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Oxidation of Aniline with Silver Nitrate Accelerated by *p*-Phenylenediamine: A New Route to Conducting Composites

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ABSTRACT: The reaction between two nonconducting compounds, aniline and silver nitrate, yields a composite of two conducting products, PANI and silver. While the oxidation of aniline with silver nitrate is slow and takes over several months, the addition of a small amount of *p*-phenylenediamine, 1 mol % relative to aniline, shortens the reaction time to a few hours and, with higher concentrations of *p*-phenylenediamine, even to tens of minutes. Nonconducting aniline oligomers, however, are also present in the oxidation products as a rule. The chemistry of individual oxidation pathways is discussed. Higher concentrations of *p*-phenylenediamine in the reaction mixture with aniline give rise to copolymers, poly[aniline-*co*-(*p*-phenylenediamine)]s, and their composites with metallic silver. *p*-Phenylenediamine alone can similarly be oxidized with silver nitrate to poly(*p*-phenylenediamine) composite with silver. Silver is present in the composites both as nanoparticles of ~50 nm size and as larger objects. The composites have conductivity in the range of the order of $10^{-3}-10^{3}$ S cm^{-1} at comparable content of silver, which was close to the theoretical expectation, 68.9 wt %. The composites prepared in 1 M acetic acid always have a higher conductivity compared with those resulting from synthesis in 1 M nitric acid. The polymerizations of aniline accelerated with 1 mol % of *p*-phenylenediamine in 1 M acetic acid yield a composite of the highest conductivity, 6100 S cm^{-1}. At higher contents of *p*-phenylenediamine, poly[aniline-*co*-(*p*-phenylenediamine)] composites with silver have a conductivity lower by several orders of magnitude. The oxidation of *p*-phenylenediamine alone with silver nitrate in 1 M acetic acid also yields a conducting composite, its conductivity being 1750 S cm^{-1}. The semiconductor type of conductivity in polymers and the metallic type of conductivity in silver may compensate to yield composites with conductivity nearly independent of temperature over a broad temperature range.

Introduction

Polyaniline (PANI), probably the most studied conducting polymer, is currently prepared by the oxidation of aniline with ammonium peroxydisulfate (APS) in acidic aqueous media,[1] its typical conductivity being of the order of the units of S cm^{-1}. One of the strategies to increase the conductivity is based on the incorporation of noble metals, such as silver. When silver nitrate is used as the oxidant of aniline, a composite of PANI and silver is directly obtained[2−7] (Figure 1). Such composites combine the metallic conductivity of silver and the semiconductor charge transport in PANI. The latter component is expected to introduce materials features of polymers, especially their mechanical properties.[8] Nonconducting aniline oligomers have often constituted part of the oxidation products.[4,6] Despite this fact, composite conductivities were high,[4,6] exceeding 1000 S cm^{-1}. The potential usefulness of such composites as new conducting materials is seen in the design of flexible electronics, conducting inks, sensors, electrodes, etc.

The oxidation of aniline with APS in an acidic aqueous medium is completed within tens of minutes with the currently used concentrations of reactants,[1] and PANI is collected as a precipitate. Depending on the acidity conditions, the morphology of PANI can vary from granules, nanofibers, nanotubes, to microspheres.[9,10] The oxidations of aniline using silver nitrate are much slower,[4,6] and more than one month is needed to obtain an appreciable yield of polymer; this is hardly acceptable for the routine syntheses of conducting composites.

The reaction between aniline and silver nitrate was accelerated by an increase in temperature to 250 °C,[11] with UV-irradiation[5,7,12,13] or γ-irradiation and sonication.[2,3] The absorption maximum at 630−640 nm in the UV−vis spectra, which is typical of the PANI (emeraldine) base,[14] however, has often been suppressed or even absent.[2,3,15,16] This means that the oxidation products were composed mainly of nonconducting aniline oligomers,[17−19] rather than of PANI.[10] The conductivity of such composites was below 0.1 S cm^{-1} and, in spite of the presence of silver, even lower than the conductivity of PANI prepared by ordinary oxidation using APS,[1] ~4 S cm^{-1}. Composites contained a large fraction of aniline oligomers.[4,6] Only in two cases, high conductivities exceeding 1000 S cm^{-1} have recently been reported.[4,6] It is well-known that the oxidation of aniline with APS is accelerated by small quantities of *p*-phenylenediamine (PDA) in both the chemical[20−24] and electrochemical[25−27] oxidations of aniline. This approach has successfully been applied in the present work to the oxidations of aniline with silver nitrate.

The ability of aniline to copolymerize with PDA has been reported in several studies when APS was used as the oxidant[28−34] as well as in electrochemical preparations.[35,36] The formation of copolymers is also discussed in the present communication when the aniline and PDA have been used in comparable proportions and oxidized with silver nitrate to poly[aniline-*co*-(*p*-phenylenediamine)].

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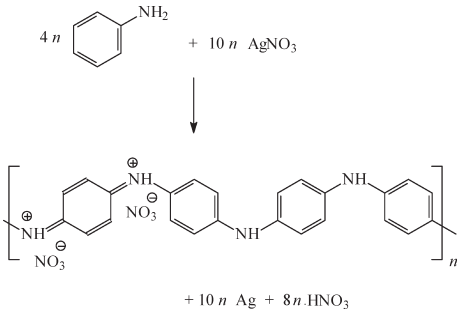

Figure 1. Aniline is oxidized with silver nitrate to PANI nitrate and metallic silver. Nitric acid is a byproduct. An acidic medium is necessary.

