MNDO-PM3 STUDY OF THE EARLY STAGES OF THE CHEMICAL OXIDATIVE POLYMERIZATION OF ANILINE

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The theoretical approach to the study of aniline polymerization mechanism has been based on the MNDO-PM3 semi-empirical quantum chemical computations of the heat of formation of aniline dimer and trimer intermediates. The oxidation in aqueous medium without added acid is analyzed. The aniline nitrenium cation is proposed to be the reactive electrophilic species generated by the oxidation of aniline with a two-electron oxidant, ammonium peroxydisulfate, in the initiation phase. 4-Aminodiphenylamine and its fully oxidized form, *N*-phenyl-1,4-benzoquinonediimine, are the main dimeric products. 2-Aminodiphenylamine and its fully oxidized form, *N*-phenyl-1,2-benzoquinonediimine, are the most important side products of aniline dimerization. The influence of protonation on the oxidizability of aniline and reaction intermediates was studied. The dominant aniline oligomers have been shown to be linear as well as branched. The importance of reactivity difference between fully oxidized aniline oligomers composed of odd or even numbers of constitutional aniline units is pointed out. The species with odd numbers of aniline units, having nitrenium cationic nature, are much more reactive. The oxidation combined with intramolecular cyclization reaction pathways leads to substituted phenazines, characteristic of two-dimensional PANI chain-growth.

Keywords: Aniline; Aniline oligomers; Conducting polymers; Polyaniline; Phenazine; Oxidations; Polymerization mechanism; Semi-empirical calculations.

The oxidation of aniline in aqueous solutions of strong acids is a typical method for the preparation of polyaniline (PANI) with a good level of conductivity, 10^0 S cm^{-1}. The polymerization starting from alkaline, neutral, and slightly acidic reaction conditions has recently been recognized as a useful synthetic route to adherent PANI films for corrosion protection[1], PANI nanotubes and nanorods produced without a template[2–4]. It seems that the morphology of the PANI produced depends on the acidity of the reaction medium, and that is why the preparation of PANI in water and in solutions of weak acids is of interest, even at reduced conductivity of products, ~10^{-2} S cm^{-1}. The oligomeric reaction intermediates have been proposed to

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act as templates for the growth of PANI nanotubes[2]. That is why the analysis of early stages of aniline oxidation is of importance for the understanding of both the molecular structure and supramolecular morphology of PANI.

The PANI chain-growth mechanism has been proposed many times in the literature and is still debatable[5]. The generation of the first reactive species by the reaction of aniline and oxidant in the initiation phase, aniline cation radical[6] vs aniline nitrenium cation[7], is still open to discussion. Based on quantum chemical calculations of the oxidizability of aniline and its reactive species, Kovalchuk[8] proposed that the first stage of PANI synthesis, in both electrochemical and chemical oxidations of aniline, is the formation of an aniline cation radical, even in the case of a two-electron oxidant, such as peroxydisulfate. The oxidative polymerization of aniline with ammonium peroxydisulfate (APS) in aqueous solution, starting from alkaline, neutral, and slightly acidic reaction conditions, was studied by Gospodinova et al.[9] The existence of two stages was demonstrated by following the pH changes during the aniline polymerization. Two steps in the course of aniline polymerization starting at pH $\geq$ 4.2, have also been found by Fu and Elsenbaumer[10] using solution calorimetry. Each of these steps gives off varying amounts of heat, the second being more exothermic. There is a long delay between the first heat evolution and the second. It has been proposed[5] that the process of PANI-chain propagation, as a redox process between the growing chain (pernigraniline form acting as an oxidant) and aniline (a reductant), resulting in the addition of monomer to the chain end, will take place until their oxidation potentials become equilibrated. This occurs on reaching the emeraldine oxidation state of the PANI chains. It was concluded that, during this redox-equilibration process, it is more favorable for the oxidant to oxidize the dimer, trimer, tetramer, ... and polymer, and for the monomer to be added to the growing chain rather than to form a new active site. It was suggested that the oxidation potential of oligomeric and PANI chains depends not only on the degree of oxidation, but also on the degree of protonation of the chains. A higher degree of protonation is accompanied by higher oxidation potentials of the chains. The relatively low oxidation potential of *N*-phenyl-1,4-benzoquinonediimine (PBQI) explains the so-called induction period of aniline polymerization[9]. The increase in the oxidation potential of oxidized forms of oligoaniline on increasing length of the growing chains from PBQI to pernigraniline, is assumed to be the most likely reason for autoacceleration in the reaction kinetics[9].

