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Spectroscopic studies of polyaniline protonation with poly(alkylene phosphates)

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Polyaniline doped with poly(alkylene phosphates) has been studied by Fourier transform infra-red, X-ray photoelectron and ultraviolet/visible spectroscopies. The protonation of the polymer was indicated by the appearance of infra-red modes characteristic of polyaniline salts and by the bands typical of polyphosphates at ca. 1000 cm^{-1}. X-ray photoelectron spectra showed a decrease in the concentration of imine groups as well as the co-existence of ionized and unionized phosphates independent of the doping level. The influence of the protonation method on the obtained product was observed.

(Keywords: polyaniline; protonation; poly(alkylene phosphates))

INTRODUCTION

Polyaniline (PANI) has recently attracted significant research interest as the most stable conducting polymer. Owing to its electrical, optical and electrochemical properties PANI can be used in a variety of industrial applications. For this reason a large effort has been undertaken to obtain processable polyaniline.

Undoped polyaniline, i.e. polyemeraldine base, has been found to dissolve in *N*-methylpyrrolidinone, NMP[1], tripropylamine[2] or pyrrolidine[2]. Solutions of the doped form of PANI were prepared by dissolving emeraldine base in concentrated strong acids such as, for example, concentrated sulfuric acid[3]. In a search for processing media other than sulfuric acid, several attempts to produce protonated PANI soluble in organic media have been reported. In particular, functionalized sulfonic acids[4] or phosphoric acid diesters[5,6] have been found to induce solubility of protonated PANI in commonly used weakly polar or nonpolar solvents. Moreover, this discovery strongly facilitates the fabrication of conducting polyblends of PANI and commercial non-conducting polymers by solution or thermal processing[4,6].

Recently, we have reported that PANI can be doped with poly(alkylene phosphates), PAPs[7]. Stable solutions of PANI protonated with PAPs can be formed in NMP or *m*-cresol, as has been proved by ultraviolet/visible/near infra-red (u.v./vis./n.i.r.) spectroscopy[8]. Similarly, solid PANI can be also protonated with PAPs. One may expect that protonation phenomena in solution and in the solid state may differ. In addition, the equilibrium of protonation can be changed after evaporation of the solvent. We have therefore undertaken a detailed study of the protonation of PANI with selected polyphosphates combining 3 spectroscopic methods (Fourier transform infra-red (*FT*i.r.), X-ray photoelectron spectroscopy (X.p.s.) and u.v./vis./n.i.r.). Two series of samples were prepared:

- PANI protonated in the solid state by treatment with PAPs in ethanol (EtOH)/H_2O solution
- PANI protonated in solution by addition of an appropriate polyphosphate solution to the solution of PANI base in NMP or *m*-cresol.

EXPERIMENTAL

Polyaniline (PANI) was synthesized chemically according to the method of Cao *et al.*[9]. Pristine PANI was

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converted to the base form by treatment with 0.1 M aqueous ammonia for 5 h. It was then washed with distilled water and methanol and finally dried in vacuum.

Poly(alkylene phosphates) (PAPs) were prepared according to the method described in refs 10 and 11. The method involves the preparation of polyphosphonates via polycondensation of dimethyl phosphate with corresponding diols followed by their oxidation to polyphosphates with N_2O_4. Number average molecular weight, M_n, as determined by osmometry varied from 9000 to 14 000.

Polyemeraldine base powder was protonated in 8×10^{-3} M solutions of PAPs in $EtOH/H_2O$ (2 : 3). The product was filtered, washed with EtOH and dried in vacuum. Solutions of PANI protonated with PAPs were prepared by direct mixing of PANI/NMP solution with an appropriate polyphosphate dissolved in the same solvent. Solid films were fabricated from the solutions by evaporation of the solvent at 50°C. The samples with the thickness $\ll 1\,\mu$m were treated as 'thin' films and the samples with the thickness of several μm as 'thick' films.

