

# Evolution of Polyaniline Nanotubes: The Oxidation of Aniline in Water

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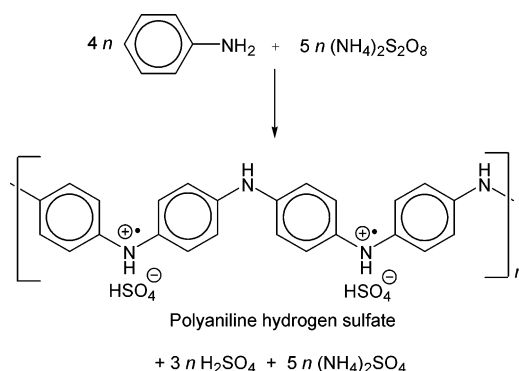
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The course of aniline oxidation with ammonium peroxydisulfate in aqueous solutions has been investigated. The reaction was terminated at various times and the intermediates collected. Besides the precipitates, the films deposited in situ on silicon windows have also been studied. The kinetic course of polymerization is controlled by the acidity level, which changes during the polymerization from pH 8 to a final value close to pH 1. It has two distinct exothermic phases. Gel-permeation chromatography indicates that aniline oligomers are produced at first at high pH, while polyaniline follows after the pH becomes sufficiently low. The growth of polyaniline nanotubes was observed by optical microscopy and confirmed by electron microscopy. The molecular structure of the reaction intermediates was studied in detail by FTIR spectroscopy. Oxidation products are markedly sulfonated, and they contain phenazine units. Aniline oligomers are more soluble in chloroform than the polymer fraction, which contains nanotubes.

## Introduction

Polyaniline (PANI) is one of the most investigated conducting polymers. It is prepared easily by the oxidation of aniline in aqueous medium (Figure 1). The reaction itself seems to be simple, yet it represents interplay of complex multilevel processes. Various supramolecular structures of the final product are obtained, depending on the conditions of the reaction, but the mechanism of their formation has not yet been elucidated. When aniline is oxidized in an acidic aqueous medium with ammonium peroxydisulfate, a PANI precipitate is produced.<sup>1,2</sup> The blue pernigraniline form present during the polymerization converts to a green protonated emeraldine at the end of the polymerization.<sup>3–5</sup> The reaction is exothermic and yields, in addition to PANI, sulfuric acid as a byproduct. The progress of polymerization thus can be followed in situ by recording either the temperature<sup>6–8</sup> or the pH.<sup>9,10</sup> Open-circuit potential measurements<sup>5,11,12</sup> and UV–visible spectroscopy<sup>13,14</sup> may be examples of other methods used for the same purpose. The progress of the chemical polymerization of aniline has newly been monitored in situ by ATR FTIR spectroscopy.<sup>15</sup>

Another group of techniques suitable to reflect the course of polymerization is based on the isolation of the reaction intermediates and their ex situ characterization. The oxidative polymerization of aniline with peroxydisulfate in dilute solutions of perchloric or hydrochloric acid of various concentrations was studied by Neoh et al.<sup>16</sup> The products thus obtained at various reaction times during the course of polymerization have been characterized by FTIR and X-ray photoelectron spectroscopies. The growth of PANI films on glass has been investigated by using UV–visible spectroscopy.<sup>17</sup> Studies of the development of morphology, however, are still missing.



**Figure 1.** Oxidation of aniline with ammonium peroxydisulfate in water yields PANI hydrogen sulfate. *Para* addition of constitutional units is shown, but the *ortho* addition can also be important. Sulfuric acid and ammonium sulfate are byproducts.

It has been reported recently that the courses of aniline oxidation with ammonium peroxydisulfate in aqueous solutions of strong (sulfuric) or weak (acetic) acids, followed by temperature and pH changes, are substantially different.<sup>10</sup> In solutions of sulfuric acid, granular PANI was produced; in solutions of acetic acid, PANI nanotubes were obtained. The morphology of PANI, granular or tubular, depends on the acidity conditions during the reaction rather than on the chemical structure of the acid.<sup>10</sup> The understanding of the principles of nanotube formation and knowledge of the factors that control the nanotubular morphology constitute a challenge.

It has been demonstrated by Gospodinova et al.<sup>9</sup> that the polymerization of aniline also proceeds well in water, without any added acid, when ammonium peroxydisulfate was used as an oxidant. Such a system is the simplest from the chemical point of view because it includes just two reactants and no other component, and is thus well suited for fundamental studies of aniline oxidation. The sulfuric acid produced by the decomposition of peroxydisulfate (Figure 1) gradually provides the

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necessary acidity, and the final PANI is protonated with this acid.<sup>18,19</sup> Although the conductivity of PANI thus prepared is rather low,<sup>20</sup>  $\sim 10^{-2}$  S cm<sup>-1</sup>, the observed nanotubular morphology of the products<sup>10</sup> makes such a system of substantial interest.

In the present paper, we analyze the course of aniline oxidation with ammonium peroxydisulfate in aqueous solutions in the absence of any added acid, as it is observed by temperature and pH measurement. The oxidation reaction was terminated at various stages, and the molecular structure and morphology of the reaction intermediates have been assessed. Both PANI films deposited on silicon windows and the accompanying PANI precipitates have been collected and characterized. The molecular structure of the products of aniline polymerization was studied by FTIR spectroscopy. The macromolecular parameters, like molecular weights and their distributions, were checked by gel-permeation chromatography. Finally, the evolution of supramolecular structure, that is, of the PANI nanotubes formed during aniline oxidation, has been followed by optical microscopy and confirmed by electron microscopy.

