



ENVIRONMENTAL STABILITY OF ELECTROCHEMICALLY SYNTHESIZED POLYPYRROLE CONDUCTING POLYMERS

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ABSTRACT

The long term environmental stability of polypyrrole conducting electroactive polymers is a key factor for successful commercial applications of these new polymeric materials in future technology. In this paper, polypyrrole (PPy) conducting electroactive polymers doped with some benzene sulfonates were synthesized electrochemically and then the electrical conductivity of the films was measured after synthesis. Their conductivities were also measured after 10 years storage under ambient conditions.

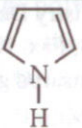


Key words : Polypyrrole, Dopant, Electrical conductivity, Environmental stability.

INTRODUCTION

Conductive electroactive polymers are materials discovered just over 20 years ago. Among the conducting polymers known to date, ones based upon PPY have attracted special interest because of their high conductivity (10^1 – 10^3 Scm^{-1}), their ease and high flexibility in preparation, their high environmental and thermal stabilities and good mechanical properties^{1,2}. Many conducting polymers are degraded over time even in dry and O_2 free environments (intrinsic instability) or vulnerable to O_2 , water and humidity (extrinsic instability). Extrinsic stability is determined by the polymer susceptibility of charged sites to attack by nucleophiles, electrophiles and free radicals. It causes irreversible chemical reactions, which lead to breaking of the conjugation system. Polyacetylene ($-\text{CH}=\text{CH}-$)_x that was synthesized and developed by Shirakawa³ in 1977, in spite of its high conductivity (10^3 – 10^5 Scm^{-1}) in doped state, it is too unstable to be of any practical value. These new polymeric materials have attracted considerable interest on account of their potential technological applications such as sensors, actuators, radar shielding, membrane separation, rechargeable batteries and anti-corrosion films, which are based on their electronic conducting and unique electrochemical properties.⁴⁻⁷ Polypyrrole (PPy) and a wide range of its derivatives may be prepared by simple chemical as a black powder or electrochemically as electrode deposited adherent film. In electrochemical synthesis, PPy is easily deposited onto the conductive surface of a given substrate from neutral

or weekly acidic aqueous solutions of monomer. The oxidation potential of some heterocyclic monomers are also summarised in Table 1.

Table 1. Oxidation potentials of some heterocyclic monomers

Compound	Formula	E(V/SCE)
Pyrrole		+0.80
Thiophene		+1.60
Furan		+1.85

The oxidant potential is lower for pyrrole (0.8V) than other heterocyclic monomers. Consequently, PPy is readily synthesised from a range of aqueous and non-aqueous solvents^{8,9}. In fact, PPy is one of the few electronically conducting polymers that can be prepared from aqueous solutions. For example, polyaniline should be synthesised from acidic aqueous media, while polythiophene must be grown from organic solvents in which the monomer is soluble. In order to prepare PPy, 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. Then with addition of chemical oxidants or applying positive potential, polymer is readily prepared as black powdered or as deposited adherent film on the surface of conducting stable electrodes. In electropolymerisation, the oxidation of pyrrole monomer yields a radical cation at the initiation step. The radical cations couple to form a dimer and deprotonate producing bipyrrole. The bipyrrole is oxidized again and coupled with another oxidized segment. Deprotonation and reoxidation follow, and the process continue with the formation of polymer (PPy). The overall electropolymerisation of polypyrrole can simply be shown as in Figure 1.

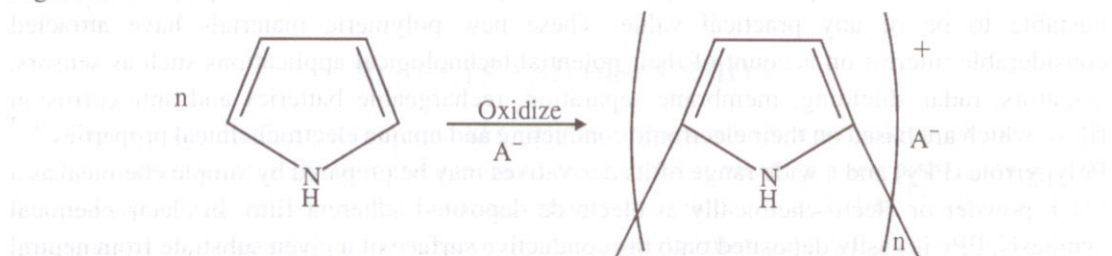


Figure 1 The overall polymerization reaction of polypyrrole conducting electroactive polymers

Where A^- is the counter ion incorporated into the polymer during polymerization in order to achieve electroneutrality.¹¹ Oxidation of pyrrole yields a positively charged polymer film, which are balanced by anions incorporated anions. A counter ion (in this case an anion, typically termed as 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 conductors.

The auxiliary electrode reactions, during the oxidation of monomer at the working electrode, will be the reduction of water or dissolved oxygen (production of OH^-). Electropolymerisation of PPy can be carried out using different techniques including potentiostatic, galvanostatic and potentiodynamic (e.g. cyclic or pulsed potential). However, more reproducibility in film preparation is usually obtained using galvanostatic method. Preparation, characterization and thermal stability of PPy conducting polymers have been extensively studied by many investigators.⁹⁻¹⁵ But very limited reports have been published about environmental stability. In this paper, the environmental stability of PPy with regard to electrical conductivity, which is the most important properties of PPy, has been investigated.

The popularity of PPy conducting polymers debts on their unique electrochemical and electrical properties. The electrochemical properties (redox processes) in polypyrrole conducting polymers involve 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.¹⁶ The electrical conductivity of PPy has metallic characteristic and is the product of two important factors, the number of carriers (e^- or holes) and charge carrier (polaron and bi polarons) mobility. The positive charges created on the polymer backbone (commonly termed polarons) are the charge carriers for the electrical conduction (Figure 2).

