Spectroscopic Properties of Polyaniline Protonated with Poly(alkylene phosphates)

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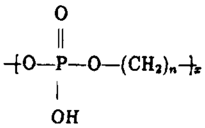
ABSTRACT: The reaction of polyaniline with new high-molecular-weight protonating agents, namely poly(alkylene phosphates), has been studied by UV/vis spectroscopy. The spectra were recorded both in the solid state and in organic solvents since polyemeraldine protonated with poly(alkylene phosphates) can be stabilized in the solution without precipitation. The influence of the molar ratio of both polymers and of the length of alkylene chain on the protonation level was observed. The protonation was evidenced by the appearance of polaron bands at 420 and ca. 900 nm. The addition of polar solvent increased the degree of protonation. The best protonation was achieved in *m*-cresol solution, whose principal features were the appearance of intrachain (free carrier) excitation at 430 nm, the decrease of the ca. 800 nm band intensity, and the increase of a long absorption tail into the near-infrared.

Introduction

Polyaniline has been considered one of the most promising conducting polymers. It shows excellent chemical stability and good electrical conductivity. The electronic properties of polyaniline can be reversibly controlled by protonation.[1]

In recent years extended research directed toward the improvement of polyaniline solution processability has been carried out. In particular, it has been demonstrated that polyaniline protonated with functionalized sulfonic acids[2] or with aliphatic diesters of phosphoric acid[3] becomes soluble in the protonated, i.e. conducting state. Taking into account this last discovery, one can consider polymeric esters with low p*K* as excellent candidates for the preparation of conducting polyaniline with interesting processing properties. Such compounds, namely poly(alkylene phosphates) of general formula



$$\left[O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-O-(CH_2)_n \right]_x$$

have been synthesized in a variety of forms.[4,5] Their chemical composition offers a unique opportunity to control the distribution of the protonating centers through the variation of the length of alkylene spacers between the acidic centers. In our previous paper[6] we have demonstrated that the solutions of polyaniline base do not precipitate when treated with poly(alkylene phosphate) but rather undergo spectral changes characteristic of the protonation reaction.

The protonation reaction of polyaniline has been studied in detail for various protonating agents and different conditions. For example, optical changes associated with the protonation of polyaniline films were studied as a function of the oxidation potential[7,8] as well as the protonation state.[9−11] Upon protonation, the absorption at 620 nm in the emeraldine base spectrum vanishes and new bands centered at 420 and ca. 900 nm appear. McManus et al.[12] and Stafström et al.[13] proposed that the new absorptions were associated with the formation of polarons in emeraldine salts. Wan[11] suggested a modified molecular structure of polyaniline by taking into consideration the degree of oxidation and protonation. Optical studies of polyaniline in its base form dissolved in *N*-methylpyrrolidinone (NMP)[14,15] show the influence of the polymerization conditions on the absorption spectra. On the other hand, Cao et al.[16] reported the absorption spectra of polyaniline in concentrated sulfuric acid solution, i.e. in the protonated state, and concluded that the intensities of the absorptions in the spectra of emeraldine salts strongly depend on both the molecular weight and the protonation level. High-molecular-weight and fully protonated emeraldine salt has three new spectral absorptions: an intrachain band at 1240 nm (with a long tail into the deep infrared), an intrachain absorption band at 415 nm, and an interchain absorption at 825 nm.[16]

In this paper the absorption spectra of polyaniline protonated with poly(alkylene phosphates) are presented and compared with those obtained with other protonating systems. New spectral features characteristic of emeraldine salt are observed upon the interaction of both polymers, i.e. polyaniline and poly(alkylene phosphate). The influence of the length of alkylene chain as well as the role of solvent composition on the degree of protonation is discussed.

Experimental Section

Polyaniline was synthesized chemically from aniline (POCH Poland) and $(NH_4)_2S_2O_8$ (POCH Poland) according to the method of Cao et al.[17] Pristine polyaniline was converted to the base form by treatment with 0.1 M NH_4OH solution for 5 h, followed by washing with distilled water and methanol, and dried in vacuum for 72 h. Emeraldine base (0.2 g) was dissolved in 20 mL of *N*-methylpyrrolidinone (NMP) (Fluka) or in 20 mL of *m*-cresol (VEB Apolda). The solutions were stirred for 12 h at room temperature and then were centrifuged to remove the insoluble material. The emeraldine base content was determined to be 8.3 mg of PANI/mL of NMP solution and 7.2 mg of PANI/mL of *m*-cresol solution. A thin film was prepared from the PANI/NMP solution on a quartz slide by spin coating.