*FT*i.r. spectra were recorded on a Digilab FTS 60V spectrometer at room temperature on pressed KBr pellets. U.v./vis. spectra were measured with a Perkin-Elmer Lambda 2 spectrophotometer. X.p.s. measurements were performed on an ESCALAB-210 (Fisons Instruments, VG Scientific) spectrometer with a Mg Kα X-ray source (1253.6 eV photons). The X-ray source was run at 12 kV and 20 mA. Vacuum-dried samples were mounted onto a standard holder by using double-sided adhesive tape. The pressure in the analysis chamber during scans was kept below 10^{-8} Torr. The binding energies were referenced to the C1s graphite carbon peak at 284.6 eV in order to compensate the charging effects for each sample. The spectra were deconvoluted into suitable components consisting of a Gaussian line shape with a Lorentzian function. All fitting parameters were freely adjustable and determined for each spectrum with an iterative, least-squares fitting routine.

RESULTS AND DISCUSSION

Polyaniline in the oxidation state of polyemeraldine can be conveniently doped with PAPs. Standard methods of doping can be used in this case, such as for example, protonation of solid polyemeraldine powder in the solution of polyphosphates in $EtOH/H_2O$ mixtures. However, macromolecular anions are not able to diffuse easily inside PANI grains. We can suppose that in this doping method anions are mainly distributed on the surface of solid PANI. Alternatively, PANI can be doped by mixing polyemeraldine/NMP solution with PAP solution in the same solvent. The polymer undergoes protonation but does not precipitate from the solution[7]. In this case molecular mixing of both macromolecular components of the resulting polyblends occurs. Therefore in this case uniform distribution of the dopant within PANI matrix is expected upon the removal of the solvent.

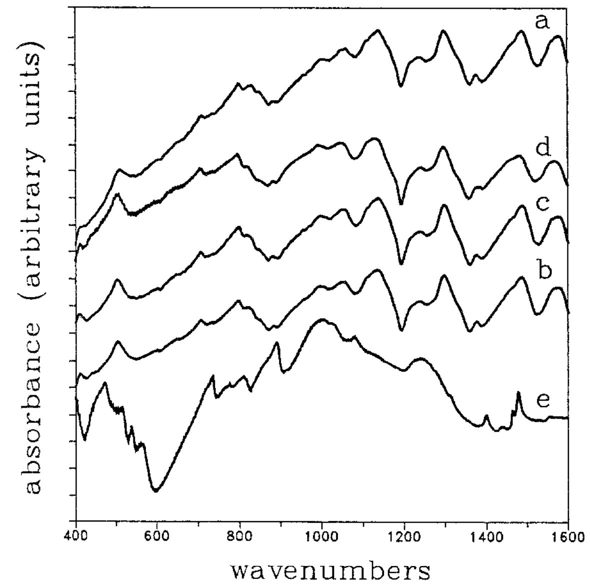

Figure 1 Infrared spectra of polyaniline protonated with poly(hexamethylene phosphate) in $EtOH/H_2O$ solution: (a) $y = 0.03$; (b) $y = 0.08$; (c) $y = 0.17$; (d) $y = 0.27$; (e) poly(hexamethylene phosphate). (y is defined as the molar ratio of PAP to PANI unit)

Table 1 I.r. wavenumbers of the vibrations of polyaniline protonated with poly(hexamethylene phosphate), PHMeP, in $EtOH/H_2O$ solution

	PANI/PHMeP				
PANI	$y = 0.03$	$y = 0.08$	$y = 0.17$	$y = 0.27$	PHMeP
			3450	3468	
3387	3380	3380			
3241	3240	3240	3231	3226	
3049	3049	3049	3049		
					2941
					2858
					1680
1583	1576	1576	1573	1571	
1493	1486	1490	1487	1479	1478
1378	1375	1376	1376	1377	1397
1304	1298	1298	1298	1296	
1238	1241	1240	1239	1242	1248
1160	1137	1137	1134	1129	
1103					1079
	1059	1057	1053	1044	1033
	999	999	996	992	1003
	882	883	882	882	889
828	818	816	818	818	
	798	797	797	795	
	706	707	708	704	723
505	509	504	504	497	473

