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Teze disertace
k získání vědeckého titulu "doktor věd"
ve skupině věd chemických

Evolution, performance, ageing and reincarnation of polyaniline

(FTIR and Raman spectroscopic story)

Komise pro obhajoby doktorských disertací v oboru Makromolekulární chemie

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Summary

Introduction

Polyaniline (PANI) is one of the most interesting conducting polymers. Polyaniline has a high level of electrical conductivity, good redox and ion-exchange properties, and excellent environmental stability [1–4]. It is easily prepared by the oxidation of aniline in aqueous medium. When discussing PANI in general, three individual forms – leucoemeraldine, emeraldine, and pernigraniline – should be recognized (Fig. 1).

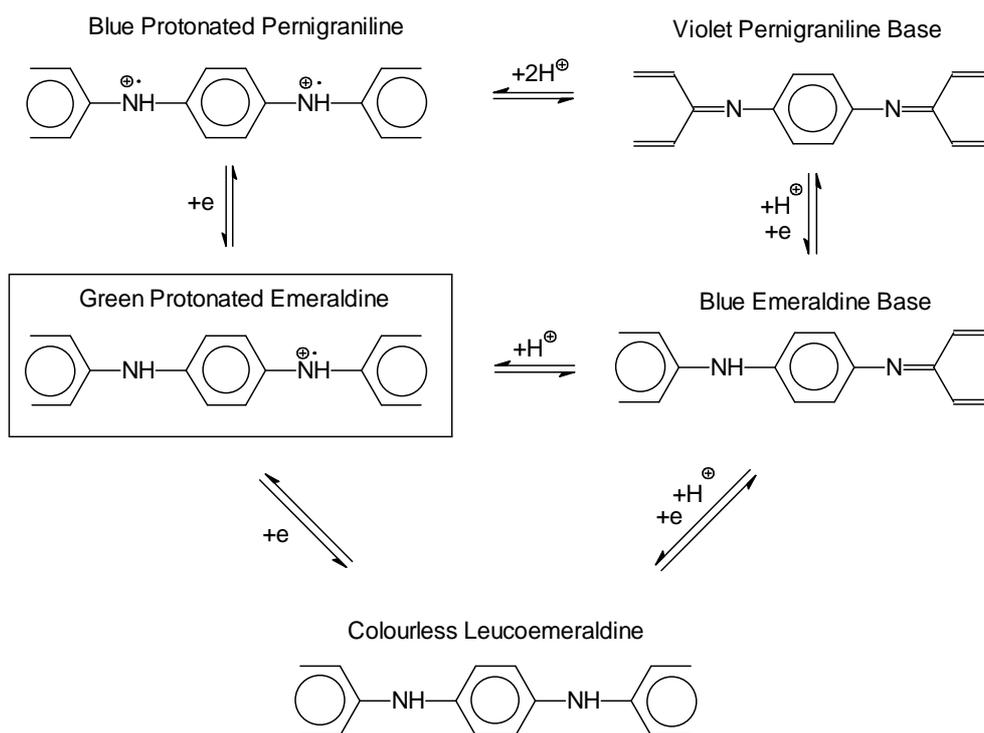


Fig. 1. Protonated emeraldine obtained after the polymerization of aniline can be oxidized to pernigraniline or reduced to leucoemeraldine. Emeraldine and pernigraniline may be deprotonated to the corresponding bases. Adapted from [5].

The fact that PANI exists in various forms that differ in the doping level and in the degree of oxidation is important for the potential applications of this polymer [5]. PANI has a good application potential in rechargeable batteries [6], erasable optical information storage [7], shielding of electromagnetic interference [8], microwave and radar absorbing materials [9], sensors [10,11], catalysts [12,13], electronic and bioelectronic components [14], membranes [15], electrochemical capacitors [16], electrochromic device [17], non-linear optical [18] and light-emitting devices [19], electromechanical actuators [20], antistatic [21] and anticorrosion coatings [22], *etc.* Thin PANI films or PANI-modified surfaces are often required for applications.

Vibration spectroscopy is extremely sensitive to the changes in electronic structure of PANI. Thus, by using infrared and Raman spectroscopy, one can easily register all interconversions between different oxidation and protonation states of PANI [23]. By using the IR spectroscopy it is possible – in addition to the characterisation of PANI – to study the changes of bonds and the mechanism of doping during the protonation and oxidation process [24].

The optical spectroscopic methods are currently used to obtain information on electronic and vibrational states in both doped and undoped states, and on the nature of structural defects in conducting polymers [25]. Conjugated polymers exhibit strong coupling between the electronic structure and certain geometric degrees of freedom. In this context, the role of conformational effects, especially phenyl ring torsional angles, on the electronic and vibration properties is one of the fundamental issues in this kind of conducting polymer [26].

1. Evolution of polyaniline

1.1. The course of aniline oxidation at various acidities

PANI is typically prepared by the chemical oxidation of aniline or anilinium salts, such as aniline hydrochloride or aniline sulfate, in acidic aqueous medium [2,4,27,28], ammonium peroxydisulfate (APS) being the most common oxidant (Fig. 2). Hydrogen atoms abstracted from aniline molecules during their coupling to oligomeric and polymeric structures are released as protons, *i.e.* sulfuric acid is a by-product. The pH thus always decreases in the course of aniline oxidation (**P1**) [29], (**P2**) [30], (**P3**) [31], [32–35]. Such process is sometimes called a "falling pH" method of PANI preparation [34,36].

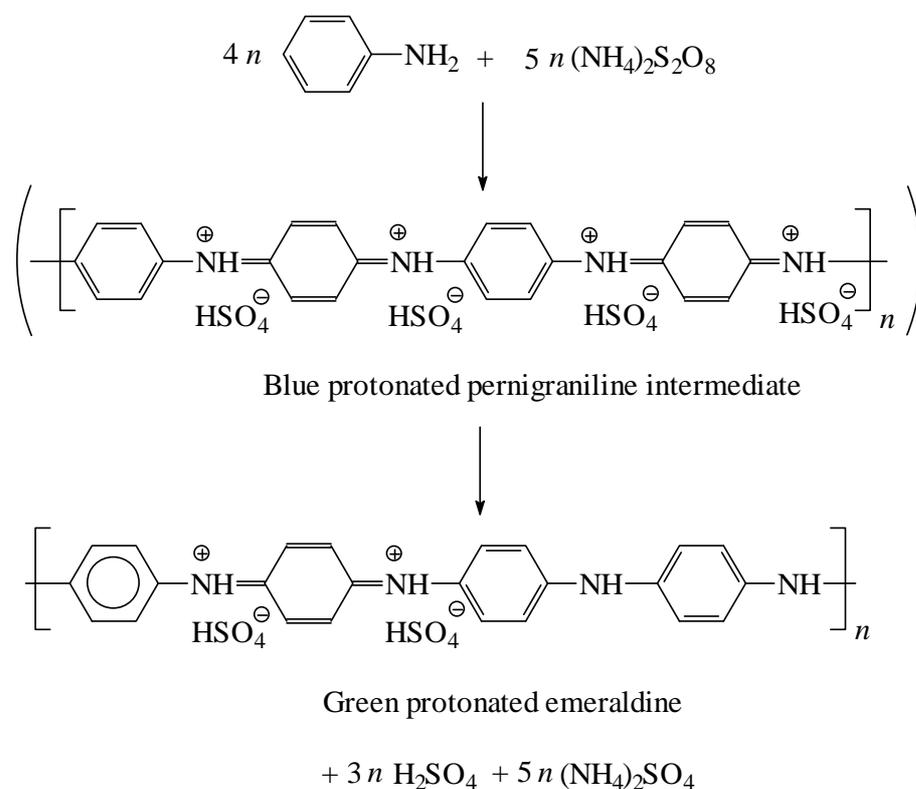


Fig. 2. The oxidation of aniline with ammonium peroxydisulfate in acidic medium yields the emeraldine form of PANI. A protonated pernigraniline is an intermediate. Sulfuric acid and ammonium sulfate are by-products.

Depending on the acidity of the reaction medium, the proportion between the neutral aniline molecules and anilinium cations varies (Fig. 3). At pH = 4.6, both species coexist in equal proportions. At higher pH, neutral aniline molecules predominate, anilinium cations being the prevailing species at low pH values. Aniline molecules and anilinium cations are two different chemical species. Anilinium cations have a higher oxidation potential than

aniline molecules, and their oxidation is, consequently, also different [37]. Generally, the oxidation of neutral aniline molecules proceeds easily, the oxidation of anilinium cations is difficult.

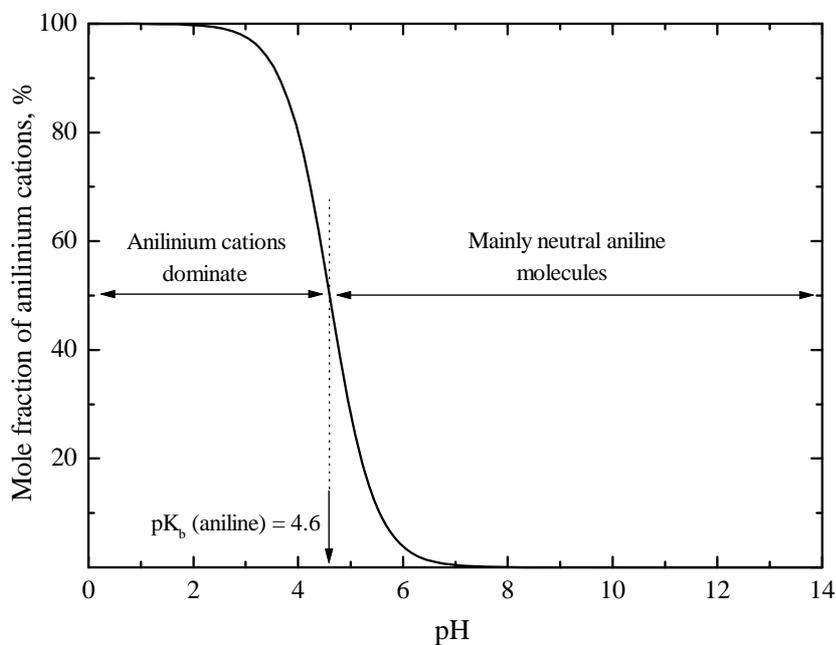


Fig. 3. Neutral aniline molecules convert to anilinium cations at low pH.

