In situ FTIR study of redox and overoxidation processes in polypyrrole films

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Dedicated to Professor E. Gileadi on the occasion of his retirement from the University of Tel Aviv and in recognition of his contribution to electrochemistry

Abstract

In situ infrared reflection spectra of thin polypyrrole films electrodeposited on platinum were obtained in aqueous KNO₃, KCl and KF solutions, within a wide potential interval ranging from the reduced, insulating state, to the oxidative degradation of the material. These spectra provide information on the molecular changes resulting from the generation of charge carriers (radical cations and dications) in this conjugated heterocyclic system, as well as the irreversible chemical changes accompanying its electrochemical oxidation at very positive potentials. The spectral region between 1000 and 1700 cm⁻¹ contains information on the relative populations of charge defects as a function of potential, and the results confirm that electronic charge transport at moderate potentials is due to formation of radical cations, which oxidize further or recombine to form dications as the potential increases. At more positive potentials the polymer degrades with formation of carbonyl and hydroxyl groups as well as CO₂. The overoxidation process occurs at less positive potential in F⁻ solution due to nucleophilic attack of OH⁻ ions originating from dissociation of the aqueous solvent, as shown by the infrared spectra and previous calorimetric evidence. In the absence of irreversible chemical changes due to overoxidation, the infrared spectra obtained in the different solutions were similar, indicating weak interactions between ions and charge defects in the backbone. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The need for new materials with specific electrical, optical, magnetic or catalytic properties has motivated the study of macromolecular systems, with special emphasis on the relations between molecular structure and specific properties. Self-assembled monolayers [1], spin transition polymers [2], metallo polymers [3] or the various conjugated polymers [4], are examples of advances on the design of molecular structures with novel properties. Conjugated polymers (such as polyaniline, polyacetylene, polypyrrole and polythiophene) have been the most studied of such molecular systems. These may be switched between electrically insulating and conductive states in response to changes in their oxidation states; the nature and behavior of the charge carriers created in the process have been subject of intense scrutiny over more than 15 years.

Conducting polymers show quasi-one-dimensional π electronic structure, charge defects are formed by chemically or electrochemically-induced oxidation. The non-degenerate fundamental state of polypyrrole is characterized by a unique aromatic structure of lower energy than that corresponding to the quinoid structure, which is the molecular arrangement favored upon formation of electronic defects, mainly polarons (radical cations) and bipolarons (dications) [5–7]. Two charge transport mechanisms account for macroscopic conductivity in these materials: charge propagation along one-dimensional conjugated domains, with tunneling across conjugation defects [8–10], and inter-chain charge propagation between localized defects, a three-dimensional electron-hopping mechanism [11–15].
Both are influenced by interaction with counterions, whose sorption and desorption from the films, during overall charging/discharging cycles, are rate-determining [16]. Electronic spin resonance (ESR) [17], [18] and spectrochemical in-situ techniques [19] have provided useful evidence about the conjugation length of polypyrrole chains, changes in the populations of charge defects with potential, the nature of interactions between counter-ions and polymer chains, as well as the kinetics of redox processes [20]. The generally accepted mechanism accounting for conductivity changes in polypyrrole with potential involves two potential-dependent entities, either regarded as a combination of lattice distortion and charge defect moieties (polarons and bipolarons), or as discrete radical cations and dications. The populations of these charge defects may be determined with careful examination of the changes on the optical properties occurring during the insulator–conductor transition.

A previous study of the growth, redox properties and irreversible oxidation of polypyrrole thin films reported the behavior of such charge-carrying moieties with potential, as obtained from the analysis of FT-IR spectra [19]. Infrared signals corresponding to the charge carrying species were identified from correlation of the potential dependent spectra with the corresponding electrochemical behavior. Integration of the band attributed to polaron led to an increase of their population during the initial stages of oxidation, followed by a constant concentration of radical cations throughout the potential range available, extending up to the positive limit of reversible doping. This is inconsistent with data obtained either by electron spin resonance (ESR) by Genoud et al. [17], or with UV–vis in-situ spectroscopy [20] in our laboratory, which indicates decreasing polaron concentrations at potentials more positive than the voltammetric anodic peak, as the bipolaron population increases. Here we provide a detailed analysis of the changes in infrared absorption with potential. Deconvolution of the infrared active vibrational bands of the polymer backbone yields clear evidence of the decreasing concentration of radical cations as the dication charge carrying species are generated upon oxidation, at potentials beyond the voltammetric anodic peak. We further address here the effects of the doping species on the vibrational spectra. As we have found also, using microcalorimetry [21], electrochemical impedance [22] and UV–vis spectroscopy [20], there are no effects on the vibrational spectra in the presence of different dopant anions, unless the dopant agent undergoes chemical reactions; as we show here this is the case of KF solution, where OH⁻ is the doping agent and promotes overoxidation at moderate positive potentials.