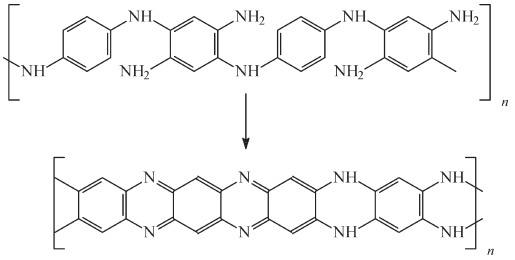

Figure 2. Idealized structure of poly(*p*-phenylenediamine) and its conversion to the ladderlike phenazine structure as proposed in the literature.[28,39,41]

The observation that the oxidation of PDA alone with silver nitrate proceeds easily in the absence of aniline led to closer investigation of this process. The oxidation of PDA has been studied so far only with APS as the oxidant.[37−40] It was proposed that the product of such oxidation is a polymer, poly(*p*-phenylenediamine) (PPDA), but in fact, the oxidation products could rather be classified as oligomers from the present point of view. The possible structure (Figure 2) may resemble a PANI chain having pendant amino groups,[41−43] especially with a mole ratio of APS oxidant and PDA equal to 1.25, which is otherwise used in the preparation of PANI. Further oxidation leads to ladder structures[28,30,38,39,41] at higher oxidant-to-PDA mole ratios. Such structures may be composed of phenazine, hydrophenazine, and dihydrophenazine constitutional units;[40,44] i.e., they may exist in various oxidation states (Figure 2). The structures actually produced in experiment, however, may be even more complex and will include cross-linked units produced by intermolecular oxidative reactions[25,34] and N=N coupling of constitutional units.[37,45] PPDA is regarded as a nonconducting polymer, its conductivity being below 10^{-9} S cm^{-1},[28,30,38,46,47] although in a single case, a conductivity of 6.3×10^{-6} S cm^{-1} was reported.[41]

Both polymers PANI and PPDA display some similarities in behavior, such as the ability to produce morphology-retaining carbonized product after pyrolysis,[48] to be active in electrorheology due to their high polarizability,[31,46,49] to provide corrosion protection of metals,[33,44,50,51] or to participate in noble-metal sensing[52] and recovery.[40,53] Also for that reason, the oxidation of aniline and PDA or their mixtures with silver nitrate is analyzed in the present communication.

Experimental Section

Preparation. Aniline, *p*-phenylenediamine (both from Fluka, Switzerland), or their mixtures of various compositions were oxidized at 0.2 M monomer concentration with 0.5 M silver nitrate (Lach-Ner, Czech Republic) in 1 M nitric acid or 1 M acetic acid at 20 °C (Figure 1). The oxidation of aniline alone was slow, without any perceptible progress even after 1 week,[4,6]

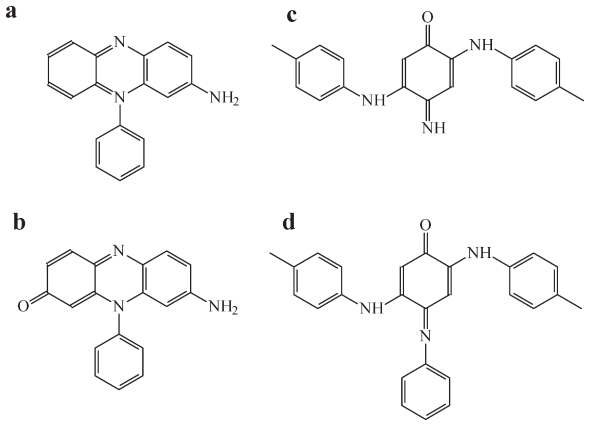

Figure 3. Examples of oligomer structures proposed by (a) Sapurina and Stejskal,[9,10] (b) Zujovic et al.,[19] (c) Surwade et al.,[17] and (d) Kříž et al.[18]

while other reactions including PDA proceeded within hours or even tens of minutes. In such cases, the solids were collected on a filter after 2 days, rinsed with the corresponding acid solution, and dried at room temperature over silica gel. Portions of the products were deprotonated in 1 M ammonium hydroxide to the corresponding bases. The ammonia solutions were collected after deprotonation and evaporated, and resulting solids were analyzed by FTIR spectroscopy. They are referred to below as "filtrates".

Characterization. UV−vis spectra of the bases dissolved in *N*-methylpyrrolidone were obtained with a Lambda 20 spectrometer (Perkin-Elmer, UK). The content of silver was determined as an ash. The conductivity was measured by a four-point van der Pauw method on pellets compressed at 700 MPa with a manual hydraulic press, using as current source a SMU Keithley 237 and a Multimeter Keithley 2010 with a 2000 SCAN 10-channel scanner card. The density was obtained by weighing the pellets with a Sartorius R160P balance in air and immersed in decane at 20 °C. Infrared spectra of the composites dispersed in potassium bromide and compressed into pellets were recorded with a fully computerized Thermo Nicolet NEXUS 870 FTIR spectrometer with DTGS TEC detector.

Results and Discussion

Aniline oxidation leads at first to an aniline dimer, aminodiphenylamine (semidine), and subsequently to trimers and tetramers.[54−56] Depending on acidity conditions, such oligomers (1) are present in the final oxidation product, (2) they grow to higher oligomers, and (3) some of them may initiate the growth of PANI chains.[56] These processes and their acceleration with PDA are discussed below.

Oligomerization. At the early stages of aniline oxidation, the aniline molecules are coupled both in *ortho*- and *para*-positions, and subsequent oxidation to phenazine units also takes place[9,10] (Figure 3a,b). Such a process proceeds especially at low acidity or at alkaline conditions and yields brown nonconducting products. Phenazine units were proposed to convert to initiation centers that later start the growth of true PANI chains if the acidity of the medium is sufficiently high.

