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# Materials combining conducting polymers and noble metals

Doctoral Thesis

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# **Materiály kombinující vodivé polymery a drahé kovy**

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Ústav makromolekulární chemie  
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This Dissertation describes my original work except where acknowledgement is made in the text. It is not substantially the same as any work that has been or is being submitted to any other University for any degree, diploma or any other qualification.

Prague, 8 February 2013

Patrycja Magdalena Bober

“The greatest joy of life is to accomplish.

It is the getting, not the having.

It is the giving, not the keeping.

I am a firm believer in the theory that you can do  
or be anything that you wish in this world,  
within reason, if you are prepared to make the sacrifices,  
think and work hard enough and long enough.”

*Frederick Banting 1923*

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# Table of Contents

List of the papers constituting the Thesis.....	1
Other papers not included in the Thesis.....	2
The results of the Thesis presented by P. Bober on scientific meetings.....	3
The results of the Thesis presented by co-authors of research papers on scientific meetings .....	4
Abbreviations .....	5
Abstract .....	6
Abstrakt (in Czech).....	7
<b>1. INTRODUCTION .....</b>	<b>8</b>
<b>1.1. Polyaniline .....</b>	<b>8</b>
1.1.1. Chemical and physical properties .....	9
1.1.2. Synthesis .....	10
1.1.3. Applications of polyaniline.....	11
<b>1.2. Poly(<i>p</i>-phenylenediamine) .....</b>	<b>11</b>
<b>1.3. Conducting polymers–noble metals composites .....</b>	<b>12</b>
<b>1.4. Applications of composites materials.....</b>	<b>14</b>
<b>2. AIMS OF THE STUDY .....</b>	<b>15</b>
<b>3. EXPERIMENTAL TECHNIQUES FOR CHARACTERIZATION OF POLYANILINE–SILVER COMPOSITES .....</b>	<b>16</b>
<b>4. RESULTS.....</b>	<b>19</b>
<b>4.1. Reaction medium for preparation of polyaniline–silver composites .....</b>	<b>19</b>
4.1.1. Oxidation in the carboxylic acids solutions .....	19
4.1.2. Oxidation in the sulfonic acids solutions .....	22
<b>4.2. Optimization of reaction time.....</b>	<b>25</b>
4.2.1. Acceleration by <i>p</i> -phenylenediamine .....	25
4.2.2. Oxidation of aniline by mixed oxidants.....	27
<b>4.3. The preparation of conducting polymer–silver composites in liquid and frozen reaction mixture .....</b>	<b>30</b>
<b>5. CONCLUSIONS.....</b>	<b>32</b>
References.....	33
Appendices 1–6	

## List of the papers constituting the Thesis:

1. N. V. Blinova, P. Bober, J. Hromádková, M. Trchová, J. Stejskal and J. Prokeš, *Polyaniline-silver composites prepared by the oxidation of aniline with silver nitrate in the solutions of acetic acid*, **Polymer International**, **59** (2010) 437–446.

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2. P. Bober, J. Stejskal, M. Trchová, J. Hromádková and J. Prokeš, *Polyaniline-coated silver nanowires*, **Reactive & Functional Polymers**, **70** (2010) 656–662.

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6. P. Bober, J. Stejskal, M. Trchová and J. Prokeš, *The preparation of conducting polyaniline-silver and poly(p-phenylenediamine)-silver nanocomposites in liquid and frozen reaction mixtures*, **Journal of Solid State Electrochemistry**, **15** (2011) 2361–2368.

IF 2.131, times cited: 0

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1. P. Bober, J. Stejskal, M. Špírková, M. Trchová, M. Varga and J. Prokeš, *Conducting polyaniline-montmorillonite composites*, **Synthetic Metals**, **160** (2010) 2596–2604.

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3. M. Špírková, P. Bober, J. Kotek and J. Stejskal, *Bi-hybrid coatings: polyaniline-montmorillonite filler in organic–inorganic polymer matrix*, **Chemical Papers**, in press. DOI: 10.2478/s11696-012-0299-z.

4. R. Moučka, M. Mrlik, M. Ilcikova, Z. Spitalsky, N. Kazantseva, P. Bober and J. Stejskal, *Electrical transport properties of poly(aniline-co-p-phenylenediamine) and its composites with incorporated silver particles*, **Chemical Papers**, in press. DOI: 10.2478/s11696-013-0351-7.

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1. P. Bober, J. Hromádková, M. Trchová, J. Stejskal, J. Prokeš, “*The oxidation of aniline with silver nitrate in the solutions of acetic acid to polyaniline-silver composites*”.  
73rd Prague Meeting on Macromolecules (PMM 2009), New Frontiers in Macromolecular Science: From Macromolecular Concepts of Living Matter to Polymers for Better Quality of Life, 5–9 July 2009, Prague, Czech Republic: Book of Abstracts p. 78.
2. P. Bober, M. Trchová, J. Stejskal, “*Polyaniline-silver composites*”.  
International Symposium "Technologies for Polymer Electronics TPE 10", 18–20 May 2010, Rudolstadt, Germany: Book of Abstract p. 188–189.
3. P. Bober, M. Trchová, I. Sapurina, J. Stejskal, “*Preparation and characterization of polyaniline-silver composites*”.  
43rd IUPAC World Polymer Congress "MACRO 2010", 11–16 July 2010, Glasgow, United Kingdom: Book of Abstracts p. 32.
4. P. Bober, M. Trchová, J. Stejskal, “*Polyaniline-silver composites: oxidation of aniline with silver nitrate accelerated by p-phenylenediamine*”.  
European Polymer Federation (EPF 2011), 26 June–1 July 2011, Granada, Spain: CD Abstract T4–035.
5. P. Bober, M. Trchová, J. Stejskal, J. Prokeš, “*Polyaniline-silver composites prepared by the oxidation of aniline with mixed oxidants*”.  
75th Prague Meeting on Macromolecules (PMM 2011), Conducting Polymers 2011, 10–14 July 2011, Prague, Czech Republic: Book of Abstracts p. 103.
6. P. Bober, J. Stejskal, M. Trchová, J. Prokeš, “*Polyaniline-silver conducting composite*”.  
International Workshop on Polymer/Metal Nanocomposites, Nanoworkshop 2011, 20–22 September 2011, Bari, Italy: Book of Abstracts p. 80.
7. P. Bober, J. Stejskal, M. Trchová, J. Prokeš, “*Polyaniline – silver composites*”.  
International Conference on Science and Technology of Synthetic Metals 2012 (ICSM 2012), 8–13 July 2012, Atlanta, USA: Book of Abstracts p. 345.

## The results of the Thesis presented by co-authors of research papers on scientific meetings:

1. M. Trchová, N. Blinova, P. Bober, J. Stejskal, “*The oxidation of aniline with silver nitrate to polyaniline-silver composites*”.  
Matériaux et nanostructures pi-conjugués (MNPC 2009), 20–30 October 2009, Arcachon, France: Book of Abstract p. 93.
2. J. Stejskal, N. Blinova, P. Bober, M. Trchová, J. Prokeš, “*The oxidation of aniline with silver nitrate to polyaniline-silver composites*”.  
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3. M. Trchová, P. Bober, E. Konyushenko, J. Stejskal, “*Deposition of silver nanoparticles inside polyaniline nanotubes*”.  
61st Annual Meeting of the International Society of Electrochemistry, 26 September–1 October 2010, Nice, France: Book of Abstracts p.134.
4. M. Varga, J. Prokeš, P. Bober, J. Stejskal, “*Electrical conductivity of polyaniline/silver nanocomposites*”.  
75th Prague Meeting on Macromolecules (PMM 2011), Conducting Polymers 2011, 10–14 July 2011, Prague, Czech Republic: Book of Abstracts p. 122.
5. M. Varga, J. Prokeš, P. Bober, J. Stejskal, “*Electrical conductivity of silver-content-controlled polyaniline-silver composites*”.  
International Conference on Nanostructured Polymers and Nanocomposites, 24–27 April 2012, Prague, Czech Republic: Book of Abstracts p. 54.
6. M. Varga, J. Prokeš, P. Bober, J. Stejskal, “*Electrical conductivity of polyaniline-silver nanocomposites*”.  
Annual Conference of Doctoral Students (WDS'12), 29 May–1 June 2012, Prague, Czech Republic: Book of Abstracts p. 52–57.
7. J. Stejskal, P. Bober, M. Trchová, J. Prokeš, M. Omastová, “*Hybrid conducting polymer-silver composites*”.  
World Polymer Congress (MACRO 2012), 24–29 June 2012, Blacksburg, USA: poster T104.

