, N. A, *Nano Lett.* **4**(9), 1785-1788, 2004.

[22] Vyas, M.K. & Chandra, A. *Appl. Mater. Interfaces,* **8**(28), 18450-18461, 2016.

[23] Saini, P. & Choudhary, V. *J. Nanopart. Res.* **15,** 1415, 2013.

[24] Koul, S., Chandra, R., & Dhawan, S.K. *Polym.* **41**(26), 9305-9310, 2000.

[25] Kim, H.K., Kim, M.S., Song, K., Park, Y.H., Kim, S.H., Joo, J., & Lee, J.Y. *ICSM International Conference on Science and Technology of Synthetic Metals,* **135**(36), 881, 2002.

[26] Burroughes, J.H., Bradley, D.D.C., Brown, A.R., Marks, R.N., Mackay, K., Friend, R.H., Burns, P.L. & Holmes, A. B. *Nature* **347**, 539-541, 1990.

[27] Baughman, R.H. *Synth. Met.* **78**(3), 339-353, 1996.

[28] Hara, S., Zama, T., Takashima, W., Kaneto, K. *Polym. J.* **36**(2), 151-161, 2004.

[29] Otero, T.F., & Broschart, M. *J. Appl. Electrochem.* **36**(2), 205-214, 2006.

[30] Massonnet, N., Carella, A., Geyer, A, Vincent, J.F. & Simonato, J.P. *Chem. Sci.,* **6,** 412-417, 2015.

[31] Xu, H., Wu, J., Li, C., Zhang, J. & Liu, J. *Electrochim. Acta* **165,** 14-21, 2015.

[32] Kumar, D., & Sharma, R.C. *Eur. Polym. J.* **34**(8), 1053-1060, 1998.

[33] Chiang, J.C., MacDiarmid, A.G. *Synth. Met.* **13**(1-3), 193-205, 1986.

[34] MacDiarmid, A.G., & Epstein, A.J. *Faraday Discuss. Chem. Soc.* **88**, 317-332, 1989.

[35] Skotheim, T.A., & Reynolds, J.R., CRC press(Ed) Taylor & Francis Group, Florida, 2006.

[36] Dong, H. & Hu, W. *Acc. Chem. Res.,* **49**(11), 2435-2443, 2016.

[37] Chen, X., Li, D.M., Liang S.F., Zhan, S. & Liu, M. *Sens. Actuator B-Chem.,* **177,** 364-369, 2013.

[38] Bredas, J.L., & Street, G.B. *Acc. Chem. Res.* **18**(10), 309-315, 1985.

[39] Dubala, D.P., Huertasa, Z.C., Holzeb, R., Romero, P.G. *Electrochim. Acta*, **191,** 346-354, 2016.

[40] H. Farrokhia O. Khanib, F. Nematia, M. Jazirehpour, *Synth. Met.* **215,** 142-149, 2016.

[41] Shi, Y., Pan, L., Liu, B., Wang, Y., Cui, Y., Bao, Z. & Yu, G. *J. Mater. Chem. A,* **2,** 6086-609, 2014.

[42] Wanekay, A.K., Nosang, W.C., Myung, V., & Mulchandani, A. *Electroanal.* **18**(6), 533-550, 2006.

[43] Mahato, N., Parveen, N. & Cho, M. H., *Mater. Lett.*, **161,** 372-374, 2015.

[44] Saini, P. & Aroraa, M., *J.* Mater. Chem. A, 1, 8926-8934, 2013.

[45] Zhao, Y., Wei, H., Arowo, M., Yan, X., Wu, W., Chen, J., Wang, Y. & Guo, Z., *Phys. Chem. Chem. Phys.,* **17,** 1498-1502, 2015.

[46] Chiou, N.R, & Epstein, A.J. *Adv. Mater.* **17**(13), 1679-1683, 2005.

[47] Jang, J., & Yoon, H. *Chem. Commun.* (6), 720-721, 2003.

[48] Liu, H., Hu, X.B, Wang, J.Y., & Boughton, R.I. *Macromolecules* **35**(25), 9414-9419, 2002.

[49] Pillalamarri, S.K., Blum, F.D., Tokuhiro, A.T., Story, J.G., & Bertino, M.F. *Chem. Mater.* **17**(2), 227-229, 2005.

[50] Huang, W.S., Humphrey, B.D., & MacDiarmid, A.G. *J. Chem. Soc., Faraday Trans.* **82**(8), 2385-2400, 1986.

