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Review Article

Polypyrrole Conducting Electroactive Polymers: Synthesis and Stability Studies

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Abstract: This paper deals with a fundamental review of preparation methods, characterizations, thermal and environmental stabilities and practical applications of polypyrrole (PPy) conducting electroactive polymers. In this article some of the most important factors affecting the electrical, electrochemical, thermal and environmental stabilities of polypyrrole conducting polymers have also been reviewed.

Keywords: Polypyrrole, conductivity, electroactivity, environmental and thermal stability

Introduction

The demand for electrically conducting polymers as used in the electronics industry has in the past been met by using high loadings of conductive powders such as silver, gold and graphite (sometime as high as 80% by weight) with the polymer matrix¹. There are, however, a number of disadvantages to this approach, including high cost and deterioration in other properties of the polymer. Intrinsically conducting organic polymers such as polyaniline, polypyrrole and polythiophene have been studied intensively during the last

decade due to their high electrical conductivity, good environmental stability. Among the conducting polymers known to date, ones based upon PPy have attracted special interest because of their high conductivity, their ease and high flexibility in preparation, their stability and good mechanical properties. Potential technological applications such as in electronic and electrochromic devices²⁻⁴, counterelectrode in electrolytic capacitors⁵ sensors⁶⁻⁸, chromatographic stationary phases⁹, light-weight batteries¹⁰, membrane separation¹¹ consequently, have attracted a great deal of attentions in recent years and this is currently one of the most active areas of research in polymer science and engineering at present.

Electroactive, conductive polymer films can be generated on electrode surfaces by the oxidation of aromatic compounds such as benzene, and heterocycles. The oxidation potential is lower for pyrrole (0.8V) than other heterocyclic monomers. This is also lower than the oxidation potential of water. Consequently, PPy is readily synthesised from a range of aqueous and non-aqueous solvents¹³. In fact, PPy is one of the few electronically conducting polymers that can be prepared in aqueous solutions¹⁴. Polyaniline should be synthesised from acidic aqueous media, while polythiophene must be grown from organic solvents in which the monomer is soluble.

Results and Discussion

Polypyrrole (PPy) and a wide range of its derivatives may be prepared by simple chemical or electrochemical methods¹³⁻¹⁹. Chemical polymerisation is a simple and fast process with no need for special instruments. Bulk quantities of polypyrrole (PPy) can be obtained as fine powders using oxidative polymerisation of the monomer by chemical oxidants in aqueous or non-aqueous solvents^{15-17, 20} or by chemical vapour deposition¹⁸. However, the use of chemical polymerisation limits the range of conducting polymers that can be produced since only a limited number of counterions can be incorporated. The chemical polymerisation of pyrrole appears to be a general and useful tool for the preparation of conductive composites^{21,22} and dispersed particles in aqueous media^{23,24}.

Iron (III) chloride has been found to be the best chemical oxidant and water is the best solvent for chemical polymerisation with respect to desirable conductivity characteristics^{15,21}. The overall stoichiometry resulting from chemical polymerisation of PPy with ferric chloride oxidant is shown in Figure 1.

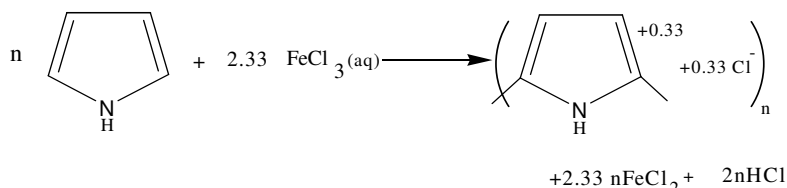


Figure 1. Chemical polymerization of polypyrrole

The optimum initial mole ratio of Fe (III)/Pyrrole for polymerisation by aqueous iron (III) chloride solution at 19°C has been found^{20,25} to be 2.25 or 2.33. During chemical polymerisation of pyrrole, electroneutrality of the polymer matrix is maintained by incorporation of anions from the reaction solution. These counterions are usually the anion of the chemical oxidant or reduced product of oxidant. For example, when FeCl₃ or Cl₂ are used as oxidants, Cl⁻ ion is incorporated as counterion or when I₂ is used as oxidant, I₃⁻ ions

are incorporated into the polymer matrix. It has been found that factors such as solvent, reaction temperature, time, nature and concentration of the oxidising agent, affect the oxidation potential of the solution. These in turns influence the final conductivity of the chemically synthesised polypyrrole^{15,16}. Elemental analysis data has shown²⁵ that the composition of polypyrrole prepared chemically is almost identical with that electrochemically prepared.

