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Polyaniline and polypyrrole: A comparative study of the preparation

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Abstract

Aniline and pyrrole have been oxidized with ammonium peroxydisulfate in aqueous solutions, in the presence of equimolar quantities of hydrochloric acid. The oxidation of pyrrole was faster; the induction period typical of aniline oxidation was absent in the case of pyrrole. As the proportion of oxidant-to-monomer molar concentration increased up to 1.5, the yield increased in both cases. Similarities between the two oxidations are illustrated and discussed. The oxidant-to-monomer molar ratio 1.25 is proposed to be the optimum stoichiometry, in the accordance with the data published in the literature. The conductivities of the polymers prepared were only slightly dependent on the oxidant-to-monomer ratio in the range 0.3–1.5, and were of the order of $10^0\,S\,cm^{-1}$ for polyaniline and $\sim 10^{-2}$–$10^{-1}\,S\,cm^{-1}$ for polypyrrole. Outside this interval, the conductivity of both polymers was reduced. Polyaniline having conductivity $\sim 10\,S\,cm^{-1}$ was produced in solutions of phosphoric acid of various concentrations. On the contrary, the conductivity of polypyrrole was reduced as the concentration of phosphoric acid became higher. The type of protonation is discussed with the help of FTIR spectra by analyzing the ammonium salts obtained after deprotonation. Sulfate or hydrogen sulfate anions produced from peroxydisulfate always constitute a part of the counter-ions.
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1. Introduction

There are many papers on optimizing the preparation of polyaniline (PANI) and polypyrrole (PPy) with respect to molecular structure, molecular weight, morphology, and conductivity [1,2]. The results reported for these most important conducting polymers, however, are difficult to compare because various research groups have used different conditions of preparation, and characterization. The studies dealing systematically with both PANI and PPy are scarce [3,4].

It is the purpose of this study to revisit the effect of oxidant-to-monomer molar ratio on the syntheses of PANI and PPy. Ammonium peroxydisulfate

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(APS) has been selected as the oxidant for this study for the sake of comparison, although we are aware that iron(III) salts are the oxidants of choice in the preparation of PPy with high conductivity [5]. We shall briefly assess the effect of acidity on the oxidation of both monomers. Phosphoric acid has been used for this study, because the acidity of the medium is more easily adjusted by selecting the acid concentration, compared with strong acids, such as hydrochloric and sulfuric acids.

We decided to check how both conducting polymers are protonated when prepared under "standard" conditions [6], and what are the counter-ions when the polymerization is carried out in the solutions of phosphoric acid. This type of experiments is important in the design of acidity sensors [7,8] and corrosion protection and, especially for PPy, this information is missing in the literature.

It is definitely not the purpose of this study to suggest that either of these two polymers, PANI or PPy, is better. Each of them has its benefits [1,2,9,10], which can be exploited and improved by using specific methods of preparation. This paper reports some selected features of PANI and PPy when prepared or used under comparable conditions, and newly seeks parallels rather than differences between these polymers.

2. Experimental

2.1. Synthesis

Aniline or pyrrole (0.2 M) was oxidized with various proportions of APS at 20 °C in 0.2 M HCl. The precipitated polymers were collected on a filter, rinsed with 0.2 M HCl, and acetone, and dried. In another series of experiments, aniline or pyrrole (0.2 M) was oxidized with 0.25 M APS in aqueous solutions of phosphoric acid of various concentrations. The products of oxidation were treated as above. So-called "standard" samples [6] have been prepared by oxidizing 0.2 M monomer with 0.25 M APS in 0.2 M HCl. All the syntheses were carried out in a volume of 100 mL.

2.2. Deprotonation

Portions of protonated polymers were suspended in excess of 1 M ammonium hydroxide for several hours. The resulting polymer bases were separated on a filter, and dried. The filtrate was evaporated to yield the ammonium salt of the acid originally protonating the conducting polymer.

2.3. Characterization

Infrared spectra in the range 400–4000 cm^{-1} were recorded at 64 scans per spectrum at 2 cm^{-1} resolution using a fully computerized Thermo Nicolet NEXUS 870 FTIR Spectrometer with DTGS TEC detector. Polymers were dispersed in potassium bromide and compressed into pellets.

The conductivity was measured by a four-point van der Pauw method on pellets compressed from polymer powders at 700 MPa with a manual hydraulic press, using a current source SMU Keithley 237 and a Multimeter Keithley 2010 voltmeter with a 2000 SCAN 10-channel scanner card. A two-point method using a Keithley 6517 electrometer was applied to samples having a low conductivity, $<10^{-5}$ S cm^{-1}. Prior to such measurements, circular gold electrodes were deposited on both sides of the pellets.