The inherent viscosity of the PANI fraction soluble in NMP was equal to 0.9 dL/g at 25 °C (0.1 wt % of polyemeraldine in H_2SO_4). According to the Baird et al.[18] estimation made from Mark−Houwink relations the average molecular weight, $\bar{M}_w$, of PANI was ca. 12 000.

Poly(alkylene phosphates) (PAP) were prepared by Pretula according to the method described in refs 4 and 5. Polyphosphonates were obtained by polycondensation of dimethyl

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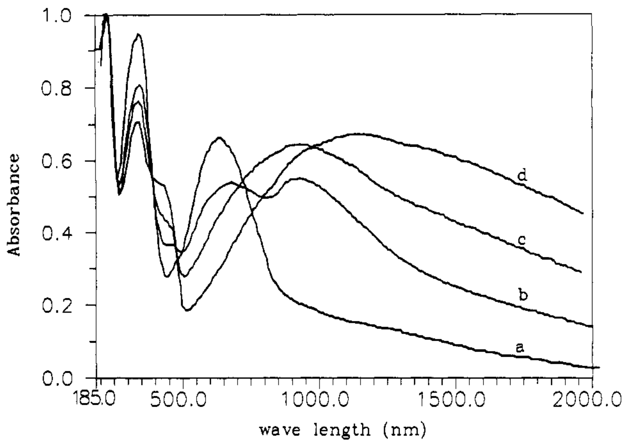

Figure 1. Absorption spectra of polyaniline film protonated with poly(hexamethylene phosphate) in C_2H_5OH/H_2O solution: PANI film cast from NMP solution (a); PANI film after 2 days (b), 7 days (c), and 14 (days (d) of protonation.

phosphate with corresponding diols and then oxidized with N_2O_4 to polyphosphates. The number average molecular weight, $\bar{M}_n$, as determined by osmometry, varied from 8500 to 14 000.

A thin film of polyaniline was doped in an 8×10^{-3} M solution of poly(hexamethylene phosphate) in $EtOH/H_2O$ (2:1). The solutions of polyaniline–polyphosphates in NMP were prepared by mixing 3 mL of PAP/NMP solution containing the appropriate amount of polyphosphates with 0.5 mL of PANI/NMP solution diluted to 4 mL with NMP. The PAP/NMP solution was added dropwise in order to avoid the precipitation of polyaniline. The upper solubility limit of PAP/PANI complexes was ca. 7×10^{-3} M. The solutions were stirred for 48 h and then diluted. For UV/vis measurements the concentration of polyaniline was equal to 3.3×10^{-4} M. The solution of polyaniline–polyphosphates in mixed solvents were obtained by stirring 0.31 mL of PANI/PAP/NMP solution with 2.62 mL of NMP and 1.47 mL of dimethylformamide (POCH Poland), acetonitrile (VEB Schwedt), or *m*-cresol (VEB Apolda), respectively. The solutions were "aged" for 72 h. The PANI/PAP/*m*-cresol solutions were prepared analogously as the solutions in NMP, but 0.1 mL of PANI/*m*-cresol solution was diluted in 5.16 mL of *m*-cresol and then mixed with 0.72 mL of PAP/*m*-cresol. The color change was very fast, but the solutions were stirred for 12 h at room temperature. No traces of precipitation were observed. For absorption measurements the concentration of polyaniline was equal to 5×10^{-4} M of PANI.

The UV/vis/near-IR (NIR) spectra were measured with a Cary 2315 spectrophotometer (Varian).

