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Polyaniline prepared in solutions of phosphoric acid: Powders, thin films, and colloidal dispersions

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Abstract

Polyaniline (PANI) has been prepared by the oxidation of aniline with ammonium peroxydisulfate in the 0–4 M phosphoric acid. The maximum conductivity of PANI, 15.5 S cm^{-1}, was found with PANI prepared in the presence of 1 M phosphoric acid. The mass loss after deprotonation with ammonium hydroxide revealed that relatively large amounts of phosphoric acid were associated with PANI if the polymerization had been carried out at higher acid concentration. This suggests the protonation of both the imine and amine nitrogens in PANI, the increased adsorption of phosphoric acid by PANI, or the presence of polyphosphate counter-ions. The increasing content of phosphoric acid is also reflected in the increase of sample density. FTIR spectra of ammonium salts collected after deprotonation proved that the counter-ions of the sulfate type, resulting from the decomposition of peroxydisulfate, always participated in the protonation of PANI. The proportion of sulfate to phosphate counter-ions was reduced as the concentration of phosphoric acid in the medium increased.

Thin PANI films were produced in situ on glass surfaces immersed in the reaction mixture during the polymerization of aniline. Optical absorption has been used to assess their thickness, 70–140 nm, which was found to be virtually independent of the acid concentration. The film conductivity was comparable with the conductivity of the PANI powders produced at the same time. Colloidal dispersions were obtained when the reaction mixture contained poly(*N*-vinylpyrrolidone). The particle size, 200–260 nm, and polydispersity, determined by dynamic light scattering, were virtually independent of the concentration of phosphoric acid. The films produced on glass during the dispersion polymerization of aniline were thinner, 20–90 nm, compared with those grown in the precipitation polymerization.

Keywords: Colloids; Conducting polymer; Conductivity

1. Introduction

The conducting form of polyaniline (PANI) is protonated with an acid. The selection of the particular acid influences both the electrical and materials properties of PANI. Most of the preparations concern the PANI hydrochloride [1]. Organic acids, like camphorsulfonic [2,3], dodecylbenzenesulfonic [4,5], naphthalenesulfonic [6], or dinonylnaphthalenesulfonic acid [7], have been used to protonate PANI to improve its processibility and miscibility with commodity polymers or to produce new PANI morphologies. Some applications require a specific method of protonation. Phosphoric acid provides the counter-ion of choice in the corrosion protection of metals with PANI [8,9].

There are several papers dealing with PANI protonated with phosphoric acid but a systematic study has not been made. Polyaniline phosphate was reported to have a good conductivity; Boara and Sparpaglione [10] optimized the synthesis that led to a product having conductivity as high as 85 S cm^{-1}. The thermal stability of the conductivity of PANI phosphate was superior to that of PANI hydrochloride [11,12]. The conductivity of PANI phosphate was reduced to 41% after being exposed for 25 h to 175 °C, while the conductivity of PANI hydrochloride was lower by a factor of 10^5 in the corresponding experiment. Hong and Choi [13] have recently used polyaniline phosphate dispersed in kerosene as an electrorheological fluid. When PANI was prepared in the presence of each of ten various acids, the polymerization in phosphoric acid yielded the product with the highest molecular weight [14]. This fact should positively be reflected in the mechanical properties which,

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along with the electrical parameters, are of importance in practical uses.

If the polymerization of aniline is carried out in the absence of any acid, the polymer conductivity is low [14,15], $\sim 10^{-2}$ S cm^{-1}. The use of hydrochloric acid in equimolar concentration with respect to aniline yielded a product having conductivity of 4.4 S cm^{-1} [1]. The best conductivity result 11.9 S cm^{-1}, was obtained in 1.2 M hydrochloric acid [1]. A high concentration of an acid reduces the conductivity of PANI [16] and, if the acid concentration is above 5 M, no conducting polymer is produced. This means that there exists some optimum concentration of an acid in the reaction mixture that yields a polymer with the best conduction properties. This trend has recently been illustrated also with respect to the polymerization yield by Ayad et al. [17]. That is why we have decided to prepare PANI similarly in media containing various concentration of phosphoric acid.