*FT*i.r. spectra of PANI protonated with polyphosphates in $EtOH/H_2O$ solution are presented in *Figure 1*. The band at 1160 cm^{-1}, assigned to Q=N–B, B–NH–B (where Q is a quinoid ring and B is a benzoid ring)[12], or to C–H bending coupled to the carbon backbone[13], shifts upon protonation to 1130 cm^{-1}. This change is so characteristic in all polyemeraldine systems that it can be treated as diagnostic of the protonated state. Similarly, the bands corresponding to quinoid (N=Q=N) and benzoid (N–B–N) stretching[12] at 1583 and 1493 cm^{-1} in the emeraldine base spectrum are shifted to 1571 and 1479 cm^{-1}, respectively. The extent of the shifts depends on the concentration of the dopant and increases with the increase of the polyphosphate content in polyblend (*Table 1*). The presence of PAP is manifested mainly by strong absorptions around 1000 cm^{-1}. The band at ca. 1050 cm^{-1} can be assigned to ν(P–O–C)$_{as}$ vibration and that at ca. 995 cm^{-1} to δ(P–OH) vibration[14–16]. In the spectrum of

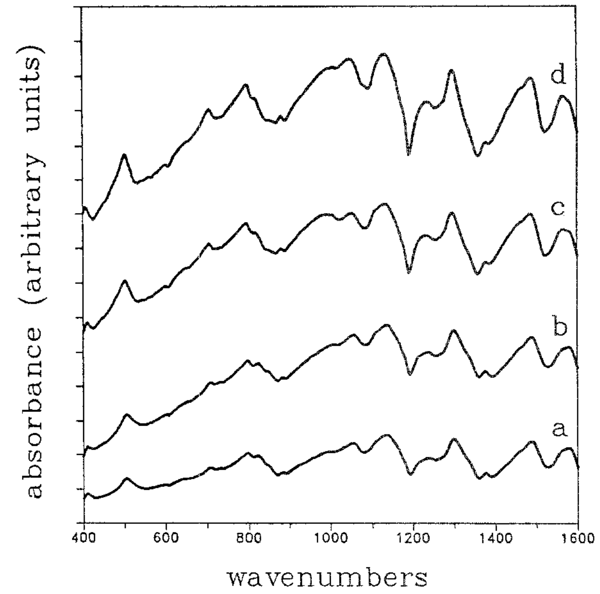

Figure 2 Infrared spectra of polyaniline protonated with poly(alkylene phosphates) in EtOH/H_2O solutions: (a) $n = 5, y = 0.11$; (b) $n = 7$, $y = 0.11$; (c) $n = 7, y = 0.32$; (d) $n = 12, y = 0.32$. (n, length of alkylene spacer)

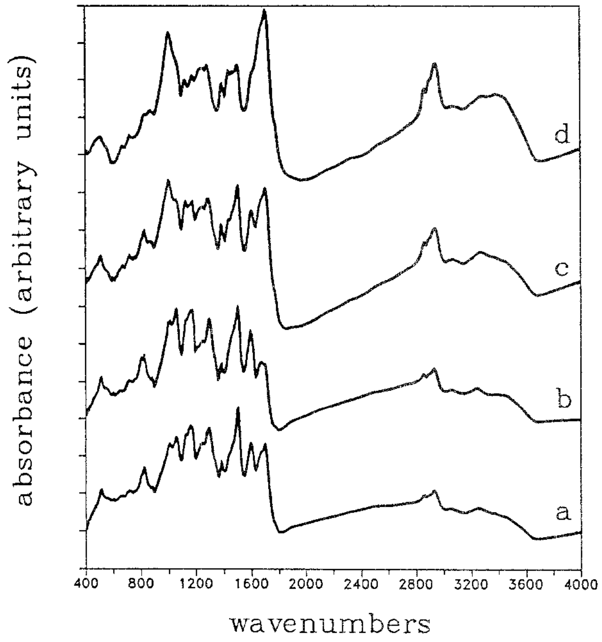

Figure 3 Infrared spectra of thin polyaniline films obtained from PANI/PHMeP/NMP solutions: (a) $y = 0.32$; (b) $y = 0.52$; (c) $y = 0.85$; (d) $y = 2.18$