Electrochemical preparation of PPy

The electrochemical approach for making electroactive/conductive films is very versatile and provides a facile way to vary the film properties by simply varying the electrolysis conditions (e.g. electrode potential, current density, solvent, and electrolyte) in a controlled way. Or the variations in the properties of polymer can be made in the selection of the monomer or the electrolyte. Furthermore, the electrosynthesis allows an easy control of the thickness of the polymers. Preparation of conducting polymers electrochemically is a complex process and the yield and quality of the resulting polymer films is affected by various factors. The nature and concentration of monomer/electrolyte, cell conditions, the solvent, electrode, applied potential and temperature, pH all have a strong effect on the electro-oxidation reaction and the quality of the film^{26, 34-39}. It is therefore not easy to optimize all parameters in one experiment.

Among these different parameters, the counterion plays the most important role. In the electrochemical method the polymer is synthesised directly in its oxidised and doped state. Then can be removed in either its conducting or insulating form. The monomer is first dissolved in a salt solution (where the electrolyte is highly dissociated and which are slightly acidic) with low nucleophilicity and solution resistance. Application of a suitable potential ($E \geq 0.65$ V vs. Ag/AgCl) initiates the polymerisation reaction. The oxidation potential used can be easily controlled and therefore the quality of the polymer can be optimised.

Also because of the good solubility of pyrrole monomer in a wide range of solvents, pyrrole is easily electropolymerised in both aqueous²⁸ and non-aqueous solvents^{27, 29}. The polymerisation reaction is very complicated and the mechanism of electropolymerisation is still not fully understood. The generally accepted mechanism^{13,26-34} is that in the first step the neutral monomer is oxidised to a radical cation followed by aromatisation and oxidation of the dimer. As the dimer, on account of its greater conjugation, is more easily oxidised than the monomer under the given experimental conditions, it is immediately reoxidised to the cation. Since the polymerisation reaction proceeds only when the potential is sufficiently high to oxidise the monomer, the coupling reaction must involve the coupling of two radical cations.

Although most of their pyrrole units are linked at the α - α (or 2,5) positions, a significant number of the units are coupled through the α - β and β - β cross linkages³², the less desirable 3,4 or 2,3 coupling contributes to the formation of soluble oligomers and reduces the conjugation length and lowers the conductivity³³ (Figure 2).

