

Conducting Polymers: Synthesis, Properties and Applications

Ravindra Kumar¹, Satyendra Singh², B C Yadav³

Research Scholar, Department of Applied Physics, School for Physical Sciences,

Babasaheb Bhimrao Ambedkar University, Lucknow, U.P., India¹

Assistant Professor, KNPG Government College, Gyanpur Sant Ravi Das Nagar, Bhadohi, U.P., India²

Associate Professor, Department of Applied Physics, School for Physical Sciences,

Babasaheb Bhimrao Ambedkar University, Lucknow, U.P., India³

Abstract: Conducting polymers (CPs) have drawn significant interest of researchers for more than 30 years because of their economical importance, superior stability, lighter weight, better workability, resistance to corrosion and satisfactory electrical conductivity. Some of the applications of CPs include: rechargeable batteries, electrochromic display devices, light reflecting or light transmitting appliances for optical information, sensors and storage for glare reduction systems and smart windows in automobiles and buildings, polymeric light emitting diodes (PLEDs), photovoltaic devices, transistors, electromagnetic shielding against electro-magnetic interferences (EMI) and printed electronic circuits.

Keywords: CPs, EMI shielding, Properties, Applications, Polyaniline, sensors.

I. INTRODUCTION

Polymers are the insulating materials. For example; metallic cables are covered in plastic to shield them. However, there are four major classes of semiconducting polymers that have been developed so far which include conjugated conducting polymers, charge transfer polymers, ionically conducting polymers and conductively filled polymers. The conductively filled polymers were first made in 1930 for the prevention of corona discharge. The invention of new substances with outstanding properties often leads to latest technology. A key invention in the growth of the CPs was the discovery in 1960 that the inorganic polymer polysulfur nitride is a metal.[1] The ambient temperature conductivity of polysulfur nitride is of the order of $10^3 (\Omega \cdot \text{cm})^{-1}$. These innovations were of meticulous importance because they proved the existence of highly CPs and encouraged the massive amount of work required to produce other polymeric conductors. Electrically CPs emerge to be a principle candidates for several applications as many of their characteristics outwit problems common with traditional Random Access memory including corrosion, weight, matrix incongruity and ecological integrity. In addition to being corrosion resistant and light weight, several important properties of CPs may be customized for different applications. The study of CPs has generated entirely new scientific concepts as well as the potential for new technologies. The importance of CPs is exemplified by the Nobel Prize award in Chemistry in 2000 to MacDiarmid, Shirakawa and Heeger for the invention and development of CPs.[2-4] Because of their extraordinary properties such as electrical characteristics, reversible doping-dedoping procedure, controllable chemical and electrochemical properties and simple processibility, a variety of CPs e.g., polyacetylene (PA), Polyaniline (PANI), polypyrrole

(PPY), poly(phenylene)s (PPs), Poly(p-phenylene) (PPP), poly(p-phenylenevinylene) (PPV), poly(3,4-ethylene dioxothiophene) (PEDOT), polyfuran (PF) and other polythiophene (PTh) derivatives, etc, have drawn special interest in the field of nanoscience and nanotechnology.[5-7]

A. Polyacetylene

In the mid 1970s, PA was accidentally fabricated by accident by Shirakawa, the first polymer capable of conducting electricity.[4] It is an organic polymer with the repeating unit $(\text{C}_2\text{H}_2)_n$. The invention of highly conducting PA led to a rapid squirt in research motion directed towards the discovery of new CPs. The high electrical conductivity discovered for these polymers lead to deep attention in the use of organic compounds in microelectronics. The discovery by Alan MacDiarmid and Alan Heeger would discover an enhancement in the electrical conductivity of 12 orders by oxidative doping, fast reverberated around the polymer and a demanding search for other CPs almost immediately followed.[5] In 1976, Alan MacDiarmid et al reported that conductivity of PA was amplified by 6 orders of magnitude when mixed with iodine is the result of charge carriers. Additionally, it was revealed that altering the level of doping yielded polymers revealing broad range of electrical properties, from insulator to metal. PA itself is too unstable to be of any practical value, its structure comprises the heart of all conjugated CPs.

Little had suggested that accurately substituted PA molecule would show superconductivity at ambient temperature.[8] Hatano et al are the first to state the electrical conductivity of the order of 10^5 S/cm for trans PA sample.[9] Polydiacetylene are prepared by the topochemical polymerization of diacetylenes.

B. Poly (thiophene)s

PTh is an important CP that manufacture the environmentally and thermally stable materials and useful as electrical supercapacitor, non-linear optics, PLEDs, electrochromics, photoresists, antistatic coatings, sensors, batteries, electromagnet shielding materials, solar cells, memory devices, transistors and imaging materials. A new PTh derivative was developed by two scientists at the Bayer AG research laboratories in Germany in 1980.[10] An influence on the chemical and physical properties of the polymeric manufactured product has not only caused by heteroatom but the preparation process of required monomer has taken in account. PTh similar to numerous other linear polyaromatic compounds is insoluble in organic solvents.[11] Schopf published a comprehensive review of the literature .[12] Roncali reported the electrochemical synthesis in 1992 [13] and demonstrated the electronic properties of substituted PTh in 1997.[14] McCullough's review concentrated on conventional synthesis method for developing conducting PTh.[15] Reddinger and Reynolds focused on general review of CPs in 1999.[16] Conjugated-polymer-based chemical sensors were examined in 2000 by McQuade.[17] These reviews are outstanding guides to emphasize the primary PTh literature since 1990.

C. Polyaniline

PANI is a CP of the semi-flexible rod polymer family. Among all the above classes PANI is of much importance worldwide because of its unique properties. PANI was first explained in the mid-19th century by Henry Lethe by who studied the electrochemical and chemical oxidation products of aniline in acidic media.[18] Lee et al investigated the effect of the electrode material on the electrical-switching type of a non-volatile resistive-memory apparatus based on an active poly(o-anthranilic acid) thin film.[19] They found that bottom-electrode material is responsible for the switching characteristics of the active polymer layer. Athawale et al studied PANI and its substituted derivatives as methanol, ethanol, propanol, butanol and heptanol sensors.[20] Author found that the PANI exhibits good responses for ethanol. Misra et al synthesized the high quality doped PANI thin films using vacuum deposition technique has been found to be appropriate for detection of CO.[21] Crawley investigated the fabrication and operation of a PANI/CuCl₂ as a hydrogen sulphide sensor.[22] Banerjee reported the fabrication of PANI nanofiber reinforced nanocomposite crystal microbalance sensor as HCl sensor.[23] The author found rapid detection of HCl at low concentration in natural water systems. Subsequently, DeSurville reported high conductivity in a PANI by electrochemical polymerization.[24] Likewise in 1980, Diaz and Logan synthesized electroactive films of PANI that can serve as electrodes.[25]

