Research Article

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Polyaniline–silver composites prepared by the oxidation of aniline with silver nitrate in acetic acid solutions

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Abstract

The reaction between two non-conducting chemicals, aniline and silver nitrate, yields a composite of two conducting components, polyaniline and metallic silver. Such conducting polymer composites combine the electrical properties of metals and the materials properties of polymers. In the present study, aniline was oxidized with silver nitrate in solutions of acetic acid; in this context, aniline oligomers are often a major component of the oxidation products. An insoluble precipitate of silver acetate is also present in the samples. The optimization of reaction conditions with respect to aniline and acetic acid concentrations leads to a conductivity of the composite as high as 8000 S cm^{-1} at *ca* 70 wt% (*ca* 21 vol%) of silver. A sufficient concentration of acetic acid, as well as a time extending to several weeks, has to be provided for the successful polymerization of aniline. Polyaniline is present as nanotubes or nanobrushes composed of thin nanowires. The average size of the silver nanoparticles is 30–50 nm; silver nanowires are also observed.

Keywords: polyaniline; silver; conducting polymer; conductivity; nanotubes

INTRODUCTION

The successful oxidation of aniline with silver ions yields composites of polyaniline (PANI) and metallic silver (Fig. 1). The chemical reaction between two non-conducting species thus yields two conducting products. The oxidations of aniline with silver nitrate reported in the literature have used nitric acid as the reaction medium[1,2] or just water.[3,4] The fact that PANI was produced mainly as nanobrushes composed of thin 10–20 nm nanowires[2] but contained also nanotubes makes such materials of interest in the design of nanostructures.[5] The induction period, typical of aniline oxidations[6] and extending with silver nitrate oxidant to months,[2] is followed by a relatively fast polymerization, which still takes at least a week or longer. The oxidation is promoted by UV irradiation.[1,3,4,7] Two strikingly similar papers[8,9] illustrated that both ultrasonic agitation and ionizing radiation accelerate the oxidation of aniline with silver nitrate.

Preliminary experiments have suggested that aqueous solutions of organic acids might be more suitable media for the oxidation of aniline with silver ions, with respect to reaction rate. Moreover, the formation of PANI nanotubes has been observed during the oxidation of aniline in solutions of acetic acid using ammonium peroxydisulfate as an oxidant.[10–12] In the study reported in the present paper we therefore investigated the feasibility of similar oxidation using silver nitrate as oxidant. Poly(2,5-dimethoxyaniline) has been claimed to have been prepared by the oxidation of 2,5-dimethoxyaniline with silver nitrate in the presence of poly(styrene sulfonic acid).[13,14] The resulting brown colour of the products, and the corresponding absence of the absorption maximum in the UV-visible spectra at longer wavelengths, suggest, however, that the product was not an analogue of a conducting PANI but rather a material based on substituted aniline oligomers.

In addition to the formation of PANI, silver is a product of silver nitrate reduction, which proceeds at the same time (Fig. 1). The resulting PANI–Ag nanocomposites are thus materials combining the semiconductor-type PANI conductivity with the metallic conductivity of silver. Except for a single paper,[2] the conductivity of bulk PANI–Ag samples has not been reported. The search for reaction conditions leading to such composites in good yield, within reasonable reaction times, and having a high conductivity, was the object of the study reported here.

EXPERIMENTAL

Oxidation of aniline

In the first series of experiments, aniline and silver nitrate (Fluka, Switzerland) were separately dissolved in 0.4 mol L^{-1} acetic acid. Both solutions were mixed to start the oxidation at 20 °C. The concentrations of aniline in the resulting mixture were 0.1, 0.15, 0.2, 0.3, 0.4, 0.6, 0.8 or 1.0 mol L^{-1}; the mole ratio of silver nitrate to aniline was 2.5. After two weeks, the brown-to-green solids

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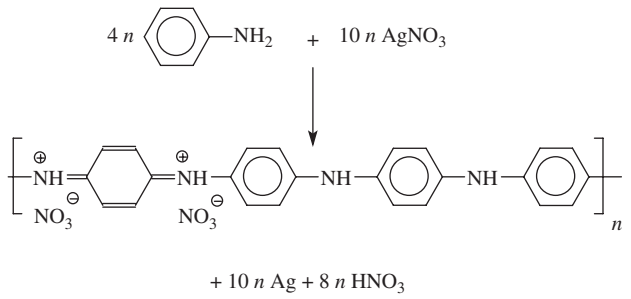

Figure 1. Aniline is oxidized with silver nitrate to polyaniline (emeraldine) nitrate. Metallic silver is produced at the same time; nitric acid is a by-product. In the solutions of acetic acid, a precipitate of silver acetate is also present in the reaction mixture.

produced in the oxidation were collected by filtration, rinsed with 0.4 mol L^{-1} acetic acid and dried at room temperature over silica gel.

In the second series of experiments, the concentration of aniline was fixed at 0.2 mol L^{-1}, the mole ratio of silver nitrate to aniline was 2.5 and the aqueous reaction medium contained various concentrations of acetic acid, ranging from zero to 99% (glacial). Reaction times were extended to four weeks. Portions of the products were deprotonated in excess of 1 mol L^{-1} ammonium hydroxide to form the corresponding bases.

Characterization

UV-visible spectra of deprotonated samples dissolved in *N*-methylpyrrolidone were recorded with a Lambda 20 spectrometer (Perkin Elmer, UK). Fourier transform infrared (FTIR) spectra in the range 400–4000 cm^{-1} were recorded, at 64 scans per spectrum at 2 cm^{-1} resolution, using a fully computerized Thermo Nicolet NEXUS 870 FTIR spectrometer with a DTGS TEC detector. Samples were dispersed in potassium bromide (KBr) and compressed into pellets. Silver acetate, used as a reference, was purchased from Sigma-Aldrich, Switzerland. Raman spectra excited with a He–Ne laser (633 nm) were collected using a Renishaw inVia Reflex Raman spectroscope. A research-grade Leica DM LM microscope with an objective magnification ×50 was used to focus the laser beam on the sample. The scattered light was analysed using a spectrograph with a holographic grating with 1800 lines mm^{-1}. A Peltier-cooled CCD detector (576 × 384 pixels) was used to register the dispersed light.

TGA was performed in a 50 cm^3 min^{-1} air flow at a heating rate of 10 °C min^{-1} with a Perkin Elmer TGA 7 thermogravimetric analyser to determine the content of silver as a residue. JEOL JSM 6400 and JEOL JEM 2000FX microscopes were used to assess the morphology. The conductivity was measured using a four-point van der Pauw method on pellets compressed at 700 MPa with a manual hydraulic press, using as current source an SMU Keithley 237 and a Multimeter Keithley 2010 voltmeter with a 2000 SCAN 10-channel scanner card. For low-conductivity samples, 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. Temperature dependences were determined for the same samples with a Janis Research VNF-100 cryostat in the range 78–320 K in a flowing stream of nitrogen vapour, which provided good control over the temperature homogeneity in samples. The density of the composites was evaluated using a Sartorius R160P balance by weighing the pellets both in air and immersed in decane at 20 °C.

RESULTS AND DISCUSSION

Varying the concentrations of reactants

In the first series of experiments, the effect of reactant concentrations, with a fixed concentration of acetic acid (0.4 mol L^{-1}), was analysed.

Silver acetate precipitate

Aniline and silver nitrate were separately dissolved in acetic acid. After mixing both solutions to start the oxidation, a voluminous white precipitate was produced. Its elemental analysis, 14.7 wt% C, 1.7 wt% H, 0.2 wt% N, 59.1 wt% Ag, suggests that the precipitate is silver acetate (14.4 wt% C, 1.8 wt% H, 64.6 wt% Ag) only slightly contaminated with aniline. While the solubility of silver nitrate in water is high (115 g per 100 g water at 0 °C), the solubility of silver acetate is much lower (0.72 g per 100 g water at 0 °C); the precipitation is thus to be expected but it occurs only when promoted by the addition of aniline.

Brown oxidation products are generated only in the surrounding aqueous phase, while the precipitate remains white. Thus, the precipitate does not directly participate in the reaction, but its

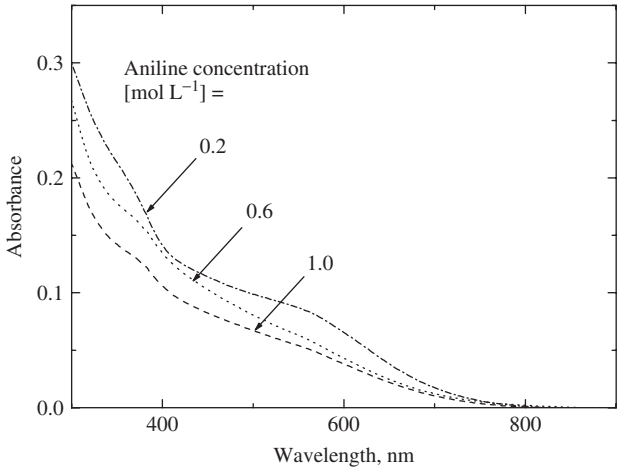

Figure 2. UV-visible spectra of the oxidation products converted to the corresponding bases and dissolved in *N*-methylpyrrolidone. The oxidant-to-aniline mole ratio was 2.5 in all cases.

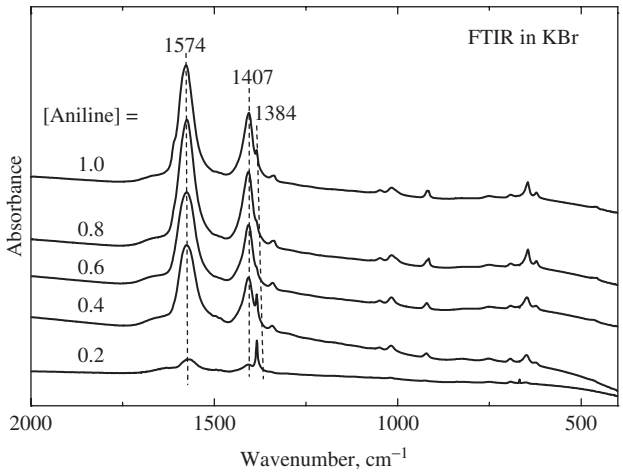

Figure 3. FTIR spectra of the oxidation products. The concentrations of aniline are given in mol L^{-1}. The oxidant-to-aniline mole ratio was 2.5 in all cases.

presence reduces the concentration of free reactants available for the oxidation in the aqueous phase. From this point of view, the presence of a precipitate of silver acetate is a drawback, because the silver acetate may constitute a significant fraction of the product.

Oxidation of aniline

The classic oxidation of aniline with peroxydisulfate in solutions of weak acids proceeds in two distinct phases.[10,12] In the first, an exothermic oxidation of neutral aniline molecules yields non-conducting aniline oligomers containing mixed *ortho*- and *para*-coupled aniline constitutional units[5,12] and quinoneimine moieties.[15] The hydrogen atoms abstracted in this process from aniline molecules are released as protons, so the acidity gradually increases and the neutral aniline molecules become protonated to anilinium cations. These are much more difficult to oxidize, and that is why the oxidation reaction virtually stops. Only later, when the acidity reaches the level needed for the protonation of pernigraniline intermediate, do the anilinium cations participate in the growth of conducting polymer chains.

The above description of aniline oxidation using ammonium peroxydisulfate can also be applied to silver nitrate oxidant (Fig. 1) but some specific features have to be mentioned. The basic difference is in the rate of oxidation; while with peroxydisulfate the reaction is completed within tens of minutes, in the case of silver nitrate weeks are needed for the progress of oxidation. By analogy with a common oxidation of aniline,[12] we assume that brown non-conducting aniline oligomers are produced at first (not shown in Fig. 1) and green conducting PANI is formed later (Fig. 1), if at all. Some products may be composed exclusively of oligomers; for others a fraction of oligomers always accompanies the polymers.

When 1 g of aniline is oxidized with silver nitrate, it theoretically produces 1.35 g of PANI nitrate and 2.90 g of silver, i.e. 4.25 g of PANI–Ag composite, according to the scheme shown in Fig. 1. The theoretical composition of a PANI–Ag composite is thus 68.2 wt% Ag. The experimental yields are much lower under our given experimental conditions (Table 1), because a portion of the silver ions is inaccessible in the precipitated silver acetate, but the compositions correspond well to the expected values (Table 1). The deviations may be due to the formation of oligomers, which are not considered in the reaction scheme (Fig. 1).

Aniline is a weak base. When its concentration in the reaction medium is increased, it reduces the acidity afforded by the acetic acid solution, and, more importantly, it neutralizes the nitric acid, which is a by-product of the oxidation (Fig. 1).[2] A sufficiently high acidity, needed for the successful polymerization of aniline to PANI, is thus not necessarily reached in most experiments carried out at high aniline concentration. For that reason, the presence of a polymeric component may be anticipated only at low concentrations of aniline.

UV-visible spectra

In the present case, using silver nitrate as an oxidant (Fig. 1), obviously only the first part of the oxidation takes place, and the acidity needed for the true polymerization is not reached within the two weeks allocated for the experiment. For that reason, the yield of the reaction is low, and the products are mainly composed of oligomers mixed with a silver acetate precipitate. This is manifested by the UV-visible spectra (Fig. 2), which do not exhibit the absorption band characteristic of the PANI base located at *ca* 630 nm but only an unpronounced shoulder extending to longer wavelengths. The products are brown; they do not have the green colour typical of true PANI.

FTIR spectra

The FTIR spectra of the oxidation products exhibit two strong absorption bands with maxima at 1574 and 1407 cm^{-1} (Fig. 3), especially with a high content of aniline and silver nitrate in the

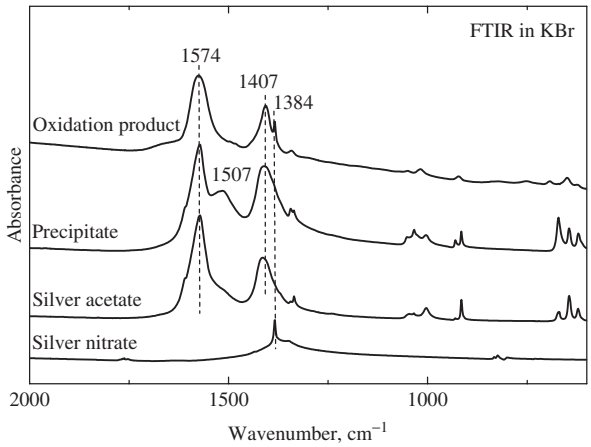

Figure 4. FTIR spectra of the oxidation product prepared at 0.4 mol L^{-1} aniline and the white insoluble precipitate of silver acetate produced after mixing of reactants. The spectra of silver acetate and silver nitrate are shown for comparison.

Table 1. The oxidation of aniline with silver nitrate in 0.4 mol L^{-1} acetic acid at various aniline concentrations

Concentration of aniline[a] (mol L^{-1})	Yield (g g^{-1} aniline)	Yield (% theory)	Composition (wt% Ag)	Conductivity (S cm^{-1})	Density (g cm^{-3})
0.1	0.50	12.6	–	5680	3.29
0.15	0.93	23.4	70.8	8000	3.33
0.2	1.30	32.7	77.0	4350	3.28
0.3	1.09	27.6	–	5300	3.34
0.4	0.602	14.2	71.1	2240	3.24
0.6	0.429	10.1	69.4	4340	3.48
0.8	0.360	8.5	70.1	20.1	3.41
1.0	0.325	7.6	69.7	50.3	3.50

[a] Mole ratio $[AgNO_3]/[aniline] = 2.5$.

reaction mixtures. They do not resemble the spectra of either PANI[12,16] or of aniline oligomers[17] at all. They are typical of the carboxylate ion, which gives rise to two bands: a strong asymmetric stretching band near 1650–1550 cm^{-1} and a weaker symmetric stretching band close to 1400 cm^{-1}.[18,19] This confirms that silver acetate is formed in the reaction and constitutes a major part of the product. To support this statement we compared the FTIR spectrum of the oxidation product with the spectrum of the white insoluble precipitate created after the mixing of reactants and with the spectra of silver acetate and silver nitrate (Fig. 4). The main absorption bands at 1574 and 1407 cm^{-1} observed in the oxidation products (Fig. 3) are also present in the spectrum of silver acetate (Fig. 4). In the spectrum of the white insoluble precipitate, we can see an additional absorption maximum at 1507 cm^{-1}. The presence of this band is connected with traces of aniline oxidation products or with aniline oligomers present at the faces of the silver acetate crystals, and detected using optical microscopy (Fig. 5). A sharp peak at 1384 cm^{-1} in the spectrum of the oxidation product is attributed to the nitrate anion, introduced by the protonation of aniline constitutional units with nitric acid, as illustrated by the spectrum of silver nitrate (Fig. 4).

Thermogravimetric analysis

TGA suggests the presence of a component with a decomposition temperature of 180–280 °C (Fig. 6), probably a mixture of silver acetate and aniline oligomers. A polymer fraction is found only when the reaction takes place at 0.2 mol L^{-1} aniline, where the major component decomposes at *ca* 320 °C. The standard PANI prepared with peroxydisulfate also starts to decompose at this temperature, but complete destruction takes place only at *ca* 650 °C.[20]

TGA is a suitable method for the determination of silver content as a residue (Fig. 6), provided the samples are homogeneous,

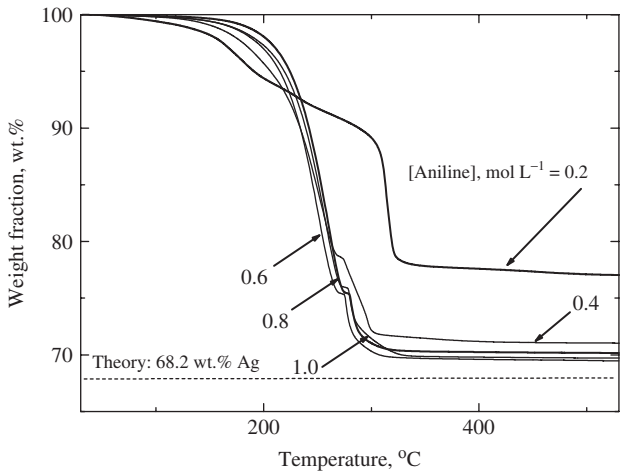

Figure 6. TGA of composites. The oxidant-to-aniline molar ratio was 2.5 in all cases.

and they do not contain macroscopic silver particles, a condition which is satisfied in the present case. The silver contents (Table 1) are close to theoretical expectations for the oxidation product, 68.2 wt% Ag (Fig. 6), as well as for the silver acetate, 64.6 wt%. The agreement is good, considering the fact that a part of the product consists of aniline oligomers, which are not considered in Fig. 1, but must have a similar structure to the aniline polymers and differ only in the bonding of the aniline constitutional units.[12]

Density

The presence of silver is also confirmed by the density measurements (Table 1). The density of 'standard' PANI salt at 20 °C is[6]

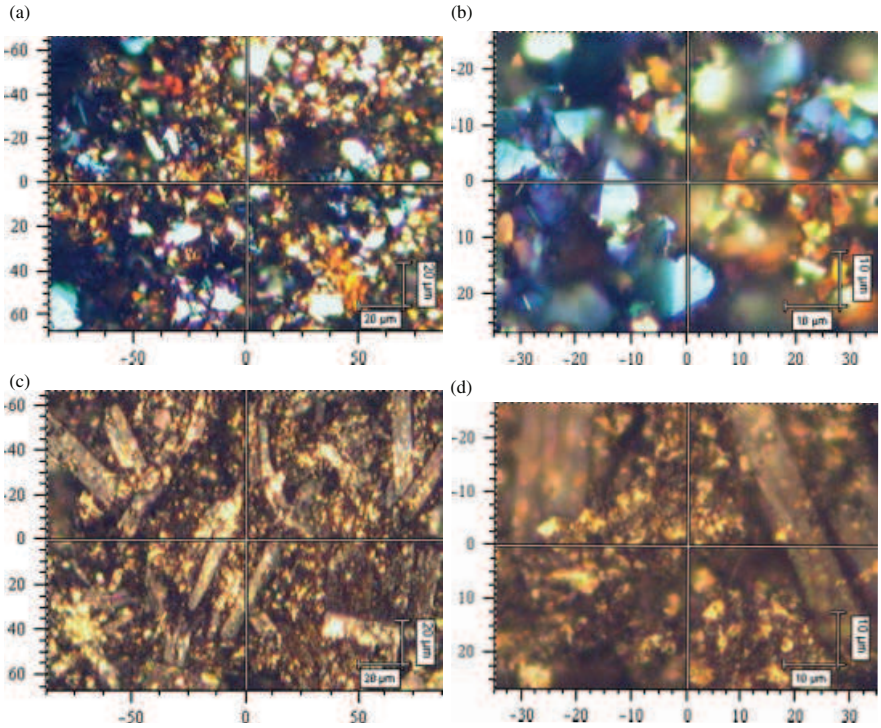

Figure 5. Images of the oxidation products prepared by the oxidation of 0.2 mol L^{-1} aniline with 0.5 mol L^{-1} silver nitrate in the solutions (a, b) 0.2 and (c, d) 5 mol L^{-1} acetic acid.

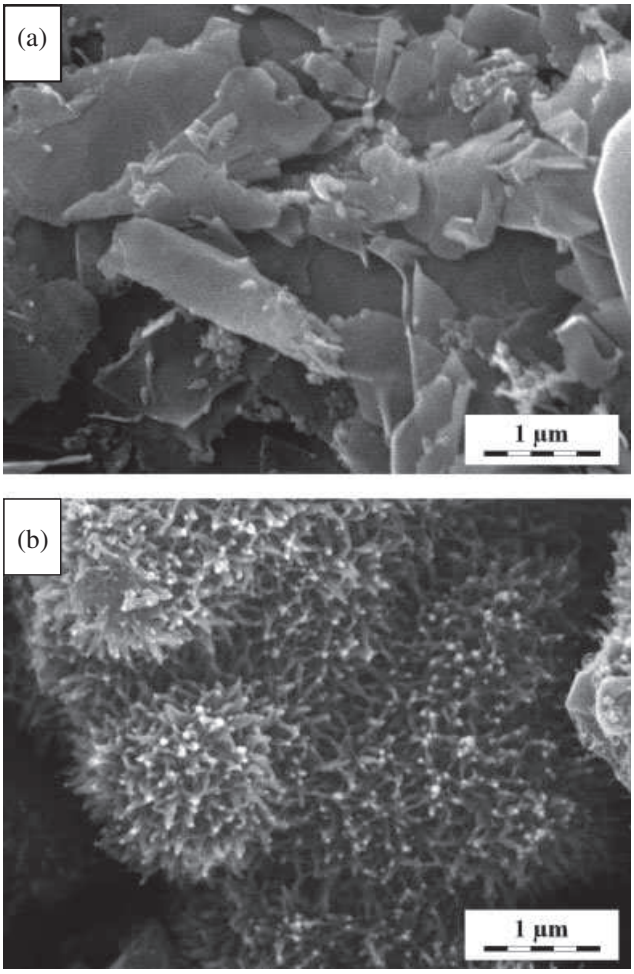

Figure 7. SEM micrographs of the oxidation products: aniline was oxidized with equimolar amount of silver nitrate in 0.4 mol L^{-1} acetic acid. Concentration of aniline was (a) 0.1 and (b) 0.4 mol L^{-1}.

1.33 g cm^{-3} and that of silver is 10.50 g cm^{-3}, the density values of PANI–Ag composites being between these two limits (Table 1). With a theoretical composition of 68.2 wt% Ag, and by assuming the additivity of volumes, this corresponds to 21.4 vol% Ag and to a density of 3.29 g cm^{-3}. The compositions are close to each other (Table 1), confirming the comparable content of silver in the samples. Both the compositions and densities are also close to the predicted values.

Morphology

The morphology of the products is complex: it is dominated by sheets at lower aniline concentrations (Fig. 7(a)), while nanobrushes composed of thin nanowires are present in the samples prepared at higher aniline concentrations (Fig. 7(b)). The latter morphology has also been produced by the oxidation of aniline with silver nitrate in solutions of nitric acid.[2] Similar PANI nanostructures have been reported in the literature, such as coralloid objects prepared in the presence of a ferrite,[21] or rambutan-like assemblies.[22–24] PANI and silver moieties can be distinguished with the help of transmission electron microscopy (Fig. 8). PANI nanotubes are found in the products (Fig. 8; marked 'A') and elongated 'hairy' objects constituted by thin nanowires (Figs 7(b) and 8(e) and (f); marked 'B') are often present in the micrographs, corresponding to a higher content of aniline in the reaction mixture. The growth of PANI nanotubes has often been observed with another oxidant, ammonium peroxydisulfate.[10,12,17,25,26]

The morphology of the silver is mainly represented by clusters of 20–50 nm nanoparticles, which are present in all the samples, often as a major component (Figs 8(a), (b), (d); marked '1'). Objects with a marble-like texture are also found in these materials (Figs 8(c), (d); marked '2'). These are probably PANI or silver acetate particles incorporating continuous silver patterns. A similar patterning has also been observed in gold substances.[27]

Conductivity

In spite of the absence of an appreciable fraction of the conducting polymer, the conductivity of the resulting materials is good, in most cases of the order of 10^3 S cm^{-1}. The maximum value of 8000 S cm^{-1} is certainly of interest, although the low yield makes it rather unattractive for practical applications. Such a conductivity is comparable to that of mercury[28] (10 400 S cm^{-1}). The conductivity is obviously controlled by the silver nanoparticles, the conductivity of silver being 6.3×10^5 S cm^{-1} at 20 °C.[28] It should be stressed that the conductivity of samples having comparable contents of silver may differ by two orders of magnitude (Table 1) and the presence of silver is not an automatic prerequisite for a high conductivity for a composite.[29,30] The size, morphology and distribution of the silver particles must also be of importance.

