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Synthesis and Applications of Conducting Polymers – An Overview

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ABSTRACT

One of the most important materials in our modern world is polymer. Each polymer type has found widespread application in a variety of disciplines, primarily optical and electronic applications such as batteries, displays, plastic wires, optical signal processing, data storage, solar energy conversion, and so on. Conducting polymers (CPs) are highly conjugated molecules with single and double bonds alternating. In the manufacture of conductive polymers, chemical and electrochemical polymerizations are commonly used processes. Other methods for polymer synthesis include photochemical polymerization, metathesis polymerization, plasma polymerization, pyrolysis, solid state polymerization, and inclusion polymerization. This overview demonstrates the synthesis of polymers using two important techniques: chemical and electrochemical polymerization.

Keywords: **Polymer, Coducting polymer, Chemical synthesis, Electrochemical synthesis, Applications**

1. Introduction

Despite the fact that conducting polymers have been known for at least 25 years (reports on their synthesis date back to the last century), it was only in the early 1990s that a tidal wave of renewed and amplified interest in these materials catalysed many new developments, both on a fundamental and manufacturing level. The discovery of light-emitting polymers in 1990 at Cambridge University's Cavendish Laboratory was a key, if not decisive, turning point in the fortunes of plastronics, i.e., the use of polymeric materials as substitutes for metal and metal derivatives in electronic systems.

In 1930, the first conductively packed conducting polymers were developed to prevent corona discharge. Because of their ease of production, strong environmental stability, and wide variety of electrical properties, the potential uses for conductively loaded polymers have subsequently proliferated. Because conductively loaded polymers are multi-phase systems in nature, they have an inherent lack of homogeneity and reproducibility. Controlling the quality of dispersion is therefore vital in order to generate homogeneous conducting polymer composites.

The 1975 report on the electrical conductivity of ionic polymers drew a lot of attention. Since then, a variety of ionically conducting polymers or polymer electrolytes have been developed for a variety of uses, including rechargeable batteries and smart windows. Polymer electrolytes are also quite easy to work with. The dissociation of opposite ionic charges and subsequent ion migration across coordination sites, which are generated by the slow motion of polymer chain segments, are required for ionic conduction. As a result, polymer electrolytes have low conductivity and a high susceptibility to dampness. When they dry, they frequently become electrically non-conducting [1].

2. Conducting polymers

Previously, polymers were thought to be electrical insulators. Four decades ago, no one would have guessed polymers could conduct as well as metals. But, thanks to a simple modification of ordinary organic conjugated polymers known as electrically conducting polymers or synthetic metals, such feats can now be accomplished. These materials combine the electrical properties of metals with the advantages of polymers, such as lighter weight, greater workability, resistance to corrosion and chemical attack, and lower cost, and have infiltrated our daily lives with a wide range of products ranging from everyday consumer goods to high-tech devices.It's no surprise that these polymers have been dubbed "materials of the twenty-first century."

Shirakawa et al. demonstrated in 1978 that polyacetylene (PA), an intrinsically insulating organic conjugated polymer, exhibits a dramatic increase in electrical conductivity when treated with oxidising (electron-accepting) or reducing (electron-donating) agents. This was the first major breakthrough in the field of electrically conducting polymers. P-doping and n-doping are the terms for the oxidation and reduction reactions that cause high conductivity in PA.

Following the discovery of highly conducting PA, there was a surge in research activity focused on developing novel conducting polymeric systems. Among the numerous unique conducting systems currently known are polypyrrole, poly(phenylacetylene), poly(p-phenylenesulphide), poly(p-phenylene), polythiophene, polyfuran, polyaniline, polycarboxylate, and its derivatives.

One of the most highly valued properties of synthetic polymers in the realm of polymer technology is their capacity to behave as effective electrical insulators. According to research, most conducting polymers undergo a transition from insulator to electric conductor when doped with minor oxidising or reducing chemicals.As a result of the synthesis of conjugated polymers, it is now possible to combine the electrical properties of a semiconductor and a metal in a single material with the ease and low cost of preparation and manufacture. Other key advantages of conducting polymers are flexibility, density, and chemical inertness; non-linear optical activity; and outstanding mechanical qualities such as tensile strength and tolerance to hostile conditions.