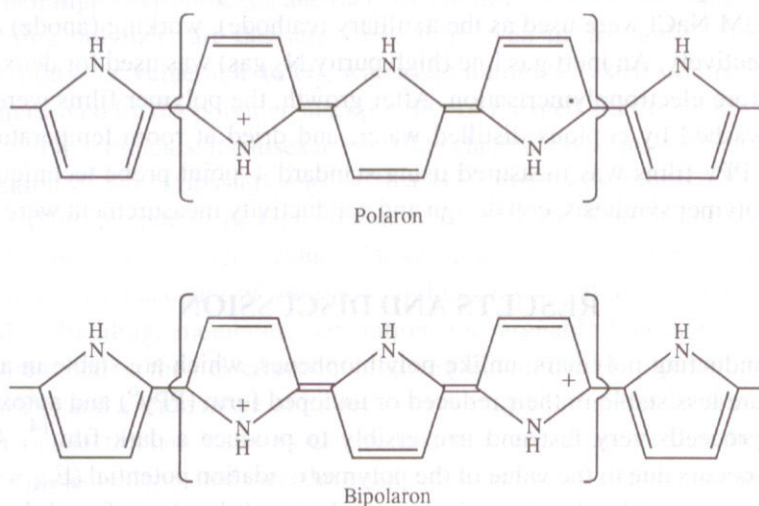


Figure 2. Proposed structures for polarons and bipolarons¹⁰

Higher mobilities will occur with more crystalline, better oriented, defect free materials. The bipolaron 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 out.

EXPERIMENTAL

In this paper, polypyrrole conducting polymer films (stand alone) were prepared electrochemically (Galvanostatic method) in a three compartment electrochemical cell ($I = 2 \text{ mA/cm}^2$). Pyrrole (monomer) was distilled before polymerization and stored in fridge. The monomer solutions (0.2M) were prepared in 0.05M of selected dopant anions (sodium salt) as shown in Figure 3.

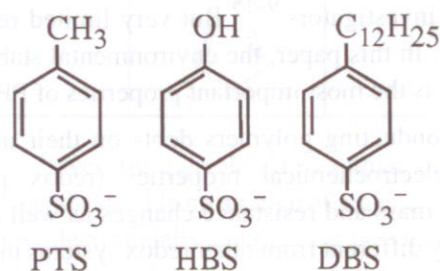


Figure 3 Selected aromatic anions used as dopant for preparation

In this investigation, the anions used for preparation of PPy membranes were sodium salts of p-toluene sulfonate (PTS), p-hydroxybenzene sulfonate (HBS), and p-dodecylbenzene sulfonate (DBS). A porous carbonaceous material (RVC), well polished stainless steel plate and an Ag/AgCl in 3M NaCl were used as the auxiliary (cathode), working (anode) and reference electrodes, respectively. An inert gas line (high purity N_2 gas) was used for deoxygenating the cell solution before electropolymerisation. After growth, the polymer films were peeled from the electrode, washed by copious distilled water, and dried at room temperature. Electrical conductivity of PPy films was measured using standard 4-point probe technique.¹² Detailed procedures of polymer synthesis, cell design and conductivity measurement were carried out as described.^{12, 17}

RESULTS AND DISCUSSION

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 (PPy^0) and autoxidation in the dedoped state proceeds very fast and irreversibly to produce a dark film¹⁴. A progressive redoping by O_2 occurs due to the value of the polymer oxidation potential ($E_{\text{ox}} = -0.3\text{V}$) which lies in the same range as that for the reduction of the O_2 . It has been found that the decay of conductivity and electroactivity of ppy CEP's is accelerated in air atmosphere especially in

presence of moisture or elevated temperatures.^{12, 13} The conductivity of PPy films has been found to increase within the first few days and then level off.¹⁴ 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 of 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 crosslinked mesh, blocking conducting pathways. The electrical conductivity of the films measured 24 hours after synthesis (year 1994) (σ^0) and after 10 years storage of the films under normal environmental conditions (σ) are summarized in Table 2.

Table 2. Environmental stability of PPy films with regard to electrical conductivity

Polymer	σ^0 (S cm ⁻¹)	σ (S cm ⁻¹)	σ/σ^0
PPy/PTS	80	18	0.22
PPy/HBS	100	23	0.23
PPy/DBS	25	5	0.20

Therefore, polypyrrole conducting polymers are relatively stable to atmospheric exposure in their electrochemically oxidised states. It was interesting that the polymer films had good mechanical properties (flexibility) even after 10 years storage under ambient conditions. This may be a positive point from application point of view. However, some degradation in conductivity was occurred during prolonged storage in air. Decay in conductivity can be related to the reactivity of the charged polymer backbone towards oxygen or water. It was also found that long term stability of conductivity in PPy is not very dependent on the nature of dopant. Conductivity decay in PPy films during a period of 10 years storage at ambient conditions was found to be about 75–80%.

CONCLUSION

Electrical conductivity of PPy films is strongly affected by the nature of its electrolyte dopant solution used for preparation. The most important factor in decay of conductivity or electroactivity in air atmosphere is attributed to the chemical reaction of O₂ with double bonds in conjugated system. Although the nature of dopant plays the most important role in determining environmental stability of PPy films but the importance of preparation conditions

should not be ignored at all. On the whole, PPy films prepared under optimized or suitable electrochemical conditions normally show higher conductivity, better electroactivity, mechanical properties and environmental stability. More research is needed in order to prepare PPy films with higher environmental or long term stability. This may be achieved via encapsulation of polymer, modification of the structure of monomer units, the counter ions or controlling the polymerisation conditions.

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