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Conducting Polymers and Composites

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Abstract

Conducting polymers (CPs) characteristically form polarons, bipolarons, or solitons and exhibit low band-gap energies. These properties make them to be suitable materials for applications in sensors, semiconductors, anticorrosion coatings, batteries, and display devices, among others. This chapter focuses on the electronics, electrochemistry, and processability of some commonly used CPs in the recent past – namely, polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), poly(3,4-ethylenedioxythiophene) (PEDOT), and polyfuran (PFu). Also included in the chapter are conducting dendritic star copolymers and polymeric nanocomposites incorporating single-walled and multiwalled carbon nanotubes.

1 Nature of Conducting Polymer Materials

Since the early 1970s, researchers have been focussed on the task of identifying organic solids that exhibit remarkable conducting properties. These organic compounds, with the ability to effectively transfer charge, can be divided into three main groups: radical-ion salt charge-transfer complexes, carbon-based small molecules, and conjugated conducting polymers (CPs). Conducting polymers (more commonly termed *synthetic metals*) are organic polymers that exhibit highly reversible redox behavior and demonstrate the properties of both metals and plastics. CPs gained in popularity owing to their interesting electrical and optical properties, which had previously only been observed in inorganic systems. One of the most remarkable features of CPs is their ability to be nanostructurally tailored for more specialized applications, through innovatively manipulated synthetic transformations. This flexibility has resulted largely in the replacement of traditional inorganic conducting materials with CPs, which, through blending or composite formation, have introduced improved processability, mechanical properties, and stability. These enhancements have allowed CPs to have practical application in various fields, including electromagnetic shielding and microwave absorption [1, 2], static electricity dissipation, heating elements [3], membrane materials [4], paint coatings for anticorrosion protection [5, 6], sensor materials, and molecular devices [7]. This chapter provides an examination of CPs and composites — their properties, synthesis, and applications. In addition, conducting star copolymers, dendritic star copolymers and dendrimers are also explored as they are inextricably connected to their progenitor molecules (the CPs).

2 Conducting Polymers and Their Properties

Conducting polymers (CPs) typically contain a linear backbone of repeating conjugated monomers as the fundamental structural unit, as exemplified by polyacetylene (PAC), polypyrrole (PPy), polyaniline (PANI), and polythiophene (PTh) [8, 9]. Two general types of conducting polymers exist. The first is a composite material (with dimensions in the nanometre range) that engages a polymer to hold together conductive filler-like metal flakes [10]. Typical examples of conductive components used to prepare this type of CP include conducting solids (carbon black, carbon fibres, aluminium flakes, stainless steel fibers, metal-coated fillers, metal particles, etc.) and conjugated conducting polymers. The latter can be had via polymerization at an electrode (anode) surface coated with a nonconducting polymer film [11]. These conducting nanocomposites (CNCs) can be synthesized from a variety of metals and conjugated polymers as well as oligomers and have attracted considerable interest because of the possibility of using them to create suitable materials for electrocatalysis, microelectronics, and chemical sensors [12]. The second group of CPs consists of a set of polymers whose backbones constitutionally propagate charge, making the polymer itself conductive [13]. The conductivity arises from the chemical bonding which produces an unpaired π-electron per carbon atom in the backbone of the polymer. The carbon atoms are π-bonded in an sp^2p_z hybridized configuration, where the orbitals of successive carbon atoms overlap, providing for delocalization of the electrons along the polymer chain [14]. Consequently, charge mobility is exerted along the polymer backbone, introducing properties such as electrical conductivity, low-energy optical transitions, low ionization potential, and high electron affinity. During doping (addition of known quantities of chemical species) and polymerization of CPs, the π-bonds are highly susceptible to chemical and electrochemical oxidation and/or reduction processes leading to the formation of nonlinear defects, namely, solitons, polarons, and bipolarons, all of which contribute to the electrical conduction in these polymeric materials [15–18].

CPs like PPy, PAC, PTh, and PANI have undergone extensive development over the past 25 years. Thus, organic conducting and semiconducting polymers can now be synthetically bespoke to optimize desirable properties such as melting point, melt viscosity, solubility, electrical and thermal conductivity, etc. Although found in oligomers of 4–10 repeating units, enhanced electrically conductive properties are frequently observed in polymers (e.g., CPs) with hundreds or thousands of repeating units by virtue of the long range ordering of the polymer chains in the solid state [19].

For CPs to be useful in multifarious applications, they need to have excellent electrical and mechanical properties, solution or melt processability, and high environmental stability. Conducting polymer composites (CPCs), resulting from the blending of an insulating polymer matrix with an electrical conductive filler (carbon black, carbon fibers, metal particles), show many interesting features owing to their electrical resistivity variations with temperature [20–22]. For instance, changing the nature of the positive temperature coefficient (PTC) effect, i.e., transition temperature and amplitude, allows for the adjustment of the CPC properties, thereby potentially giving access to a wider range of applications. As such, self-regulated heating can be coerced in a CPC with a sharp positive temperature coefficient effect. Moreover, these materials have the ability to withstand corrosion and can be prepared using common plastics processing techniques such as extrusion or injection. A list of CPs widely in use today are shown in Fig. 1 and include the well-known PAC, poly(3-alkyl-thiophene), PPy, and PANI [23].

Since the early 1990s, CPs have been reported to function as thin films for batteries, capacitors, light-emitting diodes, ion-selective electrodes, and solid-state

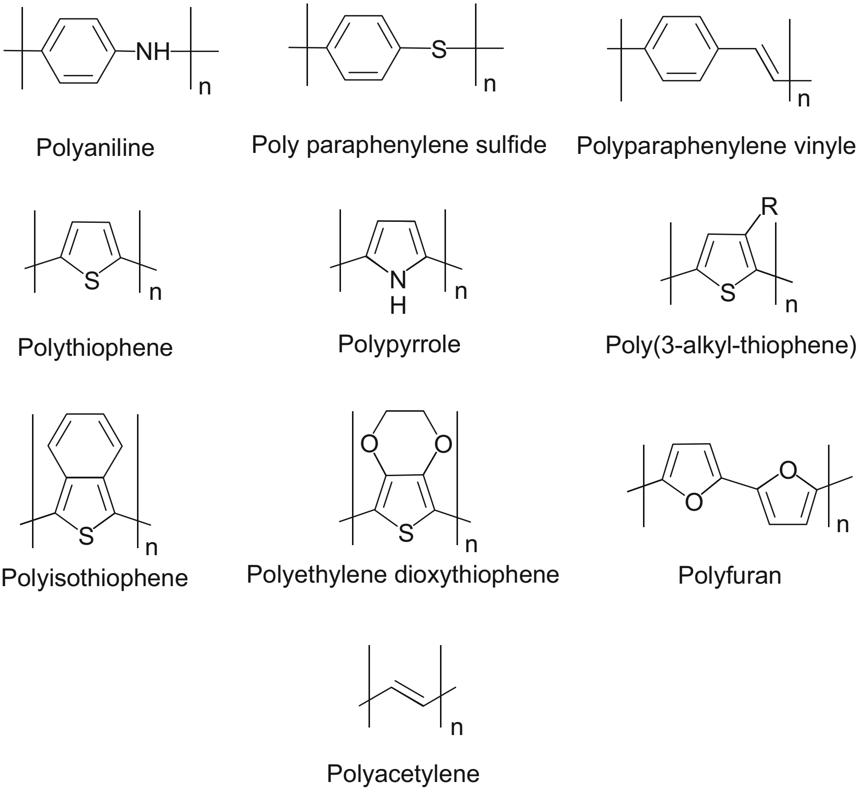


Fig. 1 Chemical structures of common conducting polymers (CPs)

devices [24, 25]. Recently, the application of CPs has extended to include sensors, actuator components in microsurgical tools, controlled drug delivery systems, corrective implantable aids, lifelike prosthetic limbs, actuators, and artificial muscles [26]. It is worth noting that a change in emphasis in the area of materials science and chemistry has opened the doorway to new approaches in analytical sensing, which influences the design of sensors, particularly those that employ electrochemical or spectroscopic transduction methods. Specifically, conducting polymers are frequently used in environmental monitoring and clinical diagnostics to achieve fast detection, high sensitivity, small size and specificity for investigation of a particular analyte through the use of electrochemical sensors [27] and biosensors [28].

2.1 Electronic Classification

Electrons are essential for conductivity and can be loosely categorized into one of four groups. The first type – core electrons – primarily exists close to the nucleus and are rarely removed owing to the relatively large magnitude of the effective nuclear charge felt by these electrons.

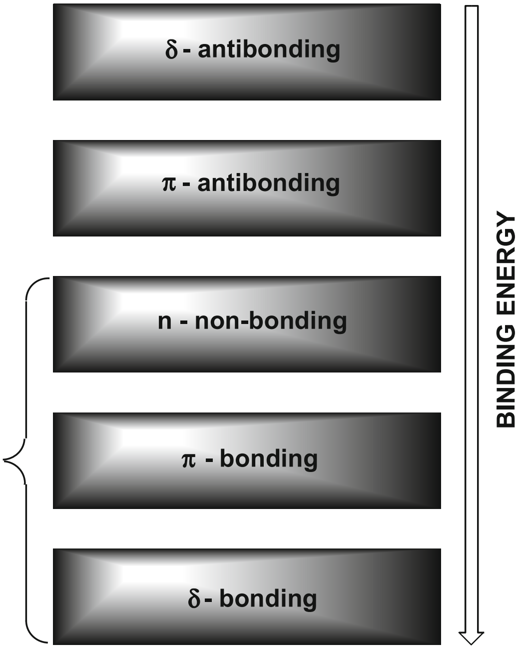


Fig. 2 Binding energy levels of σ, π, and n electron states for organic molecules. (Redrawn from Ref. [29])

σ-Electrons constitute the chemical bonds that are responsible for maintaining the structural integrity of the molecule. Nonbonding or n-electrons are usually associated with the lone pairs present on the atoms of some elements and can influence the susceptibility of a bond to reaction. Weaker and less-localized connections than the internuclear bonds of σ-electrons are also present upon the birth of molecules. These entities, known as π-electrons, are likewise involved in bonding but are often thought of as being "free" (delocalized) and hence require the least amount of energy to jump to the next energy state (Fig. 2). This π-electron "cloud" enables conduction and polymers that contain π-electrons, through double bonds, are known as conjugated polymers.

2.2 Band Theory

Band theory is widely used to explain electrical conductivity as it describes the energy states of electrons. When two identical atoms, each having a partially-filled orbital, are brought together, the two atomic orbitals interact to produce two new (molecular) orbitals – one of lower energy and one of higher energy. Two electrons occupy the lower energy orbital. The (now-filled) orbital of lower energy is a bonding orbital and the higher energy (empty) orbital is an antibonding orbital. The magnitude of the energy difference between the highest of the low-energy orbitals (highest occupied molecular orbital – HOMO) and the lowest of the high-energy orbitals (lowest unoccupied molecular orbital – LUMO) is called the energy band gap (Eg).

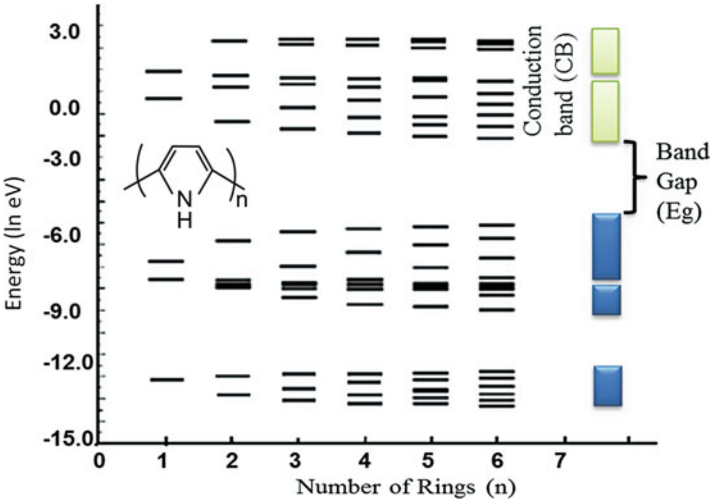


Fig. 3 The origin of band structure in polypyrrole. (Redrawn from Ref. [30])

As shown in Fig. 3, for the PPy system [30], molecular orbital perturbation effects lead to energy states that are comparable. As the length of the polymer chain increases progressively from one to infinity, the occupied valence orbitals form continuous bands called valence bands (VBs), and the empty orbitals coalesce into continuous bands referred to as conduction bands (CBs).

In other words, Eg is the energy difference between the highest energy eigenstate of the valence band (VB) and the lowest energy eigenstate of the conduction band (CB) and represents the minimum energy that is required to excite an electron up into the conduction band where it can participate in the conveyance of charge (Fig. 3). To maintain conductivity, valence electrons must move to the CB through this gain in energy.

In band theory, depending on the size of the energy gap (Eg), the material can be an insulator or a semiconductor (Fig. 4). An insulator has electrons in the valence band that are separated by a large band gap from the conduction band. Hence, these electrons are prevented from participating in conduction. Semiconductors, whose conductivities can range from 10^3 to 10^{-9} S.cm^{-1}, usually have energy gaps ≤ 1 eV. They are mainly inorganic, crystalline solids, and the magnitude of the energy gap is such that electrons may be thermally excited across it into the empty upper band, where they can conduct, leaving holes in the lower band, which can also contribute to conductivity [31].

