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Oxidation of Aniline: Polyaniline Granules, Nanotubes, and Oligoaniline Microspheres

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ABSTRACT: Aniline was oxidized with ammonium peroxydisulfate in solutions of strong acid (0.1 M sulfuric acid), weak acid (0.4 M acetic acid), or alkali (0.2 M ammonium hydroxide). The properties of the oxidation products and their morphology are controlled by the initial acidity of the medium and the acidity profile during the oxidation; the acidity increases because sulfuric acid is a byproduct. Conducting polyaniline nanogranules, nanotubes, or nonconducting oligoaniline microspheres were obtained, respectively. FTIR spectra suggest that the oligomers produced by the oxidation of neutral aniline molecules at the beginning of oxidation are similar, regardless of the acidity of the medium. Neutral aniline molecules, prevailing under alkaline conditions, are easily oxidized to aniline oligomers composed of *ortho*- and *para*-coupled aniline constitutional units. *Ortho*-coupled units are further converted by oxidative intramolecular cyclization to phenazines. It is proposed that, in acidic media, *N*-phenylphenazine units constitute the initiation centers for the subsequent polymerization of aniline, which takes place at pH < 2 when the intermediate pernigraniline chains become protonated. Anilinium cations, which dominate in strongly acidic media, are difficult to oxidize to oligomers, but they easily participate in the formation of polymer chains once their growth has started. The self-organization of phenazine units is responsible for the generation of polyaniline nanotubes. Partial sulfonation of aromatic amines occurs at higher pH, especially in alkaline media. The sulfonated oligomers stabilize aniline emulsions and enable the formation of oligoaniline microspheres, when the miscibility of aniline with aqueous medium is limited. The final oxidation products obtained in alkaline conditions contain only low-molecular-weight oligomers; the polymeric component is the dominating product only in strongly acidic media. Both components are present in various proportions when the oxidation takes place at intermediate pH ranges.

Introduction

Nanostructures produced by conducting polymers are likely to exhibit new electrical and optical properties due to the various organizations of polymer chains.[1,2] Polyaniline (PANI) is one of the most important conducting polymers. The oxidation of aniline typically proceeds in strongly acidic aqueous medium and is currently used for the synthesis of conducting PANI.[3] The granular morphology of PANI is observed as a rule.

Reports on the preparation of PANI nanotubes[4–7] and nanowires[8–13] now appear in the literature frequently. The pioneering papers have been published by the Wan group.[14–16] The presence of organic acid in the reaction mixture has been a typical feature of these syntheses.[7,11,14] It has been proposed that aniline salts with these acids form a special kind of template for the subsequent polymerization of aniline.[16,17] Later, however, the nanotubes were prepared in solutions of inorganic acids[18] or even in the absence of any added acid.[19] Another type of morphology, microspheres, was the product of aniline oxidation started in an alkaline medium.[20,21] The role of the acidity, rather than the nature of the acid employed, has recently been suggested to exert control over the chemistry of aniline oxidation[5,21,22] and, subsequently, the growth of PANI nanostructures.

During the oxidation of aniline with peroxydisulfate, the pH decreases because sulfuric acid is a byproduct (Figure 1). Any coupling of aniline molecules is connected with the abstraction of two hydrogen atoms that are released as protons. The whole oxidation is thus an intricate interplay of oxidation and protonation processes, depending on the starting pH and the acidity−time profile during the reaction. The present study demonstrates the role of acidity in the formation of the molecular structure of the oxidation products, and tries to provide some chemical clues to the generation of supramolecular assemblies.

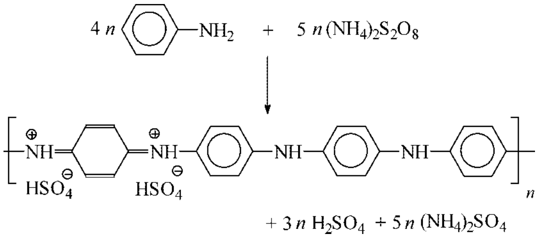

Figure 1. Stoichiometry of aniline oxidation with ammonium peroxydisulfate to polyaniline hydrogen sulfate in an acidic medium. Sulfuric acid and ammonium sulfate (or ammonium hydrogen sulfate) are byproducts.

Experimental Section

Oxidation of Aniline. Aniline (20 mmol, 1.86 g) was dissolved in various aqueous media: 0.1 M sulfuric acid, 0.4 M acetic acid, or 0.2 M ammonium hydroxide to 50 mL of solution. Ammonium peroxydisulfate (APS; 25 mmol, 5.71 g) was similarly dissolved to provide 50 mL of a solution, and the solutions of aniline and oxidant were mixed at 20 °C to start the oxidation. The reaction mixture thus always contained 0.2 M aniline and 0.25 M APS (Figure 1). The course of the exothermic polymerization was monitored with a digital thermometer, and the acidity changes were recorded with a pH meter. The solids were collected on a filter after 2 h, rinsed with water, and dried in air and then over silica gel in a

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Table 1. Properties of Polyanilines Prepared in Aqueous Media of Various Acidities[a]

	0.1 M sulfuric acid	0.4 M acetic acid	0.2 M ammonium hydroxide
starting pH	2.4	4.5	10.4
terminal pH	1.0	1.1	3.0
morphology	granules	nanotubes	microspheres
conductivity of protonated form, S cm^{-1}	3.7	0.036	$<10^{-10}$
conductivity of corresponding base, S cm^{-1}	1.1×10^{-9}	7.9×10^{-9}	$<10^{-10}$
density, protonated/base, g cm^{-3}	1.402/1.227	1.338/1.256	N/A
sulfur in PANI bases, wt %	0.9	1.8	2.0
molecular weight, M_w	39,400	32,200	4,080
polydispersity index, M_w/M_n	13.1	19.0	1.3

[a] 0.2 M Aniline was oxidized with 0.25 M ammonium peroxydisulfate at 20 °C. The corresponding bases were obtained by deprotonation with 1 M ammonium hydroxide. Conductivity was determined by a four-point method for conducting samples ($>10^{-5}$ S cm^{-1}) and with a two-point technique for nonconducting samples. Density was determined by weighing the samples in air and immersed in decane. Molecular weights and polydispersity were assessed by gel-permeation chromatography using *N*-methylpyrrolidone as the solvent.

desiccator. A portion of the products was converted to PANI bases by overnight immersion in 1 M ammonium hydroxide, followed by separation and drying. Test samples have also been isolated after 4 min of reaction.

