Characterization of Polypyrrole Films for Use in Optical Sensing

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A study has been performed on the properties of polypyrrole (PPy) as a new material for use in optical sensing. PPy was synthesized by chemical oxidation of pyrrole (Py) using various oxidizing agents including aqueous ferric chloride, and very homogeneous thin films were obtained on plastic supports such as polyester membranes and polystyrene slides after a reaction time of 25–30 min. Elemental analyses of PPy films are inconsistent with the chemical structure of a pure polypyrrole in that, in addition to the expected presence of C, H, N and Cl (for the chloride-doped forms), we find oxygen in typical fractions of 9.5%. We suggest a chemical structure of a hydroxylated PPy, which is consistent with these findings. PPy films were also analyzed by FTIR and SEM methods. The absorption spectra of PPy are characterized by a long-wavelength absorption band that extends far into the near infrared (NIR). The NIR spectra of PPy change with pH and on exposure to ammonia vapors, a fact that can be exploited for sensing purposes.

1.   Introduction

Organic conducting polymers (OCP) have been widely used in recent years for purposes of electrochemical sensing. OCPs may act as chemically sensitive matrices as well as matrices for immobilization of specific reagents and enzymes.[1] They are easily manufactured, but in order to obtain materials reproducibly the experimental conditions must be carefully chosen.[2,3] Among OCPs, polypyrrole (PPy) has been used both in pure

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form and in composite membranes.[4,5] It displays high electrical conductivity in the oxidized (charged) form, fair stability, low redox potential, and can be grown from aqueous solutions. Polyaniline[6] is another popular OCP, while polythiophene[7] and polyacetylene[8] have been used less frequently.

PPy is usually obtained by chemical or electrochemical polymerization of pyrrol (Py). Different oxidizing agents including ferric chloride,[9] cupric chloride,[10] ferric perchlorate,[11] $K_2S_2O_8$[12] and certain salts of cerium(IV)[13] were found to be suitable. Oxidation with cupric chloride is slow,[14,15] while peroxodisulfate is much faster[16] but requires addition of chloride in order to improve the properties of OCPs. The most widely employed catalyst is ferric ion. However, as in all previous methods, polymerization strongly depends on the counterion, and stable and reproducible films were obtained only when using chloride salts,[17] although ferrocyanate[18] or stearate[19] have been employed as well. Recently, phosphomolybdic acid[20] has been used as an oxidant. Photopolymerization of pyrrol[21] is an alternative method which has been recently proposed.

Techniques such as FTIR[22] or XPS[23] have been used to characterize the polymer. The morphology and chain length of PPy is known to depend on the reaction conditions and, even more strongly, on pH.[24] Polymerization does not occur at pHs > 7. Both electrochemical and chemical polymerization result in a positively charged polymer that obviously requires the presence of a counter anion. Frequently this is referred to as the "dopant". Chloride,[25] bromide or sulfate[26] are the most common dopants. However, doped PPy, after treatment with alkali or water, undergoes an exchange process of the dopant anion by hydroxy ion.[27,28] Chemical reduction of charged PPy also results in neutral PPy polymer[29] that, however, is not stable in air.

Previous work on PPy resulted in electrochemical sensors and biosensors for determination of low-levels of analytes such as glucose,[30] lactate,[31] nitrate[32] or ammonia.[27] To our knowledge, OCPs have never been used for *optical* sensing purposes. We will show that PPy is a promising novel material for optical sensing purposes in that it undergoes pH-dependent changes in its intrinsic absorption and therefore, conceivably, is a pH-responsive material superior to conventional pH sensor materials in which an indicator dye is required that needs to be incorporated into (or on) a polymeric support.

2.   Materials and Methods

2.1 *Reagents*

Pyrrole (Py) was obtained from Fluka (prod. no. 83,220) and used after distillation. Ferric chloride (Merck) was of analytical reagent grade. Pyrrol solutions (140 mM) were prepared by dissolving 2.27 g of liquid pyrrol in 100 ml of distilled water. The other oxidants, viz. copper nitrate and potassium peroxodisulfate (both of analytical reagent grade), were used as 100 to 200 mM solutions. A universal buffer solution containing sodium sulfate (100 mM), boric acid (40 mM), sodium acetate (40 mM) and sodium dihydrogen phosphate (40 mM) was used. Its pH was adjusted by addition of 2 M sodium hydroxide or 4 M sulfuric acid.