pristine poly(hexamethylene phosphate) the corresponding peaks are located at 1038 and 995 cm^{-1}, respectively. The separation of both bands is very difficult, because the ν(P–O–C) vibrations are superimposed on (P–OH) deformation in the case of aliphatic phosphates[15,16]. Significant broadening of the (P–OH) band (especially below 1000 cm^{-1}) is probably caused by its overlap with the $\nu(\text{P–O–C})_{\text{sym}}$ band which should be centered at 970 cm^{-1} (ref. 16). It should be noted that the intensity of the (P–OH) peak increases slightly with the increase of the dopant content in the polyblend (*Figure 1*). Thus we can assume that macroanions are distributed mainly on the surface of PANI grains. Surface limited doping puts additional steric restriction on the protonation and the dissociation of P–OH groups must be limited due to steric reasons despite significant flexibility of (CH_2) spacers. The spectra of PANI doped with polyphosphates are also influenced by ν(P=O) and $\delta(CH_2)$ vibrations. The ν(P=O) vibration at 1248 cm^{-1}[14–17] is superimposed on BBB stretching of PANI occurring at 1238 cm^{-1}. Also, the band characteristic of the benzoid sequence (1479 cm^{-1}) is broadened by the superposition with (CH_2) deformation of polyphosphate which occurs in the range of 1460–1470 cm^{-1}.

Protonation of PANI with polyphosphates must, of course, result in the formation of ionic phosphates PO^-. The vibrations of this group, in the case of aliphatic esters, should appear at 1150 cm^{-1} (refs 15 and 16), i.e. in the very close vicinity of 1130 cm^{-1} mode of doped PANI In all our spectra we observe only one broad peak in this region. It is difficult to state unequivocally whether this band arises only from the PANI mode or whether it must be treated as a superposition of PANI vibration with ionic phosphate vibration. Thus, analysing solely the *FT*i.r. spectra we cannot estimate an average protonation level of PANI powder.

The protonation of PANI with polyphosphates of different length of alkylene spacer ($n = 5, 6, \ldots, 12$) does not change significantly the *FT*i.r. spectra (*Figure 2*). All features characteristic of doped PANI and polyphosphates discussed above are clearly observed. The increase of dopant content causes an increase in the red shift of the PANI bands. The peak intensities at 995 and 1050 cm^{-1} show that for the same molar content of phosphates with different length of the methylene spacer, the concentration of unionized P–OH groups is very similar, i.e. the protonation level is also similar.

Figure 3 shows *FT*i.r. spectra of PANI films obtained from PANI/PAP/NMP solution after evaporation of the solvent. In this case the spectra are strongly influenced by the presence of NMP in the films. The NMP vibration appears evidently at 1698 cm^{-1}. This band corresponds to (C=O) stretching. Strong ν(C–N) vibration of NMP at 1500 cm^{-1} is superimposed on (N–B–N) stretching of PANI. Other bands attributed to NMP vibrations are superimposed on the vibrations of PANI and polyphosphate. However, several differences in the spectra as compared to those presented in *Figure 1* can be distinguished. The vibrations assigned to $\nu(\text{POC})_{\text{as}}$ and δ(POH) are slightly shifted to higher wavelengths, i.e. to 1557 and 1009 cm^{-1}, respectively. The last one can be superimposed on 1000 cm^{-1} of $\nu(\text{C–N})_{\text{sym}}$ vibration of NMP. We can observe that the NMP content in the films increases with an increase in the doping level. Significant differences between the spectra of *Figures 3* and *1* are also noticed for PANI bands. In the case of PANI films the bands corresponding to quinoid and benzoid stretching are shifted towards higher wavelengths, i.e. in an opposite direction to PANI powders (*Figure 1*). Moreover, in addition to the characteristic polyemeraldine salt (1130 cm^{-1}) band, an additional peak at 1162 cm^{-1} typical of non-protonated polymer is clearly visible for $\text{PANI(PAP)}_{0.14}$. We can suppose that the evaporation of the solvent strongly influences the equilibrium of the protonation. The films contain both protonated and non-protonated forms of PANI, although the protonation is higher for higher polyphosphate contents. Simultaneously, we observe an increase of the NMP