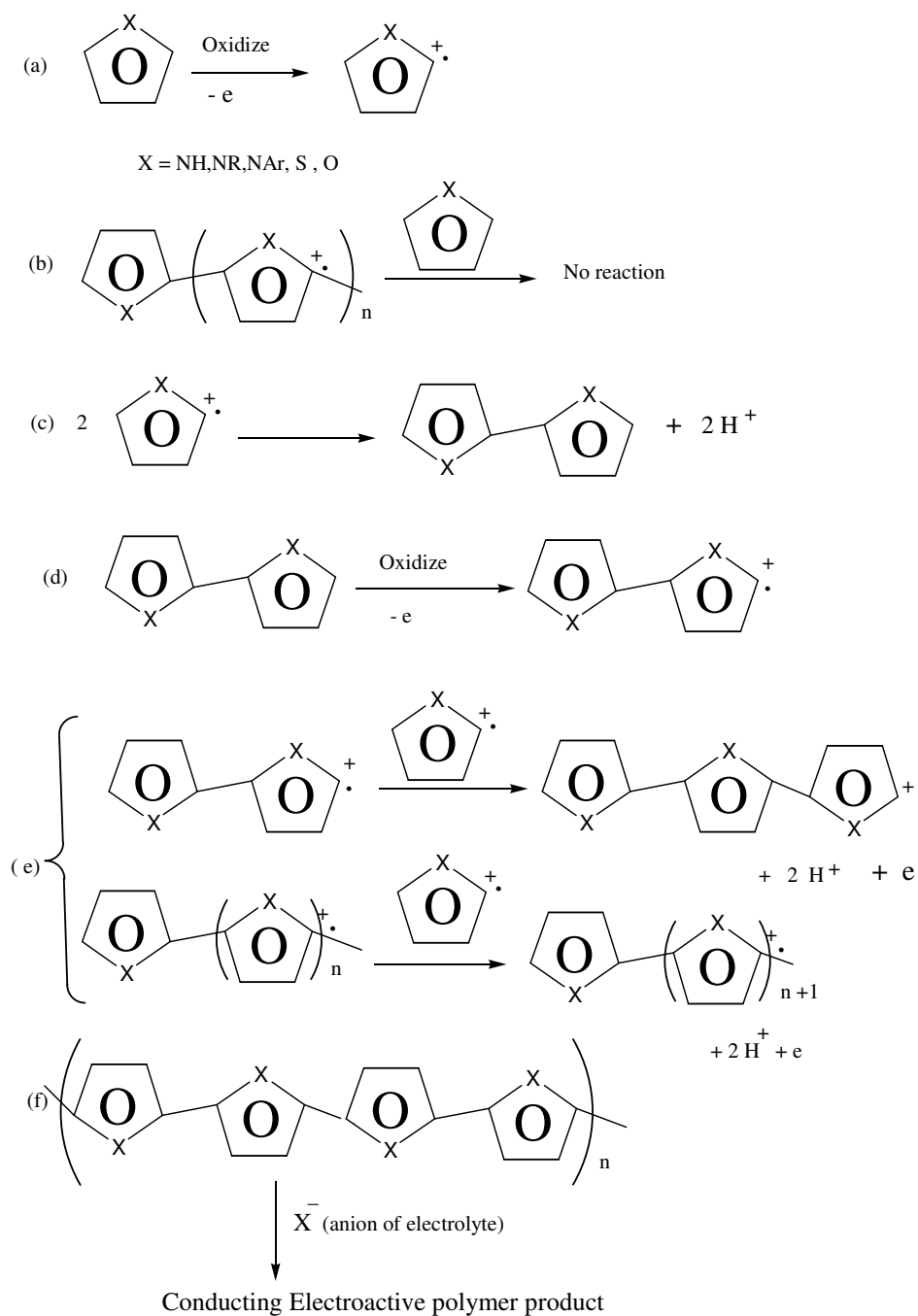


Figure 2. The accepted mechanism for electropolymerisation mechanism of polypyrrole or other aromatic heterocyclic monomers

And the overall electropolymerisation of polypyrrole can be shown as in Figure 3.

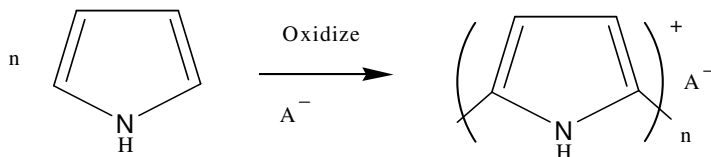


Figure 3. Electrochemical polymerisation of polypyrrole

Where A⁻ is the counterion incorporated during polymerisation. The resulting polymer is produced in the oxidised state with incorporation of counterions³¹. The value of n has been determined to be between 2.2 and 2.4. The level of oxidation of ppy is 0.25-0.32 per pyrrole unit, depending on the type and the charge of the incorporated anion⁴⁰, corresponding to one anion for every 3-4 pyrrole units in order to achieve electroneutrality, and this makes up 30-40% of the final weight of the polymer. The radical cations formed during the electropolymerisation process would quickly react with strong nucleophiles thereby preventing the growth of polymer³⁴. This places some limitations on the choice of solvent and electrolyte. For this reason, many of the reported studies have used aprotic solvents, which are poor nucleophiles, although a wide variety of other aprotic solvents have also been used³³.

Solvents like dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), HMPT, and pyridine prevent anodic electropolymerisation of pyrrole monomer unless the pH of solution is lowered³⁴. In considering the effect of solvent, it has been found that traces of water in organic solvents (e.g. CH₃CN) have a substantial influence on the polymerisation process and the structure of the films prepared^{27,35}. The mechanical properties of PPy films are also improved when the electropolymerisation is carried out in the presence of slight amount of water (e.g. 1%).

Factors Affecting Properties of Ppy

(i) Effect of substrate

PPy films can be electropolymerised on a wide range of metal electrodes. Glassy carbon, platinum (Pt) and gold (Au) are mostly used. However, Indium-tin oxide (ITO) coated glass, Titanium (Ti), Aluminium (Al), mild steel, and brass, mercury, tin-oxide and silver have also been tried^{36,37}. In comparison with Pt electrode the oxidation potential of pyrrole is increased and current density reduced when Ti, Fe, or Al are used. This is a consequence of metal-oxide film formation which impedes electron transfer during electropolymerisation³⁷. Metals such as silver or aluminum, which oxidise more readily than the pyrrole monomer, would obviously not be a good choice. The polymer may be deposited as a continuous film on the surface of the electrode in a solvent in which the polymer is insoluble. The properties of the films produced and also the detailed mechanism of their formation are a function of the conditions used for the synthesis, e.g. potential, charge, pH, anion⁴¹⁻⁴³.