2. Experimental

2.1. Electrodeposition of polypyrrole films

Polypyrrole films were deposited onto 10 mm diameter platinum disks, polished previously with successively finer grades of alumina to a mirror finish, from 50 mM pyrrole (Sigma Chemical Co, distilled before use) and 1 M KNO₃ (Riedel de Haën, analytical grade) aqueous solutions, prepared with distilled and ultrafiltered (Nanopure®, 17.4 MΩ resistivity) water. Galvanostatic deposition was carried out from solutions deaerated with oxygen-free argon at 1 mA cm⁻² during the time required to grow films to 0.1 μm thickness, assuming 100% efficiency for the anodic deposition reaction and a charge–thickness ratio of 0.4 C μm⁻¹ cm⁻² [23].

After synthesis, the films were washed with ultrafiltered water and immersed in monomer-free 1 M KNO₃ aqueous solution, where cyclic voltammograms of the polypyrrole electrode were acquired between −0.9 and 0.4 V (SCE) at 100 mV s⁻¹ to verify the quality and reproducibility of the films for subsequent spectroelectrochemical measurements. These were carried out in 1 M aqueous solutions of KNO₃, KCl, KBr and KF. In all cases, the spectroscopic measurements, to be described below, were carried out after obtaining stable cyclic voltammograms in the working solution.

2.2. Spectroelectrochemical measurements

In situ infrared studies were conducted in the thinlinear configuration, pressing the working electrode surface towards a CaF₂ (Harrick) window, fixed with epoxy to an all-glass cell [24]. A platinum ring, surrounding the working electrode, was used as a secondary electrode. A saturated calomel electrode (SCE) located in a different compartment and connected to the main cell through a Luggin capillary was used as the reference; potentials were taken with respect to SCE. The three-electrode system was controlled with an EG&G PAR 273A potentiostat/galvanostat under M270 version 4.00 software. An Equinox IFS-55 (Bruker) spectrometer was used, with a medium band (MIR, 700–6000 cm⁻¹) globar source, a wide band, liquid nitrogen-cooled MCT detector, and a variable angle specular reflectance module (Specac P/N19716). The position of the electrochemical cell was adjusted with a mount driven by micrometers, assembled from one horizontal rotator, two horizontal translators and one vertical translator (Oriel). Maximum intensity at the detector was obtained at angle of incidence of ca. 60°.

A KRS-5 infrared polarizer was placed in the optical path between the electrochemical cell and the detector. The instrument and the optical bench described were continually flushed with air free from moisture, CO₂ (< 2 ppm) and suspended particles (> 0.01 μm), using a Balston 74–5021 NA purge gas generator.
Infrared spectra are displayed as $\Delta R/R = (I_i - I_{\text{ref}})/I_{\text{ref}}$, the ratio of the difference between signals obtained at potentials $E_i$ and $E_{\text{ref}}$ and that obtained at the reference potential $E_{\text{ref}}$. Thus negative bands indicate absorption by species generated as the potential is changed from $E_{\text{ref}}$ to $E_i$. Spectra $I_i$ were obtained by Fourier transformation after averaging 500 interferograms, each acquired in 0.05 s, at 8 cm$^{-1}$ resolution using p-polarized radiation. The signal acquired at $E_{\text{ref}} = -0.8$ V was used as the reference spectrum ($I_{\text{ref}}$); at this potential the polymer is in a reduced, insulating state. Subsequent spectra were obtained at progressively more positive potentials between $-0.7$ and 1.2 V. The subtractively normalized SNIFTIRS spectra thus obtained contain only information of the molecular changes occurring from modification of the oxidation state of the polymer in a potential interval covering both the insulator–conductor transition of polypyrrole as well as its irreversible oxidation.