D. Polypyrrole

PPy is a type of organic polymer formed by polymerization of pyrrole. It was shown to be a CP in 1968. Among the numerous CPs, PPy has been widely studied, which is due to its ease of preparation, superior

redox properties [26], stabilized oxidized form, capacity to give towering conductivity [27], water soluble, commercially accessible and valuable electrical and optical properties. Pyrrole blacks have been known for a century when they were initially obtained as powders by chemical polymerization of pyrrole. These mysterious polymers have not been characterized in huge detail though they are known to be polymers of pyrrole where the bonding is mainly via α, α' carbons. Weiss and co-workers [28] explained the pyrolysis of tetraiodopyrrole to fabricate surprisingly conductive materials in 1963. In 1979, an improved electrochemical technique was used to synthesize free standing films with adequately good mechanical properties to study this system as a CP.[29]

Dall'Olio et al synthesized PPY by oxidation of pyrrole in sulfuric acid as a black powder with room temperature conductivity of 8 Scm^{-1} . [30] The work of Dall'Olio was then extended by workers at IBM who explained that films of this polymer can be achieved by electrochemical polymerization.[31] The conductivity of these films when cycled electrochemically varies from 100-200 S cm^{-1} between a conducting state and an insulating state.[32]

E. Poly (3,4-ethylenedioxythiophene)

PEDOT is a CP based on 3,4-ethylene dioxy thiophene monomer. Advantages of PEDOT are optical transparency in thin, oxidized films, very high stability and reasonable band gap and low redox potential.[33] It can be used in lots of different applications such as antistatic coating of polymers and glass, high conductive shell, organic light emitting diode displays, nano-fiber electrodes for unit stimulation, solar cells, cathode material in electrolytic capacitors, printing wiring panels, textile fibers with colour varying properties, transparent electrodes for thick-film electroluminescence, source gate and drain in the quickly developing organic semi-conductors field [34-36], A vanadium pentoxide nanofiber is used to synthesize PEDOT by nanofiber seeding method. 3,4-ethylene dioxy thiophene is added in an aqueous solution of camphor sulfonic acid and vanadium pentoxide nanofiber sol-gel and ammonium persulfate is used to initiate the polymerization.[37] Preparation of alkyl-substituted EDT derivatives EDT-C1, EDT-C6, and EDT-C10 is reported by Heywang and Jonas in 1992.[38]

F. Poly (phenylene vinylene)s

PPV is a diamagnetic substance, capable of electroluminescence and has extremely low electrical conductivity of the order of 10^{-13} S/cm having structure which is intermediate between that of PA and PP.[39] Oriented PPV is highly crystalline, mechanically strong and environmental stable. The electrical conductivity enhances upon doping with iodine, ferric chloride, alkali metals or acids but with less stability. Generally, unsubstituted unaligned PPV shows reasonable conductivity with doping ranging from 10^{-3} -100 S/cm synthesized via the popular Gilch route. The emissive layer of first PLED is prepared using PPV in 1990.[40] Although PPV-based devices have poor absorption and

photo degradation and PPV derivatives cover many applications in research cells.[41]

G. Polyphenylene and Polyparaphenylene

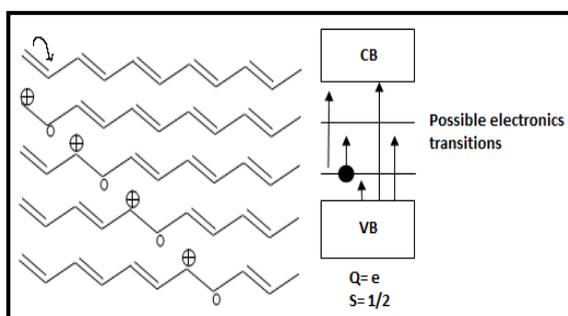
PPP is the precursor to a CP of the rigid-rod polymer host family made of repeating p-phenylene units and converted to its conducting form using an oxidant or a dopant. In 1980, PPP was doped to attain the conductivity comparable to PA.[42] This is the first case of the non-acetylenic hydrocarbon polymer that can be doped with electron acceptor or an electron donor to offer conducting properties. Ballard et al synthesized PPP via derivations of cis-dihydrocatechol achieved from bacterial fermentation using benzene as transformation substrate in a homo polymerization way.[43] Extremely high crystalline PPP films have also been synthesized by electrochemical oxidation from benzene/ 96% H₂SO₄ solution.

II. STRUCTURES, ENERGY BAND GAP AND CONDUCTIVITIES OF CPS

Polymer	Discovery	Structure	Energy band gap (eV)	Conductivity (S/cm)
Polythiophene	1981		2.1	10 ⁻¹ - 10 ³
Polyacetylene	1977		1.5	10 ³ - 1.7x10 ⁵
Polyaniline	1980		3.2	30 - 200
Polypyrrole	1979		3.1	10 ² - 7.5x10 ³
Poly(3,4-ethylene-dioxythiophene)	1980		1.1	300
Poly(p-phenylene vinylene)	1979		2.5	3 - 5x10 ³
Polyphenylene and polyparaphenylene	1979		3.0	10 ² - 10 ³

III. CONDUCTION MECHANISM OF CPS

A. Conduction mechanism of PA



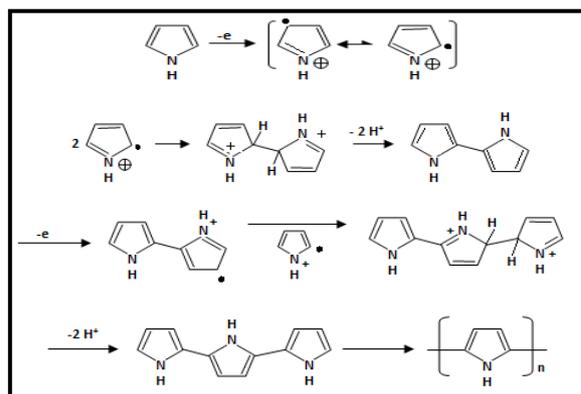
Scheme 1 Conduction mechanism of PA

The conduction mechanism of PA is shown in scheme 1. The radical cation (also known as polaron) is localized, partly because of Coulomb attraction to its counterion, which has usually an extremely low mobility, partly because of a local alteration in the equilibrium geometry of the radical cation relative to the neutral molecule. The

mobility of a polarons along the PA chain can be high and charge is carried along the chain. The possible electronic transition is also given in it.