## Experimental Section

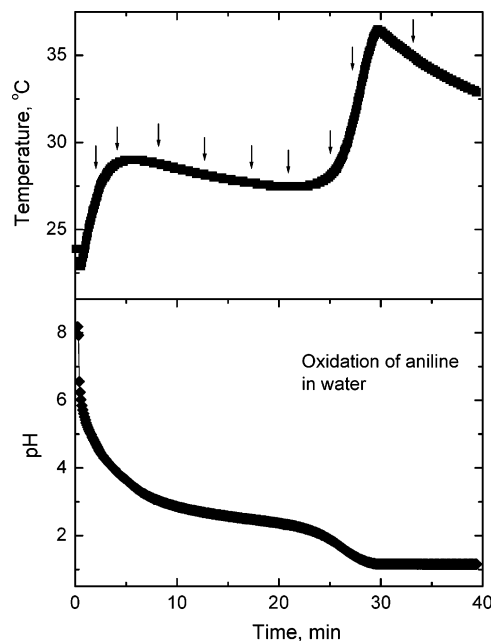
**Sample Preparation.** Aniline (0.2 M) was oxidized with ammonium peroxydisulfate (0.25 M) in water. Solutions of monomer and oxidant dissolved in water were mixed at room temperature to start the oxidation. The reaction mixture was quickly poured over silicon windows, that are used in FTIR spectroscopy (26 mm in diameter), placed in Petri dishes. The windows were slightly lifted on a support so that the reaction mixture had access to both the top and bottom sides. After a specified time, selected on the basis of the preliminary determination of the course of polymerization, the silicon windows were removed from the mixture. The oxidation reaction was stopped by rinsing the PANI films deposited on the windows with water, which removed both aniline and oxidant. The films were dried in air. After FTIR spectroscopic characterization, the windows were immersed in 1 M ammonium hydroxide to convert protonated intermediate forms to the corresponding bases, and FTIR spectra were again recorded.

The residual reaction mixture left after the removal of silicon windows was poured at the same time into excess of 1 M ammonium hydroxide to stop the polymerization. The precipitate was quickly collected on a filter, thus separated from the residual monomer and oxidant, and also dried in air. Selected samples have been suspended in chloroform for 24 h and the soluble and insoluble fractions have been separated.

**FTIR Spectroscopy.** Infrared spectra in the range of 400–4000 cm<sup>-1</sup> were recorded at 64 scans per spectrum at 2 cm<sup>-1</sup> resolution using a fully computerized Thermo Nicolet NEXUS 870 FTIR Spectrometer with a DTGS TEC detector. The spectra of thin films deposited on silicon substrates were measured in the transmission mode. An absorption subtraction technique was applied to remove the spectral features of the silicon. FTIR spectra of powders were recorded ex situ in the transmission mode, after dispersion of the samples in potassium bromide pellets. The spectra were corrected for the presence of carbon dioxide and water vapor in the optical path.

**Microscopy.** A research-grade Leica DM LM Microscope equipped with a 50 $\times$  Olympus objective lenses has been used for optical microscopy. Scanning electron micrographs have been taken with a JEOL 6400 microscope, transmission microscopy with a JEOL JEM 2000 FX.

**Gel-Permeation Chromatography (GPC).** Molecular weights were assessed by a GPC/SEC using a 8  $\times$  600 mm PLMixedB



**Figure 2.** Changes in temperature (top, squares) and acidity (bottom, diamonds) during the oxidation of 0.2 M aniline with 0.25 M ammonium peroxydisulfate in water. There are two reaction phases: the first starts after mixing the reactants at time  $t = 0$ , the second after  $t = 17$ – $21$  min. The times of sample collections are marked by arrows.

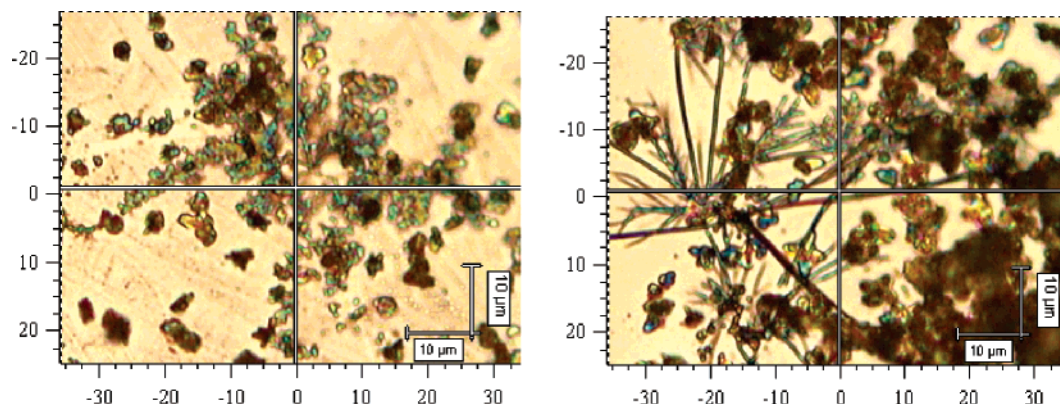
column (Polymer Laboratories, U.K.) operating with *N*-methylpyrrolidone and calibrated with polystyrene standards with spectrophotometric detection at the wavelength of 650 nm. The samples were dissolved in *N*-methylpyrrolidone containing 0.025 g cm<sup>-3</sup> triethanolamine for deprotonation of PANI, and 0.005 g cm<sup>-3</sup> lithium bromide to prevent aggregation.

## Results

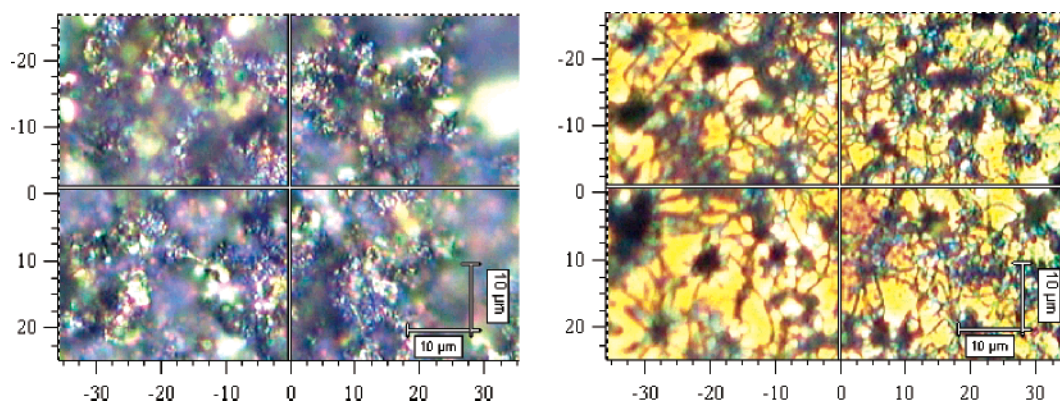
**Course of Polymerization.** The oxidation of aniline with ammonium peroxydisulfate is exothermic and its course is followed easily by monitoring the reaction temperature.<sup>2,6</sup> As aniline molecules are chained to produce PANI, the hydrogen atoms from the amino groups and from the benzene rings of the aniline are released in the form of protons, as sulfuric acid (Figure 1). Consequently, the pH of the reaction mixture decreases during the polymerization and can be recorded to assess the progress of reaction.<sup>9</sup>

