Spectroelectrochemical characteristics of Polypyrrole synthesized by different methods

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The present review summarizes several studies performed on polypyrrole (PPy) in order to emphasize the paramount importance of characterizing the conductive polymer both by electrochemical and spectroscopic techniques. The investigations take into account one or more of the following factors: type of polymerisation, temperature and pH during synthesis, dopant of choice etc. Initially, fundamental concepts concerning the charge transport within conductive polymers are presented, followed by recent developments both in PPy synthesis and PPy composites for various applications.

INTRODUCTION

The flexibility of electric character in conductive polymers (CPs) initiated substantial perspectives for their use in a variety of applications. Since the discovery of CPs [1, 2], they have been of academic and technological interest representing a significant scientific challenge for chemists, physicists and material science researchers [3].

The main objective has been achieving a thorough understanding of their electrochemical properties as derived from their chemical structure. Besides traditional electrochemical and chemical methods of synthesis, many polymerization techniques are available including but not limited at: photochemistry, metathesis, chemical vapor deposition, UV-induced polymerisation, concentrated emulsion synthesis, plasma polymerisation etc. [4]. In addition, in pursuit of an economical and environmentally benign pathway, enzymatic synthesis was extensively researched [5].

Therefore, an overview of different characterization techniques for conductive polymers along with the similarities and discrepancies observed in these materials related to their synthesis method is proposed. The main focus will be on polypyrrole as it is representative to the field and its simplicity of synthesis and adherence to many types of surfaces as well as stability and conductivity render it an illustrative model of analysis.

FUNDAMENTAL CONCEPTS IN THE CHARACTERIZATION OF POLYPYRROLE

The elementary theoretical models and experimental data which were to later become the fundaments in the characterization of conducting polymers will be assessed in this section. The first investigations of the charge mechanism in CPs were performed on electrochemically synthesized films due to simplistic and controllable deposition manner along with ability for adequate parameter setting. Factors such as: potential or current applied, solvent and supporting electrolyte are of significance affecting the structure, electrochemical and mechanical properties of the resulting polymer. The nature of the counterion, in particular, was of extended interest because the electrochemical synthesis does not render a neutral polymer in insulating state, rather it is tailoring it with conductivity and charge according to synthesis conditions [6, 7].

Yakushi et al. [8] performed an optical study on perchlorate doped PPy (33 mol %) at various stages of reduction. The as-grown PPy film was already in oxidized form as it is the case in electrochemical synthesis and applying progressive reduction potentials rendered the opportunity to analyze the polymer at intermediate oxidation stages between the conductive and the insulating form. The as-

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grown film (highly oxidized form) revealed absorption peaks at 1.0 eV (1240 nm) and 2.7 eV (460 nm) while the highly reduced form absorbed mainly at 4.5 eV (275 nm) and 3.2 eV (387 nm). It was noticed that as the reduction increases, the absorbance bands decrease in intensity and shift to higher wavelengths, however several weak bands are common for most films. The absorption peaks at most oxidized state, were still present in the most reduced films as weak bands and vice-versa. Thus, a coexistence of the oxidized and neutral forms of PPy within the same film was considered. Therefore, it must be that the polymer chain is composed of several neutral and cationic segments of different lengths, randomly distributed within the film and that the electron hopping between segments is imparting electrical conductivity. Thereupon, Bredas et al. [9, 10] developed a theoretical model involving the concept of polarons and bipolarons in conductive polymers intrigued by the fact that electron hopping within the highly conductive films did not exhibit paramagnetic behaviour. They stated that the oxidation of the conjugated polymer leads to a localized deformation associated with charge carriers which means lengthening of double bonds and shortening of single ones along the polymer chain and upon analyzing the spectra obtained for 33% perchlorate doped PPy at intermediate states of reduction, they introduced the concepts of polaron and bipolaron charge carriers. Therefore, polarons are radical cations formed within CPs at low levels of oxidations that, upon further oxidation, pair up into double charged radical dications or bipolarons. Electron spin resonance (ESR) studies revealed a spin of ½ for cationic units while for dicationic species there was no paramagnetic signal. The high conductivity in the absence of paramagnetism was thus, to be related to double charged spinless bipolarons. The theoretical model was supported by optical, magnetic and structural data.

