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Prospects of conducting polymers in molecular electronics

V. Saxena, B.D. Malhotra *

Biomolecular Electronics and Conducting Polymer Research Group, National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi 110012, India

Abstract

Molecular electronics (ME) is rapidly evolving from physics, chemistry, biology, electronics and information technology. This is because the present-day advanced silicon chip can store about 16 million bytes of information within an area less than 1 cm². Organic materials such as proteins, pigments and conducting polymers (CPs) have been considered as alternatives for carrying out the same functions that are presently being performed by semiconductor silicon. Among these, CPs have demanded the maximum attention. These ME materials differ from conventional polymers by having a delocalized electronic structure that can accommodate charge carriers such as electrons and holes. Besides, these conjugated electronic materials exhibit Peierl's instabilities due to built-in highly anisotropic interactions. It has been proposed that electrical conduction in CPs occurs via non-linear (or topological) defects (solitons/polarons) generated either during polymerization or as a consequence of doping. Solitons and polarons have recently been shown to have implications in the technical development of ME devices.

CPs such as polypyrroles, polythiophenes and polyanilines have been projected for applications for a wide range of ME devices. One of the main reasons for such a wide-spread interest is due to the reported observation that these interesting electronic materials exhibit full range of properties from insulator to superconductor depending upon chemical modification. CPs have been found to have applications as optical, electronic, drug-delivery, memory and biosensing devices. The major challenge confronting the material scientists including chemists and physicists is how do the properties of these electronic materials differ from those of conventional semiconductors. Another advantage lies in the fact that these materials possess specific advantages such as high packing density, possibility of controlling shape and electronic properties by chemical modification.

Our group has been actively working towards the application of CPs to Schottky diodes, metal-insulator-semiconductor devices and biosensors for the past about 10 years. This paper is a review of some of the results obtained at our laboratory in the area of CP ME.

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1. Introduction

Electronic technology has rapidly evolved during the past decades. The emphasis is to make better, faster and smaller electronic devices for application in modern life. Almost all electronic devices are fabricated from semiconductor silicon. The contemporary advanced silicon chip can store 16 million bits of information within an area less than 1 cm^2 . However, there is a practical limit to the density of stored information in a chip. If the size is decreased further, there is possibility of overheating

Corresponding author. Fax: +91-11-25726938.

and cross-talk between electronic components, which can affect their performance. One of the possible ways to overcome the present limitation is to use organic materials such as proteins, pigments, conducting polymers (CP) etc. to carry out the same functions that are presently being performed by conventional semiconductors. This approach led to the evolution of an interdisciplinary field, molecular electronics (ME). ME is so named because it uses molecules to function as 'switches' and 'wires'. ME is a term that refers both to the use of molecular materials in electronics and electronics at molecular level.

Among organic materials, CPs (or conjugated polymers) have attracted most attention for possible applications in ME devices [1–5] because of their unique

E-mail address: bansidhar_m@yahoo.com (B.D. Malhotra).

properties and versatility. The first conjugated polymer, polythiazyl $(SN)_r$, was discovered in 1975, which possesses metallic conductivity and becomes superconductor at 0.29 K [6]. However, the idea of using polymers for their electrical conducting properties actually emerged in 1977 with the findings of Shirakawa et al. [2], that the iodine doped trans-polyacetylene, $(CH)_x$, exhibits conductivity of 10³ S/cm. Since then, an active interest in synthesizing other organic polymers possessing this property has been initiated. As a result, other CPs having π -electron conjugated structure (conjugated polymers), such as polyaniline (PAni), polypyrrole (PPy), polythiophene (PT), polyfuran (PFu), poly(pphenylene) and polycarbazole [2-4,7] have been synthesized for exploring them in devices. The molecular structures of a few CPs are shown in Fig. 1. The conductivity of these polymers can be tuned from insulating regime to superconducting regime, by chemical modification, by the degree and nature of doping. Besides these, polymers offer the advantages of lightweight, flexibility, corrosion-resistivity, high chemical inertness, electrical insulation, and the ease of processing.

The use of CPs in ME is rapidly evolving from physics, chemistry, biology, electronics and information



Fig. 1. Structures of a few CPs.

technology. These ME materials differ from conventional polymers in the sense that they posses a π -delocalized electronic structure. Besides this, these organic materials exhibit Peierl's instabilities due to the built-in high anisotropic interactions and undergo substantial geometric modifications due to electronic excitations [3]. This results in various charge transfer processes and a substantial degree of disorder leading to various localized states in the forbidden gap due to localization. CPs can have the behaviour of metal and semiconductor. The various electronic properties of CPs result from the various type of charge carriers in these materials, which is entirely different from that of conventional semiconductors. The polymer chain is distorted when electrons or holes are injected at the electrodes, and the charge carriers couple with the polymer chain distortion to form a mobile polaron/soliton [8,9]. When the density of injected electrons/holes increases, the coupling of charge carriers with the polymer chain gives rise to the formation of bipolaron. Charge transport involves the transport rate, scattering and trapping processes, recombination, tunneling, hopping. The mechanism appears to be complex and needs to be elucidated. Several basic models of electronic transport have been described: the tunnelling model, the variable range hopping model, small polaron transport and the solitonic transport etc.