(ii) Effect of dopant

The anion incorporated into the polymer (counterion) during synthesis has the greatest influence on the general properties of the polymer and the thermal stability³⁵. The effect of

the counterion or anion(s) of the electrolyte used for electropolymerisation on the properties of the polymer has been widely discussed in the literature^{35, 45-47}. The as-formed polymers are molecular composites containing a cationic polymer backbone, with accompanying "dopant" anions for maintenance of charge neutrality. During electrochemical synthesis, as a result of simultaneous oxidation and polymerisation of the pyrrole monomer, the conducting form of the polymer with a delocalized positive charge on the π electron system is formed. Anions from the electrolyte solution in which the monomer has dissolved are incorporated into the polymer in order to achieve electroneutrality.

The counterions used as supporting electrolytes in electropolymerisation should be very soluble in the monomer solution, chemically inert (toward the solvent or electrodes), electrochemically stable at the potential of monomer oxidation or reduction potential at the cathode. Therefore, easily oxidisable anions with a lower oxidation potential than the monomer, such as iodide or bromide, decrease the electropolymerisation efficiency or reduce the selectivity for film formation. The dopant is not necessarily the adopted supporting electrolyte anion, as other negatively-charged molecules, even with much larger size, can be incorporated into PPy matrix as dopant subsequently. In addition, the use of an aqueous deposition medium would also offer considerably larger selection of supporting electrolyte anions.

For example polyelectrolytes (e.g. PVS) are readily available as water-soluble salts or free acids, but are not easily converted to acetonitrile-soluble materials. Electron donor substituents in the counterions, will also prevent polymerisation while electron withdrawal groups will encourage polymerisation. Nature, size, geometry, charge, electronic and steric structure of counterion, deposition conditions, substrate, and solvent⁴⁵⁻⁵⁰, all are important in determining the properties of the synthesised film. The degree of molecular or structural anisotropy is enhanced through the use of highly planar counterions. Scanning electron microscopy, X-ray diffraction and TEM results have shown that the dopant anion also has a profound influence on the morphology of electrodeposited conducting polymers^{35,47}. For instance, polypyrrole synthesised in the presence of substituted benzenesulfonates and long-chain n-alkyl sulfonate/sulfate dopants appear to have the highest order⁴⁷.

Electrical Conductivity in Polypyrrole

The electrical conductivity of PPy conductive polymers is one of the most important properties for analytical applications. PPy is a conducting polymer which has a non-degenerate conduction band in the ground state. The polaron and bipolarons are the dominant charge carriers in these polymeric conductors, the mechanism of conduction in PPy has not been yet conclusively established because of the persistent structural disorder of the polymer⁵⁸. The most widely accepted view of conductivity in these systems involves charge transport along the polymer chains, as well as hopping of carriers⁵⁹⁻⁶⁰ (holes, bipolarons, etc.). Electrically conducting polymers are semiconductors with a filled valence band and an empty conduction band. These bands are separated by an energy gap.

Doping of these polymers creates new bands in the energy gap, making it possible for the electrons to move to these new bands and increasing the conductivity of the materials⁶¹. In the reduced (undoped) form, PPy conducting polymers are insulators. Bipolarons (radical-di-ions) showed in Figure 1, play a major role in the electronic and transport properties of conducting polymers. The bipolaron model has been shown to provide a coherent and unified picture of the properties of doped conducting polymers and the possibility of a small

band gap has been pointed out⁵⁹. The positive charges created on the polymer backbone (commonly termed polarons) are the charge carriers for the electrical conduction (Figure 4).

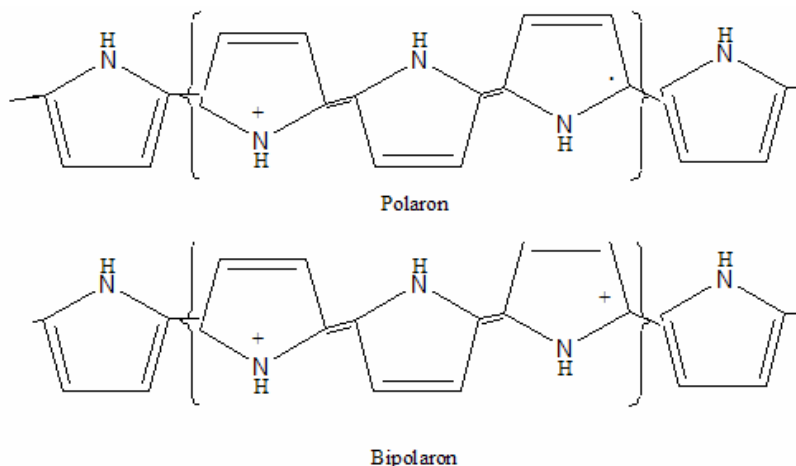


Figure 4. Proposed structures for polarons and bipolarons.