Albeit the resemblance of electric nature between conductive polymers and semiconductors, the two systems are elementary different. Conventional semiconductors display three-dimensional structures while conductive polymers consist of conjugated one-dimensional chains. Accordingly, they do not obey semiconductor type of behaviour, their conductivity being an intrinsic property upon exposing them (e.g. polyacetylene) to oxidation or reduction. This process was referred to as doping analogous with the doping of inorganic semiconductors, however it is an oxidoreduction reaction [11]. The facility of oxidation/reduction is related to the conjugated character of the polymer

which renders a facile removal or inclusion of - electrons into the chain with little disruption of bonds. The electrical susceptibility of the material is given by the width of the bandgap, the gap between the highest occupied molecular orbitals (HUMO) or valence band and the lowest unoccupied molecular orbitals (LUMO) or the conduction band. The movement of charges between these two bands leads to conductive behaviour. Taking for instance, the oxidation i.e. expulsion of an electron from the conjugated chain will lead to the appearance of localized electronic states inside the gap [12] such as two polaron levels: the lower polaron level represented by the bonding cation level (BCL) and the upper polaron level or the antibonding cation level (ACL). Removal of a second electron would generate two bonding and antibonding dication levels (BDL/ADL) [13]. Thus, the dication state is not to occur at low levels of oxidation yet predominant at high doping levels. Still, the question remained, whether if bipolaron formation is thermodynamically favorable i.e. the energy required to form a dication is less than that of generating two radical cations as well as the stability of this state. Worth noting is that polyacetylene possesses a degenerate ground state which accounts for two structures with the same energy allowing alternation of single and double bonds within the chain, while heterocycles have a nondegenerate ground state i.e. a single possible geometric structure. The polaron formation within aromatic CPs corresponds to soliton carriers in polyacetylene [3].

Genies and Pernaut [14] undertook an optical study of polypyrrole in order to characterize the kinetics of the radical cation and dication charges in correlation with the redox properties of the polymer by recording the species equilibrium during potential cycling. The electrochemical cycling of the PPy films describe a typical redox system around – 0.2 V. Extra oxidation peak is assigned to leftover monomer in the film, consequently polymerized as it is catalytically favorable at low scan speed while an extra reduction peak proves a two-step electron transfer. Extended cycling leads to polymer degradation with consequences such as electroactivity loss. In terms of optical spectroscopy, PPy exhibits absorption peaks according to its redox state, as expected. The absorbance band at 3.4 eV (370 nm) due to – * or valence band (VB) conduction band (CB) transition is specific to the reduced state of the polymer. The oxidized state corresponds to several peaks: 2.8 eV (440 nm) related to valence band

(VB) antibonding cation/dication level (ACL/ADL); 2.3 eV (540 nm) due to bonding cation level (BCL) antibonding cation level (ACL). The transition from valence band to bonding cation/dication level (BCL/BDL) was not recorded. The experiment consisted of plotting the absorbance areas described previously against the oxidation level.

The peak at 3.4 eV (interband transition) fades as the oxidation increases probably due to the appearance of intermediate gap states. The absorption peaks at 2.8 eV and 2.3 eV are increasing as the oxidation increases as long because charge is distributed along polaron species. Decreasing of these two absorption peaks leads to the belief that radical cations are starting to pair forming dications. The results are consistent with the transition from neutral PPy to the formation of cationic (PPy+) and dicationic (PPy2+) as molecular orbitals move closer to each other within the gap corresponding to the structure modification from non-conjugated to conjugated aromatic and to quinoid type units, respectively [15]. Nechtschein et al. [16] varied the redox properties of a polypyrrole film by applying different voltages and assessed the doping level by ESR and optical analysis stating that the bipolaron species is more difficult to characterize due to lack of paramagnetic signal. However, for CPs with a non-degenerate ground state it has been of essential importance. Patil et al. [17] published an extensive review regarding optical properties of conductive polymers assigning the 1.4 eV absorption band recorded previously [8, 10] in the spectra of mildly oxidized PPy as polaronic peak seeing how it fades at higher oxidation state, while the absorption at 1 eV and 2.7 eV was correspondent to bipolaronic charges. A discussion on solitons versus polarons and bipolarons is presented by constructing an analogy between polyacetylene and polythiophene. It is also disclosed that charged species are not confined to a solid state of the material they are present in liquid solution as well, owing to their intrinsic molecular nature.