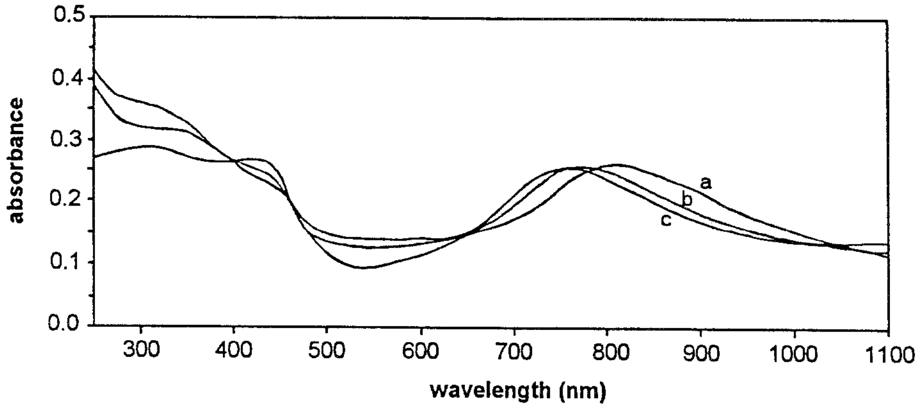

Figure 4 U.v./vis. spectra of thin polyaniline films obtained from PANI/PHMeP/NMP solutions: (a) $y = 0.32$; (b) $y = 0.52$; (c) $y = 0.85$

content. Thus, PANI chains are strongly solvated by the NMP molecules. In the range of ν(N–H) vibrations (*Figure 3*) we can distinguish the vibrations at 3467, 3380 and 3270 cm^{-1}. Furukawa *et al.*[18] suggested that the 3380 cm^{-1} peak is attributed to (N–H) stretching of $-C_6H_4NHC_6H_4-$ groups. The band at 3467 cm^{-1} can be assigned to (N–H) vibration free of H-bonding and that at 3270 cm^{-1} to (N–H) vibration with strong H-bonds[18]. The intensity of the 3467 cm^{-1} band decreases with an increase in NMP content in the film and for the spectrum 3d, only the two last peaks (i.e. 3271 and 3377 cm^{-1}) are observed. We can conclude that PANI chains are strongly solvated by the NMP molecules.

U.v./vis. spectra of thin films obtained from PANI/PAP/NMP solutions (*Figure 4*) show only the features characteristic of the protonated PANI, i.e. the bands at ca. 436 and 780 nm[19]. As in the case of PANI/PAP/NMP solution[8] the maximum of the second peak shifts towards higher energy with the increase of dopant content. It should be noted that by u.v./vis. we cannot observe the non-protonated form of PANI detected by *FT*i.r. for 'thick' films.

Useful information about the protonation of PANI can be obtained from X.p.s. studies. We have investigated 'thin' and 'thick' PANI films as well as PANI powders. The C1s core level spectrum of pristine polyemeraldine base film is slightly asymmetric and centered at 284.6 eV. The N1s spectrum (*Figure 5a*) is nearly symmetric and can be deconvoluted into two major peaks: one located at 398.2 eV and the second at 399.2 eV. The respective peaks can be assigned to the imine and amine nitrogens[20–22]. The interaction of PANI with polyphosphates induces significant changes in the N1s spectrum. The peak envelope shifts towards higher energies and becomes asymmetric. It can be deconvoluted into four components (*Table 2*). The peak attributed to the imine nitrogens decreases in intensity with an increase in dopant content. The peak corresponding to the amine nitrogens remains essentially unchanged. Two new peaks of the high energy grow and increase in intensity with increasing doping level. These two last peaks can be assigned to NH^+ radical–cation and to imine cation $=NH^+$, respectively[22,23]. Chan *et al.*[24] proposed an opposite interpretation. A decrease of the intensity of the imine components and the presence of two high-energetic peaks show unequivocally that PANI is protonated with polyphosphates. However, there exist significant parts of the polymer which remain unprotonated. These results are in good agreement with our *FT*i.r. measurements. The protonation level estimated from the N1s spectra (estimated from