Characterization. Infrared spectra in the range of 400–4000 cm^{-1} were recorded at 64 scans per spectrum at 2 cm^{-1} resolution using a Thermo Nicolet NEXUS 870 FTIR spectrometer with a DTGS TEC detector. Samples were dispersed in potassium bromide and compressed into pellets. The spectra were corrected for the presence of moisture and carbon dioxide in the optical path. Optical spectra of the oxidation products dissolved in *N*-methylpyrrolidone were recorded with a Lambda 20 spectrometer (Perkin-Elmer, UK).

Results

Oxidation of Aniline in Media of Various Acidities. The oxidation of aniline in the solutions of strong acids, e.g., 0.1 M sulfuric acid, has become standard procedure for the preparation of a conducting polymer,[3] with the conductivity of the product of the order of at least units S cm^{-1} being the criterion of successful preparation. The oxidation products are polymers having a broad molecular-weight distribution (Table 1) and are obtained as fused nanogranules (Figure 2a). The characteristic absorption maxima in the UV–visible spectra recorded for solutions of PANI base in *N*-methylpyrrolidone are located at 324 and 618 nm, and correspond to the blue color of PANI base (Figure 3).

When the oxidation is started under mildly acidic conditions, e.g., in 0.4 M acetic acid, the conductivity of the product is reduced but its polymeric character is still retained (Table 1). The high polydispersity index is due to the bimodality of the distribution; the product is composed of polymeric and oligomeric components.[22] The formation of nanotubes is the most interesting feature of the reaction (Figure 2b). When the conductivity is not the main goal and the preference is given to the nanoscale morphology of the products, the oxidation of aniline under mildly acid conditions is the priority strategy. In the optical spectra, the first maximum is shifted to 336 nm and the second is shifted to 602 nm, in accord with the reduced conductivity and the presence of an oligomeric fraction (Figure 3).

Oxidation started in an alkaline medium, 0.2 M ammonium hydroxide, yields nonconducting aniline oligomers (Table 1) but the microspheres they create (Figure 2c) make them of interest. The single absorption maximum at 336 nm in the visible spectra corresponds to the brown color of the solution and reflects the absence of conjugation (Figure 3).

The Course of Oxidation. The oxidation process itself can be analyzed by following the time-dependence of the acidity (Figure 4) which increases in the course of reaction because sulfuric acid is a byproduct (Figure 1), and/or temperature (Figure 5), because the oxidation is exothermic. The oxidation in 0.1 M sulfuric acid starts at pH 2.4 and the decrease in pH is well visible (Figure 4). An athermal induction period is followed by exothermic polymerization,[3,23] during which the temperature of the reaction mixture increases (Figure 5). Similar oxidation under mildly acidic conditions, in 0.4 M acetic acid, starts immediately, as illustrated by the sudden drop in pH (Figure 4) and the evolution of heat (Figure 5). After the pH falls below ~3.5, the oxidation virtually stops and the mixture cools, just to be followed by the second exothermic phase, starting below ca. pH 2.5. The oxidation of aniline started in alkaline conditions, 0.2 M ammonium hydroxide, is fast, without any induction period (Figures 4 and 5). The ammonium hydroxide constituting the medium is neutralized in the course of oxidation by the sulfuric acid produced (Figure 1), and the final pH thus falls in the mildly acidic region.

Molecular Structure. FTIR spectra of *the final oxidation products* substantially differ from each other (Figure 6). The base forms of the oxidation products are better suited for the comparison of molecular structure rather than the protonated counterparts, because the spectral features of counter-ions are absent. In addition to the main absorption bands of PANI base, located at 1585 and 1497 cm^{-1}, a shoulder at about 1630 cm^{-1} and bands at 1445 and 1414 cm^{-1} are present in the spectra of the products obtained in 0.4 M acetic acid and under alkaline conditions. We suppose that they correspond to the presence of *ortho*-coupled aniline units and phenazine-like units.[5,19] These peaks are not visible in the spectra of samples prepared in 0.1 M sulfuric acid. The peak at 1374 cm^{-1}, typical of standard PANI base and assigned to C–N stretching in the neighborhood of a quinonoid ring,[24] becomes reduced in the product prepared in less acidic conditions, e.g., in acetic acid. The peak located at 1040 cm^{-1} suggests the presence of sulfonate groups attached to the aromatic rings;[25] this is supported by the presence of sulfur in the samples (Table 1).

FTIR spectra of oxidation products collected in *the early stages of oxidation* in the solutions of a strong and a weak acid are, on the other hand, virtually identical (Figure 7). This is one of the most important observations of the present study. They are also identical with the spectra of the first oligomeric products of the oxidation of aniline in water, reported earlier,[19] and are very close to those observed for the oxidation products in an alkaline medium (Figure 7). The presence of the peaks at 1625, 1445, and 1414 cm^{-1} is a common feature of the all the early oxidation products. The last peak may be assigned to a totally symmetric stretching of the phenazine ring.[26,27] Phenazine-like units can also be detected by the bands at 1208 and 1136 cm^{-1} (Figure 7) and their contribution to the band at 1145 cm^{-1} is possible. The bands observed at 1445 and 1414 cm^{-1} in the spectrum of *o*-semidine (2-aminodiphenylamine), where they are much stronger than in the spectrum of *p*-semidine (4-aminodiphenylamine), support the presence of *ortho*-linked aniline constitutional units in the oligomers. The band at 1625 cm^{-1}, with a shoulder at ~1630 cm^{-1}, corresponds to the C=C stretching vibration in a phenazine-like segment,[28] including a contribution from C=N stretching vibrations.[29] The spectrum of phenazine itself displays the band at 1627 cm^{-1}. The ring-sulfonation of oligomers is especially favored when the oxidation proceeds in an alkaline medium, as is demonstrated by the absorption peak located at 1040 cm^{-1}.