A multitude of parameters can affect the mobility and distribution of charge carriers thus optical spectroscopy is not to be solely relied upon but further investigations through electrochemical and structural techniques are to be performed. Furukawa et al. [18] correlated Raman and optical absorption spectroscopy to distinguish the vibrational signals correspondent to charge carriers in polypyrrole at intermediate oxidation stages. Their study indicated that radical cations and dications coexist in highly oxidized form of PPy and as the polymer is reduced, dications turn into cations, which are further converted in neutral species. Zhong et al. [19] performed a comparison between theoretic kinetic predictions based on the polaron/bipolaron model and experimental in situ ESR data. As seen from an electrochemical perspective, the formation of the polaron state and evolution to bipolaron is a function of the potential applied. Different investigation had led to contradicting theories about the species accountable for the charge transfer in PPy chain. While Bredas et al. [10] stated that bipolaron formation is thermodynamically more favorable than formation of two different polarons, Nechtschein et al. [16] estimated that the energy necessary for both processes is similar which is why the bipolaron state is questionable. Since the electric properties of PPy do not rely only on bipolaron formation and proof of polaron state was attained at least at low doping levels, determining the stability of the charge carriers was demanded. Raman spectroscopy was employed in order to observe the structural changes of the polymer chain simultaneously with charge carrier detection by ESR. Charge injections onto a reduced film of PPy led to following observations at intermediate oxidation stages: paramagnetic signal increases until a certain point after which it decreases; C=C backbone stretching vibration band is blue shifted upon applied potential as double conjugated bonds are lengthened and the polymer chain is transitioning from benzenoid to quinoid structure.

John et al. [20] employed resistometry in analogy with voltammetry for the characterization of redox properties for PPy-nitrate films. The insights gained were related to the kinetics of the switching mechanism in conductivity such as the degree of change in resistance, the potential at which it occurs and the rate versus applied potential. Both voltammetry and resistometry revealed how the intrinsic conductivity of CPs varies with potential and provided information about the charge required to trigger this mechanism. Kaplin and Qutubuddin [21, 22] tested five different potentials for synthesizing PPy for two different electrolyte systems: sodium perchlorate and p-toluenesulfonate. The redox behaviour of polypyrrole consists of electron transfer either to or from PPy along with counterion insertion or repulsion from polymer matrix for reaching charge neutrality. In this sense the polymer exhibits switching ability from conductor to insulator. Upon voltammetric cycling, it was observed that the films prepared at potential of 1.0 V display one redox exchange with oxidation-

reduction peaks positioned symmetrically, while the films prepared at lower potentials such as 0.6 or 0.75V reveal an oxidation yet two reduction peaks.

Films obtained at potentials higher than 1.0 V such as 1.5 V or 2 V do not display symmetrical peaks. It was determined that two reduction peaks are proof of the presence of both polarons and bipolarons within the polymer chain. Bipolarons are attained in this case due to the perchlorate ion, such behaviour not being observed for the toluenesulfonate-doped PPy. In addition, by analysis of the chronoamperometric response to the applied potential during electrosynthesis, the incorporation of hydroxyl or carbonyl groups into the polymeric chain can be detected by distinctive ceasing of the process. Lower potential leads to a polymer film less susceptible for overoxidation because the oxidation of the electrode occurs slowly, while for higher potentials the electrode oxidizes faster contributing to adhesion of termination groups to the electrode surface blocking pyrrole. Thus, overoxidation of the polymer starts after 1.0 V and can be considered independent on the electrolyte. However, structural properties are subordinate to the dopant of choice. ESR spectroscopy was employed for studying the polaron:bipolaron ratio in the polymer film according to applied potential and results showed that films prepared at lower potentials had lower spin concentration i.e. preponderance of bipolaron states while in films prepared at 1.0 V, cationic species prevailed rendering higher paramagnetic signal.