2.2 *Materials*

Polymerization of pyrrole was carried out in various forms and on various supports. The supports included (a) disposable 1 × 1-cm polystyrene cuvettes (Brand, prod. no. 7590.05), (b) a 175-μm polyester film (Mylar™, from Du Pont), and (c) glass slides 1 mm thick.

2.3 *Instruments*

Absorption spectra were measured using a Genesys UV-VIS spectrophotometer operating over the 400 to 1100 nm wavelength range. Fourier transform infrared (FTIR) spectra were obtained on a Perkin-Elmer FTIR spectrometer having a resolution of 4 cm^{-1}. Scanning Electron Microscopy (SEM) data were collected at the Center for Electron Microscopy of Joanneum Research (Graz).

2.4 *Film preparation*

Typically, 3 ml of a 140 mM solution of ferric chloride were placed in a polystyrene cuvette, mixed with 30 μl of pyrrole, and rapidly stirred to obtain a homogeneous solution. After several minutes, the solution starts to turn dark, and a film is deposited on the walls. The polymerization of pyrrole was terminated after 27 min (at 22°C) by removing the inner solution. The cuvettes were washed with distilled water and stored at room temperature until used. This procedure resulted in very thin (less than 1 μm) and homogeneous PPy films deposited on the walls of the cuvette.

2.5 *Analyses*

The PPy film, which was washed several times with distilled water, was removed from the polystyrene walls by scratching, dried in vacuum over diphosphorus pentoxide, and subjected to elemental analysis (on a Carlo-Erba mod. 1106 C/H/N elemental microanalyzer). Chloride and oxygen contents were determined at the Microanalytical Laboratory of the University of Vienna.

3. Results

3.1 *Choice of oxidants*

Different oxidants were used to carry out polymerization in the polystyrene cuvettes. In all cases, 30 to 50 μl of pyrrole were added to 3 ml of the oxidant solution. Strongly differing materials were obtained as can be seen from the results given in Table 1. When cupric nitrate was tested in concentrations ranging from 100 mM up to 200 mM at pHs from 1 to 5 and at polymerization periods of up to 48 h, the PPy was formed in solution only (as a precipitate) but did not adhere to the walls of the cuvette. Polymerization with peroxodisulfate resulted in the deposition of fairly homogeneous films (after 60 min of reaction), particularly when hydrochloric acid was added, while no deposition was observed on addition of nitric acid. Reproducible and homogeneous films were obtained in the case of ferric chloride only, and the time of polymerization was shorter (< 30 min).

Table 1
Overview of the effects of oxidant and "dopant" and of the reaction time on the polymerization process.

oxidant[a]	dopant	solution pH	$t_{polym.}$	PPy film quality
cupric nitrate	no	5.0	48 h	no polymerization
	HNO_3[b]	1.0	48 h	no polymerization
	HCl[b]	< 1.0	48 h	polymerizes in solution only
peroxodisulfate	no	2.5	1 h	polymerizes in solution only
	HNO_3[b]	1.0	1 h	polymerizes in solution only
	HCl[b]	< 1.0	1 h	homogeneous film
ferric chloride	no	< 1.0	0.5 h	homogeneous film

(a) applied in 100 to 200 mM concentrations;
(b) 30 μl of conc. HCl or HNO_3 added

3.2 *Absorption spectra*

The PPy films obtained by oxidation with ferric chloride or peroxodisulfate display a characteristic absorption spectrum that is shown in Fig. 1. The maximum in the spectra of the films obtained with ferric chloride is at around 1,100 nm in the near infrared (NIR), and a minimum is found around 540 nm. Slight differences were observed in cases in which peroxodisulfate was used as the oxidant, as can be seen from the graphs in Fig. 1. In particular, the slope of the spectrum in the 600 – 800 nm range is smaller for the peroxodisulfate film than that for ferric chloride, and the minimum is located at longer wavelengths (590 nm).

3.3 *Optimization of parameters*

When the concentration of ferric chloride in the solution was increased, the absorption spectrum of the resulting film increased over the whole spectrum as well, but was stronger in the range between 600 – 900 nm (Fig. 2), probably due to stronger charge transfer interactions in the thicker "metallic" films. The films also were formed increasingly rapidly as concentrations of ferric chloride increased. On the other hand, a shift to lower wavelength maximum (λ_{max} 700 to 800 nm) and a less reproducible spectrum were obtained if the concentration of the ferric chloride was below 100 mM.