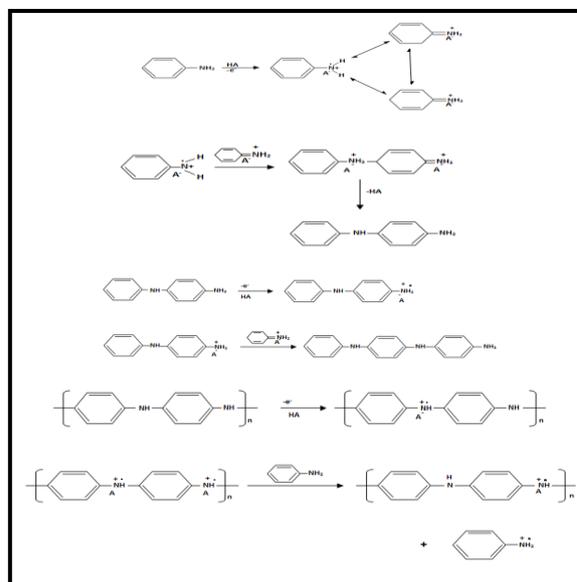
B. Conduction mechanism of PPy

The conduction mechanism of PPy is shown in scheme 2. PPy can be formed chemically or electrochemically through oxidative polymerization of pyrrole monomer. Oxidative polymerisation of pyrrole to PPy proceeds via a one electron oxidation of pyrrole to a radical cation, which subsequently couples with another radical cation to form the 2,2'-bipyrrole. This process is then repeated to form longer chains of PPy.



Scheme 2 Conduction mechanism of PPy

C. Conduction mechanism of PANI

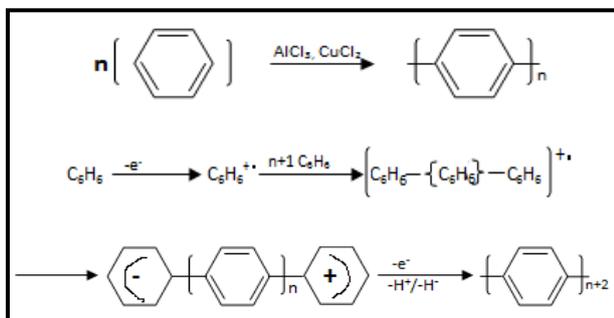


Scheme 3 Conduction mechanism of PANI

Conduction mechanism of PANI is shown in scheme 3. Polymerization of aniline involves oxidation of aniline monomer to form dimeric species as the oxidation potential of aniline is higher than those of dimers, subsequently formed oligomers and polymers. Upon creation, the dimers are immediately oxidized and then react with an aniline monomer via an electrophilic aromatic substitution, followed by further oxidation and deprotonation to afford the trimers. This process is repeated, leading eventually to the formation of PANI.

D. Conduction mechanism of PP

Conduction mechanism of PP is shown in scheme 4. The structural characteristics (meta or ortho linkages) and physical properties of the PP synthesized by oxidative coupling depend on the properties of the oxidising reagent.



Scheme 4 Conduction mechanism of PP

IV. SYNTHESIZING METHODS OF CPs

CPs can be synthesized by any one of the following methods:

A. Chemical method

CPs have been chemically synthesized through the oxidation or reduction of monomers and polymerization of corresponding monomers. One of its advantages is the chance of mass production at a reasonable price. A numeral studies have been applied to increase the yield and quality of the manufactured product attained via oxidative polymerization method. The principles of chemical route do not order the use of electrochemical methods.[44] For example, poly (3-hexylthiophene) is renowned and frequently studied CP that is almost generally produced chemically. PPy and PANI can be prepared chemically, however electrochemically prepared variants have frequently improved conductivity and mechanical properties. When preparing for a chemical polymerization, the basic need after conjugation is stability. Successful polymerization to high molecular weight entails that oligomers and low molecular weight polymers be reactive and soluble sufficient to polymerize. If an oligomer precipitates out of solution the polymerization should extend as a heterogeneous method, an increasingly unlikely view as the concentration of monomer and reactive polymer is diminishing. An unsuccessful chemical polymerization would terminate earlier to the entanglement molecular weight is attained, leaving a mechanically unstable coating on the reaction vessel walls. However, for a suitably soluble system, the chemical polymerization avows for the specific choice of oxidant to selectively produce cation radicals at the suitable location on the monomer.

B. Electrochemical method

Electrochemical synthesis of CPs is very important among the different reported methods of synthesis, since it is simple, cost-effective, can be performed in a single section glass cell, reproducible and the fabricated films have required thickness and uniformity. The most widespread electrochemical technique for preparation of ECPs is anodic oxidation of appropriate electroactive functional

monomers; cathodic reduction is used much less often. In the previous, synthesis of a polymer film and doping of counter ions as a consequence of oxidation happen simultaneously. Most frequently, the potential of monomer oxidation directing to polymerization is higher than that of charging of oligomeric intermediates polymer. A simplified means of electro polymerization of an electro active monomer, such as pyrrole or thiophene engaged alternate chemical and electrode reaction steps.[45] For example, in potentiodynamic electro polymerization of thiophene, a radical cation is generally probably formed in the initial, electrode reaction stage of thiophene electrooxidation, cleared by an anodic peak of high positive potential [46] and at the next chemical reaction stage, radical cation reacts with the monomer and the protonated dimer of a radical cation is produced. After that protonated dimer of a radical cation is electro oxidized to dication at the electrode reaction step.



Fig. 1 CHI 660C Electrochemical Workstation

C. Photochemical Method

Chemical and ECP methods have been the main procedures of finding polymers in industry and scientific research laboratories.[47] However during the previous two decades, photochemical preparation, though awfully studied, has been reported to present few advantages in that it is a quick and inexpensive method and it is not destructive to the surroundings. The method is useful to the fabrication of some CPs. For examples, pyrrole has been effectively polymerized to PPy by irradiation through visible light using either as the photosensitizer or a suitable electron acceptor. Currently, the polymerizations of aniline in the presence of hydrogen peroxide through oxidative free radical coupling reactions have been initiated via horseradish peroxidase. The polymerization of aniline can be conceded at environmentally mild circumstances compared to the chemical and electrochemical techniques.

