

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

Patrycja Bober · Jaroslav Stejskal ·
Miroslava Trchová · Jan Prokeš

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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 S cm⁻¹ for poly(*p*-phenylenediamine)–silver, and remained high after deprotonation with 1 mol L⁻¹ ammonium hydroxide.

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

P. Bober (✉) · J. Stejskal · M. Trchová
Institute of Macromolecular Chemistry,
Academy of Sciences of the Czech Republic,
Heyrovsky Sq. 2,
162 06 Prague 6, Czech Republic
e-mail: bober@imc.cas.cz

J. Prokeš
Faculty of Mathematics and Physics, Charles University Prague,
V Holešovičkách 2,
182 00 Prague 8, Czech Republic

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

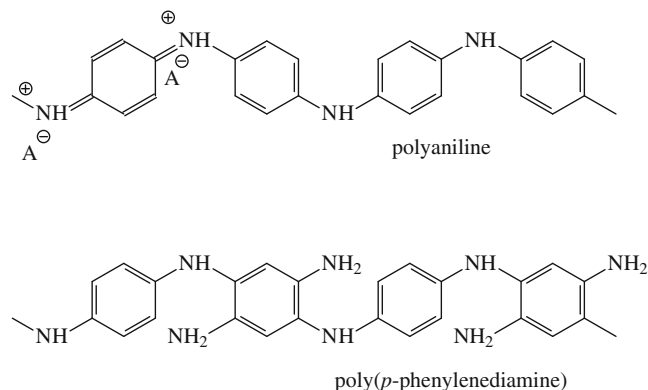


Fig. 1 Polyaniline (a protonated emeraldine form) and a possible structure of poly(*p*-phenylenediamine)

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

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 10¹ and 10³ 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

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)

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

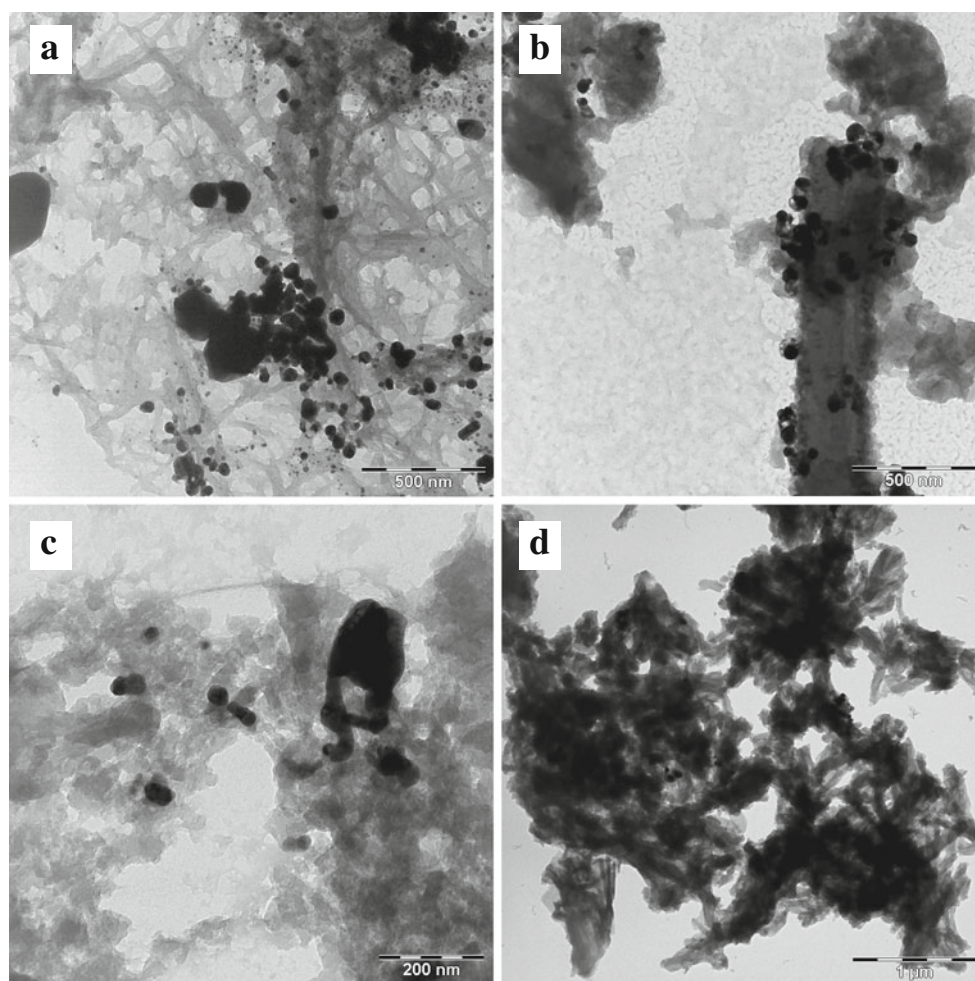
Table 2 The yield (Y) of the oxidation of aniline and p -phenylenediamine mixtures of various mole fractions of PDA (x_{PDA}) with silver nitrate in 1 mol L⁻¹ acetic acid in *frozen* reaction mixture, in ice, at -24 °C; for the meaning of symbols, see Table 1