3. Results and discussion

3.1. Polymerization

The oxidation of aniline with APS yields PANI (Fig. 1a), and similarly pyrrole is oxidized to PPy (Fig. 1b). The polymerization of 0.2 M aniline with 0.25 M APS in 0.2 M hydrochloric acid is characterized by an athermal induction period followed by the exothermic polymerization [6] during which the temperature of the reaction mixture increases (Fig. 2). After the oxidation has been finished, heat evolution stops, and the mixture cools down [11,12].

The absence of an induction period is a typical feature of pyrrole oxidation (Fig. 2). Aniline behaves in a similar manner only if oxidized in water or in media of low acidity [11–14]. Under the conditions of low acidity, aniline is present in a form of neutral molecules. They are much easier to oxidize than anilinium cations dominating at higher acidity [15]. The similar acidity-dependent behaviour may also be anticipated for pyrrole. The oxidability of neutral pyrrole molecule and protonated pyrrole is likely to be different. The oxidation of aniline and pyrrole will be controlled by their pK, 4.9 for the former and −3.8 for the latter monomer, which determine proportions between the neutral and protonated forms.
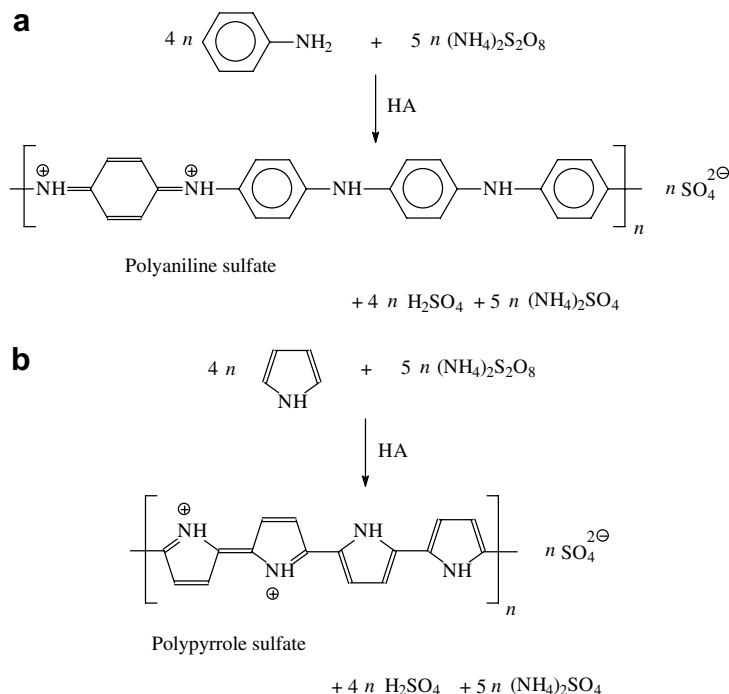
Fig. 1. (a) The oxidation of aniline with ammonium peroxydisulfate in acidic aqueous medium yields protonated polyaniline (emeraldine form). (b) The oxidation of pyrrole similarly produces protonated polypyrrole.
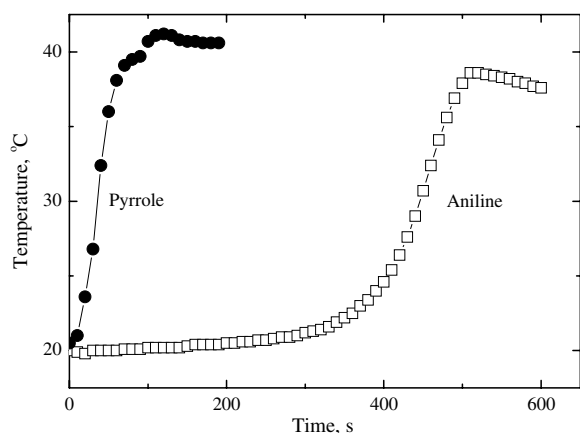

Fig. 2. The temperature profile in the oxidation of 0.2 M aniline (open squares) or pyrrole (full circles) with 0.25 M ammonium peroxydisulfate in 0.2 M HCl.

It is worth noting that peak temperatures, which are proportional to the reaction enthalpies, are comparable for both monomers (Fig. 2). This fact is important for safety reasons, because an increase in the concentrations of the reactants also increases the evolved heat and, consequently, the temperature of the reaction mixture. High concentrations of reagents resulting in an increase of peak temper-

ature to the boiling point of the aqueous medium should be avoided. This applies to the syntheses using monomer concentrations over 1 M, especially with large reaction volumes [6]. The risks met in the oxidations of aniline and pyrrole are thus similar.