Lee et al. [23] synthesized PPy in a chemical manner using dodecylbenzensulfonic acid (DBSA) as dopant and ammonium persulfate (APS) as oxidant. The polymer was soluble in m-cresol and mildly soluble in other solvents. Even though PPy is usually hard to process due to strong intra and interchain crosslinking, doping a large molecule able to reduce such interactions as well as the monomer:oxidant ratio made it accessible. The PPy obtained was slightly overoxidized as shown by elemental analysis and had low molecular weight, yet exhibited prolonged reactivity during CV. Demoustier-Champagne and Stavaux [24] synthesized PPy in an electrochemical manner in polycarbonate membranes with different pore sizes using four different dopants discussing the consequences on the morphology and conductivity of the polymer.

Aguilar-Hernandez and Potje-Kamloth [25] performed a spectroelectrochemical study on a polypyrrole – polyoxyphenylene composite prepared by potentiostatic technique at alkaline pH using 4-hydroxybenzenesulfonate (4HBS) as dopant. A slight overoxidation of the composite film was observed, however, the polymer retained a conductive character. It was stated that an increased polymerisation potential led to the evolution of polypyrrole from a quinoid to a benzenoid type structure as observed from infrared spectra which is generally associated with intrusion of carbonyl groups within the polymer's backbone which can terminate the conjugated length and affect the conductivity. C=O groups disrupt the delocalization of electrons along the polymer creating defects in the - conjugated chain. Their presence is regarded as imparted by the high deposition potential and high pH. Zhou and Heinze [26-28] defined three types of structural PPy entities differentiated by the degree of conjugation and conductivity focusing on the analysis of the electrolyte used in the electrosynthesis. Hence, pure conductive PPy or PPy (I) can be obtained in non-acidic media, even low acidity leads to PPy (II) while high acidity passivates the electrode due to formation of nonconductive low conjugated PPy (III). Elemental analysis can provide an approximation of the doping content by the ratio between different nitrogens. Three types of N atoms were identified in oxidized PPy while in neutral form only one type of nitrogen was detected. Further Raman spectroscopy connected with cyclic voltammetry was employed for studying the charging/discharging mechanism of a nitrate PPy film upon doping as reported by Liu et al. [29]. The structural change in PPy during redox switching was examined by in situ cyclic voltammetry - surface enhanced Raman spectroscopy (CV-SERS). SERS measurements were performed while the film was being cycled and for each potential the corresponding Raman peaks were identified. Thus, the peak corresponding to C-H in plane deformation did not shift either in the anodic or cathodic scan, the peak assigned to C=C backbone, correspondent to reduced form of PPy in cathodic scan, shifted toward higher frequency during anodic scan as expected [19] and the peaks assigned to ring deformation and N-H in-plane deformation transited to lower and higher wavenumbers with anodic and respectively, cathodic scan. It can be assessed that the C-H in plane deformation is autonomous of the PPy redox behaviour, the conjugated lengthening occurs during oxidation while the nitrate counterions are incorporated into the cationic polymer to neutralize the charge. Joo et al. [30] reported a comparison between charge transport and structural properties of three differently synthesized pyrrole polymers. While the

electrochemically prepared PPy was doped with hexafluorophasphate (PF6) the chemical ones included dodecylbenzensulfonic acid (DBSA) or naphtalenesulfonic acid (NSA). The comparison concluded that the PPy-DBSA and PPy-NSA displayed the insulating soluble polymer state due to the large size dopants which reduced interchain links, while PPy-PF6 had a high concentration of interchain links contributing to charge hopping and conductive behaviour. Density of states was higher in electrochemically prepared polymer rather than in chemical ones. However, neither the effects of large dopants within electrosynthesized polymer films nor the influence of highly mobile species in chemically prepared polymer were evaluated.

Upon attaining these fundamental concepts, innovation in the field of conductive polymers was impeding. For further inquiry in the elementary mechanisms of pyrrole synthesis either by chemical or electrochemical means and the resulting properties, the reader is referred to Sadki et al. [31] and Ansari [32] for comprehensive reviews.