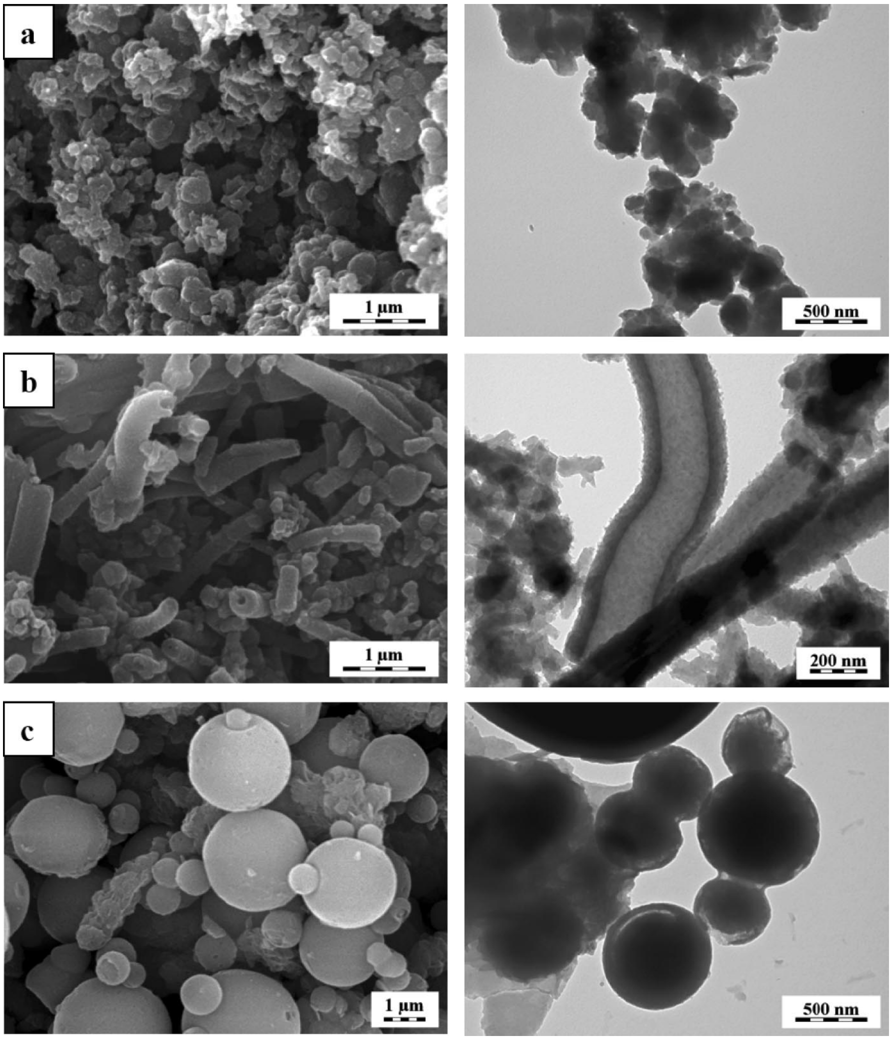

Figure 2. Scanning (left) and transmission (right) electron microscopy: (a) granular morphology typical for polyaniline prepared in strongly acidic solutions (0.1 M sulfuric acid); (b) oxidation of aniline under mildly acidic conditions (0.4 M acetic acid) produces nanotubes; (c) oligomeric microspheres obtained when the oxidation is initiated in alkaline medium (0.2 M ammonium hydroxide).

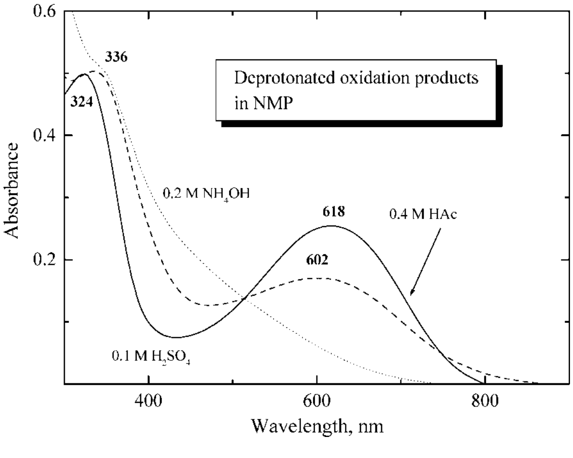

Figure 3. UV–visible spectra of the oxidation products converted to the base form and dissolved in *N*-methylpyrrolidone. Polyaniline was prepared in 0.1 M sulfuric acid (full line), and 0.4 M acetic acid (dashed line), and oligoaniline in 0.2 M ammonium hydroxide (dotted line). The first two products are blue, the last one is brown.

Discussion

Aniline is a weak base, pK_a = 4.6 at 25 °C.[30,31] In alkaline media, it exists mostly as neutral aniline molecules while, under strongly acidic conditions, the anilinium cations dominate (Figure 8). The neutral aniline molecules and anilinium cations have different electron density distributions and, consequently, different oxidation reactivity and reaction fate.[30]

Oxidation in an Alkaline Medium. Neutral aniline molecules are easily oxidized to produce a dimer (semidine), and to add further aniline molecules to produce higher oligomers (Figure 9). Both the *ortho* and *para* coupling of aniline molecules is possible.[32,33] That is why the oxidation products prepared in 0.2 M ammonium hydroxide do not produce a conjugated system and they are nonconducting. The degree of oligomerization is low, typically up to tens of aniline constitutional units (Table 1).

The *ortho*-coupled aniline units can further undergo oxidative cyclization to yield phenazine structures[34,35] (Figure 9). This type of reaction is well-known from the oxidation of *o*-phenylenediamine.[36,37] or branching and cross-linking reactions in PANI.[38–40] Phenazine units can be produced at any point in an oligomer chain.