3. Results and discussion

3.1. The insulator–conductor transition in the reversible redox region

Fig. 1 shows cyclic voltammograms of polypyrrole films in 1 M KNO$_3$ aqueous solution, acquired at 100 mV s$^{-1}$ scan rate in the thin layer configuration used for spectroscopic studies, after exposing the films to various potentials in both regions of reversible and irreversible oxidation. The voltammograms show that the reversible redox transition in the presence of nitrate ions occurs reversibly in the thin layer cell as long as the potential remains below 0.4 V, and that the voltammetric response degrades irreversibly at more positive potentials. External reflection spectra obtained in situ at 0.1 V intervals between $-0.7$ and 0.4 V, subtractively normalized with respect to the spectrum at $-0.8$ V, are shown in Fig. 2 in an extended scale, covering the complete wavenumber range experimentally available, from 7000 to 1000 cm$^{-1}$. As the applied potential becomes more positive, a strong absorption in the background, especially in the 2000–7000 cm$^{-1}$ region, develops. This is related to a low energy electronic transition within the polymer. Indeed, absorption within this region increases markedly and continuously together with the initial stages of polymer oxidation up to $-0.2$ V, i.e. the potential corresponding to the voltammetric anodic peak maximum [25,26].

Spectra obtained in aqueous solutions of different anions were found to be very similar, thus suggesting that the structural changes occurring during generation of charge carriers are independent of the nature of the dopant anions used. This is consistent with previous in-situ UV–vis spectroscopy [20], microcalorimetric [21], and electrochemical impedance [22] studies. Fig. 3 shows the region between 1700 and 1000 cm$^{-1}$ of spectra obtained in KNO$_3$ solution. This is the region of infrared active vibrations (IRAV region) in the polymer backbone, where a number of bands with absorption intensities depending on the oxidation-state of the polymer are observed. These have been associated with changes in the conjugated structure of conducting polymers, resulting from generation of charge defects [5], and have been correlated to charge carriers either em-
Fig. 3. SNIFTIRS spectra of 0.1 mm PPy films in contact with 1 M KNO₃, obtained at 0.1 V intervals between −0.7 and 0.4 V. (a) The ‘IRAV’ region; (b) detail of region between 1110 and 1260 cm⁻¹. E_ref = −0.8 V, p, polarization. The dotted lines represent the baseline correction applied to obtain the absorption peaks shown in Fig. 4.

Fig. 4. Deconvolution of infrared bands observed around 1200 cm⁻¹ (cf. Figs. 2 and 3) into gaussian components, at three values of electrode potential: (a) −0.4 V; (b) 0.0 V and (c) 0.4 V. The dots correspond to experimental data and the dotted lines are results of data fitting.
that of the band at 1186 cm$^{-1}$ increases. At 0.4 V, the positive limit of the reversible oxidation region, the polymer exhibits maximum conductivity and the band at 1186 cm$^{-1}$ clearly dominates. These bands have already been assigned to the polaronic (1222 cm$^{-1}$) and bipolaronic (1186 cm$^{-1}$) species [19].

Fig. 5 shows the area under both gaussian components as a function of electrode potential. The area under each component is proportional to the population of charge carriers and the potential-dependent behavior is in agreement with results obtained from the intensity of electron spin resonance spectra [17,29,30], indicating that the maximum concentration of radical cation species occurs in the vicinity of the voltammetric maximum observed at ca. −0.2 V, decaying at more positive potentials in spite of the continual rise of the conductivity due to the increased concentration of dicationic charge carriers, produced from further oxidation or recombination of radical cations.

Fig. 6 shows for both gaussian components of the spectra at ca. 1200 cm$^{-1}$, the frequencies of maximum intensity as a function of the potential. The 1222 cm$^{-1}$ component is associated with the population of radical cations and its frequency remains practically invariant throughout the potential range studied, covering the reversible redox transition of polypyrrole. The 1186 cm$^{-1}$ component is displaced towards lower wavenumbers as the sample becomes more conducting, particularly at potentials more positive than 0 V where, as observed from Fig. 5, the population of radical cations has decreased considerably and dications turn into majority carriers. It has been postulated [31] that the frequency of IRAV bands characteristic of charge carriers in conducting polymers can be used for the estimation of conjugation lengths in charge defects, the wavenumbers being inversely proportional to the respective lengths. However, the change of wavenumber of maximum intensity amounts to ca. 45 cm$^{-1}$ V$^{-1}$, comparable to values observed for adsorbed species at the electrochemical interphase [32], a response in the case of Ppy, to substantial variations of dipolar moment due to coupling between the charge carrier and the corresponding vibrational mode.