The progress in the field of ME is dependent upon the synthetic routes and molecular tailoring. CPs can be prepared both by chemical and electrochemical methods. By varying the nature of the groups, specific interactions with external physical and chemical phenomena can be developed in these materials leading to molecular devices such as transducers, memories and logic operators.

Characterization of CPs is another important part for understanding the basic science underlying various physical and chemical processes. A variety of techniques such as electrochemical, optical, electron spin resonance, scanning electron microscopy (SEM), atomic force microscopy (AFM), gel permeation chromatography (GPC) have been widely used to delineate the physical properties of the conjugated polymers [10–14]. For example, the changes in the optical spectra accompanied with doping have been considered very significant in elucidating the mechanism of structural changes in the polymer chains. Information on morphological changes has been found very helpful towards the fabrication of light-weight batteries [15]. It is to be noted that the experimental data collected from various characterization methods play a crucial role in the application of CPs in ME.

Owing to the unique electronic, electrical and optical properties of these conjugated materials, several potential, technological and commercial applications such as optical, electronic, memory, biosensing devices and display devices have been developed [16–18]. Among these, the application of CPs to ME has attracted the maximum attention. The major challenge confronting the materials scientists is to provide the basic mechanisms behind these devices in order to explore them in several applications. Our group has been actively engaged in the research and development of CP based ME devices for more than a decade [19–25]. The present paper is based on some recent research findings in the highly fascinating field of ME.

2. Synthesis and characterization of conducting polymer films

Conjugated polymers can be prepared by both electrochemical and chemical methods [25,26]. If polymeric materials can be made soluble, then, these materials can be purified by dissolution and subsequent re-precipitation. Therefore, differences in the synthetic methods become less important. In general, both methods have their own advantages. Electrochemical methods have advantages over chemical methods in the sense that they offer control on the polymerization and doping level, and could be produced over a number of substrates in order to fabricate devices directly. On the other hand, chemical synthesis is expected to produce polymers with high yield and ordered structures. By using electrochemical methods, these polymers can be synthesized by anodic oxidation of the monomers in suitable electrolytes (aqueous or non-aqueous) either at constant potential, or at constant current, or by cycling the potential. PT has been synthesized by both electrochemical [27] and chemical techniques [28]. Pandey et al. [29] have reported the chemical synthesis of poly(anilineco-orthoanisidine) that has been found to be soluble in common organic solvents such as acetone, chloroform and *n*-methylpyrrolidone (NMP). Wang and Quirk [30] later systematically investigated the effect of temperature on the synthesis and properties of poly(aniline-co-orthoanisidine). Other methods such as photopolymerization and plasma polymerization have also been used to cast thin films of CPs. PPy has been reportedly synthesized from pyrrole using tris (2,2'-bipyridyl ruthenium) complex as a photosynthesizer. The advantage of this technique lies in the easier control of polymerization reaction to any desired surfaces. Plasma polymerization makes use of molecules occurring in various plasma environments. This technique results in very thin but uniform polymeric layers that strongly adhere to a desired substrate. It has been found that the plasmapolymerized films are usually highly cross-linked and are resistant to higher temperatures and chemicals. Success in synthesizing processable CP has promised their potential application in ME devices.

Characterization of a CP is an important aspect before it can be used for any technological application. Physical and chemical properties of CPs have been investigated by a number of experimental techniques such as GPC, thermal techniques, spectroscopic and microscopic methods [3,5,22,27,29]. For example differential scanning calorimetry has been utilized to study the air-stability of CPs [29]. Spectroscopic methods have yielded important information on charge transport behaviour in conjugated polymers. ¹³C NMR studies have been conducted on polyazulene, polybithiophene and PFu in their respective doped and undoped states [31]. The ¹³C NMR data obtained on the electrochemically prepared pyrrole polymers indicate the presence of α - α' bonding in conducting PPy films [32]. It has been shown that the origin of magnetic properties in a conjugated polymer lies in its π -electron system that has also been considered as the reason for the observed chemical properties [33]. The structures of copolymers of 3cyclohexylthiophene and 3-n-hexylthiophene were confirmed by IR and NMR studies. Distinct peaks observed in the IR (Fig. 2) spectrum of copolymer have been found to confirm the copolymerization of ingredient monomers [24]. Morphology of CP films has been investigated using optical microscopy, SEM/transmission electron microscopy, scanning tunneling microscopy (STM) and AFM techniques [34-36]. Studies conducted on the morphology of conducting PPy films containing different anions such as NO3, F-, ClO4, BF4 and $CH_3C_6H_4SO_3^-$ have revealed that topology of growing conducting PPy surface is influenced by the nature of the electrolyte [37]. For instance, it has been shown that the fibrillar structure of polyacetylene is often advantageous since it can store up to about 7% of electrical charge [38]. AFM and STM methods [39] have recently provided valuable information on the presence of microdomains in poly(3-hexylthiophene)/stearic acid films.