Oligomer-based systems normally have limited attraction for polymer chemists but, in contrast, the good conductivity of the composites makes them of interest. The formation of a polymer, PANI, can potentially be encouraged by increasing the concentration of acid. For that reason, we mainly tested the effect of acid concentration in the following experiments. A reasonable reaction time is another parameter to be considered.

Varying the concentrations of acetic acid

In the second series of experiments, two factors were changed: (1) the aniline concentration was fixed at 0.2 mol L^{-1}, that of silver nitrate at 0.5 mol L^{-1} and the concentration of acetic acid was varied; and (2) the reaction time was increased from two to four weeks. The strategy was generally successful. The yield increases (Table 2), a high level of conductivity is maintained and, as discussed below, the fraction of green polymer increases. One should be aware that the product also contains silver acetate and that the true yield is lower.

UV-visible spectra

The spectra of the oxidation products clearly demonstrate the absorption maximum at 574–618 nm (Fig. 9), close to 638 nm, typical of standard PANI base prepared by the oxidation of aniline with peroxydisulfate.[31] The occurrence of the maximum thus clearly proves the presence of PANI in the samples. The maximum shifts to shorter wavelengths at higher acid concentrations due to convolution with the spectrum of the oligomeric component and then disappears for acid concentrations above 1 mol L^{-1}.

Thermogravimetric analysis

A similar picture is provided by TGA (Fig. 10), which demonstrates that only products prepared at low acetic acid concentration contain a major PANI component, while those prepared at high acid concentration are composed of oligomers only. Acetic acid at

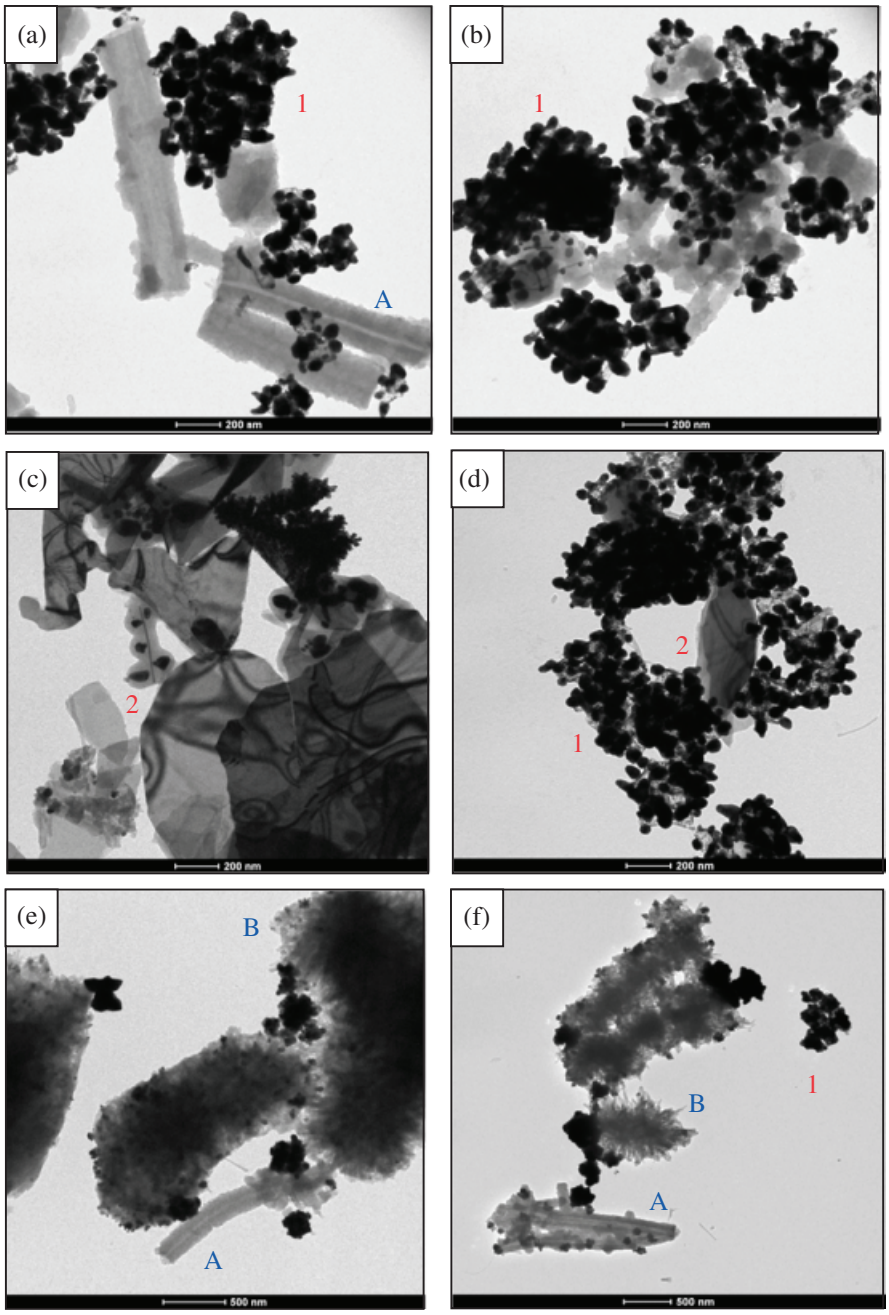

Figure 8. Transmission electron micrographs of the oxidation products when aniline was oxidized with equimolar amount of silver nitrate in 0.4 mol L^{-1} acetic acid. Concentration of aniline was (a, b) 0.1, (c, d) 0.4 and (e, f) 1.0 mol L^{-1}. Silver morphology: 1, clusters of silver particles; 2, marble-like texture. PANI morphology: A, nanotubes; B, 'hairy' objects.

high concentration obviously buffers the increasing acidity due to the formation of nitric acid as a by-product (Fig. 1) and the pH does not reach a level below 2.5, which is needed for the polymerization of aniline.[5,12]

Density

The densities of all the products are comparable (Table 2), in accordance with the practically invariant content of silver (Table 2). The density increases after the deprotonation of PANI to the corresponding base (Table 2). This is logical: the mass of the PANI decreases after deprotonation and so does the mass fraction in the composite.

FTIR spectra

For high concentrations of acetic acid (5 and 10 mol L^{-1} and 99%), the FTIR spectra (Fig. 11) are analogous to those of PANI oligomers, as discussed above (Fig. 3). They reflect the presence of silver acetate, formed in the reaction mixture. The FTIR spectra of products corresponding to lower concentrations of acetic acid (0.2, 0.5 and 1 mol L^{-1}) are completely different. The absorption of the samples is very small and it is necessary to multiply the spectra by a factor of 10 to see any details (Fig. 11).

The FTIR spectrum of the sample prepared in 0.2 mol L^{-1} acetic acid was analysed in more detail (Fig. 12). The spectra before and after subtraction of the contribution of the pure KBr

Table 2. The oxidation of aniline with silver nitrate in solutions of acetic acid of various concentrations (0.2 mol L^{-1} aniline was oxidized with 0.5 mol L^{-1} silver nitrate)

Concentration of acetic acid (mol L^{-1})	Yield (g g^{-1} aniline)	Yield (% theory)	Composition (wt% Ag)	Conductivity (S cm^{-1}) PANI salt	Conductivity (S cm^{-1}) PANI base	Density (g cm^{-3}) PANI salt	Density (g cm^{-3}) PANI base
0.2	2.77	65.1	72	239	15.9	3.50	3.64
0.5	3.21	75.7	69	326	67.7	3.42	3.67
1	1.76	41.5	72	3550	1390	3.47	3.63
5	0.55	13.0	69.5	2320	– [a]	3.55	– [a]
10	1.03	24.2	68	1.95	– [a]	3.50	– [a]
>99%[b]	1.72	40.5	67	0.078	47.8	3.46	3.98

[a] Insufficient amount of material for characterization.
[b] Glacial acetic acid.

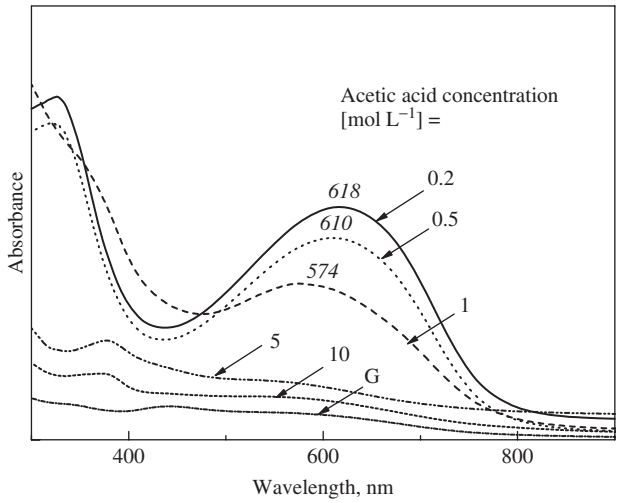

Figure 9. UV-visible spectra of the oxidation products converted to the corresponding bases and dissolved in *N*-methylpyrrolidone prepared by the oxidation of 0.2 mol L^{-1} aniline with 0.5 mol L^{-1} silver nitrate in solutions of acetic acid of various concentrations (G, glacial acetic acid (99%)).

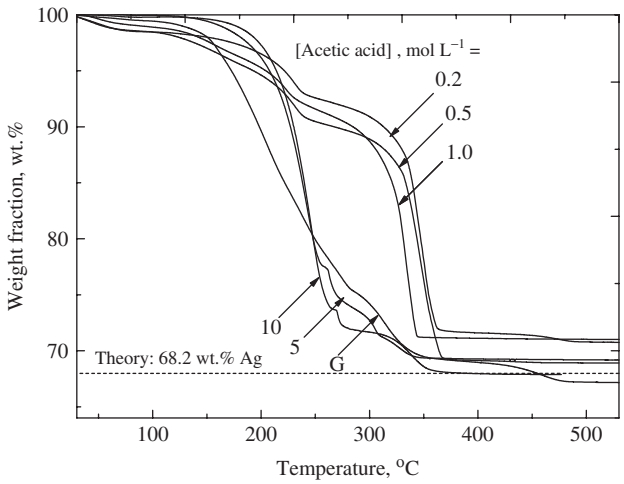

Figure 10. TGA of composites prepared by the oxidation of 0.2 mol L^{-1} aniline with 0.5 mol L^{-1} silver nitrate in solutions of acetic acid of various concentrations (G, glacial acetic acid (99%)).

pellet, including bands corresponding to water, were compared with the spectra of nanotubular PANI prepared by oxidation with ammonium persulfate in the presence of 0.4 mol L^{-1} acetic acid.[10,12] The spectrum of the oxidation product was multiplied by a factor of 50. Only then is it possible to see that the main bands of protonated PANI, represented by the absorption bands at[16] 1566 and 1490 cm^{-1}, are present in the spectra of the products of oxidation. The peak at 1444 cm^{-1}, typical for the infrared spectra of nanotubular PANI,[10,12] is also well detected in the spectra. A sharp peak situated at 1384 cm^{-1} reflects the presence of nitrate anions. This means that the polymerization of aniline by silver nitrate was successful and that PANI with nitrate counterions was produced with medium concentrations of acetic acid in the reaction medium.

Raman spectra

The samples were further analysed using Raman microscopy. In an optical microscope it is possible to see the inhomogeneous nature of the structure (Fig. 5). For the sample obtained in 0.2 mol L^{-1} acetic acid, one observes various objects of different colours; a blue colour corresponds to the presence of PANI. In the second sample prepared in 5 mol L^{-1} acetic acid, a brown colour of oligomers dominates (Fig. 5) and crystals of silver acetate are detected. The Raman spectrum of the first sample, prepared in 0.2 mol L^{-1} acetic acid and taken at the stage corresponding to the blue object, corresponds well to the spectrum of protonated PANI (Fig. 13). After deprotonation, the spectrum transforms to the spectrum of the PANI base. When the spectrum of a brown part of the sample was taken, it is found to correspond to that of the white insoluble precipitate, and the peaks of silver acetate can also be observed in the Raman spectrum.[19] Some peaks of aniline oligomers are also apparent. This supports our concept that the surface of the silver acetate crystals produced after the mixing of reactants is subsequently contaminated by the products of aniline oxidation.

Morphology

In this series of experiments, the choice of morphologies is richer (Fig. 14). Probably the most interesting structure is represented by silver rods of 300 nm diameter coated by PANI nanowires ('3' in Fig. 14(a)). Similar objects with a broken silver core are seen in Fig. 14(b) (marked 'B'). The next morphology is represented by silver nanorods about 80 nm thick and uniformly coated with PANI ('4' in Figs 14(c) and (d)). The clusters of silver nanoparticles ('1'

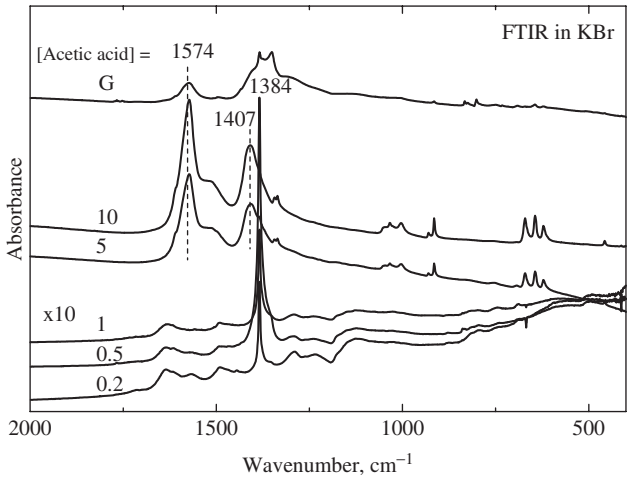

Figure 11. FTIR spectra of the oxidation products prepared by the oxidation of 0.2 mol L^{-1} aniline with 0.5 mol L^{-1} silver nitrate in solutions of acetic acid of various concentrations. The concentrations of acetic acid are given in mol L^{-1} (G, glacial acetic acid (99%)).

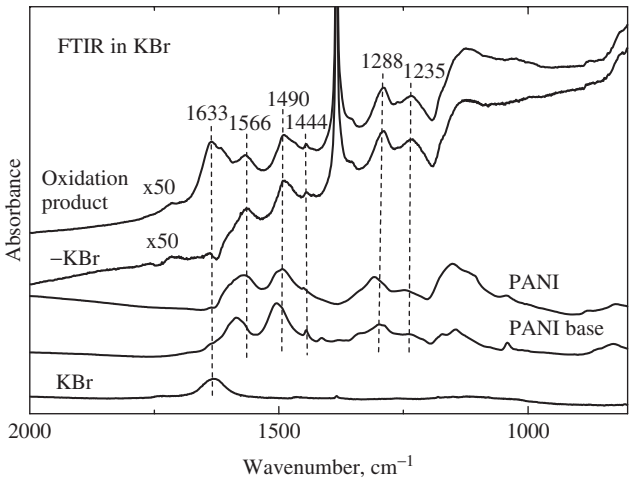

Figure 12. FTIR spectra of the oxidation product prepared by the oxidation of 0.2 mol L^{-1} aniline with 0.5 mol L^{-1} silver nitrate in a solution of 0.2 mol L^{-1} acetic acid before and after subtraction of the spectrum of KBr pellet. The spectra of PANI and corresponding PANI base prepared by the oxidation of 0.2 mol L^{-1} aniline with 0.25 mol L^{-1} ammonium persulfate in a solution of 0.4 mol L^{-1} acetic acid are shown for comparison.

in Figs 14(c) and (d)), and the objects with a marble-like texture seen in Fig. 8(a), are observed also here ('2' in Figs 14(d) and (f)). The formation of silver nanowires has often been reported in the literature,[32] the most relevant case with respect to the present study being the reduction of silver nitrate with sodium citrate carried out in the presence of aniline.[33] At a high acetic acid concentration, the isolated silver nanoparticles are preferentially deposited on elongated objects (Fig. 5; '5' in Figs 14(e) and (f)), which could be both PANI or silver acetate. Various PANI and silver objects are obviously produced under different reaction conditions and at various reaction stages. There is no information about the participation or proportions of individual forms in the samples. A simple link between the morphology and conductivity reported below thus cannot be established.

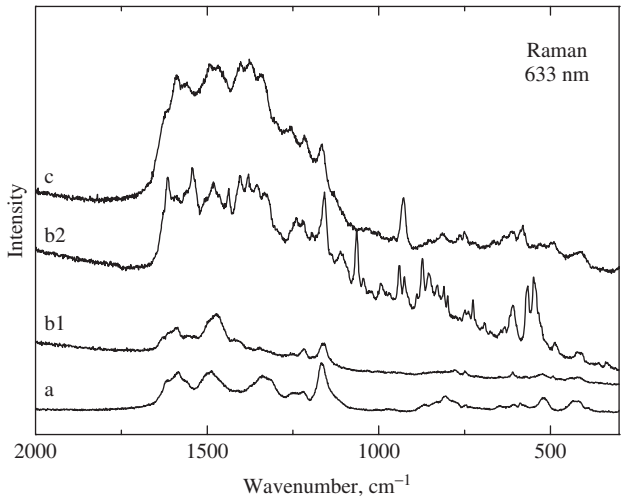

Figure 13. Comparison of the Raman spectra of (a) the oxidation product prepared by the oxidation of 0.2 mol L^{-1} aniline with 0.5 mol L^{-1} silver nitrate in a solution of 0.2 mol L^{-1} acetic acid in protonated form, and after deprotonation obtained from (b1) blue and (b2) brown parts (Fig. 5), with (c) the spectrum of white insoluble precipitate of silver acetate.

Conductivity

The conductivity has a maximum value of 3550 S cm^{-1} for the sample prepared in 1 mol L^{-1} acetic acid. It is tempting to associate it with the presence of silver nanowires (Fig. 14(c)). It is somewhat surprising to find that, despite the presence of the conducting PANI matrix, the conductivity of these composites is lower when the silver is embedded in non-conducting oligomers (Table 2). This may be due to the different morphology of silver in such composites or different distributions in the samples. The composites with a uniform distribution of silver objects would have a lower conductivity compared with the case if the same volume fraction of silver particles were concentrated in the space between silver acetate crystals.

The fact that the conductivity of the composites decreases after the deprotonation of PANI, i.e. when the conducting emeraldine salt is converted to the non-conducting emeraldine base, is to be expected (Table 2). The reduction in conductivity, however, illustrates the fact that the PANI matrix contributes to the overall conductivity of the composites. On the other hand, the conductivity of the composites decreases with increasing temperature (Fig. 15). Such behaviour is typical of metals; with semiconductors, such as PANI, the inverse trend is usually observed.[34] This confirms that the overall conductivity of the composites is controlled by silver.

CONCLUSIONS

1. The oxidation of aniline with silver nitrate in solutions of acetic acid produces PANI–Ag composites only at a moderate concentration of acetic acid, 0.2–1 mol L^{-1}, and if sufficient time (several weeks) is allowed for the reaction. Substantial fractions of aniline oligomers and of silver acetate are always present in the samples and, in many other cases, PANI is absent. The composition of composites is close to the theoretical expectation, 68.9 wt% Ag, but this fact alone is not a proof of the successful preparation of a PANI–Ag composite. Such evidence is provided by UV-visible, FTIR and Raman spectroscopy, and further supported by TGA.

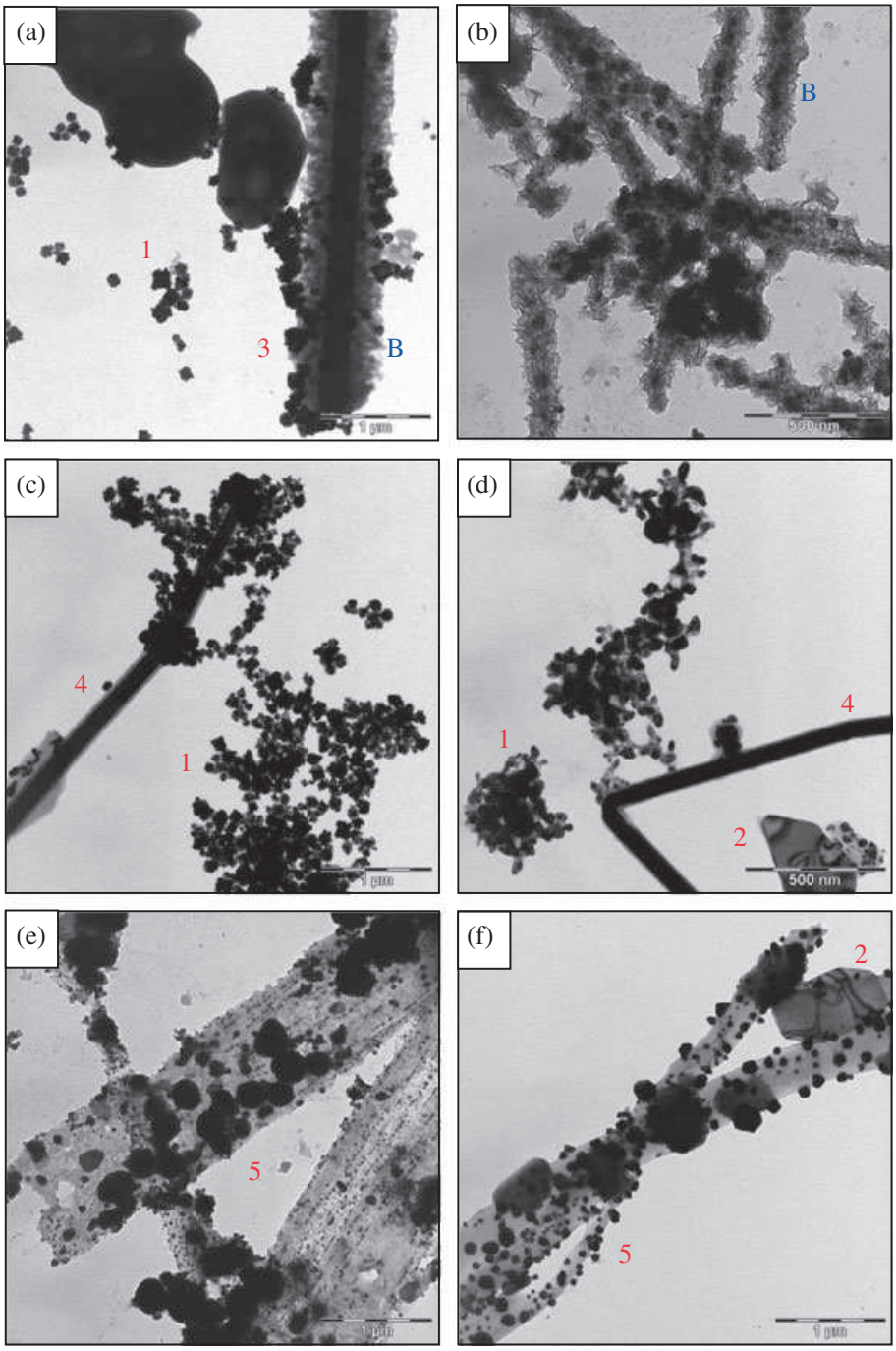

Figure 14. Transmission electron micrographs of PANI–Ag composites produced in solutions of various concentrations of acetic acid: (a) 0.2, (b) 0.5, (c) 1, (d) 5 and (e) 10 mol L^{-1} and (f) 99% acetic acid. Silver morphology: 1, clusters of silver particles; 2, marble-like texture; 3, 'hairy' nanorods with silver core; 4, coated silver nanorods; 5, isolated particles. PANI morphology: B, 'hairy' objects.

2. The morphology of the oxidation products includes PANI nanotubes, brushes constituted by nanowires, as well as other objects. Silver is present mainly in clusters of particles having a size of 30–50 nm, nanowires or nanorods coated with PANI, and a marble-like texture decorating some objects.
3. The highest conductivities of the composites are of the order of 10^3 S cm^{-1}. Such conductivities are surprisingly found especially in composites of silver with non-conducting aniline oligomers. This means that the morphology of silver and its content and distribution are the factors controlling the conductivity. The decisive role of silver in the conductivity of the composites is also confirmed by the temperature dependences, which correspond to the metallic character of the samples.