In practical oxidation experiments, different types of oxidation manifest themselves by different acidity profiles, *i.e.* by the time-dependence of pH (Fig. 4) **(P1)** [29], **(P2)** [30], **(P3)** [38], [32–35,39,40]. When, for the sake of simplicity, the oxidation of aniline is started in water, *i.e.* under mildly acidic conditions due to the presence of APS, three oxidation phases can be distinguished with respect to the oxidized species and the oxidation products (Fig. 4):

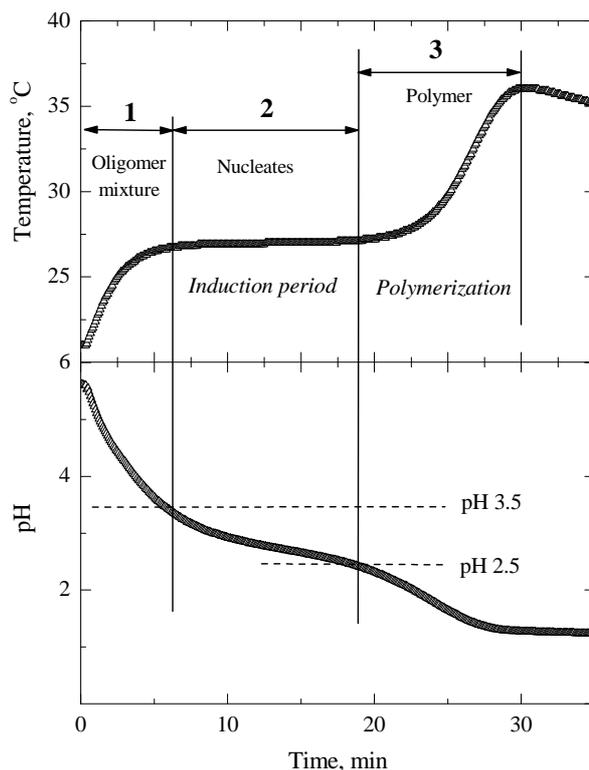


Fig. 4. Various phases of aniline oxidation at different pH. 0.2 M aniline was oxidized with 0.25 M APS in water.

(1) A fast exothermic oxidation of neutral aniline molecules characterized by an immediate increase in the temperature and a corresponding drop in pH. This phase takes place at $\text{pH} > 3.5$ and produces an *oligomer mixture*. The temperature stops rising and levels off, because the fraction of aniline molecules becomes low, and the less-reactive anilinium cations dominate. Non-conducting aniline oligomers are produced at this stage and they include semidines, other aniline dimers, and aniline trimers. These are partly further oxidized along with aniline to larger oligomers. Sulfonation, hydrolysis, and cross-linking may also be operative at this oxidation level.

(2) A so-called *induction period* follows. The much lower level of heat evolution during this phase just compensates the heat losses to the environment, and the temperature virtually does not change. The pH still moderately decreases, indicating that the oxidation continues. The highly deficient aniline molecules (Fig. 3) are still the main reactive species due to their easy oxidation. We assume that such oxidation leads to short aniline oligomers at the trimer level, which do not grow further. The induction period was observed also during the electrochemical oxidation of aniline [41].

(3) The fast polymerization of anilinium cations takes place only at $\text{pH} < 2.5$. A typical blue color of protonated pernigraniline intermediate (Fig. 2) is observed during this phase. Rapid heat evolution is accompanied by the massive generation of protons, reflecting the fast coupling of aniline molecules to form PANI chains. The final product of aniline oxidation in water is thus composed of both oligomeric and polymeric parts. It has to be stressed that the transition pH values 3.5 and 2.5 are not strictly fixed, and may vary by approximately ± 0.5 depending on concrete reaction conditions.

The oxidation of aniline can be started in acidic as well as in alkaline media. Some phases may be missing in the course of the oxidation, depending on the starting pH of reaction mixture (Fig. 5). When the oxidation starts under alkaline conditions in 0.2 M ammonium hydroxide, aniline oligomers are rapidly produced, and the reaction mixture becomes brown. The short oligomers, even at the dimer stage, become insoluble in water and form crystals. Especially the surface of crystals in contact with APS becomes oxidized to brown products constituted by larger oligomers. The pH drops as sulfuric acid is generated (Fig. 2), but not below the level where the polymerization of anilinium cations would be possible. A mixture of various oligomers is therefore the only product of the oxidation.

A conducting polymer, PANI, is typically prepared in an acidic medium, in solutions of strong acids. When the oxidation of aniline is carried out at high acidity, *e.g.*, in 0.1 M sulfuric acid, the exothermic formation of brown oligomers is not observed due to their low amount (Fig. 5); a small initial increase in temperature is due to the heat of mixing. Because of very low concentration of neutral aniline molecules (Fig. 3), only short oligomers, dimers and trimers, are slowly produced. A light blue colour is observed at this stage. It was assigned to the oxidized aniline dimer, *N*-phenyl-*p*-benzoquinonediimine. They subsequently participate in the formation of the nucleates, which initiate the growth of PANI chains. A polymer is thus virtually the only product, oligomers being present only as traces.

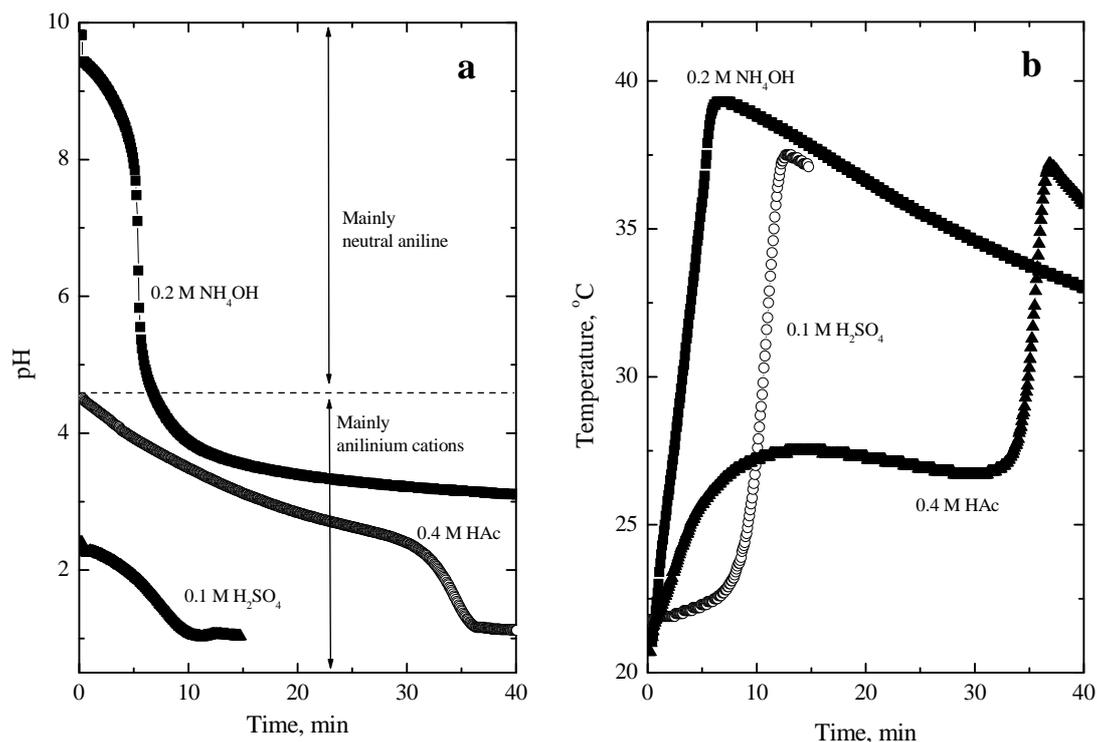


Fig. 5. (a) Acidity and (b) temperature profiles during the oxidation of 0.2 M aniline with 0.25 M ammonium peroxydisulfate started in the media of high acidity (0.1 M sulfuric acid), low acidity (0.4 M acetic acid), and in alkaline solutions (0.2 M ammonium hydroxide (**P3**)) [31].

1.2. Evolution and control of morphology

The granular morphology is typical for polyaniline prepared at the strongly acidic solutions. The oxidation of aniline at mildly acidic conditions produces nanotubes. Microspheres are obtained when the oxidation is started in alkaline media (Fig. 6). The morphology of PANI, granular or tubular, depends on the acidity conditions during the reaction rather than on the chemical structure of the acid (**P1**) [29].

Mechanisms of the formation of PANI nanostructures have recently been proposed and the formation of PANI nanotubes and related nanostructures have been reviewed [42–46]. The PANI nanotubes are probably the most complex from nanostructures produced by this polymer. The understanding of their formation is thus most valuable in the discussion of the genesis of other morphologies. The analysis of the early stages of the oxidative polymerization of aniline is the clue to understanding the evolution of the molecular and supramolecular structure of PANI. In mildly acidic aqueous media, where PANI nanotubes are typical produced, the oxidation of aniline proceeds in two exothermic steps, which are separated by an induction period (Fig. 4).