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 $-24\text{ }^{\circ}\text{C}$ 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 $20\text{ }^{\circ}\text{C}$ 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

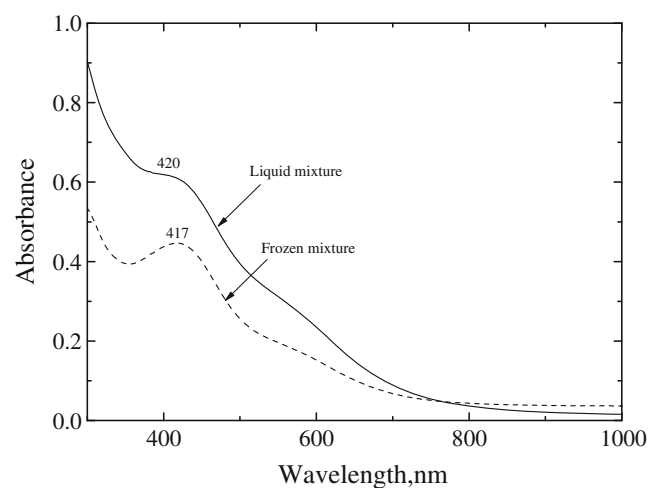


Fig. 3 UV-visible spectra of poly(*p*-phenylenediamine) prepared 1 M acetic acid at room temperature (solid line) and at $-24\text{ }^{\circ}\text{C}$ in frozen reaction mixture (broken line). The products were converted to bases and dissolved in *N*-methylpyrrolidone