Polyaniline is usually obtained as a precipitate and is collected after drying as a powder. There are other forms available. Thin PANI films are produced on surfaces immersed in the polymerization mixture used for the oxidation of aniline [12,16,18–20]. The surface polymerization of aniline [21,22] can be used for the coating of various substrates with a PANI overlayer [23–26]. Polyaniline phosphate has been used in the coating of wood sawdust [27]. That is why the films produced on glass surfaces in solutions of phosphoric acid have also been investigated in the present study.

Finally, the colloidal forms of PANI [20,28,29], produced in the presence of a suitable polymeric stabilizer, are of interest for the processing of conducting polymers. Thin films and colloids have similar roots of their formation [30]. The preparation of such colloids, stabilized in the solutions of phosphoric acid with poly(*N*-vinylpyrrolidone), is also discussed below.

2. Experimental

2.1. Preparation of polyaniline powders, films, and colloids

Aniline (0.2 M; Fluka, Switzerland) was oxidized with ammonium peroxydisulfate (0.25 M; Lachema, Czech Republic) in an aqueous medium containing 0–4 M phosphoric acid (Lachema, Czech Republic). A precipitate of aniline phosphate, produced after mixing aniline with phosphoric acid solution, dissolved to yield a clear solution. The reaction was started at ~20 °C by mixing solutions of aniline phosphate and ammonium peroxydisulfate. The progress of polymerization was monitored by following the temperature changes with a digital thermometer. Typically, 100 mL of reaction mixture was prepared in each experiment. The mixture was gently stirred with a magnetic bar. The polymerizations were completed within 10 min. Polyaniline precipitate was collected on a filter, rinsed with corresponding phosphoric acid solution, and then with copious portions of acetone. The PANI powder was dried in air and then over silica-gel beads. The yield of polymerization was calculated from the mass of collected PANI. To obtain colloidal PANI dispersions, the reaction mixture included, in addition, 2 wt% poly(*N*-vinylpyrrolidone) (Fluka; type K90, $M=360{,}000$) [20].

A few millilitres of fresh reaction mixture was poured over three circular glasses of 13 mm diameter and 1 mm thickness attached to an adhesive tape, and placed in a Petri dish. The thin PANI films grew on glass supports during both the precipitation and dispersion polymerization of aniline. After polymerization, the glasses were separated from the tape, rinsed with a corresponding phosphoric acid solution, then with acetone, and dried in air.

2.2. Deprotonation of polyaniline

A 500 mg of protonated PANI was immersed in 20 ml of 1 M ammonium hydroxide. The resulting PANI base was collected on a filter and the mass reduction was determined after washing the base with acetone and drying. The ammonium hydroxide solution containing the ammonium salts of the acid originally protonating the PANI was evaporated. The salts were weighed and then characterized by FTIR spectroscopy.

2.3. Characterization of polyaniline powders

Polymers were compressed with a manual hydraulic press at 700 MPa into pellets, 13 mm in diameter and 1 mm thick. The conductivity was measured by a four-point van der Pauw method using a current source Keithley 238, a scanner Keithley 706 with switching cards, and a Solartron-Schlumberger 7081 Precision Voltmeter. For PANI bases, a two-point method using a Keithley 6517 electrometer was applied. Before such measurements, circular gold electrodes were deposited on both sides of the pellets. The density of PANI was evaluated with a Sartorius R160P balance by weighing the pellets in air and immersed in decane.

Polyaniline powders were dispersed in potassium bromide and compressed into pellets to record the FTIR spectra of protonated PANI, PANI base, and ammonium salt. The measurement was made with a fully computerized Thermo Nicolet NEXUS 870 FTIR Spectrometer with a DTGS TEC detector. The spectra were taken in the transmission mode in the range of 400–2000 cm^{-1} with 64 scans per spectrum at 2 cm^{-1} resolution. All spectra were corrected for the presence of moisture and carbon dioxide in the optical path.