In practice, the oligomers are found to contain oxygen atoms. The oxidation of aniline with aerial oxygen is known to be responsible for brown color of stored aniline, caused by quinoneimine. Its copolymerization with aniline gives quinoneiminoid constitutional units in oligomers[17] (Figure 3b−d), and such units have indeed been identified in NMR experiments.[18,19] Preliminary analysis of oligomers suggests that they are short, up to the tetramer level. The presence of oxygen

atoms prevents their growth to regular PANI chains. The formation of higher oligomers, however, have been proposed,[17] and they constitute insoluble part of oligomeric products, which is not available for the characterization by solution methods, such as size-exclusion chromatography.[57]

Oligomers produced by the oxidation of aromatic amines in general, and aniline in particular, have often been regarded as inferior from the standpoint of polymer chemistry and also due to the lack of electronic conductivity. Yet, recent studies make them more attractive. The composites of such oligomers with silver have often had a higher conductivity than analogous products with conducting polymers.[4,6] The oligomers may also turn as candidates for proton-conducting materials. The role of oligomers in guiding the growth of PANI nanostructures, such as nanotubes, has recently also been stressed.[9,56−58]

Oxidation of Aniline to PANI. When oxidizing aniline in strongly acidic media, pH < 2.5, with ammonium peroxydisulfate, the formation of high-molecular-weight PANI chains is a preferred route. Aniline oligomers are produced only in trace amounts, and they readily convert to initiation centers that start the growth of polymer chains.[10] When using silver nitrate as oxidant, having a lower oxidation potential compared with APS, the formation of initiation centers of polymer growth and subsequent polymerization of aniline is not the exclusive process anymore, even in media having sufficient acidity,[9,10] needed for the growth of PANI chains. Both brown nonconducting aniline oligomers and green conducting PANI are produced, and only their proportions vary depending on experimental conditions.

There are differences between the oxidation products prepared in the two media of various acidity, in 1 M nitric acid and 1 M acetic acid. PANI dominates in the former case, and a UV−vis spectrum is typical of emeraldine with an absorption maxima at 336 and 630 nm.[14] The presence of oligomers is identified by the increased absorption at the 336 nm with respect to 630 nm (Figure 4a). The displacement of the maximum to 566 nm for the samples prepared in acetic acid solutions is caused by the presence of aniline oligomers in large amount (Figure 4b). The superposition of their spectra, characterized by the strong absorption at 350−380 nm and with an absorption tail extending to the red region,[9,10,19] with the spectrum of PANI leads to an apparent displacement of the maximum at 630 nm to shorter wavelengths.

Acceleration of Aniline Oxidation with *p*-Phenylenediamine. The formation of any polymer has three important phases: (1) the initiation, (2) the chain propagation, and (3) the termination. This applies also to the preparation of PANI. The conditions for the propagation step are satisfied by the sufficient acidity of the medium, but the polymerization still does not take place. This means that the initiation is slow. It has been proposed that the coupling of aniline molecules produces a semidine dimer at first and later a *N*-phenylphenazine trimer,[10,19,59] a so-called nucleate[9,10] (Figure 3a). Only after the addition of another aniline molecule, the nucleate converts to a tetramer initiation center which triggers the growth of PANI chains.[9,10] The addition of small amounts of PDA, < 1 mol % with respect to aniline, substantially increased the rate of PANI formation when APS was used as the oxidant.[21−24] A dramatic increase in the rate of aniline oxidation has also been observed with silver nitrate, and this is the most important effect reported in the present study. We propose that PDA alters the formation of initiation centers, increases their number, and, in this way, promotes the polymerization of aniline (Figure 5).

This concept is supported by two observations: (1) Only small amounts of PDA are needed for the initiation of aniline polymerization. If PDA participated only as a comonomer in the propagation step (and PDA indeed copolymerizes with aniline[28−33]), much larger quantities would be needed to produce a marked effect. (2) The phenazine nucleates are able to self-assemble and to guide the subsequent growth of nanogranules, nanofibers, or nanotubes.[9] The fact that the addition of PDA changes the morphology from granules to nanofibers[22−24] implies that the chemical nature of the nucleates and, consequently of the initiation centers, has been altered. It should be noted that both processes, (1) the conversion of nucleates the to initiation centers followed by the polymerization and (2) the formation of inactive oligomers, are both enhanced by the presence of PDA, which is easier to be oxidized compared with aniline.

The acceleration with small amounts of PDA in both media, solutions of nitric (Table 1) and acetic acids (Table 2), has led to (1) faster oxidation, (2) an increase in the conductivity of the resulting composites to thousands of S cm^{-1}, and (3) to an increase in the yield. An increase in the PDA fraction above 0.5−1 mol % further promoted the oxidation rate and increased yield, but the conductivity of the product was reduced (Tables 1 and 2). This is explained by the incorporation of PDA units into PANI chains by a copolymerization mechanism and the disturbance of its regular structure. PDA also promotes the alternative reaction route leading to the formation of nonconducting inactive oligomers.

Copolymers of Aniline and *p*-Phenylenediamine. The oxidation of 1 g of aniline according to Figure 1 produces theoretically 1.31 g of PANI nitrate and 2.90 g of silver, i.e., 4.21 g of composite. Such a composite would contain 2.90/4.21 = 68.9 wt % silver.[4] When aniline and PDA are present in comparable concentrations, copolymerization with aniline takes place. The situation is thus more complex. Nevertheless, the yields of composites per gram of monomers, Y, are close to the value of 4.21 g g^{-1} expected for the oxidation of aniline (Tables 1 and 2) once even a minute amount of PDA had been present in the reaction mixture. Under such conditions, also the compositions of composites, w_{Ag}, are close to the theoretical expectation, 68.9 wt % (Tables 1 and 2). This observation is also supported by the densities, d, which are little dependent on the content of PDA in the reaction mixture (Tables 1 and 2). The content of silver, fixed by the stoichiometry of the reaction (Figure 1), however, may be regarded as a drawback of the synthesis because the content of silver cannot be varied.