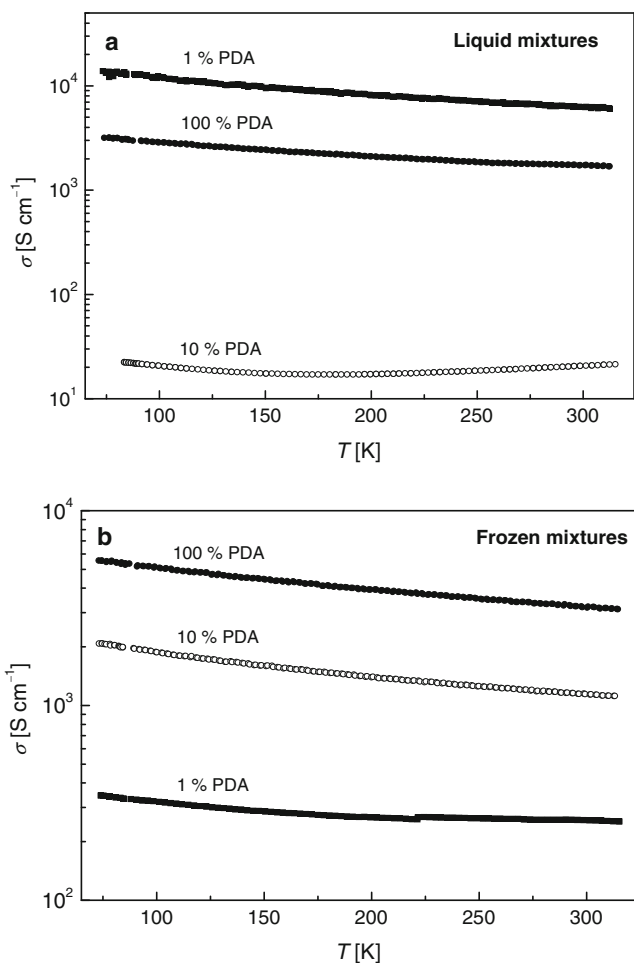


Fig. 4 Temperature dependence of conductivity of samples prepared **a** at 20 °C in liquid reaction mixtures and **b** at -24 °C in frozen media: (1) polyaniline (accelerated with 1 mol% PDA), (2) a copolymer of aniline and 10 mol% PDA, and (3) poly(*p*-phenylenediamine)

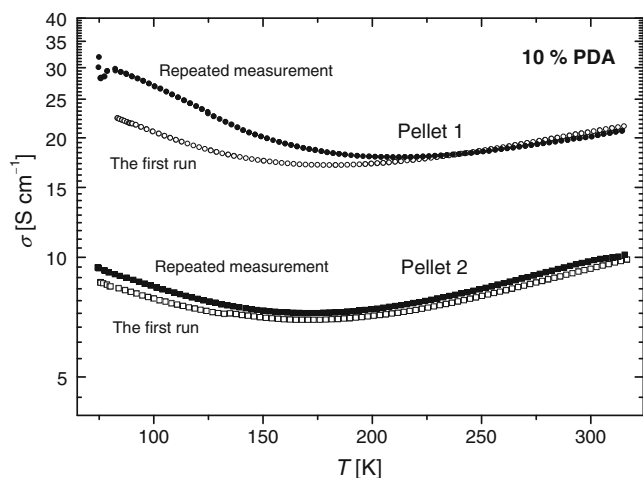


Fig. 5 The temperature dependence of conductivity σ of two pellets prepared in the liquid reaction mixture containing 10 mol% PDA: the first run and the repeated measurement

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

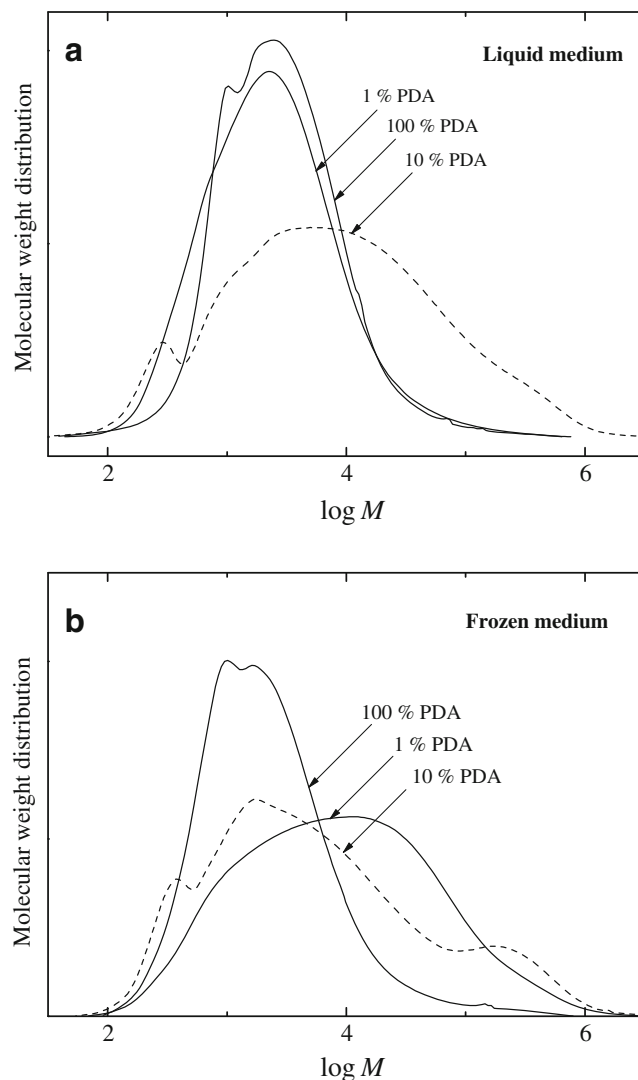


Fig. 6 Molecular weight distributions of the oxidation products prepared **a** in the liquid (20 °C) and **b** in the frozen (-24 °C) 1 M acetic acid

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 $-24\text{ }^\circ\text{C}$, 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 $1,572\text{ cm}^{-1}$ (quinonoid ring stretching), $1,490\text{ cm}^{-1}$ (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).