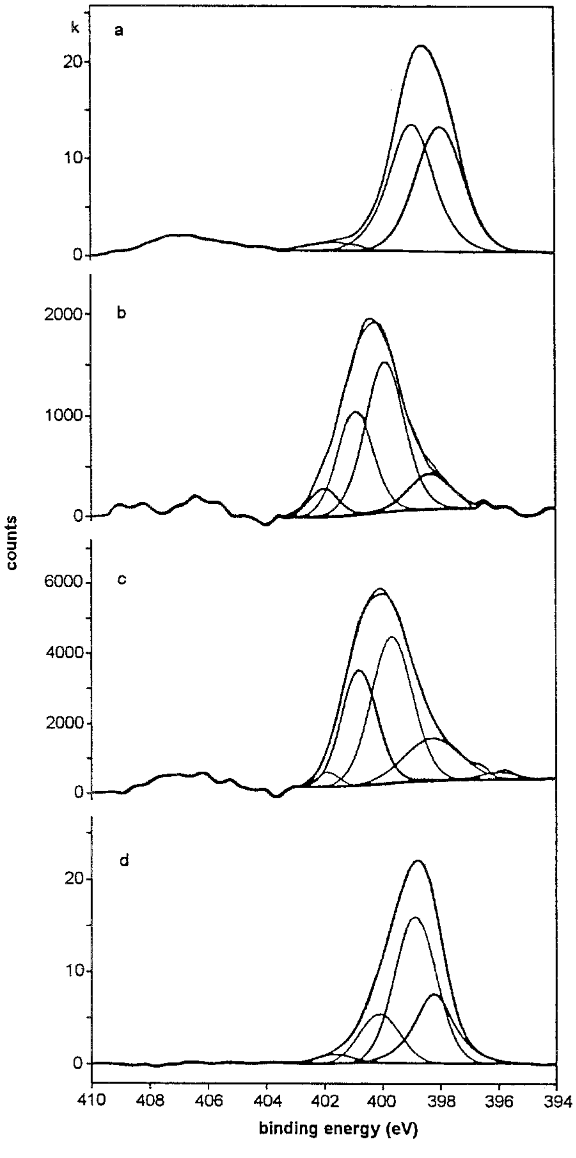

Figure 5 The N1s core-level spectra of polyaniline film (a) and polyaniline films obtained from PANI/PHMeP/NMP solutions, $y = 0.52$ (b), $y = 0.85$ (c), $y = 2.18$ (d)

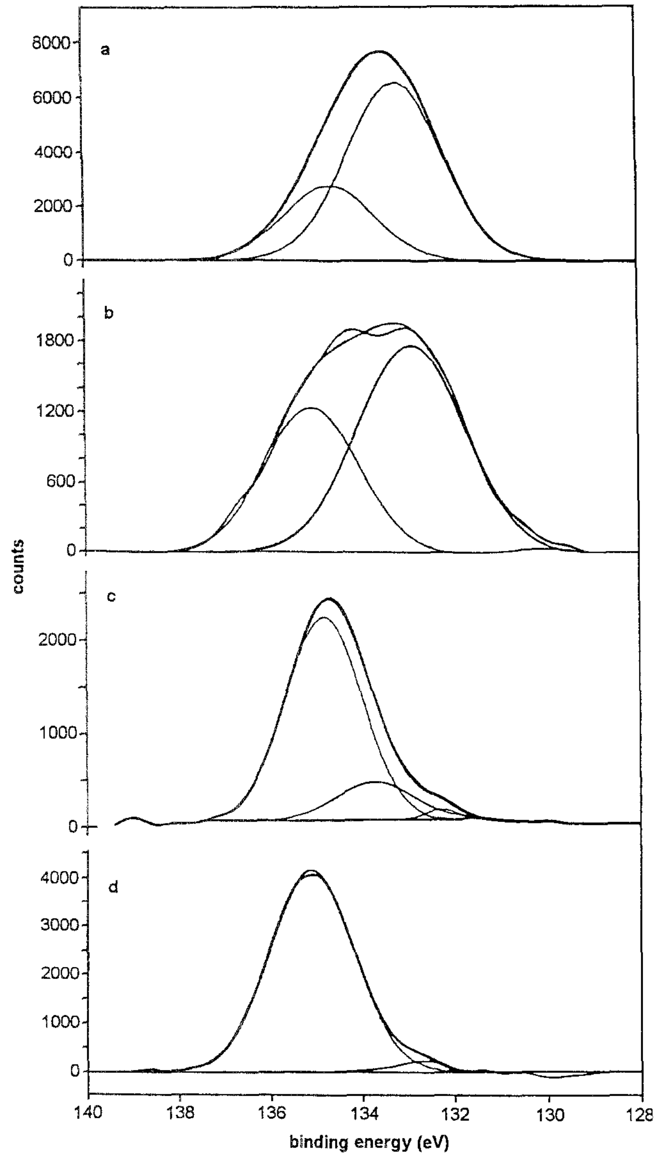

Figure 6 The P2p spectra of polyaniline films obtained from PANI/PHMeP/NMP solutions: (a) 0.52; (b) $y = 0.85$; (c) $y = 2.18$; (d) PHMeP