Contrastingly, a conductive material such as a metal has overlapping of the conduction and valence bands. This means that orbitals are freely available and electrons are “free” to move into the conduction band, increasing the possibility of transference of charge. Metals generally have conductivities of order of magnitude of 10^6 S.cm^{-1}, while insulators are at the other end of the conductivity gamut with magnitudes around 10^{-22} S.cm^{-1} owing to their very large band gap which renders thermal excitation impossible.

Highly conjugated CPs can display semiconductor properties without the inorganic, crystalline structure. The difference between band energy levels in these materials is such that the bands may be regarded as being continuous, and the electrons can adopt any energy that falls within the upper and lower boundaries of the bands. Both inorganic solids and CPs can be doped using charged chemical species [32, 33] to increase the conductivity (Fig. 5); however, the concentration of dopant is the discerning factor; in the case of semiconductors of the crystalline type, concentrations usually lie in the parts per million (ppm) order of magnitude while the polymer type can have dopant constituents, the concentration levels of which are as high as 50% (relative to the weight of the polymer).

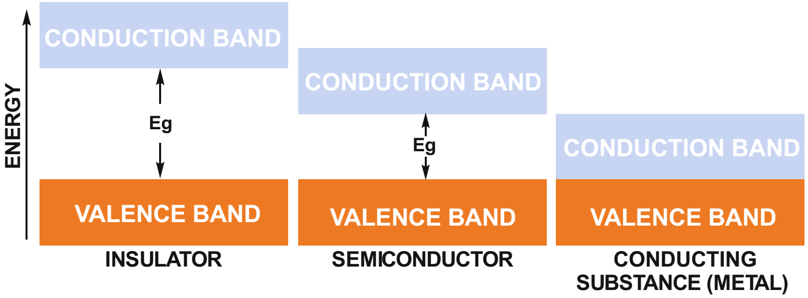
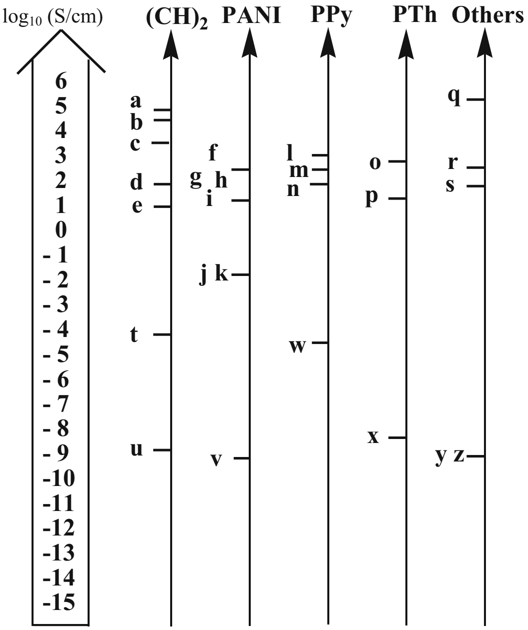


Fig. 4 Energy gap representation of an insulator, a semiconductor, and a metal

Fig. 5 The conductivity of various conducting polymers at 24 °C. (**a**–**e**) forms of [CH(I$_3$)]$_x$, (**f**–**k**) forms of PANI, (**l**, **m**) PPy doped with PF$_6$, (**n**) PPy (TSO), (**o**, **p**) forms of PTh, (**q**) PPV (H$_2$SO$_4$), (**r**) PPP (AsF$_5$), (**s**) Kr-implanted poly(phenylenebenzobisoazole), (**t**–**z**) undoped versions of the respective polymers [32] with kind permission of Cambridge University Press.



2.2.1 Band Theory of Conductive Polymers

While traditional band models have prevailed, for the most part, in explaining the semiconductor physics of inorganic crystalline materials, they have tended to break down when applied to CPs. Although it has been postulated [34] that conducting polymers and conducting inorganic crystalline materials have similar properties, fundamental differences lie in how the electrons move from one location to another. For instance, oxidation or reduction of CPs creates structural deformations along the polymer backbone, where transmission of charge will most likely occur.

When an electron in the valence band of a conducting polymer is exposed to a stimulus that causes it to become excited, a polaron forms. Generally speaking, a polaron is a spin-bearing charge-carrier that is typically linked with radical cations or radical anions. It is thought to consist of two defects – a charged defect (ion) and a neutral defect (radical) (Fig. 6a). Instead of the energized electron leaving a completely empty hole, partial delocalization occurs to offset the new energy level created by the excited electron. This deconfinement of the electrons means that the surrounding monomer units become anatomically distorted – a polaron [35]. Further, conductivity is influenced by the number of polarons (or other quasiparticles such as bipolarons or solitons) generated in the material and their movement across the mass of the material. Doping can, therefore, influence the conductivity of a material as defects in the form of radical cations or anions are introduced.

At low doping levels, charges are stored as polarons and bipolarons (Fig. 6) and so beget an electrically conductive partially filled band. For most conducting polymers such as PPy, bipolarons (pairs of defects) are created when two polarons form on the same polymer chain [38] and since PPy is a highly disordered polymer there are as many as one defect for every three rings [37]. Polarons and bipolarons can also hop to nearby chains to carry the electric current. In single polaron hopping, only one electron moves back and forth between two defect states whereas in bipolaron hopping, two electrons migrate simultaneously between two randomly created defect states. When

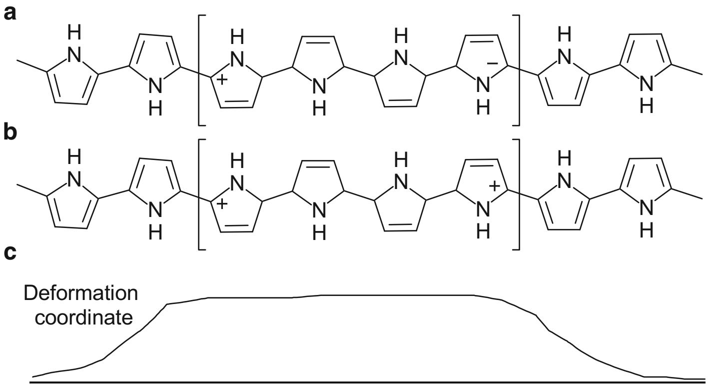


Fig. 6 Schematic of (**a**) a polaron and (**b**) a bipolaron on a PPy chain. (**c**) The bottom schematic represents the deformation of the polymer lattice created from the charge defect. (Redrawn from Refs. [36, 37])

PPy is oxidized and becomes more conductive, it is a polycation with many of these delocalized positive charges (defects) on its backbone, countered by dopant anions.

3 Conductivity

The conductivity of polypyrrole (PPy) can range from nothing tangible (~ 10^{-5} $\Omega^{-1}cm^{-1}$) as found in insulators, to 100 $\Omega^{-1}cm^{-1}$ [37]. Electrical conductivity in conducting polymers (CPs) involves movement of positively charged carriers or electrons along polymer chains and hopping of these carriers between chains. It is generally believed that the interchain hopping resistance is much greater than the intrachain transport resistance. PPy is conductive because of the ability of electrons to hop along and across the polymer chains owing to the π-conjugating bonds. In spite of these simple generalizations, conductivity within conducting electroactive polymers is a complex issue. A polymer that can exhibit conductivity across a range of some 15 orders of magnitude, most likely utilizes different mechanisms under different conditions. In addition to the electronic conductivity exhibited by conducting electroactive polymers, ionic conductivity, owing to the solvent/electrolyte incorporated during synthesis, is also a contributing factor [39].

Doping ions help to decrease the band gap (Eg) between the energy levels and hence increase conductivity (Fig. 7). As such, by using small counter anions that are coplanar with the polymer chains, the conductivity can be boosted [40]. Hydrogen peroxide, polyethylene oxide, and dodecylbenzenesulfonate, among others, have all acted as doping ions [41–43]. In addition to the introduction of dopants, conductivity and stability have been reported to result from lower temperatures and plating potentials (as well as degree of roughness of the plating surface), higher concentrations of monomer, electrolyte, and water together with longer deposition times [40, 44, 45].

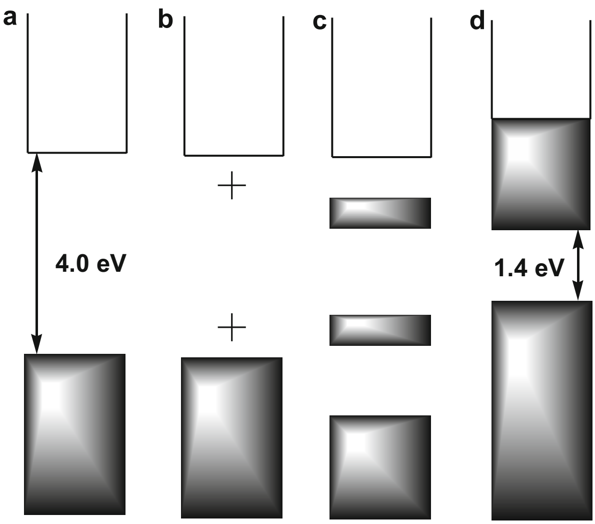


Fig. 7 Band structure representation of PPy and how Eg is modified with doping: (**a**) no dopant, (**b**) intermediate doping level – bipolarons are noninteracting at this point, (**c**) 33% dopant per monomer, and (**d**) 100% dopant per monomer. The material has changed from an insulator with a band gap of 4.0 eV to a semiconductor with full doping at 1.4 eV. (Redrawn from Ref. [46])

3.1 The Hopping Process

Conduction via localized electrons implies discrete jumps across an energy barrier from one site to the next. In other words, if two molecules are separated by a potential barrier, a carrier on one side can move to the other side via two mechanisms – either by tunnelling through the barrier or by moving over the barrier via an activated state. The latter process is called hopping. This carrier mobility is the main reason for the transport of the charges in CPs. The mobility of the charge carriers can be restricted as the degree of overlapping decreases at molecular or atomic levels. However, as the electronic states become increasingly localized, transport of the particles escalates through the hopping process. The relative importance of the two mechanisms depends on the shape of the barrier and on the availability of thermal energy, the latter resulting in a thermally activated type of mobility that increases with an increase in temperature and is mainly found in the hopping process. We can learn a lot about the conduction process by determination of the carrier mobility, e.g., its temperature dependence provides a good criterion by which we can distinguish band and hopping types of mechanisms. Though polymers are amorphous materials, a short-range order prevails. Hence, the theory that is used to explain the electronic band structure in a crystalline phase can also be applied to amorphous polymers. If the spatial fluctuations in the interatomic distances are large, the correspondingly large and random fluctuations in the height or depth of the potential wells may lead to the localization of states below a certain critical and well-defined energy. Accordingly, when the carrier mobility is low, and the mean free path is comparable with the interatomic distance, conduction can be expected to take place by a hopping process in the localized states. In order to obtain conduction through hopping, it is necessary to have an insulating or semiconducting material exhibiting a few intrinsic thermal free carriers, at least over a limited energy region, thereby establishing a large density of sites through which charge transfer can take place. There are three principal pathways that ensure carrier mobility – single chain or intermolecular transport (intrachain), interchain transport, and interparticle contact [47]. The intrachain movement depends on the effective conjugation of the polymer, while the interchain hopping is determined by the stacking of the polymer molecules. In a hopping mechanism, only those carriers with an energy kT, where k is the Boltzman constant and T is the temperature, below the Fermi level have a significant probability of hopping. Mott showed that for strongly localized states, the conductivity at low temperatures must follow a relationship of the form

$$\delta \approx \exp\left(\frac{-B}{T^{1/4}}\right)$$

where δ is the conductivity and B is a constant related to the hopping mechanism. At high temperatures, deviations from $T^{1/4}$ occur, which can be understood in terms of interchain hopping [48]. A carrier trapped in a chain, after detrapping through large energy input, may drift along the same chain or may hop onto an adjacent chain. As such, in amorphous polymers, the conduction occurs due to two distinct processes: a temperature-dependent trap hopping and a comparatively less temperature-dependent interchain hopping.

3.2 Solitons, Polarons, and Bipolarons

Polymer doping leads to the formation of conjugational defects – solitons, polarons, and bipolarons – in the polymer chain. The presence of localized electronic states of energies less than the band gap, arising from changes in local bond order – including the formation of solitons, polarons, and bipolarons – has led to the possibility of new types of charge conduction [8]. The ground state structure of such polymers is twofold degenerate, thus the charged cations are not bound to each other by a higher energy bonding configuration and so can freely separate along the chain. The effect of this is that the charged defects are independent of one another and can form domain walls that isolate two phases of opposite waveform with identical energy (solitons).

Solitons are subdivided into three categories: a neutral soliton, positive soliton, and negative soliton. An interesting observation is that charged solitons have no spin; however, neutral solitons have spin but no charge. A positively charged soliton occurs when an electron is removed from a localized state of a neutral soliton by oxidation. A negatively charged soliton is produced when an electron is inserted by reduction (Fig. 8). Solitons produced in polyacetylene (PAC) are believed to be delocalized over about 12 CH units, with the maximum charge density existing next to the dopant counterion (A^-). The bonds closer to the defect show decreased bond alternation compared with those further away from the center. Soliton formation results in the creation of new localized electronic states that appear in the middle of the energy gap. At high doping levels, the charged solitons interact with one another to form a soliton band, which can eventually merge with the band (VB and CB) edges (Fig. 8) to create true metallic conductivity [49–51].