Results and Discussion

It has been demonstrated that the protonation of polyaniline with diesters of phosphoric acid renders it conductive.[3] We could suppose that polyphosphates, for example poly(alkylene phosphates), can also be used as protonating agents. Typical absorption spectra of polyaniline thin films interacting with polyphosphates for varying protonation times are presented in Figure 1. The spectrum of pristine emeraldine base is typical and shows the absorptions at 320 nm ascribed to the $\pi-\pi^*$ transition and at 615 nm characteristic of the exciton formation in the quinoid rings.[10–12] Upon the interaction with the solution of polyphosphate the absorption at 615 nm decreases and shifts to 660 nm (Table 1). Moreover, new bands appear at 440 and 910 nm, characteristic of protonated polyaniline. When the reaction time is increased, the band due to the excitation of quinoid units vanishes completely, the $\pi-\pi^*$ band decreases its intensity, and the absorption at 910 nm shifts to 920 nm and then changes to 1140 nm with a long tail into the near-infrared. These features are essentially the same as those observed by Monkman[19] in the case of polyaniline protonated with HCl vapors and almost similar to that reported by Cao[16] for polyaniline film obtained from sulfuric acid solution. However, we should suppose that the protonation level (and the conductivity) of polyaniline protonated with polyphosphates was lower than that protonated with mineral acids. Table 2 shows the elemental analysis and the conductivity of the PANI film (thicker than that used for UV/vis measurements) protonated in PAP/$EtOH/H_2O$ solution. One can observe that even for a thin film the $\pi-\pi^*$ band was still observed, after 2 weeks of interaction of both polymers. Our spectra differ from those presented by Wan[11] who did not observe the absorption at ca. 420 nm.

Table 1. Absorption Data for Polyaniline Film Protonated with Poly(hexamethylene phosphate) in $EtOH/H_2O$ Solution

sample	time[a] (days)	absorption (nm)			
(a) PANI	0	320		615	
(b) film 1	2	320	450	660	910
(c) film 2	7	320	440		920
(d) film 3	14	320	440		1140

[a] Time of the protonation.

Table 2. Elemental Analysis and the Conductivity of PANI Film (Thickness of 30 μm) Doped in 8×10^{-3} M PAP/$EtOH/H_2O$ Solution

time (days)	y[a]		elemental analysis % C	% H	% N	% P	% O[b]	σ (S/cm)
2	0.01	theor.	78.76	5.02	15.17	0.36	0.69	8×10^{-4}
		exp.	77.84	5.09	15.28			
7	0.03	theor.	77.33	5.10	14.60	0.97	2.00	3.5×10^{-3}
		exp.	76.98	5.62	14.15	0.88	2.43	
14	0.06	theor.	75.34	5.21	13.82	1.84	3.79	1.4×10^{-2}
		exp.	75.29	5.25	13.75	1.81	3.90	

[a] y, the doping level was determined by mass uptake. [b] The amount of oxygen was determined from the difference $100 - \Sigma\%$ C + % H + % N + % P.

It has been found that the features typical of protonated polyaniline can be also observed in a diluted NMP solution of both polymers. The solution of polyaniline in NMP was mixed with the solution of poly(alkylene phosphates) in the same solvent. The spectra changed gradually depending on the PAP to PANI "molar" ratio. "The molar unit" was taken as $[C_6H_4NH_{0.5}]$ for polyaniline and $[PO_4H(CH_2)_n]$ (where $n = 5-8$) for polyphosphates. The spectrum of the emeraldine base (Figure 2) in NMP solution is typical and shows the absorptions at 325 and 635 nm with a red shift with respect to the absorptions observed for the PANI film (Figure 1). Upon the interaction of polyaniline with polyphosphates in NMP solution the bands characteristic of the emeraldine base shift gradually from 325 and 635 to 340 and 650 nm, respectively, and decrease in their intensities depending on the solution composition. New absorption features typical of protonated polyaniline appear at ca. 420 and ca. 900 nm. The location of the new absorptions and the appearance of a tail extending into the infrared depend on the PAP/PANI molar ratio (Table 3). It can be noticed that for the molar ratio equal to 0.52, polyaniline was not fully protonated and the absorption at 650 nm was still observed. Almost full protonation occurred for the molar ratio, $x = 0.85$. The subsequent increase of the PAP/PANI molar ratio caused only minor changes in the spectrum.