3. Basic concepts of conducting polymers

Conducting polymers (CPs) are highly conjugated molecules with single and double bonds alternating. The expanded p-orbital system allows electrons to travel from one end of the polymer to the other in these molecules. As a result, CPs are classified as either semiconductors or conductors, depending on how electron bands and shells are produced within a compound. Because of the electronics in CPs, the Band theory is used to describe the conduction mechanisms. The notion is based on the creation of energy bands in polymer materials as a result of discrete orbital energy levels in single atom systems. It is critical to review band theory in this regard.

There is no energy range in metals that is considered unavailable to electrons, which basically means that the forbidden gap or band gap in metals is E = 0 eV. Because the conduction and valence bands overlap, metals always have a partially filled free-electron band. As a result, the electron can easily enter the conduction band. The energy gap between VB and CB is too large for the electron to make the jump to detach from its atom and be promoted to the valance band in insulators with a band gap greater than 3 eV. As a result, at room temperature, they are poor electrical conductors.

There are two events that can lead to a substance becoming a conductor. When the valence band is not entirely filled, an electron might boost its energy to a higher level within the valence band and therefore depart from its atom. This is known as conduction within the same band, and it only requires a minimal amount of energy, so many electrons can do it. When the band gap is tiny, such as E = 0.1–3 eV, electrons can increase their energy and depart from their atoms by leaping to a higher energy level in the CB.

Exciting electrons into the conduction band can be done in a variety of ways, including thermal or photochemical excitation. These electrons contribute to electrical conductivity once they reach the conduction band. Furthermore, the holes formed in the valence band by electrons leaping to the conduction band contribute to electrical conductivity, i.e., the transfer of charge (electrons or holes) across the backbone of a polymer induces conduction. As a result, the number of electrons in the conduction band and the number of holes in the valence band dictate the electrical properties of intrinsic semiconductors. However, a technique known as "doping" is also employed to create charge carriers (electrons and holes).

As previously explained, the amount of the energy band gap is determined by conjugation and the extent of delocalization in CPs. The wider the energy band gap, the more conjugated the CP is, hence most CPs are unstable in their undoped state. A semiconductor can be classified as intrinsic or extrinsic depending on whether it is pure or doped.

4. Synthesis of conducting polymers

Although there is no single method for synthesising polymers that can be converted into conductive polymers, the use of prolonged p-electron conjugation is critical. In the manufacture of conductive polymers, chemical and electrochemical polymerizations are commonly used processes. Photochemical polymerization, metathesis polymerization, plasma polymerization, pyrolysis, solid state polymerization, and inclusion polymerization are some of the other approaches.

4. 1. Chemical synthesis

Condensation and addition polymerization are the two most common chemical polymerization processes. During condensation polymerization, atoms or groups are often broken away from monomer molecules and liberated in the form of low-molecular-weight compounds. Condensation polymerization necessitates high monomer purity to avoid cross-linking, branching, and premature termination. One example of condensation polymerization is the electrochemical polymerization of polypyrrole, which is generated by oxidising pyrrole and thereby removing two hydrogen atoms from the 2- and 5-positions.

In addition polymerization, all of the atoms of monomer molecules remain in the polymer and we can introduce the traditional nomenclature of initiation, propagation and termination steps:

Initiation: A reactive radical intermediate (•) is formed by the reaction of an initiator (R, a chemical agent such as ferric chloride) with the monomer (M):

$R + M \rightarrow RM^{\bullet}$

Propagation:

$RM^{\bullet} + M \rightarrow RMM^{\bullet}$

$RMM^{\bullet} + M \rightarrow R(M)_2M^{\bullet}$

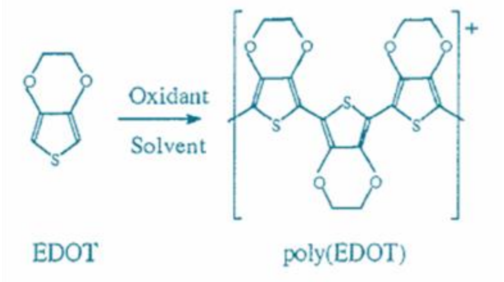
$RM^{\bullet} + nM \rightarrow R(M)_nM^{\bullet}$

Termination: Any process that ends the reaction. It may be a contaminant that reacts with the reactive radical, two radicals may react for one another, etc.