A neutral polymer has full VB and empty CB, separated by the band gap. Formation of polarons and bipolarons generates new energy levels located at mid-gap. Bipolarons and polarons are self-localized particle-like defects associated with characteristic distortions of the polymer backbone and with quantum states deep in the energy gap owing to strong electron–lattice coupling. Polarons are obtained through a combination of a neutral and a charged soliton existing on the same polymer chain. Two mechanisms have been put forward to explain the transition from polaron to bipolaron states: polaron recombination into bipolarons [52–54], where the bipolaron is generated when polarons of the same electric charge meet each other; and single-polaron to bipolaron transitions [55–57], where the polaron structure is transformed by the addition of one extra charge. Oxidation causes additional polarons to form and eventually the unpaired electron of the polaron is removed, or two individual polarons combine to form a dication or bipolaron (Fig. 9) [58]. A polaron has a spin ±1/2 and an electric charge ±e, whereas a bipolaron is spinless with a charge ±2e and is of lower energy than the two distinct polarons from which it was created. For example, the bipolarons are located symmetrically with a band gap of 0.75 eV for PPy. With continued doping, continuous bipolaron bands form [59], and the band gap also increases as newly formed bipolarons are made at the expense of

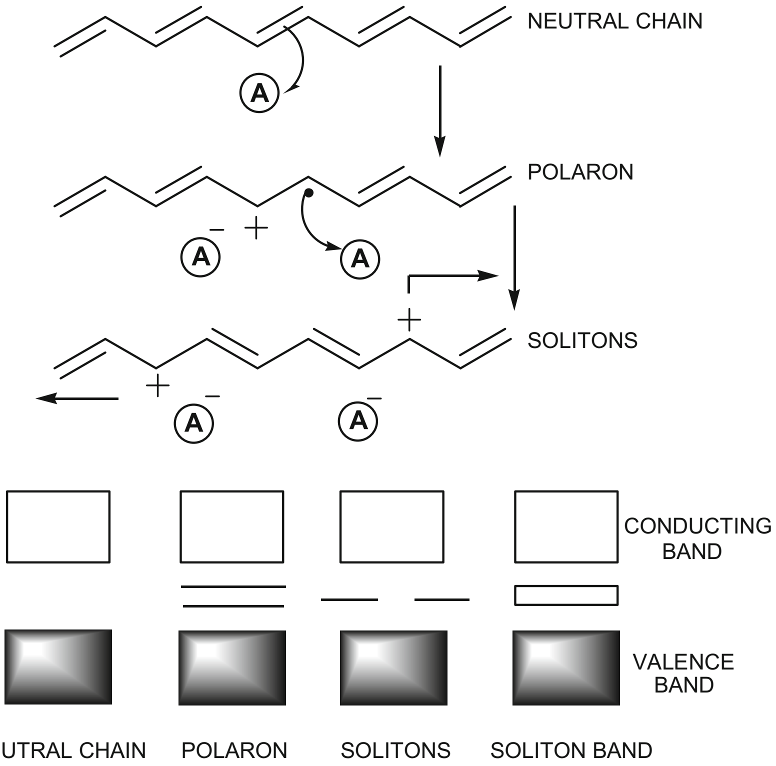


Fig. 8 Soliton structures of polyacetylene

the band edges. For a very heavily doped polymer, it is conceivable that the upper and the lower bipolaron bands will merge with the CBs and the VBs, respectively, to produce partially filled "conducting-like" bands rendering metallic-like conductivity to the polymer, as shown in Fig. 9. Conjugated polymers, e.g., PPy, with a degenerate ground state exhibit a slightly different mechanism. However, in either case, polarons and bipolarons are produced upon oxidation [60]. Indeed, density functional theory calculations showed that the charge carrier in oxidized polypyrrole are bipolarons [61].

The oxidative doping of polypyrrole (PPy) proceeds in the following way. An electron is removed from the π-system of the backbone, producing a free radical and a spinless positive charge. The radical and cation are coupled to each other through local resonance of the charge and the radical, via a sequence of quinoid-like rings, the number of which is limited by the prohibitive amount of energy required for the creation and separation of the defects. For the polaron state of the PPy, it is believed that the lattice distortion extends over four pyrrole rings and can be either a radical cation or radical anion thereby creating a new localized electronic state in the gap, with the lower energy states being occupied by a single unpaired electron. The polaron state of PPy is symmetrically located about 0.5 eV from the band edges [59, 60, 62].

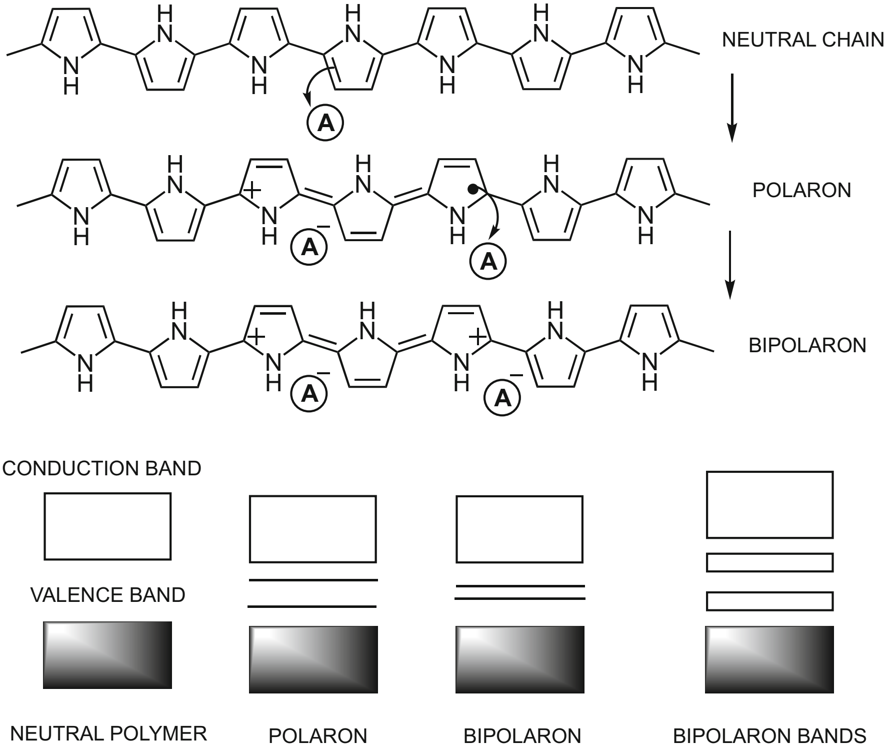


Fig. 9 Formation of polarons and bipolarons for polypyrrole (PPy)

A consistent description of the dynamics of the mechanism of creation, stability, and transition of polarons, and bipolarons constitutes a critical problem in the understanding of these materials. The polaron–bipolaron transition problem was explicitly addressed by Čík et al., in poly(3-dodecyl thiophene) in connection with temperature changes [52]. They found that when the sample was heated and subsequently cooled, there was an amplification of the diamagnetic inter- and intrachain bipolarons. Kaufman et al. studied PPy [53] using optical absorption spectroscopy and electron spin resonance and found that the metastable states possess spin, while the stable states do not. Their data revealed a slow transition, consistent with the diffusion rate limited by the mobility of the dopant.

4 Synthesis and Characterization of Conducting Polymers

It is well known that the conductivity of a polymer is influenced by a number of factors including polaron length, conjugation length, overall chain length, and by charge transfer to adjacent molecules, most of which can be influenced by the method of preparation. Conducting polymers (CPs) are synthesized, either chemically or electrochemically. Each method has advantages and disadvantages, as summarized in Table 1 [9].

Chemical synthesis includes the usual methods of condensation polymerization (i.e., step growth polymerization) or addition polymerization (i.e., chain growth polymerization). The standard CPs – PPy, PTh, PANI, and poly(3,4-ethylenedioxythiopene) (PEDOT) – can be polymerized both chemically and electrochemically [62]. With chemical synthesis of polymers, it is feasible to synthesize CPs that are currently not possible with electrochemical synthesis. However, because the latter method is relatively straightforward and reproducible [9, 64], it is rapidly becoming the preferred alternative for making CPs and consists of dissolving a monomer in a solvent/electrolyte medium followed by the electrodeposition of a polymer film onto an electrode surface using pulse, galvanostatic, potentiostatic, or sweeping techniques [65]. One advantage associated with the electrochemical polymerization of conducting polymers is that the reactions can be performed at room temperature, either by varying the potential or current for specified periods of time, thereby permitting the thickness of the film to be monitored and controlled. CPs such as PTh, polycarbazole, polyindole polyazulene, and PPy can all be synthesized using this technique [66].

4.1 Polypyrrole

Polypyrrole (PPy), as a model for the CPs, can be obtained chemically or electrochemically. The electrochemical polymerization of pyrrole (Py) has been extensively studied since it is easily obtained in the form of freestanding films and has good environmental stability and conductivity. Electrochemical polymerization is performed using a three-electrode configuration (working, counter, and reference) in a solution of the monomer (Py), appropriate solvent, and electrolyte (dopant) (Fig. 10).

Current is passed through the solution and electrodeposition occurs at the positively charged working electrode or anode. Monomers (Py) at the working electrode surface undergo oxidation to form radical cations that react with other pyrrole monomers or radical cations, forming insoluble polymer chains on the electrode surface

Table 1 Comparison of chemical and electrochemical CP polymerization

Polymerization approach	Advantages	Disadvantages
Chemical polymerization	Larger scale production possible Postcovalent modification of bulk CP possible More options to covalently modify CP backbone	Thin films inaccessible Complicated syntheses
Electrochemical polymerization	Thin film synthesis possible Ease of synthesis Entrapment of molecules in CPs Doping is simultaneous	Difficult to remove film from electrode surface Postcovalent modification of bulk CP is difficult

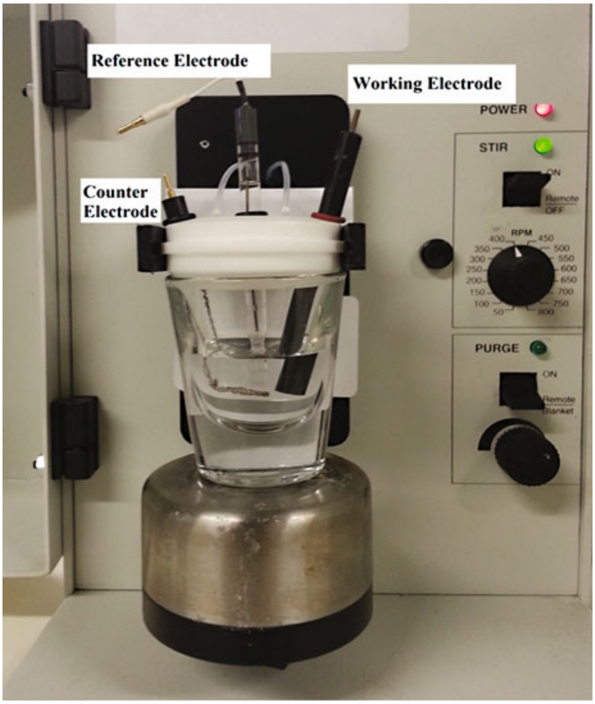


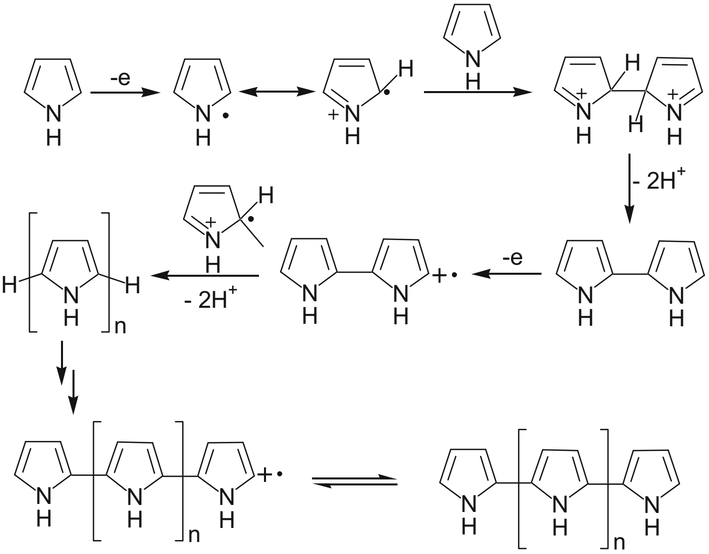
Fig. 10 Three-electrode setup for electrochemical synthesis of conducting polymers – reference electrode, working electrode, and counter electrode

(Scheme 1) [67]. A number of important variables, including deposition time, temperature, solvent system (water content), electrolyte, electrode system, and deposition charge need be considered. Each of these parameters has an effect on film morphology (thickness and topography), mechanics, and conductivity, which are properties that have a direct impact on the utility of the material for specific applications [63].

4.2 Polythiophene and Its Derivatives

In its doped oxidized state, a poly(3,4-ethylenedioxythiophene) (PEDOT) layer/film shows exceptional stability, transparency, and high conductivity (300 $S.cm^{-1}$) [68]. The electrosynthesis of polyalkylenedioxythiophenes was carried out in 1994 by the anodic oxidation of 3,4-ethylenedioxythiophene or 3,4-trimethylenedioxythiophene. This resulted in polymers that were extraordinarily stable during charging and discharging, owing to a narrow band gap [69]. The electropolymerization process may also be executed through *in situ* polymerization of 3,4-ethylenedioxythiopene (EDOT) or via oxidative means [70].