2.4. Characterization of polyaniline films and colloids

The optical spectra of PANI films have been recorded with a spectrometer Lambda 20 (Perkin–Elmer, UK). The thickness of the films, d_f, was estimated with three samples from the optical absorption at 400 nm, A_{400}, by using the relation $d_f(\mathrm{nm}) = 185\, A_{400}$, determined earlier on the basis of optical interferometry calibration [16]. The conductivity of the films was measured by a four-point van der Pauw method as with pellets [16].

Polyaniline dispersions were diluted 60× with 1 M HCl and the particle diameter, D, was determined by dynamic light scattering with an Auto-Sizer Lo-C (Malvern, UK). The apparatus also provided a parameter characterizing the polydispersity, a relative standard deviation of the particle size distribution, *P*.

3. Results and discussion

3.1. Polymerization of aniline

Polymerization of aniline (Fig. 1) is exothermic; its progress can be thus followed by recording the changes of temperature of the reaction mixture [1,31] (Fig. 2). After an induction period, during which the temperature is about constant, a marked increase in the temperature has been observed as the polymerization took place. After the monomer or an oxidant or both have been consumed, the reaction mixture cools down. The induction period became shorter as the concentration of the acid increased (Fig. 2). The rate of polymerization, given by the slope of the temperature dependence, was about the same. The maximum temperatures are also comparable; this means that the reaction heat released in the polymerization is approximately constant and, consequently, the conversion of aniline to PANI roughly equivalent. This is confirmed by the high yield of polymer in all polymerizations (Table 1). The apparent increase in the yield of polymerization at higher acid concentrations is rather due to the increasing content of phosphoric acid in the samples. This effect is discussed below.

From 1 g of aniline, the polymerization produces theoretically 0.972 g of PANI base at a 100% conversion of aniline to PANI (Fig. 1). If each imine nitrogen of the base were protonated with one molecule of phosphoric acid, we would get 1.50 g of PANI salt. The yields are often considerably higher (Table 1). This stimulated a more detailed study of the type and extent of the protonation.

3.2. Protonation and conductivity

The classical protonation concept assumes that the acid reacts with the imine nitrogens in PANI (emeraldine) base (Fig. 3, **1**) and PANI 'salt' is produced as a result (**2**). The protonation of the imine nitrogens (**2a**) has the following consequence: two electrons from the electron pairs located at imine nitrogens are injected into the adjacent quinonoid ring, which is thus converted to the benzenoid form (**2b**). The remaining unpaired electrons on imine nitrogens, two cation-radicals, act as charge carriers in the electric conduction. That is why the increased degree of protonation on imine nitrogens leads to a higher conductivity. Indeed, we observe that the conductivity of PANI increases as the concentration of phosphoric acid increases from 0 to 1.2 M (Table 1). The degree of protonation was determined from the mass loss after deprotonating PANI with ammonium hydroxide. This quantity is discussed below.

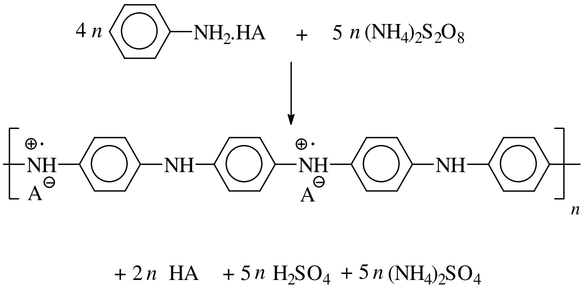

Fig. 1. When aniline is oxidized with ammonium peroxydisulfate, polyaniline is obtained. In the present case, phosphoric acid (HA = H_3PO_4) was used as the acidic medium.

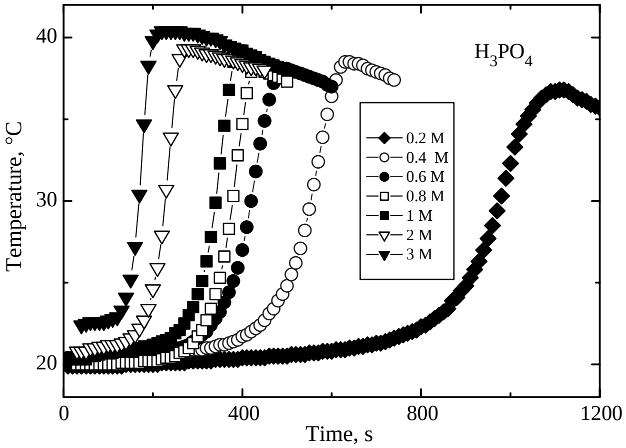

Fig. 2. The temperature profile of aniline polymerization in solutions of phosphoric acid of various concentrations.