## Abbreviations

APS – Ammonium peroxydisulfate

CSA – Camphorsulfonic acid

EB – Emeraldine base

ES – Emeraldine salt

FTIR – Fourier transform infrared spectroscopy

MSA – Methanesulfonic acid

NMP – *N*-methyl-2-pyrrolidone

PANI – Polyaniline

PANI–Ag – Polyaniline–silver composite

PDA – *p*-Phenylenediamine

PPDA – Poly(*p*-phenylenediamine)

PPDA–Ag – Poly(*p*-phenylenediamine)–silver composite

SFA – Sulfamic acid

TEM – Transmission electron microscopy

TSA – *p*-Toluenesulfonic acid

UV–Vis – Ultraviolet–visible spectroscopy

## Abstract

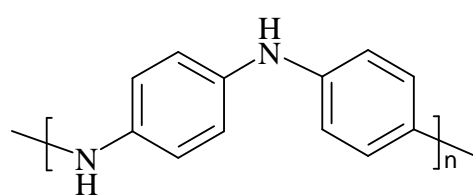
Polyaniline–silver composites combine the electrical properties of metals and the material properties of polymers. Polyaniline is one of the most studied conducting polymers on account of high electrical conductivity (units  $\text{S cm}^{-1}$ ), environmental stability, ease of preparation from common chemicals, good processibility and low cost. Silver is well known because of its highest conductivity among metals ( $500\,000\text{ S cm}^{-1}$ ), antibacterial properties, and low price compared to other noble metals. Aniline was oxidized with silver nitrate in acidic aqueous medium to polyaniline–silver composite. The presence of different organic acids was studied. The most promising became methanesulfonic acid solution, in which most problems (such as inhomogeneity of samples and limited solubility of silver salts) got solved. The oxidation of aniline with silver nitrate is slow and takes over several months to get a reasonable yield. An addition of a small amount of *p*-phenylenediamine, even 1 mol. % relative to aniline, shortens the reaction time to several hours or even to tens of minutes. Small amounts of ammonium peroxydisulfate had similar effect. The content of silver in composites is fixed by the stoichiometry of reaction, and composites always contain  $\approx 70$  wt.% of silver. By using mixed oxidants, silver nitrate and ammonium peroxydisulfate, silver content can be controlled. The molecular structure of composites was characterized by Fourier-transform infrared, Raman and UV–visible spectroscopies. Morphology of the sample was investigated by optical and transmission electron microscopies. Molecular weight was estimated by gel permeation chromatography operating with *N*-methylpyrrolidone and calibrated with polystyrene standards. For measurement of conductivity, four-point van der Pauw method was used. The content of silver was determined by thermogravimetric analysis or by ash. The highest conductivities of composites were of the order of  $1\,000\text{ S cm}^{-1}$ .

## Abstrakt

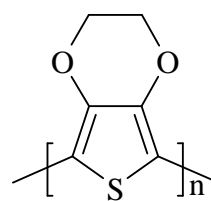
Kompozity polyanilinu se stříbrem kombinují elektrické vlastnosti kovů a materiálové vlastnosti polymerů. Polyanilin je jedním z nejvíce studovaných vodivých polymerů díky vysoké elektrické vodivosti (jednotky  $\text{S cm}^{-1}$ ), stabilitě, jednoduchosti přípravy z běžných chemikálií, dobré zpracovatelnosti a nízkým nákladům syntézy. Stříbro je dobře známo pro svou vodivost, nejvyšší mezi kovy ( $500\,000 \text{ S cm}^{-1}$ ), antibakteriální vlastnosti a nízkou cenu, ve srovnání s jinými drahými kovy. Anilin byl oxidován dusičnanem stříbrným ve vodném kyselém prostředí za vzniku kompozitu polyanilin–stříbro. Byl studován vliv různých organických kyselin a jejich koncentrace. Nejslibnější se ukázala kyselina methansulfonová, pro níž se podařilo vyřešit četné problémy, jako jsou nehomogenita vzorků a omezená rozpustnost stříbrných solí. Oxidace anilinu dusičnanem stříbrným je pomalá a trvá i několik měsíců, nežli se získá přiměřený výtěžek. Přidání malého množství *p*-fenylendiaminu, i jen 1 mol.% relativně vzhledem k anilinu, zkracuje reakční dobu na několik hodin nebo dokonce i desítky minut. Malé množství peroxidvojsíranu amonného má podobný účinek. Obsah stříbra v kompozitu je dán stechiometrií reakce, a kompozity vždy obsahují  $\approx 70$  hm.% stříbra. Použitím smíšených oxidantů, dusičnanu stříbrného a peroxidvojsíranu amonného, lze obsah stříbra ovládat. Molekulární struktura kompozitů byla charakterizována pomocí FTIR infračervené, Ramanovy a UV–viditelné spektroskopie. Morfologie vzorku byla studována optickou a transmisní elektronovou mikroskopií. Molekulová váha byla odhadnuta gelovou permeační chromatografií v *N*-methylpyrrolidonu s použitím polystyrenových standardů. Pro měření vodivosti byla použita čtyřbodová van der Pauw-ova metoda. Obsah stříbra byl stanoven pomocí termogravimetrické analýzy nebo popela. Nejvyšší vodivosti kompozitů dosahovaly řádu  $1\,000 \text{ S cm}^{-1}$ .

## 1. INTRODUCTION

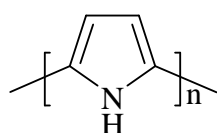
Conducting polymers are organic polymers that conduct electricity; they may exhibit metallic conductivity but usually they are semiconductors. A common feature of conducting polymers is the presence of conjugated double bonds along the polymer backbone. Figure 1 shows some examples of the most important conducting polymers. They possess ability to respond to various stimuli by the change in their optical, electrical, chemical and mechanical properties. During last years, broad range of conducting polymers have been described and studied. In 2000 the Nobel Prize for Chemistry was awarded to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa “for the discovery and development of conductive polymers”.



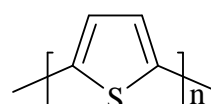
**Polyaniline**



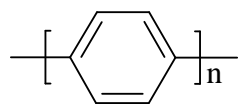
**Poly(3,4-ethylenedioxythiophene)**



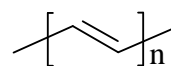
**Polypyrrole**



**Polythiophene**



**Poly(*p*-phenylene)**



**Polyacetylene**

**Figure 1.** Various conducting polymer structures.

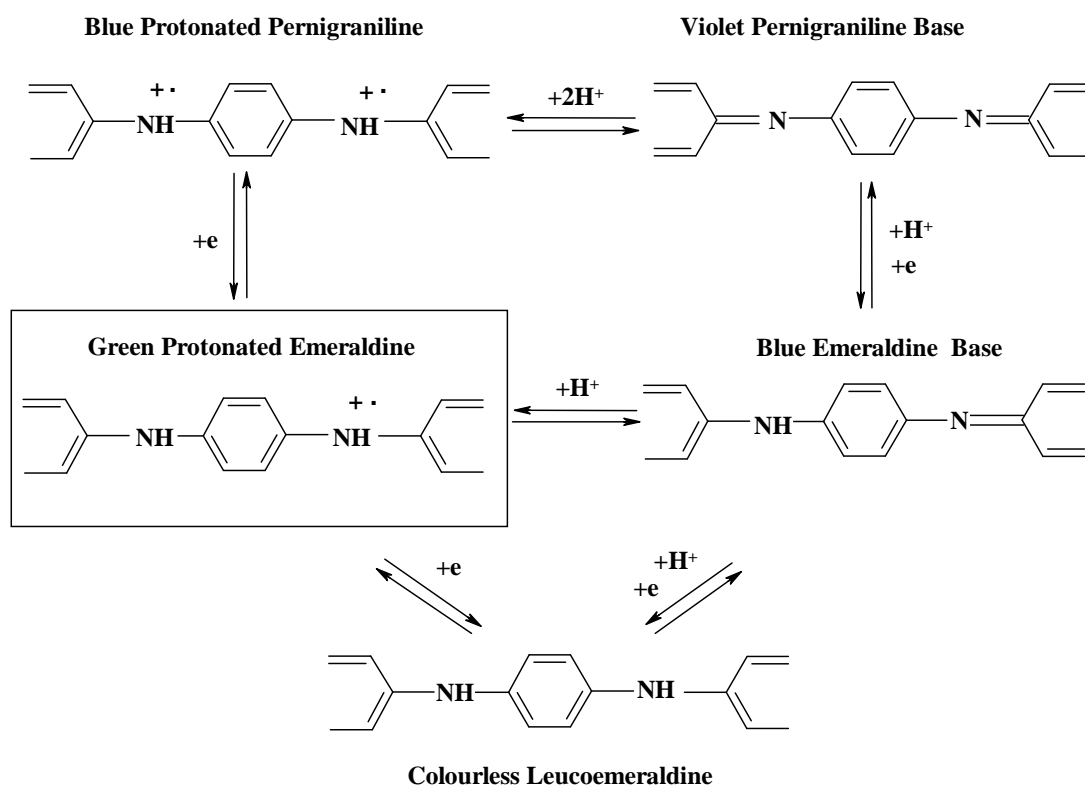
## 1.1. Polyaniline

Polyaniline (PANI) is one of the most famous conducting polymers on account of high electrical conductivity, excellent electronic and optical properties, good redox and ion-exchange activity, environmental stability, ease of preparation from common chemicals, and relatively low cost. Since reported in 1862, when polyaniline was prepared by oxidation of aniline in sulfuric acid for the first time [1], and up to now we can observe growing interest in this polymer (In January 2013 Web of Science lists 18 912 papers about PANI).

### 1.1.1. Chemical and physical properties

Polyaniline exists in a variety of forms [2], differing in the degree of oxidation or extent of protonation (Figure 2). The most important form of PANI, protonated emeraldine, is typically prepared by the chemical oxidation of aniline or anilinium salts, such as aniline hydrochloride or aniline sulfate, with ammonium peroxydisulfate (APS), the most common oxidant, in acidic aqueous medium [2–4]. It is green, stable and conducting (conductivity  $\sigma \approx 4 \text{ S cm}^{-1}$  [5]). Emeraldine salt (ES), however, is difficult to process and it is insoluble in any solvent [6].

The transition of conducting ES to the non-conducting emeraldine base (EB) is located at  $\text{pH} \approx 4\text{--}6$  [7], and the conducting polyaniline salt, such as hydrochloride, converts to the non-conducting base at higher pH. EB is highly stable at room temperature, but non-conducting (conductivity  $\sigma \approx 10^{-9} \text{ S cm}^{-1}$  [5]) and partially soluble in some organic solvents, e.g., *N*-methyl-2-pyrrolidinone (NMP) [8, 9]. Emeraldine can be reduced to colourless leucoemeraldine by phenylhydrazine [10], sodium dithionite [11], hydrazine dihydrochloride [12], etc., or oxidized by strong oxidants to pernigraniline [13, 14].