3.2. Oxidant-to-monomer molar ratio

Equimolar quantities of aniline and peroxydisulfate are needed for the hypothetical coupling of aniline molecules to the leucoemeraldine form of PANI [6], because each newly formed bond requires the abstraction of two electrons. Additional oxidation of the hypothetical leucoemeraldine to the experimentally obtained emeraldine additionally demands the removal of two electrons per four aniline constitutional units [11,16]. That is why five APS molecules are needed for the oxidation of four aniline molecules, and the oxidant-to-aniline molar ratio is thus 1.25 (Fig. 1a) [6,11,16]. The optimum experimental value 1.15 with respect to yield and conductivity has been reported in the pioneering paper by Armes and Miller [17]. Sulfuric acid and ammonium sulfate are by-products (Fig. 1a) but, in fact, their equimolar mixture is isolated mainly as ammonium hydrogen sulfate [11,18].
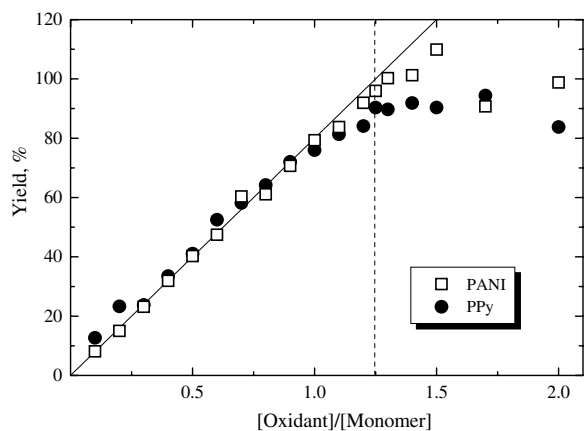
Fig. 3. The yield of PANI (% of theory, open squares) and PPy (full circles) prepared at the various oxidant-to-monomer molar ratios. The oxidation of 0.2 M monomer solution with ammonium peroxydisulfate in 0.2 HCl was started at 20 °C.

When the APS-to-aniline molar ratio gradually increases, the yield of PANI increases correspondingly (Fig. 3). At the ratio 1.25, all the aniline is expected to be consumed by the reaction (Fig. 1a). A higher ratio should not increase the yield but may cause its decrease as over-oxidation converts a part of the PANI to quinone. A slight degree of over-oxidation may thus be of advantage when the content of potential residual aniline has to be reduced, without deterioration in the yield or, as we shall see below, the reduction of conductivity.

The coupling of pyrrole units into polymer chains should follow similar principles to those established in the oxidation of aniline, i.e. the coupling of pyrrole molecules would be followed by their partial oxidation (Fig. 1b) by analogy with PANI (Fig. 1a). The oxidation product would contain imine-like and amine-like nitrogens, similarly to PANI. This hypothesis is tested against the experimental results because, if proved true, knowledge available on the synthesis of PANI could be transferred to PPy and *vice versa*.

By using the stoichiometry given in Fig. 1, we calculate that the oxidation of 1 g aniline yields 1.236 g of PANI sulfate, and similarly 1 g pyrrole provides 1.328 g of PPy sulfate. These expectations are represented by a straight line in Fig. 3. The experimental results follow this prediction closely up to the limit of oxidant-to-monomer ratio 1.2–1.3. This means that the oxidations of aniline and pyrrole both proceed quantitatively to the proposed products as shown in Fig. 1.

The situation would be somewhat different if the counter-ions in the polymers were hydrogen sulfate anions instead of the sulfate anions considered in Fig. 1. Then, we would find higher yields because twice the amount of sulfuric acid would be associated with the polymer. The presence of hydrogen sulfate counter-ions has indeed been reported in PANI [11,19]. More detailed recent studies [20] show that, at low concentration (0.1 M) of sulfuric acid, the counter-ions to the PANI are sulfate anions, while at a higher concentration of sulfuric acid (0.5–1.0 M), hydrogen sulfate anions predominate. The assumption of the presence of sulfate counter-ions in the present case (Fig. 1) is thus justified. Similarly, for pyrrole polymerization performed in water, Cassignol et al. [21] reported the creation of PPy sulfate when APS was used as oxidant.

3.3. Conductivity

Conductivity is the most important property of conducting polymers. Its nature is explained by the ability of PANI to form polarons, cation radicals [2] (Fig. 4a). Four double bonds constituting the quinonediimine constitutional unit in protonated PANI (Fig. 4a, top formula) convert to three double bonds in benzene ring and two unpaired electrons (Fig. 4a, middle formula) that act as charge carriers. The polarons can eventually spread over the polymer chain (Fig. 4a, bottom formula) to produce a polaron lattice. The analogous behaviour may be anticipated in PPy (Fig. 4b).

The dependence of the conductivity on the oxidant-to-monomer molar concentration ratio has common features for PANI and PPy (Fig. 5). Over a broad range, the fluctuations of conductivity are within the experimental error of conductivity determination. Both at low and high values of the oxidant-to-monomer molar ratio, the conductivity is reduced below that in the middle range. This is especially true for PANI. When APS has been used as the oxidant, the conductivity of PANI reported in the literature is generally higher than that of PPy [1,2], as in the present case. If similar experiments are carried out with iron(III) salts, the situation is reversed; conductivities over 200 S cm^{-1} have recently been reported for PPy [22], typical values being in the range of tens of S cm^{-1} [23–25].

