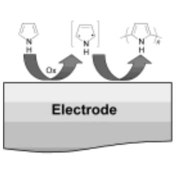

The mechanisms of pyrrole electropolymerization

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Over the past twenty years, polypyrrole has appeared as the most extensively studied conducting polymer. However, despite the volume of work already done in this area, there has been little focus put on the mechanism of polypyrrole synthesis, especially concerning the most efficient method, electropolymerization. Numerous analytical techniques have been used to study polypyrrole electrodeposition and/or doping. However, the mechanism itself is still a controversial subject as there is not one mechanism which is universally accepted. The mechanism proposed by Diaz is the one most commonly referred to in the literature although several other mechanisms are not lacking in support. The controversy lies in the initiation step as each mechanism proposes a different way of beginning the reaction, varying between electron transfer, proton transfer and direct radical pyrrole formation. Without considering the initiation step, there are many other factors including electrolyte, solvent, temperature and pH which can influence the reaction mechanism during the electropolymerization of pyrrole, thus impacting the characteristics of the polymer formed at the electrode.

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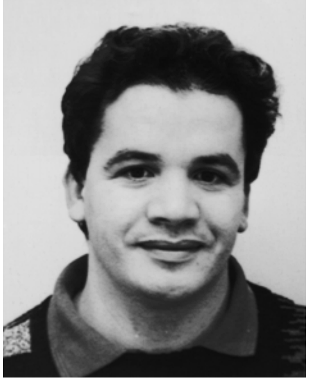
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1 Introduction

Following the first report of electrical conductivity in a conjugated polymer (polyacetylene) in 1977 by Shirakawa, Heeger and MacDiarmid,[1] the field of conducting polymers has attracted the interest of thousands of academic and industrial researchers. The possibility of combining in these new materials the properties of organic polymers and the electronic properties of semiconductors has been the driving force for various applications[2–4] including anti-static and anti-corrosion coatings, sensors, batteries and supercapacitors, and more recently light emitting diodes (LEDs),[5] electrochromic devices[6] and transparent electrode materials.[7] Conducting polymers can be prepared *via* chemical or electrochemical polymerization.[8] The latter is generally preferred because it provides a better control of film thickness and morphology, and cleaner polymers when compared to chemical oxidation. Films of electronically conducting polymers are generally deposited onto a supporting electrode surface by anodic oxidation (electropolymerization) of the corresponding monomer in the presence of an electrolyte solution. Different electrochemical techniques can be used including potentiostatic (constant-potential), galvanostatic (constant current) and potentiodynamic (potential scanning *i.e.* cyclic voltammetry) methods.[9] Electrical conductivity is achieved in the film of conducting polymer by oxidation (p-doping) or reduction (n-doping), followed respectively by the insertion of anionic or cationic species.[9] Due to the double bond alternation in the conjugated polymer backbone, the charged species formed upon doping are able to move along the carbon chain (delocalization) allowing electron transport and thus giving an electronically conductive material.[10]

Among the numerous conducting polymers prepared to date, polypyrrole is by far the most extensively studied. The reasons for this intense focus on polypyrrole certainly lie in the fact that the monomer (pyrrole) is easily oxidized, water soluble and commercially available. Hence, polypyrrole presents several advantages including environmental stability, good redox properties and the ability to give high electrical conductivities.[11–13] As a result of its good intrinsic properties, polypyrrole has proven promising for several applications including batteries, supercapacitors, electrochemical (bio)sensors, conductive textiles and fabrics, mechanical actuators, electromagnetic interference (EMI) shielding, anti-static coatings and drug delivery systems.[12,14] The intrinsic properties of polypyrrole are highly dependent on electropolymerization conditions. Therefore, understanding the different steps, *i.e.* the mechanism involved in the polymer electrodeposition, is of particular importance. With this knowledge, a better control of the properties can be envisioned thus giving polypyrrole films with improved chemical and physical properties.

We present here a condensed review of the different mechanisms proposed to date for pyrrole electropolymerization with an emphasis on the chemical structure of the polymer. It is noteworthy that these mechanisms are complex and still a controversial subject. The problems encountered in the elucidation of the mechanism are mainly caused by the difficulty of following the growth of the species *in situ* at the electrode/solution interface. However, several research groups have overcome these difficulties by coupling electrochemistry and analytical methods including electron paramagnetic resonance (EPR), ellipsometry and quartz crystal microbalance (QCM) enabling them to propose different mechanisms. Other analytical techniques like X-ray photoelectron spectroscopy (XPS), surface electron microscopy (SEM) and atomic force microscopy (AFM) have provided interesting information giving further insight into the pyrrole electropolymerization mechanism. In this review, after an overview of the deposition and characterization techniques, the different mechanisms proposed to date are compared. Finally, the influences of several parameters such as nature of the electrolyte, solvent, pH, temperature and monomer substitution are discussed.

2 Electropolymerization and characterization techniques

2.1 Different techniques

2.1.1 Electropolymerization. In an electrochemical polymerization, the monomer, dissolved in an appropriate solvent containing the desired anionic doping salt, is oxidized at the surface of an electrode by application of an anodic potential (oxidation). The choice of the solvent and electrolyte is of particular importance in electrochemistry since both solvent and electrolyte should be stable at the oxidation potential of the monomer and provide an ionically conductive medium. Organic solvents like acetonitrile or propylene carbonate have very large potential windows,[15] and high relative permittivities, which allow a good dissociation of the electrolyte and thus a good ionic conductivity. Since pyrrole has a relatively low oxidation potential,[12] electropolymerization can be carried out in aqueous electrolytes which is not possible for thiophene or benzene. As a result of the initial oxidation, the radical cation of the monomer is formed and reacts with other monomers present in solution to form oligomeric products and then the polymer. The extended conjugation in the polymer results in a lowering of the oxidation potential compared to the monomer. Therefore, the synthesis and doping of the polymer are generally done simultaneously. The anion is incorporated into the polymer to ensure the electrical neutrality of the film and, at the end of the reaction, a polymeric film of controllable thickness is formed at the anode. The anode can be made of a variety of materials including platinum, gold, glassy carbon, and tin or indium–tin oxide (ITO) coated glass.[10] The electropolymerization is generally achieved by potentiostatic (constant potential) or galvanostatic (constant current) methods. These techniques are easier to describe quantitatively and have been therefore commonly utilized to investigate the nucleation mechanism and the macroscopic growth. Potentiodynamic techniques such as cyclic voltammetry correspond to a repetitive triangular potential waveform applied at the surface of the electrode. The latter method has been mainly used to obtain qualitative information about the redox processes involved in the early stages of the polymerization reaction, and to examine the electrochemical behavior of the polymer film after electrodeposition.[10]