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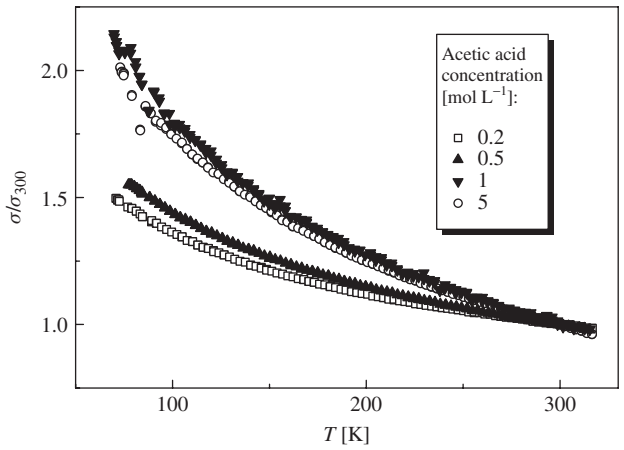

Figure 15. Temperature dependence of the relative conductivity, σ/σ_{300}, of the composites prepared in solutions of acetic acid of various concentrations (σ_{300} is the conductivity at 300 K (Table 2)).

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Polyaniline-coated silver nanowires

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ABSTRACT

Two non-conducting chemicals, aniline and silver nitrate, dissolved in formic acid solutions, yielded a composite of two conducting products, polyaniline and silver. As the concentration of formic acid increased, an alternative reaction, the reduction of silver nitrate with formic acid to silver became dominant, and the content of silver in the composites increased. The formation of polyaniline was confirmed by UV–visible, FTIR, and Raman spectroscopies. The typical conductivity of composites was 43 S cm^{-1} at 84 wt.% of silver. Silver nanowires coated with polyaniline nanobrushes are produced at low concentrations of formic acid, the granular silver particles covered with polyaniline dominate at high acid concentrations.

1. Introduction

The nanocomposites composed of conducting polymers [1–4], such as polyaniline (PANI) or polypyrrole, and noble metals, such as silver, are of interest in producing new materials with high conductivity and exploiting mechanical properties typical of polymers. The development of PANI–silver composites is important for the design of conducting patterns using ink-jet printing techniques in electronics [5,6]. The incorporation of metals is the most promising way to increase the conductivity of PANI, which is currently at the level of units S cm^{-1} [7]. The same principle applies to the construction of sensors based on conducting polymers [8].

Direct oxidation of aniline with silver nitrate is the most straightforward way of composite preparation [9,10]. Unless the oxidation of aniline was promoted by external stimuli, such as increase in reaction temperature [11], UV-irradiation [5,12–14], γ-irradiation or sonication [15,16], the reaction was slow and extended to several weeks or even months [9]. The ability of insoluble silver salts, such as silver cyanoferrate(III), to oxidize aniline to PANI was also reported [17]. The unpronounced absorption maximum in the optical spectra in the region 600–800 nm or its absence [9,15,16,18,19] indicate that many oxidation products have been composed mainly by non-conducting aniline oligomers. The oxidation of pyrrole with silver nitrate similarly required UV-irradiation [20] or the presence of a porphyrin accelerator [21].

The improvement of the syntheses is sought, which would lead to: (1) highly conducting and (2) macroscopically uniform materials, (3) produced at reasonable reaction time and (4) in high yield. It is not easy to satisfy these requirements simultaneously.

The composites prepared by the oxidation of aniline with silver nitrate in the solutions of nitric acid had the conductivity as high as 2250 S cm^{-1} at 52 wt.% silver content [9]. The homogeneity, however, was poor and macroscopic silver flakes were present in the samples along with *ca* 50 nm silver nanoparticles. The yields were at the same time low, <30% of theory, even after several weeks of reaction time. Similar experiments in the solutions of acetic acid have resulted in the product having the highest conductivity 8000 S cm^{-1} and they were macroscopically homogeneous [10]. In spite of high conductivity, the polymer matrix was not produced in many cases, and materials contained mainly non-conducting aniline oligomers.

Formic acid solutions have been selected as reaction media for the oxidation of aniline in the present series of experiments. It has earlier been demonstrated that aniline can be oxidized in the solutions of formic acid to PANI with classical oxidants, such as ammonium peroxydisulfate [22]. In the contrast to acetic acid, however, formic acid is able to reduce silver nitrate to metallic silver, similarly like aniline does. Some synergistic effect thus may be anticipated, which would be of benefit in the synthesis.

2. Experimental

2.1. Preparation of PANI–Ag composites

Aniline (0.2 M; Fluka, Switzerland) was oxidized with silver nitrate (0.5 M; Lach-Ner, Czech Republic) in the 0.1–5 M aqueous

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solutions of formic acid. After mixing the solutions of aniline and silver nitrate, the mixture was left to stand at room temperature for 2 weeks, being just occasionally shaken. A green precipitate gradually formed within few days. The solids were isolated by filtration, rinsed with the corresponding formic acid solution, then with acetone, dried in air, and then over silica gel. A part of samples was converted to a base form by immersion in large excess of 1 M ammonium hydroxide, and dried as above.

2.2. Characterization

The UV–visible spectra of the samples dissolved in *N*-methylpyrrolidone were obtained from 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 in the range 400–4000 cm^{-1} were recorded using a fully computerized Thermo Nicolet NEXUS 870 FTIR Spectrometer with DTGS TEC detector. Samples were dispersed in potassium bromide and compressed into pellets. Raman spectra excited in the visible range with a HeNe 633 nm laser were collected on a Renishaw in Via Reflex Raman spectrometer. A research-grade Leica DM LM microscope was used to focus the laser beam on the sample. The scattered light was analyzed by a spectrograph with a holographic grating with 1800 lines mm^{-1}. A Peltier-cooled CCD detector (576 × 384 pixels) registered the dispersed light. Reduced beam power was always used to avoid degradation of the samples.

Thermogravimetric analyser Perkin Elmer TGA7 was used to pyrolyse PANI–silver composites in air of in nitrogen atmosphere. Silver residues were observed with scanning electron microscopy.

3. Results and discussion

3.1. Oxidation of aniline with silver nitrate

The feasibility of the oxidation of aniline with silver nitrate to PANI–Ag composites (Fig. 1) have been illustrated in number of cases, aqueous solutions of nitric acid being a typical reaction medium [9]. In the solutions of formic acid, however, the reaction may be more complex. This acid does not only adjust the acidity of the medium but it is involved in the chemistry of aniline oxidation. When silver nitrate was dissolved in 99% formic acid, a strongly exothermic reaction took place, $H{\cdot}COOH + 2AgNO_3 \rightarrow 2Ag + CO_2 + 2HNO_3$, before the aniline solution was added and a red colour of colloidal silver was observed after the mixture had been diluted with water. In dilute solutions of formic acid and in the presence of aniline, however, this reaction was inhibited. After the induction period extending for several days, the formation of a green precipitate, PANI, was observed. PANI is protonated by nitric acid, because this acid is produced in the course of reaction as by-product (Fig. 1). The ability of PANI to constitute a salt with formic acid is limited; PANI base exposed to 1–5 M formic acid solutions has not converted to a PANI formate [23]. It should also be noted that potential reduction of emeraldine form of PANI with formic acid to leucoemeraldine has never been observed in the present or earlier reprotonation experiments [23]. The scheme given in Fig. 1 well reflects the overall chemistry of the process, but does not account for details, such as the formation of aniline oligomers, which could be generated at mildly acidic conditions along with PANI [24].

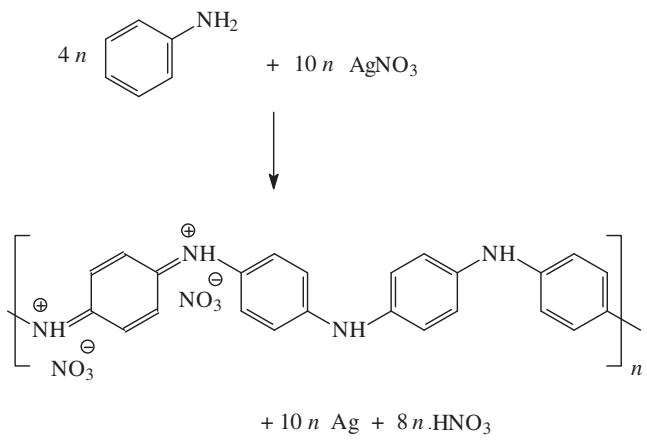

Fig. 1. Aniline is oxidized with silver nitrate to polyaniline, metallic silver and nitric acid are by-products [9]. An arbitrary acid HA present in the polymerization medium, here formic acid, adjusts the starting acidity.

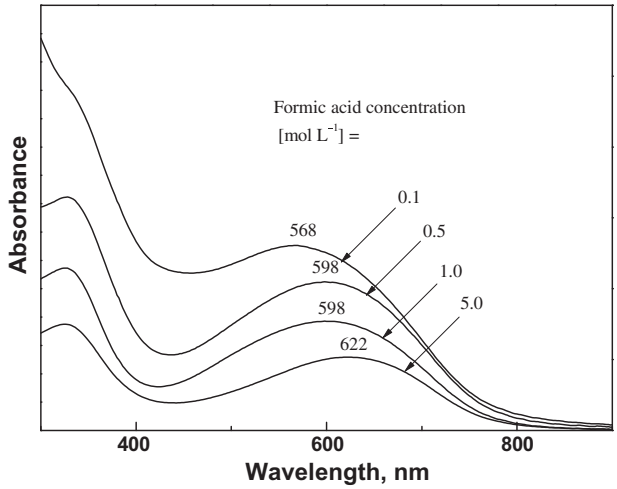

Fig. 2. The UV–visible spectra of the oxidation products converted to the corresponding bases and dissolved in *N*-methylpyrrolidone prepared by the oxidation of 0.2 M aniline with 0.5 M silver nitrate in the solutions of formic acid of various concentrations.

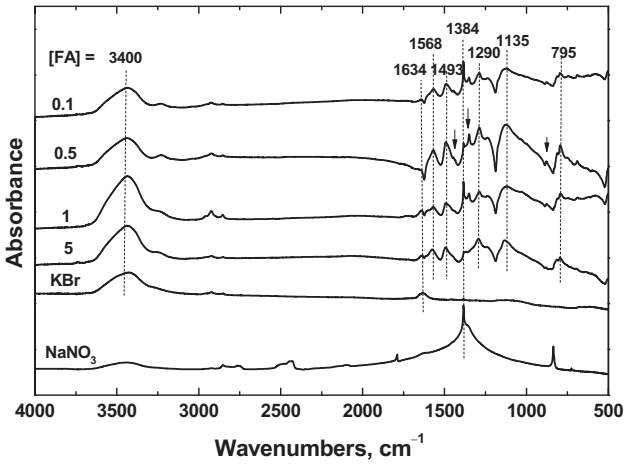

Fig. 3. The FTIR spectra of the oxidation products prepared by the oxidation of 0.2 M aniline with 0.5 M silver nitrate in the solutions of formic acid of various molar concentrations [FA]. Spectrum of pure potassium bromide pellet and sodium nitrate is shown for comparison.

3.2. UV–visible spectra

The fact that PANI is produced is documented by UV–visible spectra. The PANI prepared in 5 M formic acid and converted to PANI base displays the typical absorption spectrum of emeraldine base [25] with an absorption maximum at 622 nm (Fig. 2). This absorption maximum shifts to shorter wavelengths as the concentration of formic acid is reduced. This is probably due to the presence of aniline oligomer fraction, which absorbs strongly below 400 nm and has a long absorption tail extending to longer wavelengths [1,10]. The superposition of both types of spectra is responsible for the blue shift of the absorption maximum. Other explanations, based on the change in the oxidation state of PANI, are not relevant.

The silver nanoparticles display a plasmon band that is located between 400 and 520 nm depending on the particle size [26]. Such absorption band has not been observed in the present experiment. It is probably overlapped by stronger absorption of PANI [26], and may cause the shift of the absorption maximum of emeraldine base to lower wavelengths, similarly like aniline oligomers discussed above.

3.3. FTIR spectra

The samples were analyzed by FTIR spectroscopy (Fig. 3). They were difficult to disperse in potassium bromide pellets and, consequently, the overall absorption was small. The spectra contained relatively high absorption bands in the region of stretching and

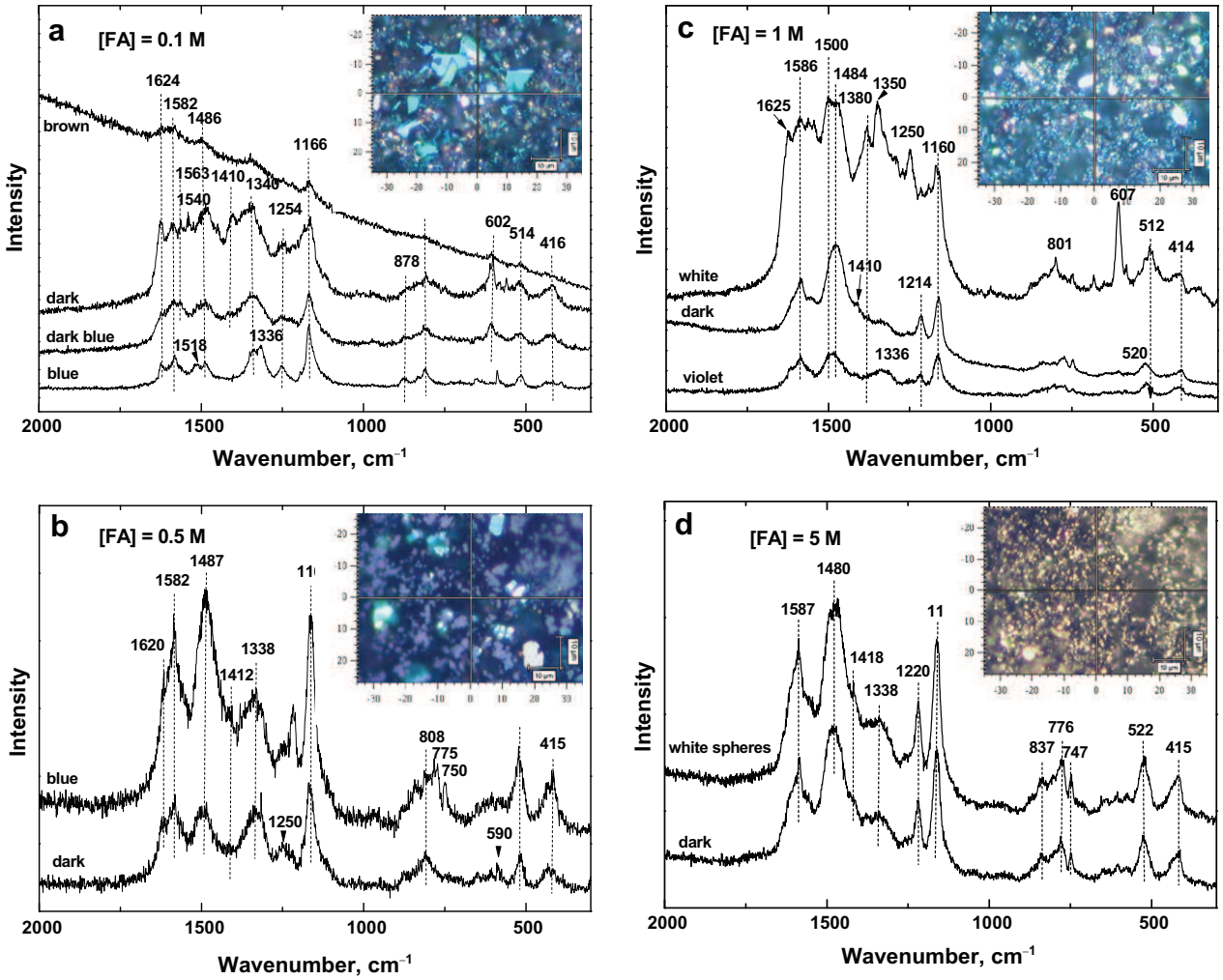

Fig. 4. Raman spectra of the oxidation products prepared by the oxidation of 0.2 M aniline with 0.5 M silver nitrate in the solutions of (a) 0.1, (b) 0.5, (c) 1, and (d) 5 M formic acid at various places of the sample.

Table 1
The oxidation of aniline with silver nitrate in the solutions of formic acid of various concentration. 0.2 M aniline was oxidized with 0.5 M silver nitrate.

Concentration of formic acid, mol L^{-1}	Yield, g g^{-1} aniline	Yield, % theory[a]	Composition, wt.% Ag	Conductivity, S cm^{-1}		Density, g cm^{-3}	
				PANI salt	PANI base	PANI salt	PANI base
0.1	3.05	71.8	74	47	4.5	3.95	4.32
0.4	3.39	79.8	72.6	0.85	0.011	3.66	4.12
0.5	2.13	50.1	76.2	5.0	–	4.13	–
1.0	2.80	65.9	84.3	43	2400	4.75	5.26
5.0	2.17	51.1	95.9	14,000	1300	8.01	8.10

[a] 1 g of aniline theoretically produces 1.35 g of PANI nitrate and 2.90 g of Ag, i.e. 4.25 g of PANI–Ag composite according to the Fig. 1. The theoretical composition of PANI–silver composite is 68.2 wt.% Ag.

bending vibrations of water molecules at about 3400 cm^{-1} and 1634 cm^{-1} respectively. They reflect the presence of residual water in potassium bromide. The main bands of protonated PANI [27], represented by the absorption bands at 1568 and 1492 cm^{-1}, together with the bands at about 1290 and 1135 cm^{-1}, are visible in the spectra of oxidation products. Additional peaks at 1444, 1350 and 880 cm^{-1}, marked by arrows in the Fig. 3, belong most probably to oxidized aniline oligomers containing *ortho*-coupled and/or oxazine-like units. They manifest themselves especially in the composites prepared at low concentrations of formic acid, where the oligomeric fraction may be substantial (Fig. 2). The sharp peak situated at 1384 cm^{-1} belongs to nitrate anions, as it is evident by comparison with its position in the spectrum of $NaNO_3$ (Fig. 3). This fact also confirms the protonation of the products by nitric acid.

3.4. Raman spectra

Raman spectra support the observed heterogeneous structure of the PANI–Ag composites (Fig. 4). The samples prepared at low concentration of formic acid, 0.1 M, are more heterogeneous, they contain dark, blue, brown and white triangular regions corresponding to silver crystals (Fig. 4a). Raman spectra of these regions are different. The spectrum measured at blue regions in the sample corresponds to the spectrum of protonated aniline oligomers. The band at about 1624 cm^{-1} is due to the C∼C stretching vibration of benzenoid ring [28] and the band observed at ∼1582 cm^{-1} to the C=C stretching vibration in the quinonoid ring. The dominating band positioned at 1486 cm^{-1} corresponds to the C=N stretching vibration in quinonoid units. A less intense peak observed at ∼1518 cm^{-1} is attributable to the N–H bending vibrations. Two bands corresponding to charged nitrogen segments, C∼N^+, (where ∼ denotes the bond intermediate between the single and double bond) are observed at ∼1340 and ∼1336 cm^{-1}. The band due to C–N stretching in benzenoid units is observed at ∼1254 cm^{-1} and the band of C–H bending in-plane vibrations at 1166 cm^{-1}, corresponding most probably to semi-quinonoid rings (cation-radical segments) [28]. The band at ∼880 cm^{-1} is attributed to the benzene-ring deformation in a protonated form. The spectrum typical to the protonated PANI with an additional peak of phenazine units at 1410 cm^{-1} is obtained at dark blue regions and the deprotonated oligomer at brown spots [28]. The spectrum of various oxidized oligomeric products and nitrates is obtained at dark regions.

The product prepared in 0.5 M formic acid is more homogeneous (Fig. 4b). Raman spectrum at the dark region corresponds to the protonated pernigraniline form of PANI with a well developed band at 1487 cm^{-1} corresponding to the C=N stretching vibration in quinonoid units and the band of charged nitrogen

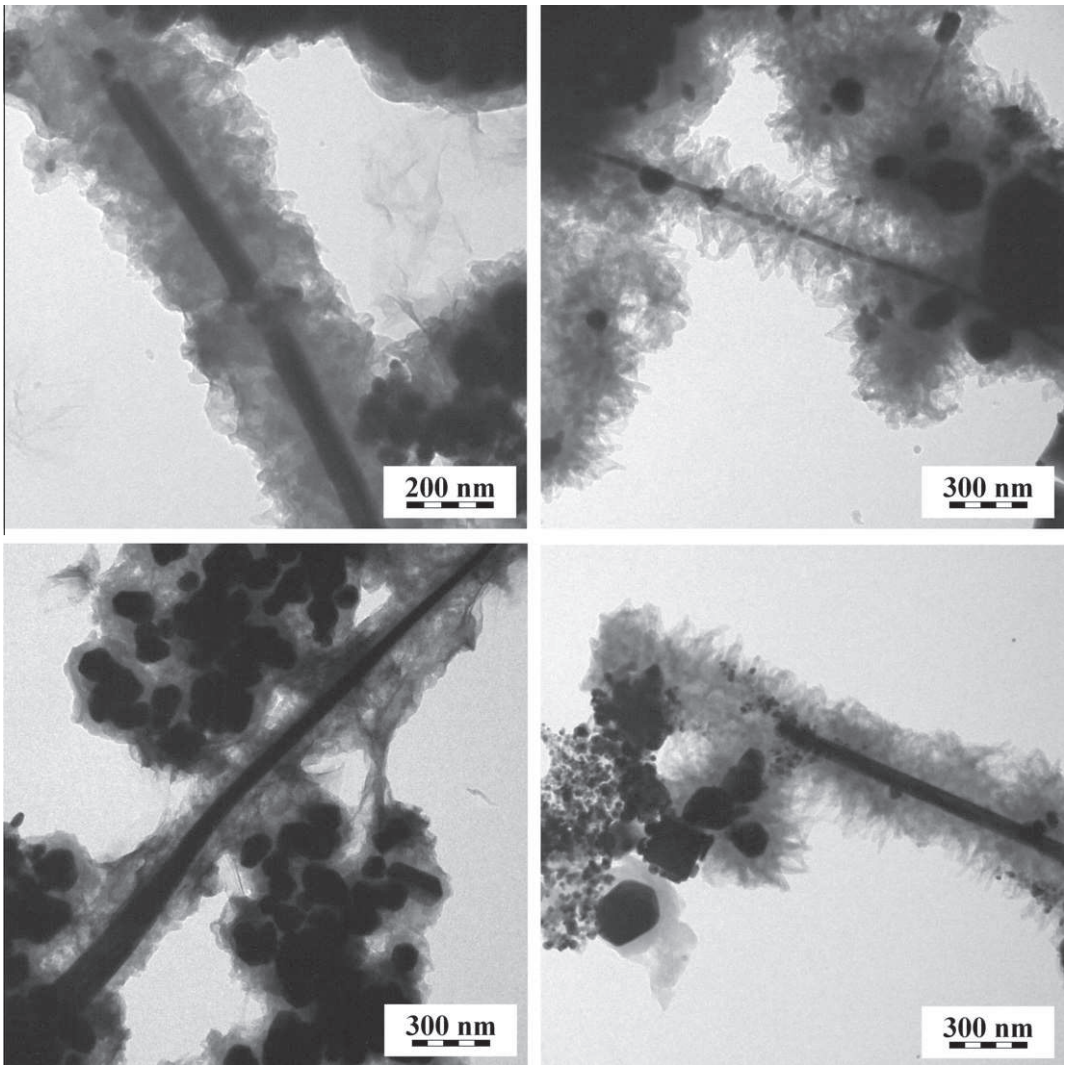

Fig. 5. Transmission electron microscopy of silver nanowires coated with polyaniline. Aniline was oxidized with silver nitrate in 0.4 M formic acid.

segments, $\nu(C{\sim}N^+)$ at about 1338 cm^{-1} at the same time [29]. At blue regions, the bands of quinonoid units are more intense and they correspond to partly deprotonated sample.

The product prepared in 1 M formic acid displays the features usually observed in PANI base at dark regions and partly protonated PANI at violet regions [30]. At bright regions the spectrum is complicated, and reflects most probably the resonantly enhanced peaks of the first oxidation oligomeric products on silver surface (Fig. 4c). The peak of nitrate at 1380 cm^{-1} is present in the spectrum. The relatively strong band at ~1500 cm^{-1} due most probably to N–H bending vibrations associated with the semi-quinonoid structure and the band of $C{\sim}N^+$ stretching vibrations of delocalized polaronic structure detected at 1350 cm^{-1} correspond to the charged aniline oligomers on the surface of the silver nanoparticles.

3.5. Conductivity

The conductivity of the composites varies between 10^{-2} and 10^{1} S cm^{-1} orders of magnitude (Table 1). This is rather disappointing, considering the high content of silver in the composites. On the other hand, the conductivities reported so far in the literature have never exceeded 10^{-1} S cm^{-1}, except for two cases where the conductivity reached the order of 10^{3} S cm^{-1} [9,10]. It should also be realized that the high mass fraction of silver still corresponds to a relatively low volume fraction of silver, below 20 vol.% in the most cases. The high conductivity of composites after the deprotonation of PANI to its non-conducting base form suggests that the overall conductivity is controlled rather by silver than by PANI.

The variation of the percolation limit with the changing proportions of globular and extended silver morphologies (see below), and the close proximity of a percolation threshold of silver in the samples, are responsible for some unexpected results. The increase in the composite conductivity after the deprotonation of conducting PANI belongs among such results (Table 1). The accompanying increase in density after deprotonation, however, suggests that mass loss during the protonation of PANI is partly caused by a removal of oligomeric fractions. This also leads to the reduced volume fraction of PANI in the composite. The increased volume fraction of silver thus reflects the higher conductivity observed after deprotonation.