**Figure 2.** Oxidation and protonation forms of polyaniline [2].

### 1.1.2. Synthesis

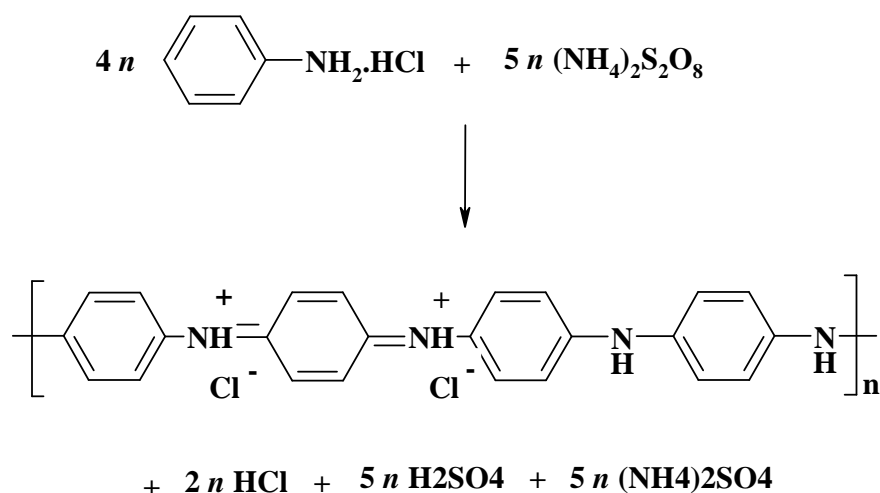
PANI can be prepared by chemical or electrochemical polymerization of monomer. Electropolymerization of aniline can be carried out in acidic aqueous solutions (e.g., sulfuric acid [15, 16], perchloric acid [17], nitric acid [18], phosphoric acid [19], etc.) or organic solvent (e.g., acetonitrile [20–22], dichloromethane [22], etc.) solution galvanostatically at a constant current density or by cyclic voltammetric scanning. The three-electrode cell for electropolymerization contains a working electrode (metals such as platinum or gold, glassy carbon and conductive oxide, e.g., ITO), a counter electrode (the same or different as working electrode) and a reference electrode (e.g., saturated calomel electrode). Polyaniline nanostructures are deposited on the surface of working electrodes as films.

Chemically prepared PANI is usually obtained by the oxidative polymerization of aniline with ammonium peroxydisulfate [2–4], the most common oxidant (Figure 3). A wide range of other oxidants also have been successfully tested, such as iron(III) chloride [23–25], cerium(IV) sulfate [26], potassium iodate [27, 28], potassium



dichromate [29], periodic acid [30], sodium chlorite [31], manganese(IV) oxide [32], copper perchlorate [33, 34], as well as vanadic acid [35]. Occasionally even oxidant mixtures have been used [36]. Silver(I) nitrate has recently become of interest because the oxidation of aniline leads to PANI–Ag composites [37, 38].

Based on polymerization conditions (pH or temperature), PANI can be obtained as precipitates of various morphologies or thin films deposited on a variety of supports [39, 40]. In strongly acidic media granular [41–43] and nanofibrillar [44] nanostructures are gained. The oxidation of aniline at mildly acidic conditions yields PANI nanotubes [42, 43, 45, 46]. Synthesis in alkaline media leads to micro- and nanospheres [42, 43] but, in this case, the products are composed of aniline oligomers only. When polymerization is carried out in the presence of a suitable steric stabilizer, e.g. poly(vinyl alcohol) [47–49], poly(*N*-vinylpyrrolidone) [47], carboxymethylcellulose [50], or hydroxypropyethylcellulose [51], PANI colloids are produced.



**Figure 3.** Oxidation of the aniline hydrochloride with ammonium peroxydisulfate to emeraldine salt.

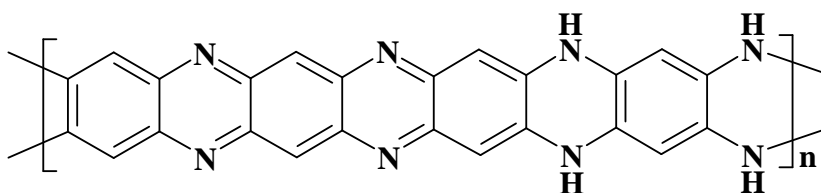
### 1.1.3. Applications of polyaniline

Great variety of properties of PANI has led to a large array of applications that include electromagnetic shielding for computers and other electronic instrumentation [52–55], gas sensors to identify the presence of small quantities of various gases [56], transparent electrodes [57], battery applications [58–60], membranes to separate ions from solutions

[61], potentiometric all-solid-state ion-selective electrodes [62–64], anti-corrosion coatings [65, 66], and many others. For that reason, the fundamental research of PANI is needed.

## 1.2. Poly(*p*-phenylenediamine)

Poly(*p*-phenylenediamine) (PPDA), (Figure 4) belongs to the most frequently studied polyaryldiamines, which show more novel multifunctionality due to free amino groups on the polymer chain [67]. Chemical and electrochemical oxidations of *p*-phenylenediamine are reported in literature [68–71]. Potassium [69, 70] and ammonium [71] peroxydisulfate was usually used as oxidizing agents. Poly(*p*-phenylenediamine) is slightly soluble in most of the common organic solvents [72] and is low conducting semiconductors [69]. To improve conductivity of these materials PPDA was copolymerized with PANI [71] as well as poly(aniline-*co-p*-phenylenediamine)/MWCNT (multi-walled carbon nanotubes) [73], PPDA/MWCNT [74] or PPDA–Ag [75, 76] composites were investigated.

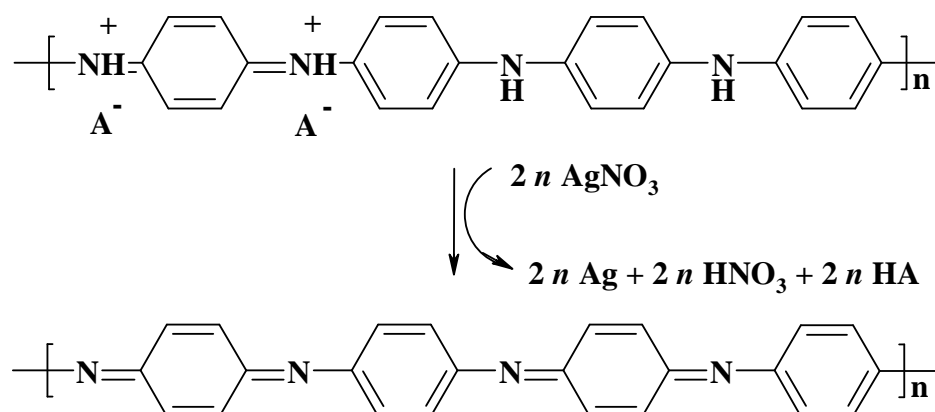


**Figure 4.** Ladder-like phenazine structure of poly(*p*-phenylenediamine) as proposed in the literature [69, 70].

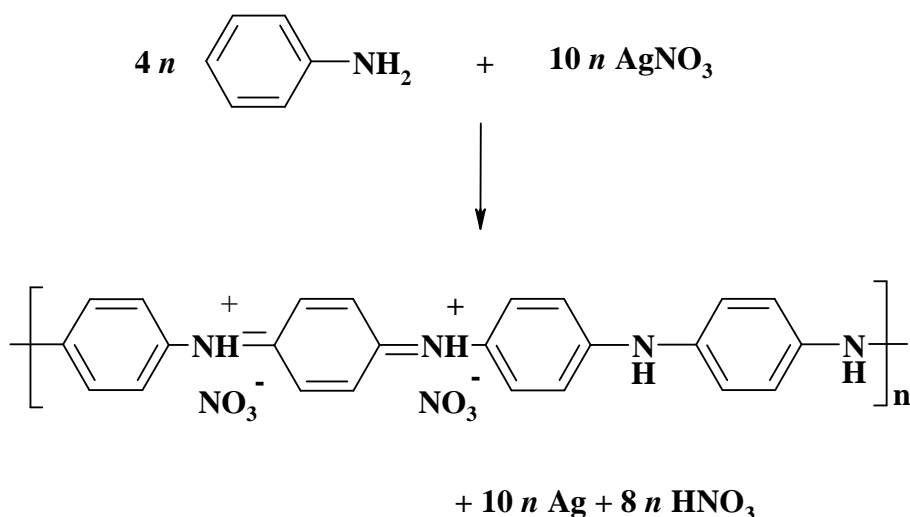
## 1.3. Conducting polymers-noble metals composites

The composites of conducting polymer such as PANI, polypyrrole, PPDA, poly(3,4-ethylenedioxythiophene), and noble metals, e.g., silver, gold or platinum combine materials properties of polymers and electrical properties of metals [37, 38, 77–91]. They also contain two types of electric conductors, conducting polymers are organic semiconductors and metals are metallic conductors. Conducting polymers–noble metals composites can be prepared by five basic ways:

- by the reduction of noble-metal compounds with polymer, such is PANI [81–84] (Figure 5);
- by simple blending of noble metals nanoparticles with conducting polymers [85, 86];
- by the polymerization of monomer in the presence of preformed metal nanoparticles [87, 88];
- by the oxidation of corresponding monomer with noble-metal compounds [38, 89] (Figure 6);
- by the electrodeposition or chemical deposition of metal, such as silver [90], gold [91] or platinum [92] on conducting polymer.



**Figure 5.** Emeraldine salt reduces silver nitrate to metallic silver. It is oxidized to the pernigraniline form at the same time [84].



**Figure 6.** Aniline is oxidized with silver nitrate to polyaniline nitrate. Metallic silver is produced at the same time; nitric acid is a by-product [38].