Polymerization of PEDOT is typically carried out in acetonitrile, employing $LiClO_4$ as electrolyte, which results in a sky-blue doped PEDOT layer containing ClO_4^- as counter ions. Oxidative polymerization, with iron(II) chloride, has been demonstrated to be a satisfactory method of synthesizing neutral, fully undoped



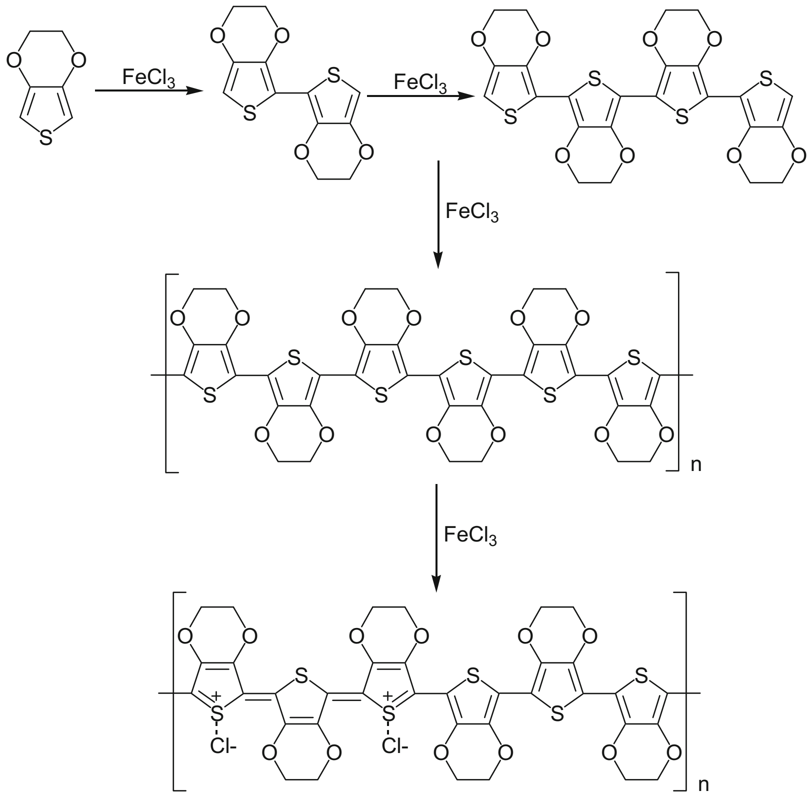
Scheme 1 Mechanism for heterocycle polymerization via electrochemical synthesis. This pathway is initiated by the oxidation of a monomer at the working electrode to give a cation species, which can then react with a neutral monomer species or radical cation oligomeric species to generate the polymer, redrawn from Ref. [67]

molecules with considerable yield [70]. PEDOT (Scheme 2) is an intermediate in the preparation of doped, highly conductive PEDOT and can be isolated through the adjustment of selected reaction conditions.

5 Principal Conducting Polymers

5.1 Polypyrrole (PPy)

Polypyrrole, composed of a number of connected pyrrole rings, has been lauded for its conductivity (resulting from interchain hopping) and high stability. In addition, the ease of oxidation and availability of its monomer, pyrrole, ensured that it would be extensively studied and characterised by thermal analysis and electrochemical techniques that include cyclic voltammetry (CV) and impedance spectroscopy. The chemical synthesis of polypyrrole, through the oxidation of pyrrole, was first accomplished in the early twentieth century. Pyrrole itself is ubiquitous in nature, making appearances in the building blocks of chlorophyll, hemoglobin, bile pigments, and mold metabolites, among others. Much later, the first electrochemical deposition of PPy was accomplished in 1968 [71]. Since then, PPy has been prepared by the electropolymerization of pyrrole onto a variety of conductive substrates, for example, stainless steel, nickel, and platinized silicon wafers, with promising results [72–76]. The properties – physical, chemical, and electrical – of



Scheme 2 Synthesis of poly(3,4-ethylenedioxythiophene) and doped poly (3,4-ethylenedioxythiophene)

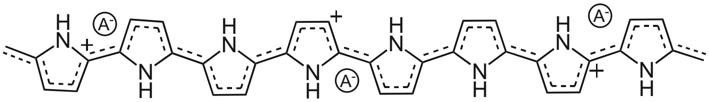


Fig. 11 Polypyrrole (PPy), with counter ions (A^-) to balance charge. (Redrawn from Ref. [81])

electrochemically deposited PPy (Fig. 11) can be reshaped through doping and changeable plating conditions [41, 42, 77–80] thereby increasing its versatility. The easy alteration of these properties, through the judicious choice of dopants, places PPy in a very select group of conducting polymers, increasing its attractiveness for application in biosensor technology, among others.

PPy exhibits good electrical conductivity and high air stability (its conductivity decreases by only 20% per year in an exposed environment) and, by its very nature, has been used in a variety of technological applications in various research areas, namely, secondary batteries [82–85], electrochromic display devices [86, 87], light-emitting diodes [88, 89], capacitors [90–92], sensors, [93–97] membranes [98], and enzyme electrodes [99–101]. It has been reported that the electrical conductivity is stable even at 200 °C [36, 102]. Consequently, conducting polymeric materials [103, 104], such as PPy, have become an area of increasing research interest as they show great potential for application in solid-state devices [105].

The ability to control polypyrrole's surface properties, such as charge density and wettability, holds promise for effective interaction between biological tissue and the polymer [106–109]. However, polypyrrole itself reveals rather poor properties in terms of electrochromic behavior [110], and often, further enhancement through doping and sensitizing with various dyes is required to obtain good optical properties [109–114]. Additionally, the syntheses of conducting star, graft, and block copolymers are some of the ways to effectively improve electrical and mechanical properties of conducting polymers and polypyrrole is no exception. In order to make conducting polymers processible, several approaches have been developed, one of which is to prepare graft and block copolymers with desired end groups like pyrrole or thiophene [115–118].

5.2 Polythiophene (PTh)

Polythiophenes (PThs) are an important representative class of π-conjugated polymers that exhibit a sought after combination of high environmental/thermal stability, processability, and electrical conductivity. PTh has been used in a variety of applications such as electrical conductors, nonlinear optical devices, light-emitting diodes, transistors, electrochromic or smart windows, photoresists, antistatic coatings, sensors, batteries, electromagnetic shielding materials, artificial noses and muscles, solar cells, microwave absorbing materials, new types of memory devices, nanoswitches, imaging materials, and polymer electronic interconnect batteries [119–121]. PThs have a regular polymeric backbone (Fig. 12) which can be modified by varying the nature of the dopant and through facile ring modifications. Owing to their chemical and electrochemical stability, high conductivity upon doping, and nonlinear optical properties, PThs are among the most widely studied conjugated organic polymers, experimentally and theoretically. However, polythiophene is generally insoluble in common organic solvents and decomposes readily, thereby limiting its use in practical applications. The real interest in this class of CPs was sparked when it was realized that three-carbon substitution of the thiophene ring yielded a wide variety of versatile CPs. The substituted PThs, namely, poly(3-methylthiophene) and poly

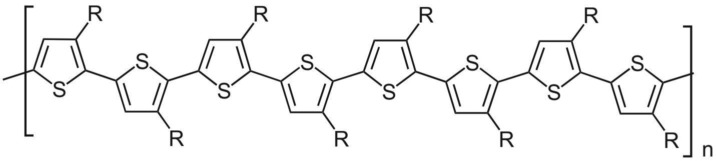


Fig. 12 Structure of polythiophene (PTh) where R = H, poly(3-methylthiophene) where R = CH_3 and poly(3-hexylthiophene) where R = C_6H_{13}

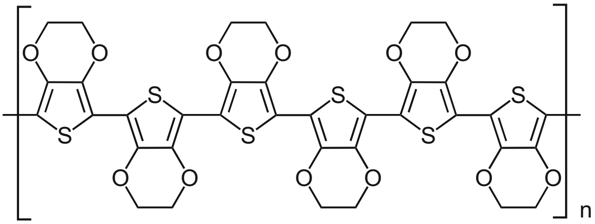
(3-hexylthiophene), etc., all exhibit good solubility in common organic solvents with the latter finding importance as a benchmark hole conductor in organic photovoltaics [122]. The chemical method for the synthesis of PTh is used in bulk production while, electrochemically, very thin and better-ordered films can be prepared. Chemically synthesized PThs are produced in their undoped state and can be doped chemically or electrochemically to increase conductivity [123].

5.3 Poly(3,4-ethylenedioxythiophene) (PEDOT)

The first synthesis of PEDOT was successfully done by scientists at the Bayern A G Laboratories in the late 1980s. The commercial name, Baytron, was given to PEDOT following the chemical polymerization of 3,4-ethylenedioxythiophene [70]. PEDOT [124] has been of interest in numerous studies because of its high transparency, high conductivity, excellent environmental stability, and relatively low band gap [125]. These unique properties make PEDOT an excellent material for utilization in electrochromic devices, antistatic coatings, biocorrosion coatings, light-emitting diodes, sensors, and synthetic textiles [126–129]. PEDOT has also been reported to be excellent for the synthesis of nanostructured materials and devices whose electrical, electronic, magnetic, and optical properties are comparable to those of metals or semiconductors. Compared to other unsubstituted PThs and derivatives, PEDOT exhibits a distinctly low oxidation potential and a small band gap in the oxidized state [130, 131]. It has been revealed that undoped PEDOT has a band gap energy of –1.6 eV and can be electrochemically cycled between its reduced and oxidized states. This superior electrochemical stability may be attributed to the presence of the ethylenedioxy binding group at the α and β position of the thiophene ring in EDOT (Fig. 13), which blocks coupling along the backbone, making the resulting polymer regiochemically defined [130, 132].

Conducting polymers may be employed in their unmodified state or they may be doped to enhance their electrical capability; PEDOT is one of the few examples within the conjugated polymer family which is both p- and n-dopable [133]. It is acknowledged that upon electrochemical p-doping or n-doping, conducting polymers undergo a redox process which involves ion transport into and out of the polymer matrix to balance the electronic charge, resulting not only in an increase in electronic conductivity but also structural transitions which give rise to spectral changes [134–137] which allowed for their exploitation in the field of sensors.

Fig. 13 Structure of poly (3,4-ethylenedioxythiophene) (PEDOT)



Indeed, Nien et al. [138] used PEDOT as the matrix to fabricate an amperometric glucose biosensor; the biosensor showed a detection limit and sensing sensitivity of 0.13 mM and 12.42 mA cm^{-2} M^{-1}, respectively. Other incorporations of PEDOT in sensors include a direct detection DNA sensor, that quantifies the targeted single-strand DNA [139], and a self-absorbing piezoelectric sensor consisting of conducting PEDOT [140]. In addition, an amperometric sensor coated with PEDOT for the measurement of chromate ions and an enzyme modified biosensor entrapped by PEDOT for the detection of phenolic compounds, with high catalytic activity have been reported [141]. Moreover, it was found that the increased surface area of the polymer led to a high rate of electron transfer between the electrode and *p*-benzoquinone, when the latter was employed as an electron mediator.

Electrochemical polymerization is widely used to construct conducting polymer films, but the option of using a conducting substrate from which a conducting polymer is formed may limit practical applications [142]. Recently, the incorporation of nanomaterials into a polymer matrix and the study of nanoparticles-matrix interactions have been of interest to material scientists [143]. Polymers are considered a good choice as host matrices for composite materials, because they can easily be designed to yield a variety of bulk physical properties [144, 145]. PEDOT coatings prepared by electrochemical polymerization in aqueous solution allows the direct incorporation of water-soluble anions [146], into its matrix. Xiao et al. developed an adenosine 5’-triphosphate (ATP) doped PEDOT for neural recording devices that displayed great stability and biocompatibility [147]. Balamurugan et al. [124] demonstrated a silver nanograins (AgNGs) incorporated PEDOT modified electrode for electrocatalytic sensing of hydrogen peroxide. The modified electrode exhibited good electrocatalytic activity towards the reduction of hydrogen peroxide without an enzyme or mediator immobilized on the electrode. It showcased a detection limit of 7 μM and a response time of 5 s. Vasantha et al. disclosed the electrochemical synthesis of a poly(3,4-ethylenedioxythiophene)-(PEDOT)|ferricyanide film modified electrode by cyclic voltammetric and chronoamperometric techniques, for the determination of ascorbic acid in aqueous solution with a detection limit of 5×10^{-5} M [148]. Olowu et al., in 2010, constructed an aptasensor for the detection of 17β-estradiol, an endocrine disrupting chemical, based on a poly(3,4-ethylenedioxythiopene)-gold nanocomposite platform; the detection limit was 0.02 nM [149].

5.4 Polyfuran (PFu)

Furan is one of the five-membered heteroaromatic ring compounds that can be converted into a conducting polymer by both chemical and electrochemical methods in aqueous and organic media. It is lesser known than pyrrole and thiophene because of its high oxidation potential. Polyfuran (Fig. 14), through chemical synthesis, has found application in industry as an insulator and is very sensitive to humidity – its electrical resistivity decreases considerably and reversibly upon contact with moisture.

Ali et al. [150] studied the dispersion of normal modes in polyfuran and this conducting polymer was used in optoelectronic devices, as upon doping the color

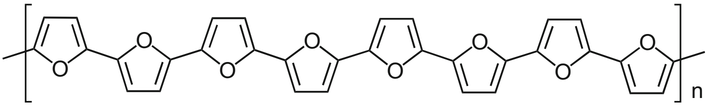
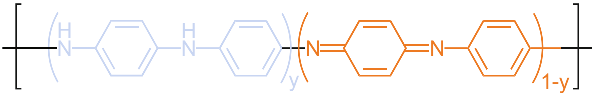


Fig. 14 Chemical structure of polyfuran (PFu)

Fig. 15 General polymeric structure of polyaniline



changes from yellow-brown to black-brown [151, 152]. Meanwhile, Galal et al. developed a promising electrochemical biosensor to determine dopamine, epinephrine and norepinephrine, ascorbic acid, and paracetamol. The sensor was fabricated via electrodeposition of palladium nanoclusters on a polyfuran film modified platinum electrode and saw exceptional improvement in the detection limit. Moreover, diffusion coefficient measurements confirmed the fast electron transfer kinetics of the electrochemical oxidation of the analyte molecules at the sensor/solution interface [153].