The efficiency of the reaction can also be assessed by a parameter t, calculated as a fraction of silver in the composites relative to the amount of silver entering the reaction as silver nitrate. These values in many cases exceed 90% (Tables 1 and 2) and illustrate a high conversion of silver ions to metallic silver. From this point of view, the progress and efficiency of reaction carried out both in nitric and acetic acid solutions are similar.

Oxidation of *p*-Phenylenediamine with Silver Nitrate. When using silver nitrate as an oxidant of PDA in the absence of aniline, a violet precipitate is obtained as a product of a fast exothermic oxidation to PPDA. In the UV−vis spectra of deprotonated PPDA, the absorption maximum is found at 430 nm, along with a long tail extending to the red region (Figure 4). Poly(*p*-phenylenediamine) prepared by the oxidation of PDA with APS displayed absorption maxima at 330 and 420 nm[44] or bands at 344−355, 404−420, and 540−543 nm.[41,43] The last absorption band may correspond to phenazine units. The absorption maximum of substituted *N*-phenylphenazines, safranines, and also of their oxidation products is located at 538 nm.[60] Such an absorption band has not explicitly been observed in the

Table 1. Products of the Oxidation of Aniline and *p*-Phenylenediamine Mixtures of Various Composition, x_{PDA}, with Silver Nitrate in 1 M Nitric Acid[a]

x_{PDA}, mol % PDA	Y, g g^{-1}	w_{Ag}, wt %	t, %	σ, S cm^{-1}	σ_B, S cm^{-1}	d, g cm^{-3}	d_B, g cm^{-3}	Δ, wt %
0[b]	1.21	57.0	23.7	425	3.7×10^{-7}	3.20	2.73	9.14
0.5	3.67	72.0	91.0	5450	0.06	4.11	3.98	10.9
1	3.65	69.5	90.7	0.88	9.5×10^{-11}	3.65		10.5
3	3.80	70.6	92.8	3.2×10^{-2}	4.4×10^{-10}	3.80	3.89	13.8
5	3.78	69.4	91.0	7.2×10^{-3}	5.3×10^{-11}	3.75	3.93	12.5
10	3.84	67.7	90.1	2.6×10^{-3}	1.6×10^{-10}	3.72	3.96	
20	4.17	68.0	100.8	1.0×10^{-3}	3.9×10^{-9}	3.76		27.3
40	4.15	57.4	87.4	5.0×10^{-5}	4.4×10^{-9}	3.33	3.60	13.2
60	3.87	65.7	96.0	5.0×10^{-3}	1.0×10^{-3}	3.53	3.87	8.60
80	3.55	69.6	94.7	4.8×10^{-3}	6.5×10^{-4}	3.68	3.87	7.92
100	3.34	71.8	95.9	60	6.8×10^{-3}	3.77	3.80	5.85

[a] Y is the yield of composite per unit mass of aniline, w_{Ag} is the content of silver in the composite, t is the ratio of the mass of silver in the composite to the mass of silver entered into the reaction as silver nitrate, σ and σ_B are the conductivities of the prepared composite and of a composite in which the polymer was deprotonated to the base form, d and d_B are the corresponding densities, and Δ is the loss of mass after deprotonation. [b] One month was allocated for the oxidation in the absence of PDA, while other products of accelerated reactions were collected after 2 days.

Table 2. Products of the Oxidation of Aniline and *p*-Phenylenediamine Mixtures of Various Composition, x_{PDA}, with Silver Nitrate in 1 M Acetic Acid[a]

x_{PDA}, mol % PDA	Y, g g^{-1}	w_{Ag}, wt %	t, %	σ, S cm^{-1}	σ_B, S cm^{-1}	d, g cm^{-3}	d_B, g cm^{-3}	Δ, wt %
0[b]	1.17	69.4	28.1	5510	4300	3.40	3.74	19.5
1	1.28	71.5	31.5	6100	4000	3.48	3.72	21.9
3	2.80	70.0	67.9	350	54	3.50	3.77	8.78
5	3.53	70.4	86.2	120	22	3.58	3.79	6.24
10	3.80	67.1	89.2	18	0.06	3.30	3.55	
20	3.69	69.5	91.1	99	14	3.43	3.65	8.40
40	3.67	68.8	92.7	810	380	3.42	3.65	6.75
60	3.61	69.5	94.9	540	195	3.41	3.68	7.72
80	3.68	69.5	99.4	885	0.090	3.21	3.54	7.06
100	3.56	68.1	96.9	1750	0.075	3.31	3.45	9.55

[a] For the meaning of the symbols, see Table 1. [b] See footnote in Table 1.

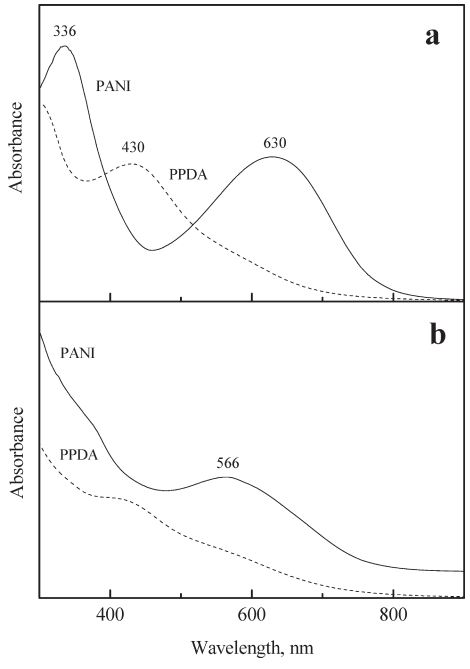

Figure 4. UV−vis spectra of polyaniline−silver composite (full lines) and poly(*p*-phenylenediamine)−silver composite (broken lines) prepared (a) in 1 M nitric acid or (b) in 1 M acetic acid (the spectrum of PANI was vertically shifted for clarity).

present experiments but may be hidden in the absorption tail.