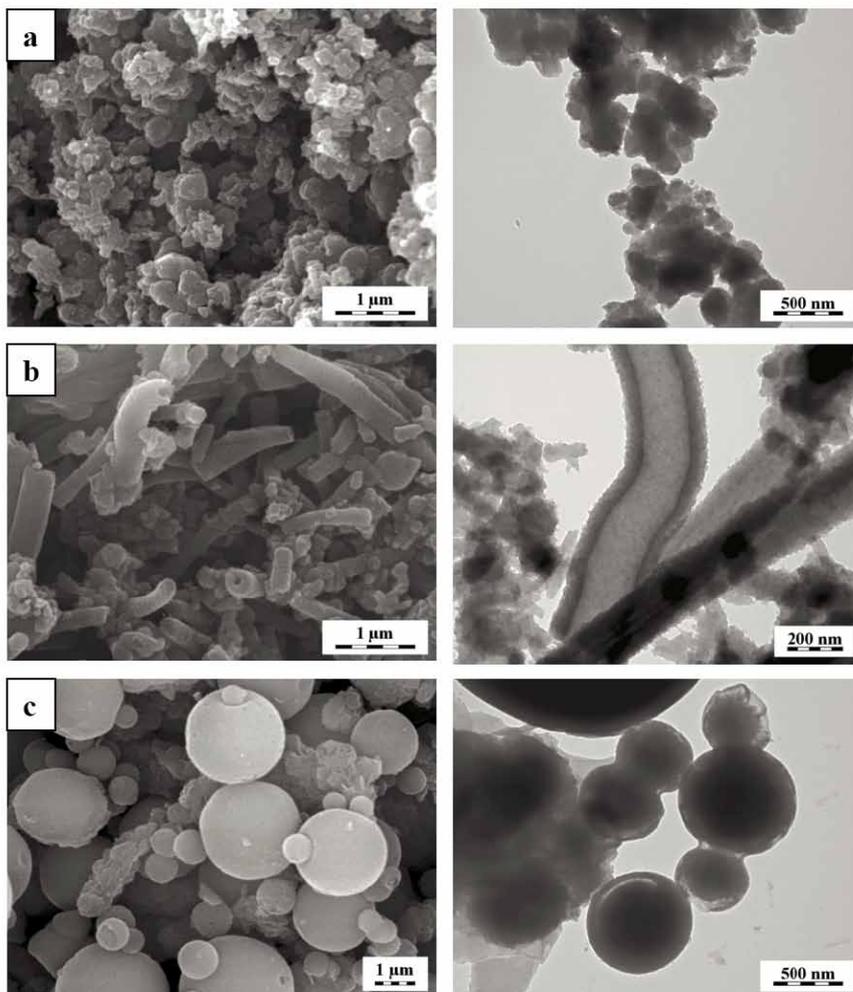


Fig. 6. Scanning (left) and transmission (right) electron microscopy of PANI prepared at: (a) strongly acidic solutions, (b) mildly acidic conditions, (c) in alkaline media (**P3**) [31].

We have studied the evolution of aniline oligomers in the first part of the reaction and of a polymer in the subsequent regime using FTIR and Raman spectroscopies in (**P2**) [30], (**P3**) [31], (**P4**) [38], and (**P5**) [47]. The role of the first products of oxidation in the nanotubes formation is also discussed. One of the techniques suitable to reflect the course of polymerization is based on the isolation of reaction intermediates and their *ex-situ* characterization (**P2**) [30], (**P3**) [31], (**P4**) [38], (**P5**) [47]. The oxidation reaction is terminated at various stages and the molecular structure and morphology of the reaction intermediates is assessed.

The infrared spectra of the precipitated reaction intermediates converted to bases can be divided into two groups with an intermediate spectrum recorded for the sample isolated at induction period, $t = 17$ min (Fig. 7a). In the early stages of the reaction ($t < 17$ min), they are similar to the spectra of aniline oligomers. For longer times, the spectra resemble those of

standard PANI [48] with some additional peaks marked by dashed lines (Fig. 7b). Their come evidently from oligomeric part of the samples.

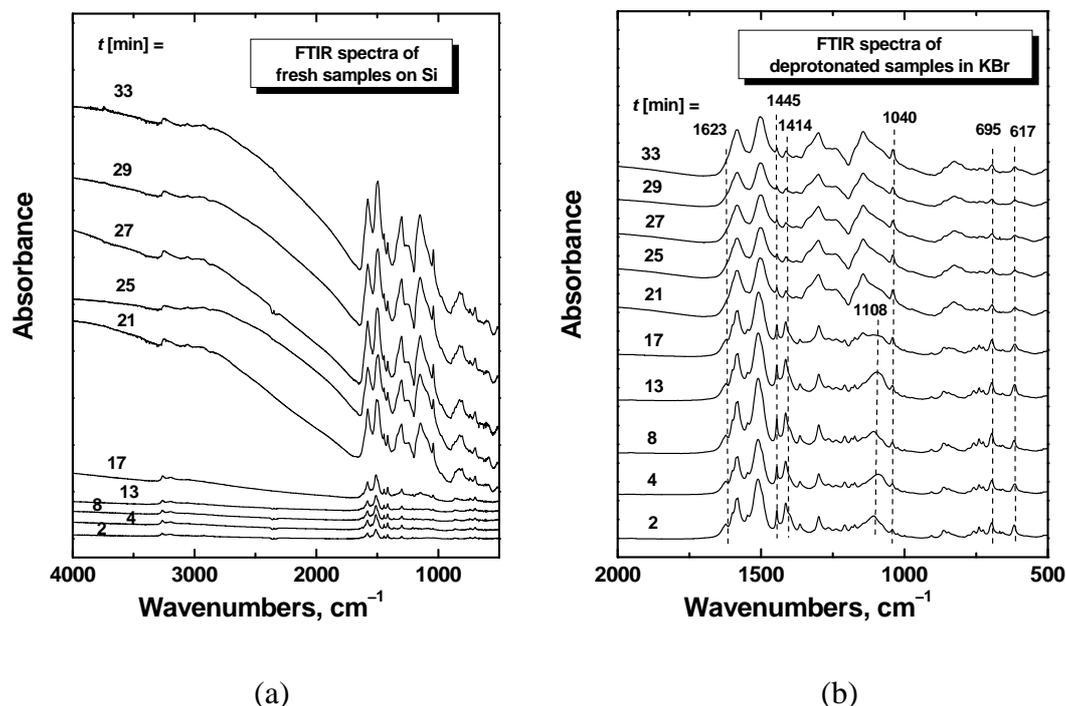


Fig. 7. FTIR spectra of (a) the reaction intermediates prepared by the oxidation of aniline in water deposited on silicon windows removed from the reaction mixture after times t , and (b) the corresponding spectra of deprotonated precipitates (**P4**) [38].

We have observed that the evolution of the morphology, molecular weight and infrared spectra of oxidation products obtained in the solution of strong and acids, and also in alkaline medium are similar and their kinetics correspond only to different acidity profiles, *i.e.* to the time-dependence of pH (Fig. 5) (**P2**) [30], (**P3**) [31]. The FTIR spectra of the oxidation products collected in the *early stages of oxidation* in the solutions of a strong acid after deprotonation are identical and are very close to those observed for the oxidation products in weak (acetic) acid (**P2**) [30] and also in alkaline medium (**P3**) [31]. The fact that the bands at 1445 and 1414 cm^{-1} are observed in the infrared spectrum of *o*-semidine (2-aminodiphenylamine), where they are stronger than in the spectrum of *p*-semidine (4-aminodiphenylamine), support the presence of the *ortho*-linked aniline constitutional units in oligomers [49]. The presence of the peaks at 1625, 1445 and 1414 cm^{-1} is a common feature of all early oxidation products of aniline, irrespective of the acidity of the medium. They have been assigned to the presence of *ortho*-coupled and phenazine-like units (**P3**) [31], (**P4**) [38]. Their interpretation is still not definitively solved and the impact of early-stage intermediate species on bulk polymer morphology is of interest [50,51].

For longer times, the spectra resemble those of standard PANI [48]. In addition, a shoulder at about 1630 cm^{-1} and especially the bands at 1445 and 1414 cm^{-1} are present in the spectra of products prepared at lower acidity (**P3**) [31]. They belong to deprotonated first products of oxidation of aniline with APS, which are crucial for the growth of nanotubular morphology. Their amount in case of oxidation in strong acid is very low and granular morphology is observed.