Oxidation in a Solution of a Weak Acid. When the oxidation of aniline starts in mildly acidic conditions, at pH 4.5 in 0.4 M acidic acid (Figure 4), the reaction mixture is rich in both neutral aniline molecules and anilinium cations (Figure 8). Neutral aniline molecules are easily oxidized to oligomers as described above (Figure 9), and the released protons reduce the pH (Figure 4). The equilibrium between the aniline

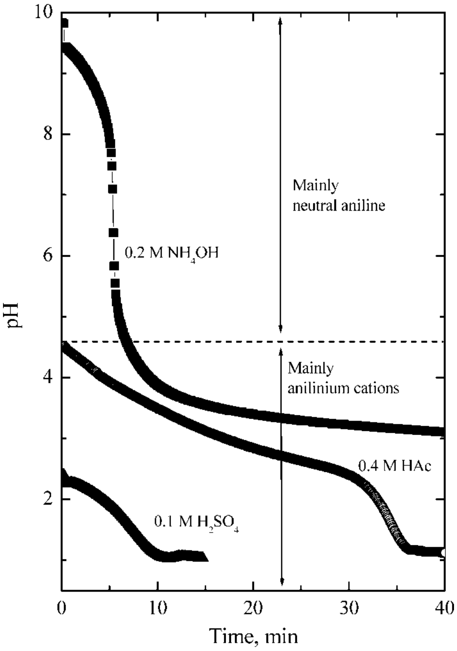

Figure 4. Acidity profiles during the oxidation of 0.2 M aniline with 0.25 M ammonium peroxydisulfate started in media of high acidity (0.1 M sulfuric acid), low acidity (0.4 M acetic acid), and in alkaline solutions (0.2 M ammonium hydroxide).

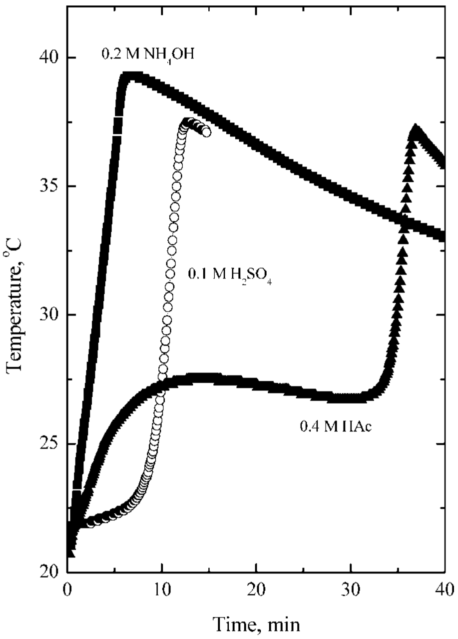

Figure 5. Temperature profile during the oxidation of 0.2 M aniline with 0.25 M ammonium peroxydisulfate started in media of high acidity (0.1 M sulfuric acid), low acidity (0.4 M acetic acid), and in alkaline solution (0.2 M ammonium hydroxide).

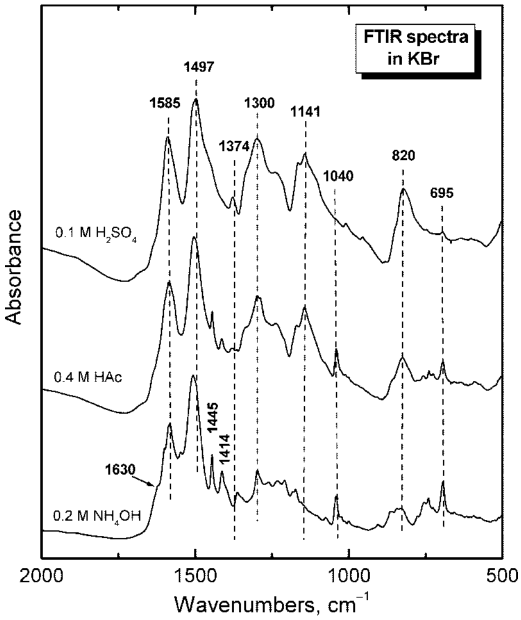

Figure 6. FTIR spectra of bases obtained by the deprotonation of samples prepared by the oxidation of aniline in 0.1 M sulfuric acid, 0.4 M acetic acid, or in 0.2 M ammonium hydroxide.

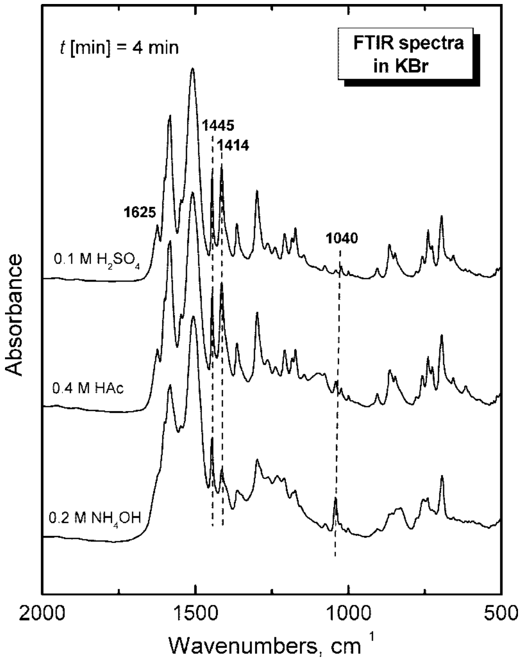

Figure 7. FTIR spectra of products isolated in the early stages of aniline oxidation (after 4 min) in 0.1 M sulfuric acid, 0.4 M acetic acid, or in 0.2 M ammonium hydroxide.

molecules and anilinium cations shifts in favor of the latter species (Figure 8). Anilinium cations are much more difficult to oxidize directly, because the electron pair on nitrogen, which is delocalized in neutral aniline molecules, becomes localized in the anilinium cation.[30] That is why the reaction virtually stops,[5,41] and the temperature starts to decrease (Figure 5). Yet, there is always equilibrium between the protonated and neutral species (Figure 8), both species always coexist, and the oxidation of neutral aniline molecules still proceeds with preference even if their content is very low. This is manifested by a continuing decrease in pH under such conditions (Figure 4). The situation corresponds to the induction period observed in the classical polymerization of aniline in acidic media. The circumstances change when pH < 2 (Figure 4). Such conditions correspond to those of oxidation in strong acids, and indeed sulfuric acid is produced in the course of oxidation (Figure 1). The exothermic polymerization then follows (Figure 5).