Due to the reduction of bond order caused by addition polymerization, it is currently only employed for polyacetylene and its derivatives. With conjugated polymers, condensation polymerization is more typically used. Takeo Ito et al. developed a direct technique of polymerizing and producing acetylene monomer at the same time to make uniform thin films of polyacetylene. They looked at the catalyst system, catalyst concentration, and polymerization temperature.

Because conjugated polymers are often insoluble, soluble substituents such as big aliphatic groups or ionic ions can be used to improve solubility. However, while the polymer's solubility is improved, the intermolecular conductivity falls at the same time. Another option is to make a precursor polymer from which conjugated polymers can be produced by an elimination reaction. Because conjugated polymers are so difficult to work with and purify, it's better to start with a simpler precursor and work your way up to the final polymer from the pure precursor polymer.

Furthermore, due to their limited solubility, the required conjugated polymers may precipitate out of solution quickly, preventing the formation of lengthy chains. A longer chain length and hence greater conductivity can be achieved by first synthesising a precursor. Finally, altering the precursor before reacting it to generate conjugated polymers makes it much easier to get the desired shape. Conjugated polymers are difficult to obtain in a useful physical state due to their insolubility, and morphological change can be problematic. Instead, a thin film of the precursor polymer can be produced and transformed to the appropriate conjugated polymers using a straightforward method. In chemical polymerization, stoichiometric amount of oxidizing reagent (eg $FeCl_3$) is used to produce polymer that is in its doped or conducting form.



Poly (3,4-ethylenedioxythiophene) (PEDOT) with a conductivity of 20 S/cm was synthesised using $FeCl_3$, $Ce(SO_4)_3$, and $(NH_4)_2Ce(NO_3)_6$ as oxidants. PEDOT was synthesised in an emulsion polymerization using an anionic surfactant, sodium alkyl naphthalene sulfonate (NaANS), as an emulsifier, and $Fe_2(SO_4)_3$ as an oxidant. A solventless oxidative chemical vapour deposition (oCVD) approach was also used to deposit PEDOT. The PEDOT fibre was made by polymerizing 2,5-dihalo-3,4-ethylenedioxythiophene in the presence of BF_3 without using a template with a conductivity of 150–250 S/cm. PEDOT was produced using the vacuum vapour phase polymerisation (V-VPP) process on glycol/oxidant (Fe (Tos) 3) coated substrates, with a maximum conductivity of 1487 S/cm [3].

PEDOT/PSS composites were created from aqueous acetonitrile solutions of EDOT and NaPSS, and conductivities as high as 10 S/cm were achieved after oxidation with Fe(III) salts.The oxidative CVD method was used to deposit heavily doped poly (3,4-ethylenedioxythiophene) thin films with high carrier mobility.

Chemical oxidation with $FeCl_3$ in neutral media produced a copolymer of 3,4-ethylenedioxythiophene (EDOT) and diclofenac (DCF).

Chemically oxidative polymers, including thiophene and carbazole moiety, were produced in the presence of $FeCl_3$, and conductivity was determined to be around 10 S/cm. Using a tri-thiopheneacetic-acid (TAA) monomer, anhydrous iron–chloride ($FeCl_3$), Bu_4NBF_4, nitrobenzene (NB), and dimethylformamide, conducting polymer-based magnetic composites poly (3-thiopheneacetic-acid)–Fe_3O_4 hybrids have been created by the co-precipitation method (DMF). Chemical oxidative coupling of the basic monomer 3-methyl-thiophene with $TiCl_4$ as an oxidant in chloroform medium yields Poly (3-methyl-thiophene) (P3MTh).