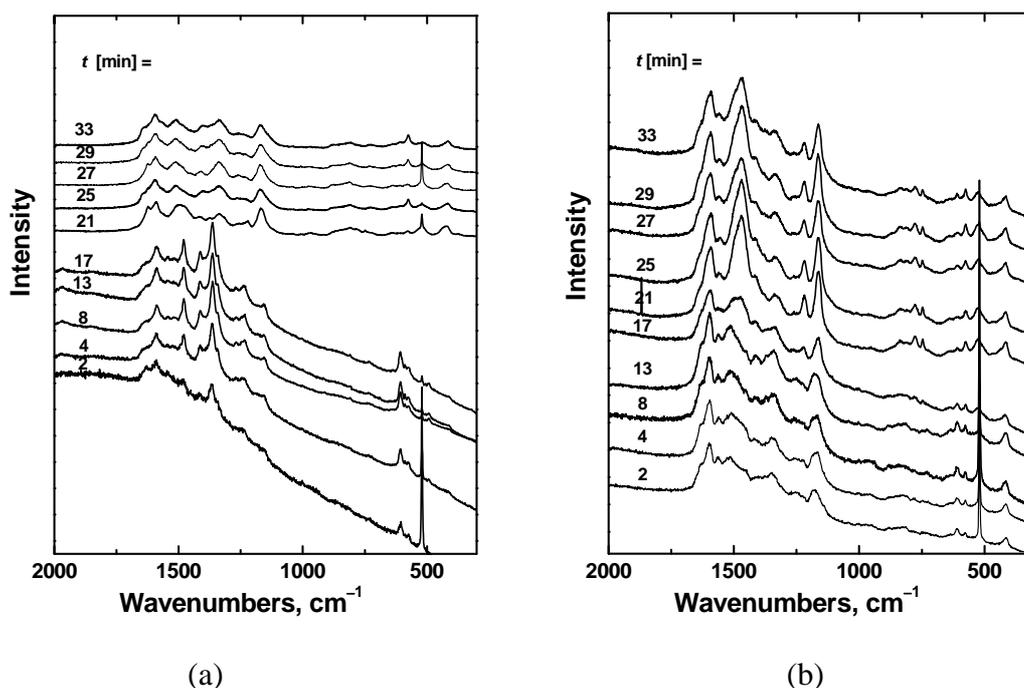


Fig. 8. Raman spectra of the reaction intermediates deposited on silicon windows at the oxidation of aniline in water taken after time t : (a) as-synthesized and (b) deprotonated samples. Excitation wavelength was 633 nm (**P5**) [47].

Raman spectra. As in case of FTIR spectra, also the Raman spectra can be divided in case of oxidation in water into two groups (**P5**) [47] (Fig. 8). The most prominent bands are dramatically changed at the induction period, $t \sim 21$ min, when pH of the reaction mixture decreased to ~ 2.5 (Fig. 4) and the chain-propagation started. The remarkable differences of the Raman spectra of oligoanilines, collected in the first stage of oxidative polymerization, and PANI nanotubes formed in the second stage of reaction, have been discussed in detail (**P5**) [47]. They confirm again that oligomers are produced during the first oxidation phase and the polymerization of aniline takes place in the second part of reaction.

1.3. In-situ polymerized polyaniline films

The progress of the chemical polymerization of aniline has been monitored *in situ* by attenuated total reflection (ATR) FTIR spectroscopy (P6) [52], (P7) [53], (P8) [54]. This method allows us to observe the early stages of polymerization directly during the oxidation process (Fig. 9). The growth of PANI films on the crystal surface, together with the changes proceeding in the surrounding aqueous medium, are reflected in the spectra.

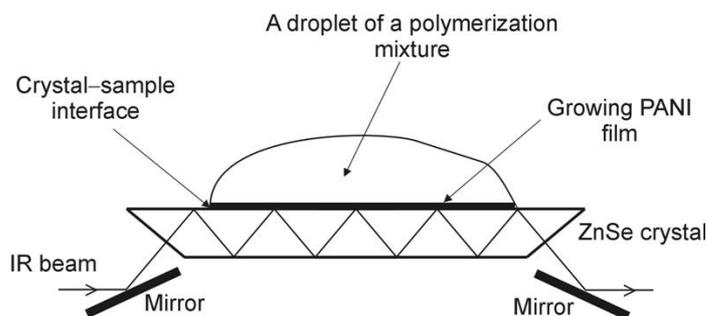


Fig. 9. The growth of the polyaniline film at the interface between of the polymerization mixture and ATR crystal in *in situ* FTIR ATR mode (P6) [52].

The solutions of aniline hydrochloride and APS were mixed, a droplet of the reaction mixture was placed into the spectrophotometer, and the spectra were successively recorded in (P6) [52]. The electric field at the interface penetrates into the deposited sample, here a droplet of reaction mixture on a ZnSe crystal (Fig. 9), in the form of an evanescent field whose amplitude decays exponentially with distance from the interface. The evolution of the spectra recorded during the oxidation of aniline hydrochloride is shown in Fig. 10. A very weak band at 1148 cm^{-1} and a shoulder at 1250 cm^{-1} in the APS band of 1277 cm^{-1} already appear after 2:15 min, and they probably reflect the formation of aniline oligomers. The intensity of the sharp band of APS at 1050 cm^{-1} remains unchanged. This means that APS has not yet been consumed in the polymerization of aniline. The mass of a PANI film is very low, of the order of μg , and the consequent reduction of reactant concentrations in the bulk is negligible. The most significant feature in the spectrum is a new strong band observed at 1133 cm^{-1} , appearing after 4:30 min, which corresponds to the formation of ammonium sulfate (Fig. 2). This is associated with the onset of the polymerization in the bulk (Fig. 10a).

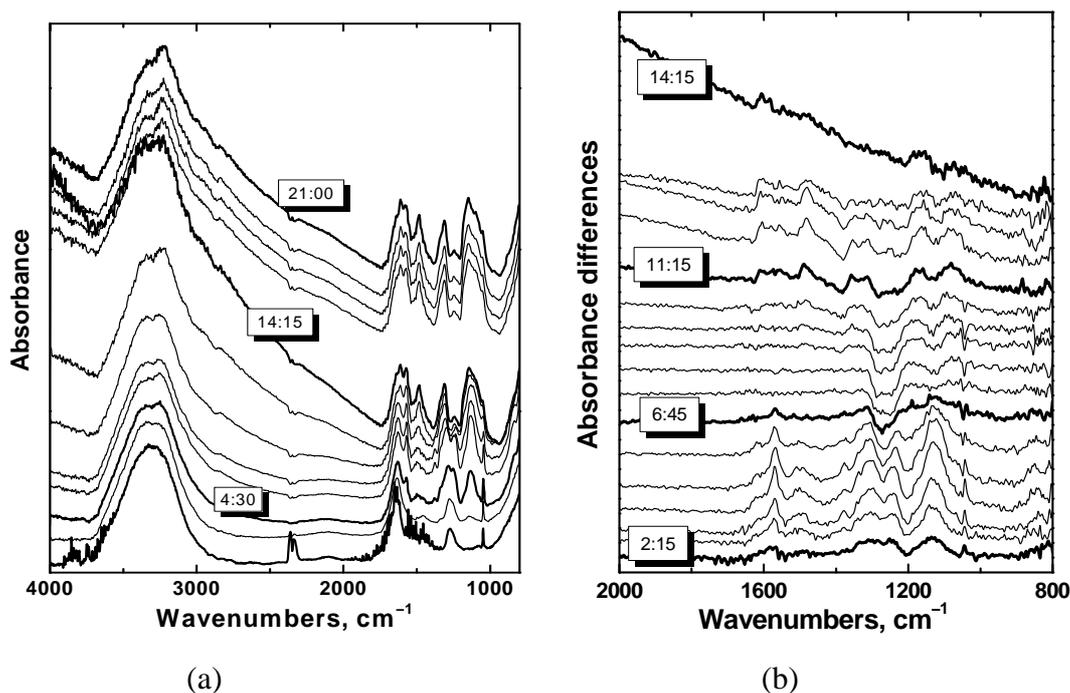


Fig. 10. (a) The evolution of ATR FTIR spectra during the polymerization of aniline hydrochloride on ZnSe crystal. (b) Differences of two consecutive ATR FTIR spectra recorded at various stages of polymerization. The selected reaction times (min:s) are shown at the spectra (**P6**) [52].

To detect the changes in the spectra in more detail, we have plotted the corresponding differences of two consecutive spectra (Fig. 10b); three stages can be distinguished. According to these spectra, the film grows on the crystal from the very beginning of the measurements, *i.e.*, already during the induction period (Fig. 5) where no polymerization in the bulk takes place. This is an important conclusion: the surface polymerization precedes the polymerization in the whole volume. The development of PANI forms and the conversion of pernigraniline to emeraldine structure at the end of polymerization are also well visible by FTIR technique (**P6**) [52].

The product contains generally both the chloride counter-ions as well as the sulfate or hydrogen sulfate ones, originating from the reduction of peroxydisulfate oxidant. The influence of various acids on the start and progress of polymerization of aniline on the surface of the ATR crystal, which was in contact with the reaction mixture, has been analysed in (**P7**) [53]. The oxidation reaction in hydrochloric acid was compared with the polymerization in sulfuric and phosphoric acids. The influences of chloride, sulfate, and phosphate counter-ions on the initiation and progress of aniline polymerization were analyzed.

The polymerization of aniline with APS in water, described with the help of the terminated polymerization in paragraph 1.2, was investigated also *in situ* by the ATR FTIR spectroscopy and compared with the aniline polymerization in the presence of weak (acetic) acid and strong (sulfuric) acid (**P8**) [54]. The aim was to understand the influence of acidity on the observed morphology of the final PANI products, granular or nanotubular. The results of the *in-situ* ATR FTIR spectroscopy support the results obtained from the termination of polymerization at various stages (**P8**) [54]. The differential spectra and the factor analysis (FA) were used to observe the evolution of the molecular structure. In contrast to the differential spectra, where averaging was necessary to obtain reasonable information, the FA worked with the as-measured spectra. The FA results helped us to determine the time scale of the polymerization in detail. Thus, the course of polymerization known from the acidity and time dependence could be thus precisely correlated with the changes taking part at the level of the molecular structure.