3.6. Morphology of composites

The silver nanowires have been observed in the literature to be a product of silver-nitrate reduction under variety of experimental conditions [31]. It has been reported that the reduction of silver nitrate with sodium citrate yielded granular silver nanoparticles, and in the presence of aniline, it led to rod-like silver particles [32]. This

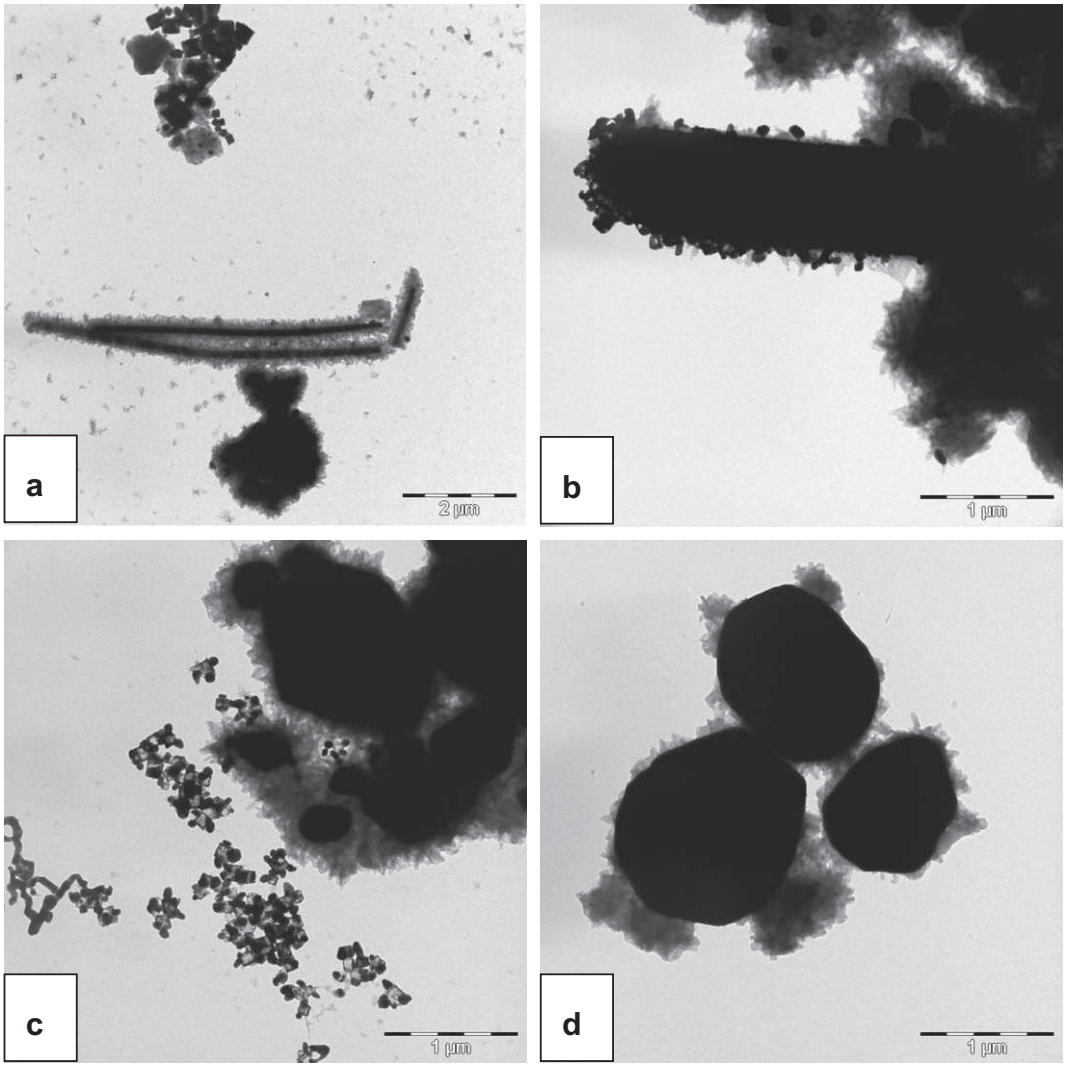

Fig. 6. Transmission electron microscopy of the product of the oxidation of aniline with silver nitrate in (a) 0.1, (b) 0.5, (c) 1.0, and (d) 5.0 M formic acid.

is analogous to the present situation where formic acid takes over the role of a reductant of silver salt.

When the reaction between aniline and silver nitrate takes place, silver nanowires of 20–80 nm in diameter were produced, and were accompanied by granular silver particles in the similar size range (Fig. 5). Silver nanowires as well as silver particles were coated with PANI, the hairy polymer overlayer having a thickness of 50–150 nm. Such thickness is typical of PANI films grown on various surfaces immersed in the reaction mixture during the oxidation of aniline with other oxidants, such as ammonium peroxydisulfate [33,34]. We conclude that silver nanowires are produced at first and PANI coating grows on them in close succession. Polyaniline nanotubes could, in principle, also grow under low-acidity conditions [1,24] and silver could later be deposited inside them [35]. The latter explanation, however, is not likely, because it could not explain the observed coating of granular silver particles with PANI (Fig. 6). It should be mentioned that similar silver nanowires coated with polypyrrole have been obtained after the oxidation of pyrrole with silver(I) oxide at elevated temperature [36].

As the concentration of formic acid in the reaction mixture increases, the silver nanowires (Fig. 6a) become less frequent and become replaced with globular silver particles (Fig. 6b–d). In all cases, they are coated with PANI. This suggests that silver particles were produced at first and only later became coated with PANI.

3.7. Morphology of silver

A slightly different but complementary picture is obtained when observing the morphology of silver. When 0.4 M silver nitrate is prepared in 99% formic acid in the absence of aniline, a fast exothermic reaction produces silver as granules of ~500 nm size (Fig. 7). No silver nanowires are observed. Similar granular particles are visible when the oxidation takes place in the presence of aniline (Fig. 5), especially when the reaction is carried out at high acid concentration (Fig. 6d), but in this case they are accompanied by silver nanowires.

PANI–Ag composites prepared in 0.4 M formic acid, after being exposed to 830 °C [37], yielded fused silver nanoparticles (Fig. 7). The silver microstructure was different if the pyrolysis has been carried out in nitrogen (Fig. 8a) or in air (Fig. 8b), even though the melting point of silver, 962 °C, has not been reached.

It is well known that PANI is carbonized in nitrogen atmosphere above 650 °C to nitrogen-containing carbon and preserves its morphology [37–39]. In air, PANI is slowly decomposed at 400–700 °C, leaving no residue [37]. In the present case of PANI–Ag composites, the decomposition of PANI in air is much faster, and occurs below 400 °C (Fig. 9), being catalyzed with silver nanoparticles. Similar effect was reported earlier [9]. In nitrogen atmosphere, the carbonization of PANI takes place, and the residue above 700 °C is considerably larger. Under such conditions, PANI coating of silver objects converts to carbon coating and prevents the amalgamation of the individual silver particles into larger structures. These are found when the samples are exposed to elevated temperature in air. Then PANI decomposes, and the protective coating is absent.

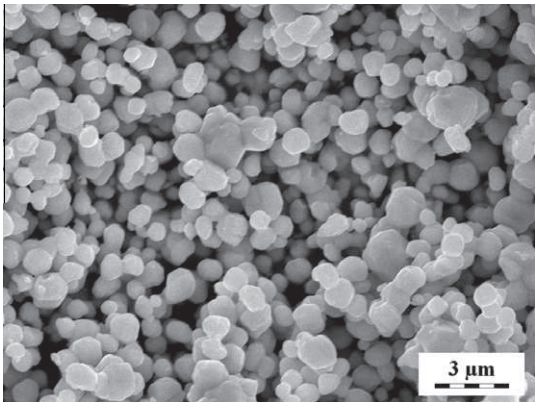

Fig. 7. Scanning electron microscopy of silver particles obtained by the reduction of silver nitrate with 99% formic acid in the absence of aniline.

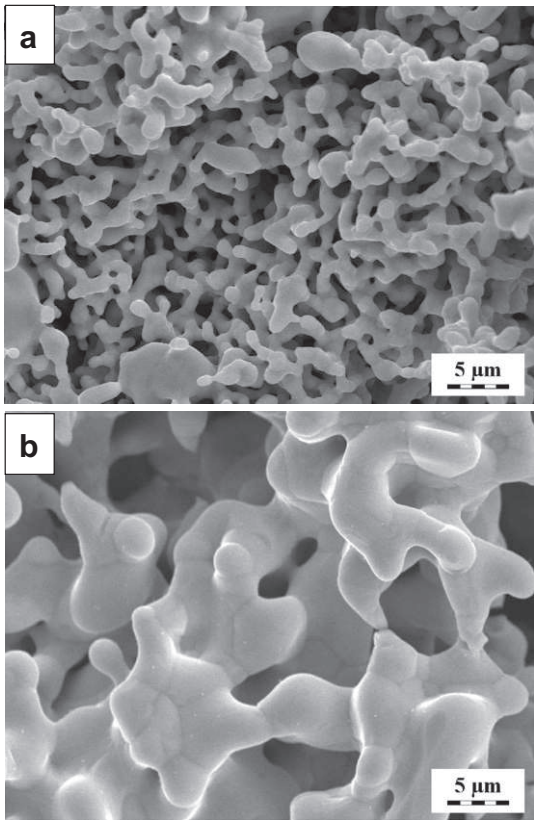

Fig. 8. Scanning electron microscopy of silver obtained as a residue after pyrolysis, i.e. after heating to 830 °C, in nitrogen (top) and in air (bottom). The original sample was prepared by the oxidation of 0.2 M aniline with 0.5 M silver nitrate in 0.4 M formic acid.

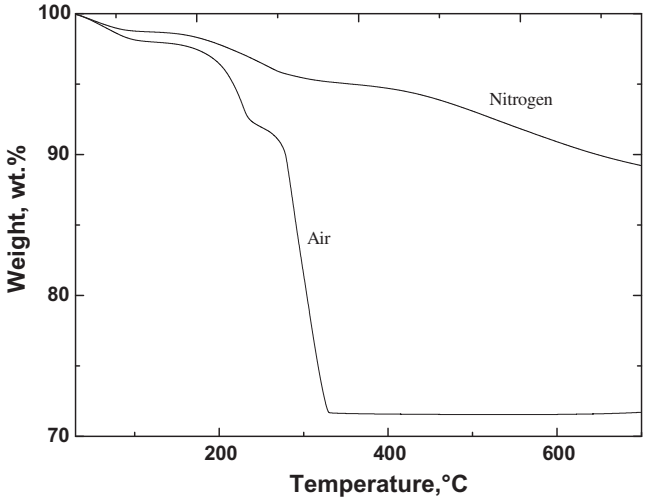

Fig. 9. Thermogravimetric analysis of PANI–silver composite in air and in nitrogen atmosphere. The composite was prepared in 0.4 M formic acid.

It should be noted that thermogravimetric analysis could be used for the determination of silver content only in the case of homogeneous composites because of small amounts of samples used in experiments. In microheterogeneous composites, such as in the present case, the determination of silver as an ash, using larger and more representative samples, is appropriate.

4. Conclusions

Polyaniline–silver composites can be prepared by the oxidation of aniline with silver nitrate in the solutions of formic acid. Two chemical processes are combined in this case: (1) the oxidation of aniline with silver nitrate to PANI–silver composite, and (2) the reduction of silver nitrate with formic acid to silver. The first process dominates at low concentrations of formic acid, the second when the concentration of formic acid is high. Silver nanowires coated with PANI are present in the preparations using low concentration of formic acid; the globular silver particles are produced when the concentration of formic acid is high. In spite of successful preparation of PANI–silver composites, the products still suffer from drawbacks: (1) a slow rate of aniline polymerization, (2) the homogeneity of samples was poor, (3) and the conductivities of the order of 10^2 S cm^{-1} may still need improvement.

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Polyaniline–silver composites prepared by the oxidation of aniline with silver nitrate in solutions of sulfonic acids

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ABSTRACT

Aniline was oxidized with silver nitrate in aqueous solutions of sulfonic acids: camphorsulfonic, methanesulfonic, sulfamic, or toluenesulfonic acids. Polyaniline–silver composites were produced slowly in 4 weeks in good yield, except for the reaction, which took place in sulfamic acid solution, where the yield was low. Polyaniline in the emeraldine form was identified with UV–visible, FTIR, and Raman spectra. Thermogravimetric analysis was used to determine the silver content, which was close to the theoretical prediction of 68.9 wt.%. Transmission electron microscopy demonstrated the presence of silver nanoparticles of *ca* 50 nm average sizes as the dominating species, and hairy polyaniline nanorods having diameter 150–250 nm accompanied them. The highest conductivity of 880 S cm^{-1} was found with the composite prepared in methanesulfonic acid solution. Its conductivity decreased with temperature increasing in the 70–315 K range, which is typical of metals such as silver. The conductivity of composites prepared in solutions of other acids was lower and increased with increasing temperature. Such dependence is typical of semiconductors, reflecting the dominating role of polyaniline in the conductivity behaviour. It is proposed that interfaces between the polyaniline matrix and dispersed silver nanoparticles play a dominating role in macroscopic level of conductivity.

1. Introduction

Conducting composites based on polyaniline (PANI) and silver can be prepared in several ways: (1) by a simple blending of both components [1–3], (2) by the reduction of silver compounds with PANI [4–11], or (3) by introducing silver compounds during the oxidation of aniline with ammonium peroxydisulfate [12,13]. Probably the most interesting approach consists in (4) the direct oxidation of aniline with silver nitrate [14–16], when the reaction between two non-conducting compounds yields a composite of two conducting components, PANI and silver. Such a procedure is analyzed in the present study. The goal consists in the preparation of materials having (a) a defined nanostructure with respect to both the polymer and the metal, (b) a homogeneous distribution of both components at the micrometer level, and (c) a good conductivity. In addition, the composites should be produced within a reasonable time and in high yield. Such materials may potentially be useful in applications such as electrode materials in electrocatalysis, in energy conversions, sensors, flexible electronics, *etc*.

The ability of silver(I) salts to oxidize aniline has recently been demonstrated in several papers [13–16]. The resulting polyaniline–silver (PANI–Ag) composites are composed of a polymer semiconductor and metallic silver, the most conducting element among metals. The preparation of quantities sufficient for conductivity measurements have been reported for the oxidation of aniline in aqueous solutions of nitric acid. The conductivity of the products reached 2250 S cm^{-1} at 51.8 wt.% silver content [15]. The induction period extending over several weeks, which precedes the polymerization, is a drawback in the routine preparation of composites. UV irradiation was reported to promote the polymerization [4,16] but this technique is not efficiently applicable when the oxidation is not carried out in thin layers.

The oxidation of aniline to PANI proceeds in an acidic medium [17]. Except for nitric acid solutions, the choice of inorganic acids is limited because most acids produce insoluble salts with silver ions. Carboxylic acids also form salts of limited solubility with silver cations. This has recently been illustrated for the oxidation of aniline in solutions of acetic acid, where silver acetate was present in the products in significant amounts [18]. Moreover, aniline oligomers have often been the only products or their major component but, despite this fact, the conductivity of the composites was as high as 8000 S cm^{-1}.

The oxidation of aniline in solutions of sulfonic acids proved to proceed relatively easily and in good yields in exploratory tests. No precipitate was formed after mixing the reactants, aniline and silver nitrate, and the oxidation of aniline thus started in a homo-

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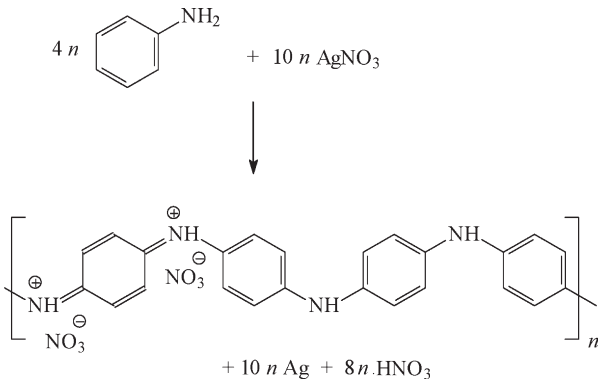

Fig. 1. Aniline is oxidized with silver nitrate to polyaniline, metallic silver is also a product and nitric acid is a by-product. A sulfonic acid present in the polymerization medium may participate in the protonation of PANI along with the nitric acid.

geneous medium. The present study reports the results of such reactions.

2. Experimental

2.1. Oxidation of aniline

Aniline (Fluka, Switzerland) and silver nitrate (Lach-Ner, Czech Republic) were separately dissolved in 50 mL of 1 mol L^{-1} aqueous solutions of sulfonic acids. Four acids (Fluka, Switzerland) were selected: camphorsulfonic acid (CSA), methanesulfonic acid (MSA), sulfamic acid (= aminosulfonic acid, SFA), and toluenesulfonic acid (TSA). The silver nitrate-to-aniline mole ratio was always 2.5 (Fig. 1). Aniline and silver nitrate solutions were mixed to start the oxidation of aniline at room-temperature. After 4 weeks, green solids were collected on a paper filter, rinsed with a solution of the corresponding acid, and dried at room-temperature in air, and then in a desiccator over silica gel. For spectroscopic characterization, parts of the products were deprotonated by overnight immersion in 1 M ammonium hydroxide to convert PANI salts to the corresponding bases, and dried as above.

2.2. Characterization

Infrared spectra were recorded in the range 400–4000 cm^{-1} using a fully computerized Thermo Nicolet NEXUS 870 FTIR Spectrometer with DTGS TEC detector. Samples were dispersed in potassium bromide and compressed into pellets. Raman spectra excited in the visible range with a HeNe 633 nm laser were collected on a Renishaw inVia Reflex Raman spectrometer. Reduced beam power was always used to avoid degradation of the samples. The UV–visible spectra of PANI bases dissolved in *N*-methylpyrrolidone were recorded with a Lambda 20 spectrometer (Perkin-Elmer, UK).

The content of silver was determined as an ash. Thermogravimetric analysis was performed in a 50 cm^3 min^{-1} air flow at a heating rate of 10 °C min^{-1} with a Perkin-Elmer TGA 7 Thermogravimetric Analyzer. The density was obtained by weighing the pellets with a Sartorius R160P balance in air and immersed in decane at 20 °C.

The conductivity was measured by a four-point van der Pauw method on pellets compressed at 700 MPa with a manual hydraulic press, using a SMU Keithley 237 as current source and a Multimeter Keithley 2010 as a voltmeter with a 2000 SCAN 10-channel scanner card. Temperature dependences of conductivity were determined on the same samples in a Janis Research VNF-100 cryostat in the range 78–315 K in a flowing stream of nitrogen vapour which provides good control over the temperature homogeneity in the samples. Before such measurements, samples were placed in vacuum (≈10 Pa) for several hours at about 305 K to remove moisture. When the conductivity of the samples was $<10^{-4}$ S cm^{-1}, a two-point method using a Keithley 6517 electrometer was used. Circular gold electrodes were deposited on both sides of the pellets prior to such measurements.

3. Results and discussion

3.1. Oxidation of aniline

Aqueous solutions of four sulfonic acids were selected to constitute the medium for the oxidation of aniline because these acids do not precipitate silver ions: camphorsulfonic acid (a bicyclic aliphatic acid often used with PANI), methanesulfonic acid (the simplest aliphatic acid), sulfamic acid (aminosulfonic acid, NH_2SO_3H, representing a borderline between the organic and inorganic acids), and *p*-toluenesulfonic acid (an aromatic acid).

Except for sulfamic acid solutions, the oxidation yields of PANI–silver composites were close to each other for other three acids (Table 1), 77–87% with respect to the calculated expectation for full conversion (Fig. 1). The simple reaction scheme assumes that PANI is protonated by nitric acid, which is a by-product (Fig. 1), but all four sulfonic acids are strong enough to protonate PANI [19] and become a part of the products. Due to the presence of amino group in sulfamic acid, the acidity of its solutions would be lower compared with other three acids. This may become important in the early stages of aniline oxidation, where the initiation centers are produced and sufficient level of acidity is needed for the chain propagation [17].

The content of silver was determined as a white residue after heating the samples to 1100 °C in air (Table 1), and independently confirmed as a residue in the thermogravimetric analysis, which gave a similar result (Fig. 2). The former method used larger samples and provided more reliable results when the samples were not perfectly homogeneous. The content of silver, 63–69 wt.% (Table 1), is close to the value of 68.9 wt.% expected on the basis of simple stoichiometry (Fig. 1), again except the product obtained in solutions of sulfamic acid (Fig. 2). The contents of silver correlate reasonably well with the densities of the composites (Table 1).

PANI–silver composites have been obtained but the time needed for their preparation extends to several weeks. Only after 11–13 days, the first traces of PANI precipitate became visible. Such a reac-

Table 1
Yield, composition, conductivity, and density of PANI–silver composites prepared in solutions of camphorsulfonic, methanesulfonic, sulfamic, or toluenesulfonic acids.

Acid	Yield(g g^{-1} aniline)	Yield(% theory)[a]	Composition(wt.% Ag)	Conductivity (S cm^{-1})[b]		Density (g cm^{-3})	
				Salt	Base	Salt	Base
CSA	3.43	81	63	1.7 (1.5)	2.1×10^{-9}	3.11	–
MSA	3.27	77	69	880 (709)	0.003	3.88	4.28
SFA	0.5	12	12	42 (25)	0.018	2.29	–
TSA	3.69	87	69	1.4 (0.86)	2.2×10^{-10}	3.31	3.96

[a] 1 g of aniline in the reaction according to Fig. 1 produces theoretically 1.31 g of PANI nitrate and 2.90 g of silver. Such a composite would contain 68.9 wt.% silver [15].
[b] In air. Values in parentheses were measured after the samples were kept *in vacuo*.

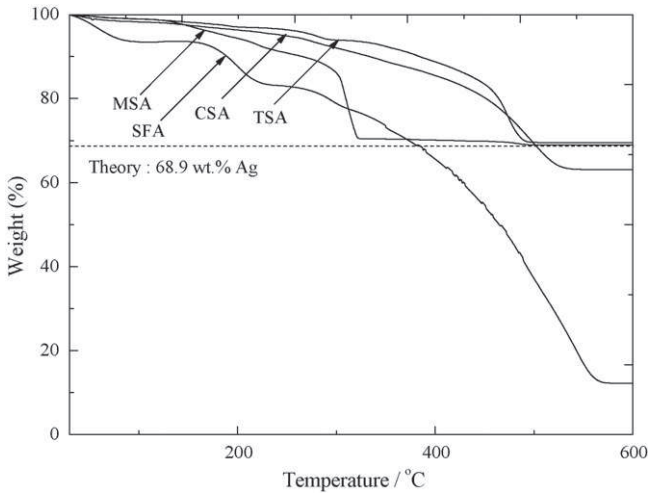

Fig. 2. Thermogravimetric analysis of PANI–silver composites prepared by the oxidation of aniline in solutions of camphorsulfonic, methanesulfonic, sulfamic, or toluenesulfonic acids. Theoretical expectation of 68.9 wt.% (Fig. 1) is marked by broken line.

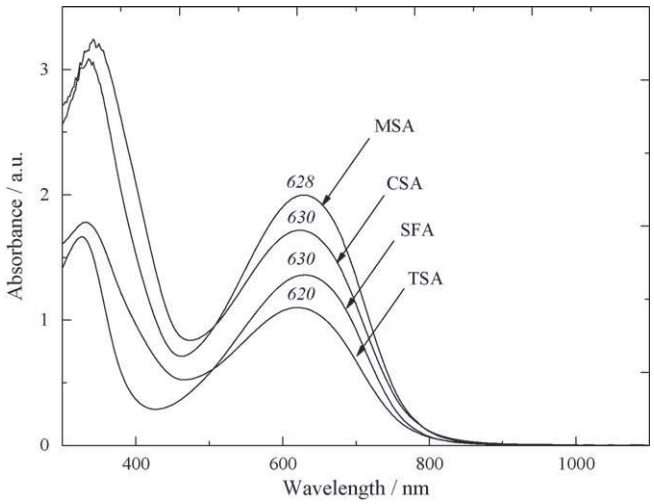

Fig. 4. The UV–visible spectra of the oxidation products (converted to the corresponding bases and dissolved in *N*-methylpyrrolidone) prepared by the oxidation of aniline in 1 mol L^{-1} camphorsulfonic, methanesulfonic, sulfamic, or toluenesulfonic acids. The wavelengths corresponding to the second maxima are shown at the individual curves.

tion rate is hardly acceptable for the practical syntheses and ways to accelerate the generation of composites are sought. No PANI was produced when the reaction was carried out in water, *i.e.* in the absence of acid.

The morphology of both silver and PANI is rich. Silver is usually present as nanoparticles of *ca* 50 nm average size but with a broad particle-size distribution (Fig. 3). Silver particles often form clusters. Polyaniline forms as hairy nanorods, 150–250 nm in diameter, as well as objects of unresolved shape. Silver nanoparticles are usually located outside PANI nanorods.