Oxidation in a Solution of a Strong Acid. The induction period is a typical feature when anilinium cations are the dominating monomer species (Figure 5): the aniline molecules that can be oxidized are deficient, anilinium cations that are available are difficult to oxidize, and the reaction proceeds only very slowly. This reaction stage is followed by an exothermic polymerization (Figure 5). It is well-known that under such conditions the growth of PANI chains in the protonated

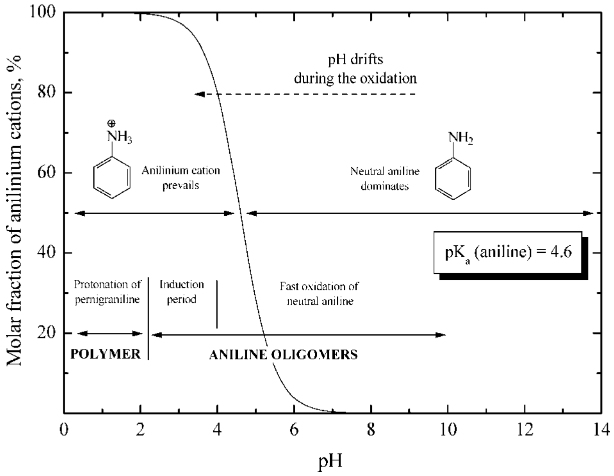

Figure 8. pH drifts to lower values during the oxidation of aniline (Figure 4). The equilibrium between neutral aniline molecules and anilinium cations shifts in favor of the latter species.

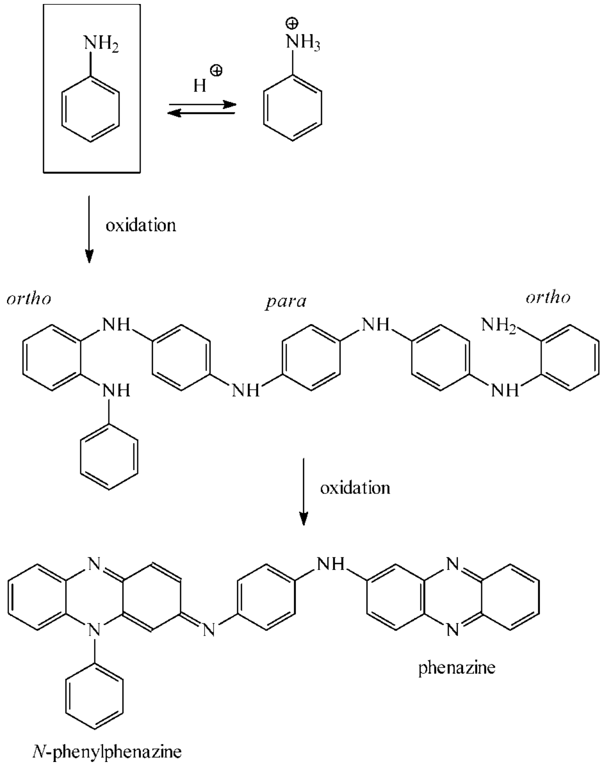

Figure 9. Proportions between neutral aniline molecules and anilinium cations depend on pH. Neutral aniline molecules are oxidized to oligomers having mixed *ortho-* and *para*-coupled aniline constitutional units. *Ortho*-coupled units may undergo intramolecular cyclization to produce phenazine structures.

pernigraniline form becomes feasible[42] (Figure 10). Anilinium cations cannot be oxidized directly but they are easily added to propagating PANI chains, once their growth has started. After the oxidant becomes depleted, pernigraniline is reduced by the residual aniline to the final product, a green emeraldine form of PANI.[23] Macromolecules are composed with a high preference by *para*-linked aniline constitutional units[43] (Figure 10).

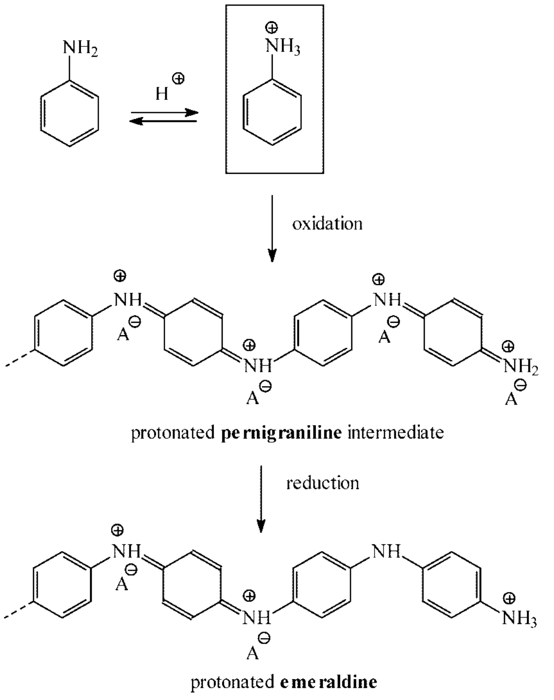

Figure 10. Polyaniline chains grow in blue protonated pernigraniline form by adding anilinium cations in *para* positions. At the end of oxidation they are reduced by excess aniline to the green emeraldine form.