1.4. Brush-like ordering of polyaniline films

Many applications of PANI, such as sensors, antistatic and anticorrosive coatings, require thin films. The technique of *in-situ* surface polymerization, giving rise to thin PANI films, has often been used in the coating of various materials with a conducting polymer overlayer [55]. The concept of brush-like ordering of macromolecules chains in produced film has been proposed in [56] and studied by FTIR spectroscopy in [57]. Thermal deprotonation and stability of such prepared films has been studied by FTIR spectroscopy (**P9**) [58]. Five so-called “H-peaks” located at 3220, 3140, 3050, 2920, and 2830 cm^{-1} correspond to the hydrogen bonding between regularly aligned PANI chains as has been reported by Wu *et al.* [59]. This absorption peaks remain unchanged during the heating of films to 120°C. The presence of peaks in the region 3300–2800 cm^{-1} has been confirmed by independent preparation and FTIR characterization in various laboratories. Only very weak H-peaks are observed in the spectrum of PANI hydrochloride powder prepared under the same conditions. The absorption bands in the region 3300–2800 cm^{-1} reflect the organization of PANI chains within the film by hydrogen bonding involving NH and NH^+ groups (**P9**) [58].

2. Performance of polyaniline

2.1. Protonation and oxidation of polyaniline

We have proved with help of the infrared spectroscopy that emeraldine base can be protonated by organic acids by the blending of components in the solid state [60]. The protonation by camphorsulfonic acid was compared from the spectroscopic point of view with the solid-state oxidation of emeraldine base by ammonium peroxydisulfate in **(P10)** [61].

The protonation reaction between two non-conducting compounds, polyaniline base and 3-nitro-1,2,4-triazol-5-one (NTO), an insensitive explosive, yields conducting products **(P11)** [62]. Three ways of preparation have been tested: the interaction of PANI base with NTO dissolved in water, the polymerization of aniline in a medium containing NTO, and solid-state blending of both components. The FTIR spectra were used to discuss changes in the molecular structure of PANI and NTO occurring during the protonation.

The properties of PANI can be modified by controlling the way of protonation **(P12)** [63]. PANI base was immersed in aqueous solutions of 42 inorganic or organic acids in order to find out, which is able to constitute a salt with the polyaniline base and what are the properties of products. The structure and properties of conducting polymers were studied by the infrared spectroscopy to investigate the doping process and structural transitions in PANI.

2.2. Polyaniline composites

2.2.1. Polyaniline–fullerene

The investigation of composites based on conjugated polymers and (C_{60}) is of both scientific and technological interest. The photoinduced electron transfer from semiconducting polymers (as donors) to C_{60} and its derivatives (as acceptors) has been demonstrated in blends as well as in heterostructures prepared from these two materials. The latter interpenetrating phase-separated donor–acceptor composites appear to be ideal photovoltaic materials for the preparation of various types of optical devices, such as switches, dynamic memory units, etc.

In **(P13)** [64] two new ways of PANI– C_{60} composite preparation are investigated. PANI–fullerene composites were prepared either by solid-state blending of both components (composite I) or by the introduction of fullerene during polymerization of aniline (composite II). The composite I had a lower conductivity ($1.5 \times 10^{-7} \text{ S cm}^{-1}$) than the composite II ($7.2 \times 10^{-5} \text{ S cm}^{-1}$). Investigation of composites by solid-state ^{13}C NMR and FTIR spectroscopy indicated the interaction between PANI and fullerene. X-ray diffractograms

suggest that the mechanical blending of components lead to a decrease in the size of fullerene crystallites. In composite II, diffractograms proved the formation of PANI–fullerene complex comprising the structure corresponding to a doped PANI.

2.2.2 Polyaniline–carbon nanotubes

The composites of CNT with PANI have been reported in many papers [65–71]. Their possible applications have also been proposed. Such composites can be used in fuel cells, pH sensors or gas sensors, supercapacitors, batteries, electromagnetic shielding and for the design of anti-corrosion coatings.

PANI is typically prepared by the oxidative polymerization of aniline with ammonium peroxydisulfate in the acidic aqueous medium [72]. In **(P14)** [73] CNT were suspended in the reaction mixture. They become coated and, depending on the amount of PANI generated, may be accompanied by a PANI precipitate. The ethanol (50 vol.%) has been added into the polymerization medium. The goal of the synthesis was to improve the wettability of carbon nanotubes as required in some applications, *e.g.*, in the fuel-cell electrodes. The surface-modified CNT are hydrophilic when coated with protonated form of PANI, as proved by contact-angle measurements. The composites of CNT with PANI have been characterized with a FTIR and Raman spectroscopies.

After the coating of CNT with PANI, the Raman spectrum of this polymer dominates in all samples. This observation confirms that good coating of CNT with PANI has been achieved. The positions of all PANI bands remain practically unchanged for all contents of CNT. We have observed the relative decrease and a shift of the second-order of the disorder-induced band D' which indicates a less perfect structure for the nanotubes embedded in the polymer [66]. In some cases [74], Raman spectroscopy showed indications of possible interaction between single-wall CNT and conducting polymers. In our study, no interaction between CNT and PANI could be proved (Fig. 11).

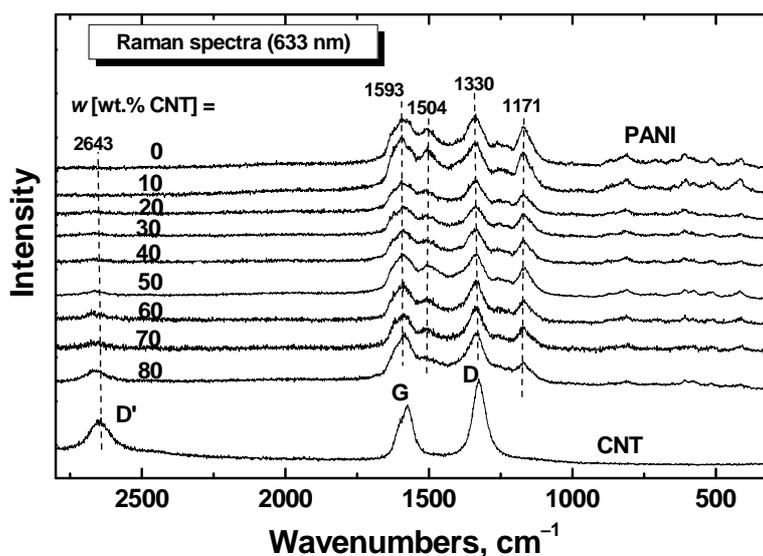


Fig. 11. Raman spectra of multi-wall carbon nanotubes (CNT) coated with PANI. The content of CNTs (wt.%) is given at the individual curves (**P14**) [73].

2.2.3. Polyaniline–silver

The composites based on conducting polymers and noble metals, such as silver, can be prepared by five basic ways: (1) by simple blending of both components [75,76], (2) by the polymerization of aniline in the presence of preformed metal nanoparticles [77,78], (3) by the deposition of metal on conducting polymer while using various oxidants, such as glucose [79, 80], (4) by the reduction of noble-metal compounds with PANI [81], (**P15**) [82], [83], and (5) by the oxidation of aniline with noble-metal compounds (**P16**) [84], (**P17**) [85], [86]. From the point of view of PANI nanostructures, last approach is the most interesting. Aniline can be oxidized with noble-metal compounds to produce PANI and the corresponding metal at the same time. Silver nitrate may serve as an example of such an oxidant (Fig. 12) (**P16**) [84], (**P17**) [85], [86].

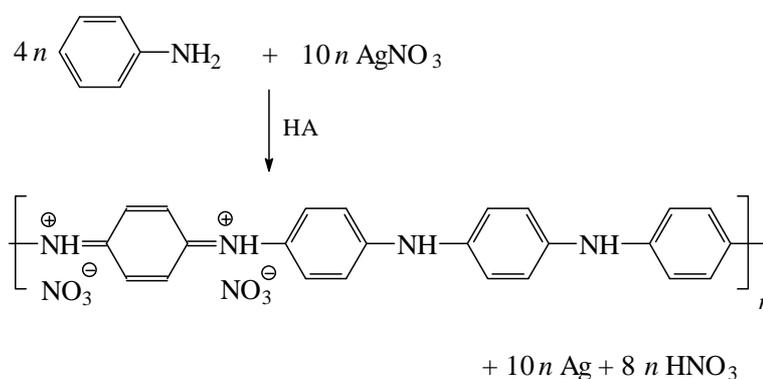


Fig. 12. Aniline is oxidized with silver nitrate to PANI nitrate and metallic silver. Nitric acid is a by-product.

Silver nitrate oxidizes aniline in the solutions of nitric acid to conducting nanofibrillar PANI. Nanofibres of 10–20 nm thickness form assembled brushes. Nanotubes, having cavities of various diameters, and nanorods have also been present in the oxidation products. Metallic silver is obtained as nanoparticles of ~50 nm size accompanying macroscopic silver flakes. The reaction is slow and it took weeks to reach a good yield, 87 % of theory. The emeraldine structure of the PANI has been confirmed by FTIR (Fig. 13) and UV–visible spectra. The resulting PANI–silver composite containing 50 wt.% of silver had a conductivity of 6 S cm^{-1} , and 709 S cm^{-1} at 71 wt.% of silver (**P16**) [84].