In the last years, the interest in polyaniline–silver composite is growing (Web of Science lists 169 papers); the presence of silver still improving their conductivity. Silver exhibits the highest electrical and thermal conductivities among all the metals; conductivity  $\sigma = 6.3 \times 10^5 \text{ S cm}^{-1}$  at  $20^\circ \text{C}$  [93], and it has relatively low cost compared to other noble metals. Silver can be present in the composites as microspheres, nanotubes, nanofibers, nanorods or nanowires, or various microparticles [38, 48, 88]. Electrical properties of such composites can be determined by the proportion of both components or by their morphology [94].

#### 1.4. Applications of composite materials

Composites materials based on conducting polymer and noble metals are potentially useful in many applications. The most obvious is the metal recovery from the industrial waste waters [95] that produces such composites. PANI is able to reduce silver ions from the aqueous solution of their compounds to metallic silver [96, 97]. Silver is well known for its antibacterial properties [98] and a similar activity has been reported for PANI [99, 100]. The combination of silver nanoparticles and PANI has a synergistic antimicrobial efficiency on *Escherichia coli*, gram-positive *Staphylococcus aureus* and

fungous yeast bacteria [101]. Incorporation of silver may be also a source of modified selectivity or sensitivity of various sensors. Gas sensors have a wide range of applications, such as industrial production, food processing, environmental monitoring, health care, etc. PANI–Ag composites have been offered in the literature as sensors for acetone [102], ethanol [84], toluene [103] and ammonia [104] vapors. The incorporation of silver nanoparticles into PANI reduced the response time of the order of tens of minutes. It is well known that PANI has been proved to catalyze various organic reactions, and similar effect is expected from PANI composites. For example, the electrocatalytic activities of PANI–Ag materials have been tested for the determination of hydrazine in environmental samples within the concentration range of 20–100  $\mu\text{M}$  [105]. Usually conducting polymers have high specific capacitance values and can be an alternative in the development of energy-storage devices. The PANI–Ag composite with ultrahigh specific capacitance, higher than that of PANI alone and stability with 94 % retention of its original capacitance after 2000 cycles have been reported [106]. Composite materials containing silver particles can be also used in neural tissue engineering, artificial muscles, and various monitoring devices [107], conducting printing inks [108] and many others.

## **2. AIMS OF THE STUDY**

The main focus of this Thesis was to develop new highly conducting hybrid composites containing conducting polymers, especially PANI, and noble metal, such as silver. The specific aims of the study were to prepare materials which should be:

- high conducting (conductivity  $> 10^3 \text{ S cm}^{-1}$ );
- produced in reasonable time (hours);
- macroscopically homogenous;
- not contaminated by other components, e.g., insoluble silver salts.

In order to carry out these tasks, PANI–Ag composites were prepared. Different types of acidic media (acetic, formic, camphorsulfonic, methanesulfonic, sulfamic, or toluenesulfonic acid solutions) have been investigated. Only methanesulfonic acid

solution, however, was found to be a good medium for the preparation of PANI–Ag composites. Aniline was oxidized with silver nitrate using a one-step reaction procedure. Highly conducting materials (conductivity  $\sigma = 880 \text{ S cm}^{-1}$ ) with satisfactory yield were obtained. Adding of the small amount of *p*-phenylenediamine as was expected to reduce the reaction time from a few months to several hours. In order to obtain composites with different amount of silver particles, mixture of two oxidants, silver nitrate and APS have been studied. Possible application has been proposed.

Obtained PANI–Ag composites have been studied by array of methods in order to understand the relation between electrical properties and molecular, macromolecular, or supramolecular structure. Molecular structure was analyzed by UV–Vis, FTIR and Raman spectroscopies. To determine the molecular weight, gel permeation chromatography was used. Optical, scanning and transmission electron microscopies were employed to study the supramolecular structures and morphology. Materials properties have been studied by thermogravimetric analysis (TGA), conductivity and its temperature dependence, and density measurements.

The present Thesis consists of six papers published in international journals (Appendices 1–6) with an extended introduction and a discussion of the content of the papers. Another two papers have been published but have not been included in the present Thesis. Finally, another two papers have been accepted for the publication in the special issue of the Chemical Papers dedicated to PANI.

### **3. EXPERIMENTAL TECHNIQUES FOR CHARACTERIZATION OF POLYANILINE–SILVER COMPOSITES**

- **Ultraviolet–visible (UV–Vis) spectroscopy**

UV-Vis spectroscopy is an absorption or reflectance spectroscopy used to obtain the absorbance spectra of a compound in solution or as a solid. The UV-Vis region of energy for the visible spectrum covers 1.5–6.2 eV, which corresponds to a wavelength range of 200–800 nm. When light is absorbed by a material, valence electrons are promoted from their normal states to higher energy states. The fact that PANI has been

obtained can be confirmed by UV-Vis spectra, when PANI base is dissolved in *N*-methylpyrrolidone, by the observation of absorption maximum at  $\approx 630$  nm [110].

- **Fourier transform infrared (FTIR) spectroscopy**

FTIR spectroscopy is an analytical tool used to identify molecular components and their structures by measuring the absorption of infrared radiation by the material in dependence on wavenumber. The position of the peaks in the spectrum is a direct indication of the molecular structure of the material constituting the sample. Infrared spectra of PANI–Ag components were recorded in the range  $400\text{--}4000\text{ cm}^{-1}$ . Samples were dispersed in potassium bromide and compressed into pellets.

- **Raman spectroscopy**

Raman spectroscopy is based on inelastic Raman scattering of monochromatic light, usually from a laser (in the present case 633 nm He-Ne laser) in the visible, near infrared, or near ultraviolet region. This method provides information about molecular vibrations that can be used for sample identification and quantitation.

- **Transmission electron microscopy (TEM)**

TEM image is formed from the interactions of the electron beam which travels through the specimen. The electron microscope operates on the same basic principles as the light microscope; however, TEM is capable of imaging at a significantly higher resolution due to the shorter wavelength of electrons ( $0.02\text{--}0.05$  nm). In present study also optical and scanning electron microscopies have been used, however TEM is better suited for the morphology assessment because of higher contrast between polymer phase and silver.

- **Gel permeation chromatography (GPC)**

GPC is a technique commonly used in polymer science for determination of polydispersity index (PDI) and molecular weight of polymers. GPC is a separation technique based on hydrodynamic volume. Analysis by GPC is first performed by measuring a series of standards of known molecular weight (usually polystyrene standards), and then the calibration curve is created based on the retention times for these standards. PANI–Ag composite was converting to corresponding base and solubilized in NMP. It should be stressed that it was just part of the product which is soluble, which was characterized; the solubility of PANI was not complete.

- **Conductivity**

Electrical conductivity is a materials ability to conduct an electric current. Room temperature conductivity was determined by a four-point method in van der Pauw arrangement on pellets compressed at 700 MPa with a manual hydraulic press. The sample has a flat shape of uniform thickness, no holes or defects and it is homogeneous. When the conductivity of the samples was below  $10^{-3} \text{ S cm}^{-1}$ , a two-point method was applied. Before such measurements, circular gold electrodes were deposited on both sides of the pellets including ring electrode allowing to measure both, surface as well as volume resistivity.

- **Thermogravimetric analysis (TGA)**

TGA is used to measure the rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Analysis of composites was performed in a  $50 \text{ mL min}^{-1}$  air flow at heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  to determine the content of silver in samples. The TGA curves provide also additional information about the composition of the oxidation products. In the present case, silver content in the composites corresponds to the residue after the analysis.

All characterization techniques have been used in the cooperation with research teams represented usually by co-authors of the published papers. These were Dr P. Holler (GPC), Dr J. Kovářová (TGA), J. Hromádková (microscopy), Dr M. Trchová (FTIR and Raman spectroscopies) from the Institute of Macromolecular Chemistry, and Dr J. Prokeš and Mgr. M. Varga (electrical measurements) from Charles University in Prague. Their help and enthusiasm is thankfully acknowledged.



## 4. RESULTS

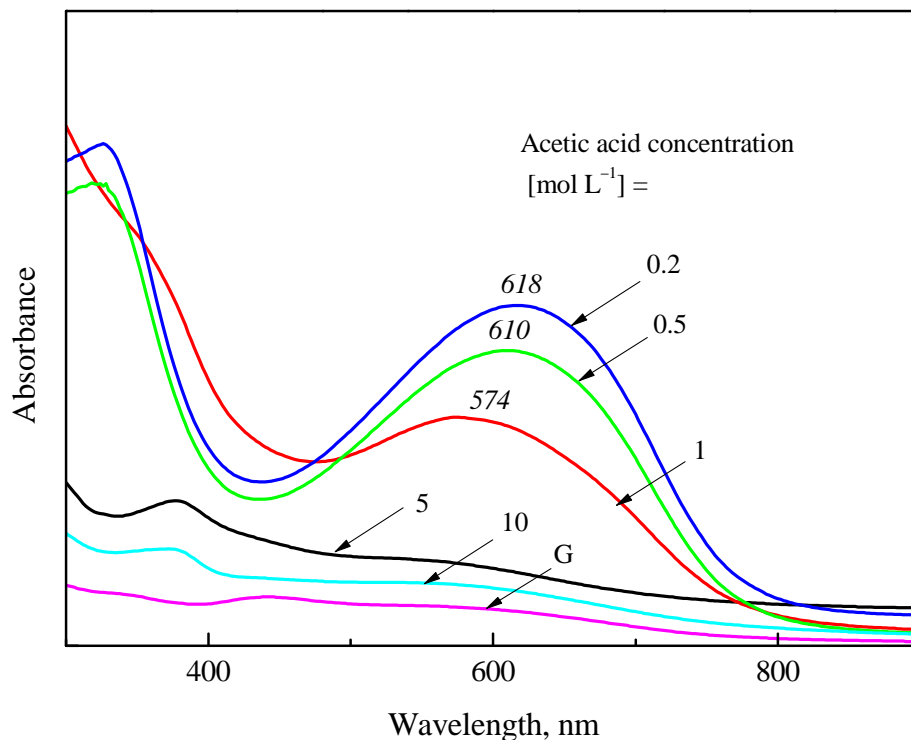
### 4.1. Reaction medium for preparation of polyaniline–silver composites

The oxidation of aniline with silver nitrate is the most direct way to obtain PANI–Ag composites [38]. In this way two non-conducting chemicals, dissolved in acidic aqueous medium yield a mixture of two conductors, PANI and silver. The oxidation of aniline has to be carried out in strongly acidic media [109],  $\text{pH} < 2.5$ , in order to produce the conducting form of PANI. As most acids precipitate silver ions, the choice is limited mainly to nitric, carboxylic or sulfonic acids. The polymerization in the presence of nitric acid leads to PANI–Ag composites with conductivity of the order  $10^3 \text{ S cm}^{-1}$ , has been demonstrated in the literature [38]. The sample, however, was not homogenous, and contained macroscopic silver flakes and the reaction was slow.