2.2 Characterization methods

2.2.1 Electrochemical methods. Cyclic voltammetry is very often used to characterize conducting polymer films. This is the method of choice for studying the reversibility of electron transfer because the oxidation and reduction can be monitored in the form of a current–potential diagram.[16] Intermediate species of very short lifetimes can be observed with microelectrodes using high scanning speeds.[17] These intermediate species (radical cations) are extremely important for the understanding of the polymerization mechanism. Another electrochemical technique, coulometry, measures the amount of electricity involved in the oxidation process. The knowledge of the initial charge used to polymerize the monomer, and the charge involved in the doping process allows the estimation of the doping level in the conducting polymer which is usually between 0.200 and 0.33 for polypyrrole.[12]

Chronoamperometry, *i.e.* measuring the current as a function of time, is a method of choice to study the kinetics of polymerization and especially the first steps.[10] Impedance spectroscopy is a more advanced and very powerful method which allows the investigation of the electron transport, the electronic resistance (electron transfer) and the ionic conductivity and enables the measurement of film porosity in the polymer. Note that the interpretation of impedance spectroscopy results is based on equivalent circuits, which are compatible with a variety of different physical and theoretical models.[18]

Rotating ring–disk electrode (RRDE) voltammetry provides for the quantitative, *in situ* measurement of ion transport between solution and conducting polymer films.[19] Cation flux in and out of the polymer can be obtained from the mass-transport-limited reduction current for the dopant cation(s) measured at the ring during redox cycling of the polymer. Note that there are some limitations to this method because it requires the use of a supporting electrolyte in order to eliminate migration effects. However, this electrolyte must be sterically inhibited from passing into the film, *i.e.* participating in polymer doping. In addition the dopant ion must be electrochemically inactive over the entire potential range applied to the polymer, and must give mass-transport-limited voltammetry at the ring within the solvent window.

2.2.2 Other analytical techniques. Numerous analytical techniques have been employed for the *in situ* monitoring of the electrodeposition and/or doping of conducting polymers. Among them, electrochemical quartz crystal microbalance (EQCM) has been widely used for the study of electrochemical systems.[20] The linear relation between the mass accumulated on the electrode and the changes in quartz oscillator frequency allows the study of the electrochemical processes involving mass changes. With this technique, the mass changes induced by the ion influx/efflux can be correlated to the change in polymer oxidation state monitored by cyclic voltammetry or coulometry.[21,22] EQCM is a very sensitive method for the *in situ* investigation of the incorporation of counterions. However, it suffers from a lack of selectivity in identifying specific dopants and in differentiating solvent molecules from ions.[23] Therefore, new methods have been developed to monitor exclusively the dopant ions. Luminescence is selective and sensitive but requires counterions such as pyrenesulfonate and naphthalenesulfonate which are fluorescent and electrochemically stable over the potential window of the polymer.[24,25] The use of these luminescence probes allows the measurement of the diffusion coefficients of the counterions. Positively charged luminescent probes like $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridyl) can also be used to study the influence of cation transport.

Another original *in situ* method, scanning electrochemical microscopy (SCEM), providing information about oxidation and reduction of conducting polymers has been used for polypyrrole.[23] The responses of a polypyrrole (PPy) modified electrode, and an ultramicroelectrode tip positioned close to the PPy surface are simultaneously monitored during cyclic voltammetry or coulometry experiments. The rate of ejection of anions (bromide or ferrocyanide) during PPy reduction was found to be dependent on the reduction potential. Direct evidence of cation incorporation was also obtained and the nature of the cation was identified as an important factor. SCEM has also been used as an *in situ* probe of thickness and morphological changes at the interface between a polymer-coated electrode and the solution.[26]

Ellipsometry is a technique which involves the measurement of the change in the state of polarization of an incident light beam after reflection from a surface.[27] The polarization state changes are usually described by two parameters, the ellipsometric angles Ψ and Δ. Note that these experimental parameters do not have a direct physical interpretation and therefore do not give direct information about the processes in conducting polymer films. However, they provide a good overview of the general behavior of the system and can serve as a basis for obtaining the physicochemical properties of the film by assuming a model behavior.[27,28] Kim *et al.* have extensively employed this technique to study the mechanism of pyrrole electropolymerization by following ellipsometric data as a function of time during the growth on a gold electrode.[29] Note also that Christensen and Hamnett have investigated the growth, cycling and overoxidation of PPy in aqueous solutions by ellipsometry and FT-IR. In particular, a decrease of the thickness has been observed upon oxidation which is explained by the electrostriction associated with the formation of dications (bipolarons).[30] In addition, overoxidation of PPy was found to produce pyrrolinones, thereby decreasing the conjugation length and inducing an expansion of the film stemming from an influx of solvent into the film. An electrochemical reaction occurring at the electrode/solution interface induces changes in the refractive index of the electrolyte which can be detected either by interferometry or by probe beam deflection (PBD).[31] The ‘mirage’ deflection stems from the appearance of a temperature and a concentration gradient in the electrolyte.[32] In the case of conducting polymers, the concentration gradient is induced, for example, by the expulsion of ions from the polymer film into the solution.[33,34] This technique can be employed to monitor the response of a polymer film to various electrochemical stimuli including potential steps or ac perturbation.

In situ Raman spectroscopy has been used to investigate the structure and doping mechanism of several conducting polymers including PPy.[35] Note that Raman and FT-IR spectroscopy are generally *ex situ* techniques for the characterization of conducting polymers.[36] The structural information obtained can be correlated to the conjugation length in the conjugated polymer and therefore to the electrical conductivity. Basically, any spectroscopic technique can be utilized for *in situ* measurements in an electrochemical cell (spectroelectrochemistry) and many techniques have proven useful for the study of the electrogenerated species including UV–visible–near-infrared (UV–VIS–NIR) spectroscopy, electron paramagnetic resonance (EPR), Raman and FT-IR spectroscopy.[9]

In the early stages of the discovery of PPy, the fact that α,α′ substituted pyrrole was not polymerizing led to the conclusion that polymerization was occurring *via* α bonding.[37] X-Ray photoelectron spectroscopy (XPS), which allows the analysis of chemical composition in the near-surface region of a solid sample, demonstrated the presence of a significant amount of α,β bonding between pyrrole units.[38] This fact was further supported by the XPS results obtained from poly(3,4-dimethylpyrrole) where the polymerization can only occur *via* α bonding.

Atomic force microscopy (AFM) has also proven useful for the determination of surface properties of PPy.[39] Surface morphology has a great impact on the kinetics of doping–undoping processes and on the electrochemical responses. The influence of dopant nature and film thickness on the roughness of PPy films has been studied *ex situ* by AFM.[40,41] More recently, AFM has been used *in situ* to investigate the morphology and thickness changes of PPy films during growth and oxidation/reduction processes.[42,43] Note that the variations of surface morphology and swelling/contraction of PPy films have also been investigated by *in situ* STM during the doping–dedoping processes.[44]

Other methods of investigation include radioisotopic labeling[45] for monitoring ion fluxes at the film/solution interface, and *in situ* electrical conductivity for studying the doping level in the polymer.[46] Note also that some attempts have been made to assess the molecular weight of electrodeposited PPy. For instance, the electropolymerization of α,α′-tritium labelled β,β′-dimethylpyrrole and further comparison of the amount of tritium in the polymer and monomer indicated a degree of polymerization of 100 to 1000 pyrrole units.[47]

3 Polypyrrole mechanism

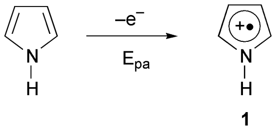
The electropolymerization mechanism is a controversial subject as there have been a number of mechanisms proposed to date. One of the principal difficulties encountered in the determination of the different stages of reaction is the rapidity of the polymerization. In addition, the insolubility of the polypyrrole coupled with its non-crystalline nature makes structure characterization and analysis of physical properties exceedingly difficult. As a result, there has not been unanimous agreement among researchers concerning this mechanism.