Molecular Structure of Oxidation Products. FTIR spectra of the oxidation products of aniline and PDA in 1 M nitric acid (Figure 6), of the bases obtained by their deprotonation

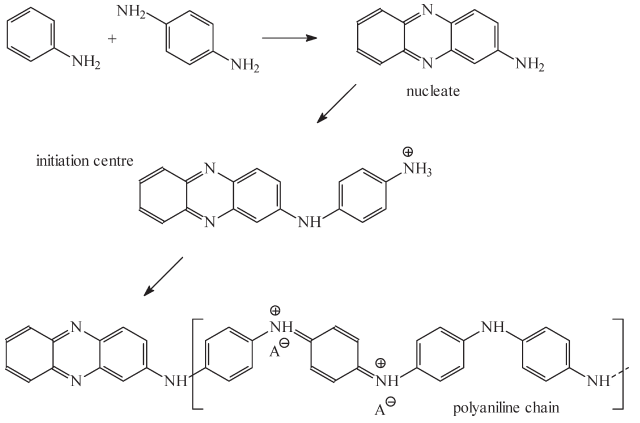

Figure 5. Role of *p*-phenylenediamine in the oxidation of aniline: the possible formation of a phenazine-containing nucleate and of an initiation center that starts the growth of a PANI chain having a phenazine head and PANI tail. A^- is an arbitrary anion.

by 1 M ammonium hydroxide (Figure 7), and of the corresponding ammonium salts obtained after evaporation of ammonia filtrates (Figure 8) can be divided into several groups, depending on PDA content, with different representative spectra.

The spectrum of the sample obtained by the oxidation of aniline in the absence of PDA (0 in Figure 6) has typical features of the spectrum of PANI synthesized with APS,[61] with absorption peaks located at 1568, 1488, 1303, 1148, and 825 cm^{-1}. Additional peaks belonging to the spectrum of aniline oligomers (marked by arrows in Figure 6) are observed in the spectrum of the corresponding deprotonated sample (0 in Figure 7) at 3226, 1638, 1144, and 1287 cm^{-1}. In the spectrum of the as-prepared sample we observe a strong

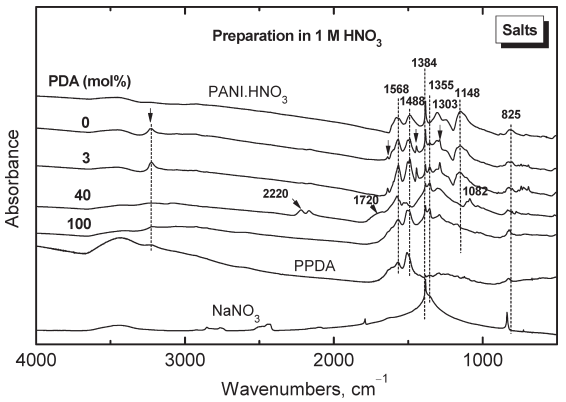

Figure 6. FTIR spectra of the selected oxidation products of aniline and *p*-phenylenediamine in 1 M nitric acid. The mole fraction of PDA in the reaction mixture with aniline is specified at the individual spectra. The spectra of PANI nitrate, PPDA prepared with APS as oxidant, and of sodium nitrate are shown for comparison.

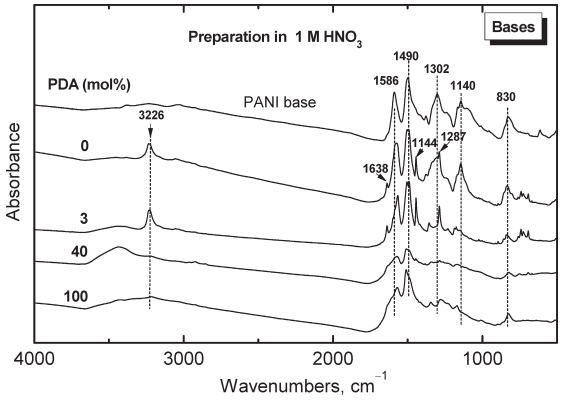

Figure 7. FTIR spectra of selected oxidation products of aniline and *p*-phenylenediamine in 1 M nitric acid deprotonated by 1 M ammonium hydroxide. The mole fraction of PDA in the reaction mixture with aniline is specified at the individual spectra. The spectrum of PANI base prepared with APS oxidant is shown for comparison.

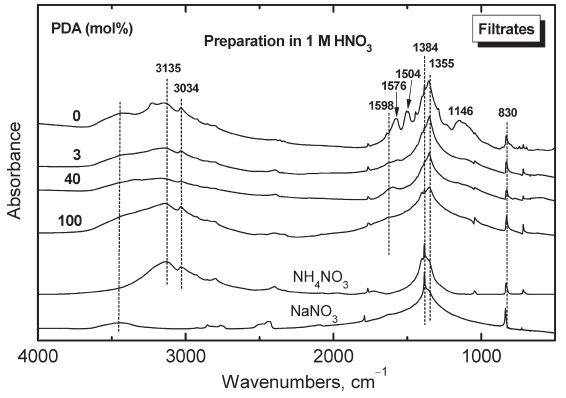

Figure 8. FTIR spectra of selected filtrates, i.e., of solids obtained after the evaporation of the ammonia solutions used for the deprotonation of the oxidation products of aniline and *p*-phenylenediamine. The mole fraction of PDA in the reaction mixture with aniline is specified at the individual spectra. The spectra of ammonium and sodium nitrates are shown for comparison.

sharp peak of the nitrate anion at 1384 cm^{-1}, which reflects the protonation of PANI by nitric acid. This peak is observed in the spectra of PANI nitrate and of sodium nitrate (Figure 6). In addition to this peak, we observe a local maximum at 1355 cm^{-1} which increases with the mole ratio of PDA in the sample. The spectrum of the corresponding ammonium salts in filtrates, besides the broad bands of ammonium nitrate, displays bands with local maxima at 1576, 1504, 1146, and 830 cm^{-1} (Figure 8). They correspond most probably to aniline oligomers. The presence of the small sharp peaks at 1638, 1444, and 1287 cm^{-1} supports this idea. The broad band with maximum at 1145 cm^{-1} is also present in the spectrum, corresponding to higher oligomers. The maximum at 1355 cm^{-1} is also detected in the spectrum of the filtrate. It corresponds most probably to another mode of the nitrate anion vibrations detected as a shoulder in the spectrum of sodium nitrate.