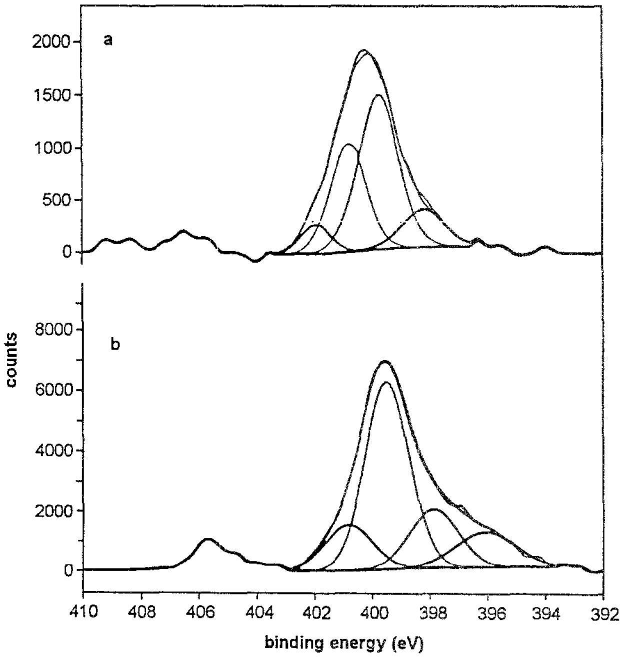

Figure 7 The N1s core-level spectra of polyaniline: (a) 'thin'; (b) 'thick' films obtained from PANI(PHMeP)$_{2.18}$/NMP solution

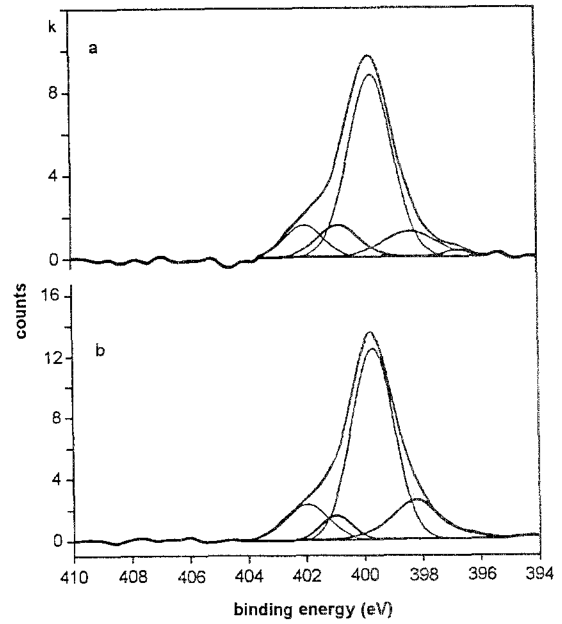

Figure 8 The N1s spectra of polyaniline powder protonated with PHMeP in EtOH/H$_2$O solution: (a) $y = 0.06$; (b) $y = 0.14$

the ratio of the surface of high-energetic components to the total N1s peak surface) is equal to 0.21 for PANI(PAP)$_{0.52}$, 0.33 for PANI(PAP)$_{0.85}$ and 0.38 for PANI(PAP)$_{2.18}$. Additional information about the extent of the ionization of the dopant can be extracted from P2p spectra (*Figure 6*). The spectra can be deconvoluted into two peaks at 133.8 eV and 134.9 eV. The surface ratio of both peaks changes from 2.45 for PANI(PAP)$_{0.52}$, 1.61 for PANI(PAP)$_{0.85}$ to 0.19 for PANI(PAP)$_{2.18}$. The P2p spectrum of poly(hexamethylene phosphate) can be fitted with only one peak located at 135.1 eV. Comparing these data we can assign the first peak (at 133.8 eV) to ionized phosphate (P–O$^-$) and the second one (at 134.9 eV) to unionized phosphate[25,26]. These results confirm our observations of *FT*i.r. spectra of the coexistence of ionized and unionized dopant molecules.