ADVANCES IN THE PREPARATION AND CHARACTERIZATION OF POLYPYRROLE

Having established the basic redox processes as well as structural modifications occurring within PPy when switching between its conducting and insulating state, a series of modifications were proposed for tailoring the polymer for specific applications. Continuous involvement in the characterization of polypyrrole is imperative in order to find an equilibrium between functionality and processability. Several pathways for modification are available either by functionalization of the monomer with functional groups preceding the polymerisation or by in situ inclusion of counterions and/or template molecules [33].

Liu et al. [34] synthesized PPy by chemical vapor deposition on metallized Nafion® electrodes for diminishing the aging issue encountered in hydrogen sensors. The results were adequate for anti-aging properties, however a loss in sensitivity emerged. Heinze and co-workers [35] have made further progress in preparing different entities of polypyrrole providing new insights in the structural diversity of the polymer. Two types of transporters within different PPy variants, mobile and immobile charge carriers are considered, the former contributing to polymer conductivity and the latter to the formation of a crosslinked network. PPy (I) and PPy (III) are able to transfer only anionic compounds, while PPy (II) is capable of motioning both anions and cations. Morphological and mass

changes within the polymer on this basis were addresses by Cohen et al. [36]. Masuda and Asano [37] provided a short note consisting of the spectroelectrochemical characterization of PPy synthesized galvanostatically with sodium alkylbenzenesulfonate dopants. The UV-Vis-NIR spectra were fairly independent of the chosen dopant molecule while in voltammetric cycling just the cathodic peak, otherwise associated with removal of counterions from the polymer matrix, was distinct dopant-wise.

Omastova et al. [38] employed chemical synthesis of pyrrole in aqueous media in the presence of different types of surfactants (anionic, cationic, neutral) in an attempt to identify the nature of the interaction between them. Conclusions were that anionic surfactants develop an ionic bond with the polymer adding to the process as dopants, increasing the polymerisation rate, while cationic ones have the reverse effect. The surfactant addition to polypyrrole led to good conductivity as well as stability towards deprotonation due to the hydrophobic nature of the surfactant. He et al. [39] synthesized novel structures of PPy so-called "coral-like nanowires" in a ferric chloride – based aqueous chemical polymerisation with the addition of dodecyl-benzene sulfonic acid (DBSA) and poly(vinyl-alcohol) (PVA). The improved structural morphologies increased the electrochemical properties of PPy as assessed by temperature-dependent conductivity measurements.

Can et al. [40] investigated the interactions between protons or Lewis acids and pyrrole from both theoretical and experimental perspectives. It was ascertained that both proton and Lewis acids act through similar mechanisms leading to pyrrole oligomers and possible addition to the polymer's backbone. Pokrop et al. [41] reported the preparation of processable PPy by using ammonium peroxydisulfate as oxidant and salts of sulfosuccinic acid diesters as dopants attempting a counter-ion provided processability [42]. A highly conductive polymer is known to be intractable due to its ionic nature, so hardly solvable, while a certain degree of processability leads to a decrease in conductivity. A compromise between the two is to be attained. Spectroelectrochemical properties of the obtained PPy were assessed with UV-Vis-NIR and cyclic voltammetry techniques.

Benabderrahmane et al. [43] functionalized pyrrole with N-succinimidyl ester and performed in situ copolymerization in presence of polystyrene latex particles using FeCl3 as oxidizer. Spectroscopy and elemental analysis of the composite particles were performed pursuing

reactivity towards amine and thiol groups for further attachment of proteins in biomedical applications. Hien et al. [44] tested a double layer of PPy for protection against iron corrosion. They manipulated the PPy by doping the outer film with dodecyl sulfate anions and the inner one with tetraoxalate anions in order to modify the permselectivity of the film from anion to cation exchanger impeding the intrusion of chloride anions. Xu et al. [45] took advantage of the redox switching mechanism of PPy and explored the hydrophobic – hydrophilic switch, the wettability of solid surfaces being of increased interest. Certainly, the dopant of choice has prevalent influence upon water contact behaviour and the switchable wettability resulted to be a function of applied potential.