The oxidative polymerization of aniline in the absence of any acid has been studied recently.<sup>10</sup> Unlike the oxidation in acid media, where an athermal induction period is followed by exothermic polymerization, two exothermic oxidation phases are well separated in water (Figure 2). The acidity of the medium, and the consequent protonation of the monomer and reaction intermediates, seem to be responsible for the existence of two reaction steps. In the beginning of the reaction, at pH > 4, aniline exists as a neutral molecule and is easily attacked by an oxidant. This is manifested by the fast increase in the temperature (Figure 2). At pH < 4, aniline is protonated to anilinium cation and the reaction mechanism changes. The oxidation then proceeds as in strong acids; an induction period is observed, followed by the exothermic polymerization of aniline.

**Morphology.** The polymerization of aniline in solutions of sulfuric acid has invariably lead to the granular morphology that has often been reported in the literature.<sup>21</sup> Polyaniline prepared in the presence of acetic acid has been produced mainly as nanotubes<sup>10</sup> accompanied by a globular precipitate; the



**Figure 3.** Morphology of the oligomeric products obtained after 8 min (left) and 13 min (right) of reaction time.



**Figure 4.** Top (left) and bottom side (right) of the silicon window observed after the 29 min polymerization time. Note the PANI nanotubes at the right micrograph.

nanotubes were produced, even in the absence of any acid. Here, we have investigated the genesis of such nanotubular structures.

During the oxidation of aniline beginning in neutral media, we have observed the evolution of the water-insoluble products of the reaction. The silicon windows were placed into the reaction mixture and removed at various stages of aniline oxidation. The oxidation products, deposited on the windows, have been studied by optical microscopy (Figures 3 and 4). There is a link between the course of polymerization and the supramolecular morphology produced at various times. The products obtained in the first stages of aniline oxidation, after 2–8 min, are composed mostly of crystals, which are obviously insoluble in water, having the size of several micrometers (Figure 3, left). They grow to trees (dendrimers) with branches of tens of micrometers in length, after the reaction time of 13 min (Figure 3, right). Brown granular objects several micrometers in size are also present. On the window removed at  $t = 17$  min, we observed, in addition to the granular precipitate, the first nanotubes growing on the top side of the window. Later, at  $t = 29$  min, only the unresolved structure is found on the top side of the windows, as a result of precipitate sedimentation (Figure 4, left). On the bottom side of silicon windows, we have observed the formation of nanotubes (Figure 4, right). Their occurrence increased at longer times of reaction.

The presence of nanotubes is confirmed by transmission electron microscopy (Figure 5), which shows the internal cavity of the nanotubes in the final precipitated product of polymerization ( $t = 33$  min). The nanotubes extend often to a few micrometers, their external diameter being ca. 200 nm and internal diameter of the cavity ca. 20 nm. Nanorods of similar morphology, but without a cavity, have also been detected in the samples, and occasionally a nanosphere was spotted in the micrographs. Some nanosheets seem to be accompanying

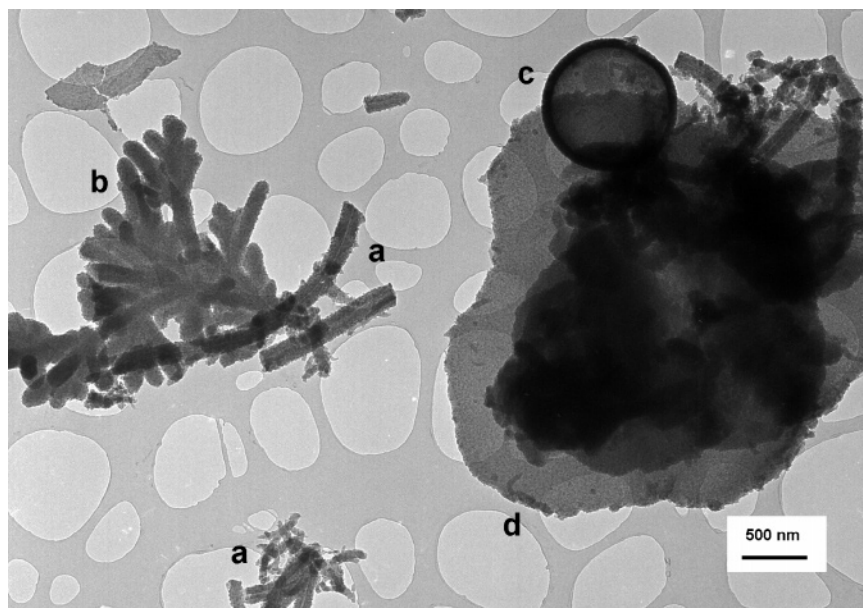
nanotubes (Figures 5 and 6) and, of course, a PANI precipitate of undefined morphology is also found in the final product.

**Molecular Weights.** GPC reveals that the reaction intermediates can be divided into two distinct groups. All of the samples separated before  $t < 17$  min, that is, produced by the oxidation of neutral aniline, have a molecular-weight distribution similar to that shown for  $t = 2$  min (Figure 7a). This corresponds to oligomers having the weight-average molecular weight  $M_w = 5000$ – $6000$  (Table 1). All of the products obtained at longer times, when the oxidation of anilinium cations has taken place, have bimodal distributions resembling that shown in Figure 7a for the reaction time  $t = 33$  min. This is reflected in a high polydispersity index,  $M_w/M_n$  (Table). This means that oligomers are produced at the first stage of reaction, and polymers in the second. The average molecular weight of the polymer part could be estimated as  $M_w = 40\,000$ – $70\,000$ . We conclude that, at higher pH (lower acidity, Figure 2, bottom), oligomeric products are obtained. Only at lower pH  $< 2$  (at high acidity) are polymeric products produced in addition to the oligomers originated earlier.