The time of polymerization was varied, at a constant Py concentration, from 12 to 35 min, and an increase in absorbance recorded. As can be seen from Fig. 3, the absorbance increases over the first 25 to 30 min but then levels off. No significant differences were found on adding Py to the ferric chloride solutions in quantities ranging from 20 to 60 μl. The films obtained after prolonged polymerization adhered to the support quite well, but if polymerized for less than 12 min they tended to delaminate.

3.4 *Membrane characterization*

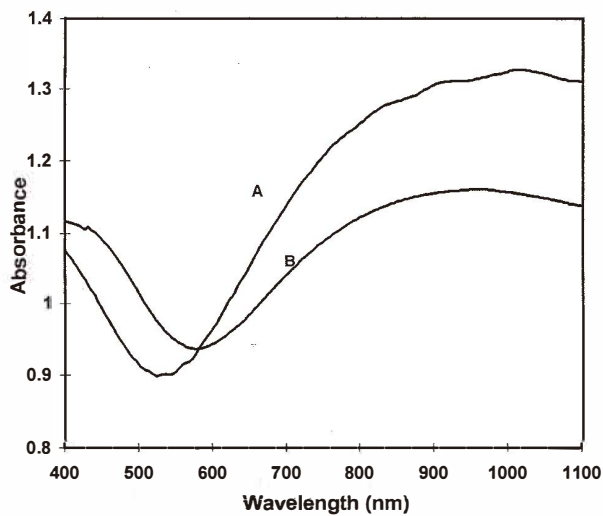We have performed elemental analyses of doped PPy since our results (see below) have

Fig. 1. Absorption spectra of polypyrrol films obtained by oxidative polymerization in a cuvette employing (A) 3 ml of a 140 mM ferric chloride solution and 30 μl of pyrrole for 27 min and (B) 3 ml of a 100 mM peroxodisulfate solution, 30 μl of HCl conc. and 30 μl of pyrrole for 60 min.
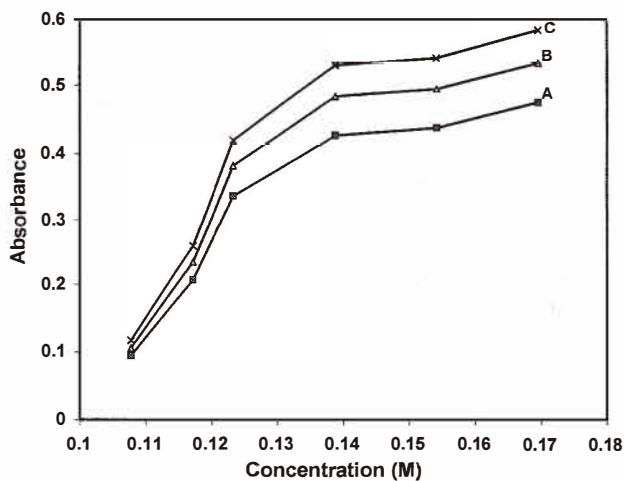

Fig. 2. Effect of the ferric chloride concentration on the absorbance of the PPy film (on polystyrene) as monitored at (A) 600 nm, (B) 700 nm and (C) 800 nm. The reaction time was 30 min, and the amount of pyrrole added was 30 μl in each case.
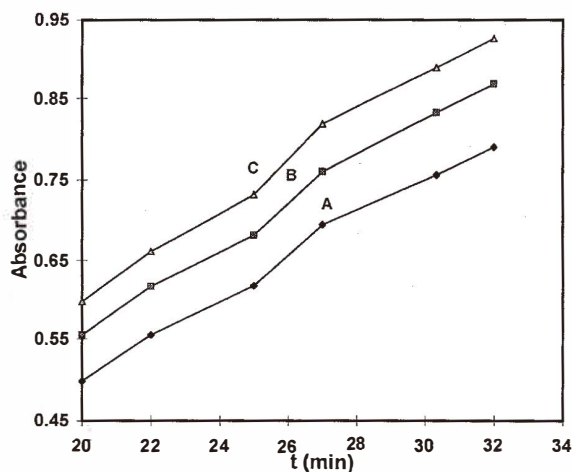
Fig. 3. Kinetics of the polymerization process as monitored via the absorbances at (A) 600 nm, (B) 700 nm and (C) 800 nm. In each case, 30 μl of pyrrole were added to 3 ml of aqueous ferric chloride (140 mM).