Their transport occurs via mobility along segments of conjugated polymer chain and the hopping of charges from chain to chain. The number of these charges contained in a material and their relative mobility controls the bulk electrical conductivity. A counterion (in this case an anion, typically termed a dopant anion) stabilises the charge on the polymer but is not very mobile within the dry material. Thus these polymers are truly electronic and not ionic conductors⁶¹. The electrical conductivity of PPy is the product of two important factors, the number of carriers (e^- or holes) and charge carrier mobility. Higher mobilities will occur with more crystalline, better oriented, defect free materials. Increasing the doping level will increase the density of charge carriers. The conductivity decreases with falling temperature just like that of semiconductors. In contrast, the conductivities of typical metals, like silver, increase with falling temperature⁶¹. The electrical conductivity of the ppy films are strongly influenced by the preparation conditions such as the nature/concentration of electrolyte or counterion^{46,49}, doping level⁶² current density⁶³, synthesis temperature^{63,64} and solvent⁶⁵.

It has been indicated⁴⁶ that highly conducting PPy films with an electrical conductivity higher than 500 S/cm have been prepared with the electrochemical method by selecting suitable polymerisation conditions. It has also been found that the preparation method also affects the properties of the produced films. For example the use of a pulsed potential technique in the growth of ppy films leads to an enhancement in electrical conductivity, molecular anisotropy and surface smoothness as compared to equivalent films synthesised by constant potential mode⁵⁰. The electrical conductivity of the produced polypyrrole films are also affected by synthesis temperature⁵³⁻⁵⁷. Polypyrrole synthesised at lower temperature exhibits longer conjugation length, structural order, fewer structural defects, and higher conductivity.

Detailed investigations of conducting polymers show that many of the chemical and physical properties are influenced by the microscopic structure. This varies depending on the dopant anion, current density and synthesis temperature⁵¹. It has also been previously reported that with increasing current density, the surface of the polymer becomes rough which leads to inaccurate values for the film thickness⁴⁹. A decrease in conductivity at high current densities (high anodic potential) can also be caused by the reaction of nucleophiles, like H₂O and/or OH⁻ with the polymer backbone. This interrupts the conjugated structure and lowers the intrinsic conductivity of the polymer⁴⁹. It has already been found⁶² that the electrical conductivity and mechanical properties are also strongly influenced by the molecular structures of the dopant and the doping level. That is, the doped PPy film has high mechanical strength and conductivity, but its strength or conductivity decreases remarkably after undoping⁶².

Munstedt *et al.*^{66,67} have reported that by a treatment of PPy with NaOH solution the conductivity of all PPys drops with time. This effect can be reversed if the sample is treated with HCl. This may be due to the stabilisation of charge carriers (polarons or bipolarons). The doped ppy chain undergoes a deprotonation process in aqueous basic media (with pKa in the range 9-11), which causes a profound change in its electronic structure (probably the formation of quinoid structure)⁶⁸ leading to de-doping and a low conductivity of 10⁻⁵ S/cm known as chemical compensation. It has been shown that after exposure to sulphuric acid solution, the PPy films shrank, became hard, somewhat brittle and weaker. Sodium hydroxide, treatment also caused severe embrittlement of the films⁶⁴. Scanning electron microscopy (SEM) investigations of PPy has also showed that the surface morphology of the ppy changes with base or acid treatment⁶⁸.

Electroactivity of PPy

The electroactive behavior of the film is unique because it is an example of a redox polymer reaction which is accompanied by a change in the electrical properties of the film from an insulator to an electrical conductor involving both electron and ion transport within the film^{69,73}. Owing to the high conductivity and thermal stability of PPy the conducting polymer, the electroactive nature or the switching properties of PPy have been utilized as the basis of most proposed applications such as sensors, separation devices and rechargeable batteries. Reduction-oxidation processes in polypyrrole conducting polymers involves mass and resistance changes as well as electron transitions, and this makes these materials very different from other redox systems in electrochemistry in which only electrons are involved during reduction and oxidation processes. Oxidation of pyrrole yields a charged polymer film with incorporated anions.