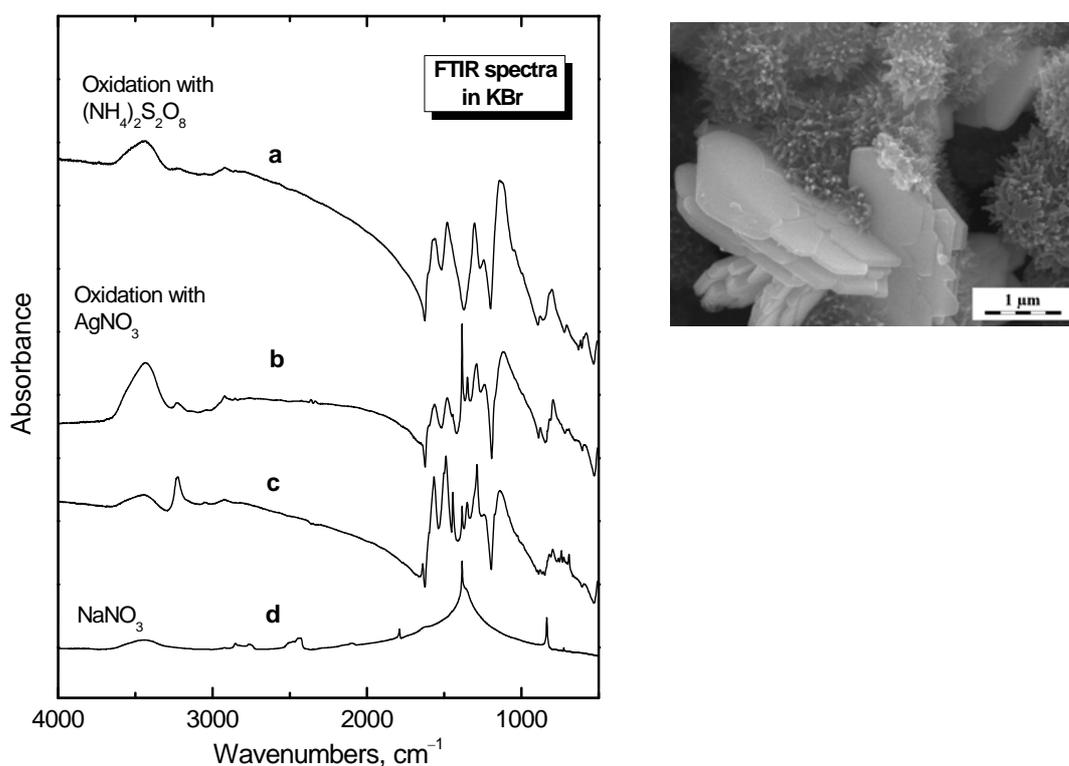


Fig. 13. FTIR spectra of PANI prepared by the oxidation of (a) 0.2 M aniline with 0.25 M APS in 0.1 M sulfuric acid (a "common" polyaniline sulfate), (b) 0.2 M aniline with 0.5 M silver nitrate in 1 M nitric acid, (c) 0.4 M aniline with 1.0 M silver nitrate in 1 M nitric acid, and (d) FTIR spectrum of sodium nitrate (**P16**) [84].

Aniline was oxidized with silver nitrate in solutions of acetic acid; in this context, aniline oligomers have often been a major component of the oxidation products. The presence of an insoluble precipitate of silver acetate in the samples was proved by FTIR spectroscopy (**P17**) [85]. The optimization of reaction conditions with respect to aniline and acetic acid concentrations has nevertheless led to a conductivity of the composite as high as 8000 S cm^{-1} at ~70 wt.% (~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. The emeraldine structure of the polyaniline has been confirmed by FTIR (Fig. 14) Polyaniline was present as nanotubes or nanobrushes composed of thin nanowires. The average size of the silver nanoparticles was 30–50 nm; silver nanowires have also been observed (P17) [85].

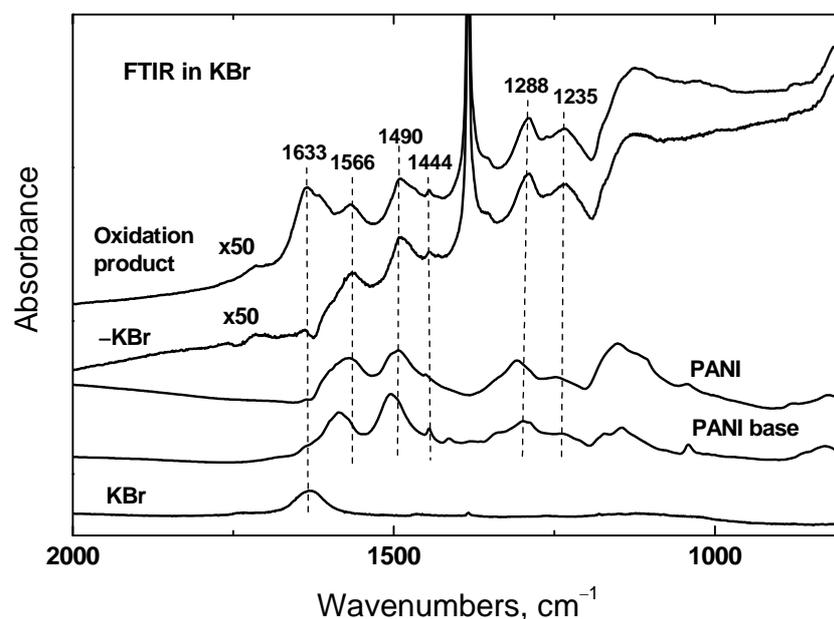


Fig. 14. FTIR spectra of the oxidation product prepared by the oxidation of 0.2 mol L^{-1} aniline with 0.5 mol L^{-1} silver nitrate in the solutions of 0.2 mol L^{-1} acetic acid before and after subtraction of the spectrum of potassium-bromide pellet. The spectra of PANI and corresponding PANI base prepared by the oxidation of 0.2 mol L^{-1} aniline with 0.25 mol L^{-1} APS in the solutions of 0.4 mol L^{-1} acetic acid are shown for comparison (P17) [85].

Alternatively, the PANI in emeraldine form can be used as a reductant for noble metal salts (Fig. 15). In this case, the emeraldine is oxidized to pernigraniline [83,87,88]:

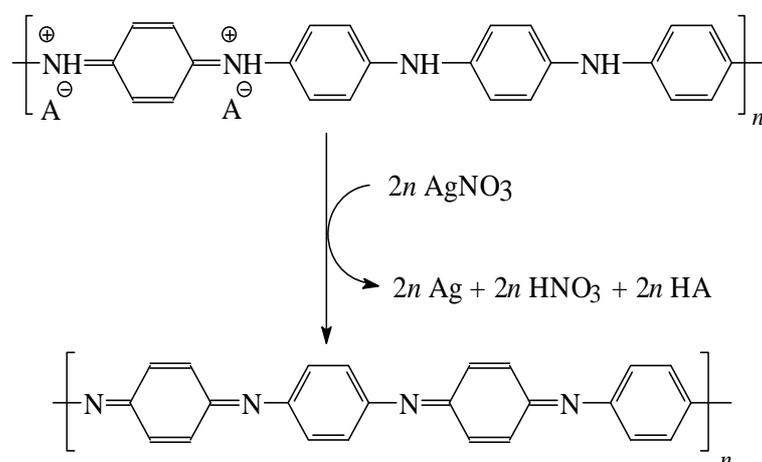


Fig. 15. The emeraldine form of PANI reduced silver nitrate to metallic silver. It is oxidized to the pernigraniline form at the same time.

The reduction of silver nitrate with PANI base in the solid state also leads to similar composites (**P15**) [82]. The changes occurring in the structure of PANI were discussed on the basis of FTIR and Raman spectroscopies. Raman spectroscopy could identify the “bright” areas composed of silver coated with pernigraniline and “dark” areas represented by PANI (pernigraniline), which become gradually protonated by nitric acid (Fig. 16). Surface-enhanced Raman scattering was observed due to the presence of a pernigraniline–silver interface in the “bright” regions. The ease of the reaction between PANI (emeraldine) base and silver nitrate was explained by the transfer of electrons and protons from the reductant, a PANI (emeraldine) base, to the oxidant, silver nitrate, assisted by the conducting PANI (pernigraniline) nitrate, which was generated *in situ* during the reaction (**P15**) [82].

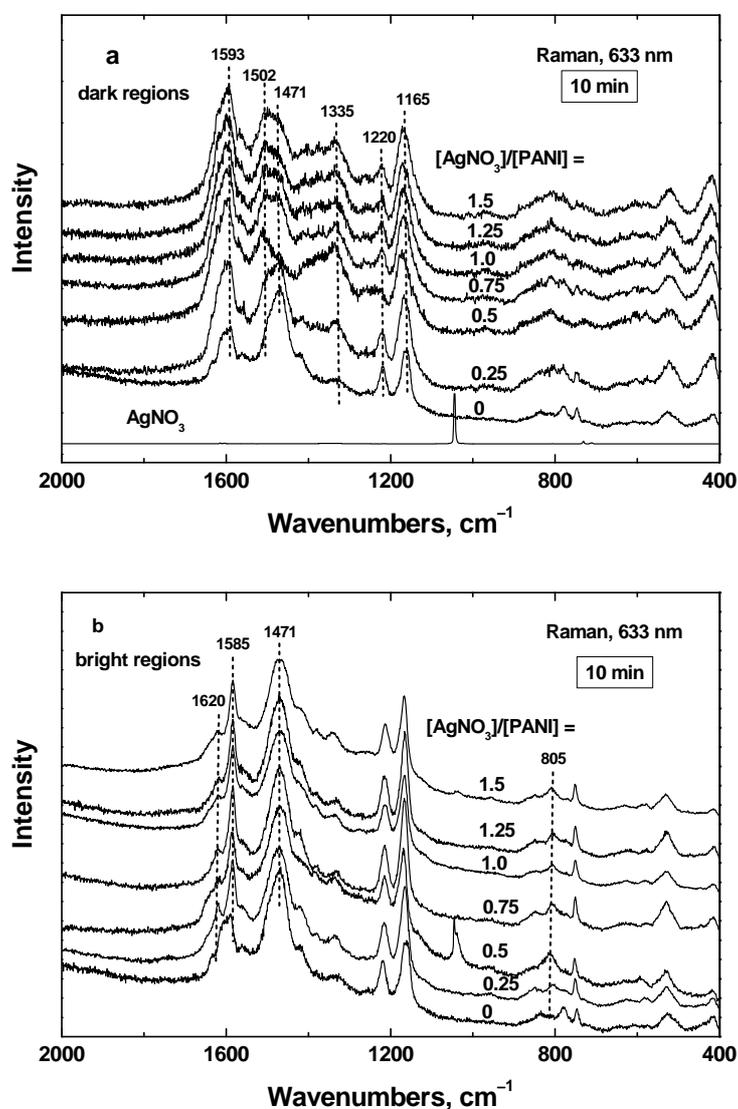


Fig. 16. Raman spectra of the PANI (emeraldine) base processed in a ball mill with silver nitrate at various mole ratios for 10 min and measured as pellets with excitation at 633 nm. The spectra were separately recorded in (a) dark and (b) bright regions of the samples (**P15**) [82].