When the content of phosphoric acid in the reaction mixture increased above 1.2 M, the conductivity of the produced PANI had an unpronounced tendency to decrease (Table 1). A similar conductivity maximum has been also reported for PANI protonated with hydrochloric acid [16,32,33]. In our opinion, this trend is due to the protonation of amine sites in the PANI chains. The secondary amine group is less basic than the imine nitrogen, yet the protonation of amine groups may be feasible in media of high acidity [34,35]. The protonation of amine nitrogens does not produce any new charge carriers (Fig. 3, **3**). On the contrary, the structure may be less favourable for the conduction.

The accompanying structural changes in the FTIR spectra PANI 'salt' prepared in the media of various concentration of phosphoric acid are presented in Fig. 4. The spectra of the PANI prepared in the presence of phosphoric acid are similar to those reported in the literature [36]. The presence of phosphoric acid in the samples is manifested by the broad band of the tetrahedral PO_4^{3-} vibration. The position of this band observed in the spectra of phosphoric acid at 950 cm^{-1} gradually shifts to 997 cm^{-1} for PANI prepared in 4 M phosphoric acid (Fig. 4). The different position of this band in the spectrum of PANI proves the interaction of acid with PANI backbone. For high contents of phosphoric acid (3 and 4 M) we observe a broad diffuse band above 2000 cm^{-1} characteristic for the protonated imine group [37]. The band inherent to phosphates is missing in the spectrum of PANI prepared in the absence of any acid (Fig. 4), which is protonated only with sulfate counter-ions.

Table 1
Conductivity, σ, and density, ρ, of PANI prepared in solutions of phosphoric acid of various molar concentrations, [H_3PO_4], and of the corresponding PANI bases

[H_3PO_4] (mol L^{-1})	Yield[a] (g g_a^{-1})	Protonated PANI		PANI bases		Acid content	
		σ (S cm^{-1})	ρ (g cm^{-3})	σ (S cm^{-1})	ρ (g cm^{-3})	δ (wt%)	x_A
0	1.04	0.055	1.35	6.0×10^{-8}	1.30	0.10	0.20
0.2	0.87	2.6	1.42	3.0×10^{-7}	1.26	0.31	0.83
0.4	1.48	5.5	1.43	1.6×10^{-6}	1.25	0.33	0.91
0.6	1.68	8.0	1.52	2.5×10^{-6}	1.27	0.42	1.34
0.8	1.77	10.9	1.54	8.0×10^{-7}	1.26	0.39	1.18
1.0	1.96	15.5	1.56	4.3×10^{-7}	1.25	0.52	2.00
1.2	1.86	13.8	1.56	3.3×10^{-6}	1.25	0.55	2.26
1.5	2.63	10.4	1.59	3.2×10^{-6}	1.26	0.67	3.75
2.0	2.99	7.7	1.56	2.2×10^{-6}	1.23	0.68	3.93
3.0	–	9.8	1.57	5.6×10^{-6}	1.26	0.65	3.43
4.0	–	11.3	1.51	1.9×10^{-6}	1.25	0.68	3.93

The mass loss after deprotonation, δ, i.e. the content of acid in PANI, and the number of acid molecules per constitutional unit composed of two aniline molecules, x_A, are also included.

[a] The mass of protonated PANI obtained per gram of aniline monomer.