During the following reduction, electroneutrality can be maintained either by expulsion of these anions or by incorporation of cations⁷⁰. The pyrrole units have positive charges, which are balanced by anions. When a sufficient negative potential is applied to the polymer, the anions are expelled (undoping), thus reducing it to the neutral state. Conversely, when a positive potential is applied to oxidise the neutral film (doping), the anions are taken up. The counterion can be released, e.g. by applying a negative potential. Release can be specifically controlled, offering interesting possibilities for active counterions of medical significance that can be incorporated into ppy^{43,71}. The properties or characteristics of the PPy films can therefore be modified with regard to the nature of its dopant or counterion⁷¹. The dopant anions (small size) in the PPy film can be exchanged relatively easily with electrolyte anions in aqueous solutions during potential sweeping.

The anion exchange processes offer an alternative chemical route for the preparation of some conductive and anion specific PPy complexes⁷². However, the anion exchange processes do not result any significant alteration of the basic structure of the polymer⁷².

It has also been found that in the case of immobilised polymeric dopants such as anionic polyelectrolytes or large surfactant anions^{73,74}, the incorporated dopant or counterion is not released during electrochemical reduction of the polymer and the electroneutrality of the polymer is conserved by the penetration of the electrolyte cation into the PPy matrix. Consequently, in contrast to PPy doped with small anions, where the anions move during switching, the electrochemistry of PPy/polyanion composites involves cation transport. The polyanions become trapped within the polypyrrole matrix due to their large size and, perhaps more importantly their entanglement with the polypyrrole chain. Consequently, this increases the stability and mechanical strength of the film⁷³. The extent to which anions leave during reduction or cations are taken in depends upon the identity of counterion and the solvent that is used^{75,76}. The contribution of both processes to the overall charge transport has been found to depend strongly on the formation potential during polymerisation.

The redox process of PPy formed at +1.0 V vs. Ag/AgCl is accompanied by a change in mass, which can be interpreted by simultaneous transport of anions and cations. A lower formation potential leads to a separation of the charge transport in either an anion or cation dominated region⁷⁰. The mass transport processes which are necessary for the electrochemical activity of polymer coated electrodes are strongly dependent on: the morphology of the polymer matrix and the conditions of film preparation⁷⁷, the nature of counterion⁷⁸⁻⁷⁹, solvent⁸⁰⁻⁸¹, thickness⁶⁹, type of the electrode³⁷, film conditioning in the solution⁷⁹, and the doping anion's solubility in the solvent and also by the history of electrochemical treatments in different electrolyte solutions⁸².

It has been shown that PPy can be used as a redox electrode in the potential range where it is conducting. The PPy electrodes should not be used at potentials more positive than +1.0V due to overoxidation of the polymer, which would result in irreversible loss of the electrochemical activity⁸²⁻⁸⁴. In polypyrrole, anodic overoxidation is an irreversible intrinsic redox reaction as shown in Figure 5.

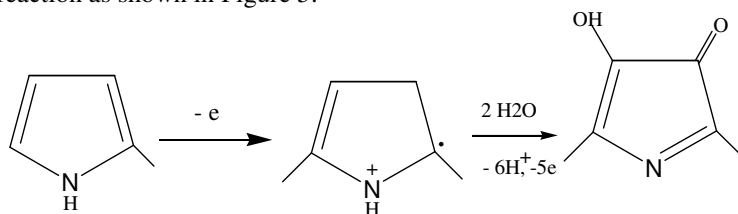


Figure 5. Proposed mechanism for anodic overoxidation of polypyrrole

The conjugation is interrupted and conductivity breaks down; hence the rechargeability of the polymer is lost⁸⁴. Higher electrochemical capacity of PPy films has been found in non-aqueous solvents under rigorous exclusion of oxygen and water⁸⁵. Electroactivity of PPy's is also degraded by strong oxidative compounds when exposed to these chemicals^{64, 86}. The electrochemical stability of PPy conducting polymers is also dependent on the pH of the solution⁸⁴.