#### 4.1.1. Oxidation in the carboxylic acids solutions

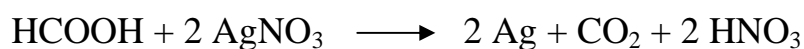
Carboxylic acids are the most common type of organic Brønsted acids because they are proton donors, characterized by the presence of at least one carboxyl group. The simplest examples are formic acid,  $\text{H}\cdot\text{COOH}$ , and acetic acid,  $\text{CH}_3\cdot\text{COOH}$ . Due to successful oxidation of aniline with APS in acetic acid solution to PANI [111], these solutions have been selected as reaction media for the oxidation of aniline with silver nitrate [**Appendix 1**]. Concentration of monomer and oxidant was fixed: 0.2 M aniline was polymerized with 0.5 M silver nitrate in the aqueous reaction medium containing various concentrations of acetic acid (from 0 to 99%) for four weeks. UV–Vis spectroscopy clearly demonstrated that true PANI–Ag composites have been produced only at moderate concentration of acetic acid, 0.2–1 mol  $\text{L}^{-1}$  (Figure 7). The absorption maxima are close to 630 nm, typical of standard PANI base [14]. Products prepared at high acid concentration contained mainly aniline oligomers. This is confirmed also by FTIR and Raman spectroscopies. They reflect also in the presence of silver acetate, formed in the reaction mixture. The highest conductivity,  $3550 \text{ S cm}^{-1}$ , was found for the sample prepared in 1 M acetic acid. It is tempting to associate this result with the presence of silver nanowires. The decisive role of the silver in the conductivity of composites is also proved by the temperature dependences, which correspond to metallic character of the samples. Polyaniline was present as nanotubes or nanobrushes composed of thin nanowires, as well as other morphological objects. Silver is produced

mainly in clusters of nanoparticles having 30–50 nm size, nanowires or nanorods about 80 nm thick, uniformly coated with PANI, and as the marble-like texture decorating some objects.

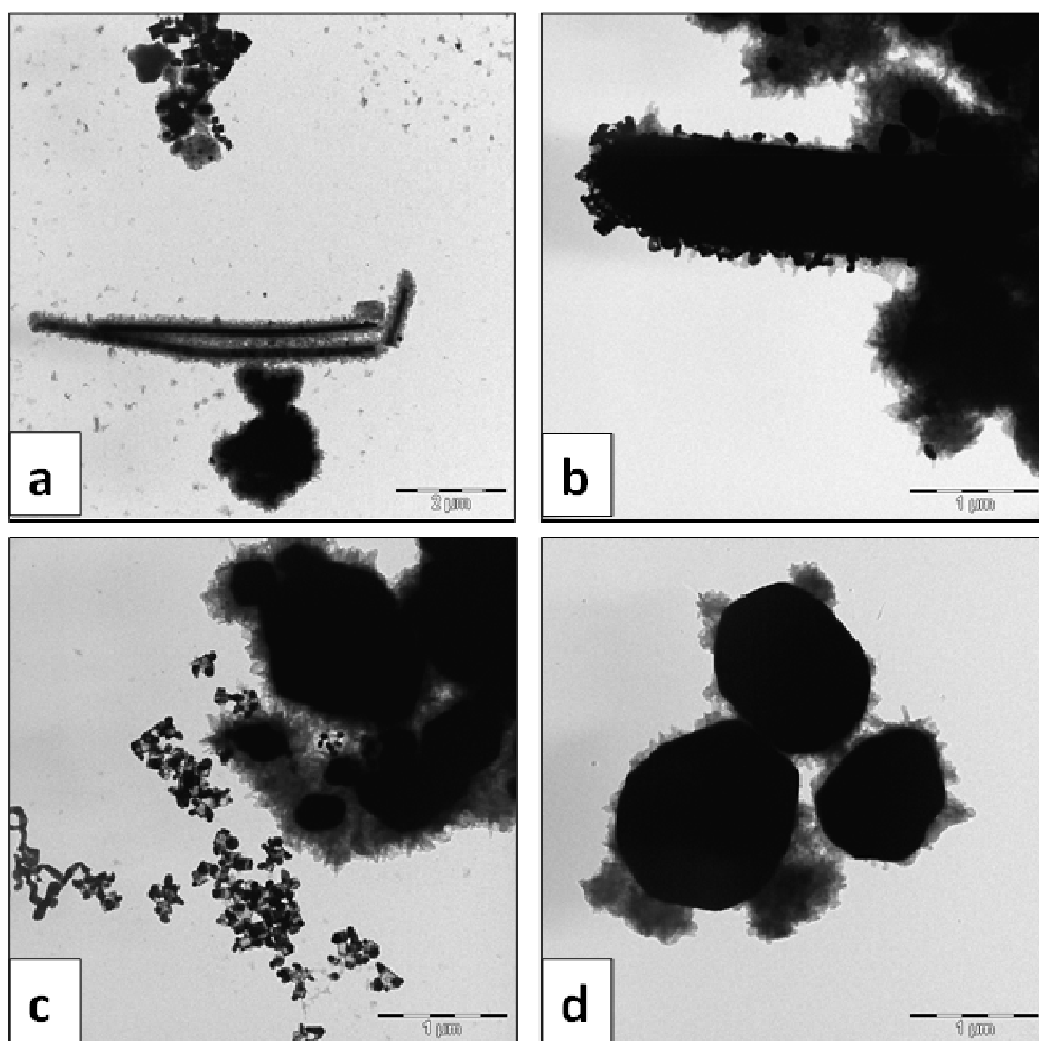


**Figure 7.** The UV–Vis spectra of the oxidation products converted to the corresponding bases and dissolved in *N*-methylpyrrolidone prepared by the oxidation of 0.2 M aniline with 0.5 mol M silver nitrate in the solutions of acetic acid of various concentrations. G stands for glacial acid. The molar concentration of acetic acid is shown at the individual curves [Appendix 1].

On account of notable fraction of aniline oligomers in the samples, in next series of experiments, formic acid solutions have been chosen as reaction media [Appendix 2]. In the contrast to acetic acid, however, formic acid is able to reduce silver nitrate to metallic silver, similarly to aniline. This makes the reaction chemistry rather complex. When silver nitrate was dissolved in 99 % formic acid, exothermic reaction took place and red colour of colloidal silver nanoparticles was observed:



When the solution of formic acid was diluted and aniline was added, this reaction was inhibited. The formation of PANI–Ag composites was confirmed by UV–Vis, FTIR and Raman spectroscopies. The conductivity of the composites varies between  $10^{-2}$  and  $10^1$  S  $\text{cm}^{-1}$  orders of magnitude. After the deprotonation of PANI to its non-conducting base form; the high conductivity of resulting composites suggests that the conductivity is controlled rather by silver than by PANI. At low concentration of formic acid silver nanowires of 20–80 nm in diameter coated with PANI nanobrushes of 50–150 nm thick were produced (Figure 8a). With increasing of acid concentration, the silver nanowires become less frequent and at high acid concentration silver particles in the similar size-range, also covered by PANI, dominated (Figure 8).

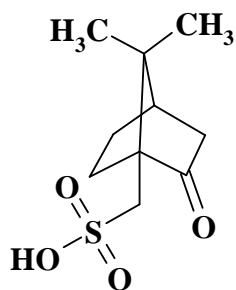


**Figure 8.** The product of the oxidation of aniline with silver nitrate in (a) 0.1, (b) 0.5, (c) 1.0, and (d) 5.0 M formic acid [Appendix 2].

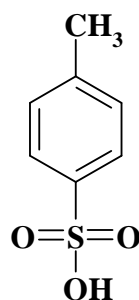
The polymerization using acetic and formic acids solutions as reaction media leads to PANI–Ag composites, however, the products still suffer some drawbacks, e.g., the homogeneity of samples was poor. Also in the case of acetic acid, the samples contain silver acetate as impurity. On the other hand, the samples prepared in the presence of formic acid had low conductivity, which still needs to be improved.