Well-defined isosbestic points at 460 and 770 nm can also be observed. It implies the coexistence of a neutral

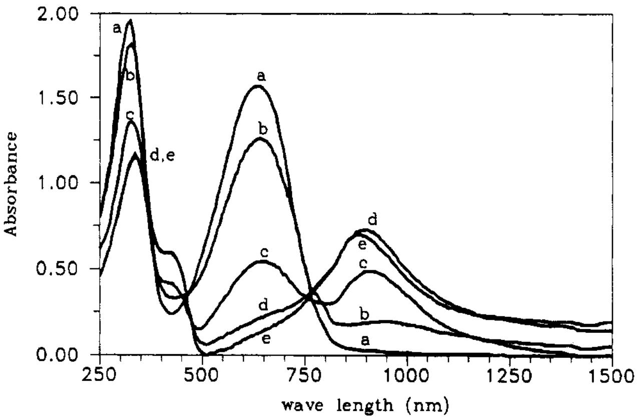

Figure 2. Absorption spectra of PANI protonated with poly(hexamethylene phosphate) in NMP solution: emeraldine base soution (a); PAP/PANI solutions with molar ratios of $x = 0.32$ (b), $x = 0.52$ (c), $x = 0.85$ (d), and $x = 2.18$ (e). The concentration of PANI was equal to 3.3×10^{-4} M.

Table 3. Absorption Data for Polyaniline Protonated with Poly(alkylene phosphate) in NMP Solution

sample	n^a	x^b	y^c	absorption (nm)			
PANI				325		635	
PANI/PHxP	6	0.32	0.15	330		635	930
PANI/PHxP	6	0.52	0.29	335	424	650	910
PANI/PHxP	6	0.85	0.44	340	418	650	885
PANI/PHxP	6	2.18	0.45	340	415		875
PANI/PPnP	5	0.53	0.34	335	427	650	910
PANI/PHpP	7	0.52	0.32	335	424	650	895
PANI/POP	8	0.53	0.13	330		645	880

[a] n = number of methylene groups in poly(alkylene phosphate). [b] x = molar ratio of PAP/PANI. [c] y = the protonation level of polyaniline estimated from the absorption spectra.

region with quinoid units and the region surrounding the positively charged nitrogen atoms.

This phenomenon is not unique to polyphosphates since it was also observed for other protonating agents.[20]

Taking into consideration the absorption bands characteristic of the excitation of quinoid units at ca. 650 nm and that of the polaron band at ca. 900 nm, one can estimate the degree of polyaniline protonation by assuming that the concentration of "absorbing species" is proportional to the peak surface, the molar absorption coefficients do not change with the PAP/PANI molar ratio, and the maximum level of protonation is equal to 0.5. Estimated in this manner, protonation levels, y, were 0.15, 0.29, 0.44, and 0.45 for PAP/PANI molar ratios, x, equal to 0.32, 0.52, 0.85, and 2.18, respectively. It should be underlined that the protonation of polyaniline was slow and varied significantly with time. For example, in the case of the PAP/PANI solution with $x = 0.52$, the protonation level changed from 0.23 after 15 h to 0.29 after 48 h.

The protonation of the emeraldine base in NMP solution was studied using poly(alkylene phosphates) with different lengths of $(CH_2)_n$ (with $n = 5-8$) (Figure 3). One can notice that the best protonation was achieved for the solution containing poly(pentamethylene phosphate) and gradually decreased for longer alkylene chains. The polaron band appeared at 910 nm for the solution with poly(pentamethylene phosphate) and shifted to ca. 880 nm for the solution with poly(octamethylene phosphate) (Table 3). The intensity ratios of the peaks at ca. 900 and 650 nm decreased in the order 1.42, 0.90, 1.18, and 0.21 for the PANI solution containing polyphosphates with $n = 5-8$, respectively. The protonation levels estimated in the same way as previously from the spectra were the following: $y = 0.34$ for $n = 5$, $y = 0.29$ for $n = 6$, $y = 0.31$ for $n = 7$, and $y = 0.13$ for $n = 8$. It seems that protonation of polyaniline with poly(hexamethylene phosphate) and poly(heptamethylene phosphate) was almost similar and decreased dramatically for poly(octamethylene phosphate).