Fig. 2. Infrared spectra of (a) P3CHT, (b) copolymer and (c) P3nHT, taken in KBR matrix [24].

3. Preparation of ultrathin conducting polymer films

To realize ME, one of the key issues is how to fabricate the ordered structures in a planned manner since various properties of organic molecules are of anisotropic nature, and consequently the functions of molecular assemblies depend strongly on the way molecules are arranged in them. The assembling process, called molecular engineering, can be accomplished in many ways among which Langmuir–Blodgett and self-assembly technique have been considered most promising.

3.1. Langmuir–Blodgett films

Langmuir-Blodgett films of CPs have attracted considerable attention not only as active elements of ME but also in terms of their low-dimensional nature. Typical LB films are prepared by transferring monolayers of amphiphilic molecules at the air-water interface onto solid substrates. The amphiphilic molecules are first dissolved in an organic solvent that is immiscible with water, spread on water surface, and compressed by decreasing the area in which the molecules are confined, to form a monolayer at the air-water interface. Then the monolayer is transferred onto a solid substrate by moving the substrate vertically or horizontally. The procedure can be used to obtain ultrathin films with the structure and thickness controlled at molecular level. Three possible structures possible by LB technique are shown in Fig. 3.

The LB film of a CP was first prepared by Iyoda et al. using an amphiphilic pyrrole derivative mixed with octadecane [40–43]. This precursor LB film is electropolymerized to give a lateral conductivity of 0.1 S/cm, with the conductivity in the perpendicular direction being 10^{-11} S/cm. Several other methods were also demonstrated to fabricate PPy films. Hong et al. have shown



Fig. 3. X-, Y- and Z-mode in Langmuir-Blodgett film deposition.

that the electrically conducting LB PPy films can be formed using a solution containing surface-active pyrrole monomer and excess pyrrole on a sub-phase containing ferric chloride [44]. It was found that the properties of resultant polymer are strongly influenced by the type of surface-active monomer used. Ultrathin films of 3-octadecylpyrrole and 3-octadecanoylpyrrole (30DOP) were subsequently obtained using LB technique. The pyrrole/3ODOP film was found to be highly anisotropic with conductivity in the plane being two orders of magnitude higher that across the perpendicular direction. LB films of PAni were also prepared and electrochemical studies on these films were performed using cyclic voltammetry coupled with quartz microbalance [45]. Aghbor et al. have obtained LB films of polymeraldine base (PEB) by dissolving PEB in a NMP/ chloroform mixture in an aqueous subphase containing acetic acid [46]. On the other hand, Ram et al. demonstrated that it is possible to obtain LB films of PEB without incorporating fatty acid tails in the molecule [47,48]. However, electrochemical studies of these films show quasi-ordered structure, resulting in reduced electroactivity. Recently, LB films of a poly(p-phenylene vinylene) (PPV) precursor were prepared using an amphiphilic precursor, where the counter ion chloride was partially exchanged by a long chain dodecylbenzenesulfonate ion [49]. These films were then used to accomplish both circular dichromism, and circularly and linearly polarized luminescence. The formation of such optical active superstructures was found to be due to the induced order in these LB films. In addition, LB films of PT, poly(o-anisidine) and poly(ethoxyaniline) were prepared and studied for possible applications in ME devices [50-52]. These devices include microactuators, high-density information storage, diodes, transistor, molecular switches etc. It is appropriate to mention here that LB technique provides an efficient way to control the thickness and organization of CPs at molecular level for application to the potential field of ME.

3.2. Self-assembly technique

The drawbacks of using LB technique are that it is a time-consuming process and films tend to be fragile. The self-assembly technique offers an alternative route to prepare monolayer/multilayer thin films of highly ordered multifunctional compounds in a more effective and time-saving manner. This technique is advantageous than the LB technique in the sense that each layer in self-assembled (SA) film can be covalently linked and no excessive deposition can take place as it is limited by the reactive sites on the layer surface [53]. In this technique, the molecules are transferred to the surface of a solid substrate from the liquid phase containing self-assembling material by a dipping process and subsequently, a highly organized and densely packed molecular layer