PBDTTPA-CHO, a copolymer of 4-(Bis(4-bromophenyl) amino) benzaldehyde (TPA-CHO) and 4,8-bis-(2-ethylhexyloxy)-oxybenzo-[1,2-b: 3,4-b'] dithiophene (BDT), was successfully synthesised using Stille coupling polymerization, and the pendant aldehyde groupA vapour phase polymerization (VPP) method was used to make poly (3,4-ethylenedioxythiophene)–tosylate–polyethylene glycol–polyethylene glycol–polyethylene glycol–polyethylene glycol–polyethylene glycol–polyethylene glycol–polyethylene glycol–polyethylene glycol–polyethylene glycol–polyethylene glycol–polyethylene glycol–polyethylene The electrical conductivity of this film was 1550 S/cm.

4.2. Electrochemical synthesis

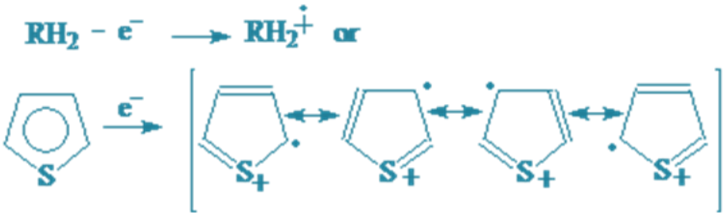
Conducting polymers can be generated via electrochemical polymerization from a monomer solution including an electrolyte like tetrabutylammonium tetrafluoroborate (TBATFB) (TBATFB). The electrochemical polymerization takes place in a three-electrode setup in a single compartment cell. Platinum or gold is commonly used as the working electrode. The reference electrode (pseudo Ag electrode) is made of silver/silver chloride (Ag/AgCl) or plain silver wire. A Pt wire or sheet is frequently used as an auxiliary. Radical cation production is used in electrochemical polymerization. The electropolymerization process is broken down into the following steps:

- Oxidation of monomer
- Dimmer formation
- Oxidation of dimmer to its radical cation
- Reaction of dimmer radical cation with another radical cation
- Oxidation of the film to the conducting polymer

Reductive or cathodic electropolymerisation is nearly never utilised, while oxidative or anodic electropolymerisation is only performed on rare occasions. The popularity of electrodeposition can be attributed to two factors: simplicity and repeatability. The experimental setup is simple and inexpensive, and the thickness of the films can be regulated using commercially available materials.

A current is transferred between two electrodes separated by a salt and monomer solution in a very simple way. A polymer layer forms on the anode surface continuously in proportion to the amount of current passing through. Authentication can be done with the film and anode. In cyclic voltammetry, changing the number of sweeps or top potential, or the time or current in a galvanostatic experiment, can readily alter film growth and doping level. Platinum, gold, and glassy carbon are the most popular substrates for film deposition. Sometimes, indium tin oxide (ITO) glass and other semiconductors are utilised, although the films made on these substrates do not have the same flat surface as those made on platinum or gold [4].

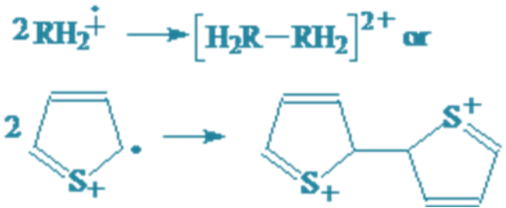
According to the reaction, the electrooxidation of thiophene to create a thienyl radical cation is the initial step in the commonly acknowledged process for the electrostart polymerization of thiophene.



The newly formed cation radical may then lose its proton to any proton acceptors in solution, such as the solvent itself, the monomer or its cation radical, or residual water:

$$RH_2^{\overset{\bullet}{+}} + B \longrightarrow RH^{\bullet} + BH^{+}$$

This is why, in acid buffered or neutral solutions, an inferior polymer of polypyrrole forms, while the reaction with thiophene does not occur in the presence of proton acceptors. Without interfering proton acceptors, the radical cation quickly joins a second radical.