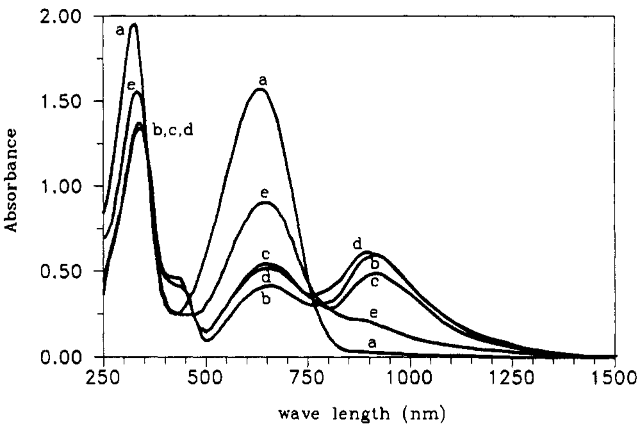

Figure 3. Absorption spectra of polyaniline protonated with poly(alkylene phosphates) in NMP solution: emeraldine base spectrum (a); PAP/PANI spectra $n = 5, x = 0.53$ (b), $n = 6, x = 0.52$ (c), $n = 7, x = 0.52$ (d), and $n = 8, x = 0.53$ (e). n is the number of methylene groups in poly(alkylene phosphate) chains. The concentration of PANI was equal to 3.3×10^{-4} M.

It should be underlined that the location of the absorption peaks in the spectra strongly depended on the solution composition. Especially the maximum of polaron band at ca. 900 nm varied with the PAP/PANI molar ratio as well as with the type of polyphosphates used. In addition, the dependence of the peak position on the protonation level was different in the solid films and in solutions. In the solid film the peak moves to higher wavelengths as the protonation level increases, whereas in the solution the opposite effect is observed (compare Tables 1 and 3). It can be supposed that in the case of the protonation of emeraldine base with polyphosphates the reaction is more complex than in the case of the protonation with discrete molecules (for example simple inorganic acids). The protonation of PANI can be accompanied by some kind of "solvation" or "complexation" of polyaniline chains in the near vicinity with the chains of polyphosphates, which causes a shift of the 900 nm peak to a higher energy. Such an effect is not observed in the case of the PANI film, because the penetration of large polymer molecules should be impeded in the already formed solid matrix.

It has been stated before that the protonation of polyaniline with poly(alkylene phosphates) was slow in the NMP solution. The addition of some solvent can change the equilibrium of this reaction. Solvents such as dimethylformamide, acetonitrile, and *m*-cresol were poured into already formed PAP/PANI solution in NMP. The addition of all these solvents increased the degree of polyaniline protonation manifested by the increase of polaron absorption intensities at 420 and ca. 900 nm (Figure 4). A blue shift of both absorptions was also observed. The most remarkable changes occurred in the case of the NMP/*m*-cresol mixture. *m*-Cresol was recommended as an excellent solvent of polyaniline complexes by Cao et al.[2] The absorption spectra of the PAP/PANI solution in *m*-cresol were significantly different from those in NMP (Figure 5). The polaron band appeared at 435 nm for PAP/PANI molar ratio $x = 0.32$ and shifted slightly to higher energy for a higher molar ratio ($x = 0.52$, $x = 0.85$). The absorption at ca. 800

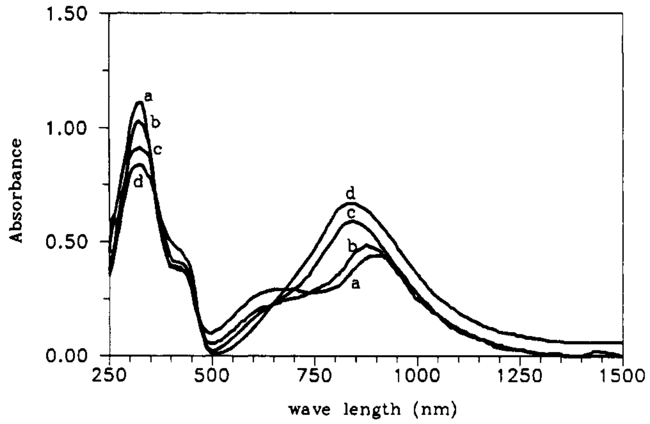

Figure 4. Absorption spectra of polyaniline protonated with poly(hexamethylene phosphate) in mixed solvents: NMP (a), NMP/DMF (b), NMP/CH_3CN (c), NMP/*m*-cresol (d). PAP/PANI molar ratio $x = 0.52$. The concentration of PANI was equal to 3.3×10^{-4} M.