5.5 Polyaniline (PANI)

Polyaniline (Fig. 15) has been studied extensively as an important conducting material owing to its promising electronic and optical properties [65, 154]. It has also generated considerable interest because of the many synthetic pathways available to scientists, its chemical stability, good environmental stability, low cost, and ease of redox doping [155]. Although PANI boasts good environmental stability and conductivity, processing of the polymer into useful products has been problematic because of its insolubility in common nontoxic organic solvents and the fact that its ready decomposition before melting. PANI is unique among inherently conducting polymers such as PPys and PThs because its N heteroatom can directly participate in the polymerization process and in the conjugation of the conducting form to a greater extent than the N and S heteroatoms in PPy and PTh.

PANI can be synthesized by either chemical or electrochemical oxidation of aniline under acidic conditions. The most widely used technique is oxidative coupling, involving the oxidation of the monomers, to form radical cations which couple to form dications. Repetition of this propagation step leads to the polymer. Electrochemical synthesis is preferred to chemical synthesis because of the accessibility to thin films and better ordered polymers. The best films are reported to be produced from electrochemical techniques using three electrode systems [156]. The film can be deposited at the working electrode through electropolymerization of monomeric aniline from a suitable medium that limits the dissolution of the substrate. This electropolymerization process is preferably conducted in acidic media at a $\text{pH} < 1$ [157, 158]. PANI-coated electrodes, as components of sensors, presents some advantages such as acceleration of electron transfer reactions, immobilization of biological compounds, amplification of signal, and elimination of electrode fouling.

5.5.1 Polyaniline Derivatives

Similar to unsubstituted PANI, polyaniline derivatives are also synthesized by chemical or electrochemical oxidative polymerization of the respective substituted aniline monomers in acidic solution, although some other approaches such as plasma polymerization [159, 160], electroless polymerization [161], solid-state polymerization [162, 163], enzyme-catalyzed polymerization, and photochemically initiated polymerization [164] have also been reported. Conditions related to the formation of PANI and its derivatives, such as the type of supporting electrolyte, monomer concentration, applied potential, the type of solvent, and pH of the electrolyte [158, 164], as well as the influence of anions on the electrodeposition of polyaniline and on polyaniline redox reactions, have also been extensively described in literature [165, 166]. These factors are known to dictate the morphology and properties of the generated polyaniline.

It is well known that the low solubility of PANI, in common organic solvents, ultimately restricts processability. To overcome this challenge, substituted PANI was investigated and polymerization of a typical derivative of aniline resulted in a soluble conducting polymer. The substituent groups present in the units of the polymer chain are thought to contribute to a decrease in the stiffness of the polymer chain resulting in better solubility. Unfortunately, substitution of the phenyl ring or the N-position of polyaniline units has been shown to decrease the conductivity [167]. However, poly (2,5-dimethoxyaniline) (PDMA), bearing anilines substituted with two methoxy groups (2,5-dimethoxyaniline), has been reported to be a soluble polymer (Fig. 16) with a conductivity similar to PANI [168, 169] though the redox transitions occur at lower potentials in comparison with PANI (0.70 V for PANI and 0.27 V for PDMA) [170].

5.5.2 Oxidation States of Polyaniline

Polyaniline has the general formula $[(\text{—B—NH—B—NH})_n(\text{—B—N=Q=N—})_{1-n}]_m$, in which B and Q are the rings in the benzenoid and quinonoid forms, respectively.

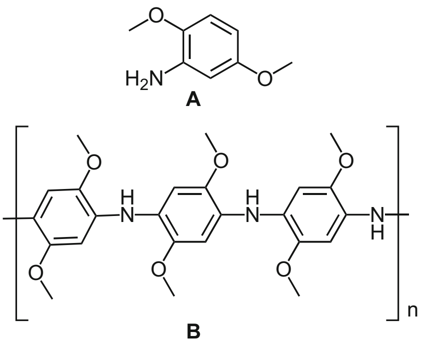


Fig. 16 Structures of (**a**) 2,5-dimethoxy aniline and (**b**) PDMA

PANI can be rapidly converted between the base and salt forms by treatment with acid or base, thus, the general polymeric structure shown in Fig. 15 is now accepted by the scientific community.

PANI can exist in three basic forms depending on the existing oxidation state, which ranges from the fully reduced ($y = 1$) leucoemeraldine state to the half oxidized ($y = 0.5$) emeraldine form to the fully oxidized ($y = 0$) pernigraniline configuration. Reduction of the emeraldine salt to leucoemeraldine and oxidation to pernigraniline both see a decrease in conductivity [171]. In fact, the fully oxidized and fully reduced states of PANI are insulators, although they possess other interesting physical and chemical properties. Beside changes in oxidation levels, different forms of PANI are also characterized by a change in color [172]. For instance, the emeraldine salt obtained by electrochemical polymerization in acidic media is green in color and can be converted into the dark blue form by further oxidation to the fully oxidized pernigraniline salt and even further into the violet pernigraniline through treatment in basic media. It can also be reduced to colorless leucoemeraldine or further converted into the blue nonconducting form of emeraldine in basic media [173] (Scheme 3). Interestingly, the two blue forms of PANI – pernigraniline salt and emeraldine – are of different shades [172].

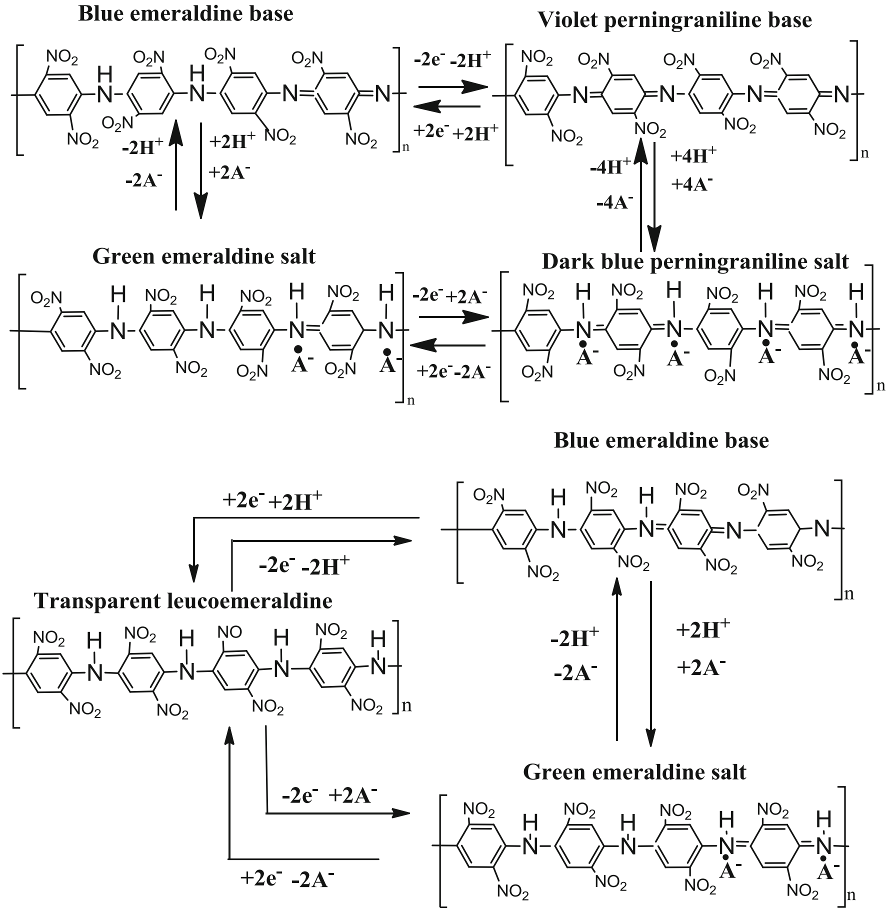
Among the three oxidation states of PANI, the emeraldine salt is the one that displays the highest conductivity, by doping or protonation of the emeraldine base [174] – and is composed of an alternating sequence of three benzenoid units and one quinonoid unit. Further, it consists of amine (–NH–) and imine (=N–) sites in equal proportions [175]. The imine sites are protonated by acids to the bipolaron (dication salt) form. However, further rearrangement occurs to form the delocalized polaron lattice, which is a polysemiquinone radical-cation salt and is responsible for the high conductivity of PANI [164].

6 Conducting Copolymers

Practical use of polypyrrole and other conducting electroactive polymers are limited by their brittle structure, insolubility and poor mechanical and physical properties, all of which restrict their processability [176]. Improvements to the processability of conducting polymers can be had by copolymerizing them with other monomers resulting in star, graft or block copolymers [177, 178]. Copolymerization permits the chemical linking between the insulating matrix (end groups) and the conjugated polymer [179]. Structural modification of conducting polymers via copolymerization has been used to obtain materials with a broad range of electronic, optical, and mechanical properties [180]. Thus, electrochemical syntheses of pyrrole copolymer films with substituted pyrroles, [181], thiophene [182], terthiophene [183], and other combinations of aromatic compounds [184, 185], have been reported. The resulting copolymers have properties different from those of the homopolymers of the constituent monomers.

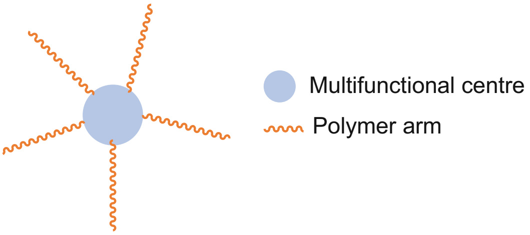
6.1 Conducting Star Copolymers

Star copolymers are a class of branched macromolecules that have a central core to which multiple linear polymer chains are attached – the core consists of a moiety with multiple branching points (Fig. 17). The cores may be formed from



Scheme 3 Different oxidation states of PANI. Redrawn from Ref. [166]

Fig. 17 Representation of a star copolymer



hyperbranched polymers, dendrimers, or other symmetric or semi-symmetric molecules which have multiple attachment sites. The three dimensional (3D) structure, with extended conjugated linear polymer chains, gives star copolymers properties that are different from the typical two-dimensional, linear polymers [19].

Conducting star copolymers are used in their undoped state for applications in which the conductivity requirements are not too high, for example, static dissipation, or where the optical property of the polymer coating is of chief importance as in a pigment or reflective layer. Materials with conductivities in the range of 10^{-6} to 1 $S.cm^{-1}$ are suitable for these purposes. Furthermore, the conducting chains surprisingly can provide sufficient intermolecular overlap to give solid materials with electrical conductivities higher than the corresponding linear, non-star conducting polymers [19, 186–188].

The regular 3D structure of star copolymer gels combines the properties of hardness and flexibility and is being investigated as materials that are hard without being brittle [19]. The combination of star copolymer and conducting polymer structures realises an approach to make materials that possess the favorable properties of both – improved processability and electrical conductivity. The former results from the spheroidal structure of hyperbranched, dendrimeric, and starburst polymers. A conducting star copolymer may be constructed in which two or more different conjugated arms radiate from the central core [86]. Doping of the conducting star copolymers, to increase the electrical conductivity, may be achieved using methods applicable to the conjugated radiating chain moieties. For conjugated chains based on pyrrole, thiophene units or their derivatives, doping may be achieved by treatment with oxidizing agents such as iodine, ferric chloride, ferric tosylate, gold trichloride, and antimony chloride. If the polymer side chains are composed of polyaniline, doping can be brought about by treatment with hydrochloric acid [189]. Doping can also be obtained electrochemically by confining the polymer to an electrode surface and subjecting it to an oxidizing or reducing potential in an electrochemical cell.

6.2 Dendrimer Star Copolymers

Dendritic copolymers (Fig. 18) are a specific group of dendrimers. These exist as two different types of copolymers – segment-block dendrimers built with dendritic segments of different constitution, obtained by attaching different wedges to one polyfunctional core molecule and layer-block dendrimers consisting of concentric layers around the central core. Hawker and Fréchet [190] synthesized a layer-block dendrimer as well as a segment-block dendrimer which consisted of one ether-linked segment and two ester-linked segments. The inner two generations were ester-linked and the outer three ether-linked.