3.3. Polyaniline bases

The conductivity of PANI bases, ~10^{-7}–10^{-6} S cm^{-1} (Table 1), is about 6–7 orders of magnitude lower than conductivity of the corresponding forms protonated with phosphoric acid, but is considerably higher than that of the bases prepared from PANI hydrochloride [1], 10^{-11}–10^{-8} S cm^{-1}. This is probably caused by the introduction of phosphate or sulfonic groups on aromatic rings in the course of aniline oxidation. These groups, fixed on the PANI chains, provide the internal protonation of imine sites on the neighbouring macromolecules. The FTIR spectra of the bases are about the same irrespective of acid concentration in the reaction mixture (Fig. 5) and correspond to other PANI prepared in the presence of strong acids [15]. The peak at 1378 cm^{-1} corresponds to C–N stretching in the neighbourhood of a quinonoid ring typical for the base state of PANI [38]. The band observed in the spectra of bases at 954 cm^{-1} is most probably connected with adsorbed phosphoric acid. The structure of PANI chains has not been affected by the presence of acid during the polymerization.

Only the polymer prepared in the absence of any acid has a spectrum which is different. The peak at 1044 cm^{-1} observed in this spectrum is due to the S=O stretching vibration of

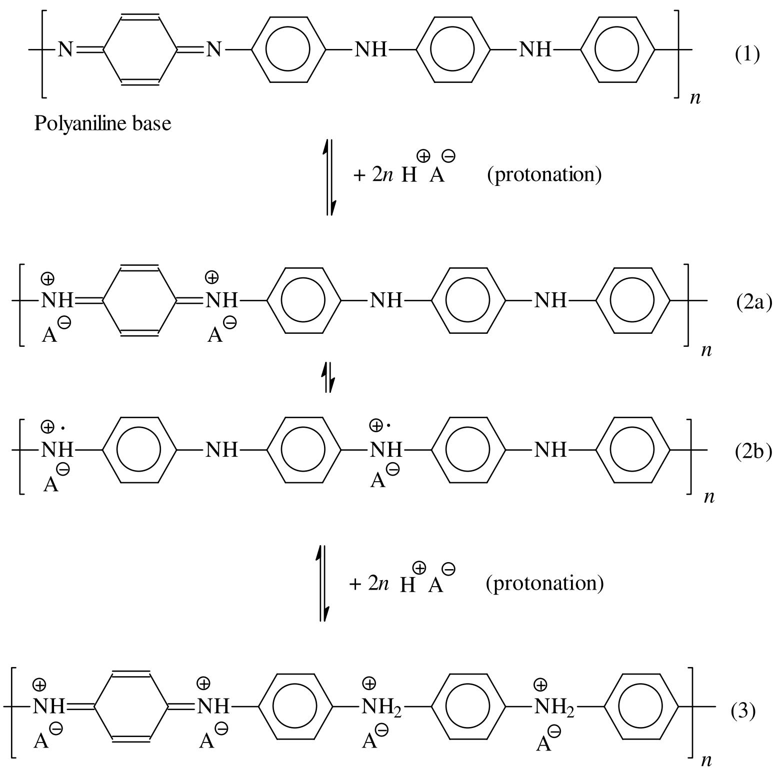

Fig. 3. Polyaniline base (**1**) is protonated on the imine nitrogens with acid to yield polyaniline 'salt' (**2**). The dication structure (**2a**) is in equilibrium with delocalized dication–diradical (**2b**). Further protonation of amine nitrogens (**3**) is feasible in strongly acidic media.

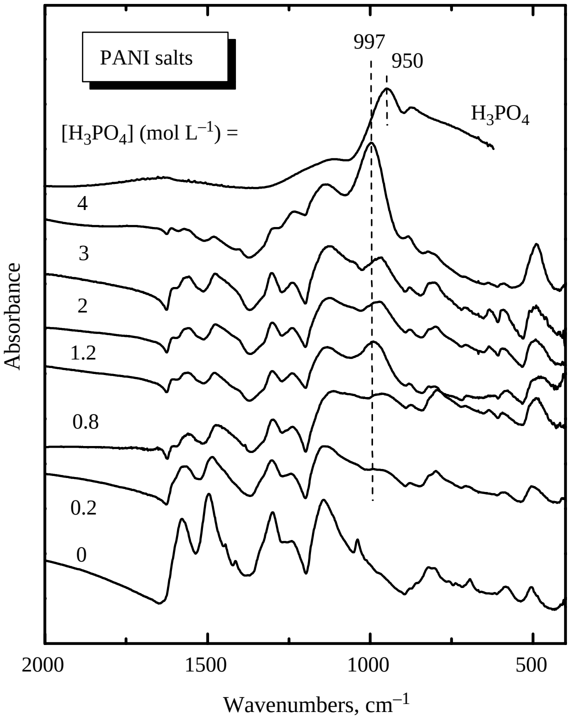

Fig. 4. FTIR spectra of polyaniline prepared in media containing various concentrations of phosphoric acid. The spectrum of phosphoric acid is shown on the top.