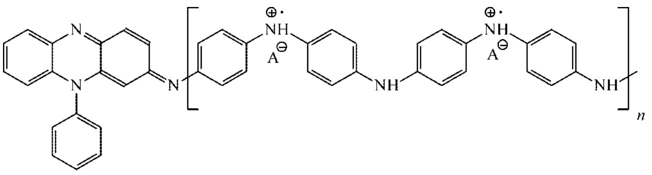

Figure 11. Structure of polyaniline chains, based on the proposition that a *N*-phenylphenazine head initiates the growth of an attached linear *para*-coupled polyaniline tail.

While the propagation of PANI chains seems to be well established, the chain initiation mechanism is still open to discussion. We propose that species of the *N*-phenylphenazine type (Figure 9) act as initiation centers. During the induction period observed in acidic media, the highly deficient aniline is still the only species which is oxidized; the predominating anilinium cations are not prone to direct oxidation. The *ortho*-coupled aniline units produced by oxidation of neutral aniline are converted by intramolecular cyclization to *N*-phenylphenazine (Figure 9). Such structures have been identified in "aniline black" and synthetic dyes obtained by the oxidation of aniline, such as mauveine and pseudomauveine.[35,44] The formation of a phenazine heterocycle is promoted by an acidic medium.[45] Further oligomer growth, however, is suppressed due to their high oxidation potential of *N*-phenylphenazine and the low concentration of available neutral aniline. At pH < 2, mainly aniline dimers, trimers, and tetramers can be produced simultaneously by direct oxidation of neutral aniline molecules.[35] When the pH becomes sufficiently low, chain propagation from these initiation centers becomes feasible (Figure 10). The low number of initiation centers and the high propagation rate result in the formation of high-molecular-weight chains. Such polymer chains are then likely to contain a *N*-phenylphenazine head and a linear *para*-coupled PANI tail (Figure 11).

This concept is supported by FTIR spectra reported above. The formation of phenazine units was also suggested to explain the "middle peak" observed in cyclic voltammograms during the early stages of electrochemical oxidation of aniline.[46] Nonconducting aniline oligomers were produced, which passivated the electrode surface,[47] and only later a conducting PANI film grew on this layer. The UV–visible spectra recorded during the onset of aniline oxidation included absorption peaks,[32,48] which could be associated with the phenazine cycles.[49,50]

Polyaniline Nanotubes. The structure proposed in Figure 11 seems to explain some features of the supramolecular morphology produced by PANI. When the oxidation was carried out in the solution of a weak acid, e.g., 0.4 M acetic acid,[5,22] PANI nanotubes were obtained (Figure 2b). The ability of phenazines to self-organize into microfibrils or nanobelts has been demonstrated in the literature.[51] The stacking of phenazine-based molecules was proposed to be due to the interplay of $\pi-\pi$ interactions, hydrogen bonding, and to be assisted by phase separation caused by hydrophobic effects.[51] The oligomers produced at the first stage of aniline oxidation similarly produce extended nanocrystallites by stacking mechanism.[5,19] These act as templates for the adsorption of *N*-phenylphenazines arising in solution during the induction period. The starting template place for nanotubular growth is thus produced by the short *N*-phenylphenazines stacked around the oligomeric nanocrystallite.[5] We can speculate that the further addition of phenazine units on the front of the tubular *N*-phenylphenazine stack guides its growth beyond the nanocrystallite template.[5] One-dimensional crystal growth is a distant but pertinent analogy. The subsequent growth of PANI chains from stacked *N*-phenylphenazines initiation centers (Figure 11) then gives rise to the walls of nanotubes. We believe that the nanowires grow by a closely related mechanism.

Oligoaniline Microspheres. The formation of microspheres, which is observed in the oxidation of aniline[20,21,52,53] or aniline derivatives[54] under weakly acidic or alkaline conditions, has another background. The neutral aniline is not always completely miscible with the aqueous medium and constitutes a separate phase. The oxidation then proceeds at the interface between the aniline droplets and the aqueous phase containing the oxidant. The nonconducting aniline oligomers (Table 1) form microspheres (Figure 2c) having a diameter of a few micrometers. They can be hollow or may possibly be partly filled with aniline (Figure 2c, right); the presence of aniline encapsulated in an overoxidized oligomeric shell facing the oxidant-rich medium may be responsible for some of the differences observed in the FTIR spectra (Figure 7).

The generation of microspheres can be understood by using the concept of surfactant-free emulsion polymerization. Such polymerization has been used for the preparation of polystyrene nanospheres and microspheres by introducing ionic moieties into the polymer structure during the radical polymerization, e.g., as end-groups from the peroxydisulfate,[55–57] other initiator fragments,[58] or by copolymerization with an ionic comonomer.[58,59] The process may be regarded as an *in situ* formation of a surfactant in emulsion polymerization. The polymerization then proceeds in the monomer droplets stabilized by the produced oligomers,[60] and the resultant polymer microspheres are stabilized by the surface charge of the ionic groups.

A similar scenario is offered in the case of aniline. The limited miscibility of 0.2 M aniline with 0.2 M ammonium hydroxide solution is clearly visible to the naked eye during the experiment. The substituted anilines are even less miscible with water, and that is the reason for the frequent observation of microspheres.[61,62] Aniline oligomers produced at the beginning of oxidation in alkaline media are partly sulfonated, as is confirmed by the presence of the absorption peak at 1040 cm^{-1} in the FTIR spectra[19] (Figure 7), and by the content of sulfur in the base (Table 1). Such oligomers may stabilize monomer droplets at micrometer-size dimensions, just as surfactants do, with the sulfonic groups being oriented at the droplet surface toward the aqueous phase with the aniline constitutional units in the direction of its interior.

Some microspheres seem to have a “stopper”, a small sphere, on the surface (Figure 2c). Similar microspheres, composed of aniline oligomers, have been reported to have an opening, a hole.[20,21,54,62] These effects may be connected with the heat evolution during the polymerization leading to protrusion of aniline outside the spheres or with the evaporation of aniline encapsulated in the spheres during the drying of the samples at elevated temperature *in vacuo*.[63] No proof of any hypothesis has been provided so far.