Dendrimer-star copolymers [191] are a novel type of molecular architecture, in which many linear homo- or block copolymer chains are attached to the dendrimer. They have been developed because they combine the properties of star copolymers with those of dendrimers [192–197]. Two general methods have been used to prepare

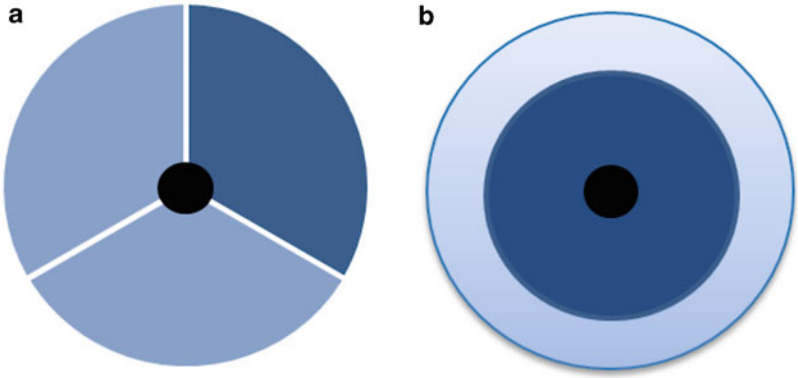


Fig. 18 Copolymers: (**a**) segment-block dendrimer and (**b**) layer-block dendrimer

the dendrimer-star copolymers – one is to link monofunctional linear polymers onto the dendrimer surface [192, 196–198] and the other is to grow armed polymer chains from the surface of the dendrimer by "controlled/living" polymerizations, such as anionic polymerization [199], ring-opening polymerization (ROP) [200], and atom transfer radical polymerization (ATRP) [201]. Synthesis of a hybrid dendrimer-star copolymer, through the reversible addition-fragmentation transfer (RAFT) polymerization process, has been reported by Zheng et al. [202]. Wang et al. discussed a conducting star-shaped copolymer, consisting of a regioregular poly(3-hexylthiopene) arm attached to a polyphenylene dendrimer core [203]. Miller and Tomalia announced the conductivities of polyamidoamine (PAMAM) dendrimers modified with cationically substituted naphthalene diimides; the study showed that the conductivity increased with increased humidity, to as high as 18 $S.cm^{-1}$ at 90% relative humidity. The conductivity was, in all cases, electrical and isotropic [204].

In 2011, Baleg et al. reported on the synthesis and characterization of a star copolymer based on a PPI dendrimer core (generations 1–4) and polypyrrole [205] (Fig. 19). In the same year, a star copolymer which involved the electro-copolymerization of (3,4-ethylenedioxy thiophene) (EDOT) with G2PPT was developed by Olowu et al. [149, 206].

Poly(propylene imine) (PPI) dendrimers are highly branched macromolecules having terminal amino groups which exhibit a number of interesting characteristics. The dendrimer can be used as a hydrogen donor because of the high density of amino groups; many of the properties of dendrimers are strongly influenced by these terminal groups [207–209].

The use of dendrimer-oligothiophene hybrid macromonomers for the preparation of a soluble, highly conducting PTh, having only dendritic substituents, has been communicated [210]. Roncali et al., in 1999, described electrogenerated poly (dendrimers) containing conjugated poly(thiophene) chains. In his approach, an electroactive conjugated polymer was synthesized by electropolymerization of increasing generations of dendrimer derivatives by a bithiophene group [211]. Deng and others described the synthesis and application of amine-terminated

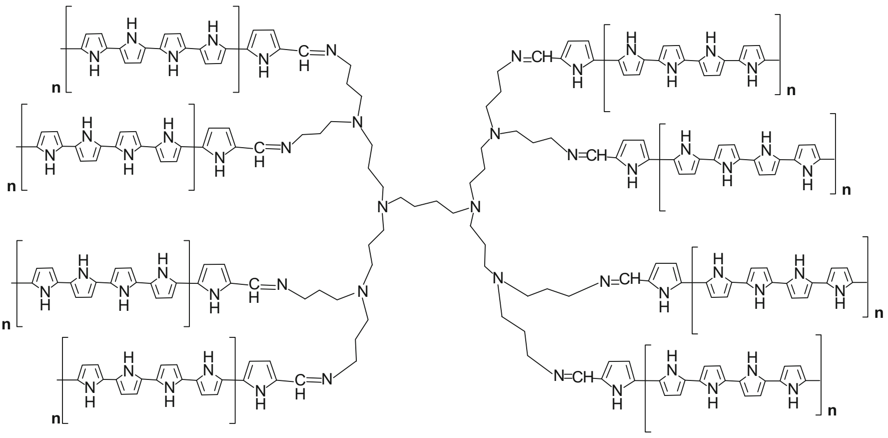


Fig. 19 Poly(propylene imine)-co-polypyrrole

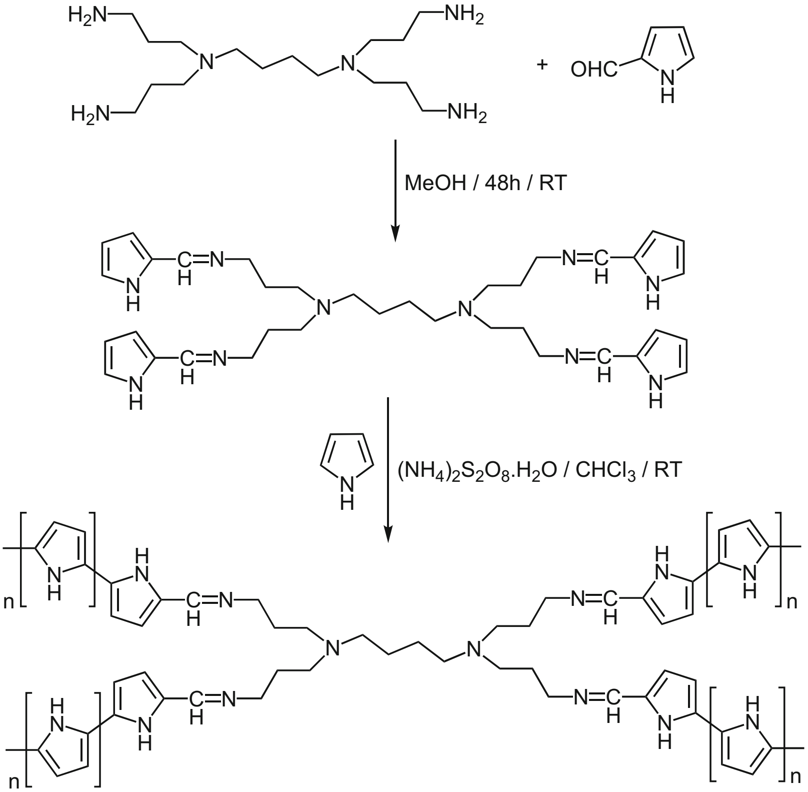
fourth-generation PAMAM dendrimers functionalized with thiophene dendron jackets and their roles in the preparation of dendrimer-encapsulated nanoparticles for energy-transfer and fuel cell application [212]. A series of star-shaped copolymers, using first generation (G1) to the fifth generation (G5) PPIs as the core, were prepared [213, 214] in order to investigate their miscibility properties with linear polystyrene. The unsaturated end groups of polyisobutylene were converted into anhydride termini by Alder-ene reaction with maleic anhydride, and the product was reacted with the PPI dendrimers to generate PPI-polyisobutylene star copolymers [215]. The formation of dendritic stars with conducting polymers such as PANI, PTh, and PPy saw an increase in the conductivity which was attributed to a nanostructural change in the product owing to elongation of the conjugation chains and unhindered π-stacking of the polymer molecule with the dendrimer [205, 212, 216].

Dendrimer-like star-branched polymers have recently appeared as a new class of hyperbranched polymers and are recognized as nano-ordered globular macromolecules. Based on their architectures which bear many characteristic structural features such as hierarchical hyperbranched structures, generation-based radial architectures, differing branch densities between core (inside) and shell (outside), and many junction points and end-groups [217, 218].

It is also possible to synthesize a variety of dendrimer block copolymers by introducing different polymer segments at each dendrimer branch. Interesting morphologies and nanostructured materials have been reported by several research groups [219–226]. Thus, dendrimer-like star-branched polymers and block copolymers are promising specialty functional materials with many possible applications as drug, vaccine, and gene encapsulated delivery devices, surface modifiers, functional nanosize spheres and micelles, surfactants, molecular recognition systems, and microelectronic materials to name a few. Yoo et al. [227] synthesized a series of dendrimer-like star-branched polystyrenes by developing an iterative methodology based on the “arm-first” divergent approach. This resulted in high-generation and high-molecular-weight polystyrenes with narrow molecular weight distributions [227].

6.2.1 Poly(propylene imine)-co-polypyrrole Dendritic Star Copolymer

Synthesis of novel star copolymers based on the PPI dendrimer core (generations 1–4) and PPy shell was rendered via a condensation reaction (Scheme 4) between the PPI surface amine moieties and 2-pyrrole aldehyde to give the pyrrole-functionalized PPI dendrimer (PPI-2Py). Subsequently, the pyrrole units on the dendrimer backbone underwent chemical oxidative copolymerization, using ammonium persulfate as an oxidant, providing the conducting star copolymer with polypyrrole side chains in 75% yield. Electrochemical synthesis was achieved via cyclic voltammetric scans of a PPI-2Py drop-coated platinum electrode (Scheme 4). In both cases, the resulting star copolymer, poly(propylene imine)-co-polypyrrole, exhibited higher conductivity than the pristine pyrrole and improved thermal stability over PPI-2Py [205].



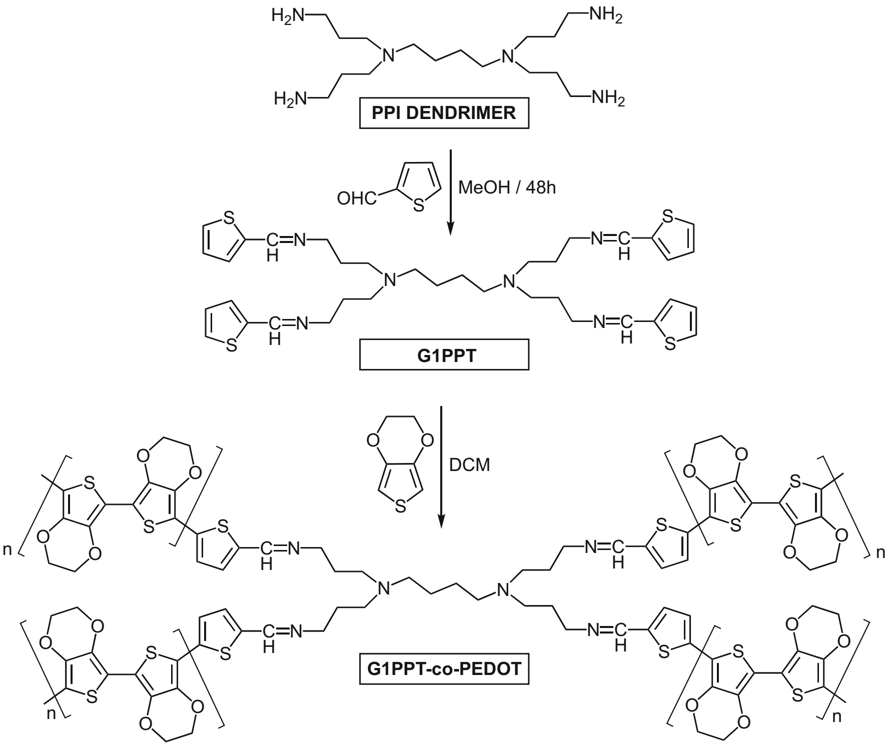
Scheme 4 Chemical synthetic procedure for poly(propylene imine)-co-polypyrrole – a dendritic star copolymer. Redrawn from Ref. [205]

6.2.2 Dendritic Poly(propylene thiophenoimine)-co-poly(3,4-ethylene dioxythiophene) Dendritic Star Copolymer

In another development, Olowu et al., in 2011 [149], also synthesized a star copolymer which involved the electrocopolymerization of 3,4-ethylene dioxythiophene (EDOT) with a G1 poly(propylene thiophenoimine) (G1PPT) modified gold electrode using cyclic voltammetric techniques (Scheme 5) to produce a generation 1 poly (propylene thiophenoimine)-co-poly(3,4-ethylene dioxythiophene) dendritic star copolymer (G1PPT-co-PEDOT) for use in the detection and quantification of the endocrine disrupting compound, 17*β*-estradiol. Electrochemical impedance spectroscopy confirmed the more desirable conductive behavior of the star copolymer over PEDOT.