D. Methathesis Method

Metathesis is defined as the chemical reaction between two compounds that results in the interchange of one part of each to form two different compounds. Metathesis polymerization is divided into three categories: ring-opening metathesis of cyclo-olefins; metathesis of alkynes, acyclic or cyclic; and metathesis of diolefins. Evans et al

studied the metathesis of aniline and 1,2-Dihydroquinoline derivatives.[48] Synthesis of acetylene-based typically conjugated polymers by metathesis polymerization and polymer properties are studied by Masuda.[49]

E. Concentrated Emulsion Method

The emulsion polymerization method is a heterophase polymerization procedure where three segments can be classified: the water segment, the latex particle segment and the monomer droplet segment. The main mechanism in it is a radical polymerization. Methods with one segment present in the arrangement are bulk and solution polymerization, where the monomer as solvent and the initiator are in identical segment.[50] The synthesized polymer remains soluble either in the monomer or in the solvent until high modification. This method contains generally a micelle-forming surfactant, a water soluble initiator in a mixture through a water insoluble monomer. The chief loci of polymerization, compare to suspension polymerization, are the monomer swollen micelles and latex particles. Thus, the word emulsion polymerization is a misnomer; the initial point is an emulsion of monomer droplets in water, however the manufactured product is a distribution of latex particles. In microemulsion polymerization, the monomer droplets generally are very small and they turn out to be the locus of polymerization. It is also feasible to execute inverse emulsion polymerizations where the uninterrupted segment is organic in mixture with a water-soluble monomer in small water droplets. The use of it in the acrylic fiber industry is limited to the production of modacrylic masterpieces.

F. Inclusion Method

Inclusion polymerization generally manufactures composite materials at the atomic or molecular level. So, this kind of polymerization can unlock the path to unique low-dimensionality composite materials with enormous potential. For instance, the inclusion of an electroconductive polymer might fabricate a molecular wire. On the basis of inclusion, composites of such polymers with organic hosts have been synthesized. Miyata et al declared that this polymerization can be observed as a common space-dependent polymerization and should not be considered merely from the perspective of stereoregular polymerization.[51] The author overlooked in other studies on conventional solution and bulk polymerizations.

G. Solid State Method

Solid State polymerization is a procedure in which the polymer chain lengths are enlarged by heat in lack of oxygen and water, either by vacuum or removal with an inert gas to push away the by-products of reactions. The reaction is controlled by temperature, pressure and the diffusion of by-products from the core of the pellet to the shell.

It is a key move often used after melt-polymerization for the intention of enhancing the mechanical and rheological properties of polymers prior to injection blow molding.[52] This method is extensively useful in industrial production of bottle-grade PET, films and

advanced industrial fibers. The chief industrial advantages of solid state polymerization focus on the use of simple and cheap apparatus and on avoiding some of the problems of conventional polymerization procedures.

H. Plasma Polymerization

Plasma polymerization is a novel process to manufacture thin films from a group of organic and organometallic preliminary materials. Plasma polymerized films are pinhole-free and highly cross linked and thus are insoluble, thermally stable, chemically inert and mechanically strong. Additionally such films are extremely coherent and adherent to a range of substrates comprising conventional polymer, glass and metal surfaces.[53] Because of these outstanding properties they have been used massively in the last few years for a range of applications such as perm selective membranes, protective shells, biomedical materials, electronic, optical devices and adhesion supporters.

I. Pyrolysis Method

Pyrolysis is described as the chemical decay of organic materials by heating to elevated temperatures. It has established as a precious process for the investigation and detection of organic polymeric substances in the plastic and rubber production, dentistry, ecological shelter and in the failure testing. This method permits the direct study of very small sample quantity without the necessity of time consuming sample preparation. Spectroscopic methods can give a detection of the monomeric species present; though, pyrolytic degradation plays a significant function in the concluding assignment of the structure. Synthetic and natural polymers analysis is extensively done by pyrolysis gas chromatography.[54] Through chemical polymerization, conjugated monomers mix with a surplus quantity of an oxidant in an appropriate solvent, such as acid. The polymerization takes place suddenly and needs continuous stirring. The subsequent technique is by electrochemical polymerization, which entails both the counter and reference electrodes placed into the solution having diluted monomer and electrolyte in a solvent. After applying an appropriate voltage, the polymer thin film instantly begins to deposit on the working electrode.

V. PROPERTIES OF CPS

CPs exhibits conduction, electronic, magnetic, wetting, mechanical, optical and microwave-absorbing properties.

Some of the properties of CPs are given below:

A. Electrical Conducting Properties

The conductivity of polymers depends upon the doping percentage, arrangement of polymer chains, conjugation length and the purity of the samples. ECPs are molecular in nature and be short of long range order. The molecular nature of polymers produces electronic movement around the individual macromolecules. The nature of procedures creating high conductivity is different for polymers and inorganic semiconductors. The elevated conductivities depend upon doping in the polymers are related with creation of self-localized excitons such as solitons, polarons and bipolarons. These particles which create

from a powerful interaction among the charges on the chain attained as a result of doping. CPs having degenerate ground state for example trans-polyacetylene, charged solitons are the charge carriers, whereas in CPs with non-degenerate ground state for example cis-PA, PPy, PTh or PPV primarily polarons are produced on doping. These polarons then join to form spinless bipolarons which employ as the charge carriers. The potential for molecular engineering of the desired properties and the low cost of the polymers have made them extremely delightful materials for electrically-conductive applications. Hideki Shirakawa examined the electrical conductivity in doped PA.[55] The same author also studied the synthesis of highly conducting films of derivatives of PA $(CH)_x$. [56] Leung et al calculated the electrical and optical properties of PA copolymers.[57] Tanaka et al investigated the optical and electrical properties of doped PA and their temperature dependence.[58] The same author studied the results of impurities and thermal isomerization on the electrical properties of PA.[59] The electrical properties of p-doped highly oriented PA are investigated by Begin's and his coworkers in 1989.[60] The conductivity of the doped PA is the maximum conductivity attained so far for any polymeric material.[61] But due to its less stability and problems in processibility commercialization has not been achievable. The effects of pressure on the electrical resistivity of iodine doped PA was explained by Matsushita in 1999.[62] Long et al synthesized electrical properties of carbon nanotube PANI composites.[63] Huang prepared the highly conductive, self assembled gold PANI nanocables and PANI carbon nanotubes.[64] Sarma et al investigated the synthesis of Au nanoparticle conductive PANI composites as oxidizing as well as reducing agent.[65] Chapman et al showed low energy conductivity of PF-doped PPy.[66]

Factors that affect the electrical conductivity are

- Density of charge carriers
- Their mobility
- The direction
- Presence of doping materials
- Temperature