The behaviour of aniline and pyrrole with respect to oxidant-to-monomer molar ratio (Fig. 5) has a consequence for the *in situ* coating of various mate-
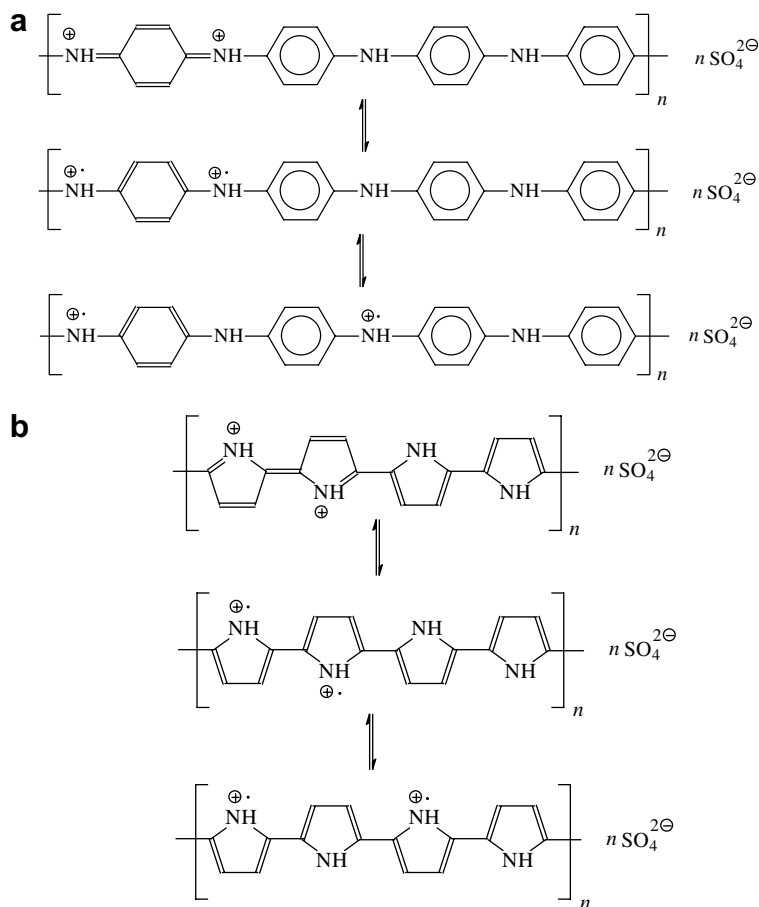
Fig. 4. (a) Two electrons are injected from charged nitrogens in PANI salt into quinoneiminoid constitutional unit (top), which converts to a benzenoid ring (middle). Remaining unpaired electrons are located at nitrogen atoms as polarons. These can delocalize along the polymer chain (bottom). (b) The similar scenario can be offered for polypyrrole. All resonance structures are present simultaneously in various proportions.
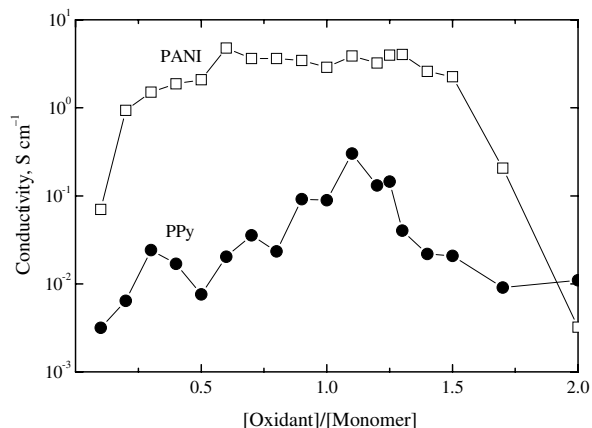

Fig. 5. Conductivity of PANI (open squares) and PPy (full circles) prepared at the various oxidant-to-monomer molar ratio. The oxidation of 0.2 M monomer solution with APS in 0.2 M HCl was started at 20 °C.

rials with conducting polymers. It is often required that a voluminous material, like carbon nanotubes [26,27], carbon black [28], or textile fibres [29], is coated with a thin overlayer of a conducting polymer. A low amount of polymer has to be generated to avoid the formation of an accompanying polymer precipitate. The total volume of the reaction mixture cannot be reduced in such cases, because it would not accommodate all the material to be coated. The use of lower concentrations of reactants would result in the slow-down of the reaction rate [11] or the polymerization would not take place at all. The present results (Fig. 5) suggest that, if the monomer concentration were maintained, a decrease in the oxidant concentration, even to 20% (0.05 M), would reduce the total amount of PANI produced five-fold, its conductivity being preserved.