### 3.2. Irreversible degradation of Ppy during overoxidation

Irreversible oxidation of polypyrrole occurs at potentials more positive than +0.4 V versus SCE in all solutions studied here. The results obtained in fluoride solutions deserve special consideration and will be discussed further below. Overoxidation of the polymer causes loss of electroactive capacity, as oxidation at positive potentials interrupts conjugation by formation of hydroxyl and carbonyl species and, eventually, loss of material through formation of CO$_2$. These electrical and chemical changes are indeed detected by SNIFTIRS [33] and IRRAS [34]. In comparison with spectra of PPy in the reduced state, spectra obtained at potentials more positive than 0.4 V show the gradual disappearance of the intense absorption between 4000 and 1700 cm$^{-1}$, as shown in Fig. 7, related to the loss of electroactivity.

![Fig. 5. Area of gaussian components centered at 1222 (○) and 1186 (●) cm$^{-1}$, of infrared spectra ca. 1200 cm$^{-1}$ as a function of potential.](image-url)
Fig. 6. Potential dependence of the frequency of maximum intensity, for the gaussian components at 1222 cm\(^{-1}\) (■) and 1186 cm\(^{-1}\) (●). Error bars represent spectral resolution.

Fig. 7. SNIFTIRS spectra of 0.1 μm PPy films electrodeposited on Pt, immersed in 1 M KNO\(_3\) solution and acquired at potentials between 0.4 and 1.2 V, at 0.1 V intervals. \(E_{\text{ref}} = -0.8\) V, p, polarization of electronic conduction of the film, as conjugation is disrupted by irreversible oxidation of the polymer chains, occurring simultaneously with the rise of bands corresponding to formation of carbonyl groups (1720 cm\(^{-1}\)), and at sufficiently positive potentials, CO\(_2\) (2340 cm\(^{-1}\)) with increasing intensities as the potential increases over the limit of reversible oxidation.

Fig. 8 shows the 1000–2500 cm\(^{-1}\) region of the SNIFTIRS spectra of PPy thin films in aqueous solutions of KNO\(_3\), KCl and KF, recorded at 0.1 V intervals between 0.4 and 1.2 V, with \(E_{\text{ref}} = -0.8\) V; the spectra have been displaced along the vertical axis to facilitate comparisons between different potentials. In the region between 1000 and 2500 cm\(^{-1}\), the changes occurring during overoxidation of polypyrrole were very similar in the various solutions studied. The bands corresponding to formation of carbonyl groups (1720 cm\(^{-1}\)) and CO\(_2\) (2340 cm\(^{-1}\)) are defined clearly with increasing magnitude as the potential becomes more positive.

Due to water absorption, the throughput in the region around 3600 cm\(^{-1}\) is low, leading to the so called ‘ghost loss effect’ [19]. Nevertheless, Fig. 9 shows single beam intensities obtained from Ppy films in F\(^-\) solution at consecutive potentials in the overoxidation region. The intensities are significant at 3600 cm\(^{-1}\), and furthermore, are potential dependent. The differential absorption bands in this region are shown in Fig. 10, the spectra obtained in fluoride solution display a narrow absorption signal, which is not observed in KNO\(_3\) or KCl solutions. This signal is characteristic of free (i.e. non-hydrogen bonded) –O–H.

Prior microcalorimetric studies of polypyrrole anodic doping processes in aqueous solutions of several anions [22] have shown that the enthalpies of doping in the presence of F\(^-\) are considerably higher than those observed in the presence of other anions, possibly due to participation of the solvent in the doping process, given the strong hydration of fluoride ions in aqueous solution. It is well known that in alkaline aqueous solutions polypyrrole easily overoxidizes due to nucleophilic attack of hydroxide ions to the polymer producing 3-hydroxy-pyrrole, and that loss of electroactive capacity due to breakdown of electronic conjugation ensues as further oxidation to pyrrolinone occurs [34]. The distinct behavior of polypyrrole in the presence of F\(^-\) is apparent also from impedance spectra. These have shown that overoxidation commences at ca. 0 V versus SCE, and that at more positive potentials the conductivity decreases [22] as the film becomes electroinactive.