cast doubts as to its chemical composition, which is reported to be $(C_4H_3NX_a)$ where X is the respective dopant anion (such as chloride) and the subscript a indicates the fractional doping level (typically on the order of 0.3). Recently, the presence of oxygen has been demonstrated by others.[33] Our results, obtained by using PPy prepared with ferric chloride, show the films to be typically composed of 56.9% carbon, 3.9% hydrogen, 16.2% nitrogen, 11.5% chloride and, most significantly, 9.5% oxygen. This corresponds to a molecular formula of $(C_4H_3NCl_{0.3}O_{0.9})_n$ and falsifies previous assumptions that PPy is composed of C, H, N and chloride only.

3.5 *FTIR spectra*

The FTIR spectrum (shown in Fig. 4) is characterized by a series of sharp peaks between 600 and 1,600 cm^{-1}, and this is in agreement with the spectrum of doped PPy.[34,35] The absence of a strong carbonyl band is obvious. A featureless increase in absorbance at above 1,600 cm^{-1} indicates the presence of NH and, possibly, hydroxy groups, which are all strongly hydrogen bridged.

3.6 *EDAX/SEM studies*

Scanning electron microscopy using energy dispersive analytical x-rays (EDAX/SEM) is known to be a powerful method for elemental characterization of solid phases. An analysis of different areas of the PPy films made with ferric chloride revealed the presence of chloride as the only inorganic species in the matrix (Fig. 5). The micrographs also demonstrated this film to be very smooth and highly homogeneous (Fig. 6).
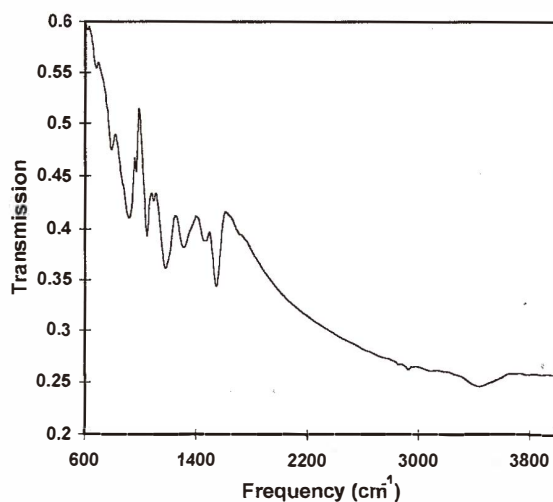
Fig. 4.   FTIR spectrum (average of 240 scans; resolution 4 cm^{-1}) of a PPy film obtained by oxidative polymerization (27 min) employing 3 ml of 140 mM ferric chloride solution and 30 μl of pyrrole. The strong and featureless absorption between 200 and 4000 cm^{-1} is particularly significant for doped PPy and is in contrast to the spectrum of undoped ("pristine") PPy.
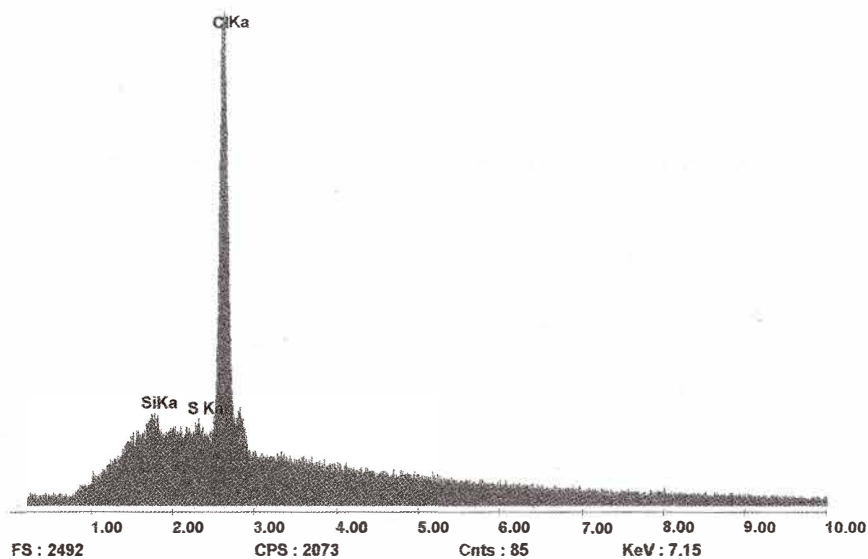