3.2. UV–visible spectra

The most simple proof that PANI has indeed been prepared is obtained by UV–visible spectra (Fig. 4). Two absorption maxima

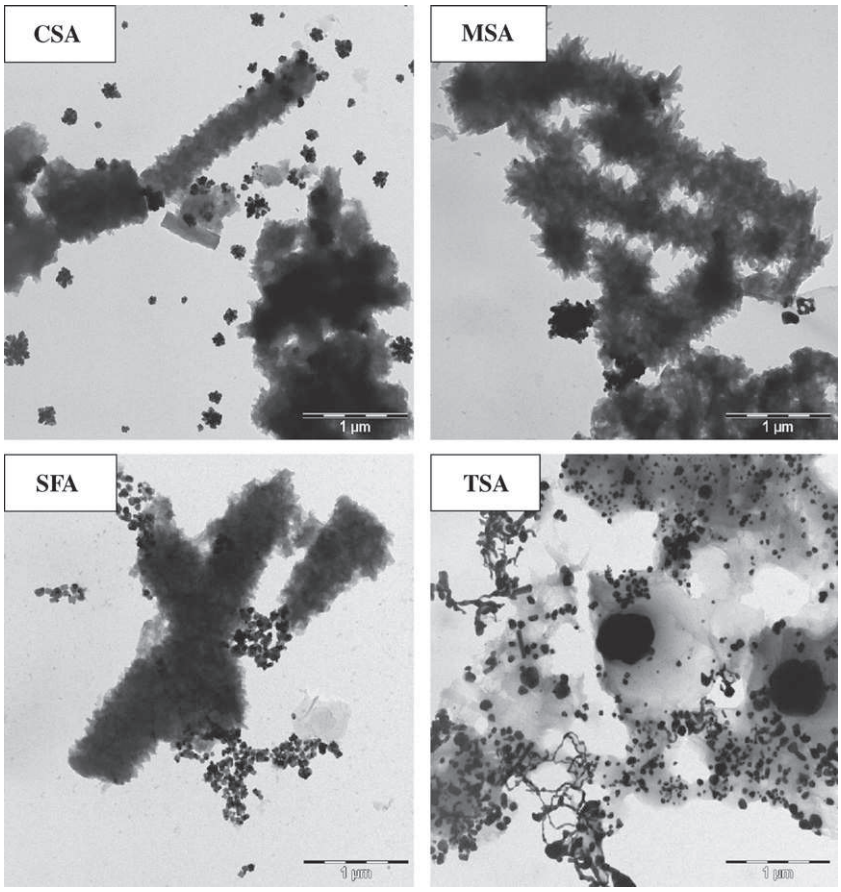

Fig. 3. Transmission electron microscopy of polyaniline–silver composites prepared in 1 M camphorsulfonic, methanesulfonic, sulfamic, or toluenesulfonic acids.

located at 350 and 630 nm are typical of a "standard" PANI base [20]. The former band is often associated with a π–π^* in the benzenoid structure. The latter absorption band in the visible range is assigned to the exciton formation in the quinonoid rings. Polyaniline in the emeraldine form has therefore been produced in all cases. However, the ratio A_{350}/A_{630} of the absorbance at the maxima of these two bands is somewhat higher in case of MSA and CSA in comparison to TSA and SFA acids. This may be connected with the higher content of oligomers in the first two samples, which contribute especially to the absorption at 350 nm [18,21].

3.3. FTIR spectra

The molecular structure of PANI is confirmed also by the FTIR spectra, which exhibit all the typical features of the emeraldine form (Fig. 5). The main bands observed in the spectrum of PANI sulfate, 1574 and 1488 cm^{-1}, due to quinonoid (Q) and benzenoid (B) ring-stretching vibrations [22], are red-shifted in the spectra of PANI–silver composites to 1565 and 1485 cm^{-1}. Additional peaks at 3226, 1638, and 1444 cm^{-1} are clearly visible in the spectra of composites prepared in the presence of toluenesulfonic, camphorsulfonic and methanesulfonic acids. They have been assigned to the presence of *ortho*-coupled aniline and oxazine-like constitutional units which are observed in aniline oligomers [23,24]. Other peaks, marked by arrows in Fig. 5, belong to sulfonic and nitric (the peak at 1384 cm^{-1}) acids that constitute salts with PANI (Fig. 1). The spectrum of a composite prepared in the presence of sulfamic acid is the closest to the spectrum of PANI sulfate (shown for comparison in Fig. 5) and the oligomeric component in this sample is relatively low. The absorption band at about 1300 cm^{-1} corresponds to π-electron delocalization induced in the polymer by protonation and it is relatively high in the case of methanesulfonic and sulfamic acids. The strong and broad band centered at 1145 cm^{-1}, which has been assigned to the vibration mode of the $-NH^+=$ structure in PANI sulfate, is very strong in the spectrum of sulfamic acid solutions. The slope of the broad absorption band at wave numbers above 2000 cm^{-1} due to the absorption of free charge-carriers in the PANI salts is, surprisingly, the lowest in the case of methanesulfonic acid, which exhibits metallic character in the temperature dependence of the conductivity (see Section 3.5).

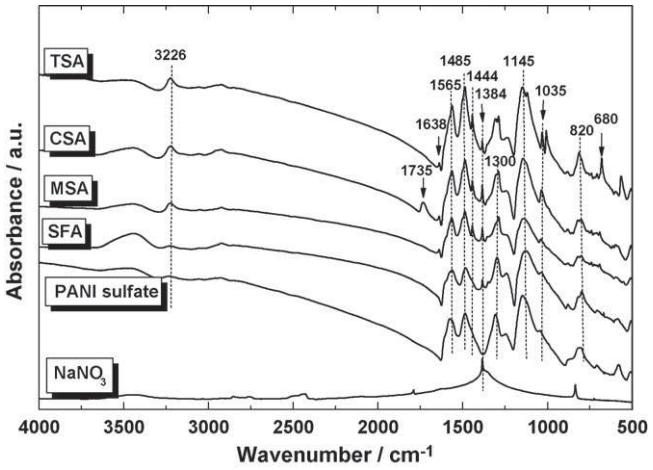

Fig. 5. FTIR spectra of PANI–silver composites prepared by the oxidation of aniline in solutions of 1 mol L^{-1} camphorsulfonic, methanesulfonic, sulfamic or toluenesulfonic, acids. The spectra of PANI sulfate, prepared by oxidation with APS in 0.1 mol L^{-1} sulfuric acid, and of sodium nitrate are shown for comparison.

3.4. Raman spectra

As the PANI–silver samples are heterogeneous at the micrometer level, the Raman spectra of powders have been measured at different locations (micrographs in the insets of Fig. 6). In micrographs, we can distinguish bright regions, corresponding mainly to metallic silver, and green, dark blue, violet, and light-violet regions. (For interpretation of the references to color in this text, the reader is referred to the web version of the article.) This means that PANI is present in various oxidation states. The colours observed in reflected light, however, cannot be simply associated with the colours observed in the transmission mode.

Raman spectra of samples obtained in the presence of camphorsulfonic acid, and measured in the blue and light regions contain the band at 1622 cm^{-1} (C–C stretching of the benzenoid ring), 1586 cm^{-1} (C=C stretching vibration in the quinonoid ring), 1490 cm^{-1} (C=N stretching vibration in quinonoid units), 1345 cm^{-1} ($C–N^{+\bullet}$ vibration of delocalized polaronic structures), 1248 cm^{-1} (C–N stretching vibrations of various benzenoid, quinonoid or polaronic forms, and benzene-ring deformations), 1165 cm^{-1} (C–H bending vibration of quinonoid rings), 807, 580, 508 and 412 cm^{-1} (Fig. 6, CSA). In the white regions the intensity is enhanced but the spectrum is noisy. The spectra correspond to the protonated pernigraniline form of PANI [25].

In the case of methanesulfonic acid solutions, the Raman spectra show maxima at about 1598 cm^{-1} (C=C stretching vibration of the quinonoid ring), 1522 cm^{-1} (N–H deformation vibration associated with the semi-quinonoid structures), 1335 cm^{-1} ($C–N^{+\bullet}$ vibration of the shorter and/or crosslinked structures), 1180 cm^{-1} (C–H in-plane bending vibrations in benzenoid rings) and 520 cm^{-1}, corresponding to protonated emeraldine [22]. In brown and white regions they exhibit enhanced fluorescence (Fig. 6, MSA). This corresponds to the presence of larger amounts of the oxidized oligomers which is in agreement with the UV–visible spectra.

The Raman spectra of the sample obtained in sulfamic acid solutions recorded in light-violet and violet spots (see the inset in Fig. 6, SFA) are similar. They contain strong bands at 1618 cm^{-1} (C–C stretching of the benzenoid ring), 1578 cm^{-1} (C=C stretching vibration in the quinonoid ring), 1500 cm^{-1} (N–H deformation vibration associated with the semi-quinonoid structures mixed with C=N stretching vibration in quinonoid units), 1335 cm^{-1} ($C–N^{+\bullet}$ vibration of delocalized polaronic structures), 1249 cm^{-1} (C–N stretching vibrations of various benzenoid, quinonoid or polaronic forms, and benzene-ring deformations), 1166 cm^{-1} (C–H bending vibration of quinonoid rings), 876 (C–N–C wag and/or benzene-ring deformation in the polaronic or bipolaronic form of the emeraldine salt), 809 cm^{-1} (benzene-ring deformations), and 587 cm^{-1}, 514 and 420 cm^{-1} (out-of-plane deformations of the ring), corresponding most probably to protonated oxidized pernigraniline form of PANI [22].

The Raman spectra of the sample obtained in toluenesulfonic acid solutions, and recorded in dark, light-blue and violet regions, are composed of the band with the local maxima located at about 1594 cm^{-1} (C=C stretching vibration in the quinonoid ring), 1512 cm^{-1} (N–H deformation vibration associated with the semi-quinonoid structures), 1335 cm^{-1} ($C–N^{+\bullet}$ vibration of delocalized polaronic structures of the shorter and/or crosslinked structures), and 1177 cm^{-1} (C–H bending vibration of the semi-quinonoid rings) correspond to protonated emeraldine form of PANI (Fig. 6, TSA) [22]. The spectrum measured in the bright part of this sample has an enhanced intensity and several sharp peaks at 1700, 1594 cm^{-1} (C=C stretching vibration of the quinonoid ring), 1573, 1404 cm^{-1} (phenazine units), 1330, 1352 cm^{-1} ($C–N^{+\bullet}$ vibration of the shorter and/or crosslinked structures), 1245, 1177 cm^{-1} (C–H bending vibration of the semi-quinonoid rings), 1119 cm^{-1} (C–H in-plane bending vibrations in benzenoid rings), 1073, 842, and

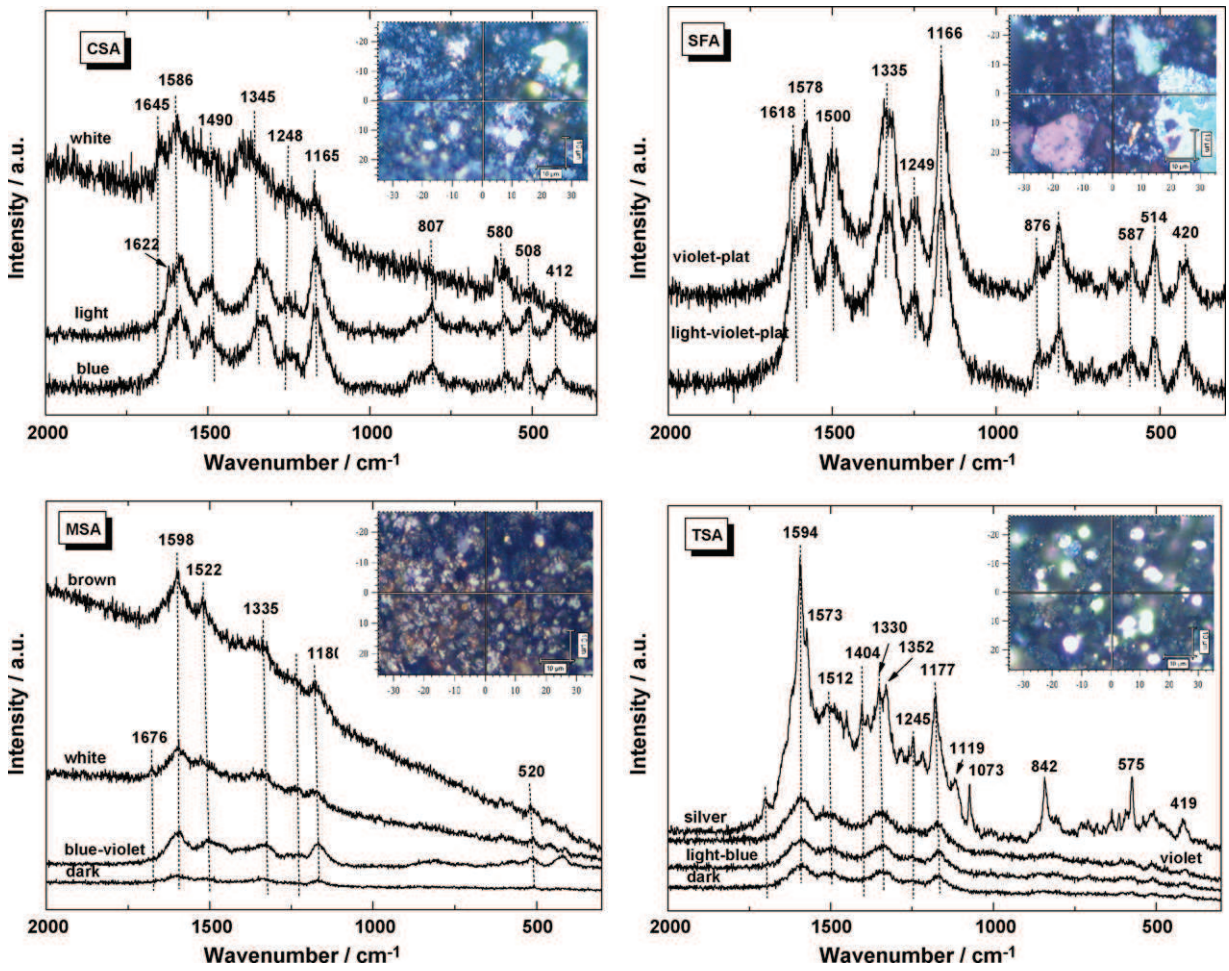

Fig. 6. Raman spectra of PANI–silver composites prepared by the oxidation of aniline in 1 mol L^{-1} camphorsulfonic, methanesulfonic, sulfamic or toluenesulfonic acids, and taken at various sample regions from the micrographs shown in the insets of the figures. Laser excitation line used was 633 nm.

575 cm^{-1} (phenoxazine-type units) are well distinguished in the spectrum. They belong to the oxidized aniline oligomers which are in contact with silver nanoparticles and their intensity is surface-enhanced with laser excitation at 633 nm [27]. The vibrations of nitrate and sulfonate anions may be also present.

3.5. Conductivity

The conductivity is the most important parameter of conducting polymers and their composites. The highest conductivity of 880 S cm^{-1} was found with the PANI–silver composite prepared in methanesulfonic acid solution (Table 1). Please note that the conductivity of the sample synthesized in a solution of toluenesulfonic acid is two orders of magnitude lower, despite the same content of silver in both samples. Obviously, the content of silver alone is not decisive for the overall conductivity of the composite. This conclusion has been already reached in previous studies [15,18]. Even though the weight fraction of silver seems to be high, *e.g.*, 69 wt.% (Table 1), one has also to realize that the corresponding volume fraction is considerably lower, ~22 vol.%. The morphology of the silver, however, is also similar in all samples (Fig. 3); the differences in the conductivity are hard to explain on account of various particles shape and distribution.

It is proposed that the interfaces between PANI and silver play the determining role in the level of conductivity. Such interfaces may produce barriers to the charge-carriers and restrict the participation of silver in conduction. The surface oxidation of silver nanoparticles to silver oxide may be offered in the case of silver. The pernigraniline oxidation state, revealed by Raman spectra, may represent a similar barrier in PANI. The situation becomes even more complex when considering the fact that the interface is created between an organic semiconductor and a metal. The formation of Schottky-like barriers thus cannot be ruled out.

For the sample prepared in methanesulfonic acid solution, the conductivity decreased with increasing temperature (Fig. 7). Such

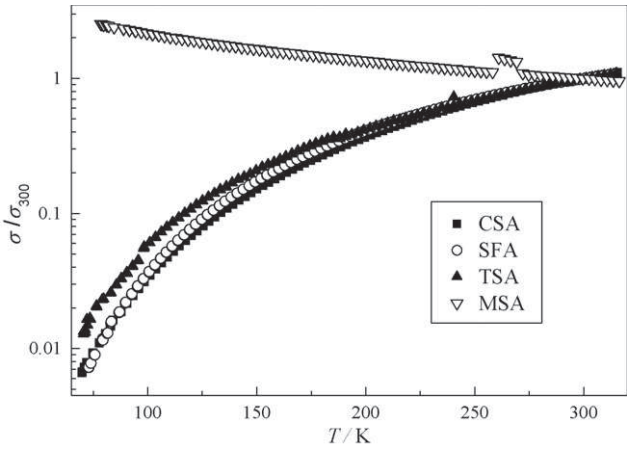

Fig. 7. Temperature dependence of the conductivity, σ, relative to the conductivity at 300 K, σ_{300}, of PANI–silver composites prepared in 1 M camphorsulfonic, sulfamic, toluenesulfonic or methanesulfonic acids.

behaviour is typical of metals, and illustrates the dominating role of silver in the conduction. This is understandable because only silver can be responsible for the room-temperature conductivity of 880 S cm^{-1}, the typical conductivity of PANI alone being of the order of units S cm^{-1} [26]. In all other cases, however, the conductivity increased with increasing temperature. This is characteristic of semiconductors and PANI obviously controls the overall conductivity of the composites.

The conductivity determined at room-temperature after the samples were kept *in vacuo* was always lower compared with the measurements made in air (Table 1). This reflects the well-known fact that the humidity increases the conductivity [28,29], because of the ionic contribution to the conduction [30].

In all composites, the conductivity decreased after the conversion of a conducting PANI salt to a non-conducting PANI base (Table 1). This means that the PANI matrix assists in the electron transfers between the individual silver objects, in the case of camphorsulfonic and toluenesulfonic acids, where the drop in conductivity amounts to 10 orders of magnitude.

4. Conclusions

Composites of PANI and silver were prepared by the oxidation of aniline with silver nitrate in solutions of sulfonic acids. The reaction media containing camphorsulfonic, methanesulfonic, or toluenesulfonic acid gave products of comparable yield and silver content, in agreement with expectation. The reaction carried out in sulfamic acid solution led to an inferior type of product with respect to the yield. The conductivities of the products differed. The highest conductivity of PANI–silver was obtained after preparation in solutions of methanesulfonic acid, 880 S cm^{-1}. The temperature dependence of conductivity had metal-like character illustrating the dominating role of silver in conduction. Other composites exhibited much lower conductivity, ~1 S cm^{-1}, of the semiconductor type. The conductivities thus differed by orders of magnitude at the same content of silver in the composites. The differences in the morphology of composite components or their distribution, which could explain the conductivity behaviour, have not been identified.

It is suggested that phenomena at the PANI–silver interfaces produce various barriers that control the conductivity of the composites. We speculate that the nature of the barriers may depend especially on the oxidation states of the PANI and silver at their mutual contact.

A high yield and good conductivity belong to the positive features of PANI silver composites prepared in methanesulfonic acid solution. A time extending to several weeks needed for the synthesis, however, can be regarded as a serious drawback. The heterogeneity of the samples is also a rather negative factor. Finally, the fact that this procedure allows for the preparation of a composite with a single close-to-stoichiometric composition, limits the potential applications of the composites. Ways to overcome these problems are currently being investigated.

Acknowledgments

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ARTICLE

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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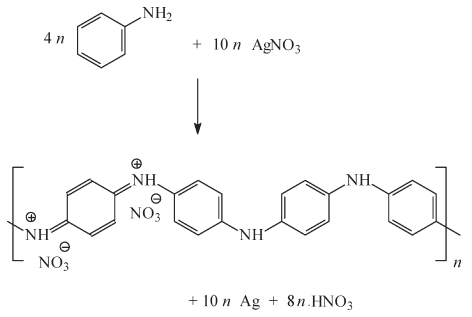

Figure 1. Aniline is oxidized with silver nitrate to PANI nitrate and metallic silver. Nitric acid is a byproduct. An acidic medium is necessary.

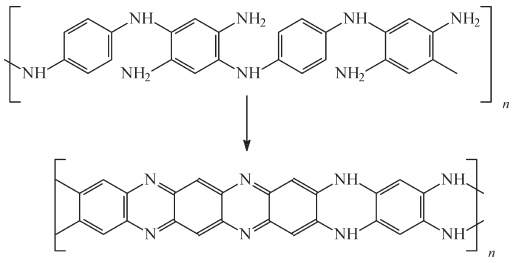

Figure 2. Idealized structure of poly(*p*-phenylenediamine) and its conversion to the ladderlike phenazine structure as proposed in the literature.[28,39,41]

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]

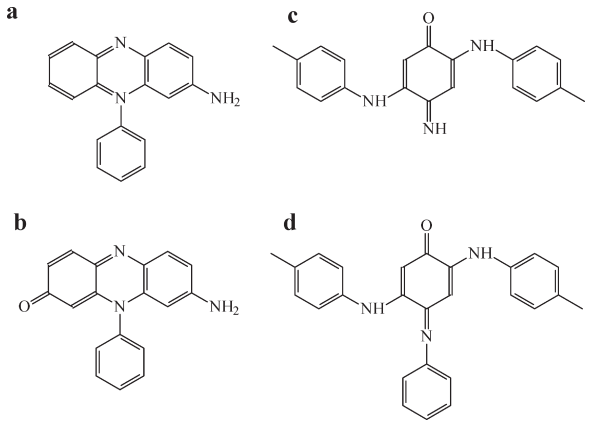

Figure 3. Examples of oligomer structures proposed by (a) Sapurina and Stejskal,[9,10] (b) Zujovic et al.,[19] (c) Surwade et al.,[17] and (d) Kříž et al.[18]

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.

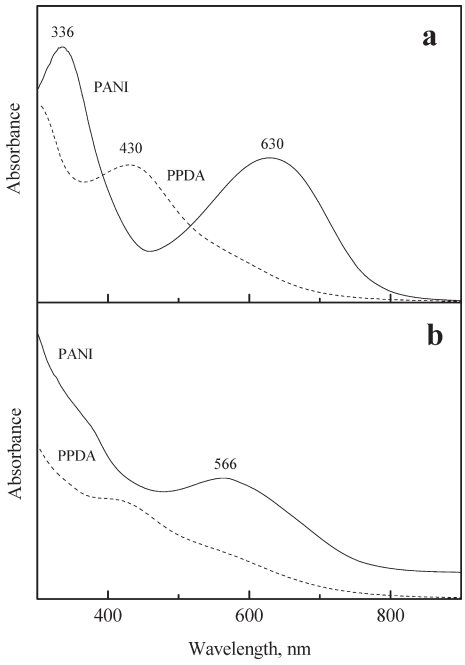

Figure 4. UV−vis spectra of polyaniline−silver composite (full lines) and poly(*p*-phenylenediamine)−silver composite (broken lines) prepared (a) in 1 M nitric acid or (b) in 1 M acetic acid (the spectrum of PANI was vertically shifted for clarity).

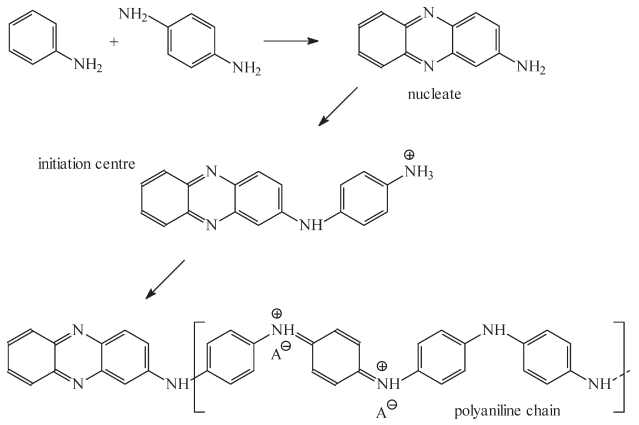

Figure 5. Role of *p*-phenylenediamine in the oxidation of aniline: the possible formation of a phenazine-containing nucleate and of an initiation center that starts the growth of a PANI chain having a phenazine head and PANI tail. A^- is an arbitrary anion.