forms spontaneously on the substrate. The formation of the SA monolayer is driven by a strong interaction between the substrate and a surface-specific functional group of the adsorbent, e.g. the interaction between organo sulphur compounds and a gold substrate. The high specificity of the sulphur-gold interaction allows the introduction of various functional groups into the monolayer without disturbing the self-assembly process. Multilayered films of required thickness and layer sequence can also be obtained by using this technique, e.g. alternate layers of p- and n-type polymers. In this approach polymer is converted into a polycation or polyanion by using appropriate acidic solution and the molecules are held by electrostatic attraction of alternately charged polymers [54-58]. Different conjugated and non-conjugated polymers in the form of bilayers have been used to make heterostructures. Collard and Fox reported a highly ordered lamellar polymer by using this approach [59]. The interlayer spacing was found to be 42.2 ± 0.2 A using XRD data. A self-assembly of poly(3-octylthiophene) (POT) on gold electrode was found to be stable [60]. Subsequently, it was shown that such POT monolayer can undergo reversible doping and undoping as revealed by cyclic voltammetry experiments [61]. Self-organization from solution-processed CPs can form complex structures where ordered microcrystalline domains are embedded in an amorphous matrix [62,63]. It has been shown that regioregular poly(3-hexylthiophene) (RRPHT) can form nanocrystals with lamellar structures where the interchain coupling is subsequently increased. This results in the mobility increase by more than two orders of magnitude [64]. Further, in a recent study of such films, it was found that polarons/excitons become delocalized over several chains as confirmed by a strong, red-shifted absorption band in the mid-IR range with superimposed anti-resonance (AR) bands [65]. These AR bands may provide an important tool for the study of electron-phonon coupling and vibrational spectroscopy in these materials. Lately, multilayer SA films of poly(2,5-methoxy-propyloxy sulfonate phenylene vinylene) (MPS-PPV) were prepared and characterized [66]. A red-shift in both absorption and fluorescence spectra with increasing numbers of active MPS-PPV layer were observed, which were attributed to the change in polymer conformation and efficient energy transfer. Capping a C_{60} or C_{60} copolymer layer on top of these highly luminescent multiplayer films results in quenching of the photoluminescence with $\sim 95\%$ efficiency. The good optical properties of these films are very useful for their potential application in photosynthesis and photovoltaic cells. Self-assembly technique has also been used to fabricate stable and improved electroluminescent devices [67,68]. Rubner and coworkers have reported the preparation of SA multilayer films of PPV and polyanion. The polyanion influences the amount of conjugated PPV deposited per bilayer,

the thickness of each layer, and eventually the electrical properties of the films [69]. They showed that it is possible to tune the wavelength of light emitted by the device without chemically modifying the PPV structure. Further, it was shown by Cho et al. that the conjugation bond length could be adjusted by the ionic strength of the polyanion solution and thereby the light emitted by the device made of such SAM [70]. In a subsequent report they showed that the electrical properties of PPV could be simply tuned by the variation of simple physical parameter such as ionic strength of polyanion [71]. There has also been a vast interest in polymer lasers with microring structures. Laser emission form the microring structure of poly(2,5-dialkoxy-p-phenylene vinylene) has been observed [72] and electroluminescent device with microcavity structure has been fabricated [73]. Subsequently, alternating multilayers of poly(1,4-{2-(5-carboxypentyloxy)-5-methoxyphenylene} vinylene) and PPV have been adsorbed onto the positively charged substrates and Fujisawa et al. have studied their optical properties. They also fabricated the periodic multilayers with microring geometry around the quartz fibers and observed a yellow luminescence from a light-emitting device using such structures [74]. Recently, there has been much interest in the preparation of self-organized super molecules based on CPs i.e. supra-molecular assembled films [75–77]. Super molecules are moieties held together by molecularly matching physical bonds (recognition) [78]. Such assemblies have potential applications to achieve 'molecular wires' and 'molecular switches'.

4. Applications of conducting polymers in molecular electronic devices

Much research has been carried out on the use of CPs as active materials in ME devices. Undoped and doped conjugated polymers, such as polyacetylene, PPy, PT and its derivatives exhibit interesting semiconducting behaviour that can be used in device applications as revealed in the following sections.

4.1. Diodes

Rectifying junctions are the basic elements of many electronic components. Since the discovery of the CPs, rectifying junctions such as p–n junction and Schottky junction have been studied so as to explore the possible application of CPs.