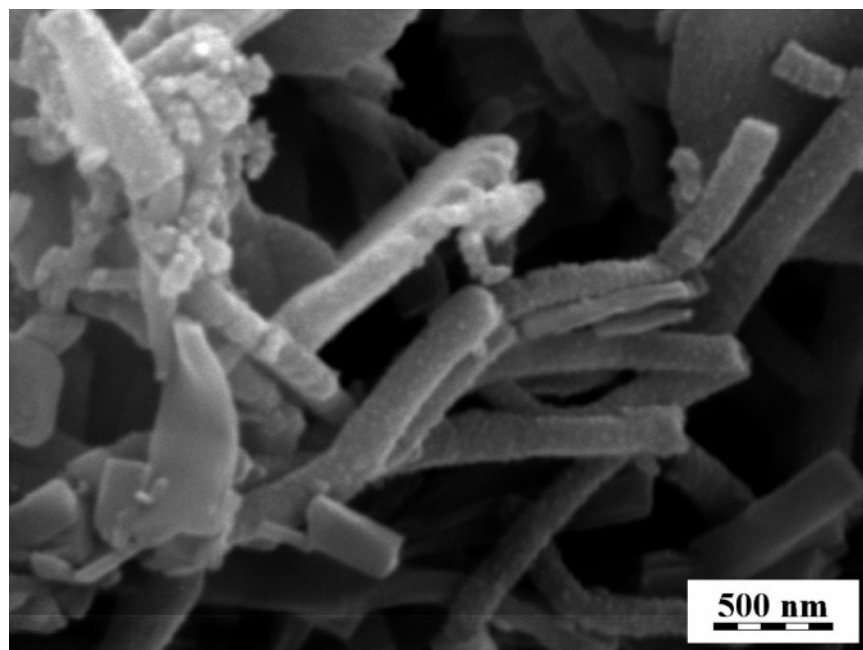
We have also determined the distributions of the molecular weights of the chloroform-soluble and chloroform-insoluble fractions of the final product (Figure 7b). The soluble portion contains mainly oligomers. The fraction insoluble in chloroform has a polymeric character, but it also contains an oligomeric part, which is either entrapped in the polymer or due to the crystallization became insoluble. This again leads us to conclude that the oligomers are produced at the beginning of oxidation and the polymers in its advanced stage.

**Sulfonation of Polyaniline.** There is practically no difference in the elemental compositions of the intermediates. There is, however, a notable amount of sulfur, 5–6 wt %, present in the samples (Table). The observed content of sulfur corresponds





**Figure 5.** Nanotubes (a) are present along with nanorods (b), nanospheres (c), nanosheets (d), and objects of unresolved morphology in the final product of polymerization ( $t = 33$  min).

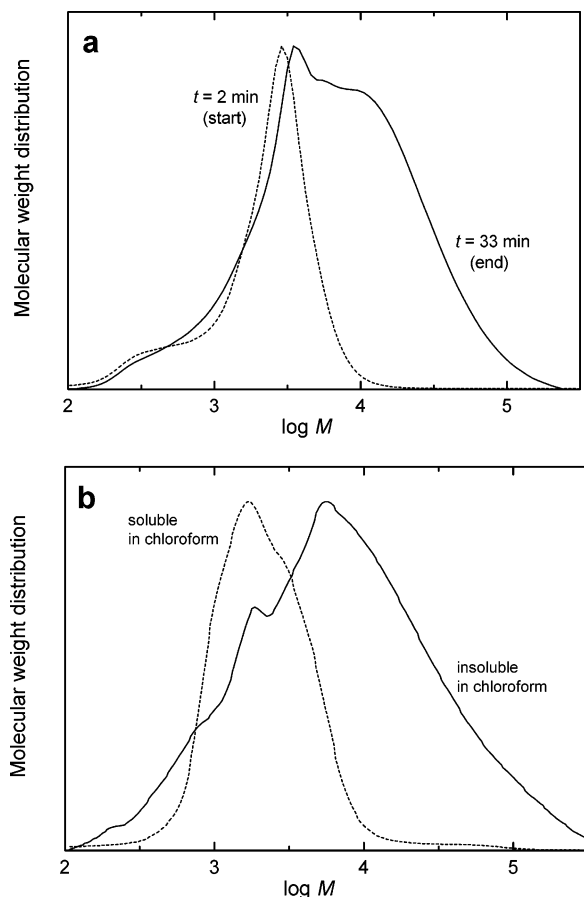


**Figure 6.** Polyaniline nanotubes as observed by scanning electron microscopy.<sup>10</sup> The nanosheets, 2D analogy of nanorods, accompany the nanotubes in the final product of polymerization ( $t = 33$  min).

to approximately one sulfonate group per five nitrogens, that is, five aniline constitutional units. Such a degree of sulfonation should have a marked effect on the properties of the PANI, and could account for the reduced conductivity of such PANI in the protonated state.<sup>22</sup> The sulfonation is typical of oxidation products prepared in the presence of weak acids or in the absence of any acid.<sup>10</sup> It has to be stressed that the samples are PANI bases, and the sulfur cannot come from the hydrogen sulfate counterions (Figure 1) associated with imine nitrogens, and it has to be mainly in covalently bound sulfonate groups. When the polymerization has been carried out in solutions of strong acids, the PANI bases contained only 0.3 wt % of sulfur.<sup>2</sup>