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 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

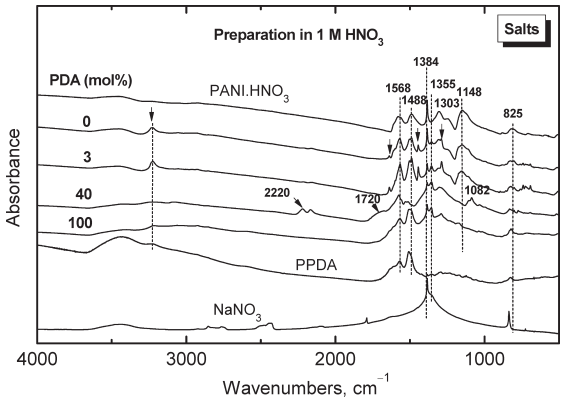

Figure 6. FTIR spectra of the selected oxidation products of aniline and *p*-phenylenediamine in 1 M nitric acid. The mole fraction of PDA in the reaction mixture with aniline is specified at the individual spectra. The spectra of PANI nitrate, PPDA prepared with APS as oxidant, and of sodium nitrate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

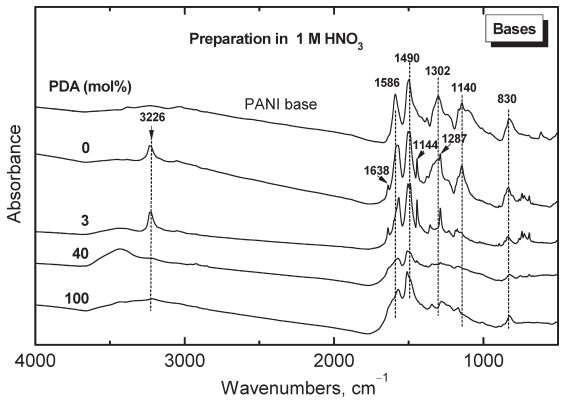

Figure 7. FTIR spectra of selected oxidation products of aniline and *p*-phenylenediamine in 1 M nitric acid deprotonated by 1 M ammonium hydroxide. The mole fraction of PDA in the reaction mixture with aniline is specified at the individual spectra. The spectrum of PANI base prepared with APS oxidant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

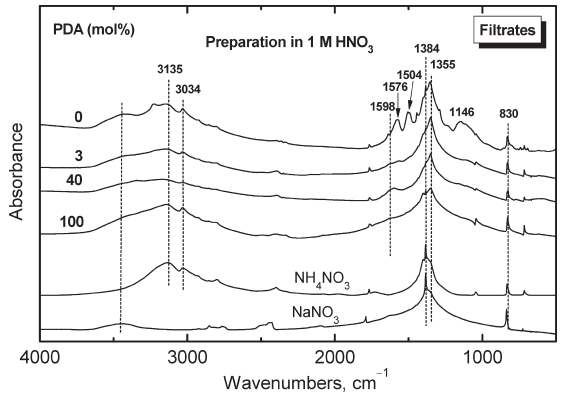

Figure 8. FTIR spectra of selected filtrates, i.e., of solids obtained after the evaporation of the ammonia solutions used for the deprotonation of the oxidation products of aniline and *p*-phenylenediamine. The mole fraction of PDA in the reaction mixture with aniline is specified at the individual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

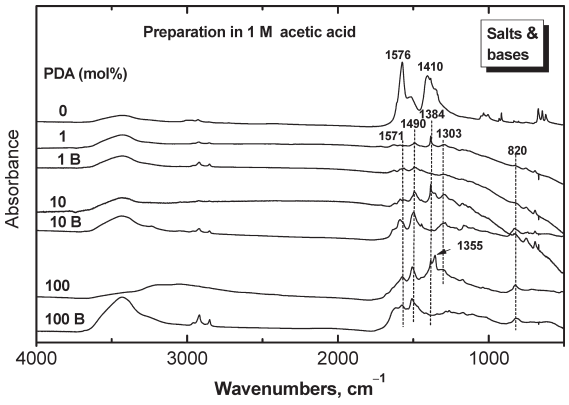

Figure 9. FTIR spectra of selected oxidation products of reaction between aniline and *p*-phenylenediamine in 1 M acetic acid and the spectra of the corresponding bases (B). The mole fraction of PDA in the reaction mixture with aniline is specified at the individual spectra.

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

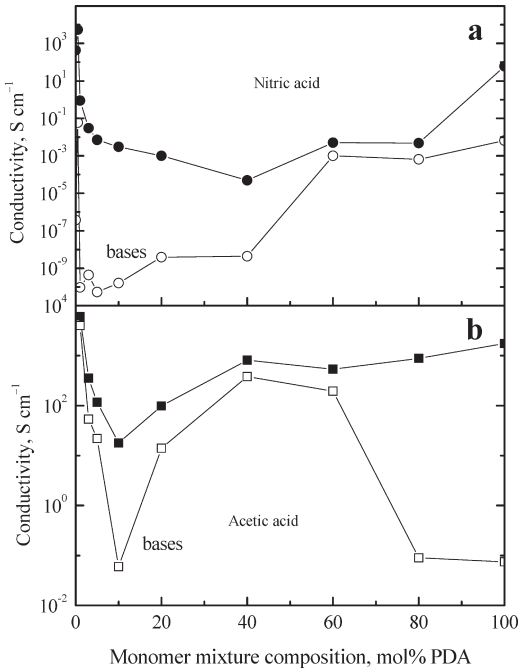

Figure 10. Dependence of the conductivity of PANI−silver composites prepared (a) in 1 M nitric acid (circles) and (b) in 1 M acetic acid (squares) on the mole fraction of PDA in the monomer mixture for as-prepared protonated samples, salts (full symbols), and after conversion to bases (open symbols).

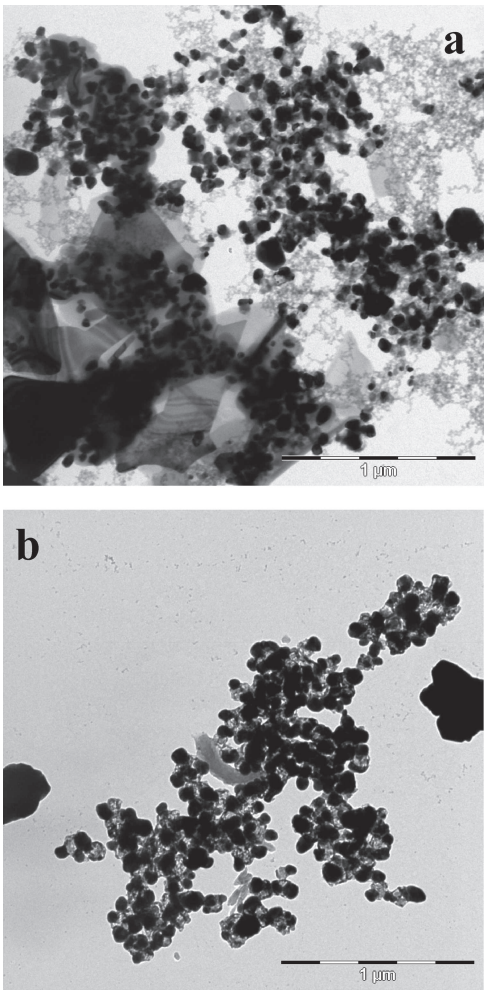

Figure 11. Micrographs of composites prepared with (a) 5 mol % PDA and (b) 60 mol % PDA in 1 M acetic acid.

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.

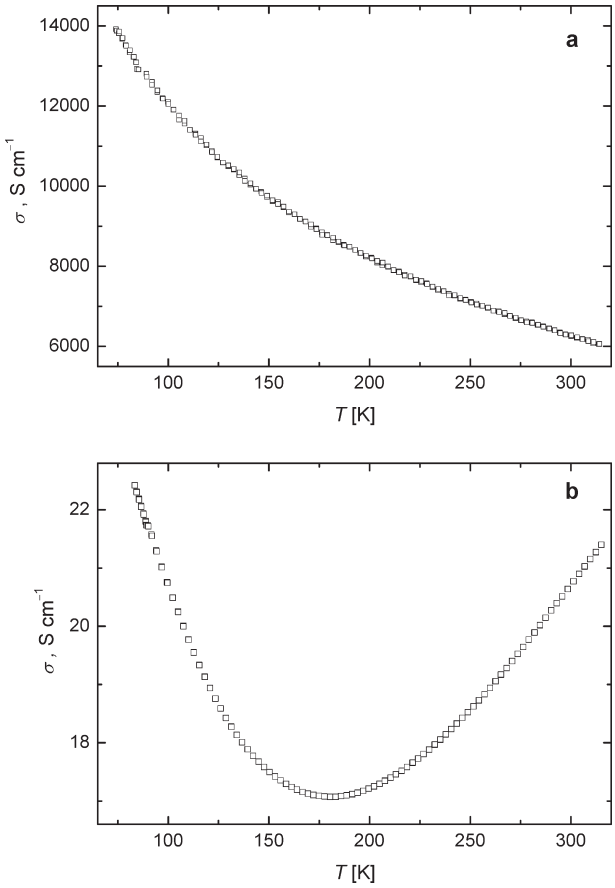

Figure 12. Temperature dependence of the conductivity, σ, of PANI−silver composites prepared (a) with 1 mol % PDA and (b) 10 mol % PDA in 1 M acetic acid.

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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Polyaniline–silver composites prepared by the oxidation of aniline with mixed oxidants, silver nitrate and ammonium peroxydisulfate: The control of silver content

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ABSTRACT

Aniline was oxidized with mixtures of two oxidants, ammonium peroxydisulfate and silver nitrate, to give polyaniline–silver composites with variable content of silver in the composites. The presence of peroxydisulfate has a marked accelerating effect on the oxidation of aniline with silver nitrate. Oxidations in 1 M methanesulfonic acid produced composites in high yield. The molecular structure of the polyaniline was confirmed by UV–visible and FTIR spectra, and the polymeric character was established by gel-permeation chromatography. The content of silver varied between 0 and 70 wt.%. The silver nanoparticles were smaller than 100 nm. The conductivity of the composites was of the order of units S cm^{-1}. Only at high silver nitrate contents in the reaction mixture, the conductivity of products exceeded 100 S cm^{-1}. The conductivity of the composites sometimes increased after deprotonation of the polyaniline salt to a non-conducting base. Such conductivity behaviour is discussed in terms of the percolation model.

1. Introduction

Composites of conducting polymers and noble metals receive increasing interest due to the variety of nanostructures displayed by both components [1]. Potential applications have been oriented to the region of catalysis [2,3], where both components are active. Electrical properties are also attractive and the development of conducting inks may serve as another example [4,5]. The combination of metallic and semiconductor types of conduction may provide materials having a reduced dependence of conductivity on temperature [6].

The highest conductivity among metals, 6.3×10^5 S cm^{-1} at 20 °C, makes silver the best candidate to participate in the design of conducting composites, this fact being supported by its reasonably low price. Polyaniline (PANI) and polypyrrole are the most promising conducting polymers [7] having the typical conductivity of the units of S cm^{-1}. Simple mixing of the components is possible and has been reported in the literature [8–10] but more exciting possibilities are seen in their *in-situ* preparation.

Pyrrole is easily oxidized with silver salts to polypyrrole–silver composites [11,12]. Similar oxidation of aniline proved to be much more difficult and requires time extending to months [13,14]. UV–visible [5,15,16] or γ-irradiation [17–20], ultrasonic agitation [21], or high temperatures [22] were needed to speed up this process. It has only recently been found that the oxidation of aniline with silver cations is accelerated by small amounts of *p*-phenylenediamine to proceed within hours at the currently-used concentrations [6]. For the classical oxidation of aniline with ammonium peroxydisulfate, this accelerating effect has been known for many years [23–28].

The oxidation of aniline with silver nitrate has been investigated in solutions of nitric [29], acetic [14], formic [13], and sulfonic acids [30], in search of conditions which produce homogeneous composites having a high conductivity in a reasonable time. The composition of composites produced by the oxidation of aniline with silver nitrate is fixed by the stoichiometry of the reaction to 68.2 wt.% silver [29]. This fact may not satisfy practical requirements, which would tend to reduce the content of silver while maintaining the high conductivity. The use of mixed oxidants, silver nitrate and ammonium peroxydisulfate in various proportions, thus allows for the control of the silver content from zero (APS oxidant only) to ≈70 wt.% (silver nitrate oxidant only). Such an approach has been used in the present study.

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2. Experimental

2.1. Oxidation of aniline

Aniline (0.2 M; Fluka, Switzerland) was oxidized with silver nitrate (Lach-Ner, Czech Republic) or ammonium peroxydisulfate (APS; Lach-Ner, Czech Republic) and their mixtures in 1 M aqueous solutions of methanesulfonic acid (≥99%; Fluka, Switzerland). The oxidant-to-aniline mole ratio varied in the various proportions p, from 1.25 for APS ($p = 0$; [APS] = 0.25 M) to 2.5 for silver nitrate ($p = 1$; [$AgNO_3$] = 0.5 M), because the former is a two-electron oxidant and the second is a one-electron oxidant. For example, at $p = 0.5$, the molar concentrations of the oxidants were [APS] = 0.125 M and [$AgNO_3$] = 0.25 M, *i.e.* each oxidant was expected to oxidize a half of the aniline. After mixing the solutions of aniline with those of oxidants, the mixture was left to stand at room temperature for 5 h, except for the oxidation with silver nitrate alone, which took place for 4 weeks [30]. The solids formed were isolated by filtration, rinsed with the corresponding acid solution, then with acetone; they were dried, first in air, and then over silica gel. Part of each sample was converted to the base form by immersion in a large excess of 1 M ammonium hydroxide, and dried as above.

2.2. Characterization

Infrared spectra were recorded in the range 400–4000 cm^{-1} using a fully computerized Thermo Nicolet NEXUS 870 FTIR Spectrometer with DTGS TEC detector. Samples were dispersed in potassium bromide and compressed into pellets. The UV–visible spectra of PANI bases dissolved in *N*-methylpyrrolidone were recorded with a Lambda 20 spectrometer (Perkin Elmer, UK).

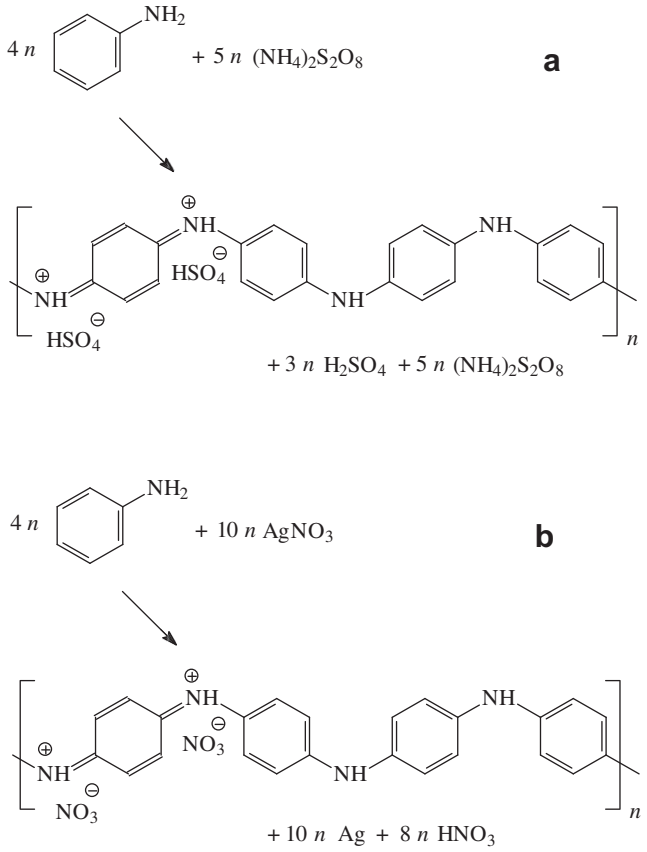
The conductivity was measured by a four-point van der Pauw method on pellets compressed at 700 MPa with a manual hydraulic press, using an SMU Keithley 237 as current source and a Multimeter Keithley 2010 as a voltmeter with a 2000 SCAN 10-channel scanner card. Temperature dependences of conductivity were determined on the same samples in a Janis Research VNF-100 cryostat in the range 78–315 K in a flowing stream of nitrogen vapour which provides good control over the temperature homogeneity in the samples. Before such measurements, samples were placed in vacuum (≈10 Pa) for several hours at about 305 K to remove moisture.

The density was obtained by weighing the pellets with a Sartorius R160P balance in air and immersed in decane at 20 °C. The content of silver in the samples was determined as a residue after burning the samples by the procedure currently used for the analytical determination of ash. Molecular-weight distributions were determined by gel permeation chromatography operating with *N*-methylpyrrolidone and calibrated with polystyrene standards. Transmission electron microscope (TEM) JEOL JEM 2000 FX was used to assess the morphology.

3. Results and discussion

The oxidation of aniline with APS in an acidic aqueous medium yields PANI (Scheme 1a). The similar oxidation with silver nitrate results in a PANI–silver composite having ≈70 wt.% silver content (Scheme 1b). The use of the oxidant mixtures thus allows for the control of the silver in the composite.

Solutions of methanesulfonic acid have some benefits as a reaction medium. Methanesulfonic acid did not precipitate silver ions even at high concentrations when silver nitrate was used as oxidant [30]. In addition, PANI prepared with APS in methanesulfonic acid had excellent stability of conductivity at elevated temperature [31].



Scheme 1. (a) The oxidation of aniline with ammonium peroxydisulfate yields polyaniline (emeraldine) hydrogen sulfate. (b) Similar oxidation using silver nitrate results in polyaniline nitrate–silver composite. Acids are by-products in both cases.

3.1. The yield and composition

Oxidations of aniline with silver ions are slow and may take months at room temperature [14,29,30]. The presence of APS, however, makes the reaction sufficiently fast, even with only a small fraction of APS with respect to silver nitrate. This is the first important finding. The mass yield of reaction increases as composites contain more silver (Table 1) due to high density of this metal. The content of silver in the composites increases with increasing fraction of silver nitrate used in the oxidation of aniline, as expected. In this sense, the goal of the synthesis was achieved.

3.2. Molecular weights

The oxidation of aniline with APS in 1 M methanesulfonic acid yields a true polymer, PANI, having weight-average molecular weight $M_w = 220\,000$. The very broad molecular-weight distribution ($p = 0$ in Fig. 1), characterized by a high weight-to-number average molecular weight ratio, $M_w/M_n = 19$, suggests the presence of an oligomeric fraction. Bimodality of the distribution, however, was not observed. It should be noted that GPC characterizes only that part of the product which is soluble in *N*-methylpyrrolidone; the solubility was not complete.

The use of the second oxidant, silver nitrate, causes the two low-molecular weight components to appear in the molecular-weight distribution ($p = 1$ in Fig. 1, Table 1) in addition to a broad polymer tail extending to high molecular weights. When silver nitrate was present in the reaction mixture along with APS, two oligomeric peaks appeared in all the chromatograms but were shifted to

Table 1
The products of the oxidation of 0.2 M aniline with various molar concentrations of ammonium peroxydisulfate, [APS], and silver nitrate, [$AgNO_3$], in 1 M methanesulfonic acid: The participation of silver nitrate in the oxidation with respect to the second oxidant, ammonium peroxydisulfate, p, The yield of composite per 1 g of aniline, Y, the content of silver, w_{Ag}, the loss of mass after deprotonation, Δ, the conductivities of composites in protonated and base forms, σ and σ_B, corresponding densities, d and d_B, weight-average molecular weight, M_w, and weight-to-number-average molecular weight ratio, M_w/M_n.

p, %	[APS], mol L^{-1}	[$AgNO_3$], mol L^{-1}	Y, g g^{-1}	w_{Ag}, wt.% Ag	Δ, wt.%	σ, S cm^{-1}	σ_B, S cm^{-1}	d, g cm^{-3}	d_B, g cm^{-3}	10^{-3} M_w	M_w/M_n
0	0.25	0	1.41	0	39.5	9.4	2.6×10^{-6}	1.41	1.27	220	19
10	0.225	0.05	1.56	15.8	32.5	11	1.2×10^{-5}	1.66	1.58	–	–
20	0.20	0.10	1.85	26.8	33.7	8.1	1.0×10^{-4}	1.80	1.90	130	30
30	0.175	0.15	2.60	29.3	41.0	2.5	2.2×10^{-5}	1.83	2.24	–	–
40	0.15	0.20	2.61	42.2	36.2	1.3	4.6×10^{-5}	2.00	2.53	–	–
50	0.125	0.25	2.50	55.6	19.8	2.3	3.9×10^{-4}	2.47	2.68	47	3.5
60	0.10	0.30	2.65	71.1	17.9	1.8	2.6×10^{-6}	2.77	3.23	–	–
70	0.075	0.35	2.96	72.0	15.0	2.0	5.2×10^{-4}	3.15	3.72	–	–
80	0.05	0.40	2.95	73.0	9.5	6.1	1100	2.79	3.89	54	4.2
90	0.025	0.45	3.19	78.2	10.2	310	1050	3.10	3.42	–	–
100	0	0.50	3.27	73.5	8.8	1490[a]	0.068[a]	3.88	4.28	46	14

[a] The conductivities of 880 S cm^{-1} and 0.003 S cm^{-1} were reported earlier [30] for PANI–silver composite prepared in 1 M methanesulfonic acid and for the corresponding base form.

higher molecular weights. Obviously, there are different oxidation routes leading to different products, at least with respect to molecular weight. This can be explained by the difference in the oxidation potentials of APS (E^0 = 2.0 V) and silver nitrate (E^0 = 0.8 V); some reactions that take place with the former oxidant cannot happen with the latter [32,33].

3.3. UV–visible spectra

The absorption band with a maximum at ≈ 610–630 nm is characteristic of the PANI base in emeraldine oxidation state [34,35]. The oxidations of aniline in aqueous solutions of methanesulfonic acid yield PANI, as unambiguously proved by the presence of the absorption maximum in the 620–630 nm region (Fig. 2), regardless of the oxidant used.

3.4. FTIR spectra

The FTIR spectra of PANI–silver composites prepared by the oxidation of aniline in 1 M methanesulfonic acid with APS and silver nitrate mixed in various proportions are given in Fig. 3a. The infrared spectrum of the product of aniline oxidation with APS in presence of strong acid has already been interpreted in many papers and summarized in a recent review [36]. In the case of oxidation in 1 M methanesulfonic acid, we observe the bands at 1557 and 1477 cm^{-1} due to quinonoid (Q) and benzenoid (B) ring-stretching vibrations, respectively. The absorption band at 1302 cm^{-1} corresponding to π-electron delocalization induced in the polymer by protonation is also present in the spectrum, as well as the band at 1240 cm^{-1} interpreted as a C–$N^{+\bullet}$ stretching vibration in the polaron structure, a strong band centred at 1130 cm^{-1} assigned to the vibration mode of the –NH^{+}= structure, and the band at 803 cm^{-1} due to the C–H out-of-plane bending vibrations of two adjacent hydrogen atoms on a 1,4-disubstituted benzene ring (spectrum p = 0 in Fig. 3a). This spectrum differs from the spectrum of PANI sulfate [36] by slightly shifted position of above bands, and by the presence of the peaks of variously substituted benzene ring or out-of-plane ring deformation vibrations at 877, 705, 580 and 504 cm^{-1}. The contribution of the vibrations of hydrogen sulfate or sulfate counter-ions is possible. The peak observed at 1045 cm^{-1} corresponds to the symmetric SO_3 stretching in the hydrogen sulfate or methanesulfonate counter-ion.

When silver nitrate is added to the reaction mixture, a sharp peak of nitrate anion at 1384 cm^{-1} appears in the spectra (p = 0.1 and 0.2 in Fig. 3a). For p = 0.3 and 0.4, the shape of spectra dramatically changes, and a broad band with a maximum at

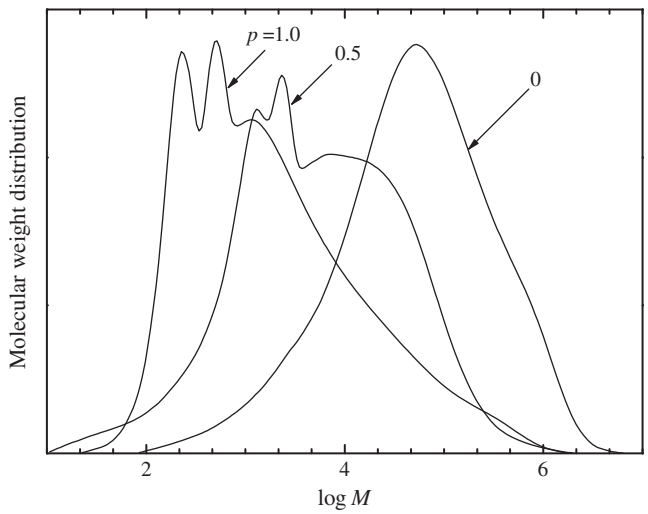


Fig. 1. Molecular-weight distributions of PANI fractions in PANI–silver composites prepared in 1 M methanesulfonic acid with various oxidant proportions, p = 0 (APS only), 0.5, and 1 (silver nitrate only).