The standard method of adjusting the conductivity of a semiconductor and choosing the nature of the dominant majority carriers is by controlled doping. This allows the construction of p–n junction in which the concentration profiles of the dopants and therefore, the spatial dependence of the energy-level positions remain stable despite the existence of high internal electric fields. In 1978, Chiang et al. have made a p-n junction device by pressure contact of a p-type polyacetylene film (doped with Na) to an n-type polyacetylene film (doped with AsF5) [79]. However, stable p-n junctions could not be developed successfully. This is because the preparation of p-n junction by diffusion of two dopants eventually led to compensation of the donor by the acceptor and thereby, led to a homogeneously insulating material. The alternative attempt to fabricate CP based rectifying junctions is to use a heterojunction between a semiconductor and a CP or Schottky junction between CP and metal. p-type Si [80], n-type Si [81], and CPs [82] have been used as semiconductor in order to achieve stable junctions. The electronic properties of heterojunctions have been studied in the case of poly(sulfur nitride) and poly(acetylene) [83,84]. However, fabrication of such junctions is usually difficult due to the inherent difficulty in casting desired CP films directly on the semiconductor surface. Several Schottky junctions have been fabricated using PPy [85], PAni [86], polyacetylene [87], and poly(3-alkylthiophene) (P3AT) [88], respectively. These contacts were studied the most, primarily due to possible applications in photovoltaicenergy conversion. Unfortunately, the photovoltaic yield of CPs never exceeded about 1% [89]. Recently, poly(alkylthiophene) based Schottky diode has been reported [90] that is sensitive to different gaseous species. In contrast to inorganic semiconductors, which exhibit low selectivity, CPs offer high selectivity, room-temperature operation and low-cost [91]. Nitric oxide and ammonia sensitive Schottky diodes have been reported by Inganas and coworkers [92].

Free-standing films of PAni have been used to make Schottky junction by Chen and Fang [93] and effect of doping on rectification and photovoltaic characteristics were studied. The undoped toluene-4-sulfonic acid doped and polyacrylic acid doped PAni behave as a ptype semiconductor. The acid doping of PAni can cause a higher rectifying behaviour and photovoltaic conversion efficiency. On the other hand metal/polymer junction using vacuum evaporated PAni films was reported by Misra et al. [94]. They found that the structure of PAni remains unchanged after vacuum evaporation due to polymerization and conjugation of chains broken during evaporation. This was confirmed by infrared and optical spectroscopy. The large degree of defects possible in vacuum deposited metal/polymer junction were attributed to the fact that the defects and dangling bond readily react with various gases.

Electronic properties of PPy/metal and PPy/n-Si junctions have also been investigated in detail by several researchers [95–97]. Watanabe et al. reported energy band diagrams of PPy/n-Si junction on the basis of electrical and optical data [95]. The higher values of ideality factor in comparison to that of inorganic semi-

conductors were found to be due to the discontinuous structure at the interface between polymer and semiconductor. Lei et al. discovered that it is possible to make Schottky junction on the PPy films with a metal electrode using interfacial polymerization method [96]. Various physical characteristics of the polymer, work function, Fermi level and carrier concentration have been estimated and Al/PPy formed by this method was found to have better performance characteristics than those by other methods. Singh and Narula reported results of their systematic studies using capacitancevoltage measurements on the Al/PPy Schottky diodes [97]. The results obtained have been explained on the basis of thermoionic emission theory revealing that polymers having higher carrier concentration indicate bad rectifying behaviour. On the other hand, the I-Vmeasurements on p-type indium phosphide/PPy Schottky diode show a deviation from thermoionic emission theory as the temperature is reduced, as evident by the increase of quality factor and the curvature in Richardson plot [98]. Such deviations have been explained by the barrier inhomogeneity model, in which the barrier becomes voltage dependent due to the interaction of a small low-barrier region with a higher surrounding potential, termed the 'pinch-off' effect. In addition, leaky Schottky barriers at the interfaces between PPy and reactive metals and the absence of Schottky barrier at the junction of PPy/Al contacts have also been reported [99,100].

Diodes made of PT including its derivatives and copolymers were also studied in details. Poly(3-methylthiophene) (P3MT) was prepared using an electrochemical technique to fabricate Si based devices [101]. The results obtained from current-voltage measurements, chronopotentiometry, SEM and Fourier-transform infrared spectroscopy suggested that the rectifying behaviour was induced by covalent bond formation between P3MT and the silicon. However, the I-Vcharacteristics of the poly(4-dicyanomethylene-4Hcyanopenta (2,1-b: 3,4-b') dithiophene based device showed no rectification [102]. On the contrary, I-V plots were essentially independent of voltage polarity. The observation of two stable, voltage-controlled conductance states was related to a thin depletion region formed at the device interface. It was postulated that the field-induced changes in space-charge (SC) density in the depletion layer cause a change from electrode to bulk limited transport in the device. Recently, the effect of regioregularity [103] and electron withdrawing/donating substituents [104] on the junction properties of Schottky diode based on PT has been reported. It was found that better performance of the device could either be achieved with regioregular polymers having a short alkyl substituent or by the presence of electron withdrawing group. The effect of steric hindrance on the junction properties of Schottky devices using chemically synthesized poly(3-cyclohexylthiophene) (P3CHT) and poly(3*n*-hexylthiophene) (P3nHT) have been investigated in detail [105]. Based on the current–voltage and capacitance–voltage curves, thermoionic emission theory was found to be suitable for the device. It was also found that better rectification property of P3CHT/metal junction to that P3nHT/metal is perhaps due to the steric hindrance produced in the thiophene ring by bulky cyclohexyl group. In addition, diodes have been fabricated using other conjugated polymers and studied in detail for the optimization of performance [106–109].