sulfonic groups on the aromatic rings. These groups could result from peroxydisulfate radical attack on the benzene rings [39]. Similar ring-substitution by the phosphonic group in PANI phosphate is demonstrated by the occurrence of a new peak at 1008 cm^{-1} [40].

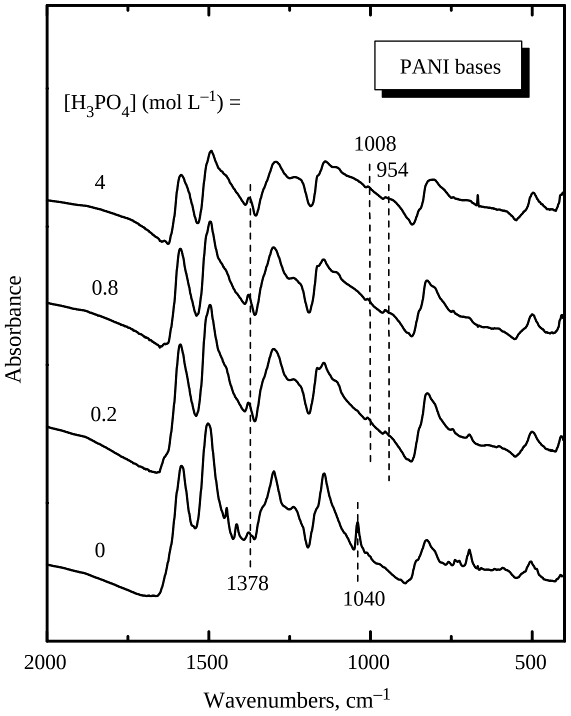

Fig. 5. FTIR spectra of bases from polyanilines prepared in media containing various concentrations of phosphoric acid.

3.4. The type of protonation

When PANI preparation is carried out in the medium of an organic or inorganic acid, one often assumes that the protonation of PANI is achieved by this acid. This need not always be correct. During the oxidation of aniline with ammonium peroxydisulfate, sulfuric acid is produced as a by-product (Fig. 1). That is why the course of polymerization can be followed by monitoring the increasing acidity [41,42]. At a typical concentration of 0.2 M aniline and 0.25 M ammonium peroxydisulfate [1], 0.25 M sulfuric acid is produced at complete conversion of aniline to PANI (Fig. 1). This acid competes with the acid constituting the reaction medium for the protonation of PANI. When the polymerization has been carried out in a solution of acetic acid, PANI with hydrogen sulfate counter-ions has invariably been obtained [15,34].

The PANI produced at various concentration of phosphoric acid was deprotonated with ammonium hydroxide. The ammonium salts containing the original counter-ions have been collected by evaporation of the ammonia solution after deprotonation. The FTIR spectra of these salts (Fig. 6) clearly indicate that all the PANI samples contained both the sulfate (e.g. one of the four normal modes of the tetrahedral counter-ion HSO_4^- at 613 cm^{-1}) and phosphate counter-ions (e.g. some of the four normal modes of the tetrahedral counter-ion PO_4^{3-} at 1444, double peak 952 (894), and 550 cm^{-1}) [43]. The proportion of phosphate counter-ions increases with increasing concentration of phosphoric acid in the medium, as expected, but sulfate counter-ions always participate. This is in accordance with the earlier observation that PANI samples