The material comprising conducting polymers and noble metals are potentially useful in many applications. From these, the energy conversion in fuel cells is probably the most important.

3. Ageing and stability of polyaniline

For applications, the stability of the nanostructured polyaniline films is crucial and good comprehension of the degradation mechanisms is necessary. The changes at molecular level, *e.g.*, manifested by gradual conversion of the PANI salt to base, are expected to be the main processes controlling the level of conductivity. It is a consequence of a complex combination of structural changes: deprotonation, also the loss of conjugation, oxidative processes, crosslinking, and other chemical reactions on PANI chains (chlorination, sulfonation) [89]. The stability of PANI doped by various inorganic salts may be investigated by using vibrational spectroscopy. For applications of PANI nanotubes or nanofibers, the stability of the nanostructured films is crucial and good comprehension of the degradation mechanisms is necessary. The infrared and Raman spectroscopies are efficient tools to assess the changes in the molecular structure occurring during ageing.

3.1. Ageing of polyaniline

Stability of the protonated PANI films varies with the nature of protonating acid [72,90–92]. We have studied the changes in molecular structures of PANI films prepared *in situ* on silicon windows protonated with different acids in **(P18)** [93]. In addition to the most common monobasic hydrochloric acid, samples containing the dibasic sulfuric acid and tribasic phosphoric acid were included. The evolution of the infrared spectra during the annealing was recorded and compared with the conductivity curves measured under the same conditions. The most significant change in the FTIR spectra is the decrease of the polaronic band above 2000 cm^{-1} connected with the deprotonation of the PANI salt to the base. The other more subtle changes have been observed in the region of molecular vibrations under 2000 cm^{-1} and can be mainly assigned to the changes in molecular structures connected with deprotonation and to the formation of covalent bonds between the PANI chains and counter-ions of the doping acid, which appear in all three cases.

The changes in molecular structure during heating of both PANI hydrochloride and corresponding deprotonated films deposited *in situ* on silicon windows were studied by FTIR spectroscopy in **(P19)** [94]. The conformational state of the polyaniline chains affects the

kinetics and probability of various degradation processes. A dramatic change in the resistivity dependence on time was observed when temperature of ageing exceeded 85 °C. As the glass-like transition at about 70 °C had been previously reported in the literature in the case of the bulk sample degradation [95], it is believed that this effect can be caused by a similar mechanism. The study of the ageing of PANI base using FTIR spectroscopy proved the presence of the transition at the temperature around 80 °C (**P19**) [94]. We can conclude that this feature is an inherent property of PANI and is not influenced by the nature of protonating acid.

3.2. Stability of polyaniline

The stability of the PANI films prepared under different conditions on silicon windows and leading to different morphologies were tested at elevated temperature in (**P20**) [96]. The spectra of two samples with nanotubular structure, prepared in water and in acetic acid, were compared with the spectrum of granular PANI film prepared in sulfuric acid solution. The morphology of the samples was preserved during the degradation at 80 °C during three months, but the molecular structure has changed as it is reflected in the infrared and Raman spectra (Fig. 17). The changes in the infrared spectra of the films correspond to deprotonation, oxidation and thermal transition due to the chemical cross-linking reactions among PANI molecules. The molecular structure corresponding to nanotubular morphology, which contains the crosslinked, phenazine- and oxazine-like groups, is more stable than the molecular structure with granular morphology.

The extensive use of polyaniline in the design of electrode materials for fuel cells, as a mixed proton–electron conductor in acidic fuel cells, as an electron-transfer mediator in biofuel cells, and as a catalyst support in alkaline fuel cells operating at mildly elevated temperature, raise the question of the stability of PANI under such conditions. The influence of strongly alkaline or acidic media on the stability of polyaniline was reported in (**P21**) [97].

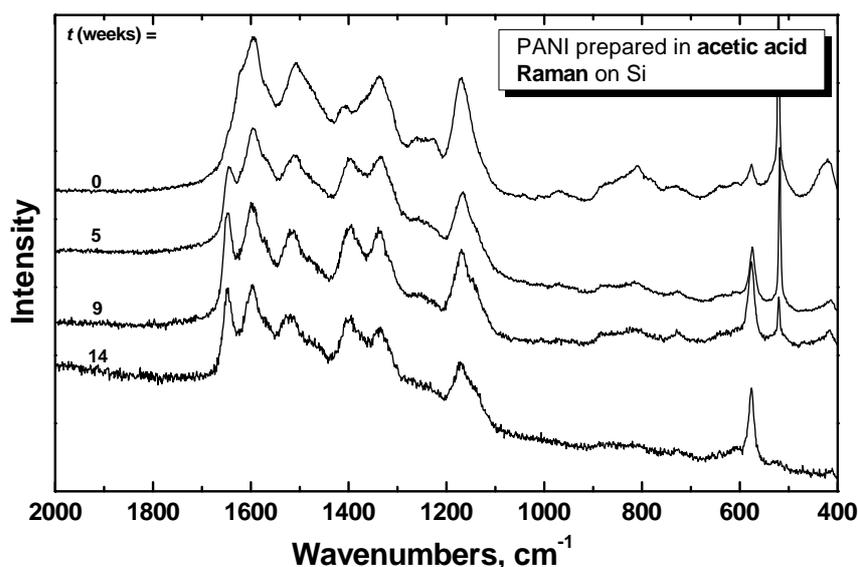


Fig. 17. Raman spectra of the PANI films as prepared in 0.4 M acetic acid deposited *in situ* on the silicon window measured at the beginning of ageing (at 80 °C) and after 5, 9 and 13 weeks (P20) [96].

4. Reincarnation of polyaniline

The carbonization of conducting polymers, such as PANI, leads to new materials, nitrogen-containing carbons. It is an important fact that the morphology of the original polymer is preserved after carbonization. The ease of preparation and the richness of morphologies that the conducting polymers display make them interesting objects of carbonization studies. Such nanostructured materials may find uses as catalyst supports [98–100], in hydrogen storage [101,102], and in applications currently using multi-wall carbon nanotubes [103].

4.1. Pyrolysis of polyaniline base

It has been observed that cellulose fibers coated with PANI leave a carcass of carbonized PANI after burning [104, 105]. The globular morphology of PANI remained preserved after the carbonization of PANI in air (P22) [106], [107]. The conductivity of the residue after treatment at 1000 °C was $7.3 \times 10^{-4} \text{ S cm}^{-1}$, but the yield was low, 6.4 wt.%. The samples had about the constant content of nitrogen, ~14 wt.%, irrespective of the processing temperature up to 800 °C, which was assigned to the formation of phenazine-like crosslinks

(P22) [106]. The evolution of the molecular structure has been studied by Raman spectroscopy (Fig. 18).

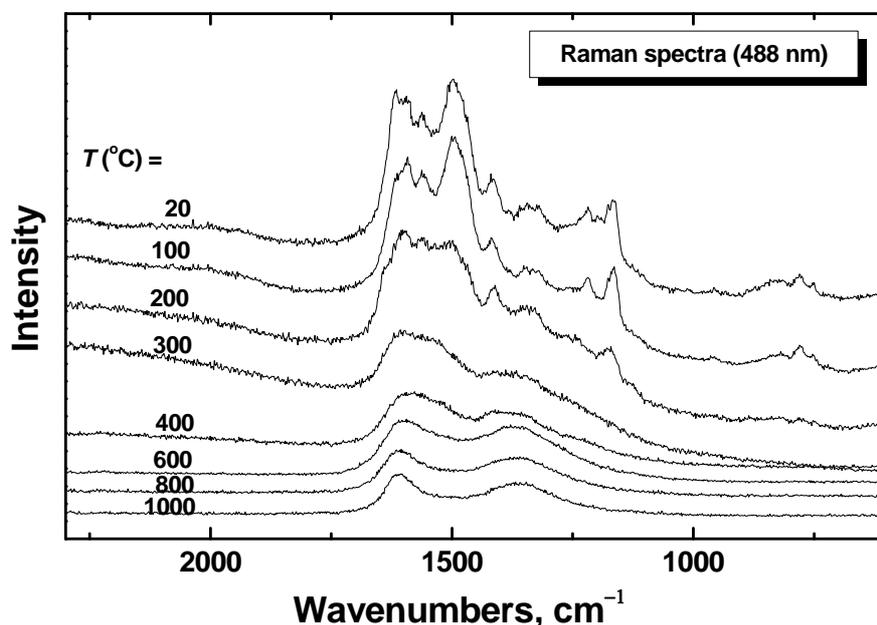


Fig. 18. Raman spectra (excitation line 488 nm) of polyaniline base exposed to elevated temperature T for 2 h (P22) [106].