Cong et al. [46] developed multi-composite electrodes consisting of polypyrrole and mixed oxides on a glassy carbon electrode: GC/PPy/PPy(Ox)/PPy. The electrocatalytic activity towards oxygen reduction (orr) was found to be highly dependent on the electrochemical properties of PPy. The oxygen reduction reaction proceeds at the oxide layer while the polymer is accounted for charge transportation. As electrochemical behaviour is highly susceptible to the anionic dopant used, samples doped with different small size anions (Cl-, ClO4-, PF6-, NO3-, SO42-) were analyzed by cyclic voltammetry. Highest redox activity was registered by chlorate doped PPy in agreement with conductivity measurements and absorption spectra which showed the effect of the doping agent by a hypsochromic shift of max from 419 nm (Cl-) to 404 nm (SO42-). Similar composite type of electrodes was developed by Singh et al. [47] using CoFe2O4 nanoparticles resulting in a desirable electrocatalytic response.

Bufon et al. [48] undertook the study of voltammetric cycling in relation to the polymeric chain length and conductivity. Two different PPy entities are identified as a function of temperature and applied potential. Shorter chains and higher conductivity are assigned to PPy II in accordance with disorder dominated transport i.e. delocalization of charge with an increased localization length occuring in shorter chains. Thus, chain length is not considered primarily relevant for assessing CPs conductivity. PPy II it is the species produced when lower temperature or potential are employed during polymerization and it readily transforms into PPy I during CV. The two types of PPy were clearly distinguished both in cyclic voltammetry and optical absorption analysis. In voltammetric cycling, an oxidation peak at -0.12 V

is assigned to PPy II, while the peak at +0.1 V relates to PPy I oxidation. Similarly, an absorption band at 386 nm corresponds to PPy II, while absorption between 450 and 470 nm is caused by PPy I owing to the significantly longer polymer chain which has higher extinction coefficient. Previously, the fact that the wavenumbers of CPs are scaling linearly to the reverse of the polymerisation degree was determined. Thereby, the longest the polymer chain is, the higher the wavelength at which will absorb light [49].

Hwang et al. [50] investigated the changes in mass and volume of PPy doped with perchlorate upon pH variation. The paramount redox switching property can be not only a measure of applied potential, but also adjustable through pH manipulation. In contact with basic solutions, PPy experiences deterioration due to the attack of hydroxyl ions on the -carbons along with anion expulsion leading to neutral and insulating forms. Contrary, immersion in acidic media recovers, at least partially, the former electric properties of PPy. Quantification of mass and volume changes in the polymer chain when variating the pH was performed using atomic force microscopy and quartz crystal nanobalance. With increasing pH, the mass of the polymer was found to decrease as anion expulsion occurs, while an increasing mass during anion incorporation due to protonation of nitrogen sites within the polymer is noticed during the pH drop. Anion incursion is a slower mechanism than anion discharge.

Kim et al. [51] prepared carbon nanotube/polypyrrole composites with controlled pore size using nanosized silica embedded into CNT during electrodeposition. The composites contained around 80% nanosized polymer and provided facile ion transport at electrode level along with conductivity and higher surface area. Ayad et al. [52] employed PPy as host for entrapping noble metals by chemical synthesis using hydrochloride and ferric chloride. Subsequently, the polymer was de-doped using ammonia and exposed to silver nitrate for reduction of the Ag ions. The silver-PPy composite can be applied for silver detection. Parakhonskiy et al. [53] developed PPy microcontainers by electrochemical synthesis in the presence of a surfactant (-naphataline sulfonic acid) for obtaining polypyrrole shells at the surface of the oxygen bubbles generated during the monomer oxidation. The resulted polymer shells exhibited high redox activity and controllable permeability.