Fig. 5.   EDAX/SEM scan of a PPy film obtained by a 27-min oxidative polymerization employing 3 ml of 140 mM ferric chloride solution plus 30 μl of pyrrole.
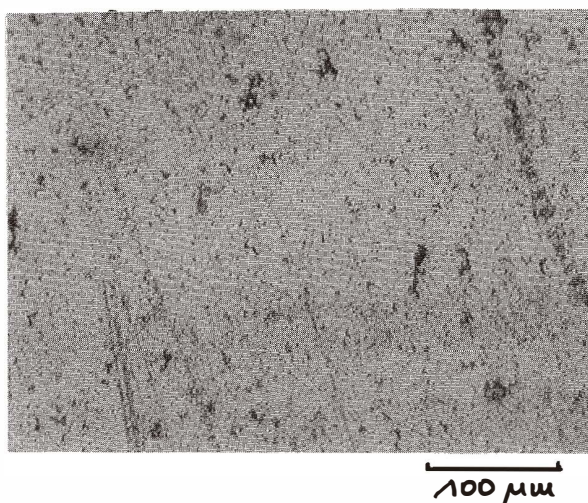
Fig. 6.   Scanning electron micrograph of the PPy film in Fig. 5.

3.7 *Supports*

Aside from polystyrene, the polymerization of pyrrole also was performed on a polyester film and a glass slide.   The 1-cm wide polyester film was placed in a vial containing pyrrol and ferric chloride in the same concentrations as in the cuvette experiments.   The PPy film obtained showed the same optical properties as the former.   Attempts to deposit the PPy on the glass support were unsuccessful.

3.8 *Solubility*

No solvents have been identified for PPy, but ultrasonic treatment of the films in dimethylsulfoxide, acetonitrile and tetrahydrofuran caused deterioration and dispersion of the PPy film.   It cannot be dispersed, however, in chloroform, carbon tetrachloride or dichloromethane.

3.9 *Effects of pH*

An interesting and novel aspect is the pH dependence of the absorption spectra of PPy. Both absorbance and shape vary with pH.   Figure 7 shows a plot of absorbance A $(= \log I_0/I)$ versus wavelength at different pHs and reveals an increase in absorbance with pH above 600 nm.   Simultaneously, the absorption minimum (at λ around 580 nm) is shifted to shorter wavelengths, while no significant changes are observed in the wavelength of the maximum.   The largest effects are observed at pHs between 7 and 10 (with an apparent pKa of 8.3), and this again is indicative of a phenolic function present in doped PPy.

Figure 8 shows the titration curve resulting from the pH-dependence of the absorption spectra of the films.   The pKa value (i.e., the turning point in Fig. 8) can be calculated to be
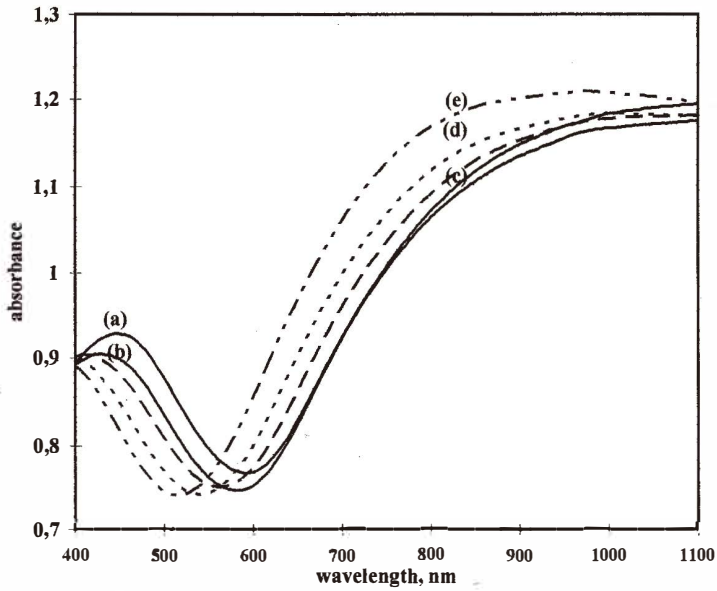
Fig. 7. Absorption spectra of the PPy film of Figure 5 at pHs of (a) 3.0, (b) 6.0, (c) 7.0, (d) 9.0 and (e) 11.0. Absorbance A is defined as $\log I_o/I$.
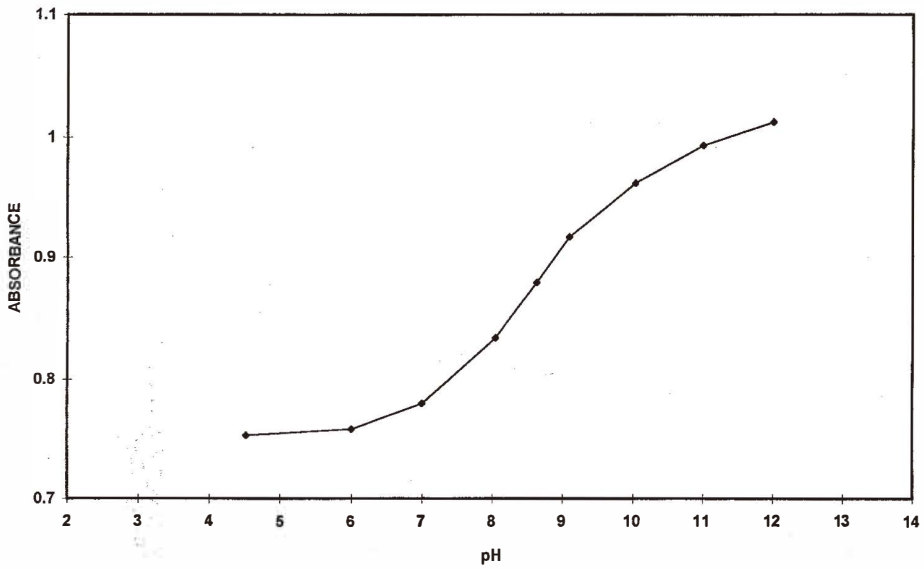