Environmental Stability of PPy

Environmental stability is related to the reactivity of the charged polymer backbone towards oxygen or water. Because of the low oxidation potential of PPy conducting polymers, the redox reactions of PPys are more sensitive to the oxygen than those polymers that are more difficult to oxidise^{13,27}. The PPy conducting polymers, unlike polythiophenes which are stable in air even in the dedoped state, are less stable in their reduced or undoped form (PPyo) and autooxidation in the dedoped state proceeds very fast and irreversibly to produce a dark film^{69,84,87}. A progressive redoping by O₂ occurs due to the value of the polymer oxidation potential (E_{ox} = -0.3V) which lies in the same range as that for the reduction of the O₂. Therefore, it is concluded that the decay of conductivity of ppy CEP's is accelerated in air atmosphere especially in presence of moisture.

The conductivity of PPy films has been found⁵² to increase within the first few days and then level off. The increase in conductivity with time during the first few days is believed to be due to the decrease in moisture or solvent content of the films on standing. The slight decrease in conductivity after long storage times is thought to be due to oxygen attack of the conjugated double-bond system. The undoped PPy reacts easily with O₂, resulting in oxidation of the polymer and lowering the mechanical strength. In contrast to the oxidised state, the reduced state of ppy films is unstable to oxygen and water. From this finding it can be concluded that PPy in its oxidised state is stable if oxygen and humidity are kept away. This is in contrast to polyacetylene which is inherently unstable. Oxygen adsorption onto the surfaces of the polymer and diffusion into the interior are the respective rate limiting steps in the incorporation of O₂ into the closely cross-linked mesh, blocking conducting pathways⁸⁸.

Polypyrrole (PPy) is changed to PPy(A⁻) when dipped in an acidic aqueous solutions (H+A⁻) and changed to PPy(OH⁻) when dipped in an alkaline or neutral solutions⁸⁹. In aqueous media these spontaneous processes are strongly influenced by the pH of the electrolyte⁸⁰. Polypyrrole is also sensitive to moisture because this leads to leaching of the counterion and thus to a decrease in conductivity. This can be avoided by using appropriate hydrophobic or polymeric counterions [e.g., camphor sulphonic acid or poly (styrene sulfonic acid)]⁴³. We have found in our research work⁹⁰⁻⁹³ that the dopant counterion affect not only electrical conductivity and electroactivity of polymers but also govern general properties of the final product such as mechanical, chemical and morphological properties as well as thermal and environmental stability of the polymer. For example Polypyrroles doped with perchlorate as a counterion are unstable even under atmospheric conditions but polymers doped with p-toluene sulfonate was electroactive even after thermal treatment at 300°C under nitrogen atmosphere and below 150°C in air. In general electrical, electrochemical, mechanical and morphological properties of PPy films strongly depends on preparation conditions and any post treatments. Among different factors, the counterion or dopant anion plays the most important role.

Thermal Stability

Because of the possible applications of conducting polymers at elevated temperatures, research on determining the thermal stability is of both fundamental and technological importance. Long term environmental stability of conducting polymers can be investigated by thermal treatment of the polymer samples at elevated temperatures.

For successful industrial applications of these fascinating new materials in future, their long term stability and thermal resistance are the key properties that should be considered first. Ageing and thermal stability of ppy conducting polymers in air and solutions have been the focus of some researchers.⁹⁴⁻¹¹¹ Exposure of conducting polymers to elevated temperatures is known to induce changes in the molecular structure. The changes may be related to the interaction between the charged polymer backbone and the counterion, or the thermal stability of the counterion and the charged polymer itself.

While the mechanism of degradation of electrical conductivity in polyacetylene (and possibly all conducting polymers) when it is exposed to air involves reaction of the polymer with oxygen to form carbonyl species and intermolecular crosslinks. It has been reported^{105,106} that conductivity of polypyrroles doped with arylsulfonates exhibit excellent stability in inert atmospheres but are slightly less stable in the presence of dry or humid air. Polypyrrole samples doped with the aromatic sulfonates such as tosylate anion were found to be the more stable than ppy films doped with longer sidechain substituted benzenesulfonates or aliphatic dopants. The main conclusion of this study was that the polymers with shorter side chains generally exhibit higher stability. Polypyrrole doped with perchlorate, tetrafluoroborate, and hexafluorophosphate lost conductivity and decomposed at ca.>150°C in air and polymer doped with toluene sulfonate did not decompose until 280°C.