Conclusions

The oxidation of neutral aniline molecules produces nonconducting oligomers composed of mixed *para*- and *ortho*-coupled aniline constitutional units, and various phenazine units, as a result of the cyclization of *ortho*-coupled units. At pH > 4, this is the only reaction that takes place.

At 4 > pH > 2, anilinium cations are the predominant aniline species in the system but they are difficult to oxidize. The oxidation reaction virtually does not proceed and this phase is known as an induction period. The highly deficient neutral aniline molecules are still the only species that are oxidized to yield short aniline oligomers, rich in phenazine units. That is why the early stages of oxidation always involve neutral aniline molecules and yield the similar type of oligomers regardless of the acidity of the medium. The acidity slowly decreases as a result of continuing oxidation. No polymer is produced at this stage. It is proposed that phenazine units act as the initiation centers for the future polymerization of aniline.

The polymerization proceeds only at pH < 2, when the intermediate pernigraniline form becomes protonated and makes this process feasible. *N*-phenylphenazine is proposed to be responsible for the initiation of chain growth. Anilinium cations easily participate in the propagation step to give high-molecular-weight PANI chains, until aniline or oxidant or both become depleted. The pH ranges given here have only informative guidance and the transition between them is smooth.

The pH decreases in the course of oxidation because sulfuric acid is a byproduct. Depending on the initial and final acidity of the reaction mixture, the mechanism of oxidation may change. The oxidation products always have an oligomeric component (produced by the oxidation of neutral aniline) and may have a polymeric fraction (generated by the polymerization involving anilinium cations) in varying proportions. Short oligomers comprising units of the phenazine type are proposed to self-assemble and promote the self-organized growth of polymer chains to supramolecular assemblies, such as nanotubes and nanowires. The limited miscibility of neutral aniline with the reaction medium is responsible for the formation of microspheres, which are stabilized by sulfonated oligoanilines.

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References and Notes

(1) Aleshin, A. N. *Adv. Mater.* **2006**, *18*, 17.
(2) Zhang, D.; Wang, Y. *Mater. Sci. Eng., B* **2006**, *134*, 9.
(3) Stejskal, J.; Gilbert, R. G. *Pure Appl. Chem.* **2002**, *74*, 857.
(4) Zhang, Z.; Wei, Y.; Zhang, L.; Wan, M. *Acta Mater.* **2005**, *53*, 1373.
(5) Stejskal, J.; Sapurina, I.; Trchová, M.; Konyushenko, E. N.; Holler, P. *Polymer* **2006**, *47*, 8253.
(6) Zhang, L. J.; Peng, H.; Hsu, C. F.; Kilmartin, P. A.; Travas-Sejdic, J. *Nanotechnology* **2007**, *18*, 115607.
(7) Zhang, L. J.; Peng, H.; Zujovic, Z. D.; Kilmartin, P. A.; Travas-Sejdic, J. *Macromol. Chem. Phys.* **2007**, *208*, 1210.
(8) Zhang, X.; Goux, W. J.; Manohar, S. K. *J. Am. Chem. Soc.* **2004**, *126*, 4502.
(9) Li, D.; Kaner, R. B. *J. Am. Chem. Soc.* **2006**, *128*, 968.
(10) (a) Huang, J. X.; Kaner, R. B. *J. Am. Chem. Soc.* **2004**, *126*, 851. (b) Huang, J. X. *Pure Appl. Chem.* **2006**, *78*, 15. (c) Huang, J.; Kaner, R. B. *Chem. Commun.* **2006**, 367.
(11) Zhang, L.; Zhang, L.; Wan, M.; Wei, Y. *Synth. Met.* **2006**, *156*, 454.

(12) Chiou, N.-R.; Lee, J.; Epstein, A. J. *Chem. Mater.* **2007**, *19*, 3587.

(13) Chiou, N. R.; Lui, C. M.; Guan, J. J.; Lee, L. J.; Epstein, A. J. *Nature Nanotechnol.* **2007**, *2*, 354.

(14) Huang, J.; Wan, M. *J. Appl. Polym. Sci.* **1999**, *37*, 1277.

(15) Qiu, H.; Wan, M.; Matthews, B.; Dai, L. *Macromolecules* **2001**, *34*, 675.

(16) Qiu, H.; Wan, M. *J. Polym. Sci., Part A Polym. Chem.* **2001**, *39*, 3485.

(17) Wei, Z.; Zhang, Z.; Wan, M. *Langmuir* **2002**, *18*, 917.

(18) Zhang, Z.; Wei, Z.; Wan, M. *Macromolecules* **2002**, *35*, 5937.

(19) Trchová, M.; Šeděnková, I.; Konyushenko, E. N.; Stejskal, J.; Holler, P.; Ćirić-Marjanović, G. *J. Phys. Chem. B* **2006**, *110*, 9461.

(20) Wang, X.; Liu, N.; Yan, X.; Zhang, W.; Wei, Y. *Chem. Lett.* **2005**, *34*, 42.

(21) Venancio, E. C.; Wang, P.-C.; MacDiarmid, A. G. *Synth. Met.* **2006**, *156*, 357.

(22) Konyushenko, E. N.; Stejskal, J.; Šeděnková, I.; Trchová, M.; Sapurina, I.; Cieslar, M.; Prokeš, J. *Polym. Int.* **2006**, *55*, 31.

(23) Pud, A. A.; Noskov, Yu. V.; Kassiba, A.; Fatyeyeva, K. Yu.; Ogurtsov, N. A.; Makowska-Janusik, M.; Bednarski, W.; Tabellout, M.; Shapoval, G. S. *J. Phys. Chem. B* **2007**, *111*, 2174.

(24) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Prog. Polym. Sci.* **1998**, *23*, 277.

(25) Sahin, Y.; Pekmez, K.; Yildiz, A. *Synth. Met.* **2002**, *131*, 7.

(26) Viva, F. A.; Andrade, E. M.; Molina, F. M.; Florit, M. I. *J. Electroanal. Chem.* **1999**, *471*, 180.

(27) Dines, T. J.; MacGregor, L. D.; Rochester, C. H. *Phys. Chem. Chem. Phys.* **2001**, *13*, 2676.