Fig. 8. Variation in the absorbance ($\log I_o/I$) of a PPy film of approx. 0.5 μm thickness with pH at 650 nm.

at pH 8.7. At first glance, the sigmoidal titration curve resembles that of pH optical sensors based on immobilized pH indicators. A more careful look reveals, however, that it is different in that the pH-dependence of the PPy-based sensor covers a larger range than conventional optical sensors whose range usually does not exceed 3 pH units. Both shape and relative signal change of such titrations plots (cf. Fig. 8) depend on the analytical wavelength as can be deduced from Fig. 7.

In terms of sensitivity, the films are comparable to conventional optical sensors and can result in a resolution on the order of 0.01 pH units. This is mainly due to the strong absorption of even thin films (see Fig. 7) which results in a favorable signal-to-noise ratio when measuring the absorption using an LED or diode laser light source. The relative change in absorption with pH (ΔAbs/pH) is 0.062 at pHs close to the pKa. Cross-sensitivities to ionic strength (known to be a major problem in conventional optical sensors) are very small and the subject of current investigations. The effect of ionic strength on the pKa (the turning point of the titration plot in Fig. 8) was tested by acquiring pH titration plots in buffers containing 100 and 200 mM concentrations of sodium chloride. In buffers of higher salinity, the pKa was lower by 0.01 to 0.02 units, which is comparably very little.

3.10   *Stability*

The stability of the PPy films at two pH values was determined by monitoring the absorption in the range from 600 to 800 nm. Both at pH 6 and 11 no changes in absorbance occurred over 3 h. However, on storage in dilute acid, the films suffer a change of their pKa values with time, typically from 8.7 to 8.9 within 1–2 weeks.

4.   Discussion

4.1 *Polymerization conditions*

So far, PPy has been used in electrochemical sensors only, since its electrical conductivity makes it an ideal coating for amperometric sensors. The preferred methods for making PPy films are electrochemical or oxidative polymerization. Deposition of the polycationic polymer on a surface occurs after a critical chain length has been reached. The resulting polymer has a net positive charge which is neutralized by incorporation of anions from the aqueous electrolyte solution.

Specifically, at least for the case of chemical polymerization in aqueous solution, we find the spectral and other properties of the PPy film not only to depend on the pH of the solution,[24] but also on the redox potential of the oxidant applied, the respective counter anion, the time of polymerization, and the concentration of the oxidant employed. This is based on the following findings: (a) Polymerization can be initiated only by oxidants whose redox potential is above a certain level. Ferric chloride and peroxodisulfate work well, while copper(II) does not cause any reaction to occur. (b) The polymer only precipitates on the walls of the cuvette in the presence of chloride. (c) On increasing the reaction time and the concentration of ferric chloride, a shift in the absorption maximum

occurs toward longer wavelengths (from 800 to more than 1,100 nm). Hence, the reproducible manufacturing of PPy films on inert supports requires reaction conditions to be carefully kept constant.