The decay of conductivity of PPy/PTS films with time in air followed first-order kinetics involving reaction of polymer backbone with air. In contrast, PPy/CIO₄ or PPy/BF₄ samples showed faster decay and more complex kinetics. It was suggested that this reflects the presence of a combination of processes, possibly the simultaneous reaction of the polymer with oxygen or moisture with the counterion being involved. The difference between the conductivity loss in dry air and humid air seems to be very small, indicating that oxygen may be mostly responsible for degrading the doped polymer. In this report the less conductivity and thermal stability of ppy samples prepared with the longer alkyl chain substituted benzenesulfonates in comparison to samples prepared with tosylate dopant has been attributed to the less dense structures of these films that makes them more susceptible to be attacked by water and oxygen.

The degradation mechanism is most likely a combination of two or more process. One is the reaction of the polymer backbone with the dopant anion, and the other is the reaction of the polymer backbone with oxygen or water. It is also possible that the dopant species itself might undergo thermal degradation and the products of this degradation could react with the polymer backbone. PPy/CIO₄ or PPy/BF₄ when heated in an inert atmosphere is examples of this degradation mechanism. In all cases of PPy conducting polymer, it has been found that the nature of the anion incorporated with polymer as counterion has the most important role in determining the thermal stability of produced polymer. The type of counterion as well as the preparation conditions, exposure temperature, surrounding atmosphere (e.g., oxidative or hydrolytic, inert), and also duration of thermal treatment play a very important role in determining the thermal stability of the conductivity in PPy conducting polymers.

The presence of the anions as dopants in the polymer matrix has made the thermal stability of these polymers more complicated than conventional polymers. It was also found that mild thermal treatment of polypyrrole conducting polymers in inert atmosphere, the electrical conductivity can be improved. The increase in conductivity may be related to annealing effects which improves the local ordering within the film and also the removal of

non-polymeric impurities trapped into the polymer matrix during growth. However, the amount of conductivity change is greatly dependent on the nature of the dopant anion incorporated during growth. However; at elevated temperatures, structural changes such as cross linking or chemical interactions between counterion and polymer that leads to blocking charge carriers' paths or shorten conjugated system will also result to a decrease in electrical conductivity.

General Conclusions

Conducting polymers have more limited stability (environmental, thermal, chemical) than conventional inert polymers due to the presence of dopant and their dynamic and electroactive nature. The effect of the counterion on the intrinsic and extrinsic stability is more indirect; the effect of the anion might be to alter the crystallinity of the polymer/dopant system, the numbers of chemical defects, or extent of backbone oxidation. All of these may affect the reactivity of the dopant/polymer system to the environment and its thermal stability. Polypyrrole conducting electroactive polymers doped with aromatic sulfonates (mainly Benzene or naphthalene sulfonates) as counterions produce flexible, and smooth films that can be readily detached from working electrode as membrane with good mechanical properties. The easily oxidizable organic or inorganic counterions were found that are not suitable for preparation of PPy as free standing films. In addition, the electrolyte should not have corrosive effect on the working electrode.

Electropolymerization of polypyrrole CEP's is also limited to using high nucleophilic anions or substituents such as $-NH_2$. Preparation conditions were found that are very important so that a small change in preparation conditions may lead to a big change in properties of resulted polymer. The counterions used during preparation of polypyrrole films have the greatest effect on total properties of the resulted polymers.

Thermal treatment at elevated temperatures affects the electrical conductivity and electroactivity depending on the nature of the counterion incorporated during synthesis. The changes are mostly an irreversible process. And the dopant anion has the greatest effect on conductivity, electroactivity, mechanical, morphological, thermal and environmental and chemical stability of PPy conducting polymers. The most important factor in decay of conductivity or electroactivity in air atmosphere is attributed to the chemical reaction of O_2 with double bonds in conjugated system. The rate of thermal degradation of conductivity is also very much dependent on temperature, atmosphere and duration of heating. The conductivity decay of PPy polymer occurs much quicker in oxidative atmospheres, such as air, as compared to inert atmospheres like nitrogen.

Future work

Polypyrrole conducting polymers still suffer from relatively poor thermal stability especially in oxidative atmospheres such as air. The future applications of conducting polymers as technological materials will certainly demand high thermal stability of their conductivity, electroactivity and mechanical properties. It should be noted that long term stability of the PPy is a key factor for application of these new polymeric material in future applications and PPy conducting polymers seem to be a good candidates. More research is needed in order to prepare PPy films with higher environmental or long term stability. It will be useful for researchers now to attempt at the synthesis of conducting polymers with improved mechanical properties and thermal stability. This may be achieved via encapsulation of

polymer, modification of the structure of monomer units, the counterions or controlling the polymerisation conditions.

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