#### 4.1.2. Oxidation in the sulfonic acids solutions

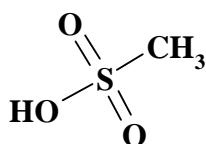
Based on preliminary results the 1 M solution of sulfonic acids seems to be the most promising medium. This acid does not precipitate silver ions and provides sufficient acidity of the reaction medium [Appendix 3]. Four sulfonic acids have been selected:



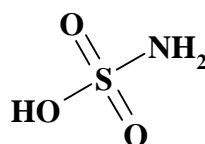
**Camphorsulfonic acid**



**Toluenesulfonic acid**



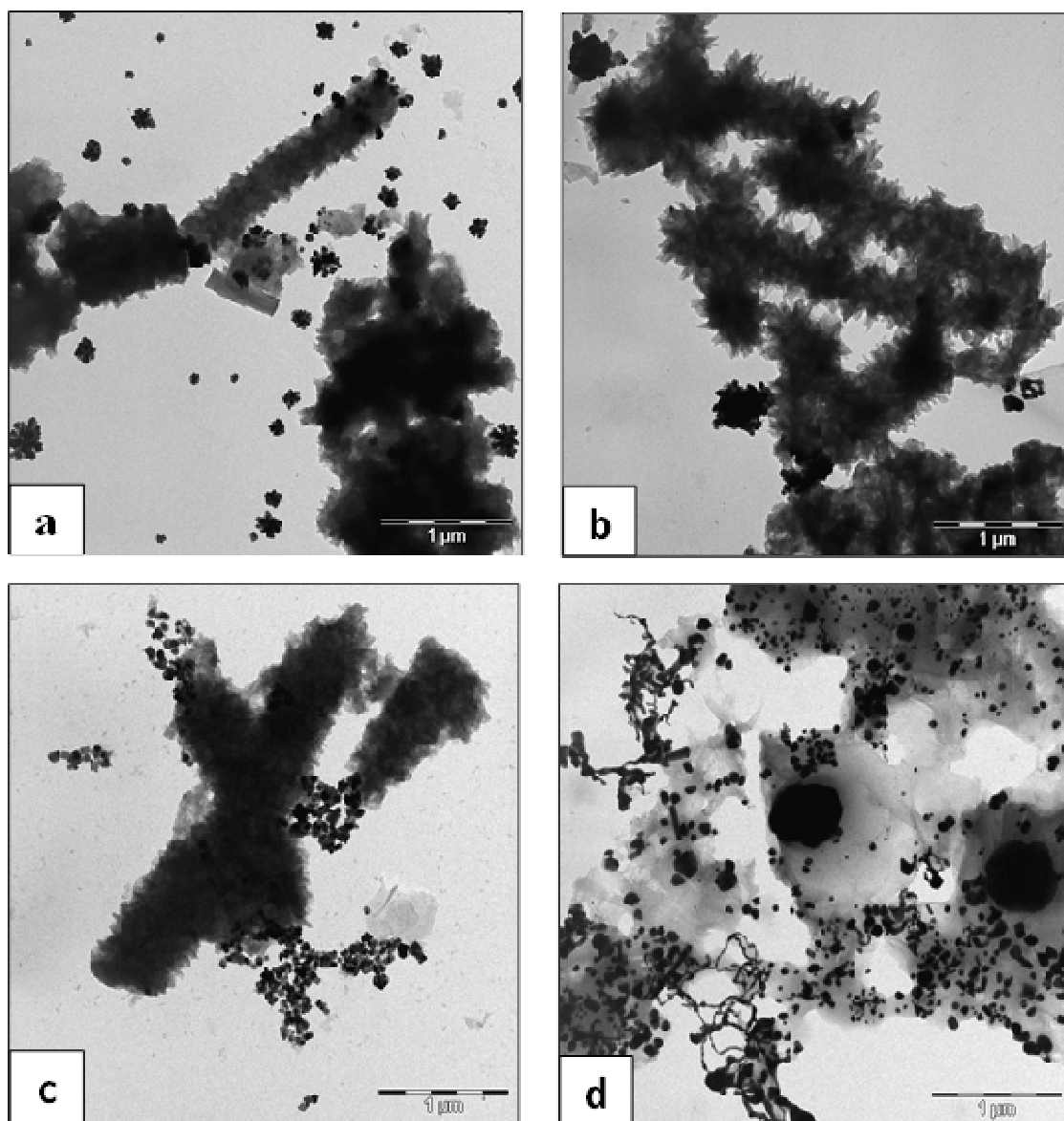
**Methanesulfonic acid**



**Sulfamic acid**

The reaction media containing camphorsulfonic (CSA), *p*-toluenesulfonic (TSA) and methanesulfonic acid (MSA) gave products of comparable yield, 77–87 % (Table 1) with respect to the calculated expectation for full conversion. The content of silver was 63–69 wt%, except the product obtained in the solution of sulfamic acid (SFA). The reason for different content of silver in the solution of SFA is obviously the different character of this acid compared to other three sulfonic acids. The presence of amino group in sulfamic acid reduces the acidity, compared with other sulfonic acids, and the reaction conditions are not favorable for the polymerization of aniline. The morphology

of both PANI and silver was rich. Silver is usually present as nanoparticles with a broad particle-size distribution; PANI forms mostly hairy nanorods of 150–250 nm in diameter (Figure 9). The reaction in MSA solution resulted in the best of PANI–Ag composites reaching the conductivity of  $880 \text{ S cm}^{-1}$ . The conductivity decreased with increasing temperature, typical behavior for metals, illustrating the dominating role of



**Figure 9.** Transmission electron microscopy of polyaniline–silver composites prepared in 1 M (a) camphorsulfonic acid, (b) methanesulfonic acid (c) sulfamic acid and (d) toluenesulfonic acid [Appendix 3].

silver in conduction. Other composites exhibited conductivity at the level of PANI alone and the contribution of silver to the conductivity was not observed. Composites prepared in MSA solution had good conductivity and high yield, as well as the best homogeneity among other composites which had been prepared. The long time needed for the synthesis, however, can be regarded as a serious drawback.

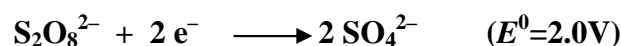
**Table 1.** Yield, composition, conductivity, and density of PANI–silver composites prepared in solutions of camphorsulfonic, methanesulfonic, sulfamic, or toluenesulfonic acids.

Acid	Yield, g g <sup>-1</sup> aniline	Yield, % theory	Composition, wt.% Ag	Conductivity, <sup>a</sup> S cm <sup>-1</sup>	
				Salt	Base
CSA	3.43	81	63	1.7 (1.5)	2.1×10 <sup>-9</sup>
MSA	3.27	77	69	880 (709)	0.003
SFA	0.5	12	12	42 (25)	0.018
TSA	3.69	87	69	1.4 (0.86)	2.2×10 <sup>-10</sup>

<sup>a</sup> In air. Values in parentheses were measured in vacuum.

#### 4.2. Optimization of reaction time

The oxidation of aniline with silver nitrate is slow and takes over several months to get a reasonable yield [38, **Appendices 1–3**]. This can be explained in part by the differences in the standard reduction potential of silver nitrate and APS:

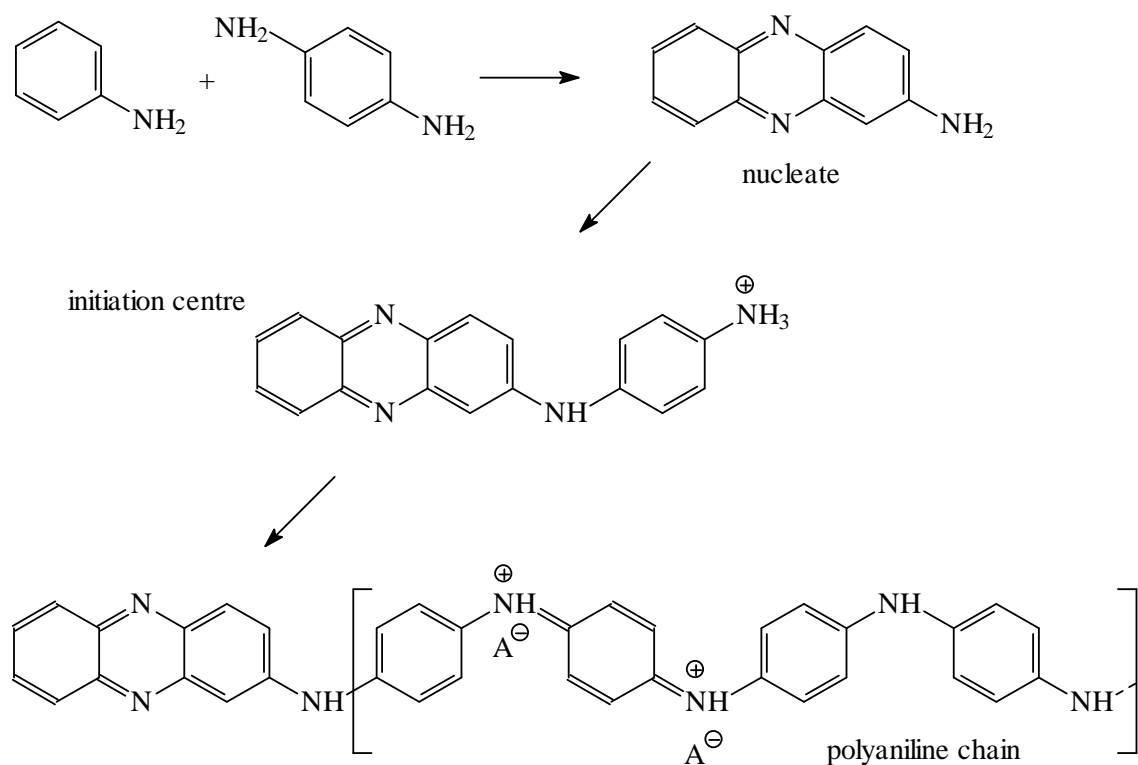


Several groups have been trying different strategies to accelerate this reaction by *physical* means, such as heating [112], irradiation with UV–Vis [24, 108, 113] or  $\gamma$ -rays

[114], or ultrasonic agitation [37]. The present Thesis concentrated on the *chemical* alteration of the reaction.