4.1. Carbonization of polyaniline nanotubes

The same approach has been used for the preparation of nitrogen-containing carbon nanotubes by the exposure of PANI nanotubes at elevated temperature up to 830 °C in a nitrogen atmosphere (P23) [108], [109] and their properties have been compared with classical multi-wall carbon nanotubes (P23) [108]. In contrast to them, they contained 8–9 wt.% of nitrogen. The morphology of both types of nanotubes is also distinctly different. The nitrogen-containing CNT have finite length up to several micrometres, they are straight or only slightly bend. The highest conductivity of carbonized nanotubes reported in these experiments was 0.7 S cm⁻¹ [109], other experiments yielded non-conducting products.

The changes in the molecular structure occurring during the carbonization are conveniently observed by Raman spectroscopy (P23) [108], [110,111] (Fig. 19). The originally complex spectrum is reduced to two dominating peaks corresponding to the graphitic (G) and disordered (D) carbon structures. Many other techniques, however, have been used to follow the carbonization process [100].

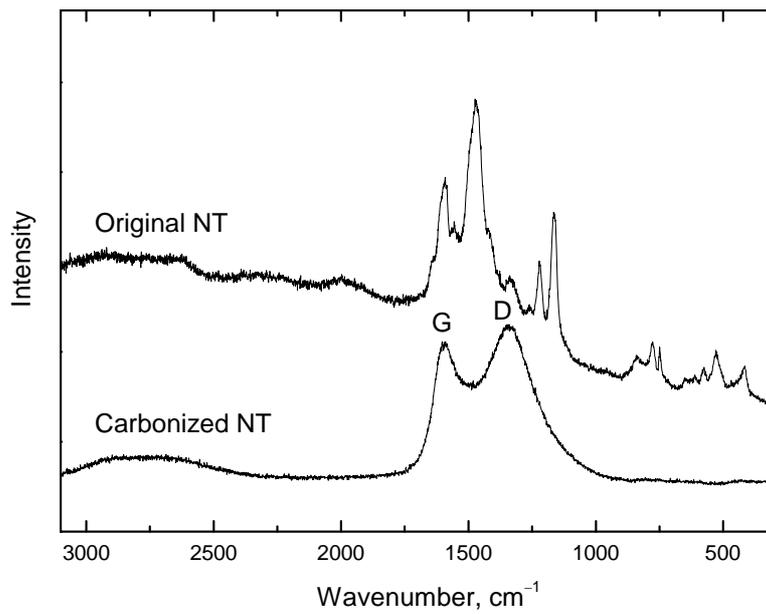


Fig. 19. Raman spectra of original nanotubular PANI and its carbonized product. Laser excitation at 633 nm.

Conclusions

The story of PANI does not end with this Thesis. On the contrary, it appears that, in fact, it is starting. Molecular structure and properties of the first oxidation products of aniline are the objects of persistent studies of teams over the whole world. The impact of aniline oligomers and their role in the formation of PANI nanostructures, *viz.* nanotubes, nanofibres, microspheres, and more complex hierarchical morphologies, are of fundamental importance. It has been proved that both infrared and Raman spectroscopy are extremely useful in this research direction.

The Thesis does not include many other papers of the authoress, in which vibrational spectroscopy also played an essential role. Those studies were devoted to the polymerization of aniline at interfaces (on silica gel, carbon nanotubes, on membranes, within ice crystals), and to the oxidation of aniline dimers, semidines, which are related to the phase on polyaniline formation. The important role of infrared spectroscopy was recognized in the studies of mixed electron and proton conductivity in polyaniline films immersed in solutions of strong acids. Additional series of papers concerns the coating of various substrates with polyaniline, and their application in the corrosion protection of metals, tuning of magnetic properties of ferrites, the electrical and chemical stabilities of polyaniline under extreme conditions, and other topics. The list of such related papers is appended in the Thesis.

Our research on the preparation and properties of polyaniline continues and extends. Various oligomers of aniline have recently been prepared for the studies by vibrational spectroscopy, including future synthesis that will use deuterated analogues. Aniline oxidations in non-aqueous media, in ionic liquids, or in the solid state, are other interesting fields that are currently being exploited. The morphology-retaining carbonization of conducting polymers produces exciting objects for Raman spectroscopy, as well as for the applications in catalysis. The same applies to the composites of polyaniline with noble metals, which are regarded as a break-through theme in the research team.

The authoress herself, however, considers the major contribution of her Thesis to be an involvement of young and promising students, and development of their enthusiasm for polyaniline. This is documented by two MSc and three PhD studies completed successfully in the recent years, and by the continuation of young researchers in the started direction. They are the best guarantee that the science of polyaniline will further be promoted.

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- P23. Trchová M.,** Konyushenko E.N., Stejskal J., Kovářová J., Čirić-Marjanović G.:
The Conversion of Polyaniline Nanotubes to Nitrogen-Containing Carbon Nanotubes and their Comparison with Multi-Wall Carbon Nanotubes,
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Summary

The Thesis is represented by a set of **23** selected papers **P1–P23** of the Doc. Dr. M. Trchová, that were produced in last ten years of active and intensive studies on conducting polymers, *viz.* polyaniline (PANI), by infrared and Raman spectroscopies, and appended by the comments of the authoress. The structure and the order of individual chapters do not correspond to the chronology of the research work. The authoress has made an effort to organize the papers constituting the Thesis into a dynamic set, describing the origin and evolution of PANI and its supramolecular structures, its properties and their improvement, aging and stability of PANI, and finally its resurrection to new and perspective materials based on carbonized PANI. Last but not least, an effort was also made to organize the papers in such a way, so that the readers would find the Thesis at least in part so exciting, as was the work, which has lead to its creation.

The first chapter concerns the origin and evolution of PANI. The PANI nanotubes are probably the most complex objects from nanostructures produced by this polymer. The understanding of their formation is thus most valuable in the discussion of the genesis of other morphologies. The analysis of the early stages of the oxidative polymerization of aniline to oligomeric intermediates is the clue to understanding the evolution of the molecular and supramolecular structures of PANI. The oxidation of aniline proceeds in two subsequent steps. In **P2**, **P3**, **P4**, and **P5**, the evolution of aniline oligomers in the first part of the reaction and of a polymer in the subsequent regime have been studied by using Fourier-transform infrared (FTIR) and Raman spectroscopies. These techniques were suitable to reflect the course of polymerization by the isolation of reaction intermediates and their *ex-situ* characterization. The role of the first oxidation products in the generation of nanotubes was discussed and the model of their formation was formulated.

The progress of the chemical polymerization of aniline has newly been monitored *in situ* by attenuated total reflection (ATR) FTIR spectroscopy in the **P6**, **P7**, **P8**. This method allowed observation of the early stages of polymerization directly during the oxidation process. The concept of brush-like ordering of macromolecules chains in the *in-situ* produced thin films and thermal deprotonation and stability of such films has been studied by FTIR spectroscopy in **P9**.

In the second chapter, the performance of PANI, especially with respect of tuning the conductivity, was studied with help of the infrared spectroscopy. The protonation by camphorsulfonic acid was compared from the spectroscopic point of view with the solid-state

oxidation of emeraldine base by ammonium peroxydisulfate in **P10**. The protonation reaction between two non-conducting compounds, PANI base and 3-nitro-1,2,4-triazol-5-one (NTO), a commercial explosive, yields conducting products **P11**. The properties of PANI, such as the hydrophilicity, can be modified by controlling the way of protonation in **P12**. Molecular structure of PANI composites with fullerenes was studied in **P13**, and with multi-wall carbon nanotubes in **P14**, again by using FTIR and Raman spectroscopies. The conducting PANI–silver composites obtained by oxidation of aniline with silver nitrate in solution of nitric or acetic acids in **P16** and **P17**, were analyzed by FTIR and Raman spectroscopies. The reduction of silver nitrate with PANI base in the solid state also leads to similar composites and the changes occurring in the structure of PANI were discussed on the basis of both FTIR and Raman spectroscopies in **P15**.

The third chapter concentrates on ageing and thermal stability of PANI. We have studied the changes in molecular structures of PANI films prepared in situ on silicon windows and protonated with different acids in **P18**. The study of the ageing of PANI base using FTIR spectroscopy proved the presence of the structural glass-like transition at the temperature around 80 °C in **P19**. The stability of the PANI films prepared under different conditions on silicon windows and leading to different morphologies were tested at elevated temperature in **P20**. The influence of strongly alkaline or acidic media on the stability of polyaniline was reported in **P21**.

The fourth chapter describes the reincarnation of PANI, *i.e.* the pyrolytic transformation of PANI to new materials, nitrogen-containing carbons. The globular morphology of PANI remained preserved after the carbonization of PANI in air. The samples had about the constant content of nitrogen, ~14 wt.%, irrespective of the processing temperature up to 800 °C, which was assigned to the formation of phenazine-like crosslinks using FTIR and Raman spectroscopic analysis in **P22**. The same approach has been used for the preparation of nitrogen-containing carbon nanotubes by the exposure of PANI nanotubes at elevated temperature up to 830 °C in a nitrogen atmosphere in **P23**.

The story of PANI does not end with this Thesis. On the contrary, it appears that, in fact, it is just starting. It has been proved in this Thesis that both infrared and Raman spectroscopies are extremely useful in this research direction.