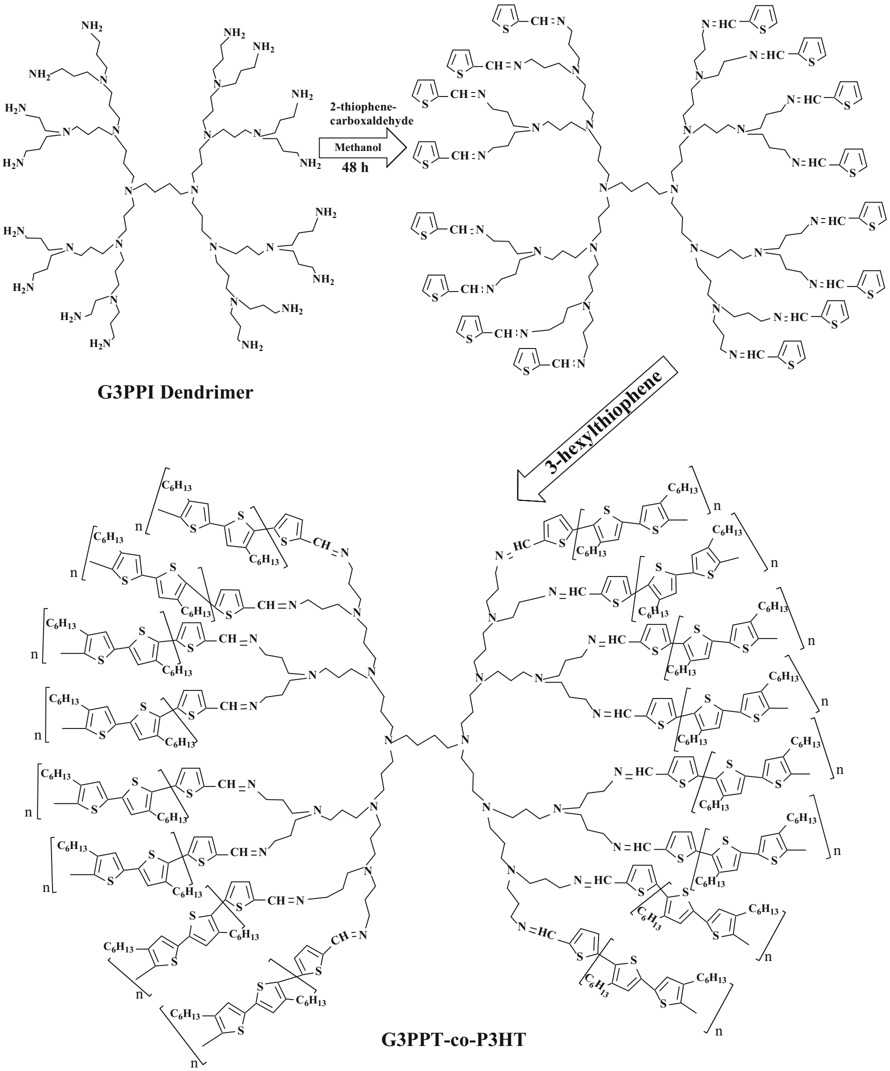
6.2.3 Dendritic Poly(propylene thiophenoimine)-co-poly(-3-hexylthiophene) Dendritic Star Copolymer

Novel star copolymers based on a G3 PPI dendrimer core and a poly (3-hexylthiophene) shell were prepared by Makelane et al. [228]. The synthesis of



Scheme 5 Synthetic pathway to poly(propylene thiophenoimine)-co-poly(3,4-ethylene dioxythiophene) dendritic star copolymer. Redrawn from Ref. [149]

the G3 poly(propylene thiophenoimine) (G3PPT) dendrimer was carried out by condensation of PPI with 2-thiophene carboxaldehyde. The thiophene units on the dendrimer backbone were polymerized electrochemically, in the presence of 3-hexylthiopene on a gold electrode coated with G3PPT using cyclic voltammetry (Scheme 6) resulting in the poly(propylene thiophenoimine)-co-poly(3-hexylthiophene) dendritic star copolymer.



Scheme 6 Synthesis of generation 3 poly(propylene thiophenoimine)-co-poly(3-hexylthiophene) dendritic star copolymer. Redrawn from Ref. [228]

7 Conducting Polymer-Based Composites

Conducting polymers and their composites have been extensively utilized in the fabrication of sensors and other technology that necessarily warrant materials that are responsive in nature. However, as previously mentioned, conducting polymers on their own suffer from low processibility and sensitivity as well as fouling [229]. The expansion of the field of CP-based composites, whose robustness and high detection limits, provided a means of overcoming these challenges associated with neat CPs, expanded.

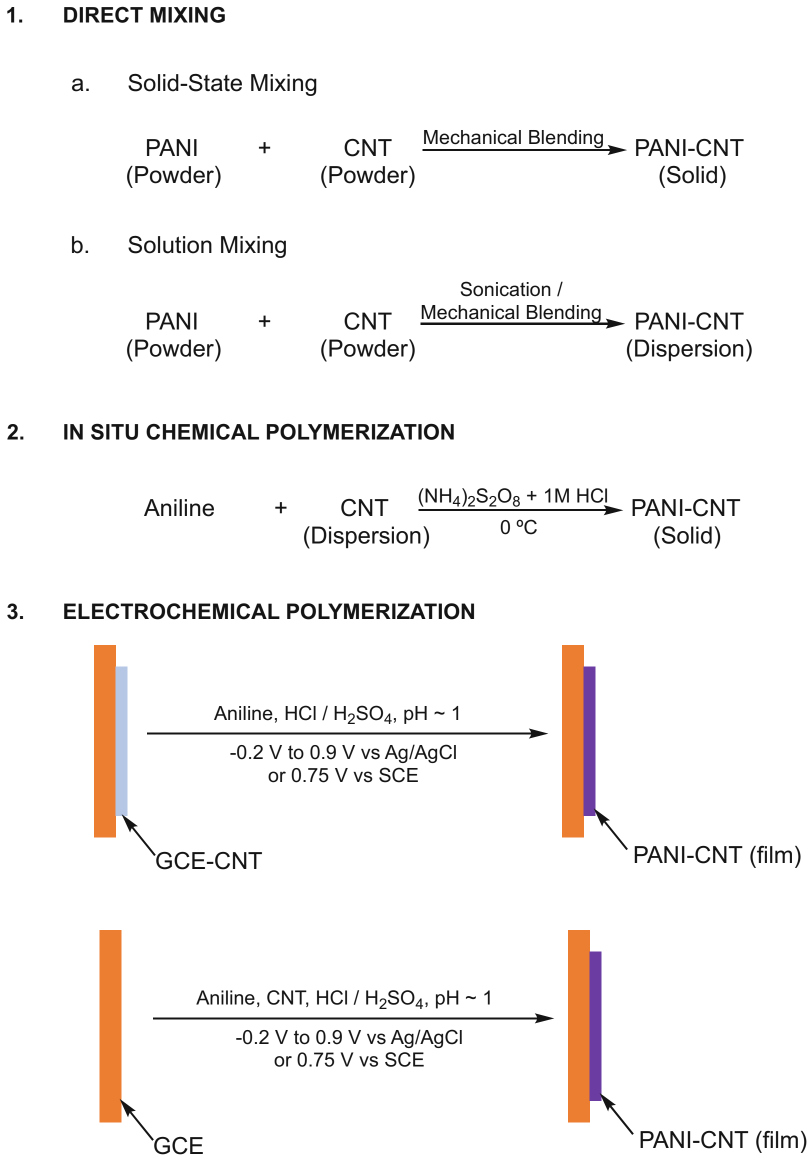
7.1 Polyaniline–Carbon Nanotubes Composites (CNCs)

The discovery of carbon nanotubes (CNTs) in 1991 [230] led to an explosion of interest in nanoscience and nanotechnology research. Although there were initial high expectations of the potential of the CNTs, it soon became apparent that working with the carbon allotrope in its natural form presented some challenges. One response to facilitate the utilization of CNTs and their extraordinary properties in real-world bulk applications was the development of CNT/polymer nanocomposites (NCs). There now exists ongoing research into new combinations of traditional stock as hybrid materials, blends, and NCs and exploitation of their complementary properties [231, 232]. In this context, the development of conducting polymer–CNT composites, as novel futuristic materials, has attracted the curiosity of investigators because the blending of the two constituents offers the possibility to observe and capitalize on synergistic effects.

Some studies have emerged in the literature explaining that certain discrete properties of the components of conjugated polymer–CNT composites are enhanced, relative to the individual units, therefore validating their suitability for selected technological applications [233–235]. Incorporating CNT as fillers into conducting polymers results in NCs that possess much higher electrical conductivities than CPs. The CNT has been shown to behave as a transport bridge between the conducting domains of CPs, thus enhancing the electrical conductivity of the CP and by extension, the nanocomposite [236]. Currently, the construction of polymer composites is the biggest area of application for CNTs owing to the nanocomposite's high durability, high strength, light weight, design, and process flexibility. The successful utilization of carbon nanotubes in the assembly of the composite depends heavily on the homogenous dispersion of CNTs individually and uniformly throughout the matrix, without negatively affecting their structural integrity or reducing their aspect ratio [237]. Additionally, the enhanced mechanical properties of the nanocomposites require good interfacial bonding to achieve significant load transfer across the CNT–matrix interface [238]. Therefore, careful processing of the composites is of utmost importance. In the next section, we will discuss the different processing techniques and properties of a polyaniline/carbon nanotube (PANI–CNT) nanocomposite as a benchmark model.

7.2 Synthesis of the Composites

Various methodologies have been developed for chemically and electrochemically [239] preparing PANI–CNT composites, with two of the most common being direct solid-state mixing [240] and dispersal of CNTs in PANI solutions [241, 242] (Scheme 7a, b). However, a cursory scan of the literature reveals that in situ



Scheme 7 General preparative methods of PANI-CNT composites

polymerization (Scheme 7c) is the most favored synthetic method for PANI-CNT NCs as it enables grafting of polymer molecules onto CNT, leading to better dispersion coefficients and augmented interactions between the CNT and the polymer matrix. Arguably, the in situ polymerization of aniline or substituted aniline in an acidic dispersion of multiwalled or single-walled carbon nanotubes, in the presence of an oxidant at low temperatures, is the simplest method reported so far [239, 243, 244]. Nevertheless, several approaches have been successfully adopted to obtain intimate mixing of nanotubes with polymer matrices in general, and polyaniline in particular, including dry powder mixing, solution blending, melt mixing, in situ polymerization, and surfactant-assisted mixing.

7.2.1 Solution Processing of Composites

Solution casting, which involves mixing of carbon nanotubes and the polymer in a suitable solvent, is the most common technique used in the preparation of CNTs/polymer. One benefit is easy deaggregation and dispersion of carbon nanotubes through agitation of the CNTs with the polymer in a solvent. This method consists of three steps:

(a) Dispersion of carbon nanotubes in either a suitable solvent or polymer solution
(b) Mixing of carbon nanotubes and the polymer
(c) Recovery of the nanocomposite by precipitation or casting of a film

The synthesis of nanocomposite CNT/polymer can be done either through an organic or aqueous medium and the choice of solvent is usually dependent on the solubility of the polymer. Lau et al. [245] revealed the influence of solvents on carbon nanotubes dispersion and the thermal and mechanical properties of the composites. Their results demonstrated that, contrary to the general belief that only small traces of CNTs are needed to strengthen the epoxy composites, the choice of solvent used in the dispersion of CNTs cannot be ignored. They concluded that only the acetone-dispersed nanocomposites displayed improvements in flexural strength over the pure epoxy. Ethanol and dimethylformamide (DMF) actually countered the benefits of CNTs in the resulting nanocomposites. Subsequently, thermogravimetric characterization (TGA) proved the existence of remaining solvent in the resulting nanocomposites bringing to the fore the importance of considering the boiling points of solvents in the interest of improving the purity of products. Further study [246] provided evidence of the solvent influence, using Fourier Transform Infrared (FTIR) spectroscopy, on the molecular structure of the final nanocomposite. The presence of remaining solvent altered the reaction mechanism by restricting the nucleophile–electrophile interaction between the hardener and epoxy, thereafter affecting the degree of cross-linking and degrading the transport and mechanical properties of the cured structures.

In general, dispersion of carbon nanotubes can be done by magnetic stirring, shear mixing, reflux or most commonly, ultrasonication. The latter technique can be executed in two ways – mild sonication in a bath or high-powered sonication. Unfortunately, the use of high-powered ultrasonication for long periods of time can cause shortening of the carbon nanotubes, i.e., reduce the aspect ratio, which is detrimental to the composite [247].

One resolution to this problem has been to disperse higher loadings of nanotubes, through the use of surfactants [246, 248, 249]. As an alternative to the covalent functionalization of CNTs, this approach preserves the integrity of the nanotubes without disrupting the extended π-conjugation [236]. When CNTs are dispersed in aqueous solutions containing surfactants, each individual nanotube (or small bundle) is encased in its own micelle-like envelope with the hydrophobic substituents of the surfactant oriented toward the nanotube and the hydrophilic groups oriented toward the solution. The insertion of aniline in the hydrophobic region within the micelle/CNT hybrid template guides the growth of PANI on the CNT surface. The utilization of surfactants including, anionic sodium dodecylsulfate (SDS) [250], dodecylbenzene sulfonic acid sodium salt [251], dodecylbenzene sulfonic acid (DBSA) [252], cationic cetyltrimethyl ammonium bromide (CTAB) [253], non-ionic poly(ethylene glycol) mono-p-nonyl phenyl ether (Oπ-10) and polyvinyl alcohol [254, 255], during the micelle/CNT hybrid template directed synthesis of CNT/PANI have produced composites with coaxial nanostructures. In such cases, cationic and nonionic surfactants are not incorporated into the CNT/PANI composites, unlike anionic surfactants that generally are integrated into the composite as a dopant. Zhang et al. [256] reported the template-directed synthesis, characterization, and electrical properties of single-walled carbon nanotube (SWNT)-based coaxial nanowires; that is, core (SWNT)−shell (conducting polypyrrole and polyaniline) nanowires in which an aqueous solution containing the cationic surfactant cetyltrimethylammonium bromide (CTAB) or the nonionic surfactant poly(ethylene glycol) mono-p-nonyl phenyl ether (Oπ-10) was employed. The results revealed that the micellar molecules could affect the surface morphologies of the resulting coaxial nanowires (SWCNT/polymer composite) but not the molecular structures of the corresponding conducting polymers.

In solvent blending, a slow evaporation step often leads to CNT aggregation. The research groups of Laplaze [257] and Chauvet [258] suggested spin-casting on substrate or drop-casting on a hot substrate CNT/polymer suspension to expedite the evaporation step and hence alleviate the aggregation problem. The solution processing method in the case of PANI/CNT composites generally consists of mixing PANI (Emeraldine Salt or Emeraldine Base) and CNT solutions or dispersions together in an appropriate solvent. Solvents, such as N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), or N,N-dimethyl propylene urea (DMPU) are good solvents for the emeraldine base (EB) and are preferred solvents for the preparation of EB–CNT composites [259]. Water processing of emeraldine salt–carbon nanotube (ES–CNT) composites utilize CNT functionalized with hydrophilic moieties, such as carboxylic acid groups [260, 261], and/or hydrophilic PANI (sulfonated [262, 263] or boric acid [264–266]), or self-doped PANI. These modifications are to ensure that the CNTs are properly dispersed in the water. Water processing also refers to the ex-situ processing of ES–CNT composites reported in the literature [242, 260, 262, 267]. The external doping of PANI is important in the preparation of stable aqueous colloids of ES, which leads to the nanofiber nanoscale structure of PANI [242, 268].