Various Schottky junctions using copolymers have also been reported. The observed deviation of poly-(aniline-co-orthoanisidine)/metal junction at higher voltages has been explained in terms of either the Poole– Frenkel effect or due to the presence of a large number of defects containing the trapped charges existing at the interface [110]. Saxena and Santhanam have reported a detailed study of copolymer/metal junctions using chemically prepared poly(3-cyclohexylthiophene-co-3-*n*cyclohexylthiophene) [111]. It was found from the I-Vand C-V measurements (Fig. 4) that deteriorated performance of the junction is due to the effect of 3-cyclohexylthiophene content which produces steric hindrance to the polymeric backbone.

Metal-insulator-semiconductor structures have also been prepared using LB films of cadmium stearate (CdSt₂) on PPy films electrochemically deposited on indium tin oxide (ITO) glass substrate. The low value of ideality factors of metal/CdS₂/PPy in comparison to the metal/PPy junction was attributed to the passivation of the semiconducting PPy [112].

4.2. Field effect transistor

In conventional semiconductor devices, 'field-effect' has been used to improve the performance of the devices [113]. The field-effect controls the current through a

'gate electrode' thereby opening the possibility of a transistor action without requiring the existence of p-n junctions. This phenomenon not only improves the device characteristics but also provides a useful tool to study semiconductor and surface states [114]. This phenomenon was first used by Koezuka and coworkers to fabricate CP based transistors [115]. They demonstrated that it is possible to control the current flowing between source and drain through Gate. Fig. 5 shows a schematic diagram of CP based field effect transistor (FET). After Koezuka many researchers applied this principle to fabricate FET devices [116–118]. Tsumura et al. fabricated an FET based on electrochemically grown PT thin film and showed that it is possible to modulate the drain current by more than two orders of magnitude by varying the gate voltage [119]. Further, Garnier et al. reported fully plastic FET fabricated by using printing technique [120]. A report on a device comprising of 'polymer grid triode' by Yang and Heeger is also worth noting [121].

The performances of CP based FETs are quite encouraging and recent use of these devices in logic circuits or active matrix emissive displays has geared up the



Fig. 5. Schematic diagram of CP based FET.



Fig. 4. Current-voltage and capacitance-voltage characteristics of metal/CP junctions.

research in this direction immensely [122-125]. One of the important parameters deciding the performance of these devices is the mobility. The charge carrier mobilities in these FETs are found to be around 10^{-5} cm²/V s depending on the applied voltage and the nature of the gate insulator. These values are significantly lower than that of inorganic semiconductor device in which mobilities are in the range 0.1-1 cm²/V s. However, sexithienyl based FETs yields values upto 3×10^{-2} cm²/Vs, which is 100 times lower than that of an amorphous Si based FET [126]. In an FET, the interface of the gate insulator and organic semiconductor layer plays an important role in charge transport. It was found that if SiO_2 is replaced by cyanoethylpulluan as the gate insulator, the mobility is increase by three orders of magnitude [127]. Waragai et al. showed similar behaviour, the highest mobility achieved in their device was 3 cm^2 / V s [128]. This value is quite higher than the amorphous Si based FETs. Field-effect mobilities above 0.1 cm²/V s have been achieved in a number of highly ordered polycrystalline or single-crystalline molecular films deposited by vacuum sublimation [129]. Most short conjugated oligomers assume a preferential orientation with their long axis close to normal to the FET substrate such that efficient charge transport can occur in the plane of the film along the direction of intermolecular $\pi - \pi$ stacking. Grain boundaries in polycrystalline films have been found to act as carrier traps resulting in a thermally activated temperature dependence of the mobility and reducing the room temperature value with respect to that of a perfectly ordered single-crystal [130]. Mobilities of the order of $0.1 \text{ cm}^2/\text{V}$ s have also been reported with the solution-processed P3CHT [131]. In contrast to the small molecules, polymers can be processed easily from solution and therefore are useful for applications on flexible plastic substrates and in multilayer device configurations. However, solution-processed polymer films are inherently more disordered than in case of molecular FETs. It has been suggested that the high mobilities are related to self-organization of the polymer chains in the solid state [132]. Recently, it has been found that highly stacked π -conjugated oligomers and polymers such as sexithiophene, antradithiophene and regioregular P3AT give high field-effect mobilities of 10^{-2} -1 cm²/V s in their neutral state [133]. These values are much greater than the mobilities for amorphous π -conjugated polymers such as polyacetylene, PT and PMT in their neutral or lightly doped states [134,135]. Apparent mobilities of positive charge carriers are found to increase by electrochemical or chemical doping [136], e.g. the mobility for the PMT film increased monotonously from $2 \times$ 10^{-5} to 0.1 cm²/V s by electrochemical ClO₄⁻ doping [134]. Apparent mobilities of positive charge carriers in a regioregular poly(3-octylthiopohene) (P3OT) film at various doping levels were evaluated by an electrochemical technique by Kunugi et al. [137]. They found