When the fraction of PDA in the reaction mixture increases from 0.5 to 10 mol %, the content of PANI part decreases and the peaks typical of aniline oligomers become sharper (3 mol % PDA in Figure 6). The sharp peak at 1384 cm^{-1} and the maximum at 1355 cm^{-1} are well observed in the spectrum. The typical spectrum of the sample obtained with a small amount of PDA after deprotonation corresponds to the spectrum of aniline oligomers (3 mol % PDA in Figure 7). The spectrum of the corresponding filtrate is close to that of ammonium nitrate, but its maximum is shifted to 1355 cm^{-1} (Figure 8).

The shape of the spectra in the group of samples with higher mole fraction of PDA, from 20 to 60 mol %, dramatically changed (40 mol % PDA in Figure 6). The dominating band of aniline oligomers at 1488 cm^{-1} practically disappeared; the bands at about 1575, 1530, 1302, and 833 cm^{-1} are present in spectrum (Figure 6). The peak at 1384 cm^{-1} and the maximum at 1355 cm^{-1} are very strong; the two new peaks at 1086 and 1035 cm^{-1} appeared in the spectrum. The last peaks are connected with nitration of the benzenoid rings, e.g., in aniline.[62] The spectrum of the corresponding filtrate is closer to that of ammonium nitrate with the maximum at 1355 cm^{-1} and with a broad band at 1598 cm^{-1} (Figure 8). We suppose that the spectrum of the as-prepared sample is a mixture of nitroaniline and PDA oligomers.

The spectra of the samples with the highest mole fraction of PDA, from 60 to 100 mol %, correspond to the spectrum of the PPDA nitrate with the peak of the nitrate anion at 1384 cm^{-1} and the maximum at 1355 cm^{-1} (100 mol % PDA in Figure 6). The spectra of the corresponding base (Figure 7) and of the filtrate (Figure 8) support this observation.

FTIR spectra of the typical oxidation products of aniline and PDA prepared in 1 M acetic acid and the spectra of the corresponding bases are presented in Figure 9. Contrary to the case of oxidation in 1 M nitric acid, silver acetate having two typical bands at 1576 and 1410 cm^{-1} is produced in the absence of PDA[4] (0 in Figure 9). When a small amount of PDA was added to the reaction mixture, the spectra dramatically changed. The samples have stonelike consistency and are difficult to disperse in potassium bromide pellets. Small bands of PANI sequences protonated by nitric acid are detectable in the spectra at 1571, 1490, and 1303 cm^{-1}. The sharp peak of the nitrate anion at 1384 cm^{-1} dominates the spectrum. For mole fractions from 10 to 100 mol %, the spectra of deprotonated samples correspond to the spectrum of the PANI base with some amount of aniline oligomers. In the case of the oxidation of PDA (100 mol % in Figure 9), the spectrum is close to the spectrum of PPDA which contains a strong peak at 1384 cm^{-1} with secondary maximum at 1355 cm^{-1} which corresponds to nitrate anions. After deprotonation, the spectrum of PPDA base is obtained.

Conductivity. The composites of aniline−PDA copolymers with silver have always had a lower conductivity than those constituted by silver and the parent homopolymers (Tables 1 and 2, Figure 10), except for the sample prepared

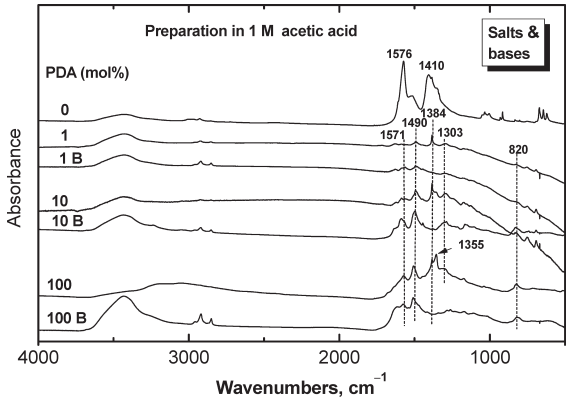

Figure 9. FTIR spectra of selected oxidation products of reaction between aniline and *p*-phenylenediamine in 1 M acetic acid and the spectra of the corresponding bases (B). The mole fraction of PDA in the reaction mixture with aniline is specified at the individual spectra.

with a small addition of PDA which improved the conductivity. This implies that both parent homopolymers are conducting and that mixed incorporation of aniline and PDA constitutional units destroyed the regularity of the PANI chains and, consequently, reduced the conductivity. The situation is similar to that of copolymers of aniline and pyrrole, which are also nonconducting, while the corresponding homopolymers are good semiconductors.[63]

The conductivity of composites prepared in nitric acid solutions differs over a range of 6 orders of magnitude despite the comparable contents of silver (Table 1). This means that the presence of silver is not an automatic prerequisite of a high conductivity. Please note that 69 wt % of silver represents only ~22 vol %[4] because of the large difference in the densities of the components. Electron micrographs, however, do not show any marked differences in the morphology of silver represented by nanoparticles of ~50 nm size and the morphology of the copolymers (Figure 11). A simple explanation of these large conductivity differences in terms of morphology thus cannot be offered and the concept of conductivity barriers at silver interfaces should be considered.