3.4. Protonated forms and bases

The emeraldine form of PANI contains equal numbers of imine and amine nitrogen atoms (Fig. 1) [30], the former being more basic and more prone to protonation compared with the amine sites, which become protonated only at high acid concentrations [31]. The secondary amine group (–NH–) in pyrrole is even less basic than the corresponding group in aliphatic compounds. We assume that protonation in PPy preferentially takes place on the oxidized units in PPy, analogous to the imine sites in PANI (Fig. 1b). The protonating acid can be removed from the conducting polymer by treatment with an alkali, such as ammonium hydroxide (Fig. 6). During this process, the corresponding polymer bases are produced. The acid–base transition in conducting polymers is well documented by the decrease in conductivity. The conductivity of "standard" PANI changes after deprotonation [6] from 4.4 S cm^{-1} to 6×10^{-11} S cm^{-1}, the conductivity of PPy from 0.5 S cm^{-1} to 3.2×10^{-9} S cm^{-1}.

On the molecular level, the deprotonation process is well illustrated by FTIR spectra (Fig. 7). A broad absorption band at wavenumbers higher than 2000 cm^{-1} in the spectrum of PANI, typical of the conducting form [32,33], disappeared after deprotonation. The metallic polaron energy band was responsible for the broad absorption. The spectrum of PANI hydrochloride exhibits main peaks at 1559 and 1480 cm^{-1}, corresponding to quinone and benzene ring-stretching deformations, respectively. These modes show a blue shift to 1593 and 1498 cm^{-1} in the PANI base. The absorption band at 1303 cm^{-1} corresponds to π-electron delocalization induced in the polymer by protonation [32,33]. The band characteristic of the conducting protonated form is observed at 1243 cm^{-1} and is interpreted as a C–N$^{+\cdot}$ stretching vibration in the polaron structure [33,34]. The prominent 1136 cm^{-1} band is assigned to a vibration mode of the –NH^{+}= structure, which is formed during protonation [35]. The intensity of these two bands decreased dramatically after deprotonation. The
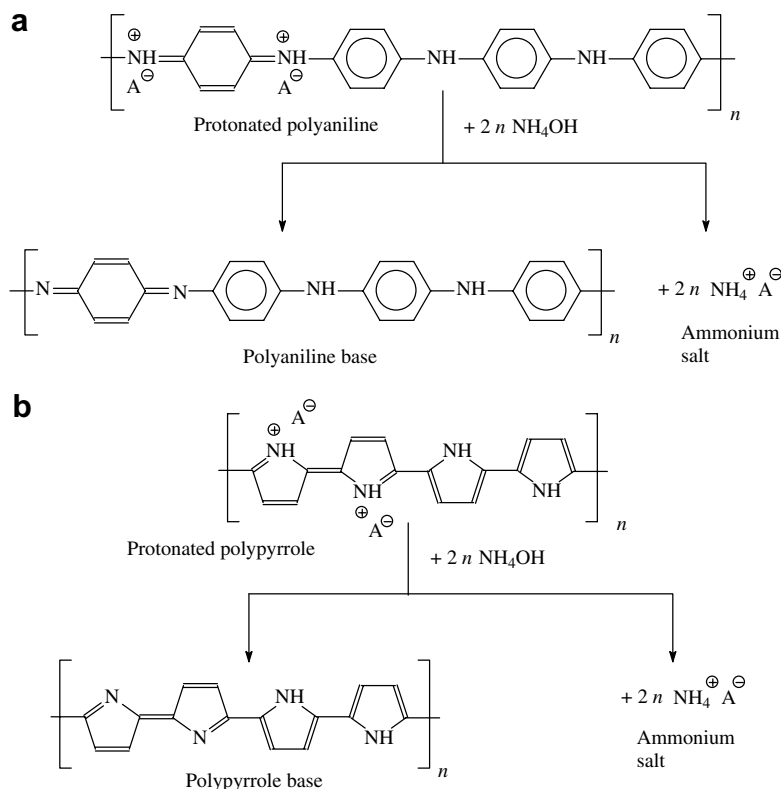

Fig. 6. (a) The protonated PANI is deprotonated by ammonium hydroxide to corresponding polyaniline base. Ammonium salt of an acid protonating PANI is produced by neutralization. The formation of water is not shown. (b) The deprotonation of PPy proceeds in a similar manner.
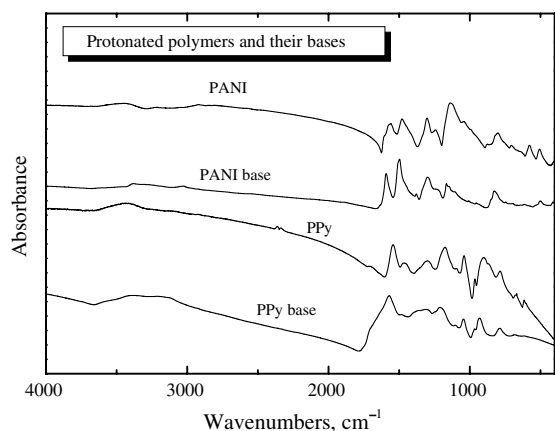
Fig. 7. FTIR spectra of PANI and PPy and their corresponding bases.