that up to 2% doping level, the decrease in the values of the apparent mobility in the P3OT films were due to the increase of molar fractions of dimers and beyond 2% doping level, the increase in the carrier mobilities is due to the formation of bipolarons leading to metallic conduction as in ordinary CPs. Recently, charge carrier mobility of RRPHT was studied within the temperature range 77-370 K using thin FETs [138] to understand the hole mobility mechanism. It was concluded from the mobility and temperature relationship that Mott's variable-range hopping model for 2D systems holds good in this case. Horowitz and Hajlaoui have studied the charge transport in vacuum evaporated polycrystalline films of sexithiophene and octathiophene [139]. They interpreted their data according to a model where charge transport is limited by charge trapping and release at states located within grain boundaries. They found that the mobility increases with grain size and a sharp contrast occurs between small grains and large grains. Recently, Burgi et al. reported high-resolution potentiometry of operating organic thin film FETs by means of scanning Kelvin probe force microscopy [140]. They demonstrated that the measured potential reflects the electrostatic potential of the accumulation layer at the semiconductor/insulator interface. It was also derived from the data that field effect mobility at temperature from 50-300 K is dependent on gate bias and lateral electric field.

It can be concluded from the above results that conjugated polymer based FETs are much cheaper than Si based device. However, the slow response and limited lifetime of the device restrict them to replace current Si technology. Nevertheless, the possibility of making flexible and flat panel with conjugated polymers open a new area of large-area low-cost plastic electronics.

4.3. Light emitting diodes

Polymeric light emitting diodes (PLED) have aroused much interest worldwide since the discovery of electroluminescence (EL) in a thin PPV layer by Friend and coworkers in 1990 [141]. CPs have been thought of as potential luminescent materials for replacing inorganic light-emitting materials when used in large-area, lightweight, flexible displays. The main advantages of these materials over conventional luminescent materials are the tuning of wavelength emitted by chemical modification, low operating voltage, flexibility, easy processing, low cost, possibility of making large area device and output colours in whole visible spectrum. Due to these unique features, a number of CPs have been synthesized that emit light across whole visible spectrum and have high quantum efficiencies. The simplest form of PLED is a layered structure consisting of a glass substrate coated with ITO as the transparent conducting anode, an emissive polymeric layer, and then a metallic cathode. The holes and electrons are injected by anode and cathode, respectively; a radiative recombination of the excitons in the polymeric layer gives light.

PPV is one of the first polymers studied for its good photoluminescent and electroluminescent properties. It gives emission in yellow-green region but substitution at the 2- and 5-positions on the phenyl ring gives a red emission [142]. Electroluminescence has also been reported from other conjugated polymers such as poly(pphenylene), polyfluorene, P3AT etc. [143-145]. The luminescent efficiency of the device is an important issue in the fabrication of LEDs. It has been reported that LEDs based on copolymers of P3AT exhibit increase in the luminescence efficiency with increase in cyclohexyl contents in copolymer [145]. Fig. 6 reveals currentvoltage and voltage luminescence curves of one of the device. The structures of the copolymer have been related to their EL property. The devices emit greenishblue light in wavelength region of 550-580 nm, which is easily visible in poorly lighted room. The quantum efficiencies are in the range of 0.002–0.01% (photons per electron) at room temperature; which are significantly higher than the corresponding values for P3CHT based LEDs. Among various approaches adopted for the purpose are:

- (i) Synthesis of high purity materials [146].
- (ii) Modification in structures of polymeric backbone or copolymers formed with segments of the chain having different band gaps [147].



Fig. 6. Luminescent-current as a function of applied voltage for LED based on copolymers of 3-cyclohexylthiophene and 3-*n*-hexylthiophene Ref. [145].

- (iii) Insertion of a carrier injecting/transporting layer or hole-blocking layer [148,149].
- (iv) Using the low work function cathode and high work function anode [150].