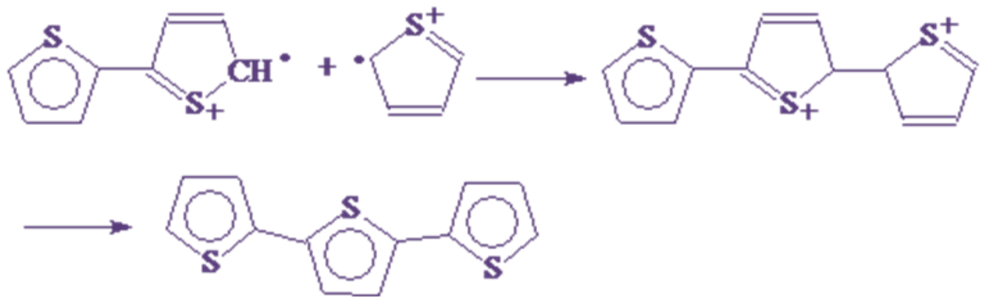
They link at the alpha locations because this is where the electron (spin) density is highest (as evidenced by the fact that replacement at the 2 and 5 positions results in no polymerization, at least for pyrroles). Deprotonation aromatizes the two cations once they have joined.

$$[H_2R-RH_2]^{2+} - 2H^+ \longrightarrow HR-RH \quad \text{or}$$

Furthermore, because the dimmer has a lower oxidation potential than the monomer, it is preferentially oxidised and becomes the preferred target for further radicalization, resulting in an ever-lengthening chain.

$$HR-RH - e^- \longrightarrow [HR-RH]^{\overset{\bullet}{+}}$$

$$[HR-RH]^{\overset{\bullet}{+}} + RH_2^{\overset{\bullet}{+}} \longrightarrow HR-RH-RH_2^{2+} \longrightarrow HR-R-RH + 2H^+$$



The terminal positions on the radical polymer chain, like the monomer, have the highest electron density. However, as the chain grows longer, the region where the electron density is spread expands, resulting in branching and discontinuous conjugation zones. When electrochemically polymerized, several heterocycle monomers are demonstrated to exhibit similar reactions.

The electrochemical polymerization method stands out because it uses very little monomer, has a short polymerization time, and can produce a regulated thickness. Potentiostatic or galvanostatic circumstances, as well as cyclic voltammetry, can be used to obtain a polymer. Unlike chemically synthesised layers, electrochemically synthesised layers are free of residual oxidants. Another benefit of electrochemical synthesis is the ability to manage the polymerization process (for example, the rate of polymerization or the thickness of the resulting polymer film) by adjusting the current, potential, scanning rate potential, or the number of voltammetric cycles. Electronically conductive polymers are produced by electrochemical oxidation of various resonance stabilised aromatic compounds such as pyrrole, thiophene, aniline, furan, carbazole, and others. It's thought that the polymerization involves either radical-cation/radical cation coupling or radical cation interaction with a neutral monomer.

Various researchers have used an electrochemical approach to make poly (3, 4-ethylenedioxythiophene) PEDOT and its copolymers. Under potentiostatic circumstances, PEDOT films were electropolymerized from an aqueous micellar solution of 3,4-ethylenedioxythiophene and 1 M camphorsulfonic acid in deionized water. The electro oxidation of EDOT solution in p-toluene sulphonic acid, phosphate buffer, borax buffer, and H_2SO_4, KCl, NaOH, and buffer (pH 4.0, 9.2) were employed as aqueous supporting electrolytes to create PEDOT films on glassy carbon electrode surfaces and ITO plates. The cyclic voltammetric method was used to make copolymers from 3,4-ethylenedioxythiophene (EDOT) and Diclofenac (DCF) in the presence of two different surfactants, sodium dodecylsulfate (SDS) (anionic surfactant) and cetyltrimethyl ammonium bromide (CTAB) (cationic surfactant) on a glassy carbon electrode surface.