(28) Li, X.-G.; Duan, W.; Huang, M.-R.; Yang, Y.-L. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3989.

(29) Malinauskas, A.; Bron, M.; Holze, R. *Synth. Met.* **1998**, *92*, 127.

(30) Cram, D. J.; Hammond, G. S. *Organic Chemistry*; McGraw Hill: New York, 1964; pp 210–211.

(31) *CRC Handbook of Chemistry and Physics*, 76th Ed.; Lide, D. R., Frederikse, H. P. R., Eds.; CRC Press: New York, 1995; pp 8–49.

(32) Zimmermann, A.; Kunzelmann, U.; Dunsch, L. *Synth. Met.* **1998**, *93*, 17.

(33) Mazeikiene, R.; Niaura, G.; Malinauskas, A. *J. Electroanal. Chem.* **2005**, *580*, 87.

(34) Ćirić-Marjanović, G.; Trchová, M.; Stejskal, J. *Collect. Czech. Chem. Commun.* **2006**, *71*, 1407.

(35) (a) Ćirić-Marjanović, G.; Trchová, M.; Stejskal, J. *Int. J. Quantum Chem.* **2008**, *108*, 318. (b) Ćirić-Marjanović, G.; Konyushenko, E. N.; Trchová, M.; Stejskal, J. *Synth. Met.* **2008**, *158*, 200.

(36) (a) Chiba, K.; Ohsaka, T.; Ohnuki, Y.; Oyama, N. *J. Electroanal. Chem.* **1987**, *219*, 117. (b) Losito, I.; De Giglio, E.; Cioffi, N.; Malitesta, C. *J. Mater. Chem.* **2001**, *11*, 1812.

(37) Li, X. G.; Duan, W.; Huang, M.-R.; Rodriguez, L. N. J. *React. Funct. Polym.* **2005**, *62*, 261.

(38) Trchová, M.; Matějka, P.; Brodinová, J.; Kalendová, A.; Prokeš, J.; Stejskal, J. *Polym. Degrad. Stab.* **2006**, *91*, 114.

(39) Zhou, C.; Han, J.; Song, G; Guo, R. *Macromolecules* **2007**, *40*, 7075.

(40) Matnishyan, A. A.; Akhnazaryan, T. L. *Polym. Sci. Ser. B* **2007**, *49*, 139.

(41) Fu, Y.; Elsenbaumer, R. L. *Chem. Mater.* **1994**, *6*, 671.

(42) Madathil, R.; Ponrathman, S.; Byrne, H. J. *Polymer* **2004**, *45*, 5465.

(43) Bacon, J.; Adams, R. N. *J. Am. Chem. Soc.* **1968**, *90*, 6596.

(44) (a) Meth-Cohn, O.; Smith, M. *J. Chem. Soc., Perkin Trans.* **1994**, *1*, 5. (b) de Melo, J. S.; Takato, S.; Sousa, M.; Melo, M. J.; Parola, A. J. *Chem. Commun.* **2007**, 2624.

(45) Tu, X.; Xie, Q.; Xiang, C.; Zhang, Y.; Yao, S. *J. Phys. Chem. B* **2005**, *109*, 4053.

(46) Geniès, E. M.; Lapkowski, M.; Penneau, J. P. *J. Electroanal. Chem.* **1988**, *249*, 97.

(47) Hong, S.-Y.; Park, S.-M. *J. Phys. Chem. B* **2007**, *111*, 9779.

(48) Neoh, K. G.; Kang, E. T.; Tan, K. L. *Polymer* **1993**, *34*, 3921.

(49) Wu, L.-L.; Luo, J.; Lin, Z.-H. *J. Electroanal. Chem.* **1997**, *440*, 173.

(50) He, D.; Wu, L.-L; Xu, B.-Q. *Eur. Polym. J.* **2007**, *43*, 3703.

(51) (a) Desvergne, J.-P.; Del Guerzo, A.; Bouas-Laurent, H.; Belin, C.; Reichwagen, J.; Hopf, H. *Pure Appl. Chem.* **2006**, *78*, 707. (b) Sun, X.; Hagner, M. *Langmuir* **2007**, *23*, 10441. (c) He, D.; Wu, Y.; Xu, B.-Q. *Eur. Polym. J.* **2007**, *43*, 3703.

(52) Zhang, L.; Wan, M.; Wei, Y. *Macromol. Rapid Commun.* **2006**, *27*, 888.

(53) Zhu, Y.; Hu, D.; Wan, M.; Wan, M. X.; Jiang, L.; Wei, Y. *Adv. Mater.* **2007**, *19*, 2092.

(54) Han, J.; Song, G.; Guo, R. *Adv. Mater.* **2006**, *18*, 3140.

(55) Žůrková, E.; Bouchal, K.; Zdeňková, D.; Pelzbauer, Z.; Švec, F.; Kálal, J.; Batz, H. G. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2949.

(56) Tuin, G.; Peters, A. C. A. I.; van Diemen, A. J. G.; Stein, H. N. *J. Colloid Interface Sci.* **1993**, *158*, 508.

(57) Ngai, T.; Wu, C. *Langmuir* **2005**, *21*, 8520.

(58) Liu, W.-J.; He, W.-D.; Wang, Y.-M.; Wang, D.; Zhang, Z.-C. *Polym. Int.* **2006**, *55*, 520.

(59) Peula, J. M.; Fernández-Barbero, A.; Hidalgo-Álvarez, R.; de las Nieves, F. J. *Langmuir* **1997**, *13*, 3938.

(60) Kühn, I.; Tauer, K. *Macromolecules* **1995**, *28*, 8122.

(61) Sanada, K.; Patil, R.; Ooyama, Y.; Yano, J.; Harima, Y. *Polym. J.* **2006**, *38*, 732.

(62) Han, J.; Song, G.; Guo, R. *Chem. Mater.* **2007**, *19*, 973.

(63) Im, S. H.; Jeong, U.; Xia, Y. *Nature Mater.* **2005**, *4*, 671.

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