3.1 Diaz's mechanism

The mechanism described by Diaz and his colleagues[48,49] is the mechanism encountered most often in the literature. Waltman and Bargon[50,51] have confirmed this mechanism by theoretical studies based on the correlation between the reactivity and the unpaired electron density of the radical cations.

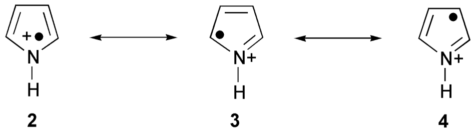
3.1.1 The different stages of reaction. This mechanism begins by electron transfer (E) followed by a succession of chemical reactions (C) and electron transfer reactions. The term $E(CE)_n$ which is an extension of the term ECE is often used to describe all the reactions involved in the formation of the film.[10] This mechanism can be described by the following stepwise reactions:

Step 1: This step implies the oxidation of monomer R at the surface of the electrode to form the cation radical $R^{+\bullet}$ (**1**), as shown in Scheme 1.



Scheme 1

The several resonance forms of this cation are represented in Scheme 2.

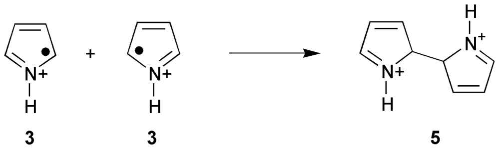


Scheme 2

Because the monomer is oxidized to $R^{+\bullet}$, the electron transfer reaction is faster than the diffusion of R in the solution at the electrode surface. As a result, at the applied potential, the monomeric molecules near the electrode find themselves in their oxidized state $R^{+\bullet}$. This results in a high concentration of $R^{+\bullet}$ maintained by the continual diffusion of R towards the electrode. These monomeric radical cations can undergo different reactions depending on their reactivity:

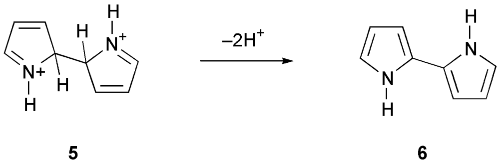
- When $R^{+\bullet}$ is relatively stable, it can diffuse into the solution and react to form soluble products with low molecular weights.
- When $R^{+\bullet}$ is very unstable, it can react rapidly near the electrode with the solvent or the anion also forming soluble products of low molecular weight.
- Between these two extremes, $R^{+\bullet}$ can also undergo dimerization reactions.

Step 2: This radical cation $R^{+\bullet}$, having a greater unpaired electron density in the α-position dimerizes *via* the resonance form **3,** as shown in Scheme 3. The coupling between two radicals results in the formation of a bond between their α-positions and the formation of the dihydromer dication **5**.



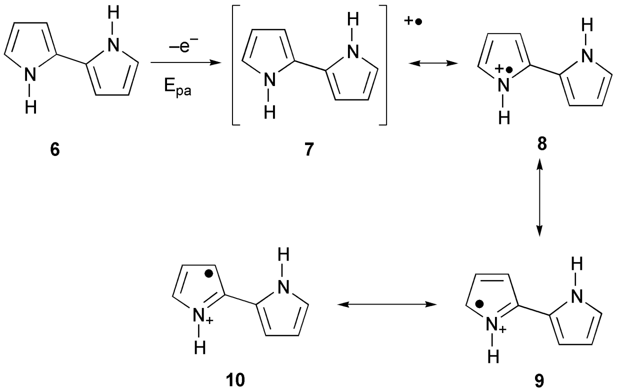
Scheme 3

Step 3: The loss of two protons forms the aromatic dimer **6** (stabilization step) shown in Scheme 4.



Scheme 4

Step 4: The polymerization reaction follows the oxidation of the dimer **6** (see Scheme 5) into the cation radical **7**. Since the unpaired electron is now delocalized over the two rings, the oxidation potential of **6** is lower than the oxidation potential of the monomer. The dimer **6** is therefore more easily oxidized at the applied potential which is the oxidation potential of the monomer. Another consequence of this stabilization is that the dimer radical cation becomes less reactive than the monomer. The positions 5-5′ are equally the most reactive areas and the resonance form **9** is predominant with respect to the other forms.

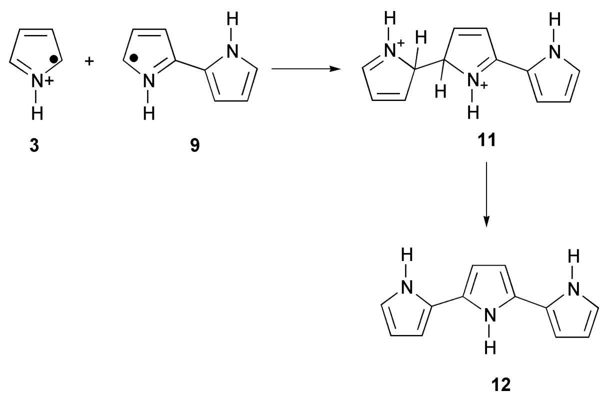


Scheme 5

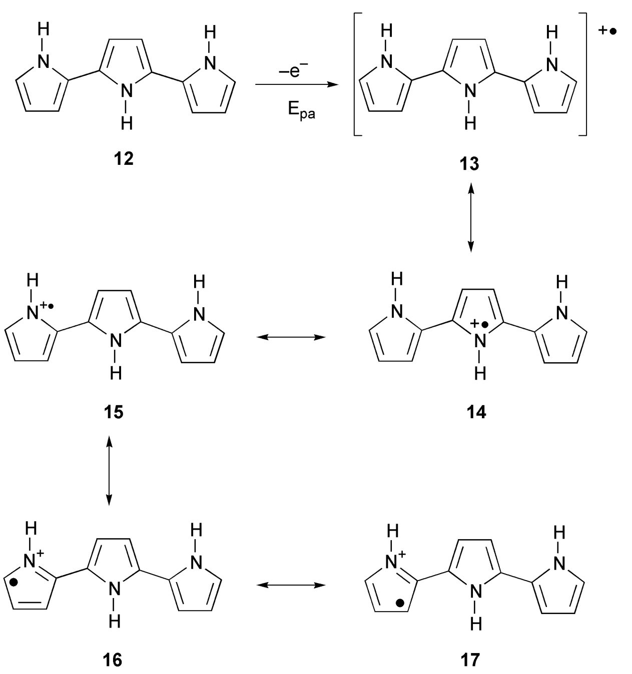
Step 5: The resonance form **9** reacts by position 5 or 5′ with a monomer radical cation **3** to form the trimer dication **11** that deprotonates to give the neutral trimer **12**, as shown in Scheme 6.