Sharifirad et al. [54] probed PPy as coating against copper corrosion and estimated the

efficacity with potentiodynamic polarization and electrochemical impedance techniques. Three different dopants were tested for the electrodeposition of polypyrrole on copper from aqueous media and the final polymer provided efficient corrosion protection despite being slightly overoxidized as observed from FTIR spectroscopy. Cui et al. [55] devised nanowires consisting of polypyrrole and SnO2 nanoparticles by one-pot chemical oxidation. The SnO2-PPy composites showed high potential for anode materials for lithium-ion batteries due to good electrochemical properties. Madani et al. [56] prepared polypyrrole/cadmium sulfide composites by electropolymerisation in presence of CdS nanoparticles for applications in optoelectronics. Even though a high concentration of nanoparticles leads to increased resistance, electroactivity is still remnant as displayed by cyclic voltammetry. Moreover, electrical impedance indicates increased capacitance and photoconductivity. Arjomandi et al. [57] prepared and characterized polypyrrole and poly(pyrrole-2,6-dimethyl- -cyclodextrin) [P(Py- -DMCD)]. Differences between the two polymers are discussed in respect to their structural and electrochemical properties.

Zhang et al. [58] developed polypyrrole/graphene nanosheets (PPy/GNS) composite electrodes by in situ chemical polymerisation to obtain higher specific capacitance for supercapacitors. Graphene represents a single atomic plane of graphite and the association with polypyrrole leads to high conductivity within a single layer network. FTIR spectroscopy reveals a shift in main peaks upon addition of graphene which is associated which so-called graphene doping of PPy i.e. introduction of GNS groups into the PPy backbone. Concerning the electrochemical properties, cyclic voltammetry and charge-discharge measurements proved good capacitive behaviour. Konwer et al. [59] studied the influence of graphene oxide (GO) in association with polypyrrole for electrode applications. Subsequently, the composites were investigated by UV-Vis and FTIR spectroscopy for identification of structural changes while conductivity and CV attested to enhanced electrochemical characteristics most probably due to extension of conjugated segments within PPy owing to the interaction with GO.

Wang and Yu [60] analyzed the dopant influence on the polaron:bipolaron ratio in PPy synthesized chemically with three different anions: chloride (Cl-), p-toulensulfonate (p-TS-) and anthraquinone-2-sulfonate (AQS-). While the conductivity of CPs is commonly determined by resistance measurements, more insights into their electrical behaviour is to be acquired by analyzing the origin of it i.e. the charged species within the polymer chain. Thus, the present study aims to prove the charge-carrier distribution dependency on the chosen dopant molecule. ESR and Raman spectroscopy techniques were employed for gathering information about paramagnetic and structural behaviour of the samples along with UV-Vis-NIR, FTIR. NIR absorption assigned higher charge mobility according to chosen dopant in the following order Cl- < p-TS- < AQS- in agreement with conductivity measurements. Raman spectra displayed both radical cation and dication bands attesting that bipolarons are prevalent in PPy: AQS- and polarons in PPy: Cl- and PPy: p-TS- which leads to adequate correlation between charge distribution and electrical properties.

Functionalization of PPy was thoroughly addressed by Singh et al. [61] in a review on the characterization and synthesis of polypyrrole composites.

CHARACTERIZATION OF BIOSYNTHESIZED POLYPYRROLE

The current requirement for environmentally friendly pathways towards obtaining technologically important polymers has been widely documented. Though not the scope of the present review, enzymatic or otherwise greener methods for the polymerisation of PPy cannot be overlooked in an attempt gain understanding on spectral and electrochemical properties of the polymer.

Nabid and Entezami [62] synthesized a water-soluble polypyrrole in the presence of horseradish peroxidase (HRP) using sulfonated polystyrene (SPS) as counterion at pH 2. The use of templates in this process was crucial for attaining chain alignment and low pH, both imperative for a qualitative final product. UV-Vis analysis was used for proving a certain redox reversibility of the polymer during adjustment of pH. Adsorption peaks at 440 and 600 nm were used as reference points. Song and Palmore [63] attempted the polymerisation of pyrrole using laccase. The investigation is significant due to its environmental benign character however the process was rather slow in the absence of a redox mediator. They employed 2,2'-azino-bis-(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) diammonium salt as mediating molecule, which is easily oxidized by laccase being able, in turn, to oxidize the pyrrole monomer. In this sense, the synthesis does not take