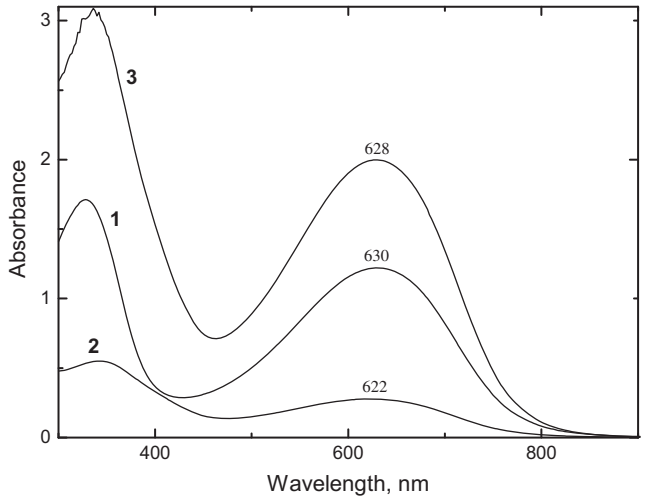


Fig. 2. The UV–visible spectra of the oxidation products (converted to the corresponding bases and dissolved in *N*-methylpyrrolidone) prepared by the oxidation of 0.2 M aniline with (1) 0.25 M ammonium peroxydisulfate (p = 0), (2) mixed oxidants: 0.125 M ammonium peroxydisulfate and 0.25 M silver nitrate (p = 0.5), and (3) 0.5 M silver nitrate (p = 1), in the solutions of 1 M methanesulfonic acid.

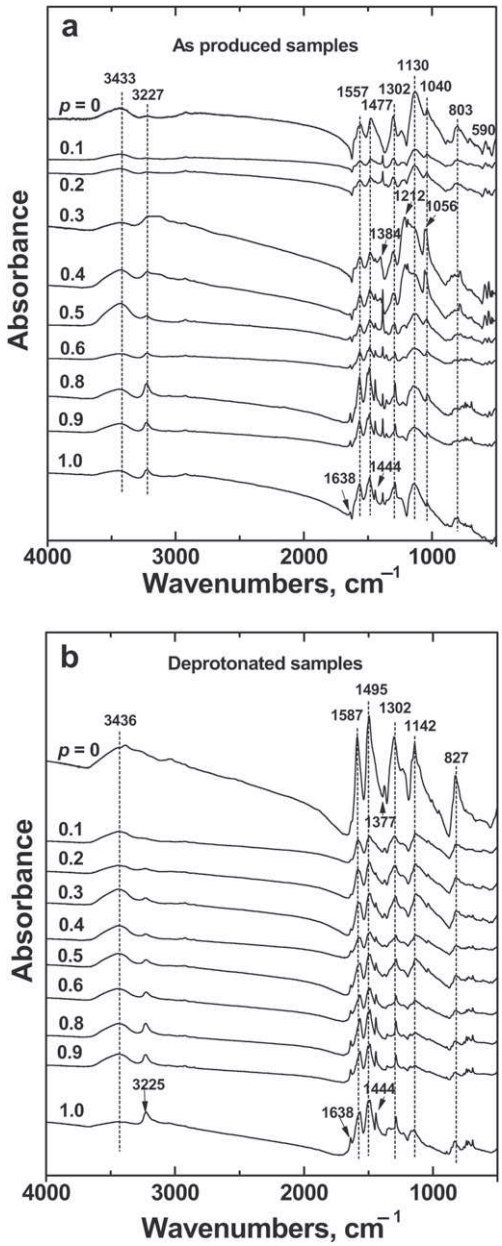


Fig. 3. FTIR spectra of PANI–silver composites prepared by the oxidation of aniline in 1 M methanesulfonic acid with APS and silver nitrate mixed in various proportions, p: (a) as prepared, and (b) after deprotonation by 0.1 M ammonium hydroxide.

1212 cm^{-1} and a sharp peak at 1056 cm^{-1} are observed in the spectra, and assigned most probably to methanesulfonate anions attached to aniline oligomers present in the products, and detected by gel permeation chromatography (Fig. 2). With increasing of silver nitrate content in the reaction mixture, new peaks at 1636 and 1444 cm^{-1} belonging to aniline oligomers [36] appear.

The evolution of the spectra of oligomeric part of oxidation products is easier observed in the spectra of deprotonated samples where the protonated low-molecular oligomers and various counter-ions have been removed (Fig. 3b). The spectrum of typical PANI base prepared with APS only, $p = 0$, with the bands of quinonoid (Q) and benzenoid (B) ring-stretching vibrations at 1587 and 1495 cm^{-1}, the band at 1379 cm^{-1} attributed to C–N stretching vibration in the neighbourhood of a quinonoid ring, the at 1302 cm^{-1} due to the C–N stretching vibrations of aromatic amines, the structured band with the maximum at 1142 cm^{-1} of the aromatic C–H in-plane deformation, and the band at 827 cm^{-1} of C–H out-of-plane bending vibrations is shown in Fig. 3b. With increasing of the silver nitrate content in the reaction mixture ($p > 0$), a new sharp band of medium-to-strong intensity at 1040 cm^{-1}, which can be attributed to the S=O stretching in sulfonate SO_3^- group substituting the aromatic ring is found in the spectra. The spectra consecutively change and the bands typical for the spectra of aniline oligomers and benzoquinones obtained with weaker oxidant than APS are observed in the spectra. The peak observed at about 1638 cm^{-1} corresponds most probably to N–H scissoring vibrations of aromatic amines or to the presence of phenazine units. The contribution of benzoquinone units is possible. The sharp band at 1444 cm^{-1} is attributed to the skeletal C=C stretching vibration of the substituted aromatic ring in aniline oligomers, the presence of C=N stretching or N=N azobenzene stretching vibrations is also possible. Band at 1377 cm^{-1} attributed to C–N stretching vibrations in the neighbourhood of a quinonoid ring, typical for the spectrum of PANI base, is not observed in the spectrum of aniline oligomers prepared at high silver nitrate fraction in oxidant mixtures. The oligomeric nature of the oxidation products is confirmed by the band of C–N stretching vibrations observed at 1230 cm^{-1} and, especially, by the peaks of the C–H out-of-plane bending and out-of-plane ring-deformations of a mono-substituted phenylene ring situated at 823, 758, 740, 724, and 690 cm^{-1}.

3.5. Morphology

Polyaniline prepared by the oxidation of aniline with APS in 1 M methanesulfonic acid has a rather nanofibrillar morphology instead of the common granular form (Fig. 4a). As the proportion of silver nitrate in the reaction mixture increased, silver nanoparticles appeared and became more frequent (Fig. 4b–d). They are smaller than 100 nm and form clusters, especially at high silver contents (Fig. 4d). For the morphology of the sample prepared exclusively with silver nitrate oxidant, the reader is referred to an earlier study [30].

3.6. Deprotonation

The expected loss of mass in PANI methanesulfonate after deprotonation by ammonium hydroxide, *i.e.* after the removal of methanesulfonic acid from the PANI salt, is 96.11/(181.22 + 96.11) = 34.66 wt.%. This value corresponds well with the results reported in Table 1 for samples prepared at low contents of silver nitrate. With increasing content of silver nitrate, the mass loss on deprotonation also decreases, because the fraction of PANI in the composite decreases as more silver is produced.

3.7. Conductivity

Salts: The conductivity of composites containing a conducting component often follows the percolation principle. Calculations based on percolation theory predict that at least 17–18 vol.% of conducting spheres in the matrix of non-conducting spheres are needed for the creation of infinite conducting pathways [37] and for the observation of macroscopic conductivity of the material. The position of the percolation threshold shifts to lower volume fractions for non-spherical conducting particles.

In the present case, an increase in conductivity above the conductivity of the PANI matrix is observed above 60–70 wt.% silver (Fig. 5a, Table 1). This corresponds to 16.8–23.8 vol.% silver if we assume the additivity of volumes, and densities of silver as

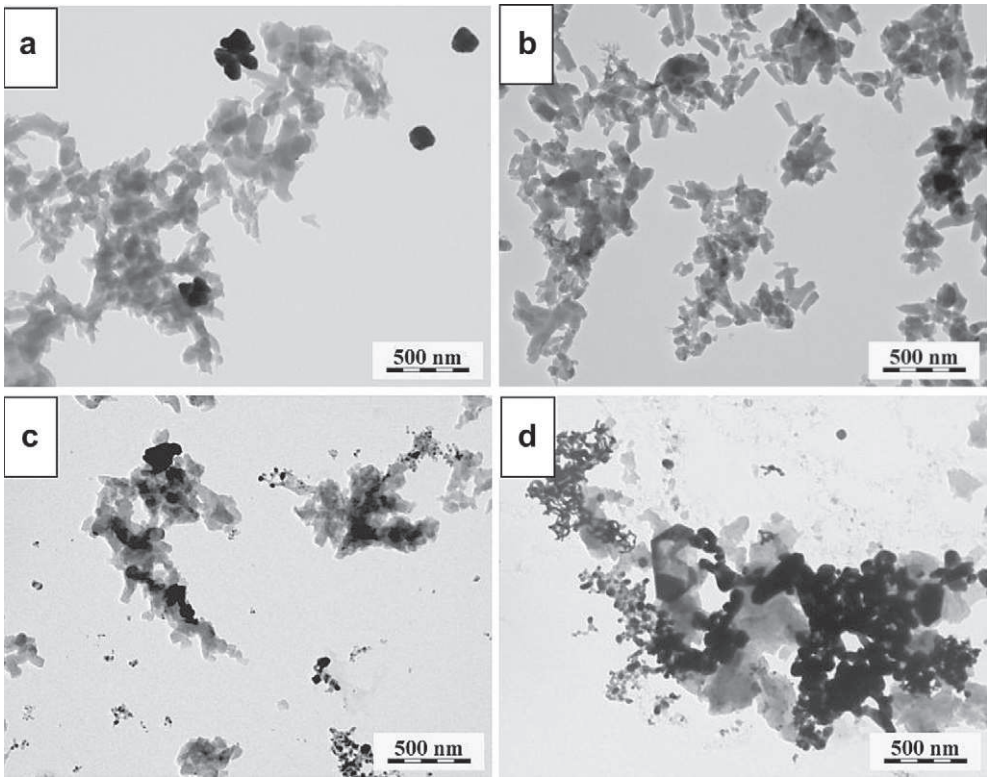


Fig. 4. Transmission electron micrographs of the PANI–Ag composites prepared in 1 M methanesulfonic acid with the oxidant proportions, (a) $p = 0.1$ (APS-rich system), (b) 0.2, (c) 0.5, and (d) 0.8 (the system rich in silver nitrate).

10.5 g cm^{-3} and of PANI methanesulfonate 1.41 g cm^{-3}. This is in accordance with the expected percolation threshold.

Bases: The percolation principle is even better visible after the deprotonation of PANI (Fig. 5b). Below 60–70 wt.% silver, the conductivity is controlled mainly by that of the matrix, a PANI base. Only above the percolation threshold does the conductivity increase steeply.

Another peculiar effect is based on the observation that the conductivity of composites sometimes increases after the deprotonation of PANI, *i.e.* after conversion of the semiconducting matrix to non-conducting one (Fig. 5, Table 1). There are two possible explanations:

The first is based on the *shift in composition*. It was proposed that this is caused by a decrease in the mass of the PANI after deprotonation (*cf.* Δ in Table 1) and, consequently, by the increase in the volume fraction of silver in the composite. This fact is confirmed by the increase in density of samples after deprotonation (Table 1). Indeed, this phenomenon, an increase of composite conductivity after the deprotonation of the PANI component, has been observed close to the assumed percolation threshold. A simple calculation shows that the deprotonation of PANI methanesulfonate in the composite containing 60 wt.% of silver increases the content of silver to 69.7 wt.%; similarly at 70 wt.% of silver in the composite there is an increase to 78.1 wt.%.

The second explanation is based on the *shift in percolation threshold*. It was observed that the percolation threshold of the conducting particles was shifted to higher fractions of the conducting component when these particles had been coated with a non-conducting overlayer and, consequently, the formation of conducting pathways was less efficient [38]. In the present case, such a layer could be afforded by silver oxide on the surface of silver nanoparticles. The dissolution of this non-conducting barrier in ammonia solution, where insoluble silver salts convert to well

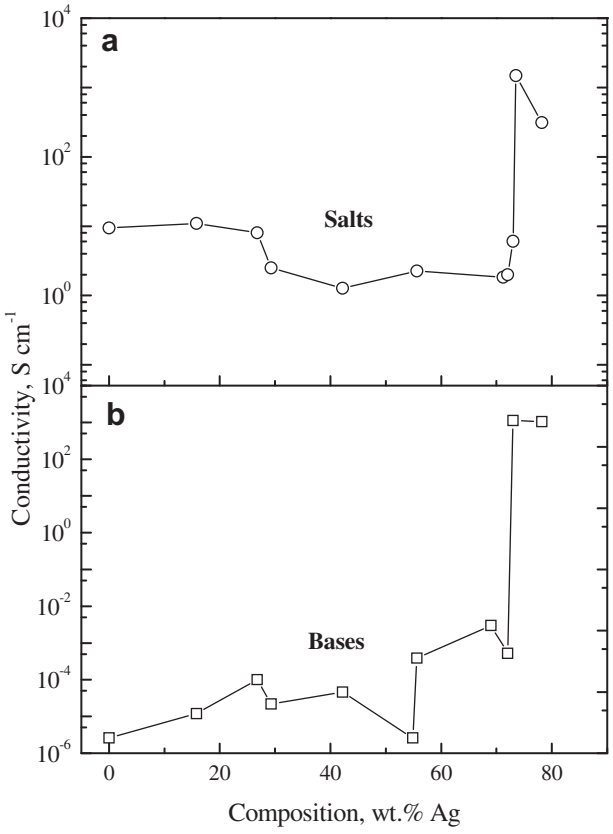


Fig. 5. The dependence of the conductivity of (a) salt and (b) base forms of PANI–silver composites prepared and in 1 M methanesulfonic acid on the weight fraction of silver in the protonated form of the composite.

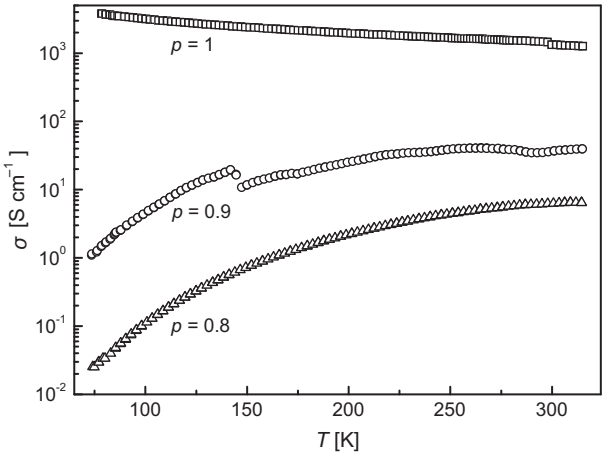


Fig. 6. Temperature dependence of conductivity of PANI–silver composites prepared in 1 M methanesulfonic acid by the oxidation of aniline with APS and silver nitrate mixed in various proportions, p (Table 1).

soluble diamosilver complex, would results in a shift of percolation threshold to lower silver contents and in a consequent increase in conductivity. It should be stressed that these effects may take place only in the close vicinity of the percolation threshold where the dependence of conductivity on the content of the conducting component is very steep, and small changes in the composition are associated with large changes in conductivity.

3.8. Temperature dependence of conductivity

The conductivity of semiconductors increases with increasing temperature. This is the case when the conductivity is controlled by the PANI part, *i.e.* below the percolation threshold with respect to silver ($p = 0.8$ and 0.9 in Fig. 6). Once the percolation threshold has been reached, as demonstrated by the increase of conductivity above the conductivity of PANI alone, the conductivity of the composite acquires metallic character, *i.e.* it decreases with increasing temperature ($p = 1$ in Fig. 6).

4. Conclusions

The content of silver in PANI–silver composites can be controlled from 0 to *ca* 70 wt.% of silver by using mixed oxidants, ammonium peroxydisulfate and silver nitrate, in various proportions for the oxidation of aniline. The corresponding control of composite conductivity, however, was not achieved. In most cases, the conductivity of the composite is determined by that of a matrix. Only at high contents of silver, above the percolation limit at 60–70 wt.% of silver, does the conductivity of this metal in the composites manifest itself and the conductivity increases above 100 S cm^{-1}.

A rather surprising effect, an increase in the conductivity of the composites after conversion of the conducting protonated PANI to the corresponding non-conducting PANI base, was demonstrated in some cases. This is explained on the basis of the percolation model, either by the higher fraction of silver in the composite after the deprotonation of the PANI component or, alternatively, the by the coating of silver nanoparticles with an insulating overlayer of silver oxide. Such an insulating coating would dissolve in ammonia solutions during the deprotonation of PANI salt to PANI base, and the percolation threshold would be shifted to lower silver contents. In the contrast to classical systems represented by a conductor dispersed in insulating matrix, the behaviour of metallic particles embedded in organic semiconductor thus has to consider interfacial electric barriers. The temperature dependence of conductivity may have a semiconductor or metallic character, if the conductivity is controlled by PANI matrix at low silver loading or by silver nanoparticles at high silver contents, respectively.

Acknowledgment

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ORIGINAL PAPER

The preparation of conducting polyaniline–silver and poly(*p*-phenylenediamine)–silver nanocomposites in liquid and frozen reaction mixtures

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Abstract The oxidation of aniline with silver nitrate in 1 mol L^{-1} acetic acid at 20 °C yielded a composite of two conducting components, polyaniline and silver; the acceleration with 1 mol% of *p*-phenylenediamine is needed for efficient synthesis. The yield and molecular weight increased when aniline was copolymerized with 10 mol% *p*-phenylenediamine. Such product displayed metallic conductivity below 180 K and semiconductor type above this temperature. As the result, the conductivity was the same at 100 and 300 K. The oxidation of *p*-phenylenediamine alone with silver nitrate also produced a conducting composite having the conductivity of 1,750 S cm^{-1} despite the assumed nonconductivity of poly(*p*-phenylenediamine). The present study demonstrates that all oxidations proceeded also in frozen reaction mixtures at −24 °C, i.e., in the solid state. In most cases, molecular weights of polymer component increased, the conductivity of composites with silver improved, to 2,990 Scm^{-1} for poly(*p*-phenylenediamine)–silver, and remained high after deprotonation with 1 mol L^{-1} ammonium hydroxide.

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Introduction

Conducting polymers have intensively been studied due to their electrical and responsive properties, polyaniline (PANI) being the typical representative of this group [1–3]. The oxidation of aniline with silver nitrate has recently been reported to produce hybrid organic–inorganic composites of two conductors, semiconducting PANI and metallic silver [4–6]. The oxidation of aniline with silver nitrate, however, takes months at room temperature. UV-visible (UV-vis) [7, 8], γ-irradiation [7, 9, 10] or temperature elevated to 250 °C [11] were needed to speed up this process.

Accelerating effect of *p*-phenylenediamine (PDA) in the oxidation of aniline with peroxydisulfate has been known for many years [12–17]. It is operative also with silver nitrate oxidant [18]. The ability of aniline to copolymerize with PDA has also been documented [19–21]. *p*-Phenylenediamine alone easily produces oligomers or polymers upon oxidation with peroxydisulfate [19, 22, 23] and silver nitrate [18].

The conductivity of the PANI matrix incorporating silver nanoparticles can be increased by increasing the molecular weight of the polymer [24–26]. This is achieved by decreasing the reaction temperature during the preparation of PANI [26–30]. The freezing of the reaction mixture at sub-zero temperatures was prevented by additions of inorganic salts, such as lithium chloride [25, 27, 28]. The oxidation of aniline to PANI, however, proceeds also in the absence of such salts, i.e., in frozen reaction mixtures [26, 31, 32], even at −50 °C [26]. The role of a conducting polymer in the transfer of electrons from the oxidant to aniline molecules has been proposed to be responsible for

this fact [3, 32]. Such concept is supported by independent experiments [33] illustrating that PANI grows like an organism devouring the aniline molecules in its vicinity and incorporates them into the polymer structure. Consequently, there is no need of the reactant molecules to diffuse and meet each other in order to react. The polymerization in frozen media was used to guide the morphology of PANI by using ice crystals as templates [34].

The present study reports on three systems using silver nitrate as oxidant in 1 mol L^{-1} acetic acid: (1) the oxidation of aniline accelerated with a minute 1 mol% amount of PDA, (2) a copolymer of aniline with 10 mol% PDA, and (3) PDA alone. The properties of products obtained in liquid media at room temperature and in frozen reaction mixtures at −24 °C have been compared.

Experimental

Preparation of hybrid composites

Monomers, aniline (Fluka, Switzerland) and *p*-phenylenediamine (Fluka, Switzerland), and oxidant, silver nitrate (Lach-Ner, Czech Republic), were separately dissolved in 1 mol L^{-1} aqueous solution of acetic acid. The silver nitrate-to-monomer mole ratio was always 2.5. The content of PDA was 1 or 10 mol% in the mixture with aniline or 100 mol% for its homopolymerization. In the first series of experiments, the monomer and oxidant solutions were mixed to start the oxidation of aniline at room temperature. After 1 week, the green solids were collected on a filter, rinsed with a solution of the acetic acid, and dried at room temperature in air, and then in a desiccator over silica gel. In the second series, the reaction mixtures were placed in polyethylene containers and frozen in liquid nitrogen, and transferred to the freezer operating at −24 °C. Again, after 1 week, the dark green frozen mixture was melted at room temperature. The solids were immediately processed as above. Parts of products were deprotonated in excess of 1 mol L^{-1} ammonium hydroxide to corresponding bases.

Characterization

UV-visible spectra of deprotonated samples dissolved in *N*-methylpyrrolidone were recorded with a Lambda 20 spectrometer (Perkin Elmer, UK). Molecular weight distributions were determined by gel-permeation chromatography operating with *N*-methylpyrrolidone and calibrated with polystyrene standards. Infrared spectra were recorded with a fully computerized Thermo Nicolet NEXUS 870 Fourier transform infrared (FTIR) Spectrometer with a DTGS TEC detector. Samples were dispersed in potassium bromide and compressed into pellets. The conductivity was measured by a four-point van der Pauw method using a current source SMU Keithley 237 and a Multimeter Keithley 2010 voltmeter with a 2000 SCAN 10-channel scanner card. The powders were compressed at 700 MPa with a manual hydraulic press to pellets of 13 mm diameter and 1 mm thickness before such measurements. Temperature dependences of conductivity were determined on the same samples in a Janis Research VNF-100 cryostat in the range 78–315 K in a flowing stream of nitrogen vapor. Before such measurements, samples were placed in vacuum (≈10 Pa) for several hours at about 305 K to remove moisture. The content of silver was determined as an ash.

Results and discussion

The oxidation of aniline in acidic aqueous media yields protonated PANI, an emeraldine salt (Fig. 1). The oxidation of PDA under similar conditions has also produced a polymer (Fig. 1) [22, 35]. Depending on the degree of oxidation, such polymer may either resemble an amino-substituted PANI [22, 36–38] (Fig. 1) or to have a ladder polyphenazine structure [20, 22, 37]. Both monomers, aniline and PDA, are able to copolymerize [19–21, 39–41]. The present study compares the polymer–silver composites prepared by the oxidation of aniline and PDA with silver nitrate in the liquid and frozen reaction mixture.

Yield and composition

In the absence of PDA, the oxidation of aniline is slow and requires months to take place [4]. The acceleration of aniline oxidation by 1 mol% of PDA results in the formation of a composite, but the yield was low (Table 1). Silver acetate is a by-product, which may be present in the samples [18]. The yield increases three times when aniline was oxidized along with 10 mol% PDA or PDA was oxidized alone. The same trend was observed for the

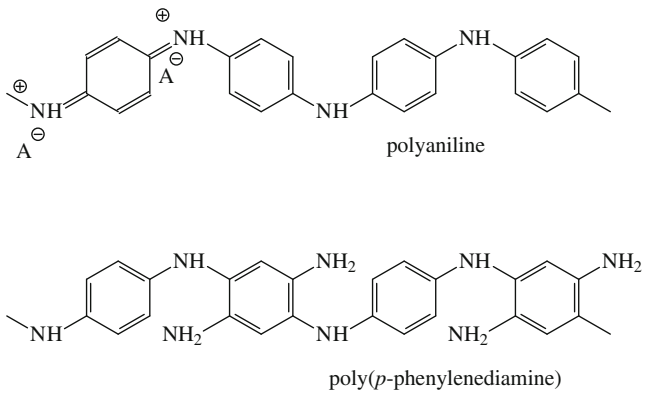

Fig. 1 Polyaniline (a protonated emeraldine form) and a possible structure of poly(*p*-phenylenediamine)

Table 1 The yield (Y) of the oxidation of aniline and *p*-phenylenediamine mixtures of various mole fractions of PDA (x_{PDA}) with silver nitrate in 1 mol L^{-1} acetic acid in *liquid* reaction mixture at 20 °C: the content of silver (w_{Ag}), the conductivity of as-prepared samples (σ) and after deprotonation (σ_B) and weight-average molecular weight (M_w), and the ratio of weight-to-number-average molecular weights (M_w/M_n)

x_{PDA} (mol% PDA)	Y[a] (g g^{-1})	w_{Ag} (wt.%)	σ (S cm^{-1})	σ_B (S cm^{-1})	M_w	M_w/M_n
1	1.28	71.5	6,100	4,000	8,800	6.2
10	3.80	67.1	18	0.06	60,800	15.1
100	3.56	68.1	1,750	0.075	7,100	2.2

[a] Grams of solids per 1 g of monomers

samples prepared both in liquid and frozen mixtures (Tables 1 and 2). For the oxidation of aniline with silver nitrate to PANI nitrate–silver composite the theoretical yield is 4.25 g of composite per 1 g of aniline [5]. For reactions including PDA these values may slightly differ. The highest conversion of monomers is close to 90%. The content of silver is comparable in all composites as it is fixed by the stoichiometry of reaction, which expects the fraction of silver 68.2 wt.% [5].