The sulfonation of benzene rings is therefore offered as a plausible explanation for the presence of sulfur in PANI. Because the sulfur content in the intermediates obtained at the different reaction times is approximately constant (Table), it

seems that the aniline monomer and low-molecular-weight oligomers, rather than the completed polymer, become sulfonated by interaction with ammonium peroxydisulfate or its derived radicals. The proposed aniline sulfonation would lead to a mixture of aniline with sulfanilic (4-anilinesulfonic acid) and orthanilic acid (2-anilinesulfonic acid). Therefore, the following process can be assumed to be a copolymerization of aniline with such sulfonic acids.<sup>23</sup> However, competitive sulfonation of low-molecular-weight oligomers cannot be ruled out. For example, in the case of aniline dimer, 4-aminodiphenylamine, its 1,4-diamino-substituted benzene ring is more reactive toward electrophilic aromatic substitution reaction, a sulfonation, than the mono-amino-substituted benzene ring. It can reasonably be expected that sulfonation of aniline trimers, tetramers, and so forth, leads mainly to products with the sulfonated aniline-oligomer head (a benzene ring with primary



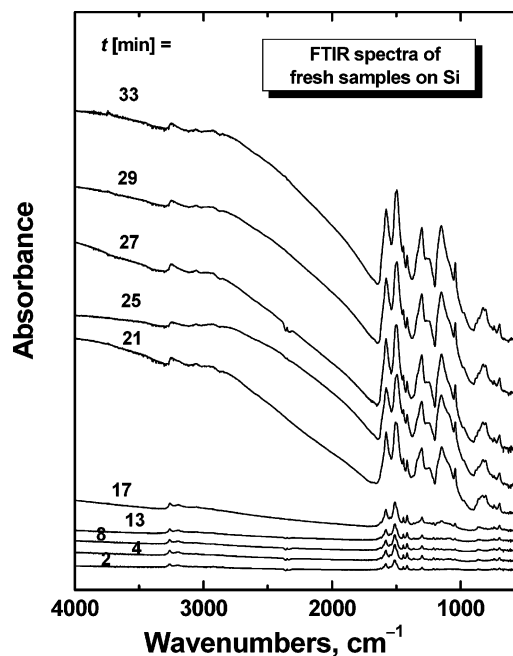
**Figure 7.** Weight distributions of molecular weights as obtained by GPC for the sample produced (a) at the start (dotted line) and at the end (full line) of aniline polymerization in water and (b) the chloroform-soluble and chloroform-insoluble fraction of the final product. The functions are normalized to a peak value.

**TABLE 1: Elemental Composition of Reaction Intermediates Isolated in Their Base Form after Time  $t$  and Their Weight-Average Molecular Weight,  $M_w$ , and Polydispersity, Weight-to-Number Average Molecular Weight Ratio  $M_w/M_n$ , Obtained by GPC**

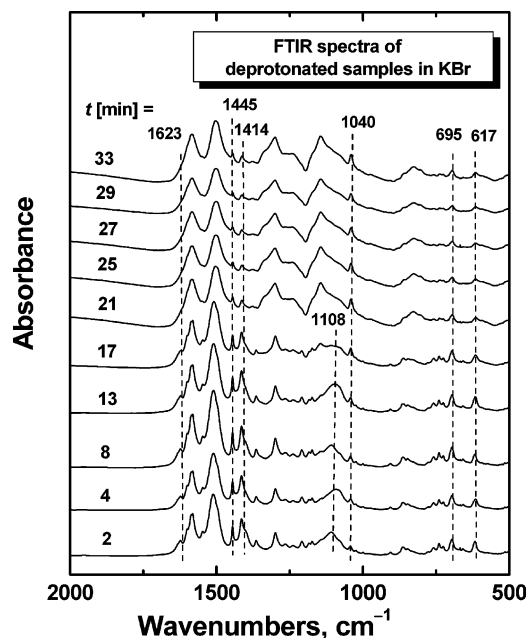
$t$ , min	%C	%H	%N	%S	$10^{-3} M_w$	$M_w/M_n$
2	58.0	5.4	15.0	6.1	6.2	3.1
4	59.3	5.5	14.7	5.5	5.2	3.3
8	63.0	5.9	14.3	4.9	6.0	3.6
13	59.5	5.3	14.5	5.6	5.4	4.0
17	58.5	5.2	14.4	6.3	14.1	5.3
21	57.8	5.1	13.8	6.0	41.8	14.1
25	56.4	5.1	13.4	5.1	38.1	11.3
27	55.6	5.1	13.4	6.0	56.5	15.9
29	54.5	5.0	13.7	6.3	87.2	15.8
33	57.9	5.1	13.5	6.3	64.8	13.1

amino group). Such aniline-sulfonated oligomers can also be copolymerized with aniline and other aniline oligomers in the reaction mixture.

**FTIR Spectra.** The molecular structure of the products arising during oxidation of aniline in water was studied by the FTIR spectroscopy. We have analyzed first the as-prepared samples deposited on silicon windows at various times after the beginning of the reaction (Figure 8). The spectra can be divided into two groups. The intensity of the absorption is very small for the samples obtained in the first stage of aniline oxidation ( $t < 17$  min) (Figure 2) and later it increased dramatically as the thickness of the films grew. The shape of



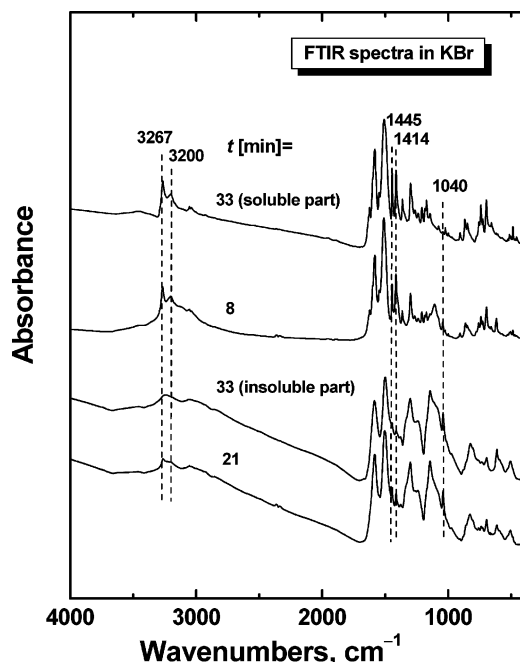
**Figure 8.** FTIR spectra of the reaction intermediates of the oxidation of aniline in water deposited on silicon windows separated after time  $t$  from the beginning of the reaction. The spectra are vertically shifted for separation in Figures 8–10.