Step 6: The electro-oxidation of **12** gives the radical cation **13** (see Scheme 7).

The trimer 5-5′ (α-position) and 3-3′ (β-position) positions can undergo coupling reactions with the following oligomers even if the β-positions are sterically inaccessible. The α-coupling will predominate. However, the oligomer chain, as well as the delocalization of the unpaired electron, increases progressively and the α-coupling will no longer be the only coupling possible. The longer the chain length the higher the number of β-bonds formed. By using XPS, Street has shown



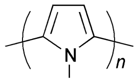
Scheme 6



Scheme 7

that one pyrrole unit in three is affected by the structural disorder.[38,52,53] These β-couplings are responsible for the poor crystallinity of PPy. Poly(3,4-dimethylpyrrole), which can only form α-couplings because the β-positions are blocked, does indeed show improved crystallinity.

Step 7: The propagation continues *via* the same sequence: oxidation, coupling, deprotonation until the final polymer product is obtained (see Scheme 8).

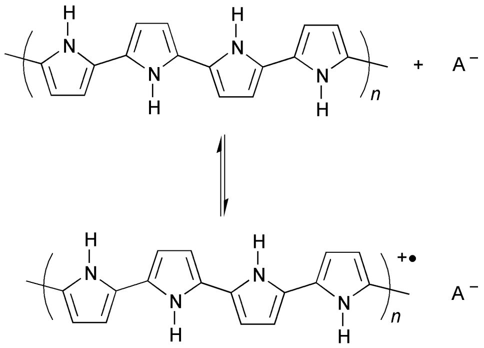


Scheme 8

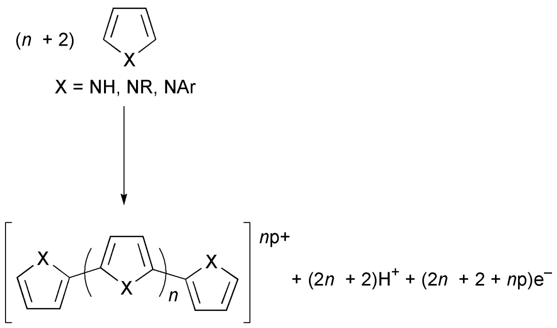
Step 8: The electropolymerization does not give the neutral non-conducting polypyrrole but its oxidized conducting form (doped). Actually, the final polymer chain carries a positive charge every 3 to 4 pyrrole units, which is counter-balanced by an anion. The structure of the doped polymer is presented in Scheme 9 where A is the electrolyte anion.

The films obtained consist of about 65% polymer and 35% anion (% in weight). The global polymerization reaction can be summarized by the equation presented in Scheme 10.

The different reactions of the film formation are often followed by stoichiometric determination of the number of electrons donated by each molecule. This value is generally found to be between 2 and 2.7 where 2 electrons serve in the film formation and the excess charge is consumed by the polymer oxidation. This number is normally in agreement with the number of anions found in the polymer by elementary analysis.



Scheme 9



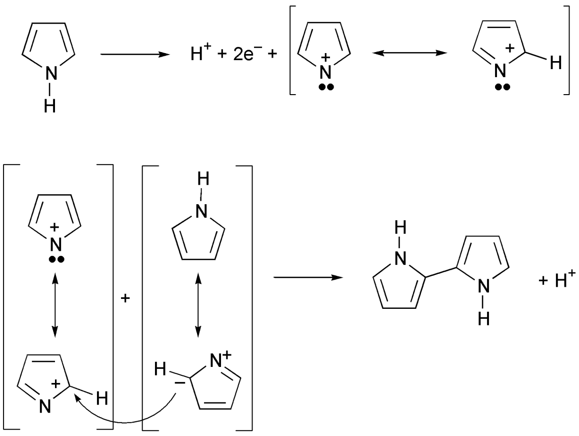
Scheme 10

There are several reasons why this mechanism is believed to be the best one representing this reaction. In the first place, this mechanism is in accord with EPR (Electron Paramagnetic Resonance) observations that show the existence of a π-type radical.[52] In addition, the elimination of H from the α-position indicated by this mechanism is in agreement with the observed drop in pH of the solution during polymerization. This mechanism is also in agreement with the number of electrons consumed during the reaction which has been determined to be 2.25 to 2.33 for pyrrole. Chronoabsorption studies have shown that the film grows linearly with respect to t and not to $t^{1/2}$. This observation shows that the rate-determining step during film growth is a coupling process and not the monomer diffusion towards the electrode.[49]

3.2 Kim's mechanism

K. J. Kim *et al.* have proposed another mechanism, shown in Scheme 11, where polymerization is initiated by the loss of two electrons and a proton from a pyrrole molecule forming the active intermediate Py^+.[54] This intermediate is dimerized by a neutral pyrrole molecule and the loss of a second proton. The polymer chain is further extended by the same procedure (loss of 2 electrons and coupling). A multilayer model has been proposed by Kim supported by a thorough ellipsometric study.[29] The polymer is deposited in three stages:

1. In the first part of the reaction, monomer absorption occurs.
2. The simultaneous formation of a dense electropolymerized polymer from the bidimensionally absorbed monomer and the nucleation of low molecular weight polypyrrole molecules in solution.



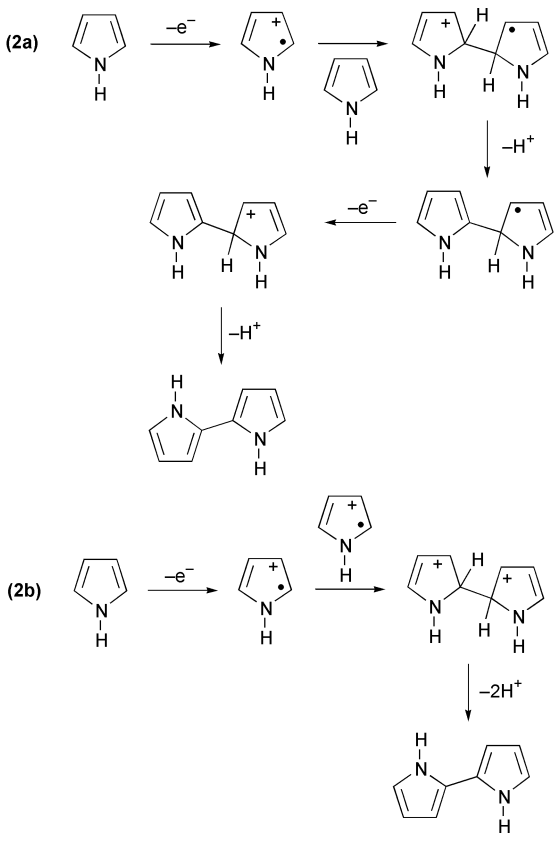
Scheme 11

3. Tridimensional growth layer by layer. Monomer oxidation occurs more easily on the polymer than on the electrode as described by Pletcher.[55]

Note that another interpretation was given by Pei *et al.* for the initial stage of electropolymerization which was found to occur in solution followed by polymer precipitation.[56]

3.3 Pletcher's mechanism

Pletcher *et al.* have proposed yet another mechanism in which the cation radical formed by the loss of an electron reacts directly with a neutral molecule giving a cation dimer.[55] The cation dimer then loses a second electron and 2 protons forming the neutral dimer. Satoh *et al.* have studied this coupling mechanism by comparing it to the classical coupling between two cation radicals.[19] They explained their experimental results by the coupling between a monomer molecule and a cation radical which corresponds to an aromatic substitution reaction of an electrophile as shown in Scheme 12.