B. Magnetic Properties

Magnetism of CPs depicts much interest due to their extraordinary magnetic properties as well as their technological applications. Moreover the structural characteristics and magnetic properties of nanomaterials to be merged into polymer matrix, transition metal oxide nanoparticles are of meticulous importance. Nandapure et al investigated the magnetic and transport properties of conducting PANI/nickel oxide in 2012.[67] It was also studied that the conductivity of the PANI/ nickel oxide nanocomposites reduced and the magnetization improved with the increase in weight proportion of nickel oxide in PANI. CP/ferromagnet film was prepared by anodic-oxidation technique by Yan.[68] A composite of PPy with ferromagnetic behaviour was produced by a chemical method in the company of p-dodecyl benzenesulfonic acid sodium salt as a surfactant and dopant. The magnetic properties of the ending composites proved ferromagnetic

behaviour such as high saturated magnetization. The highest conductivity of 10 S/cm was attained beneath the most favourable synthetic circumstances.[69] Particles of $NiFe_{1.95}Gd_{0.05}O_4$ composites with different proportion of ferrite/PANI have been effectively prepared by in situ polymerization. Different ferrite/aniline proportions were picked by Apesteguy in order to show magnetic properties with increasing proportion of PANI.[70] The modification in the magnetic and conductive properties after PANI coating were studied. The coercivity is approximately unaffected, whereas the saturation magnetization significantly decreases. Zaidi et al reported the preparation and characterization of a novel type of polymer, PANI cyanoquinodimethane prepared from PANI and an acceptor molecule tetracyanoquinodimethane.[71] Magnetic calculations concluded that the polymer is ferri- or ferro-magnetic at Curie temperature above 350 K and a highest saturation magnetization of $0.1 JT^{-1}kg^{-1}$. Gosk et al described the magnetic properties of PANI doped with $FeCl_3$. [72] Ferromagnetism in PANI is observed by Trevedi in 2001.[73] Billas and his group studied the magnetism in iron, cobalt and nickel clusters from the atomic to the bulk level.[74] Zhang and his coworkers showed the preparation and characterization of ferromagnetic PANI with conductivity in an applied magnetic field.[75]

C. Optical Properties

The distinctive optical properties of CPs have been widely investigated because of their advantage in nanophotonic devices.[76] Via Genkin-Mednis approach, Chang found an accurate expression of the third order nonlinear optical susceptibilities of CPs.[77] Novel optical features have been observed by Yoshino in CPs doped with molecular dopants such as fullerenes.[78] Tanner et al examined the optical reflectance PA doped with high concentrations of potassium and the optical properties estimated by Kramers-Kronig study.[79] Fujii et al showed the optical properties of thin films of novel di-substituted acetylene polymers that demonstrate huge photoluminescence quantum efficiency in contrast with unsubstituted or monosubstituted PA.[80] Piao have synthesized helical PA $[(CH)_x]$ for the first time with left and right-handed screw structures beneath chiral nematic reaction field.[81] Linaba et al investigated the effects of ammonium sulfide treatment on the electrical and optical properties of indium tin oxide/CP electrodes.[82]

D. Mechanical Properties

The magnetic properties of CPs have been widely investigated as they offer significant information on charge-carrying group and unpaired spins. Sulong et al studied the mechanical properties of carbon nanotube/Graphite/polypropylene nanocomposite for a conducting polymer composite (CPC).[83] The consequences of filler concentrations and chemical functionalization on the mechanical properties of the resulting CPCs were calculated by the same author. The functionalized CPC illustrates better strength and elongation than as produced CPC established on the tensile and flexural tests. The maximum flexural and

tensile strengths of it are 80 and 35 MPa, respectively. The functionalized CPC also exhibits higher hardness than as produced CPC. The mechanical properties of uniaxially oriented PPV thin film synthesized via simultaneous thermal exclusion and uniaxial extension of the poly sulphonium salt precursor have been calculated both in the machine and transverse directions.[84] These properties of it are anisotropic and dependent upon the degree of molecular orientation. Young's modulus varies between 2.3 and 37 GPa as a function of draw ratio in the machine direction and between 2.3 and 0.5 GPa in the transverse direction. Tensile properties of conducting poly (3-cyclohexyl thiophene) films at different temperatures are studied by Somanathan.[85] Sgreccia et al investigated the mechanical properties of hybrid proton CP combines based on sulfonated polyetherketones.[86]

E. Microwave absorbing properties

CPs as innovative microwave interesting materials has been traversed due to their lower density, simple processibility and low cost. Via free space method, the Ting examined the microwave absorbing properties by determining complex permittivity, complex permeability and reflection loss in the microwave frequency range.[87] The same author also proved that PANI addition was valuable for attaining a large absorption over a broad frequency range. Wai et al studied the microwave absorption performances of PANI nanocomposites including TiO₂ nanoparticles.[88-89] PANI nanocomposites reinforced with tungsten oxide nanoparticles and nanorods are synthesized using facile surface initiated polymerization technique.[90] Guo showed electrochemical impedance spectroscopy study of microwave absorbing shells on magnesium alloy in 3.5 wt.% NaCl solution.[91] Hosseini et al investigated the microwave absorbing properties of magnetic nanofiber of polystyrene polyvinyl pyrrolidone.[92] Nanofiber having a diameter varies from 30 to 40 nm at ambient temperature showed the coercive field around 25 KV and saturation magnetization was 1.1emu/g.

F. Wettability

Surface wettability plays a crucial part in the performances of materials. The control of the surface wettability is important for various applications including cookware coatings, self cleaning windows for the industry of automotive and aeronautics, water proof textiles, anti-fingerprint or anti-reflective properties for optical instruments and mobile phones, liquid transportation, separation membrane, cell and antibacterial adhesion. Xu et al investigated the preparation and surface wettability of TiO₂ nanorod films modified with triethoxyoctylsilane.[93] Darmanin et al. studied the wettability of poly (3-alkyl-3,4-propylenedioxythiophene) fibrous structures forming nanoporous, microporous or micro/nanostructured arrangements.[94] Lin et al investigated the development of the tunable wettability characteristics of poly(3-alkylthiophene) thin films.[95] Teh et al investigated the effect of redox-induced reformation of PPy on its surface morphology and wettability.[96] San et al investigated the influences of

fluoropolymer based additive at different additive/binder and additive/filler proportions on surface wettability of polymer composite bipolar plates.[97]

VI. APPLICATIONS

A. Supercapacitors

Supercapacitor (SC) is the common term for a family of electrochemical capacitors. CPs are a subject of interest for many researchers due to their multiple applications. SCs have been emphasized on the growth of new customized electrode materials with superior performance.[98] The substances for electrode of SCs are generally transition metal oxides, high surface carbons and CPs. SCs based on CPs have benefits such as superior capacitive energy density and low material cost. Superior electrical conductivity, better pseudo-capacitance and rapid doping/dedoping rate throughout the charge/discharge procedure are their key benefits. CPs have some disadvantages also such as small life cycle and slow ion transport. That's why the nanocomposite electrodes based on carbon nano tubes (CNT) coated with CPs have been extensively used for SCs.[99] The large surface area and high conductivity of CNT improved the redox property of CPs. Moreover, the structure and capacitance of the nanocomposite are essentially susceptible to the synthetic mode. SCs based on gel polymer electrolytes [100] and proton conducting membranes have been studied by various authors.[101] The proton conducting membranes in their extremely hydrated form have superior mechanical strength, elevated ionic conductivity, excellent dimensional stability compared to gel polymer electrolytes.