On the basis of these observations, it has been proposed that OH\(^-\), originating from dissociation of the solvent, maintains charge balance during formation of charge carriers in the polymer backbone upon anodic oxidation [21,22]. Nucleophilic attack of hydroxyl ion additionally occurs, as evidenced by the appearance of bands corresponding to CO–H bonds, observed in the presence of fluoride. Additional evidence was obtained observing overoxidation at potentials more positive than 0.4 V versus SCE, using D\(_2\)O as solvent. Spectra obtained in 1 M KF protic and deuterated aqueous solutions at potentials above 0.4 V are shown in Fig. 11.
The band corresponding to stretching of the CO–H bond, observed at 3615 cm$^{-1}$ in H$_2$O, displaces to 2683 cm$^{-1}$ when D$_2$O is used as solvent. The vibration frequency $v$ of the bond is proportional to $(K/\mu)^{1/2}$, where $K$ is the force constant of the oscillator and $\mu$ is the reduced mass at both sides of the bond. The ratio of square roots of reduced masses in deuterated and protic solutions, $[\mu$(CO–H)/\mu$(CO–D)]^{1/2}$ is 1.37, whereas the corresponding isotopic shift determined experimentally from the spectra in Fig. 11 is 1.35. This result provides additional evidence for the incorporation of hydroxyl groups to the polymer during its electrochemical oxidation in fluoride aqueous solutions.

Fig. 8. SNIFTIRS spectra of Ppy in aqueous 1 M KNO$_3$ (a), KCl (b) and KF (c) solutions, obtained at 0.1 V intervals between +0.4 and +1.2 V vs. SCE. $E_{ref} = -0.8$ V. p, polarization.

Fig. 9. Single beam intensities of Ppy in aqueous 1 M KF solutions collected at several overoxidation potentials. Also shown is the single beam intensity obtained at $-0.8$ V, which was taken as the reference signal for the SNIFTIRS spectra shown in Fig. 10. The inset shows the potential dependent intensities in the region between 2500–4500 cm$^{-1}$. p, polarization.
Fig. 10. SNIFTIRS spectra of Ppy in aqueous 1 M \(\text{KNO}_3\) (a), \(\text{KCl}\) (b) and \(\text{KF}\) (c) solutions, obtained at 0.1 V intervals between +0.4 and +1.2 V vs. SCE. \(E_{\text{ref}} = -0.8\) V. p, polarization.

Fig. 11. SNIFTIRS spectra of Ppy in contact with 1M \(\text{KF}\) in (a) \(\text{H}_2\text{O}\) and (b) \(\text{D}_2\text{O}\), acquired at 0.1 V intervals at potentials between +0.4 and 1.2 V vs. SCE. \(E_{\text{ref}} = -0.8\) V. p, polarization.
4. Conclusions

In situ infrared spectroelectrochemistry of redox processes in polypyrrole show that the structural modifications occurring during doping are in general independent of the nature of dopant anions, hence the changes in intensity of the different absorption bands are due only to changes occurring in the polymer backbone during formation of charge carriers upon reversible oxidation, or to the chemical changes accompanying overoxidation. Detailed analysis of the intensity of infrared bands has shown that at potentials beyond that of the voltammetric maximum, the population of radical cations decreases while that of dications continues rising. This has been established from the analysis of data obtained with a variety of experimental techniques, but had not been determined in previous in situ infrared studies of polypyrrole.

Overoxidation of polypyrrole occurs through apparition of C–OH and C=O functional groups in the polymer backbone, as well as formation of CO₂ at sufficiently positive potentials. Formation of these species disrupts the conjugated structure of polypyrrole and leads to loss of electroactive capacity. The infrared spectroscopic study provides further evidence showing that OH⁻ ions, originated from dissociation of the solvent, are the doping agents in F⁻ solution. It also confirms that the onset of overoxidation of polypyrrole occurs at less positive potentials in F⁻ as compared with NO₃⁻ or Cl⁻ solutions, as indicated by previous studies [20–22], due to the nucleophilic attack of dopant anions to positive defects generated during reversible oxidation.

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