[51] Zhang, X.T., Zhang, J., Song, W.B., & Liu, Z.F. *J. Phys. Chem. B* **110**(3), 1158-1165, 2006.

[52] Rao, J.P., & Geckeler, K.E. *Prog. Polym. Sci.* **36**(7), 887-913, 2011.

[53] Klapper, M., Neno, S., Haschic, R., Mulle, K., & Mulle, K. *Acc. Chem. Res.* **41**(9), 1190-1201, 2008.

[54] Jang, J., & Yoon, H. *Langmuir* **21**(24), 11484-11489, 2005.

[55] AlMawiawi, D., Coombs, N., & Moskovits, M. *J. Appl. Phys.* **70**(8), 4421-4425, 1991.

[56] Fleischer, R.L., Price, P.B., & Walker, R.M. University of California Press, Berkeley, 1975.

[57] Despic, A., & Parkhutik, V.P. Plenum Press, New York, 1989.

[58] Cho, S.I., & Lee, S.B. *Acc. Chem. Res.* **41**(6), 699-707, 2008.

[59] Niu, Z., Liu, J., Lee, L.A., Bruckman, M.A., Zhao, D., Koley, G., & Wang, Q. *Nano Lett.* **7**(12), 3729-3733, 2007.

[60] Fu, G.D., Zhao, J.P., Sun, Y.M., Kang, E.T., & Neoh, K.G. *Macromolecules* **40**(6), 2271-2275, 2007.

[61] Wu. C.G., & Bein, T., *Science* **264**(5166), 1757-1759, 1994.

[62] Parthasarathy, R.V., & Martin C.R. Chem. *Mater.* **6**(10), 1627-1632, 1994.

[63] Ozin, G.A. *Adv. Mater.* **4**(10), 612-649, 1992.

[64] Hulteen, J.C., & Martin, C.R. *J. Mater. Chem.* (7), 1075-1087, 1997.

[65] Huang, J., & Kaner, R.B. *J. Am. Chem. Soc.* **126**(3), 851-855, 2004.

[66] Nuraje, N., Su, K., Yang, N.L., & Matsui, H. *ACS Nano* **2**(3), 502-506, 2008.

[67] Su, K., Nuraje, N., Zhang, L.Z., Chu, I.W., Peetz, R.M., Matsui, H., & Yang, N.L. *Adv. Mater.* 19(5), 669-672, 2007.

[68] Huang, Z.M., Zhang, Y.Z., Kotaki, M., & Ramakrishna, S. *Compos. Sci. Technol.* **63**(15), 2223-2253, 2003.

[69] Greiner, A., & Wendorff, J.H. *Adv. Polym. Sci.* **219**, 107-171, 2008.

[70] Sadki, S., Schottland, P., Brodie, N., & Sabouraud, G. *Chem. Soc. Rev.* **29**(5), 283-293, 2000.

[71] Jang, J., Oh, J.H., & Stucky, G.D. *Angew. Chem. Int. Ed.* **41**(21), 4016-4019, 2002.

[72] Yan, F., Xue, G., & Zhou, M. *J. Appl. Polym. Sci.* **77**(1), 135-140, 2000.

[73] Zelenev, A., Sonnenberg, W., & Matijevic, E. *Colloid Polym. Sci.* **276**(9), 838-841, 1998.

[74] Zha, Z., Yue, X., Ren, Q., Dai, Z., *Adv. Mater.* **25**(5), 777-782. 2013.

[75] Jang, J., Oh, J.H., & Li, X.L. *J. Mater. Chem.* **14**(19), 2872-2880, 2004.

[76] Cheng, D., Zhou, X., Xia, H., & Chan, H.S.O. *Chem. Mater.* **17**(14), 3578-3581, 2005.

[77] Yang, X., & Li, L. *Synth. Met.* **160**(11-12), 1365-1367, 2010.

[78] Chronakis, I.S., Grapenson, S., & Jakob, *Polymer* **47**(5), 1597-1603, 2006.

[79] J. Feng, W. Yan, L. Zhang, *Microchim. Acta* 166(3), 261-267, 2009.

[80] Menon, V.P., Lei, J., & Martin, C.R. *Chem. Mater.* **8**(9), 2382-2390, 1996.

[81] Jang, J., Oh, J.H. *Chem. Commun.* (7), 882-883, 2004.

[82] Yang, X., Zhu, Z., Dai, T., & Lu, Y. *Macromol. Rapid Commun.* **26**(21), 1736-1740, 2005.