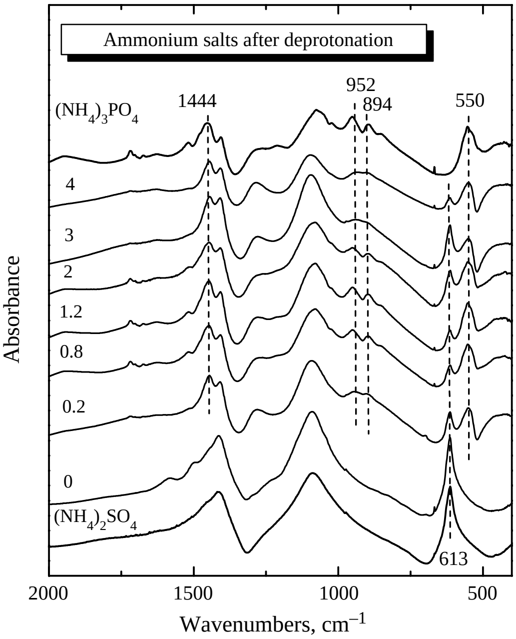

Fig. 6. FTIR spectra of ammonium salts collected after deprotonation of protonated PANI to the PANI bases. The concentration of phosphoric acid (mol L^{-1}) in the reaction mixture is denoted at the individual spectra. The spectra of ammonium phosphate (top) and ammonium sulfate (bottom) are shown for comparison.

prepared in the presence of weak organic acids are protonated exclusively by the hydrogen sulfate counter-ions [14,15,34,44].

3.5. The degree of protonation

The amount of acid in PANI can be determined as the mass loss, δ, after deprotonation (Table 1). Now we are interested to learn how many molecules of acid, x_A, are present in PANI per constitutional unit. These two quantities are related as $x_A = (M_B/M_A)\ \delta/(1-\delta)$, where $M_A = 98.00\ \mathrm{g\ mol^{-1}}$ and $M_B = 181.22\ \mathrm{g\ mol^{-1}}$ are the molar masses of phosphoric acid and the PANI-base segment comprising two aniline units, respectively. In a currently accepted model that assumes the full protonation of imine nitrogens with a monobasic acid (Fig. 3), this fraction would be $x_A = 1$.

Phosphoric acid is tribasic, so, in principle, one molecule of acid could simultaneously protonate three imine sites, the counter-ions being PO_4^{3-}, and $x_A = 1/3$. In the case of hydrogen phosphate counter-ions, HPO_4^{2-}, we would have $x_A = 1/2$, and for dihydrogen phosphate anions, $H_2PO_4^-$, $x_A = 1$. The situation is more complicated by the mixed protonation with phosphoric and sulfuric acids, as discussed above but simplified by the fact that the molecular weights of phosphoric and sulfuric acids are virtually the same, $M_A = 98.00$ and 98.08, respectively.

The experimental values of x_A are close to the theoretical value of unity, corresponding to full protonation with dihydrogen phosphate counter-ions, for polymerizations in 0.2–0.8 M phosphoric acid (Table 1). At 1 M and higher concentrations of phosphoric acid, the acid content in PANI is much higher (Table 1). This means that: (1) amine nitrogens become protonated in addition to imine ones as the concentration of an acid in the reaction mixture increases (Fig. 3, **3**), (b) phosphoric acid forms complex polyanions that are associated with PANI, or (c) there is specific adsorption of phosphoric acid in PANI. None of these possibilities is favoured at the present time.

The increasing content of phosphoric acid in PANI is also reflected by the increasing density of the products (Table 1). These are higher than those of PANI hydrochloride [1], 1.33 g cm^{-3}, or PANI sulfate [14], 1.40 g cm^{-3}. On the other hand, the density of the PANI bases is the same for all samples (Table 1), as expected on the basis of FTIR spectra (Fig. 5) discussed above.

3.6. Thin polyaniline films

The surface of glass immersed in the reaction mixture becomes coated with a thin PANI film during the oxidation of aniline. It has earlier been reported that the thickness of the films prepared in solutions of hydrochloric acid is independent of the acid concentration [16], at least compared with other factors, such as the aniline concentration or the aniline-to-oxidant molar ratio. Other studies based on quartz-crystal-microbalance experiments have suggested some dependence on acid concentration [17]. With phosphoric acid, we have not observed any conclusive trend in the film thickness as the concentration of acid in the reaction mixture increased (Table 2). The conductivity of the films was, within the experimental error, comparable with the conductivity of the corresponding PANI powders (Table 1), in accordance with the earlier observations [16].