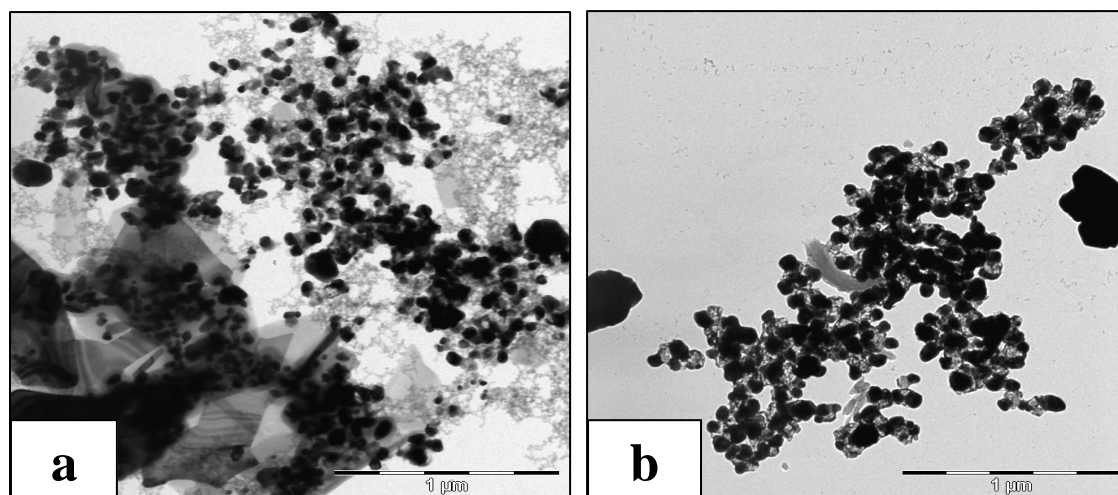
#### 4.2.1. Acceleration by *p*-phenylenediamine

Addition of small amounts of *p*-phenylenediamine (PDA), a few percent relative to aniline, can accelerate oxidation of aniline with APS in both the chemical and the electrochemical oxidations [51, 115–117]. Similar accelerating approach has been applied when silver nitrate was used as oxidant [Appendix 4]. An addition of a small amount of PDA, even 1 mol. % relative to aniline, shortens the reaction time to several hours or even to tens of minutes. Higher concentration of PDA produces conducting copolymer composites. Also *p*-phenylenediamine alone is similarly able to be oxidized to poly(*p*-phenylenediamine) and produce a composite with silver.



**Figure 10.** The role of *p*-phenylenediamine in the oxidation of aniline: the possible formation of a phenazine-containing nucleate, and of an initiation centre that starts the growth of a polyaniline chain having a phenazine head and polyaniline tail.  $\text{A}^-$  is an arbitrary anion [Appendix 4].

The formation of any polymer has three important phases: (1) the initiation, (2) the chain propagation, and (3) the termination, which also applies to the preparation of PANI. The conditions for the propagation step are satisfied by the sufficient acidity of the medium ( $\text{pH} < 2.5$ ) but the polymerization still does not take place. This means that the initiation is too slow. We proposed that PDA alters the formation of initiation centers, increases their number, and thus promotes the polymerization of aniline (Figure 10). This happens especially in 1 M nitric acid. In 1 M acetic acid, the acceleration concerns rather the formation of oligomers because of the lower acidity of the medium. The acceleration of aniline oxidation with silver nitrate by small amounts of PDA opens a new route to the preparation of PANI–Ag composites. The composites are produced in high yield and in short reaction times of some tens of minutes.

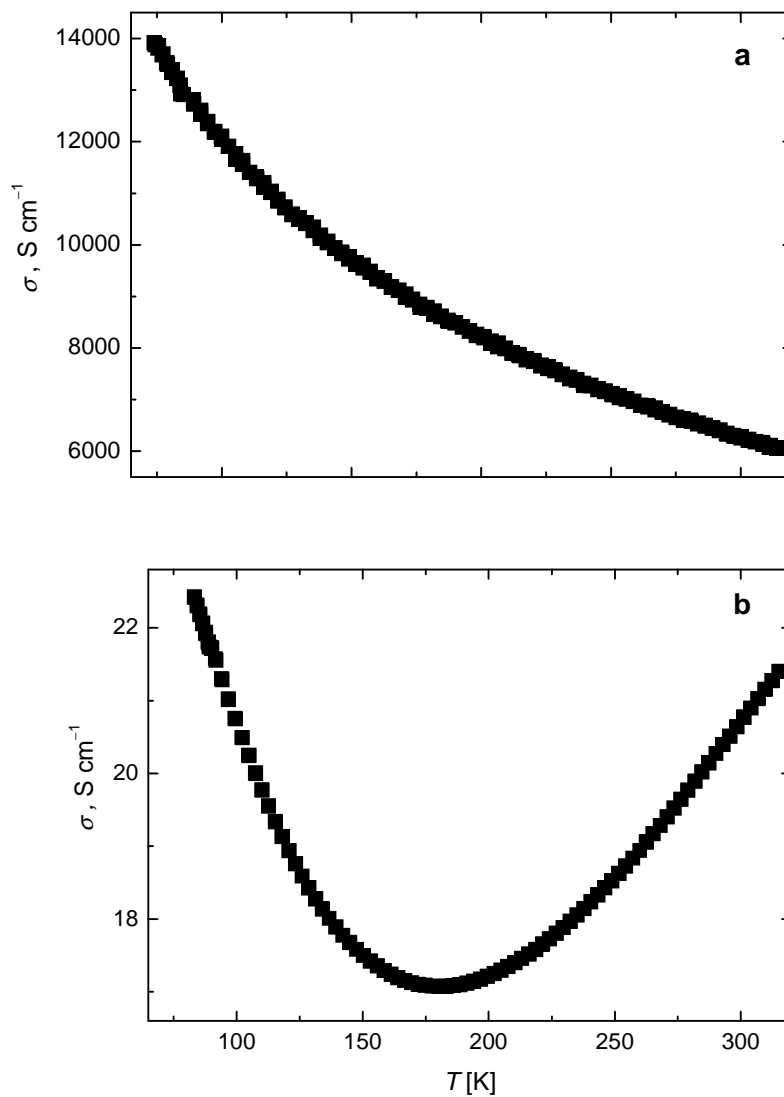


**Figure 11.** Micrographs of composites prepared with (a) 5 mol% *p*-phenylenediamine and (b) 60 mol% *p*-phenylenediamine mixtures with aniline in 1 M acetic acid, using silver nitrate as oxidant [Appendix 4].

Silver is present in all composites as nanoparticles of ~50 nm size and as larger objects (Figure 11). The composites had conductivity in the range of the order of  $10^{-3}$  to  $10^3$  S  $\text{cm}^{-1}$  at comparable content of silver, which was close to the theoretical expectation (Figure 3), 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 composite with conductivity of the order of  $10^2$ – $10^3$  S  $\text{cm}^{-1}$  behave like metals (Figure



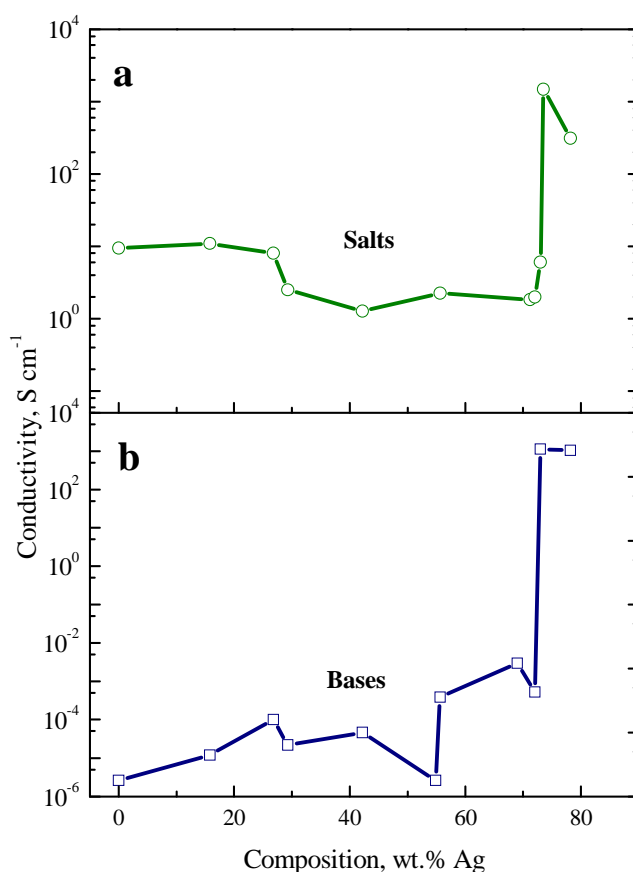
12a, conductivity decreases with temperature). Composites having a moderate conductivity of the order of  $10^1 \text{ S cm}^{-1}$ , which behave as metals at low temperature, and as semiconductors at room temperature (Figure 12b). As a result, the conductivity becomes virtually independent of temperature.



**Figure 12.** Temperature dependences of the conductivity,  $\sigma$ , of PANI-silver composites prepared (a) with 1 mol.% *p*-phenylenediamine and (b) 10 mol.% *p*-phenylenediamine in 1 M acetic acid [Appendix 4].

#### 4.2.2. Oxidation of aniline by mixed oxidants

The addition of the small amount of APS along with silver nitrate also efficiently accelerates the oxidation of aniline [Appendix 5]. Aniline was oxidizing with mixtures of APS and silver nitrate to PANI–Ag composites in 1 M MSA medium. The use of mixed oxidants, silver nitrate and ammonium peroxydisulfate in various proportions, thus allows for the control of composite composition from zero (APS oxidant only) to ~70 wt.% silver (silver nitrate oxidant only). The composites had conductivity of the order of  $1 \text{ S cm}^{-1}$ , however the composites with high silver content have conductivity of the order of  $10^2$ – $10^3 \text{ S cm}^{-1}$  (Figure 13). In most cases, the PANI determined the conductivity of the composite and only at high proportions of silver, its role in the composites manifested itself.