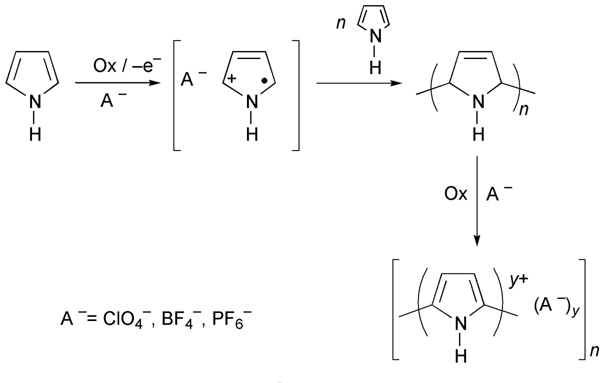
Scheme 12

Thus, this coupling reaction (**a**) and the resulting polymerization are affected by the monomer concentration. In addition, the amount of polymerization current obtained depends on the pyrrole concentration.[57] However, the conclusion formed by Satoh concerning the coupling reaction has been challenged by Takakubo who demonstrated by molecular orbital calculations that the addition of a cation radical to a neutral molecule is symmetry forbidden and thus requires a high activation energy.[58]

3.4 Reynolds' mechanism

Reynolds *et al.* have studied the polymerization of pyrrole by EQCM in various aqueous electrolyte solutions.[59] Under specific conditions in the presence of ClO_4^-, BF_4^- and PF_6^- electrolytes, three stages are observed during the polymerization process where the number of electrons involved (n) is different. The first and the second stages give n values of 1.60 and 0.12 respectively, whereas the third stage gives an n value of 2.50. This last n value is the one observed in the classical mechanism and so this last stage is representative of Diaz's mechanism. To explain the low n numbers and high rates of polymerization in the first two stages, an electrochemically initiated chain polymerization mechanism was proposed which starts the formation of the PPy film.[59] This chain polymerization process is predominant with respect to the radical cation coupling during the first two stages of the reaction.

The reaction, presented in Scheme 13, is initiated by the generation of monomer radical cations at the surface of the electrode followed by a rapid growth of the chain and by a low n value. The obtained non-conjugated polymer becomes conjugated and takes on the doped polypyrrole form by oxidation at the electrode. Note that this mechanism is only valid in aqueous solution and in the presence of the electrolytes cited above. As explained by the authors, the strong interaction between the solvent (H_2O) and the radical cations, and the anion's ability to activate the initiation step enable this type of mechanism. The polymers obtained by this mechanism have the capacity to transport cations and anions during electrochemical switching between the different redox states, unlike the polymers synthesized by radical cation coupling which are only capable of transporting the anions.

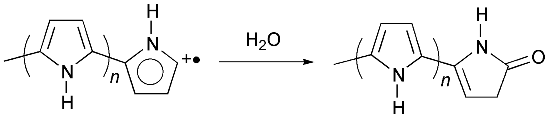


Scheme 13

3.5 Other steps in the mechanism

3.5.1 Different termination reactions. The final step in polymerization is not clear and different hypotheses have been proposed. Diaz believes that the reaction with water, shown in Scheme 14, could be one of the reactions that quenches the polymerization.

In contrast, Street[52] believes that the growth of the chain stops because the chain radical cation becomes relatively

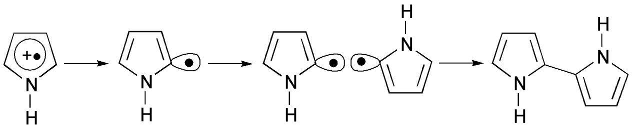


Scheme 14

unreactive towards chain propagation or because the reactive chain ends become blocked sterically.

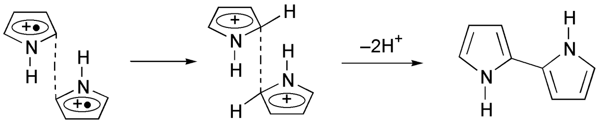
3.5.2 Other coupling steps. Tanaka *et al.*[60,61] have carried out a theoretical study of the polymerization and in particular the coupling process between two radical cation monomers. They have envisioned two possible routes involving on the one hand a σ-radical and on the other a π-radical.

Step 1: The α-hydrogen is abstracted from the radical cation monomer, as shown in Scheme 15. Following this, the two radicals couple to form a neutral dimer. In this case, it is the σ-radical responsible for the coupling reaction.



Scheme 15

Step 2: Diaz uses the π-radical to explain the coupling mechanism. Two π-radical cation monomers couple to form a dimer precursor. The dimer itself is then formed by the elimination of two protons, as shown in Scheme 16.



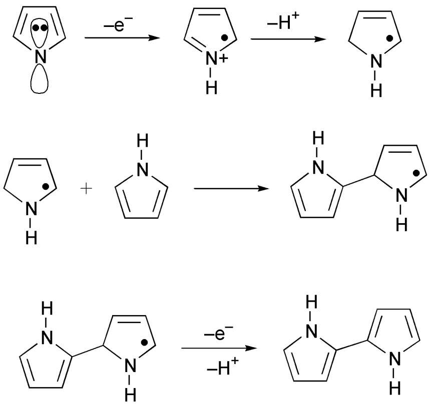
Scheme 16

The proton elimination from the radical cation by either route **a** or **b** is believed to be carried out by the solvent molecules. Tanaka's work has demonstrated that the σ-radical couples without an energy barrier but that the proton elimination induces a destabilization of the formed radicals.[61] The rate determining step of the reaction is the proton elimination. The precursor formed by the coupling of the two-cation radicals (route **b**) is relatively stable. This route is accompanied by an energy barrier because of the charge repulsion between the two positively charged radical cations. By this route, the rate-determining step will be the coupling reaction.

Tanaka has also shown by EPR that no σ-radicals were produced by this reaction. This piece of evidence suggests that the polymerization follows route **b**. The work performed by Waltman and Bargon[51] supports this result. Thus, the coupling occurs between two π-radicals.