peak observed at 1379 cm^{-1} in the spectrum of the PANI base is due to the C–N stretching vibration in the neighbourhood of a quinonoid ring, which is characteristic for the PANI (emeraldine) base [36]. The band at 1299 cm^{-1} is assigned to C–N stretch of the secondary aromatic amine whereas, in the region of 1010–1170 cm^{-1}, the aromatic C–H in-plane bending modes are usually observed in the spectrum of the PANI base. Out-of-plane deformations of C–H on 1,4-disubstituted rings are located in the region of 800–880 cm^{-1} [37]. The presence of sulfate anions in the protonated form of PANI is manifested by the bands at 1104, 1042 and 578 cm^{-1} [38]. These bands are missing in the spectrum of the PANI base.

The infrared spectrum of protonated PPy also differs from the spectrum of the PPy base (Fig. 7). A reduction in the absorption band at wavenumbers higher than 2000 cm^{-1} is observed in the spectrum of the PPy base as it was in the case of PANI. This result is in good correlation with the reduced conductivity accompanying deprotonation. The band at about 1700 cm^{-1} observed in the spectrum of PPy corresponds to the presence of carbonyl group formed by the nucleophilic attack of water during the preparation [38]. The band assigned to C–C stretching vibrations in the pyrrole ring, observed at 1543 cm^{-1} in the spectrum of protonated PPy, is blue-shifted to higher wavenumbers, 1572 cm^{-1}, in the spectrum of a deprotonated sample. This is connected with the influence of the doping on the skeletal vibrations, involving the delocalized π-electrons. The band of the C–N stretching vibration in the ring, observed at 1470 cm^{-1} in the spectrum of protonated PPy, is shifted to 1485 cm^{-1} in the spec-

trum of the PPy base. The broad band from 1400 to 1250 cm^{-1} is attributed to C–H or C–N in-plane deformation modes, and has a maximum at 1300 cm^{-1}. This maximum is shifted to 1307 cm^{-1} for the PPy base. In the region of the C–H and N–H in-plane deformation vibrations from 1250 to 1000 cm^{-1}, one can observe a maximum at 1173 cm^{-1} in the spectrum of PPy and at 1213 cm^{-1} in the spectrum of the PPy base. This shift is most probably connected with the disappearance of the expected 1183 cm^{-1} band of sulfate anions. The peak observed at 1095 cm^{-1} in the spectra of PPy corresponds to the in-plane deformation vibration of NH$^+$, which is formed on the PPy chains by protonation (Fig. 1b) [25]. A new peak shifted to 1101 cm^{-1} is found in the spectrum of the PPy base. The bands corresponding to the C–H and N–H in-plane deformation vibration situated at 1041 cm^{-1} and to C–C out-of-plane ring-deformation vibration at 965 cm^{-1} are observed at the same position in both spectra. The region of the C–H out-of-plane deformation vibrations of the ring (at about 900 cm^{-1}) and of the C–H out-of-plane ring deformation (at about 786 cm^{-1}) are shifted to 930 and 788 cm^{-1} in the spectrum of the PPy base. The peak at 678 cm^{-1} corresponding to the C–C out-of-plane ring deformation or C–H rocking vibration is only slightly influenced by deprotonation. The most important feature is the disappearance of the 620 cm^{-1} band from the sulfate anions in the spectrum of the PPy base.

3.5. Protonating acid in PANI and PPy

The polymerization of 0.2 M aniline or pyrrole with 0.25 M APS produces 0.25 M sulfuric acid as a by-product [6] (Fig. 1). Even when the polymerization is carried out in 0.2 M hydrochloric acid, the produced polymers are protonated also with sulfuric acid. The nature of the protonating acid can be identified by the analysis of the ammonium salts collected after deprotonation of the polymers (Fig. 6).

The salts obtained after the deprotonation of "standard" samples thus should be mixtures of ammonium chloride and ammonium sulfate. The presence of ammonium sulfate is well illustrated by the FTIR spectra (Fig. 8). The broad band observed above 2000 cm^{-1} has the same shape as in the spectra of ammonium salts obtained from standard PANI and PPy. The peak corresponding to NH$_4^+$ at 1404 cm^{-1}, and two peaks of the sulfate anion, localized at 1089 and 613 cm^{-1}, correspond
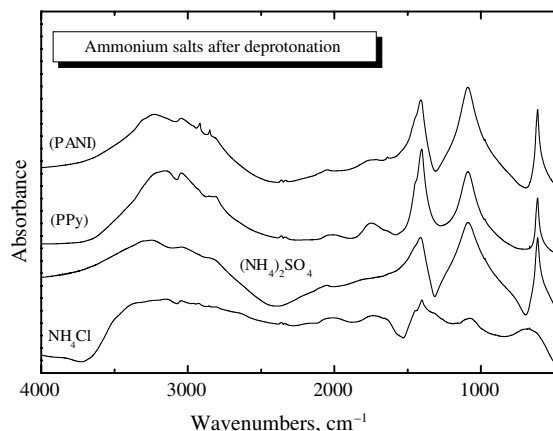
Fig. 8. FTIR spectra of ammonium salts collected after the deprotonation of PANI and PPy, and spectra of ammonium sulfate and chloride.