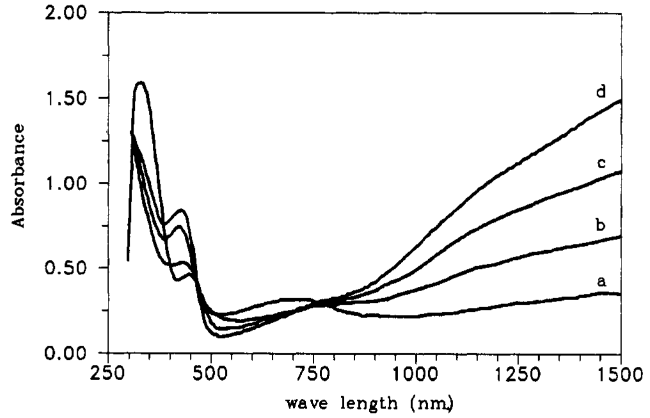

Figure 5. Absorption spectra of PANI solution in *m*-cresol: emeraldine base (a); EB protonated with poly(hexamethylene phosphate) $x = 0.3$ (b), $x = 0.5$ (c), $x = 0.8$ (d). The concentration of PANI was equal to 5×10^{-4} M.

nm decreased its intensity, while a long absorption tail extending into the near-infrared dominated with the increase of the PAP/PANI molar ratio. These observations were in agreement with the results of Cao et al.[16] One can conclude that the protonation of polyaniline with polyphosphates in *m*-cresol was significantly enhanced as compared to that in NMP solution. These results were confirmed by electrical conductivity measurements. The conductivity values measured for PANI/PAP films cast from NMP solutions were significantly lower than those obtained for the films cast from *m*-cresol solutions.

It should be mentioned that the emeraldine base forms complexes with *m*-cresol alone, but the complexes are metastable and the protonation is retired after the evaporation of the solvent. Figure 6 shows the spectra of the films obtained from *m*-cresol solutions. The spectrum of polyemeraldine contains the transitions typical of the base form, and only traces of the protonation peak at 460 nm can be observed. Contrary, the spectrum of the PAP/PANI film presents the features characteristic of the protonated state of polyaniline.

Conclusion

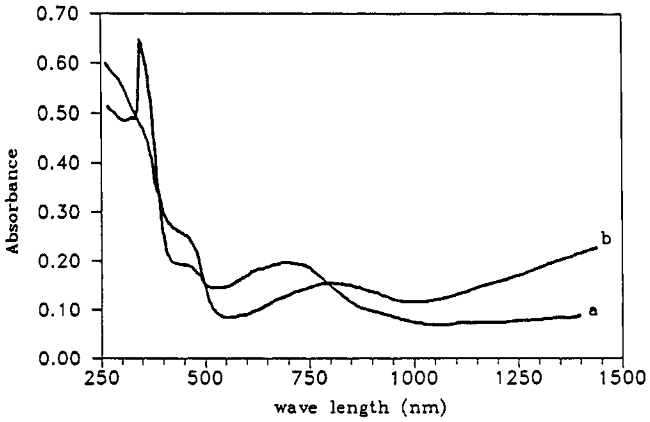

Figure 6. Absorption spectra of PANI films spin-cast from *m*-cresol: emeraldine base (a); EB protonated with poly(hexamethylene phosphate), $x = 0.3$ (b).

It has been shown that emeraldine base can be protonated with poly(alkylene phosphates) in the solid state as well as in NMP solution. The protonation level of polyaniline in NMP solution was low and depended significantly on the PAP/PANI molar ratio. The decrease of the length of alkylene chains of polyphosphates increased the protonation. The protonation was also enhanced by addition of some solvents. Full protonation can be achieved in *m*-cresol solution.

It is postulated that the protonation is accompanied by the solvation of polyaniline with polyphosphate chains which cause an increase of the interchain transition energy.

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