**Figure 9.** FTIR spectra of the precipitated reaction intermediates collected after time  $t$ .

the spectra changed, too. The products obtained in the second stage of the reaction show high absorption in the region above  $2000 \text{ cm}^{-1}$ .

We have also analyzed the spectra of the samples deposited on silicon windows after immersion in 1 M ammonium hydroxide, that is the deprotonated forms, and the spectra of corresponding powders obtained as precipitates. The spectra of samples deposited on silicon windows are very similar to the spectra of the corresponding powders; therefore, only the latter spectra are discussed (Figure 9). They can also be divided into two groups with an intermediate spectrum recorded for the sample isolated at  $t = 17$  min. In the early stages of the reaction ( $t < 17$  min), they are more similar to those of aniline oligomers.



**Figure 10.** FTIR spectra of fractions soluble and insoluble in chloroform after extraction of intermediate collected at  $t = 33$  min and comparison with the typical spectra of the first and second group of products (oligomers and polymers) collected after  $t = 8$  and 21 min.

For longer times, the spectra resemble those of standard PANI<sup>22</sup> with some additional peaks marked by dashed lines in Figure 9.

The FTIR spectra of chloroform-soluble and chloroform-insoluble fractions of precipitated reaction intermediates collected at  $t = 33$  min were compared with the typical spectra of the first and second group of products (Figure 10). One can see that the spectrum of the soluble fraction is very close to that of the aniline oligomer intermediate obtained at short reaction time,  $t = 8$  min, while the spectrum of the insoluble fraction is similar to that of the final product of the polymerization reaction. Additional peaks are still present in the spectra of the insoluble part but they have a lower intensity. This observation will be discussed later.

### Discussion Based on FTIR Spectroscopy

**Spectroscopic Evidence of Sulfonation.** The sulfonate  $\text{SO}_3^-$  groups attached to the aromatic rings have been identified by the absorption peaks at 1040, 695, and 617  $\text{cm}^{-1}$  in all of the spectra<sup>24</sup> (Figure 9). These bands correspond, consecutively, to the S=O, S–O, and S–C stretching vibration modes. The presence of these bands in the spectra of alkali-treated samples confirms that sulfo-groups are covalently bound to the reaction intermediates during reaction. The aniline molecule and low-molecular-weight aniline oligomers, available in sufficient amount in the reaction mixture in the early stage of polymerization (at pH 4–8, Figure 2), are much more suitable for electrophilic attack than the anilinium cation and protonated aniline oligomers, and can thus be sulfonated. Additionally, the sulfonate group is likely to force the chain out of planarity,<sup>25</sup> inducing changes in the product conformation and in this way to reduce conjugation in the PANI chain. The conductivity of sulfonated PANI is indeed at least 2 orders of magnitude lower compared with common PANI.<sup>2</sup> We suppose that a broad band at 1144  $\text{cm}^{-1}$  may be due to the asymmetric stretching vibration of the sulfonate group, and the band at 1108  $\text{cm}^{-1}$  is attributed to the sulfate-ion stretching vibration.<sup>26</sup>

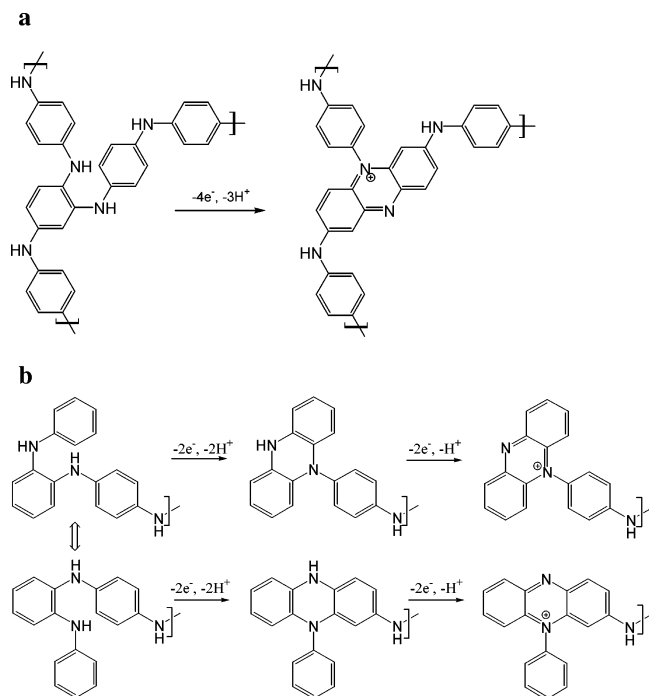
In the FTIR spectra of all the products obtained at short reaction times, one can observe two relatively strong bands with maxima at 3267 and 3200  $\text{cm}^{-1}$  (only the spectrum of the sample obtained after 8 min is shown in Figure 10). They are less pronounced in the spectra of samples collected at longer times,  $t > 17$  min (only the spectrum of the final product is shown in Figure 10). They could be assigned to terminal primary amine groups, but, considering the GPC data (Table), they are not likely to be present to a discernible extent. These bands have often been assigned to different types of intra- and intermolecular hydrogen-bonded N–H stretching vibrations of secondary amines, N–H $\cdots$ N. We also assume the presence of intramolecular hydrogen bonding in N–H $\cdots$ O, where the oxygen belongs to the sulfonate group.<sup>27–31</sup> The broad peak at 3182  $\text{cm}^{-1}$  has also been reported to reflect the presence of an intermolecular hydrogen bonding to imine groups.<sup>32</sup> The bands due to secondary amine stretching at 3460  $\text{cm}^{-1}$  and imine stretching<sup>26,30,33</sup> at 3370  $\text{cm}^{-1}$  are very broad, and weaker than bands appearing at  $\sim 3267$  and 3200  $\text{cm}^{-1}$ .