B. Light emitting diodes

During last two decades, PLEDs synthesized from CP have drawn international attention as contestants for the next generation of emissive flat panel displays and the same organic structures have been utilized as light detector appliances similar to photodiodes or solar cells. CP ultrathin film employed as a hole injection layer for organic optoelectronic equipments such as organic light emitting diode also has been a issue of importance in current time. In the hole injection layer, CPs plays a crucial role to effectively insert holes from anode into the device.[102] The first organic light emitting diode was produced with anthracene crystals in 1965 but unsuccessful to draw attention because of its poor performance. Then publication describing electroluminescence from a polymer (polyvinyl carbazole) by Partridge [103], in 1983, remained largely unnoticed. It lasted until 1990 before a large academic and industrial importance in the field of light-emitting conjugated polymers was established, initiated by a publication from Friend and co-workers describing EL from PPV films. A lot of research in the field has been focussed towards the growth of new efficient polymeric emitters. A whole range of PLEDs, producing over the entire visible wavelength region from blue to red, has been reported.[104] Furthermore, the LED performance was significantly improved, by means of additional charge-transport layers.[105] Besides PANI, PEDOT, mostly due to its

exceptional electrical conductivity and optoelectronic properties, has been launched into organic light emitting diodes as hole injection layer. Burroughes et al studied the LED based on conjugated polymers.[106] Braun improved efficiency in semiconducting PLEDs.[107] Despite the rapid progress in the field of polymeric light-emitters, no commercial displays based on PLEDs have been manufactured as yet.

C. Solar Cells

Polymer solar cells (PSCs) have grown as a capable and commercial option to silicon-based solar cells. Several considerable advantages of PSCs comprise low expenditure of production, simple processing, mechanical flexibility and versatility of chemical structure from progresses in organic chemistry. Currently, several studies have been performed on flexible and lightweight appliances using a plastic film substrate instead of a brittle glass substrate. To synthesize the fully plastic PSCs, it is compulsory to apply transparent anode via organic-based materials. Heo et al studied the patternable solution of flexible polymer solar cells using polydimethylsiloxane.[108] PSCs serve as renewable sources of electrical energy because of their various benefits, such as low cost production and simple processing on flexible substrates. The working efficiency of PSCs has been significantly enhanced by using bulk-heterojunction model as an active layer where electron donor and acceptor materials are uniformly combined in a solution and fabricate a thin film sandwiched between two electrodes. Liang et al. studied the whole simulation of a traditional bulk-heterojunction apparatus based on the poly (3-hexylthiophene-2,5-diyl).[109] The power conversion efficiency of state-of the art PSCs has been reported more than 9% for single cells, 10% for tandem cells and 11.0% for the PSC based on P3HT. Huang et al studied the photovoltaic performance of PSCs buffered by these metal oxide layers and the applicability of these interfacial layers that was demonstrated both with P3HT and a low band gap polymer PBDT-T8-TPD.[110] Efficient inverted PSCs were studied by Li.[111] Yu et al demonstrated that one-dimensional photonic crystals as distributed Bragg reflectors can effectively improve the performance of semitransparent PSCs based on the blend of P3HT: ICBA.[112] He reported a maximum power conversion efficiency of 4.12%, a highest transmittance of 80.4% at 660 nm and an average transmittance of 55.6% in the wavelength range of 600-800 nm are obtained in the case of $N = 8$, corresponding enhancement of 24.1% in PCE.

D. Transistors and data storage

CPs has established application in electronics as field effect transistors and for charge storage because of their outstanding properties. High sensitivity of CPs can be attained by operating them as field effect transistors because of their ability to magnify in-situ and to gate-modulate channel conductance. Grigorian et al studied the structural and morphological modifications of P3HT thin films in the planar geometry of an organic field effect transistor apparatus beneath an applied electric field and these changes are partially reversible in nature.[113]

Majumdera and co-workers have synthesized and characterized sandwich-type apparatus based on an oriented PTh derivative.[114] They also have shown conductance switching by calculating capacitance of the apparatus and have explored the high and low conducting states of it. Hiraoka et al. studied the characteristics of polymer light-emitting transistors with Ag-nanowire source/drain electrodes manufactured on polymer substrate.[115] The maximum external quantum efficiency is 0.6%. He also demonstrated the possibility of producing flexible polymer light-emitting transistors using Ag nano wires electrodes. Gurunathan et al have given summary of several technological applications of these polymeric materials to electronics, optoelectronics tools like energy storage applications as solid-state rechargeable batteries.[116] SnO₂ nanoparticles evenly decorate PPy nanowires which are produced by electrochemical reaction method showed porous reticular morphology and homogenous allocations.[117] In lithium ion batteries as anode materials, the distinct nanostructured hybrids have shown improved Li⁺ storage performance. Wanekaya et al studied the field effect transistors based on single nanowires of CPs.[118] He found that the performance of single nanowires conducting polymer field effect transistor was comparable to the silicon nanowire field effect transistor.

E. Sensors

The application of CPs in sensor technologies includes the CPs as an electrode modification in order to enhance sensitivity, to impart selectivity, to suppress interference and to give a support matrix for sensing materials. Few sensors employing CPs are discussed below:

E.1 Gas sensors:

The liberation of gaseous impurities like SO₂, nitrogen oxide and toxic gases from associated industries has become a severe ecological concern. Sensors are essential to identify and evaluate the concentration of such gaseous pollutants. PANI, PPy and PTh have generally been used in fabrication of gas sensor apparatus. Amrani et al studied the fabrication, characterisation and multi frequency calculations of poly N-(2-pyridyl) pyrrole for sensing applications.[119] Badhulika investigated the synthesis, characterization and subsequent assessment of PEDOT doped with poly (styrene sulfonic acid) coated single walled carbon nanotubes sensors for sensing analytes in industries.[120] Electrical characterization in terms of change in resistance, cyclic voltammetry and FET measurements was performed to confirm the presence of PEDOT: PSS coating on single walled carbon nanotubes. PEDOT nanowires were developed by wetting Al₂O₃ membrane template technique in order to find highly arranged structure of nanowires and the self-assembly film of nanowires at air/water boundary.[121] The results demonstrated that PEDOT nanowire surfactant complex at air/water interface had fine self-assembly capacity and the stable float sheet was produced with collapse pressure >50 mN/m. Waghuley et al studied the synthesis of PPy and its application as a CO₂ gas sensor.[122] He also showed that the resistance increase of the material in the presence of