Conductivity

The conductivity is the most important parameter of polymer–silver composites. In spite of comparable contents of silver in the composites (Tables 1 and 2), the conductivities considerably differ. The conductivity of the composites prepared in liquid medium at room temperature has been reported earlier [18] and varies between 10^1 and 10^3 S cm^{-1} orders of magnitude (Table 1). The decrease in conductivity after the introduction of 10 mol% PDA into reaction medium can be explained by the copolymerization of aniline with PDA resulting in the reduced PANI-chain conjugation. The high conductivity of PPDA–silver composite, however, is surprising because of PPDA which is rated as a nonconducting polymer.

After the preparation in the frozen reaction mixtures, the conductivity of PANI–silver composites was reduced, contrary to the expectation (Table 2). The conductivity of corresponding PPDA–silver composites was higher, 2,990 S cm^{-1} (Table 2), which is also difficult to interpret. These observations cannot be simply explained by any marked differences in the morphology of composites, i.e., especially by the size and distribution of silver nanoparticles (Fig. 2).

After the deprotonation with ammonium hydroxide, the conducting PANI salts convert to a nonconducting PANI base. One would expect a consequent decrease in the conductivity of the composite with silver but an increase was found (Table 2). Such effect has occasionally been reported earlier [5, 42, 43]. It was proposed that the silver particles are coated with nonconducting silver oxide, which forms an electric barrier and dissolves in ammonium hydroxide during the deprotonation. The decrease in the conductivity of polymer matrix thus can be overridden by the removal of conductivity barriers on the surface of metal nanoparticles. Alternatively, the reduction in polymer mass caused by the deprotonation results in the increase of silver fraction in the composite and, consequently, could be responsible for the increase in conductivity.

When silver particles are embedded in the PPDA homopolymer matrix, the conductivity of the matrix should not change after treatment with ammonium hydroxide, the matrix being nonconducting from the very beginning. The experiment, however, shows the decrease in the conductivity by five orders of magnitude for the sample prepared in liquid medium (Table 1). Less pronounced decrease in conductivity was observed for the sample prepared in the frozen mixture (Table 2). This suggests that PPDA undergoes the salt–base transition, similarly like PANI, the salt being conducting. This would mean that the PPDA prepared by using silver nitrate as oxidant is different than that produced with ammonium peroxydisulfate [19]. This hypothesis, however, is not supported by UV-visible spectra. The oxidation products of PDA prepared with

Table 2 The yield (Y) of the oxidation of aniline and *p*-phenylenediamine mixtures of various mole fractions of PDA (x_{PDA}) with silver nitrate in 1 mol L^{-1} acetic acid in *frozen* reaction mixture, in ice, at −24 °C; for the meaning of symbols, see Table 1

x_{PDA} (mol% PDA)	Y[a] (g g^{-1})	w_{Ag} (wt.%)	σ (S cm^{-1})	σ_B (S cm^{-1})	M_w	M_w/M_n
1	0.95	69.7	281	765	56,100	19.5
10	2.88	74.1	1,080	615	304,000	1.6
					+12,100[b]	4.6
100	2.75	67.1	2,990	680	9,900	7.4

[a] Grams of solids per 1 g of monomers

[b] Two polymeric components

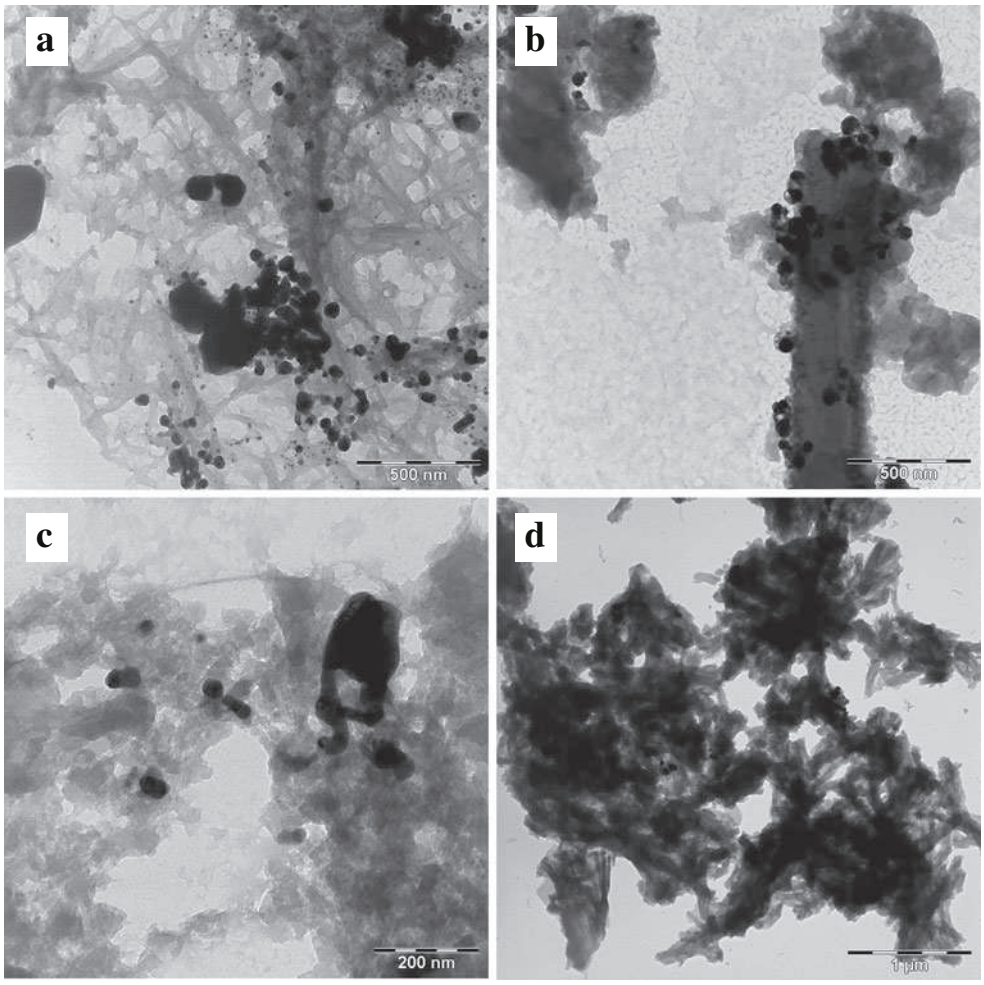

Fig. 2 Transmission electron micrographs of composites prepared in frozen reaction mixtures at −24 °C containing **a** 99 mol% aniline+1 mol% PDA, **b** 90 mol% aniline+10 mol% PDA, and **c** PDA. **d** The product of oxidation of PDA in liquid medium at 20 °C is shown for comparison

peroxydisulfate display unpronounced maximum at 420 nm [35, 38] as also illustrated in the present study (Fig. 3). The maximum becomes more pronounced when the oxidation was carried out in frozen mixtures but no marked differences in the spectra are found. The similar effect, when the conductivity of PANI was promoted by the presence of nonconducting aniline oligomers [44], should be mentioned here.

Temperature dependence of conductivity

Except for one sample, the temperature dependences of conductivity have negative slope (Fig. 4) characteristic of metallic type of conductivity. This is not surprising because the conductivities of the order of 10^2–10^3 S cm^{-1} must be due to the presence of silver.

In a single case of a copolymer of aniline with 10 mol% PDA, the composite with silver had a bowl-like dependence (Figs. 4 and 5). Such material displays the metallic conductivity at low temperature (conductivity decreases with increasing temperature) and semiconductor type of conductivity at room temperature (conductivity increases with increasing temperature), the minimum of conductivity 17.1 S cm^{-1} being located at 180 K (Fig. 5, the first run on pellet 1). The copolymer component thus participates in the conduction, and the macroscopic conductivity is thus lower than in other samples (Table 1). As a consequence, the

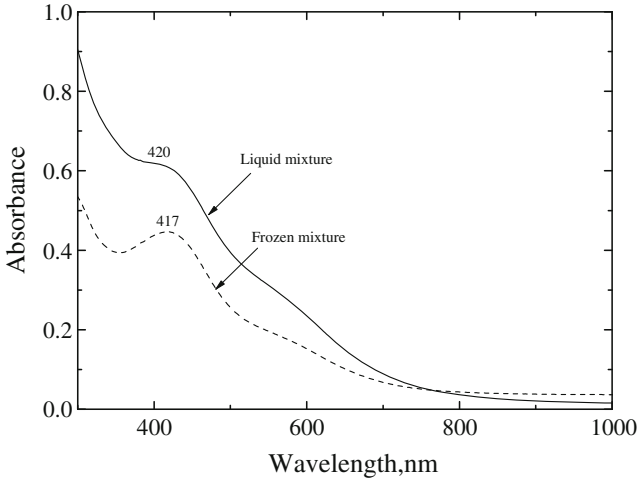

Fig. 3 UV-visible spectra of poly(*p*-phenylenediamine) prepared 1 M acetic acid at room temperature (*solid line*) and at −24 °C in frozen reaction mixture (*broken line*). The products were converted to bases and dissolved in *N*-methylpyrrolidone

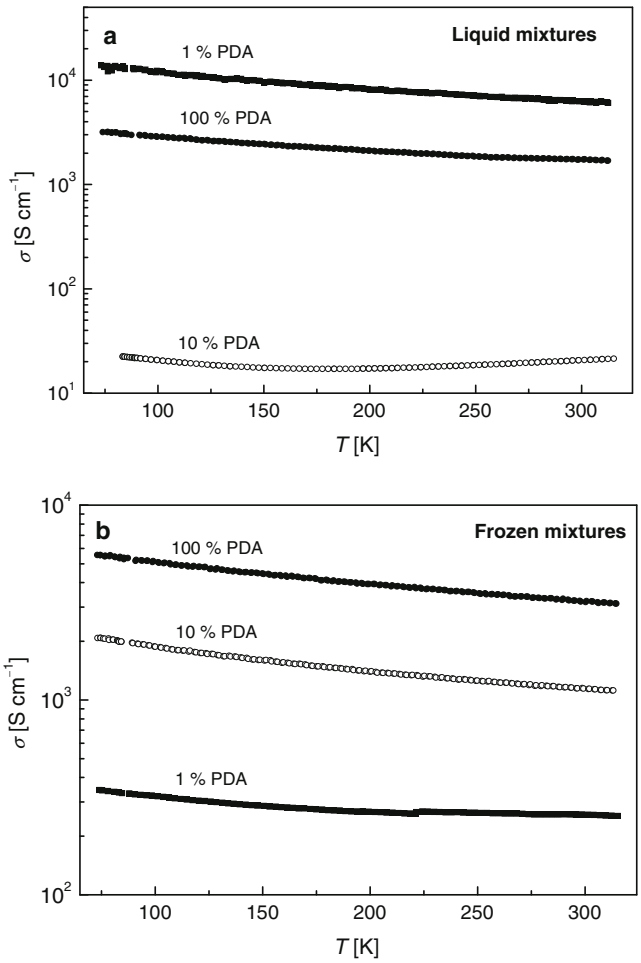

Fig. 4 Temperature dependence of conductivity of samples prepared **a** at 20 °C in liquid reaction mixtures and **b** at −24 °C in frozen media: (1) polyaniline (accelerated with 1 mol% PDA), (2) a copolymer of aniline and 10 mol% PDA, and (3) poly(*p*-phenylenediamine)

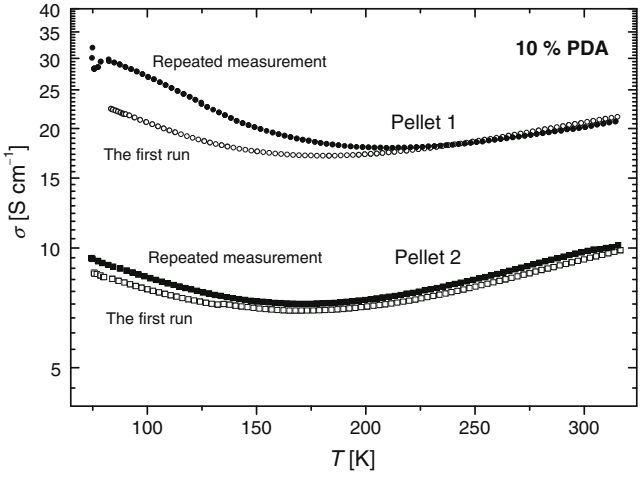

Fig. 5 The temperature dependence of conductivity σ of two pellets prepared in the liquid reaction mixture containing 10 mol% PDA: the first run and the repeated measurement

conductivity is little dependent on temperature, and has the same value of 20.7 $S cm^{-1}$ at 100 and 300 K.

The bowl-like dependence has been observed in repeated measurements and also with various pellets prepared from the same composite (Fig. 5). This experiment proves that the effect is inherent to the composite and not an experimental artifact associated with the way of pellet preparation or measurement. Differences in the temperature dependences are connected with the imperfect homogeneity of the samples.

Molecular weights

Some conductivity trends could possibly be related to molecular weight of polymers although the conductivity increased with increasing molecular weight of PANI only marginally [26]. For that reason, molecular weight distributions were determined (Fig. 6). Polyaniline prepared by

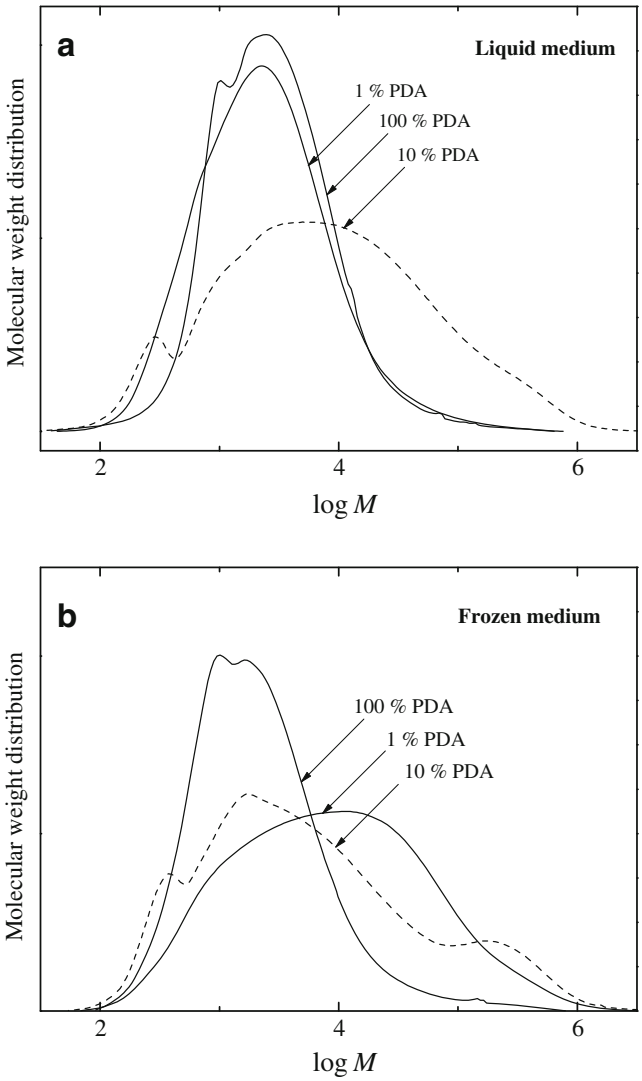

Fig. 6 Molecular weight distributions of the oxidation products prepared **a** in the liquid (20 °C) and **b** in the frozen (−24 °C) 1 M acetic acid

the oxidation of aniline with silver nitrate has relatively low molecular weight, and may rather be regarded as an oligomer (Table 1; Fig. 6a). High values of polydispersity expressed by the ratio M_w/M_n (Table 1) reflect broad distributions of molecular weights. The copolymerization with PDA leads to higher molecular weight. This is probably due to the branching of polymer chains due to the incorporation of a bifunctional monomer PDA (Fig. 1) [39]. The molecular weight distribution was bimodal, and the polymeric fraction was accompanied by a small fraction of oligomers. The molecular weight of PPDA is of the order of thousands, i.e., the oxidation product of PDA is regarded as an oligomer. The presence of two oligomeric components is clearly visible (Fig. 6a).

The decrease in the polymerization temperature to −24 °C, resulting in the freezing of reaction medium, has led to increase in molecular weight in all cases (Table 2). Such trend has been demonstrated earlier for PANI [26, 28–30]. The character of distributions remains preserved (Fig. 6b). The distribution of PANI is still monomodal but shifted to higher molecular weights. The copolymer contains the oligomeric fraction and the polymeric fraction is split into two components. The high molecular weight component which is only suspected as the shoulder in the samples prepared at room temperature (Fig. 6a) becomes clearly visible (Fig. 6b). The product of PDA oxidation has again an oligomeric character and a bimodal distribution indicates the presence of two types of oligomers.

The variations in molecular weights are thus not decisive for the level of conductivity. Even oligomers produce composites with silver having a high conductivity. Molecular weights would be thus important rather in mechanical than electrical properties.

Molecular structure reflected by FTIR spectra

The analysis of FTIR spectra with respect to molecular structure of the oxidation products has already been reported for the composites of silver and both PANI [4, 5] and PPDA [18]. In the present contribution we concentrate especially on features displayed by the corresponding copolymer and the comparison of the samples prepared in liquid and frozen media.

The FTIR spectrum of a copolymer of 10 mol% PDA and 90 mol% aniline prepared *in liquid medium* at room temperature displays the main bands typical of the spectrum of PANI salt synthesized in common way, with ammonium peroxydisulfate oxidant [18, 45]. The main absorption peaks located at 1,572 cm^{-1} (quinonoid ring stretching), 1,490 cm^{-1} (benzenoid ring stretching), and 810 cm^{-1} (aromatic C–H out-of-plane deformation vibration of 1,4-disubstituted benzene ring) are well distinguished in the spectrum of sample obtained at room temperature (Fig. 7).

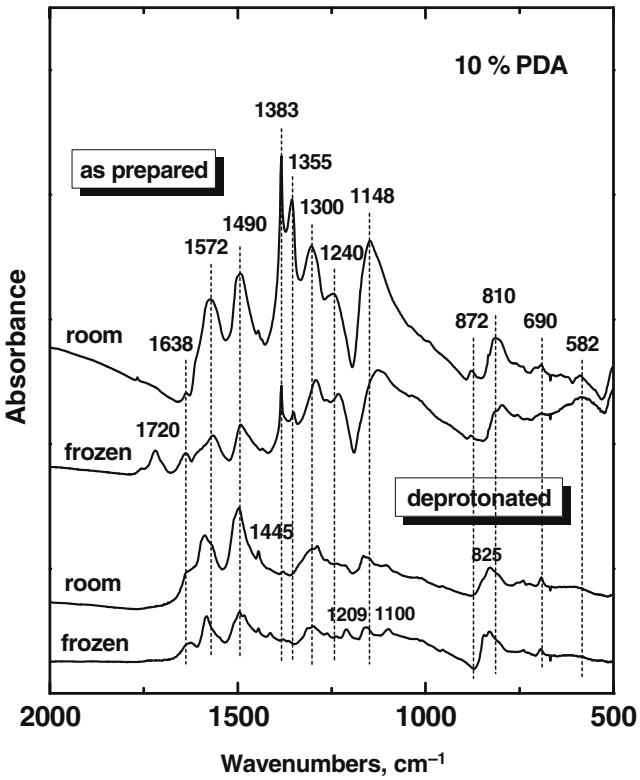

Fig. 7 FTIR spectra of a copolymer of aniline and 10 mol% PDA prepared in liquid 1 M acetic acid at room temperature or in frozen reaction mixture at −24 °C: as-prepared protonated samples and the bases obtained after deprotonation with 1 M ammonium hydroxide

The bands with maxima at 1,300 cm^{-1} (C–N stretching), 1,240 cm^{-1} (C–$N^{+\bullet}$ stretching), and 1,148 cm^{-1} (B–NH^{+}=Q stretching involving benzenoid and quinonoid rings) are characteristic of the FTIR spectrum of protonated PANI [46]. A small sharp peak at 1,445 cm^{-1} and the peaks at 872 and 690 cm^{-1} observed in the spectrum of protonated copolymer and corresponding to the presence of out-of-plane ring deformations in tri- and mono-substituted branched units signify the presence of aniline oligomers in the sample [46]. A peak at 582 cm^{-1} is observed in the spectrum. In the spectrum of the as-prepared sample, we observe a strong sharp peak of the nitrate anion at 1,383 cm^{-1} accompanied with a medium-to-strong band at 1,355 cm^{-1}, characteristic of nitrate ions. This reflects the protonation of PANI by nitric acid. Additional peaks belonging to the spectrum of aniline oligomers are better observed in the spectrum of the corresponding deprotonated sample (a shoulder at 1,638, and the peaks at 1,445 and 1,287 cm^{-1}) (Fig. 7) [46]. The bands of nitrate anion disappeared, but the peak at 690 cm^{-1} and a broad band at 582 cm^{-1} are still detected in the spectrum after deprotonation. We can conclude that the spectrum of the copolymer obtained in liquid medium corresponds mainly to the spectrum of PANI with small fraction of accompanying aniline oligomers.

The FTIR spectrum of the copolymer of aniline and 10 mol% PDA prepared *in frozen reaction mixture* differs from the spectrum of the product obtained at room temperature (Fig. 7). The absorption of the sample was very small and the contribution of potassium bromide pellet, including bands corresponding to water molecules, to the spectrum is thus possible. This may be due to higher molecular weight of the copolymer (Table 2) and difficult dispersion in potassium bromide. The main bands of protonated PANI and the peaks of nitrate anions are again well visible in the spectrum. Additional strong and broad band at 1,720 cm^{-1} corresponds to a carbonyl group and the band at 1,638 cm^{-1} increased. The peak of branched units at 872 cm^{-1} is still observed in the spectrum and the band at about 582 cm^{-1} increased and broadened. We suppose that the last peak corresponds to the in-plane rocking vibration of aromatic nitro group connected with nitration.

After the deprotonation, the band at 1,720 cm^{-1} disappeared, and the band with maximum at 1,625 cm^{-1} is observed in the spectrum. The main bands of PANI base are observed at 1,582, 1,495, 1,378, 1,298, and 830 cm^{-1}, as well as the peaks typical of aniline oligomers at 1,445 and 1,414 cm^{-1}. Additional peaks are present in the spectrum of deprotonated sample prepared in frozen mixture. The most pronounced of them is the second maximum at 1,483 cm^{-1}, corresponding to C=N vibrations in quinonoid rings. This doublet is typical for the spectrum of benzoquinone. The bands at 1,261, 1,236, and 1,209 cm^{-1} belong, in analogy with PANI, to the C–N stretching vibrations of primary aromatic amines. The aromatic ketones have a medium structured band at 1,300–1,230 cm^{-1} due to the phenyl–carbonyl C–C stretching [47]. The band at 1,100 cm^{-1} belongs most probably to the aromatic C–H in-plane deformation vibration in di- or tri-substituted benzene rings. The peaks at 825 and 690 cm^{-1} observed in the spectrum of deprotonated copolymer obtained in frozen medium correspond to the out-of-plane ring deformations in di- and mono-substituted benzene rings and confirm the presence of oligomers in the structure.

Conclusions

The feasibility of the oxidation of aniline or PDA with silver nitrate to composites of corresponding polymers with silver has been illustrated both in the liquid and solid aqueous reaction mixtures. Aniline is easily oxidized with silver nitrate in acidic media, such as the solutions of acetic acid, if the reaction is accelerated at least with a minute amount of PDA (1 mol%). Polyaniline–silver composite having the conductivity of the order of 10^3 S cm^{-1} was obtained. The oxidation of aniline proceeds at room temperature in liquid medium. When the temperature was reduced to −24 °C, the reaction took place in the frozen solid state. The yields were comparable but low. The molecular weight of polymers was of the order of 10^3, i.e., at oligomer level, when the reaction was carried out at 20 °C, and increased by one order of magnitude when the polymerization took place at −24 °C.

The copolymerization of aniline with 10 mol% PDA proceeded easily with high yield. The conductivity of composites was reduced, in spite of higher molecular weight of polymer component. Such sample had a metallic type of conductivity at low temperatures and semiconductor behavior at room temperature. As a result, the temperature dependence of the conductivity was very mild over several hundreds Kelvin. The conductivity increased by two orders of magnitude after the copolymerization had been carried out in the frozen state and became of metallic type.

The analogous oxidation of PDA alone was fast, the yield was again high, but the molecular weight was of the order of thousands, i.e., at the oligomer level. When the oxidation took place in ice, the conductivity of PPDA–silver composite was even higher than that of PANI–silver. This is surprising because PPDA is regarded as nonconducting, in the contrast to conducting PANI.

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