well to those in the spectrum of ammonium sulfate obtained after deprotonation of standard PANI [37,38]. The different ratio of the intensities of the peaks observed at 1404 and 1090 cm^{-1} confirms the presence of ammonium chloride besides of ammonium sulfate in the corresponding salt in case of PPy. The spectra also demonstrate that no other chemical species are liberated from PANI during deprotonation. This is an important observation for potential applications.

3.6. Acidity of the reaction medium

The starting acidity of the medium, in which conducting polymers are prepared, is of the greatest importance. Conducting PANI is produced only in media of high acidity, pH < 2, and the morphology, granular or nanotubular, is also pH-dependent [12,16]. The effect of the phosphoric acid concentration on the polymerization of aniline has already been reported [31], and some of these results are summarized in Fig. 9. If phosphoric acid is present in the reaction mixture, the conductivity of the products is only slightly dependent on the total acid concentration. The best conductivity, 15.5 S cm^{-1}, has been obtained when using 1.0 M phosphoric acid as the medium.

On the other hand, the conductivity of PPy steadily decreased as the phosphoric acid content grew. When the polymerization was carried out in 1 M phosphoric acid or at higher concentrations, the oxidation products could not be compressed into pellets for the conductivity experiments, and they behaved as if they were non-conducting in simple
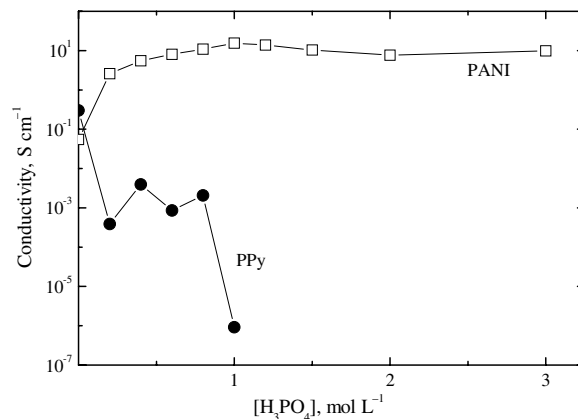

Fig. 9. Conductivity of PANI (open squares) and PPy (full circles) prepared in the solutions of phosphoric acid of various molar concentration. 0.2 M monomer was oxidized with 0.25 M APS at 20 °C.

conductivity tests. The molecular structure of the oxidation products also changed, as reflected by the FTIR spectra (Fig. 10) and the products no longer resembled typical PPy (Fig. 7). An increase in the band at about 1702 cm^{-1} corresponding to C=O group signifies the oxidation process which occurs in the polymers prepared at high concentrations of phosphoric acid. The broad band with a maximum at about 960 cm^{-1} belongs to the phosphoric acid protonating PPy in the samples
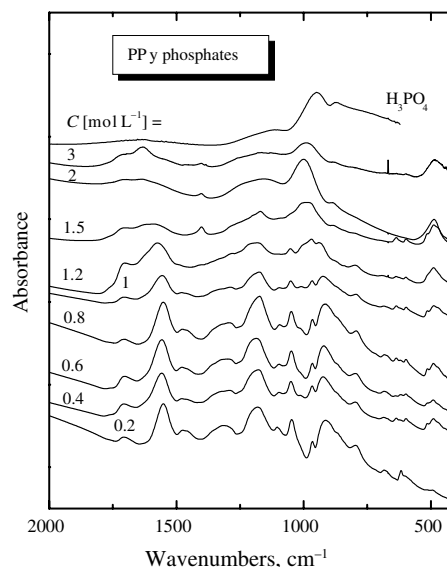

Fig. 10. The FTIR spectra of polypyrrole prepared in the solutions of phosphoric acid of various concentrations, C [mol L^{-1}]. FTIR spectrum of phosphoric acid was measured by ATR method.
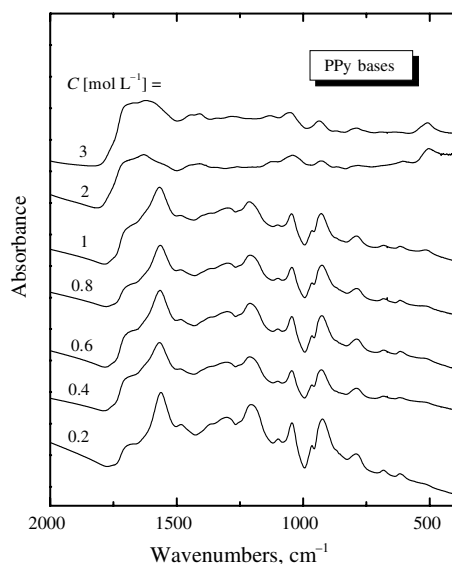
Fig. 11. The FTIR spectra of polypyrrole bases obtained after deprotonation of corresponding protonated polypyrroles prepared in the solutions of phosphoric acid of various concentrations, C [mol L^{-1}].