**Internal Protonation.** The sulfonation of PANI units<sup>25,34</sup> may lead to internal, intramolecular or intermolecular, interaction between sulfonate groups and neighboring imine sites in PANI chains.<sup>23</sup> It is obvious that interactions of this type might help to stabilize supramolecular structures produced by PANI. As we expect to analyze the spectra of products converted to the base form, there are indeed indications for reluctance of the polymer toward deprotonation. The feature of internal protonation of the products isolated at longer times of polymerization,  $t > 17$  min, is well manifested by the shape of the spectra above 2000  $\text{cm}^{-1}$  (Figure 10).

All of the spectra contain the band at 1547  $\text{cm}^{-1}$  of medium intensity, which is not expected to appear in the spectrum of undoped PANI (Figure 9). Cases et al.<sup>35</sup> assigned the band at 1547  $\text{cm}^{-1}$  to semi-quinonoid rings, and Boyer et al.<sup>36</sup> reported the band at 1558  $\text{cm}^{-1}$  for the emeraldine salt, with the proposed assignment of C=C stretching and C–H deformation vibrations in a semi-quinone structure. A strong and broad band observed at 1144  $\text{cm}^{-1}$  is reported to be a band of a conducting PANI, associated with a high degree of electron delocalization in protonated PANI,<sup>16,37–39</sup> and it is also interpreted as a B–NH–B or Q=NH<sup>+</sup>–B stretching mode<sup>37</sup> (B denotes a benzene ring, Q is a quinonoid ring in PANI chain, cf. Figure 1).

**Phenazine-like Units.** In the spectra of the present samples we have observed a set of bands corresponding to phenazine-like units (Figure 11). The presence of phenazinium structures in the structure of aniline oxidation products is not surprising. The phenazine rings are produced in chains containing both the *ortho* and *para*-linked aniline constitutional units. These are likely to be produced especially at low acidity of the reaction medium<sup>40</sup> at pH 4–8. They can constitute either branching sites (Figure 11a) or end-groups (Figure 11b). The band at 1623  $\text{cm}^{-1}$ , with the shoulder at  $\sim 1630$   $\text{cm}^{-1}$ , is observed clearly in the spectra of the products obtained for  $t < 21$  min, and for longer times they become overlapped with the band at 1582  $\text{cm}^{-1}$ . We suppose that these modes correspond to C=C stretching vibration in a phenazine-like segment,<sup>41</sup> including a contribution from C=N stretching vibrations.<sup>26,42</sup> The spectrum of phenazine itself shows the band at 1627  $\text{cm}^{-1}$ . The band at  $\sim 1600$   $\text{cm}^{-1}$  is well observed only in the spectra of products isolated at  $t < 17$  min. This absorption, corresponding to a C–C benzene ring-stretching vibration, is situated very close to the positions 1597 and 1602  $\text{cm}^{-1}$  found for aniline dimers, *p*-semidine (4-aminodiphenylamine), and *o*-semidine (2-aminodiphenylamine), respectively.





**Figure 11.** Phenazine-like unit can be formed: (a) at the branching site after oxidation of 1,2,4-trisubstituted ring structure; (b) at the beginning of the chain after oxidation of 1,2-disubstituted ring structure.

The band at  $\sim 1414\text{ cm}^{-1}$ , which is present in all the spectra, but is more intense in samples collected at  $t < 21\text{ min}$ , is a strong indication of the formation of phenazine-like segments (Figure 9). In the polymeric part produced at  $\text{pH} < 4$ , their presence becomes significantly reduced. This band is not observed in the spectra of standard PANI bases,<sup>36,37</sup> but heterocycles containing several nitrogen atoms are active in this wavenumber region. The band at  $\sim 1410\text{ cm}^{-1}$  has been observed in the spectra of pyrazine, phenazine, and polymers containing phenazine units, and it is assigned to a totally symmetric stretching of the phenazine ring.<sup>43,44</sup> Phenazine-like units can be also recognized through the bands at 1208 and  $1136\text{ cm}^{-1}$  and its contribution to the bands at 1144 and  $1108\text{ cm}^{-1}$  is possible (in the phenazine spectrum, the bands at 1210, 1136, 1147, and  $1109\text{ cm}^{-1}$  are present). Their presence may thus be expected, and is indeed observed (Figures 8 and 9), especially in oligomeric products.

**Evolution of FTIR Spectra.** The strong band at  $1582\text{ cm}^{-1}$ , observed at  $t < 21\text{ min}$  in the spectra of deprotonated samples (Figure 9), becomes even stronger and shifted to  $1585\text{ cm}^{-1}$  after this reaction time. This band corresponds to C=C stretching in newly formed quinonoid rings, (the  $\text{N}=\text{Q}=\text{N}$  stretching mode).<sup>35,37,45</sup> The massive band at  $\sim 1510\text{ cm}^{-1}$  (with a shoulder at  $\sim 1496\text{ cm}^{-1}$ ) appears in all of the spectra for the reactions times up to 21 min, and a strong band at  $\sim 1502\text{ cm}^{-1}$  is observed for longer times. This absorption is characteristic of benzenoid ring-stretching in the N–B–N mode.<sup>37,45</sup> The intensity ratio of the bands due to aromatic C=C stretching vibrations at 1445 and  $1414\text{ cm}^{-1}$  (the last one corresponding to phenazine-like segments) is changed at 21 min.