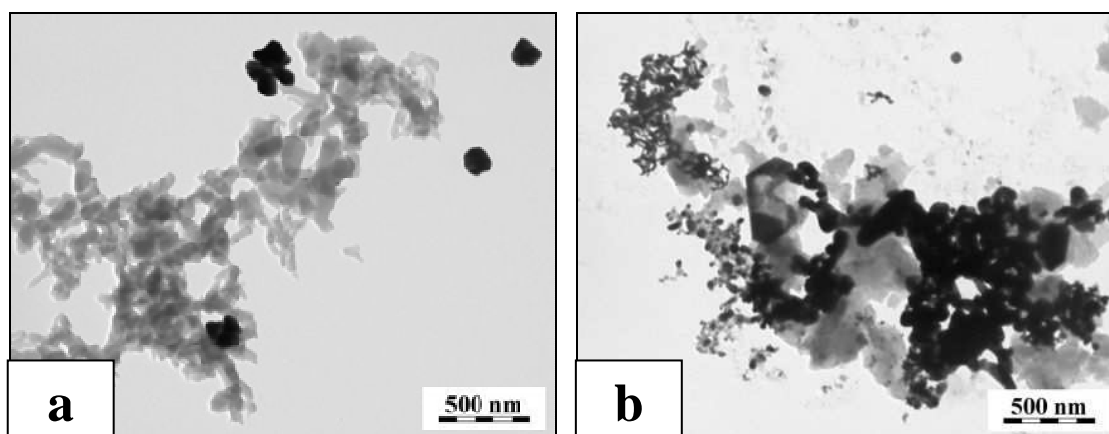


**Figure 13.** The dependence of the conductivity of (a) salt and (b) base forms of polyaniline–silver composites prepared in 1 M methanesulfonic acid on the weight fraction of silver in the protonated form of the composite [Appendix 5].

In some cases, when emeraldine salt was converted to base, conductivity of composites increased. This was surprising, as the former form is conducting and the latter is not. A similar effect has been observed earlier [Appendix 2], when aniline was oxidized with silver nitrate in the presence of formic acid, as well as in the case of PPDA–Ag composites [76]. There are two explanations offered:

- The presence of insulating interfacial barriers, such as silver oxide, covering silver particles, resulting in reduced efficiency in formation of conducting pathways [118]. These barriers can be dissolving in ammonia solution during deprotonating of PANI–Ag composites.
- A shift in composition and percolation principle. During the deprotonation of PANI, the acid is removed from the sample and the PANI mass decreases, and consequently, the content of silver increased. This means that poorly conducting sample below percolation limit may shift to or above this limit with associated increase in conductivity.

The sample prepared with APS has nanofibrillar morphology in place of granular form, typical for standard PANI [41–43]. With the increasing of silver nitrate as oxidant the silver nanoparticles around  $\approx 100$  nm become more frequent (Figure 14).

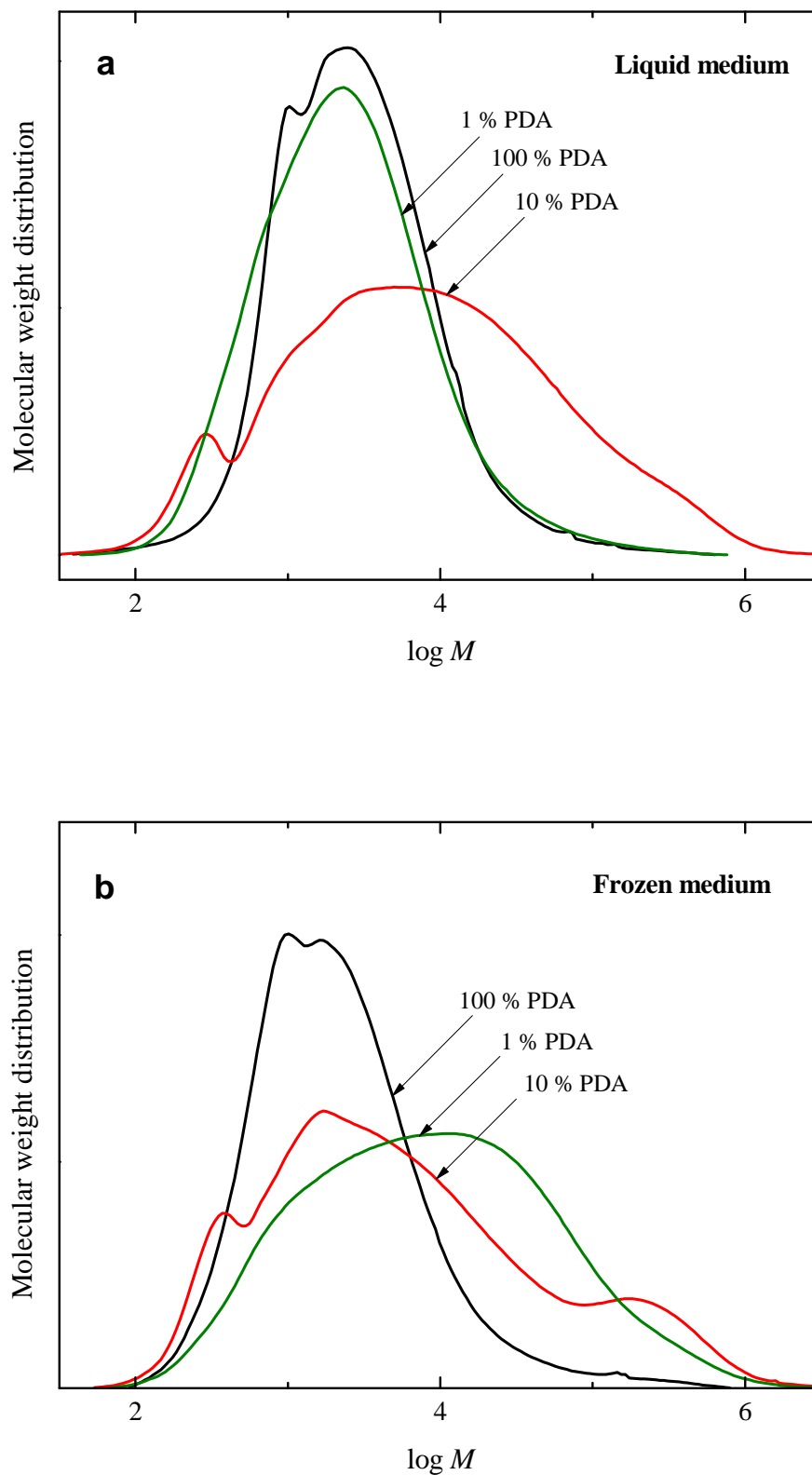


**Figure 14.** Transmission electron microscopy of the polyaniline–silver composites prepared in 1 M methanesulfonic with the various oxidant mole proportions, (a)  $p = 0.1$  (ammonium peroxydisulfate-rich system) and (b) 0.8 (silver nitrate-rich system) [Appendix 5].

### 4.3. The preparation of conducting polymer–silver composites in liquid and frozen reaction mixture

The oxidative polymerization of aniline proceeded not only at room temperature (20 °C) but also in frozen reaction mixture, even at –50 °C [119]. The polymerizations carried out at reduced temperature provided PANI with a higher molecular weight and degree of crystallinity [120]. Also the increasing of the molecular weight of the polymer can increase the conductivity of the PANI matrix incorporating silver nanoparticles [119, 121]. In the present study, we compared properties of products prepared in liquid and frozen (–24 °C) reaction mixture [**Appendix 6**]. Three systems have been selected, based on previous results: (1) the oxidation of aniline accelerated with 1 mol% amount of PDA, (2) a copolymer of aniline with 10 mol% PDA, and (3) PDA alone.

The composites of PANI–Ag or PPDA–Ag have been produced at 20 °C and –24 °C with comparable content of silver, ≈67–74 wt.%. The yields decrease in lower temperature. PANI–Ag composite having the conductivity of the order of  $10^3 \text{ S cm}^{-1}$  was obtained. The molecular weight of polymers was of the order of  $10^3$  (Figure 14), 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 leads to the decrease in conductivity. This can be explained by the fact that copolymerization of aniline with PDA results in the reduced PANI-chain conjugation. Such sample had a metallic type of conductivity at low temperatures and semiconductor behavior at room temperature. The oxidation of PDA alone was fast, the yield was high, but the molecular weight was only of the order of thousands, i.e. at the oligomer level. When the oxidation took place in ice, the conductivity of PPDA–Ag composite was even higher than that of PANI–Ag. This is surprising because PPDA is regarded as non-conducting polymer, in the contrast to conducting PANI.



**Figure 14.** 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 [Appendix 6].

## 5. CONCLUSIONS

- The oxidation of aniline with silver nitrate yields polyaniline–silver composites; two non-conducting reactants generate two conducting products. The reaction media containing acetic, formic, camphorsulfonic, methanesulfonic, toluenesulfonic or sulfamic acid has been investigated. Methanesulfonic acid does not precipitate silver ions even at high concentrations when silver nitrate was used as oxidant. For that reason, it was selected as the most promising reaction medium.
- The reaction requires acceleration (small amount of *p*-phenylenediamine or ammonium peroxydisulfate) for its efficient use. 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 centres that start the growth of PANI chains in the media of sufficient acidity, such as 1 M nitric acid.
- The highly conducting composites,  $10^3 \text{ S cm}^{-1}$ , have been prepared. They require the content of silver to be above the percolation limit, at 70–80 wt.% silver. The direct oxidation of aniline with silver salts seems to be the most efficient way how to approach this target.
- The content of silver in polyaniline–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 oxidation of aniline or *p*-phenylenediamine with silver nitrate proceeded also in frozen reaction mixtures at  $-24 \text{ }^\circ\text{C}$ , i.e. in the solid state. In most cases, molecular weights of polymer component increased, the conductivity of composites with silver improved, to  $2990 \text{ S cm}^{-1}$  for poly(*p*-phenylenediamine)–silver, and remained high after deprotonation with 1 M ammonium hydroxide.

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