place through an enzymatic mechanism, but rather through a biocatalytic mediated chemical one. ABTS was incorporated in the polymeric chain as a counterion, found to be in ratio of one to each 5 pyrrole units regardless of its concentration and improved charge transport and mechanical properties of PPy. The use of an enzyme for ABTS regeneration made continuous reaction possible as opposite to electrochemical generation of ABTS cations. Additionally, as the potential necessary for lengthening the polymeric chain decreases, the reaction between laccase and pyrrole multimers becomes thermodynamically more favorable. Cui et al. [64] prepared polypyrrole through a biocatalytic route assembling composites consisting of lactate oxidase – PPy – CNT. UV-Vis spectroscopy revealed the level of oxidation of the polymeric chain according to the polaron/bipolaron model. Absorbance bands at 460 nm and subsequently, at 570 nm are considered proof of polaron charge formation, however the mild oxidation did not lead to the development of bipolaron states. The length of the polymeric chain was considered high according to reported investigations [48]. The hybrid nanocomposites were tested for biosensors for lactate detection. Ramanavicius et al. [65] realized a spectrophotometric study of pyrrole polymerisation oxidized by hydrogen peroxide produced from glucose oxidase (GOx) - glucose reaction and further on, employed the mechanism for detecting the adhesion of oxidoreductases at the electrode surface [66].

Cruz-Silva et al. [67] employed horseradish peroxidase for pyrrole oxidation, but since the monomer is not a usual substrate for the enzyme, a redox mediator was necessary. Elemental and thermogravimetric analysis revealed high similarities with chemically synthesized PPy. Kupriyanovich et al. [68] adopted a similar system and reported an increased conductivity upon addition of sodium polystyrene-4-sulfonate among other dopants. Certainly, under synthesis conditions, infrared spectroscopy displayed vibration band corresponding to carbonyl group i.e. overoxidation of the polymer, which is the case with most enzymatic pathways of polymerisation. Further on, encapsulation of laccase in PPy shells was reported by Mazur et al. [69] by droplet/solution interface synthesis. The microcontainers as studied by visible spectroscopy, revealed increasing absorption peak at 480 nm corresponding to low level of doping. FTIR spectra displayed proof of laccase encapsulation within PPy shells while cyclic voltammetry showed a typical redox system. Bouldin et al. [70] considered

soybean peroxidase (SBP) a more suitable enzyme for pyrrole oxidation and without using a redox mediator, generated a conductive polymer as revealed from conductivity and UV-Vis absorption spectra. However, various template-dopants were tested for improving final properties. Junker et al. [71] performed a study on laccase-induced polymerisation of pyrrole using sodium bis-(2-ethylhexyl) sulfosuccinate anionic vesicles as templates. The process was optimized and the final products characterized by optical, EPR and FTIR spectroscopy indicating a conductive form of PPy. Moreover, MD simulations were performed in order to investigate the regulatory influence of the template within the synthesis.

Regarding environmentally benign routes for pyrrole polymerisation it can be concluded that the genuine enzymatic pathways proceed slowly and they must be improved by addition of redox mediators, oxidative compounds and/or templates. The aqueous media and neutral pH, while suitable for enzymes, promotes the production of low molecular weight oligomers due to the nucleophilic attack of water on the polymer. In turn, a branched structure of the polymer is consistent with loss in electric properties. Nevertheless, most enzymes are not stable at highly acidic pH. However the potential for biomedical applications is indisputable, thus intensive research is being progressively conducted [5].

CONCLUSIONS

By attempting to determine the parameters that govern the equilibrium of charged species within the redox polymers, the aforementioned researchers set the basis for the characterization of conductive polymers. Following their breakthrough, extensive research and improvement has been made. However, the significance of the fundamental concepts is not to be disregarded.

Certainly, the present review could not comprise the amplitude of research conducted within the field, but the main purpose of displaying the evolution in the characterization and application of polypyrrole was fulfilled. Even after decades of investigating conducting polymeric materials, inquiries related to synthesis, reaction mechanisms and dopant influence are still valid. Nevertheless, innovative and promising applications are widely researched.

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