The classic surfactant-free method for the preparation of CNT/PANI composites consists of mixing aniline with an oxidant such as ammonium peroxydisulfate [269], ferric chloride [270], polyphenylene sulfide [271], etc. in an aqueous acidic dispersion [272] of MWCNT or SWCNT in concentrations ranging from 2 to 70 wt% either at low temperatures (0–4 °C) [173, 273] or at room temperature [274]. Among the available surfactant-free preparation methods that have been proposed to facilitate the dispersion of hydrophobic nonfunctionalized CNTs in aqueous media, addition of ethanol to the aqueous reaction medium [274], or refluxing in aniline [275], are generally accepted as being the most efficient. Another approach is to chemically modify the carbon nanotube surface so as to disrupt the rope structure and add reactive species to the nanotubes thereby improving interfacial bonding in CNT/PANI composites. Carboxylic acid [276–278] and amine-functionalized [278–280] CNTs are also frequently used for the same purpose. The oxidation of amino groups, covalently linked to CNT in aminobenzoyl functionalized CNT, generates radical cations that initiate polymerization on the surface [281].

The morphology of CNT/PANI composites depends on the content of CNT [282]. For instance, the morphology of neat PANI is comparable to that of MWCNT/PANI formed as individual nanofibers when MWCNT loading is at 2.7 wt%. However, when the MWCNT loading increases to 10 wt%, granular nanofibers are obtained. Greater than 20 wt% results in a continuous porous matrix formed from the cross-linked smooth-surface nanofibers and increasing the content of PANI to 80 wt% in the composites leads to full encapsulation of the carbon nanotubes by polyaniline [236]. Furthermore, Li and Kim [283] found that the use of a high mass ratio of aniline/MWCNT (4:1) can lead to the formation of nanofibers, with diameters between 10 nm and 15 nm, through in situ polymerization.

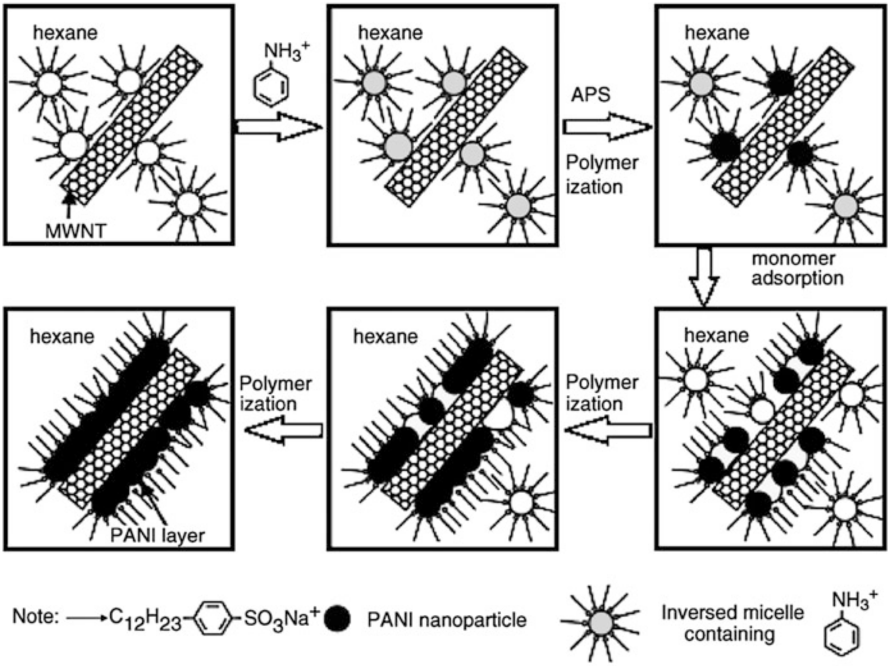
7.2.2 Melt Processing of Composites

Solution processing is an important technique for both carbon nanotubes dispersion and nanocomposite formation; it is less suitable for industrial scale processes. To facilitate large-scale production for commercial applications, melt processing is the better alternative and the most commonly used method for industrial purposes owing to the low cost and simplicity of process. This technique makes use of the fact that thermoplastic polymers soften when heated. Melt mixing generally requires high temperatures to decrease the viscosity of the substrate and high shear forces to disperse the nanofillers, such as CNTs. Thus, composites of different shapes can be fabricated by techniques such as compression molding, injection molding, or extrusion. While melt blending is presented as a very simple method [284–287], the use of high shear forces and high temperatures can cause deterioration of the nanocomposite structure. To overcome these problems during melt processing, optimization of the processing conditions is required, not only for the different nanotube types but also for the entire range of polymer–nanotube combinations [288]. For instance, high shear force is required to achieve CNT dispersion but this can lead to CNT fragmentation. Therefore an optimum shear stress is required to achieve the desired dispersion with the least amount of damage to the CNTs. On the other hand, high temperatures enhance CNT dispersion by lowering the viscosity but excessively high temperatures lead to loss of the intrinsic properties of the polymer. Studies have suggested that these challenges can be curtailed through modifications in melt compounding. Haggenmueller et al. [289] combined solution and melt blending by subjecting a solvent-cast SWCNT/polymer film to several cycles of melt pressing. Jin et al. [290] introduced polymer-coated MWCNTs (rather than pristine MWCNTs) into the polymer melt to maximize compatibility.

7.2.3 In-situ Polymerization Processing of Composites

In addition to the previously mentioned two methods, which combine nanotubes with high molecular weight polymers, in situ polymerization utilizes CNTs and monomers. In situ polymerization has advantages over other composite fabrication methods, for example a stronger interface results owing to the facile intimate interactions between the polymer and nanotubes during and after the growth stage [291]. The main advantage of this method is that it enables grafting of polymer macromolecules onto the walls of CNTs. In addition, this processing technique allows for the preparation of NCs with high nanotube loading and very good miscibility. It is particularly useful when insoluble and/or thermally unstable polymers are desired, especially when processing by solution or melt processing is not possible. A simple in situ chemical polymerization of aniline, in an acidic dispersion of multiwall carbon nanotubes (MWCNTs) or single-wall carbon nanotubes (SWCNTs), in the presence of an oxidant at low temperature, has been reported by Cochet et al. [243, 244]. Saini et al. [292] described the fabrication process for a highly conducting PANI–MWCNT NC via an in situ polymerization. Carbon nanotube-polyaniline hybrid materials were successfully prepared using in situ emulsion polymerization and an in situ inverse microemulsion route (Scheme 8) [251, 293]. In situ polymerization has also been used for the preparation of composites of substituted PANI in the presence of either SWCNTs or MWCNTs. These include poly(*o*-anisidine) [294], poly(*N*-methylaniline) [295], poly(diphenylamine) [296], and poly(aminobenzoic acid) [297–299].

Another practical approach for the preparation of PANI–CNT composites is electrochemical deposition. Early attempts included the direct electrochemical polymerization of aniline on individual CNT whiskers [299] and an aqueous dispersion containing aniline and CNT [300]. In the latter example, the aniline functionalized CNT was sometimes dispersed in the electrolyte [301], while at other times, substituted PANI was grafted to SWCNT by oxidative coupling during electropolymerization [302, 303]. In 2014, PDMA multiwall carbon nanotubes (PDMA-MWCNTs) nanocomposite films were synthesized by in-situ electrochemical polymerization of a well-dispersed solution of DMA and multiwall carbon nanotubes (MWCNTs) [304].



Scheme 8 In situ synthesis of MWCNT/PANI core-shell nanowires using inverse micro-emulsion [279]

7.3 Interactions Between PANI and CNT

Electrical, thermal, and mechanical properties observed in PANI–CNT composites are intermediate between pure PANI and CNT and is dependent on CNT content and the extent of its integration with PANI. Thus, electrochemical properties of PANI–CNT composites are enhanced compared with the two individual components. For instance, electrochemical growth, redox, and capacitive currents of the composites are several-fold higher than the pure PANI [239, 305]. The same behavior is also observed in composites of CNT with substituted PANI derivatives, but the extent of the current increase depends on the nature of the substituent present on the aniline ring [239]. Such a remarkable current enhancement appears to be unique to PANI–CNT composites and has not been observed for any other conjugated polymer–CNT composite. The augmented properties are a direct result of the intimate interactions between PANI and carbon nanotubes.

There exists various possibilities for interactions between PANI and CNT in the composites. One of the first suggestions was the attachment of aniline radicals, generated during electrochemical oxidative polymerization, onto the CNT lattice especially at defect sites [239]. However, it was also postulated that the carboxylic acid sites on the acid-treated CNTs were the most likely sites of interaction with the

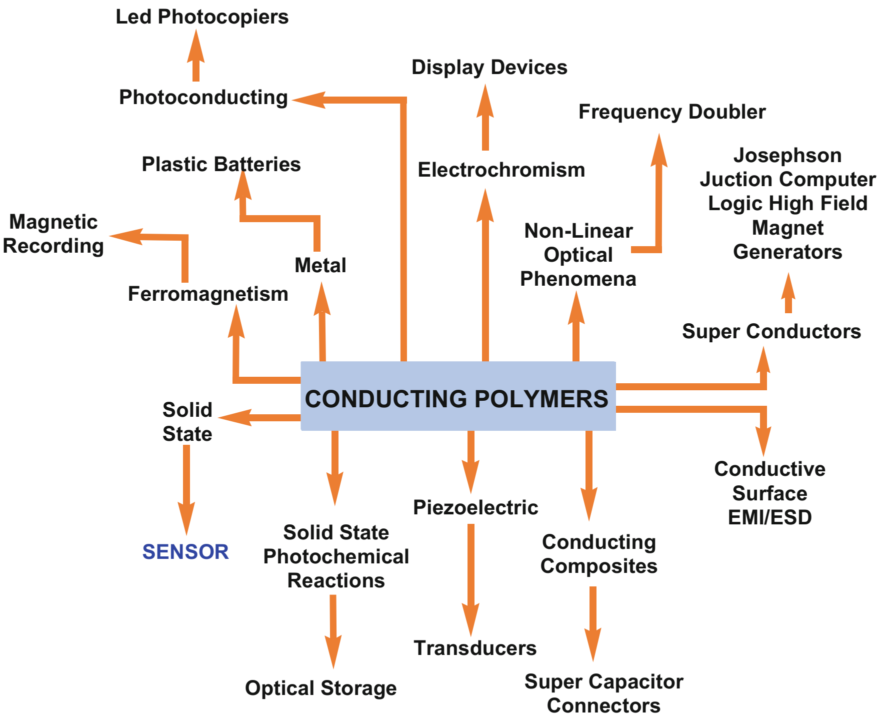


Fig. 20 Applications of conducting polymers

aniline monomer [305]. PANI can interact either with functionalized or with nonfunctionalized CNT.

8 Conclusions

CPs are characterized by a conjugated structure of alternating single and double bonds (extended π-orbital system) through which electrons can move from one end of the polymer to the other. Hence the electrons become delocalized over the whole and are shared by many atoms.

Conducting polymers (CPs) are mainly used in environmental monitoring and clinical diagnostics to achieve fast detection, high sensitivity, small size, and specificity for investigation of a particular analyte through the use of electrochemical sensors and biosensors. Conductivity values for conducting polymers vary from 10^{-10} to 10^{6} $S.cm^{-1}$, covering the range associated with semiconductors and conductive filler composites, at the lower end, to metals at the higher end. Polymers with electrical conductivity and semiconductivity are of interest as lightweight replacements for inorganic metals and semiconductors. CPs have electrical and optical properties similar to those of metals and inorganic semiconductors but also exhibit the attractive properties associated with conventional polymers such as ease of synthesis and processing.

In addition, conducting polymers have the potential to replace metal coatings and may be applied more economically utilizing nonvacuum processes from solution or from the melt. There are also clear signs that the effectiveness of conducting polymers in transferring electrical charges can be exploited for the preparation of nanocomposites (NCs) in the construction of sensors and in molecular devices. Likewise, organic semiconducting polymers may be synthetically tailored to optimize desirable properties such as melting point, melt viscosity, solubility, electrical and thermal conductivity. Conducting polymer composites (CPCs), resulting from the blending of an insulating polymer matrix with electrical conductive fillers (carbon black, carbon fibres, metal particles), show many interesting features including the variation in their electrical resistivity with thermal solicitations.

The use of pyrrole in the electrochemical synthesis of conducting polymers has proven important in allowing the development of new polymeric materials with worthwhile electrical properties. Recent studies have shown that conducting polymers – namely, PPy, PANI, and PEDOT – all have good biocompatibility and are promising alternatives for use in the development of new biodegradable conduits for restoration function of injured peripheral nerves or in the regeneration of a nerve gap by using in situ electrical stimulation.

Synthesis of conducting star, graft, or block copolymers of the conducting polymer permits chemical linkage between the insulating matrix (end groups) and the conjugated polymer. The new materials formed in this manner possess enhanced processability and chemical stability. Electrochemical copolymerization can produce a variety of conducting materials with different optical, electrical, morphological, and electrochromic properties.

Overall, these unique polymers (CPs) and their derivatives showcase a wide range of specific industrial applications (Fig. 20).

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