Table 2 X.p.s. results of polyaniline protonated with poly(hexamethylene phosphate), PHMeP

Sample	N1s					P2p	
PANI		398.2	399.2				
F, $y^a = 0.52$		398.7	399.4	400.7	402.2	133.5	134.6
F, $y = 0.85$		398.4	399.7	400.9	402.0	133.2	135.0
F, $y = 2.18^b$		398.2	399.8	400.8	401.9	133.8	134.9
F, $y = 2.18^c$	396.3	398.0	399.7	401.0			
P, $y = 0.06$		398.4	399.7	400.8	402.0	133.9	134.8
P, $y = 0.14$		398.3	399.7	401.0	402.0	134.0	134.9
PHMeP							135.1

F, film; P, powder
[a] y, molar ratio of PHMeP to PANI unit
[b] 'Thin' film
[c] 'Thick' film

It should be noted that we can observe meaningful differences between the N1s spectra measured for 'thick' and 'thin' PANI/PAP films (*Figure 7*). In the

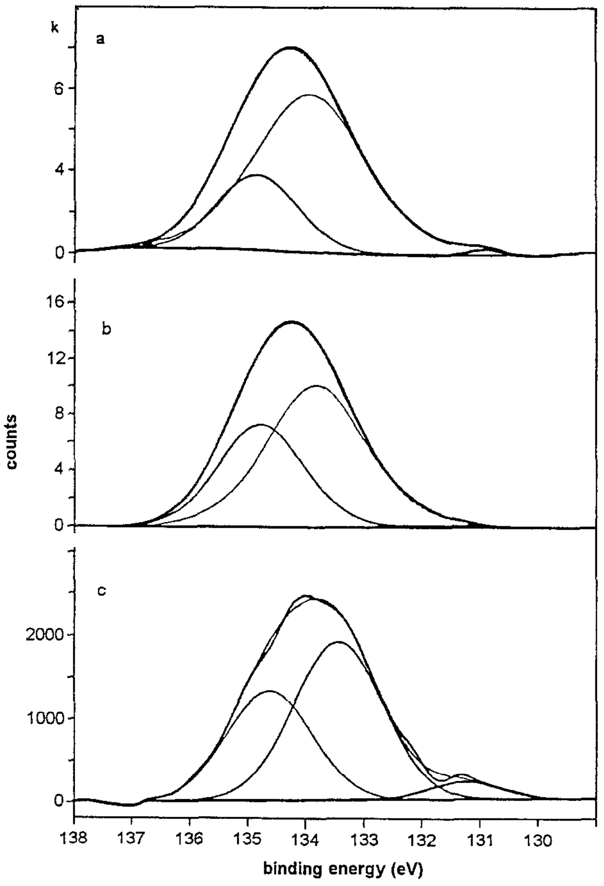

Figure 9 The P2p core-level spectra of polyaniline powder protonated with PHMeP in EtOH/H_2O solution: (a) $y = 0.06$; (b) $y = 0.14$; (c) $y = 0.27$

case of a 'thick' film a low binding energy component at 396.3 eV appears in the N1s spectrum. We can suppose that this peak is attributed to nitrogens of NMP. NMP can be evaporated totally from 'thin' films, but 'thick' films retain significant quantity of this solvent.

X.p.s. spectra measured for polyaniline powders protonated with polyphosphates are similar to that of PANI/PAP 'thin' films. The N1s and P2p spectra can be deconvoluted into corresponding components (*Table 2*). Similarly as in the previous cases the coexistence of ionized and unionized phosphate molecules can be observed. The increase of polyphosphate content causes only minor changes in the N1s spectra (*Figure 8*), although simultaneously we can notice some increase of the content of unionized phosphate (*Figure 9*).

CONCLUSION

In summary, PANI can be protonated with poly(alkylene phosphates) using different techniques. The dissociation of P–OH groups is limited for steric reasons. Unionized and ionized phosphates groups co-exist in the same sample. Unionized P–OH groups exist in the presence of non-protonated imine nitrogens of PANI. Films obtained from PANI/PAP/NMP solutions may contain NMP molecules which solvate PANI chains.

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