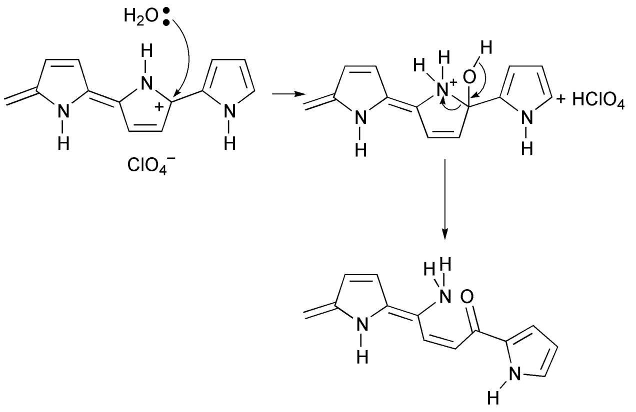
Lowen and Van Dyke have suggested that a change in hybridization could occur before the coupling which forms the σ-radical.[62] The proposed mechanism, presented in Scheme 17, begins with the formation of a radical cation at the electrode. This radical cation loses a proton and then reacts with a neutral monomer molecule. A dimer is obtained after oxidation and loss of a second proton which is available for re-oxidation and polymerization reaction.

Lowen and Van Dyke have tried to compare this mechanism to that of Diaz by studying the isotopic effect on the reaction kinetics.[62] They confirmed that it is a radical mechanism and not a cationic mechanism. They concluded that the proton loss was not the rate-determining step because they did not observe an isotopic effect on the reaction rate. This mechanism is either monomer oxidation or radical coupling in the case of the classical mechanism or radical propagation for the other mechanism. There are a number of observations which have driven them to prefer the classical mechanism.



Scheme 17

3.5.3 Secondary reactions. A number of secondary reactions taking place at the electrode/solution interface have been proposed by Otero *et al.* based on observations they made during a kinetic study of polypyrrole synthesis in the presence of perchlorate.[63,64] The importance of each proposed reaction depends on the chemical conditions and the electrochemical synthesis. The reaction with water[65] is presented in Scheme 18.



Scheme 18

In the first part of the reaction, competition between soluble oligomer formation and the nucleation process has often been observed.[66] These soluble products can react with the cation radicals at the surface of the electrode because they are more easily oxidized than the monomer. These products affect the structure and properties of the resulting polymer.

3.6 Film surface morphology

Experimental variables such as dopant, solvent and applied potential, which will be discussed in detail in the next section, are known to have a strong influence on morphology.[67] Several authors have studied the relationships between these variables and morphology because the latter greatly affects the mechanical and electrical properties of the film. Gaining a better understanding of these relationships would provide for a means of controlling and improving the properties of PPy. In the past five years, AFM has proven especially useful for the study of PPy morphology. Compton *et al.* have examined the influence of the dopant on the roughness characteristics of PPy films.[40] Surface roughness was found to increase with thickness for chloride-doped and sulfate-doped films, whereas a decrease was observed in the case of perchlorate. For thicknesses below 1000 nm, the AFM results indicated a globular-shaped surface with little influence of the dopant nature. For thicker films, chloride-doped and perchlorate-doped films have 'cauliflower' structures. An interesting point is that mainly two types of globules with different heights were noticed on the film surface and were found to be independent of film thickness and dopant nature. Miles *et al.* have investigated the formation of wrinkles on PPy surfaces using *in situ* AFM.[68] Since electronic applications require extremely smooth surfaces, the presence of defects such as wrinkles may cause interfacial problems. The wrinkles were found to be associated with the growth on ITO surfaces and are not an artifact of the handling process. These wrinkles are apparently uniquely associated with growth on porous substrates.

4 Factors affecting the electropolymerization

4.1 Monomer substitution

In a classical electropolymerization, monomers are continually oxidized while the electroactive polymer film forms at the electrode surface. Since the oxidation of the monomer occurs at a higher potential than that of the redox processes of the polymer, side reactions including crosslinking and/or over-oxidation of the polymer could take place. One disadvantage of pyrrole is the presence of available sites for coupling in the β-positions. Waltman *et al.* has shown by using theoretical calculations that the ability to distinguish between the α- and β-positions decreases as the conjugation increases for pyrrole oligomers.[69] β-Coupling leads to a conjugation break along the polymer backbone which results in an increase of the observed band gap and a decrease in conductivity. Cross *et al.*[70] have shown that the α-disubstituted monomers yield only soluble products while the α-monosubstituted monomers can give a low molecular weight polymer where β-bonding is certainly present. Substitution in the β-position prevents the β-couplings and causes an increase in the crystallinity of the polymer. However, the steric effect of β-substitution cannot be ignored. For instance, 3,4-dimethylpyrrole produces polymers with lower conductivities and lower mean conjugation length relative to pyrrole.[71] However, the substituents in position 3- or 4- of the pyrrole ring can also affect the electron density of the heterocycle. Merz *et al.* studied the effect of substitution in the 3,4-dimethoxypyrrole and showed that the electron donating effect of the methoxy groups results in a 350 mV decrease of the monomer oxidation potential. Thus, polymerization occurs exclusively through the α-positions and is likely to proceed without crosslinking and over-oxidation of the deposited polymer because of the lower potential required for the electropolymerization.[72] In order to substitute both the 3,4-positions while avoiding steric interactions between repeat units of the polymer, Reynolds *et al.* have studied the electropolymerization of 3,4-alkylenedioxypyrrole monomers.[73,74] The resulting polymers exhibit a lower band gap (2.0 to 2.2 eV) and a lower half-wave oxidation potential (*ca.* -0.3 V *vs.* SCE) compared to polypyrrole. This low half-wave oxidation potential is of particular interest for biological applications since these new polymers, which are water compatible, are not reduced by strong biological reductants such as 1,4-dithiothreitol.[73] Poly(3,4-alkylenedioxypyrrole)s have also demonstrated interesting properties as electrochromic materials, switching rapidly from a red or orange neutral state to a light blue-gray doped state.[74] Substitution by halogen atoms in the 3,4-positions was found to result in a higher doping level compared to pyrrole.[75] This phenomenon is due to the greater charge delocalization in the polyhalopyrroles because of the mesomeric effect of the halogen atoms.