The bands corresponding to C–N stretching vibrations are observed at  $1364\text{ cm}^{-1}$  (for all polymerization times),  $1378\text{ cm}^{-1}$  (arising at  $t = 21\text{ min}$ ), and  $1300\text{ cm}^{-1}$  (present in all the spectra, strengthened (and with a shoulder at  $1336\text{ cm}^{-1}$ ) for  $t > 17\text{ min}$ ). Kang et al.<sup>37</sup> attributed the  $1380\text{ cm}^{-1}$  band in the PANI spectrum to C–N stretching in QB<sub>t</sub>Q unit (B<sub>t</sub> denotes a trans-benzenoid unit), and the  $1315\text{ cm}^{-1}$  band to C–N stretching in

QB<sub>c</sub>Q, QBB, and BBQ units (B<sub>c</sub> denotes a cis-benzenoid unit). A band at  $\sim 1240\text{ cm}^{-1}$  due to C–N stretching in BBB units is noted in emeraldine-base spectra,<sup>36,37</sup> while we observed two bands at 1240 and  $1266\text{ cm}^{-1}$  for all polymerization times. The band at  $1266\text{ cm}^{-1}$  is possibly due to C–N vibrations in tertiary arylamine, in phenazine-like units.<sup>27,28</sup>

In the region  $900\text{--}650\text{ cm}^{-1}$  many bands are observed, attributed to aromatic C–H out-of-plane deformation vibrations  $\gamma(\text{C–H})$ , while the spectrum of standard PANI usually has only one band typical of a para-disubstituted benzene ring.<sup>46,47</sup> Besides the presence of 1,4-disubstituted rings as prevalent for all polymerization times, indicating linear elements of chain, FTIR spectroscopy revealed the presence of a significant number of 1,2,4-trisubstituted rings, indicative of branched and/or substituted phenazine-like elements (Figure 11). The band at  $827\text{ cm}^{-1}$  corresponding to 1,4-disubstituted rings<sup>16,26,27,46,48</sup> is drastically strengthened at 21 min, becoming the dominant band in this region. The 1,2,4-substitution pattern is revealed by the bands at 864 and  $857\text{ cm}^{-1}$  (2 H) before and after  $t = 17\text{ min}$ , respectively, at  $906\text{ cm}^{-1}$  (1 H) during all times,<sup>26</sup> and by the band at  $880\text{ cm}^{-1}$  (1 H),<sup>26,33</sup> which appears after  $t = 17\text{ min}$ . The band at  $880\text{ cm}^{-1}$  may be correlated with detected changes in the morphology of the polymeric products in this period. The band at  $848\text{ cm}^{-1}$ , well resolved only at  $t < 21\text{ min}$ , can be due to 1,4- and/or 1,2,4-substituted rings. The mono and 1,2-disubstituted rings correspond to the bands<sup>26</sup> at 726 and  $740\text{ cm}^{-1}$ . The bands at 906, 880 (1 isolated H), and  $864\text{ (}857\text{ cm}^{-1}\text{ (}2\text{H))}$  are attributable to  $\gamma(\text{C–H})$  vibrations of substituted phenazines, too.<sup>26</sup> The  $974\text{ cm}^{-1}$  band, strengthened at  $t > 17\text{ min}$ , corresponds to C–H in-plane deformation vibration of the quinonoid form of a 1,2,4-trisubstituted ring.<sup>29,33</sup>

FTIR spectra of the intermediates corresponding to longer times ( $t > 17\text{ min}$ ) may be assigned to the spectra of standard PANI base<sup>22</sup> with some features of the spectra of samples obtained for  $t < 17\text{ min}$  (Figure 10). As has been shown, the samples are only partly soluble in chloroform. The insoluble polymer fraction is composed of nanotubes and granular precipitate. We suppose that both parts of this fraction are sulfonated and that the additional peaks, which are also present in the spectra of the insoluble part, belong to the observed nanotubes. The nanotubes also contain phenazine units.

**Concluding Remark on Nanotube Formation.** It has been proposed<sup>10</sup> that the aniline oligomers produced in the early stages of the polymerization at low acidity of the medium are insoluble in water, and that they aggregate to constitute a template-like structure, which further predetermines the directional growth of PANI, that is, the production of nanotubes. The present study provides additional insight into such a concept. The PANI nanotubes are produced within an intermediate acidity interval; at lower acidity, the products are oligomers, and at higher acidity, PANI has the granular morphology.

The occurrence of nanotubes is clearly associated with the presence of oligomer crystal-like structures that act as templates where the nanotubes growth starts. The presence of phenazine-like units in PANI (Figure 11) is also invariably connected with the existence of nanotubes. We propose that phenazinium units act as discotics that guide the stacking of oligomers as they are produced during the oxidation of aniline, providing the necessary organization and order that predetermine the growth of nanotubes. The sulfonation of PANI, occurring at the same time, may help to stabilize the produced structures by internal protonation, that is, by ionic bonding between sulfonate groups and protonated imine sites in neighboring polymer chains.

Although such a model is speculative, it stimulates the further experiment work in this direction.

## Conclusions

The oxidation of aniline in water, that is, in the absence of any added acid, has two distinct exothermic phases. The acidity also increased in two steps from pH 8 at the beginning of the reaction to pH  $\approx$  1 at its end, the sulfuric acid being a byproduct. The evolution of PANI nanotubes during this process has been observed. Aniline oligomers are produced in the first part of the reaction, a polymer (PANI) in the subsequent regime. The development of oligomer crystals, and later of PANI nanotubes growing from them, has been observed by optical microscopy in PANI films deposited in situ during the polymerization on silicon windows. Precipitated oligomers thus act as a sort of a template, with nanotubes growing from them as branches. The presence of nanotubes of ca. 200 nm external diameter has been confirmed by scanning electron microscopy. The transmission electron microscopy revealed that, besides the nanotubes with an internal cavity, PANI nanorods, nanobubbles, and possibly nanosheets are found in the samples. The final oxidation products are composed of oligomers produced at short reaction times (soluble in chloroform); the polymer component is produced later and contains PANI nanotubes and precipitate (both insoluble in chloroform).

The molecular structure after deprotonation to bases is similar for both oligomers and polymers. Oligomers are not protonated during the reaction while the polymers generated later are. In contrast to the common PANI prepared in acid media, a notable content of sulfur in the samples has been found by elemental analysis. This has been attributed to the sulfonation of benzenoid rings in PANI and confirmed by identifying sulfonate vibrations in the FTIR spectra. Aniline monomers may become sulfonated in the course of the oxidation reaction and they are only later incorporated into the growing chains. The formation of phenazine units in PANI has also been proved with FTIR spectra. Such units are absent in the spectra of standard PANI. It is speculated that phenazine-like units promote the ordering of oligomers by a stacking mechanism, as with discotics. Such structures then provide a template from which PANI nanotubes emerge. The internal protonation, leading to ionic interaction between sulfonate groups and protonated imine sites of PANI chain, helps to stabilize the produced structure.

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