4.2 *Film composition*

The PPy backbone carries a net positive charge which is compensated for by a counter anion (the "dopant"; i.e. chloride in our case). We find the fraction of chloride in the total elemental composition to be around 11.5%. Given the net formula of $C_4H_3NCl_{0.3}O_{0.9}$ (see section 3.4), it can be concluded that approximately one out of 3 pyrrol moieties in the PPy backbone carries a positive charge and, hence, a chloride counter anion. The presence of around 10% oxygen in PPy is surprising and requires the established chemical structures of PPy to be revised.

Based on the grounds of a lack of strong carbonyl bands in the FTIR spectrum, the strong absorptions in the $2,000 - 3,500$ cm^{-1} range (where hydrogen bridged phenols absorb), and, in particular, the pH dependence of the spectra in the pH 7–10 range, we conclude that the oxygen is present in PPy in the form of a phenolic hydroxy group. According to elemental analyses, the phenol is present on every pyrrol ring. It may have been formed through an in-situ reaction of PPy radicals with water. Phenols are known to have pK_a's ranging from 7.5 to 10 and to undergo an increase in molar absorbance on dissociation.

From the above discussion we conclude that PPy cannot be represented simply by a chemical structure of type I as shown in Fig. 9 (with X = H). We conclude that structural elements such as II, III (with X = H or OH) and IV (with X = H or OH) are present in PPy in addition to structure I. These partial structures are assumed to be involved in acid-base chemistry, the positively charged nitrogens bearing the chloride anion, and the dissociation of the pyrrol nitrogens and the hydroxy groups to be responsible for the pH dependence of the spectra. It is difficult, however, to speculate on how they are linked to each other. Structure V is assumed not to be present in large fractions in the PPy chain because of the lack of strong carbonyl groups in the IR spectrum.

Undoped ("pristine") PPy lacks the strong IR absorptions in the 2,000 to 3,500 cm^{-1} range. However, weak bands are found for pristine PPy at 3,400 cm^{-1} (attributable to the N-H stretching) and 3,100 cm^{-1} (attributable to the C-H stretching mode for the ring carbons).[34,36]

5. Conclusion

In conclusion, we find doped PPy to be a polymer whose optical properties, in particular its long-wave absorption that extends far into the NIR, make it an interesting material for optical sensing purposes. The long-wavelength absorption band is fully compatible with diode lasers and related emitters. The pH-dependence of its spectra suggests its use as a material for optically sensing pH and basic gases such as ammonia. It also is an interesting material considering the fact that it is a polymer which does not require an indicator dye to function as a chemical sensor.
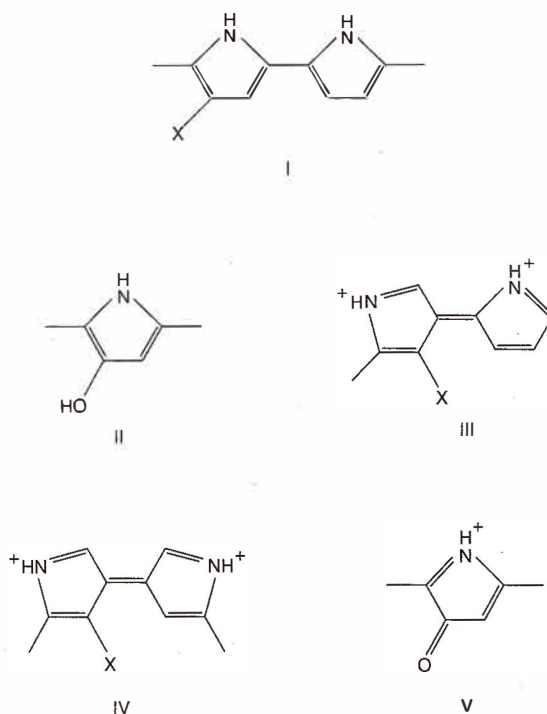
Fig. 9.   Partial structures suggested to be contained in a PPy chain. Structure I (with X = H) is the conventional representation, while II, III and IV (with X being either a hydrogen or hydroxy substituent) are suggested as additional structural elements as a result of this study.

Acknowledgments

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