The electrolyte was tetraethylammonium perchlorate (Et_4NClO_4), $LiClO_4$, or tetrabutylammonium perchlorate (TBAP) in propylene carbonate (PC) or acetonitrile (ACN) and EDOT was electropolymerized on an ITO electrode. PEDOT latex nanoparticles were made by emulsion polymerization in the presence of the surfactant dodecylbenzene sulfonic acid utilising the bi-oxidant system Fe $(OTs)_3$ and H_2O_2 (DBSA). Using PC in ACN, thin films of PEDOT-CNTs were electropolymerized onto ITO glass.

5. Applications of conducting polymers

Polymeric materials are used in a wide range of applications. In battery applications, such as high-capacity lithium batteries, ionic conducting polymers are used. Emulsion polymerization was used in the paper industry to make binders for paints and adhesives, as well as coatings. Blends of different polymers typically create two-phase systems, with the properties of the blends being determined by the polymers' mutual compatibility and interactions across phase boundaries.

The surface characteristics of polymers utilised in medical applications are critical. The free volume of a polymer, which corresponds to the unoccupied regions accessible to segmental motions, is crucial for understanding several aspects, including time and frequency-dependent electrical and mechanical properties, as well as transport properties of low molecular species.

Conducting polymers have uses in microelectronics at all levels. In the microelectronics sector, conjugated polymers in non-doped and doped conducting states have a variety of applications. Electron beam lithography, metallization (electrolytic and electroless) of plated through-holes for printed circuit board technology, superior electrostatic discharge protection for metals, and electromagnetic interference shielding are all applications for conducting polymers.

Polymers that conduct electricity, such as polyacetylene and polypyrrole, have been the focus of numerous studies during the last two decades. These materials offer features that make them useful for a variety of applications, including sensors, biosensors, rechargeable batteries, molecular electronic devices, electrochromic display devices, corrosion inhibitors, and electromagnetic shielding materials, among others. Polyaniline and its derivatives have been the focus of study among electrically conducting polymers due to their environmental stability, simplicity of synthesis, and fascinating electrochemical, optical, and electrical properties. Protonic acids or electrochemical oxidation can dope polyaniline into a highly conductive state. When doped with protonic acids, they have moderate conductivity and excellent stability in ambient settings.

According to research, conducting polymers can have conductivities ranging from semiconducting (10-5 S/cm) to metallic (104 S/cm). Polymeric conductors provide a severe challenge to established inorganic semiconductor technology with their spectrum of electrical conductivity and low density combined with low cost. Conducting polymers' electronic and chemical behavior lends them to a variety of applications, including electrostatic materials, molecular electronics, energy storage devices, conducting adhesives, optical displays, electromagnetic shielding, chemical, biochemical, and thermal sensors, photovoltaic cells, rechargeable batteries and solid electrolytes, capacitors, drug release systems, and antistatic clothing. O.A. Fraghaly et al. examined recent electroanalytical techniques utilized in industrial, pharmaceutical, and environmental applications, including cyclic, linear sweep, square wave, and stripping voltametric techniques [5].

Conductive polymers have been employed for conductive coatings, corrosion protection, and materials for sensors and separation membranes throughout the last two decades. Conducting polymers have recently been shown to be useful as an active layer in solar cells and organic light-emitting diodes. Initially, the polymer was employed for antistatic equipment in photographic materials. When compared to conventional batteries, batteries made from lithium ion polymer electrolyte have the advantages of being light and having a high energy density. One type of conjugated polymer is electroluminescence polymers, and the creation of polymer light-emitting diode devices has a lot of potential.

6. Conclusion

Polymers were once thought of as electrical insulators. Nobody would have believed it four decades ago. Electrically conducting polymers, which are simple organic conjugated polymers, have now been modified to perform such feats. Conducting polymers' electronic and chemical behavior lends them to a variety of applications, including electrostatic materials, molecular electronics, energy storage devices, conducting adhesives, optical displays, electromagnetic shielding, chemical, biochemical, and thermal sensors, photovoltaic cells, rechargeable batteries and solid electrolytes, capacitors, drug release systems, antistatic clothing, and opportunistic computing.

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