CO₂ gas is due to the orbital overlap of neighbouring molecules of the PPy structure, the π electrons delocalize along the complete chain, which offers semiconducting and conducting properties as CO₂ molecules formed weak bonds with π electrons of PPy. Doa et al studied the sensitivity of conductimetric acetone gas sensor based on PPy and PANI.[123] Parmar et al showed the ethanol sensing using CuO/Multi walled nanotubes thin film.[124] Singh et al investigated various types of metallopolymer as LPG sensors.[125-127] Pomogailo et al investigated polymer matrix nanocomposite gas sensing materials.[128] The investigations on gas sensing of Cu/Pd bimetallic nanostructures have been shown by A.K. Jaiswal et al.[129] The gas sensing setup is shown in Fig. 2.[130]

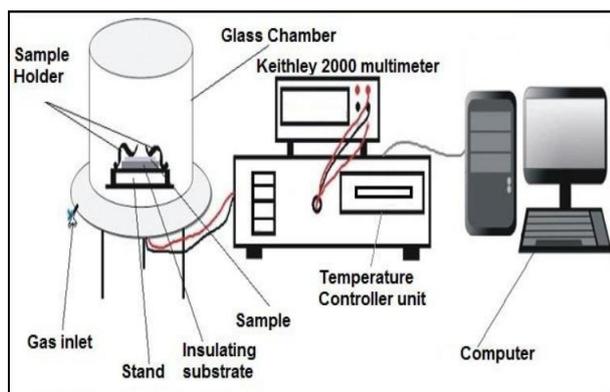


Fig. 2 Schematic diagram of laboratory gas sensing set up reprinted with permission [130]

E.2 Bio Sensors

Currently, CPs are used in chemical analysis for the detection of ions and molecules in the liquid phase at the large scale. The growth of biosensors has been a particularly important area over the last twenty years. Mahrotra et al showed the latest progress in biosensors and their uses in food investigation, environmental control, clinical detection, medicinal and farming industries, etc.[131] Adhikari et al. examined several materials for sensor applications and stated the use of CPs either in sensing mechanism or in immobilizing the ingredient responsible for sensing the analyte.[132] Freire reported the development of electrochemical biosensors by direct transfer.[133] The films synthesized by electrochemical co-deposition of enzymes on CP or conductive substrates have been used to produce biosensors.[134]

E.3 Humidity Sensors

Humidity sensors (HSs) are competent for the detection of the relative humidity in different environments with respect to electrical [135-138], optical [139-41] and other physical parameters.[141-144] These sensors drawn huge attention in the industrial and medical fields. The calculation and control of humidity are crucial in several regions such as food and electronic industry, domestic atmosphere, medical, etc. Hydrophilic properties of polymer, polymer composites and modified polymers have been used in HS devices. Jain et al studied the behaviour of HSs with PANI doped with different weak acids such as CSA, diphenyl phosphate, and maleic acid blends.[145]

Choa et al showed the influence of temperature and relative humidity of PPy sensor.[146] The author found that the initial impedance of the PPy sensor was increased with enhancement in humidity and decrement of temperature, respectively. The reproducibility of PPy sensor was outstanding at different humidity circumstances. Parvatikar et al studied the electrical and humidity sensing properties of PANI/WO₃ nanocomposites.[147] Kulkarni et al studied the poly(*N*-methyl aniline) doped with several acids by a chemical polymerization technique with ammonium persulphate as an oxidizing agent.[148] These polymers were then effectively developed as HSs. Among the several acids utilized for the doping of polymer, the H₃PO₄-doped polymer demonstrated the excellent sensing response and was found to be excellent applicant for a HS. HS based on PANI nanofibres was synthesized by Zenga and its response to humidity was studied.[149] The sensor responded to low relative humidity (<50% RH) generally by decreasing electrical resistance with enhancing humidity. Though, at higher relative humidity the sensor quashed its responses by enhancing the electrical resistance with humidity. The schematic diagram of self designated humidity controlled chamber integeneously fabricated in our lab as shown in Fig. 3.

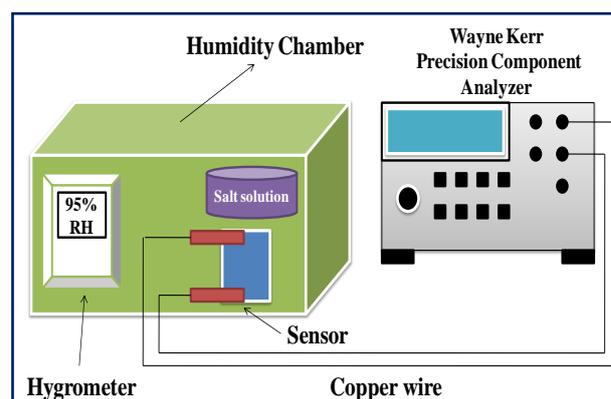


Fig. 3 Schematic diagram of humidity sensing set up.

F. Corrosion protection

CP coatings for example PANI, PPy, etc. have been revealed to suggest corrosion protection of ferrous and non-ferrous metals. Sathiyarayanan et al prepared the PANI-TiO₂ composite by chemical polymerization method in the existence of aniline and TiO₂ by APS oxidant.[150] This review summarizes the investigations made by several investigators on the corrosion resistant properties of CPs. Plesu et al have examined the performance of organic phosphorous acid doped PANI with acrylic binder on the corrosion protection of steel in 3.5% NaCl solution.[151] Gurunathan et al have synthesized and characterized the conducting PANI-TiO₂ composites and examined their application as cathode substance in rechargeable battery.[152] Xu et al have studied the nature of bonding of PANI with TiO₂ and showed the presence of hydrogen bonding between them.[153] Zhang et al have investigated the solid phase photo catalytic degradation of PANI-TiO₂ nano composite.[154] Le et al examined the corrosion of iron shielded by PPy films with a range of

thicknesses in NaCl 3% solution by open circuit potentials and electrochemical impedance spectroscopy.[155] Fenelon et al investigated the synthesis of pyrrole at a copper electrode in a near neutral sodium oxalate solution to create a uniform and adherent PPy film.[156] These films stayed stable and conducting for periods more than 8 days and revealed important corrosion protection properties in acidified and neutral 0.1 mol dm^{-3} NaCl solutions even on polarization to high anodic potentials.