Fig. 12. The FTIR spectra of ammonium salts prepared after the deprotonation of polypyrroles prepared in the solutions of phosphoric acid, C [mol L^{-1}]. The spectra of ammonium phosphate (AP) and ammonium sulfate (AS) are shown for comparison.

prepared at high acid concentrations. The FTIR spectrum of pure phosphoric acid was measured by the ATR method; this fact may influence the position of this maximum. The differences in the FTIR spectra of PPy prepared at low and high concentrations of phosphoric acid (>1 M) are even better visible for the PPy bases in the region corresponding to C=O vibrations (Fig. 11).

When looking at Fig. 9, the obvious question is what would happen if the oxidation of pyrrole had been carried out in alkaline medium. After the polymerization in water, 0.1 M, and 0.2 M ammonium hydroxide, the oxidation products had conductivity 0.055, 0.010, and 3.3×10^{-3} S cm^{-1}, respectively. The highest conductivity of PPy thus has been found when pyrrole has simply been oxidized in water.

The spectroscopic analysis of the ammonium salts obtained after deprotonation clearly shows that, at low phosphoric acid concentration (0.2 M), PPy is protonated entirely by sulfuric acid (Fig. 12). The proportion of sulfate and phosphate counter-ions in PPy shifts in favour of the phosphate type with increasing phosphoric acid concentration until, at 3 M phosphoric acid, the product is protonated entirely with phosphoric acid. A parallel spectroscopic study on PANI has been reported previously [31] with a similar result.
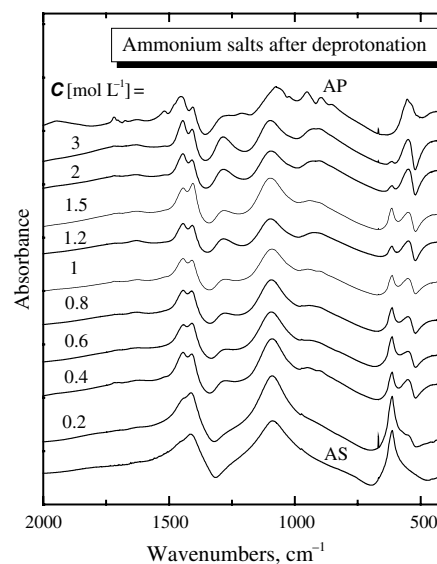
4. Conclusions

The oxidations of aniline and pyrrole, leading to polyaniline and polypyrrole, are governed by the same principles, and their formal chemistry is similar. The oxidative polymerizations of aniline and pyrrole with ammonium peroxydisulfate in aqueous solutions in the presence of 0.2 M hydrochloric acid have been investigated. The same reaction stoichiometry is proposed for both reactions. The yield of polymerization increased as the oxidant-to-monomer molar ratio increased from 0.2 to 1.5. The conductivity of the polymers was only slightly dependent on this ratio; it was of the order of 10^{0} S cm^{-1} for PANI and 10^{-2}–10^{-1} S cm^{-1} for PPy. The maximum conductivity of PANI was 4.0 S cm^{-1} at the oxidant-to-monomer molar ratio 1.3, and of PPy 0.3 S cm^{-1} at the ratio 1.1. The oxidation of aniline and pyrrole is controlled by the acidity of reaction mixture and, consequently, by the proportion between the neutral and protonated monomer molecules.

Both PANI and PPy were deprotonated to the corresponding bases. The FTIR spectra of the ammonium salts obtained after deprotonation show that PANI is protonated mainly by the sulfuric acid produced during the oxidation from ammonium

peroxydisulfate. In the case of PPy, there is a significant participation of chloride counter-ions.

Polyaniline prepared in solutions of phosphoric acid has a conductivity of 2–15.5 S cm^{-1}, virtually independent of the acid concentration over the range 0.2–3 M. On the contrary, the conductivity of PPy was reduced by several orders of magnitude as the acid concentration was raised. The highest conductivity of PPy, 0.3 S cm^{-1}, was obtained in the absence of any acid. Both PANI and PPy were in part protonated by sulfuric acid originating from peroxydisulfate. The participation of phosphate counter-ions increased with increasing concentration of phosphoric acid at the expense of sulfate counter-ions.

Acknowledgements

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