N-Substituted pyrroles are known to exhibit a conductivity three orders of magnitude lower than that of PPy as demonstrated by Diaz and coworkers for poly(*N*-methylpyrrole).[71] These results were further confirmed by monitoring the conductivity of poly(3,4-dimethoxy-*N*-methylpyrrole) which was found to be three orders of magnitude lower than that of poly(3,4-dimethoxypyrrole).[72] The larger the substituent on the nitrogen atom, the greater the steric interaction between repeat units, and subsequently the lower the conductivity. This drop in conductivity is due to the fact that the pyrrole units are not totally coplanar in the polymer, as demonstrated by the X-ray studies performed by Street on the α,α-substituted tetramer of *N*-methylpyrrole.[52] The influence of *N*-substitution on the electropolymerization characteristics was examined by Waltman *et al.*[50] The polymer yield and the rate of oxidation were found to decrease as the size of the alkyl group increases. Bonding large substituents to the nitrogen atom or to the β-carbon stabilizes the cation radical without stopping the polymerization.[17] If this intermediate is too stable it can diffuse into the solution and form soluble products. As a result, the yield and the molecular weight of the polymer will be low. It should also be noted that some specific *N*-substituents inhibit the polymerization because of their basicity, as observed for *N*-pyrrolidic pyrrole.[70]

4.2 Effect of the electrolyte

One important parameter affecting the physical characteristics and morphology of PPy is the nature and the concentration of the dopant that represents about 30% of the weight of the polymer film. The choice of an electrolyte is made by considering its solubility and its nucleophilicity. Moreover, the anion oxidation potential should be higher than the monomer. The dopant can be organic or inorganic and can be of varying sizes (from chloride to polystyrenesulfonate). The size of the anion controls the microstructure and the porosity of the polymer. Indeed, this determines the ability of the polymer to undergo an easier diffusion of the dopants during the redox process.[76] The nature of the anion has an impact on the quality of the film produced which depends on the hydrophobic character of the anion, and the interactions between the polymer and the dopant. For instance, Kassim *et al.*[77] have shown that in aqueous solution, the utilization of a large aromatic sulfate anion (surfactant in nature) gives stable conducting polymers with better mechanical properties than when a perchlorate anion is used. Because of their hydrophobic interaction with water, one of the roles played by these organic anions is to orient the polymer chain parallel to the electrode surface. This chain orientation increases the order in the polymer structure.[78] Kuwabata *et al.*[79] have shown by studying a series of carboxylate anions that the basicity of the anion plays a role in polymer growth. The higher the basicity of the anion, the lower the conductivity of the polymer. This phenomenon is due to an increase in the interactions between the positive charges of the polymer and the anions. Conversely, anion acidity leads to an increase in the conductivity of PPy.[78] On the other hand, anion nucleophilicity interferes with the reaction by increasing the formation of soluble products.

The electrolyte concentration is also important although the effect is not entirely understood. The polymers of the highest conductivity are produced when elevated concentrations of electrolyte are used.[80] For instance, the conductivity and tensile strength of the as-prepared nitrate doped PPy films increased by *ca.* 50–70% when the electrolyte concentration changed from 0.2 to 1 M. Above 1 M, no improvement was observed in the quality of the PPy films.

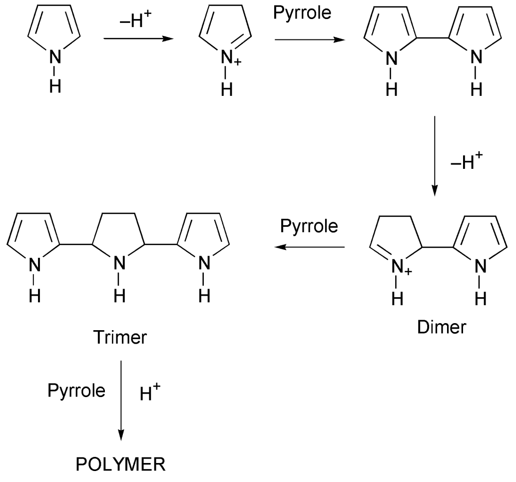
Note that the influence of the cation associated with the anion is not negligible. In fact, the size of the cation (for example tetraalkylammonium) can equally have an influence on the polymer conductivity. It has been found that the larger the cation, the higher the conductivity of the polymer.[81]

4.3 Effect of the solvent

The solvent must minimize the nucleophilic reactions. Aprotic solvents appear to be the best for PPy preparation. Among these solvents, acetonitrile is the most commonly used. Nucleophilic solvents like dimethylformamide or dimethyl sulfoxide do not allow polymer formation to occur unless a protic acid, like *p*-toluenesulfonic acid, is added.[82] In aqueous solution, high salt concentrations are necessary to give a polymer with the desired mechanical and conducting properties. Films prepared in ethanol and in aqueous and aprotic solvent mixtures have intermediate conductivities but good mechanical properties provided that the solutions contain dissociated mineral acids and not nucleophiles. In acetonitrile, the addition of a small quantity of water has a big influence on the kinetics of the reaction and the properties of the polymer formed.[48] This effect is due to the stabilization of the cation radical intermediate by the water molecules which have a larger polarity than acetonitrile.

Imanishi *et al.*[81] have attempted to explain the strong influence of the solvent by drawing attention to its basicity and polarity. Film formation is influenced by the strength of the interactions between the solvent and the cation radicals. The basicity of the solvent is the principal factor affecting the selectivity in polymer formation. On the other hand, the solvent polarity will affect the strength of the interactions between the solvent and the electrolyte anions. Ko *et al.* have studied the morphology and the film properties in aqueous and non-aqueous solution (in the case of acetonitrile).[83] They have found that the films prepared in acetonitrile are more homogeneous and better conductors than polymers prepared in aqueous solution, which are more porous. The polymers prepared in aqueous solution undergo attack by water molecules during reaction which is responsible for their irregular morphology and their weak properties. Unsworth *et al.* have shown that the adsorption of oxygen gas formed during water oxidation is a source of surface defects in the polymer.[84]

Recently, Zhou and Heinze have extensively studied the long debated ‘water effect’ on polypyrrole electropolymerization.[85] In dried acetonitrile, acid catalyzed formation of a pyrrole trimer having a broken conjugation (see Scheme 19) yields a partly conjugated and poorly conductive PPy which passivates the electrode after deposition. The favorable effect of water stems from its stronger basicity than pyrrole and therefore its ability to capture the protons released during the electropolymerization which prevents the formation of the trimer and thus avoids the passivation of the electrode. Interestingly, other additives including methanol, ethanol and tetrahydrofuran which are more basic than pyrrole but not enough to deprotonate the intermediate radical cations have proved to be as effective as water, as suggested by this mechanism.



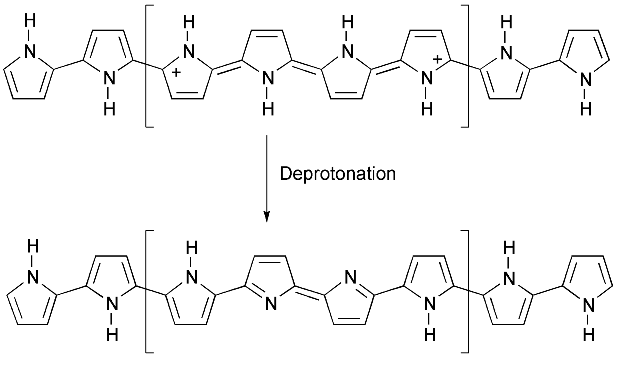
Scheme 19

4.4 Effect of pH

Even though the monomer oxidation potential is independent of the pH, the pH has an influence on the reactivity and stability of the polypyrrole formed at the electrode.[57] In general, protons are produced after each oxidation at the electrode which consequently increases the pH near the electrode. As shown by Unsworth and coworkers,[84] the optimization of the pH results in the formation of a uniform surface with very few defects. The pH which produces the best polymer depends on the species chosen to serve as solution buffers.[86] A low pH or acid solution generally favors polymerization. However, a very low pH will equally be responsible for weak conductivity because of the acid catalyzed formation of nonconjugated trimers which further react to form a partly conjugated PPy or are incorporated into the film, or even diffuse into the solution.[63] This reaction is presented in Scheme 19.