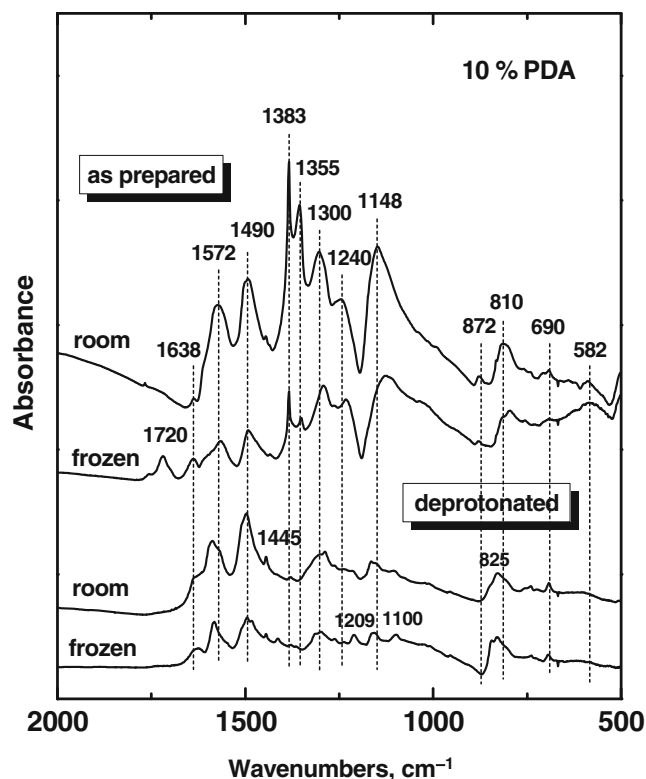


Fig. 7 FTIR spectra of a copolymer of aniline and 10 mol% PDA prepared in liquid 1 M acetic acid at room temperature or in frozen reaction mixture at $-24\text{ }^\circ\text{C}$: as-prepared protonated samples and the bases obtained after deprotonation with 1 M ammonium hydroxide

The bands with maxima at $1,300\text{ cm}^{-1}$ (C–N stretching), $1,240\text{ cm}^{-1}$ (C–N⁺ stretching), and $1,148\text{ cm}^{-1}$ (B–NH⁺=Q stretching involving benzenoid and quinonoid rings) are characteristic of the FTIR spectrum of protonated PANI [46]. A small sharp peak at $1,445\text{ cm}^{-1}$ 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 $1,383\text{ cm}^{-1}$ accompanied with a medium-to-strong band at $1,355\text{ cm}^{-1}$, 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 $1,287\text{ cm}^{-1}$) (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 $1,720\text{ cm}^{-1}$ corresponds to a carbonyl group and the band at $1,638\text{ cm}^{-1}$ 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 $1,720\text{ cm}^{-1}$ disappeared, and the band with maximum at $1,625\text{ cm}^{-1}$ 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 $1,414\text{ cm}^{-1}$. Additional peaks are present in the spectrum of deprotonated sample prepared in frozen mixture. The most pronounced of them is the second maximum at $1,483\text{ cm}^{-1}$, 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 $1,209\text{ cm}^{-1}$ belong, in analogy with PANI, to the C–N stretching vibrations of primary aromatic amines. The aromatic ketones have a medium structured band at $1,300$ – $1,230\text{ cm}^{-1}$ due to the phenyl–carbonyl C–C stretching [47]. The band at $1,100\text{ cm}^{-1}$ 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 $-24\text{ }^\circ\text{C}$, 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 $20\text{ }^\circ\text{C}$, and increased by one order of magnitude when the polymerization took place at $-24\text{ }^\circ\text{C}$.

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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