The same trend was observed for samples prepared in solutions of acetic acid (Table 2, Figure 10), but the conductivity of the samples is much higher compared with those prepared in nitric acid solutions (Table 1). This is in agreement with the results of earlier studies.[6] The explanation is not obvious because nonconducting aniline oligomers usually dominate over true PANI in acetic acid solutions,[6] and a decrease in the conductivity would be a more logical consequence of their presence.

The complexity of the system increases when the problem of chemical heterogeneity of the copolymers is considered.[64] In the statistical copolymerization of two comonomers, one type of monomer becomes preferentially incorporated into polymers chains, except at the so-called azeotropic point in the copolymerization diagram. The reaction mixture thus becomes gradually depleted of this monomer as the copolymerization proceeds. The composition of the copolymers drifts during the polymerization as the conversion increases. The product prepared at high conversions, as in the present case, is thus composed of copolymer chains widely differing in composition; i.e., it is chemically heterogeneous. It has been demonstrated that the properties of the copolymers, which are not linear functions of their composition, do depend on the chemical heterogeneity, the conductivity being a typical example.[64] This means that the microscopic regions in the polymer matrix may differ considerably in

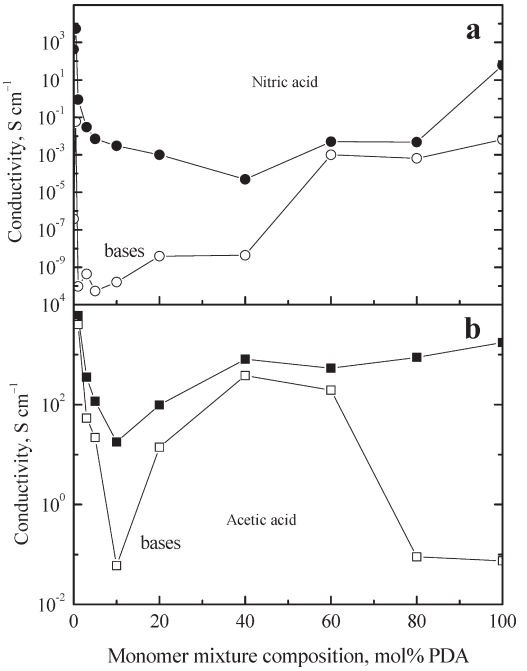

Figure 10. Dependence of the conductivity of PANI−silver composites prepared (a) in 1 M nitric acid (circles) and (b) in 1 M acetic acid (squares) on the mole fraction of PDA in the monomer mixture for as-prepared protonated samples, salts (full symbols), and after conversion to bases (open symbols).

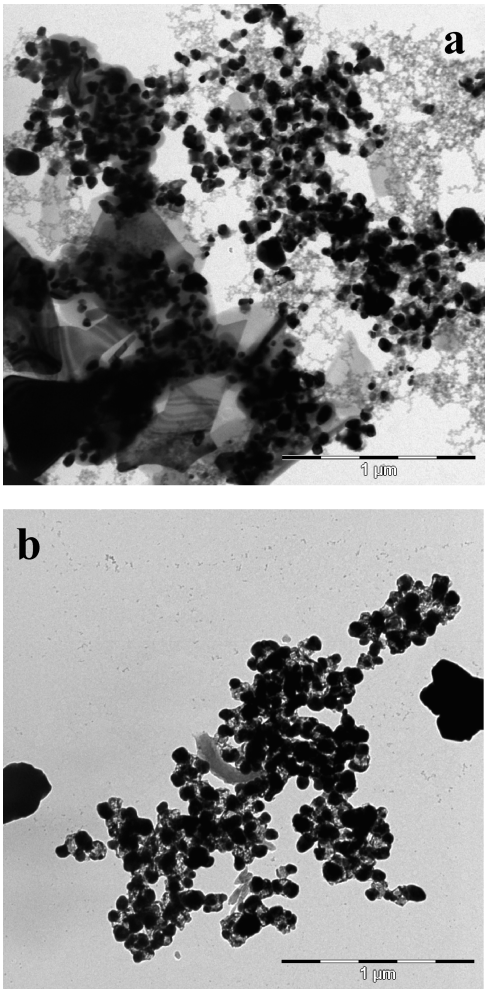

Figure 11. Micrographs of composites prepared with (a) 5 mol % PDA and (b) 60 mol % PDA in 1 M acetic acid.

conductivity. The polymer matrix thus need not be electrically isotropic.

Deprotonation of Copolymers to Bases. Organic components in the composites were deprotonated in solutions of ammonium hydroxide, when the polymer or oligomer salts convert to bases. The nitric acid constituting the salt (Figure 1) produces ammonium nitrate after reaction with ammonium hydroxide. This process is associated with the loss of mass of PANI, $\Delta = M_A/(M_A + M_P) = 25.8$ wt %, where $M_A = 63.01$ and $M_P = 181.22$ are the molecular weights of nitric acid and of a segment of polymer (PANI) base comprising two aniline constitutional units, respectively. The expected loss of mass in a composite containing 68.9 wt % silver is thus 8.0 wt %. The situation may be more complex with high contents of PDA constitutional units when the manner and the degree of copolymer protonation are not known. The reduction in mass after deprotonation corresponds to expectation in many cases (Tables 1 and 2). A higher loss of mass may be associated with the separation of oligomers and a lower loss with incomplete protonation in solutions of acetic acid. A weak acid, such as acetic acid, does not participate in the protonation of PANI,[64] and only nitric acid generated in the course of oxidation (Figure 1) is available for the formation of salts.