As a result, the films produced exhibit a lower conductivity. It should be noted that the pH also influences the electrochemical activity of the polymer. In acid solution, the insertion and deinsertion of the dopant is observed whereas in basic solution, the anion is replaced by hydroxy groups from the solution. The two phenomena are observed in neutral solution.[87]

The stability of the polypyrrole in aqueous solution depends equally on the pH. Pei and Qian have shown that the polypyrrole can undergo protonation and deprotonation processes.[56] The polymer chain undergoes a deprotonation in basic solution (with a $\mathrm{p}K_\mathrm{a}$ in the order of 9–11) which results in the modification of the electronic structure of the polymer as illustrated in Scheme 20. Conversely, a protonation process is observed in strong acids with a $\mathrm{p}K_\mathrm{a}$ in the range 2–4. Consequently, the conductivity decreases in basic solution ($10\ \mathrm{S\ cm^{-1}}$ at pH < 7 to 0.1 at pH 11).



Scheme 20

The effect of pH on the electropolymerization mechanism has been thoroughly investigated by Zhou and Heinze.[88] The formation of three forms of PPy was noticed by voltammetry. The first form, the regular PPy, is mainly obtained in neutral and weak acidic acetonitrile (1 wt% water added). An unknown structural form of PPy which is characterized by a sharp and more negative oxidation peak in the cyclic voltammogram can be found at low concentration of hydrochloric acid (10^{-5} to 5×10^{-5} M) in acetonitrile. It should be noted that treatment with basic alumina prevents its formation. The third and ill-defined form of PPy is obtained at HCl concentrations above 10^{-4} M and results from the reaction of the trimer described previously. The backbone of this third form contains both pyrrolidine and unsaturated pyrrole rings. The conjugation length and therefore the conductivity of this PPy depend on the amount of trimer formed during the polymerization by acid catalysis. In a solution of high acidity and when a low potential is applied, passivation of the electrode occurs resulting from the deposition of the third form of PPy.

4.5 Effect of the electrochemical method

Otero and DeLarreta have pointed out that the choice of the electrochemical method has an influence on the morphology, appearance and adhesion of the polymer.[89] A non-adhesive dendrite type polymer is formed when a constant current or potential is used. Note that the film obtained is poorly homogeneous and some electrolyte is present between the electrode surface and the polymer. On the other hand, films obtained from the use of alternated polarization are shiny black, very adhesive, and have a smooth and homogeneous surface. Kiani and Mitchell have put forward the hypothesis that these structural improvements come from the larger number of equivalent nucleation sites and the growth process.[90] However, they have shown that these improvements depend on other parameters such as the kind of counter-ion used and the solvent. For example, there is no improvement in film properties synthesized by potentiodynamic methods compared with other methods when SO_4^{2-}, ClO_4^-, BF_4^- are used as counter ions in an organic solvent.

Zhou and Heinze have noticed that the electrochemical method controls the structural form of the electrodeposited PPy.[91] It is well established that classical polypyrrole electropolymerization produces PPy with a single oxidation wave (*ca.* 0.01 V *vs.* Ag/AgCl) followed by a broad plateau. However, cyclic voltammetry of PPy films obtained by galvanostatic synthesis at extremely low current levels shows an additional sharp oxidation peak at a much lower potential (-0.23 V *vs.* Ag/AgCl). This is evidence of the structural diversity of PPy. It should be noted that the experimental conditions have a significant impact on the properties of the resulting polymers and that changing a single variable such as acidity may induce a more profound change in the polymer structure and properties than a change of the applied potential.

4.6 Effect of the temperature

Electropolymerization temperature has a substantial influence on the kinetics of polymerization as well as on the conductivity, redox properties and mechanical characteristics of the films.[12] The average activation energy of the polymerization process on platinum is between 15 and 20 kJ mol^{-1}.[92] It should be noted that a decrease in the redox properties is observed as the temperature increases. In general, higher conductivities are obtained at lower temperatures, both in aqueous[93] and propylene carbonate solutions.[94] For example, films prepared in propylene carbonate solution at -20 °C are much more conducting (300 S cm^{-1}) than those prepared at 20 °C (97 S cm^{-1}).[94] Spectral analysis of the material prepared at the lower temperature shows a more regular structure. At higher temperatures, side-reactions such as solvent discharge and nucleophilic attacks on polymeric radicals cause the formation of more structural defects, resulting in lower conducting films. However, Satoh *et al.* have obtained highly conductive polypyrrole films (500 S cm^{-1}) at 10 °C. This excellent conductivity has been obtained by optimizing both polymerization potential and temperature as both parameters have a great influence on the final properties of the PPy film. Note that on a different substrate like ITO, similar results are observed as PPy conductivity decreases by two orders of magnitude when temperature is increased from 2 °C to 75 °C. However, films prepared at lower temperatures have a more rugged appearance and poorer adhesion than those prepared at higher temperatures.[12]

5 Conclusion

Since the first electropolymerization of pyrrole by Diaz in 1979, many scientists have investigated the influence of experimental parameters like solvent, temperature and pH on the mechanical, morphological and electrical properties of PPy films. Because of its complexity, the mechanism itself has attracted fewer researchers though several interesting models have been presented. Among all the proposed mechanisms, the one proposed by Diaz which features a combination of several successive reactions (radical cation formation, radical coupling, and deprotonation) is certainly the most probable. In fact, the use of advanced *in situ* characterization techniques helped to confirm the first steps of this mechanism. The synthesis and electrochemical study of oligopyrroles have also shed some light on the first steps of the electropolymerization. However, the propagation and termination steps are extremely hard to probe because of the insolubility of the high oligomers and the interfacial character of the electropolymerization. In addition, the strong influence of the experimental conditions renders the study of the complete mechanism an extremely difficult task. Recent studies by *in situ* AFM have demonstrated the direct relationship between the experimental conditions and the morphology of PPy films. Different structural forms with different electrical and redox properties have been observed in PPy films depending mainly on the acidity of the polymerization medium. It is noteworthy that the numerous studies on the influence of the electropolymerization parameters have allowed a better control of the properties which are especially important for the use of PPy in industrial applications.

Chemical modification has appeared recently as a promising route toward obtaining polypyrrole derivatives with enhanced properties. For instance, the recent synthesis of 3,4-alkylenedioxypyrroles (PXDOPs) provided a way to avoid side reactions like β-coupling or over-oxidation due to high potentials. These new polymers have definitely opened new horizons for polypyrrole, especially as electrochromic materials as they can be obtained as highly homogeneous, conductive and electroactive films with colors ranging from orange/red to blue-gray depending on the doping level.

Although several steps of the electropolymerization mechanism of pyrrole are yet to be elucidated, tremendous advances have been made since the first electrosynthesis of PPy which gave rise to the continuing interest that PPy has aroused.

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