3.7. Colloidal polyaniline dispersions

It has been proposed that the formation of PANI thin films and colloidal dispersions have a common origin, i.e. that these two polymer morphologies are related [30]. It has also been reported earlier that the film thickness and the radius of colloidal particles of PANI hydrochloride prepared under similar reaction conditions have about the same dimensions [45]. The present study again confirmed this conclusion for the polymerization carried out in solutions of phosphoric acid (Table 2). The particle size is independent of the acid content, except for the extreme cases of 0 and 4 M concentrations. This applies also to the polydispersity of colloidal particles in size

Table 2

Thickness, d_f, and conductivity, σ, of PANI films deposited on glass during the polymerization of aniline in aqueous solutions of phosphoric acid of various molar concentrations, [H_3PO_4], in the absence (precipitation polymerization) and in the presence (dispersion polymerization) of 2 wt% poly(*N*-vinylpyrrolidone)

[H_3PO_4] (mol L^{-1})	Thin films				Colloidal particles	
	Precipitation polymerization		Dispersion polymerisation		*D* (nm)	*P*
	d_f (nm)	σ, S cm^{-1}	d_f (nm)	σ, S cm^{-1}		
0	84	0.78	35	0.018	(1224)	(1)[a]
0.2	128	2.1	82	1.2	244	0.25
0.4	124	6.0	79	1.5	210	0.28
0.6	120	9.8	88	2.8	211	0.29
0.8	122	14.0	–	–	208	0.24
1.0	83	22.6	–	–	207	0.27
1.2	137	21.5	81	3.8	218	0.27
1.5	90	21.6	26	5.4	216	0.25
2.0	107	20.6	18	4.2	216	0.27
3.0	73	21.3	29	1.1	258	0.25
4.0	80	17.4	–	–	1868	0.60

In the latter case, colloidal dispersion particles of diameter, *D*, and polydispersity, *P*, have been produced instead of a PANI precipitate.

[a] Relative standard deviation of the particle-size distribution. $P = 0$ for monodisperse particles, $P = 1$ for the hypothetical extreme polydispersity.

(Table 2), which is typical for the values reported in the literature [20,28].

Films produced in the dispersion polymerization on glass surfaces are thinner compared with the films grown in the precipitation polymerization (Table 2), again in accordance with earlier observations on PANI hydrochloride films (45). The conductivity of the films was found to be about the same as that of the powders (Table 2); in earlier studies [45], the conductivity of the films produced in the dispersion polymerization of aniline was higher.

4. Conclusions

Polyaniline was prepared by the oxidation of aniline with ammonium peroxydisulfate in aqueous solutions of phosphoric acid. There is an optimum 1.0 M concentration of the phosphoric acid that yields PANI with the highest conductivity, 15.5 S cm^{-1}. At higher acid concentration, the content of phosphoric acid in PANI was considerably higher than expected according to the classical concept of protonation. The protonation of amine sites, the formation of polyphosphate counter-ions, or adsorption of phosphoric acid in PANI have been proposed as possible explanations. Counter-ions of the sulfate type, produced by the decomposition of peroxydisulfate, have always been found in the products. They dominate in PANI prepared at low phosphoric acid concentrations.

The molecular structure of the produced PANI chains is independent of the concentration of phosphoric acid over a broad range, 0.2–4.0 M. All the PANI bases had identical FTIR spectra. The various levels and types of protonation, however, are reflected in the FTIR spectra.

Polyaniline films grow on glass surfaces during the polymerization. Their thickness, 70–140 nm, is generally only slightly dependent on the concentration of phosphoric acid in the reaction mixture. The conductivity of the film is comparable with the conductivity of PANI powders produced at the same time.

In the presence of poly(*N*-vinylpyrrolidone), colloidal PANI dispersions were produced in 0.2–3 M phosphoric acid. In the absence of acid or at 4 M acid concentration, a precipitate was obtained instead of a colloid. The colloidal-particle sizes, 210–260 nm, were virtually independent of the acid concentration. The films produced on glass in dispersion polymerization were thinner than those from the precipitation polymerization of aniline.

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