CPs have been demonstrated to exhibit light emission in the entire visible spectrum, quantum efficiency over 4%, fast response time, brightness of 10⁶ Cd/m² and device life-time more than two months. Recent studies on the LEDs show that the understanding of the mechanisms of charge injection [151,152], transport [153,154] and eventually trapping [155,156] in the emissive layer is a necessary step to improve lifetime and stability [157,158]. Therefore, considerable amount of work has also been devoted towards understanding the basic mechanism behind these devices. Time-of-flight measurements can determine the nature of trapped charges [159] in addition to device relaxation dynamics [160]. On the other hand, the dielectric relaxation, conductivity and the influence of interfacial polarizations have been studied by impedance spectroscopy [161] and transient capacitance measurements [162]. The frequency response of impedance spectroscopy furthermore showed that the LEDs can, in general, be described by one or a couple of parallel resistor-capacitor network combination [161]. Time resolved characteristics of EL have also received an importance as they serve as a tool to understand several aspects of carrier transport mechanism [163]. Recently, relaxation dynamics of LEDs based on P3AT derivative have been studied by transient EL and the transient capacitance measurements and the equivalent circuit of the device were found to be a series combination of two-parallel resistor-capacitor networks [164]. These methods have also been used to determine charge carrier mobility. Many reports confirm the partially reversible creation of SC distributions in organic devices upon application of a bias voltage [165]. Very recently it has been reported that the charge transport and luminescence can be strongly influenced by ionic SC distributions in polymer LEDs [166]. The dynamics of SC distributions in side-chains of PPV LEDs have been investigated by Michelotti et al. using a single wavelength electro-optic reflection technique [167]. They estimated the density of fixed charges using Debye-Huckel screening in the polymer while the dynamics of mobile charges were investigated by time dependent measurements. The measurements performed at low temperature (88 K) show the features of dispersive transport.

The current interest in exploring the luminescent properties of CPs is in flat-panel displays. Though current technologies such as inorganic LEDs, backlit liquid crystal displays and vacuum fluorescent displays are as efficient as cathode ray tubes. They, however, have limitations in size and power consumption. CPs on the other hand offer the potential applications in many battery operated devices, such as laptop computers, cellular telephones, small hand-held devices, large panel displays, notebook computer screens etc. However, some of the problems still confronting the technologists and scientists are red-shifted blue emission in large band gap polymer, durability under drive and storage conditions, degradation at the polymer-metal interface and the formation of dark spots. Nevertheless, recent advances in technologies promise to come over these problems and speedy commercialization of polymer electroluminescent devices. Several major companies such as Eastman Kodak, Hewlett-Packard, Seiko-Epson and Phillips along with several small entrepreneurial ventures, such as Uniax Corporation (USA) and Cambridge Display Technology (UK) are gearing up their research in this field to capture the huge and promising market for these devices. One hurdle is that different polymers are needed to emit light in different colours. However, it is anticipated that the two technologies are complementary to each other and will coexist.

4.4. Sensors

Sensor is referred to a device, which provide direct information about the chemical composition of its environment [168,169]. It consists of a physical transducer and a selective layer. In any sensor the sensing process can be divided into two parts, recognition which results in selectivity, and amplification which increases the power of the usually weak signals to the level at which it can be conveniently manipulated by electronics. Selectivity is the 'HEART' of the design in all the sensors. It is invariably provided by a material in which some selective interaction of species of interest takes place which results in the change of some physical parameters such as electrical current or potential or conductivity, intensity of light, mass, temperature, etc. Sensors based on CPs have been demonstrated successfully for a range of polymer types. Heteroatomic polymers can act as gas and solution sensors. PPys and PTs show conductivity changes upon exposure to both oxidizing gases (e.g. NO_2) and reducing ones (e.g. NH_3) and there is a reproducible response in solution to the sensing of the anion used as dopant [170-172]. New advanced approach to make sensors is to use FET. Several chemical field-effect-transistors have been described using the principle of field effect [173].

One of the most exciting areas of research in ME lies in the development of biosensing devices (usually called biosensors or receptrodes). The aim is to produce either discrete or continuous electronic signal(s) that is (are) specific to a single analyte (or a related group of analytes). A number of biomolecules such as enzymes, antibodies, organelles, cells and receptors have been used as sensing probes for the fabrication of biosensors [174– 176]. The transducer can either be electrical, optical,



Fig. 7. Schematic diagram showing the main components of a biosensor. The biocatalyst (a) converts the substrate to product. This reaction is determined by the transducer (b), which converts it to an electrical signal. The output from the transducer is amplified (c), processed (d) and displayed (e).

thermal or piezo-electric device [177–180]. Electrochemical method of detection is presently at the centerstage of biosensor development. Potentiometric technique relates to the dependence of the potential on the analyte concentration whereas in amperometric biosensors current is based on heterogeneous electron transfer reaction i.e. the oxidation and reduction of electroactive substances. Fig. 7 shows the principle of detection of an analyte using a biosensor.

5. Conclusions

CPs are versatile ME materials having unique electrical and optical properties. Recent researches in this class of materials include the synthesis of highly oriented materials and short-chain oligomeric systems possessing similar band-gap energies to the parent polymers. These polymers/oligomers are chemically pure and possess high crystallinity, which could be manipulated in fabricating several ME devices as discussed in this article. However, there are several problems associated with these materials, namely reproducibility, stability and processability. A better understanding of the relevant mechanisms is needed to support the drive towards the wide range of practical applications. Recent reports promise the use of regioregular CP and its composites with nanoparticles in optoelectronic devices. Besides this, the use of conjugated polymers in integrated biosensors is another future area, which needs to be exploited.

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