G. Batteries

This is the first area where CPs guarantees to have a huge commercial impact. Batteries have various parts: the electrodes allow for compilation of current and diffusion of power; the cathode material get reduced as the anode material is oxidized and vice versa; the electrolyte offers a physical partition among the cathode and the anode and supplies a source of cations and anions to balance the redox reactions. Sultana et al studied the polymer battery arrangement based on PPy doped with dopants of p-toluenesulfonic acid and indigo carmine.[157] Zhu et al synthesized a unique single ion CP electrolyte, lithium polyvinyl alcohol oxalate borate, from the reaction of poly (vinyl alcohol) with different molar ratio of boric acid, oxalic acid and lithium carbonate.[158] Its electrochemical window can be stable till 7 V which is of huge importance for high voltage lithium ion batteries with high energy density. Lewandowski et al demonstrated the Li^+ CP electrolyte based on ionic liquid for lithium and lithium-ion batteries.[159] Samsudina et al discovered the biopolymer materials based carboxymethyl cellulose as a proton conducting biopolymer electrolyte for application in rechargeable proton battery.[160] PEDOT-LiFePO₄ composite films prepared by Trinh were utilized exclusive of further changes as the positive electrode in standard lithium ion batteries.[161] Guerfi et al investigated the high cycling stability of zinc-anode/CP rechargeable battery with non-aqueous electrolyte.[162] This examination showed that the battery experiences a stern self-discharge of 48% per day. Duan et al fabricated the CP-coated sulfur composite cathode materials based on layer-by-layer assembly for rechargeable lithium-sulphur batteries.[163] Xuan and his coworkers demonstrated a thin polymer-air battery where the anode and cathode are based on the PEDOT.[164]

H. Electrochromic device

Electrochromic devices are arrangement of significant industrial engrossment due to their convenient transmission, absorption and/or reflectance. Somani et al studied the electrochromic response of PPy /Prussian blue and PANI / Prussian blue composite films in various electrolytes for example KCl, LiClO₄, K₂SO₄, KNO₃, etc., by putting the Prussian blue films on zenith of the conducting PPy and PANI films synthesized by electrochemical techniques.[165] Jensen et al studied the ion results in redox cycling of CP based electrochromic materials.[166] Tarkuc et al synthesized a soluble CP: 1-Phenyl-2,5-di(2-thienyl)-1H-pyrrole and explored it for electrochromic use.[167] Camurlu et al constructed the binary type polymer electrochromic devices based on

potentiodynamically layered films of octanoic acid 2-thiophen-3-ylethyl ester, decanedioic acid bis-(2-thiophen-3-yl-ethyl) ester and EDOT.[168] A modern method for the electrochemical description of an apparatus comprised by two electroactive films of CPs, for example electrochromic windows, artificial muscles, polymeric batteries or SCs are suggested by Padilla.[169] Shaplov et al constructed the truly solid state electrochromic devices via polymeric ionic liquids as solid electrolytes and electrodes formulated by vapour phase polymerization of EDOT.[170] Yigitsoy et al synthesized a monomer 2,5-di(thiophen-2-yl)-1-p-tolyl-1H-pyrrole using reaction of 1,4-di (2-thienyl)-1,4-butanedione and p-toluidine in the company of catalytical amount of p-toluenesulphonic acid and studied its electrochromic application.[171] Sindhu et al studied the spectral and optical performance of electrochromic PEDOT collected on translucent conducting oxide coated glass and polymer substrates.[172] Arslan et al studied the electrochromic properties of a soluble CP: Poly(1-(4-fluorophenyl)-2,5-di(thiophen-2-yl)-1H-pyrrole).[173] Maa et al fabricated the red-blue switching binary polymer electrochromic devices via room temperature ionic liquids.[174] Shen et al studied the complementary electrochromic device based on carbon nanotubes/CPs.[175]

I. Radar application

RADAR is an object-detection method that utilizes radio waves to find the range, altitude, path or speed of objects. It can be employed to identify aircraft, ships, spacecrafts, motor vehicles, weather formations and topography. CP camouflage works in a different manner, in that it replicates back in a manner i.e. different from the entity it covers and absorbs microwave emission as it has additional continuously changeable impedance. Wright et al studied the electrical characteristics of PPy composites at microwave frequencies.[176] Gama et al studied that MnZn ferrite/rubber was used as radar absorbing materials and investigated the dependence of microwave absorption properties on ferrite volume fraction in it.[177] X and Ku band of cotton fabric coated with Ni-Zn ferrite and their microwave absorption effects were demonstrated by Gupta.[178] Due to its thin and flexible properties, the coated fabric can be utilized as clothes in shielding human being from harmful microwaves and as well as radar camouflage coating display in defence. Phang et al studied the microwave absorption behaviors of PANI nanocomposites containing TiO₂ nanoparticles.[179]

J. Actuators

An actuator is a kind of device that is dependable for controlling a system and it is operated by a source of energy, usually electric current, hydraulic fluid pressure and changes that energy into action. Yamato et al fabricated tubular linear actuators using PPy in 2006.[180] Plesse described the fabrication of conducting interpenetrating polymer arrangements for actuator uses.[181] Punning explains a new self-sensing ion CP metal composite actuator.[182] This actuator provides knowledge of its own location and therefore can also be

employed as a position sensor. Temperature dependence of water vapour absorption and electro-active polymer actuating behaviour of free standing films made of PEDOT doped with poly (4-styrenesulfonate) was investigated by Okuzaki.[183] Du et al fabricated the bending actuators using the conventional double-layer beam bending theory executed by ignoring the thickness of the thin intermediate metal coatings for the sake of simplification.[184] Gaihre et al compared displacement study of bilayer actuators including of CPs, synthesized from PPy, PEDOT or poly (3,4-propylenedioxythiophene).[185] Itik et al investigated the dynamics of a PPy-based conducting electroactive polymer actuator which is required to track replicating reference instructions for location control uses.[186] Han et al synthesized the CP electrochemical actuator equipped of high-strength three layered composite films of PTh and PPy.[187] Zainudeen prepared the PEDOT and PPy bilayer and trilayer actuators.[188] Jager reported the techniques for effectively moulding and interfacing of such tri-layer PPy microactuators.[189] The PPy tri-layer actuators were moulded via modified microfabrication technology together with photolithography.

VII. CONCLUSION

This review describes the different types of CPs, synthesis techniques, conduction mechanism, properties and their applications in various fields. The research and progressive attempts of the past twenty years in the field of CPs have been discussed. To realize the importance of CPs, it is very important to enhance their processibility, environmental and thermal studies.

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