After deprotonation, the conductivity of standard PANI prepared with APS decreased by 9 orders of magnitude.[1] In PANI−silver composites, the silver becomes the only component which is conducting, and it therefore determines the overall conductivity. The conductivity indeed decreases after deprotonation (Tables 1 and 2, Figure 10). The conductivity drop is much more pronounced for samples prepared in nitric acid (Figure 10a) than for composites prepared in acetic acid (Figure 10b).

The conversion of a polymer salt to its corresponding base is always associated with a decrease in mass, Δ (Tables 1 and 2). The fraction of silver in the composite increases at the same time. This is reflected by the higher density of composites after deprotonation, d_B (Tables 1 and 2). Such effect may become important when the content of silver is close to the percolation threshold.

Temperature Dependence of Conductivity. The conductivity of semiconductors increases with temperature whereas the conductivity of metals has the opposite trend. The polymer−silver composites, which have a conductivity of the order of 10^2-10^3 S cm^{-1}, behave like metals (Figure 12a). A conductivity of this level can be reached only due to the participation of silver in the conduction because the conductivity of PANI is of the order of units S cm^{-1}, and copolymers with PDA are expected to have an even lower conductivity. An interesting situation may arise with composites having a moderate conductivity of the order of 10^1 S cm^{-1}. Such materials behave like metals at low temperature, while at room temperature they have semiconductor type of conduction (Figure 12b). As a result, the conductivity becomes virtually independent of temperature, and the same conductivity of 21 S cm^{-1} is found, e.g., at 95 and 305 K. Composites of this type might be useful in electrical applications using large differences in temperature, such as in cosmic technologies.

Concluding Remark. *p*-Phenylenediamine and its *N*-substituted derivatives are well-known developers in photography, where they reduce silver bromide to metallic silver and make the latent photographic image visible. The oxidation of PDA is not desirable, and it is prevented by various means, such as by the addition of sodium sulfite to developers. The reduction of silver salts in photography takes place in an alkaline medium, and it is stopped in a solution of acetic acid, which is used for that purpose between the developer and fixer. In contrast to the oxidation under alkaline conditions, which constitutes the basis of the developing process in photography and which has been extensively studied, little is known about the analogous process in acidic media such as that analyzed in the present paper. Yet, certain connections with the chemistry of photography should be kept in mind.

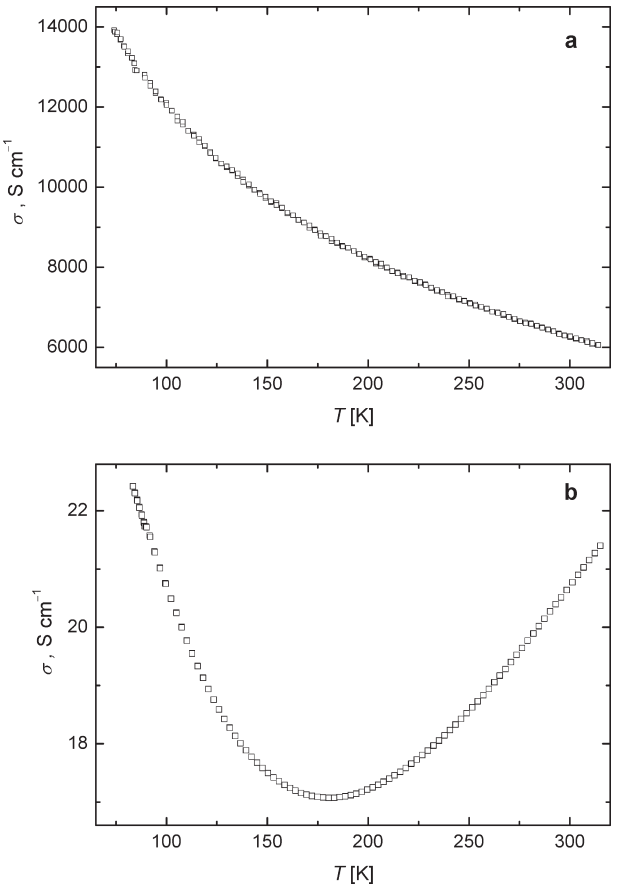

Figure 12. Temperature dependence of the conductivity, σ, of PANI−silver composites prepared (a) with 1 mol % PDA and (b) 10 mol % PDA in 1 M acetic acid.

Conclusions

1. The acceleration of aniline oxidation with silver nitrate by *small amounts* of *p*-phenylenediamine opens a new route to the preparation of PANI−silver composites. The composites are produced in high yield and in short reaction times of some tens of minutes. It is proposed that *p*-phenylenediamine participates in the formation of initiation centers that start the growth of PANI chains in the media of sufficient acidity. The oxidations in acetic acid solutions produced a conductivity as high as 6100 S cm^{-1}. The content of silver was close to the theoretical expectation, 68.9 wt %, in all composites. FTIR spectra indicate the presence of considerable fractions of aniline oligomers.

2. Aniline and *p*-phenylenediamine *mixtures* similarly produce conducting copolymer composites with silver when oxidized with silver nitrate. Oligomers may also constitute significant parts of such products. Because of copolymerization, the regular structure of the PANI chains is reduced by the incorporation of *p*-phenylenediamine units. For that reason, the conductivity of a copolymer composite with silver was generally lower than the conductivity of the parent homopolymers combined with silver. The potential chemical heterogeneity of the copolymers should always be kept in mind when discussing their electrical properties.

3. The conductivity of composites represented by silver nanoparticles embedded in the matrix of a conducting polymer is expected to be high. Nevertheless, silver nanoparticles in less conducting, or even a nonconducting, matrix often produce materials of higher conductivity. Interfacial electronic interaction between polymer semiconductor and silver metal or the formation of electrical barriers can be the cause of these results.

4. The combination of semiconducting polymers with silver may produce materials that behave as metals at low temperature and as semiconductors at room temperature. As a result, the conductivity of such composites is little dependent on temperature over a broad temperature range.

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