Recent in situ investigations of the chemical oxidative polymerization of aniline[11], using absorption spectral studies in the visible region, have revealed that the chain propagation is assisted by a redox equilibrium intermediate (REI) rather than with a fully oxidized pernigraniline. The polymerization process consists of three prominent stages called (*1*) induction period and chain initiation, (*2*) chain propagation, and (*3*) chain termination. The initial stage of polymerization manifested itself as an induction period, i.e. the time needed to produce an oligomeric REI. Madathil et al.[11] suggest that the degree of oxidation of oligomeric REI would be higher than that of emeraldine salt and lower than that of pernigraniline salt. Oligomeric REIs undergo further reductive addition of aniline and oxidation with APS while maintaining the structural characteristic of the growing polymeric REI chain. The termination of polymerization would be associated with the reduction or oxidation of polymeric REI, depending on the availability of aniline or oxidant, respectively. For an oxidant-deficient system, it was predicted that reduction continues until it reaches an emeraldine salt that is incapable of further reduction. On the other hand, an excess of oxidant results in the formation of pernigraniline salt by continuing oxidation.

Oxidative polymerization of the protonated form of aniline, e.g., of aniline hydrochloride with APS, was investigated experimentally in acidic solutions by in situ spectrophotometry and computationally by using molecular mechanics (MM+) calculations[12]. The results indicate the presence of nitrenium cations and suggest that the PANI build-up proceeds through a two-dimensional (D2) polymer with phenazine rings, which can be formed by a cross-linking reaction. This was confirmed by kinetic studies, as well as verified by MM+ calculations.

A number of theoretical approaches and computational methods have been used in the study of early stages of aniline oxidative polymerization. Properties of the aniline oligomers, such as geometry, molecular orbitals, thermodynamic stability, reactivity, redox, and acid-base character have been studied by the Hückel method[13], extended Hückel theory[14] (EHT), the Su–Shrieffer–Heeger model[15] (SSH), the valence effective Hamiltonian[16] (VEH), density functional calculations with periodic boundary conditions[17], as well as by molecular mechanics[12] (MM), ZINDO/1 [18], AM1 [19], DFT [20–22], and MP2 [23] calculations. It has to be noted, however, that most of these theoretical studies have been performed for the reactive species in vacuum, neglecting solvation effects.

Our recent gel permeation chromatography (GPC) and FTIR spectroscopic studies of the oxidative polymerization of aniline in aqueous solution[2,24], leading to the formation of PANI nanotubes and nanorods, cannot be correlated simply with the one-dimensional PANI growth mechanism proposed by Gospodinova et al.[9] The aim of the present work is to elucidate the mechanism of aniline oxidative polymerization with APS, in aqueous solution without added acid, taking into account the hydration of reactive species and pH changes that occur in the course of polymerization. Semi-empirical quantum chemical computational methods are seen to be well balanced: they are accurate enough to have useful predictive powers, yet fast enough to allow large systems such as aniline oligomers to be studied. The semi-empirical modified neglect of diatomic overlap – parametric method 3 (MNDO-PM3) quantum chemical computational method, proved to be reliable in its application to organic nitrogen compounds[25–27], is a distinct improvement over Austin model 1 (AM1) because overall errors in the heat of formation are reduced by about 40% relative to AM1. In a recent computational study focused on the torsion angle between rings, known to affect strongly the electronic and optical properties of conjugated polymers, Dávila et al.[19] suggest that the AM1 method is preferred over the PM3 for ring-structured oligomeric chains in the gas phase. Therefore, we performed comparative MNDO-PM3/AM1 study for some selected dimeric and trimeric hydrated intermediate species. Special attention has been paid to the possible formation of branched low-molecular-weight aniline oligomers and substituted phenazines, the presence of these structural features being confirmed by FTIR spectroscopy[24].

COMPUTATIONAL METHODS

The computational methods used here to obtain the molecular orbitals, ionization energy, heat of formation, charge distribution (Mulliken charges), and spin density of individual species are semi-empirical MNDO-PM3 and AM1 models[25,28,29] (included in molecular orbital package[30] MOPAC 97, part of the Chem3D Pro 5.0 package, CambridgeSoft Corporation) taking into account the solvation effects in water (using conductor-like screening model – COSMO technique to approximate the effect of a solvent model surrounding the molecule[31]), with full geometry optimization by eigenfollowing procedure[32,33]. Input files for semi-empirical quantum chemical computations of aniline dimeric and trimeric species were the most stable conformers of investigated molecular structures, with minimized steric energy using MM2 molecular mechanics force-field method[34]. The restricted Hartree–Fock method has been used for the molecular structures and the unrestricted Hartree–Fock method for radical species.

RESULTS AND DISCUSSION

Initial Oxidation of Aniline

When aqueous solutions of aniline and APS are mixed at room temperature, PANI (emeraldine) hydrogen sulfate is produced (Fig. 1) and sulfuric acid is a by-product. That is why the acidity of the reaction mixture gradually increases, i.e. the pH decreases (Fig. 2). At the beginning of the oxidation, a slightly alkaline solution is obtained (pH ~ 8.0) as a result of alkaline

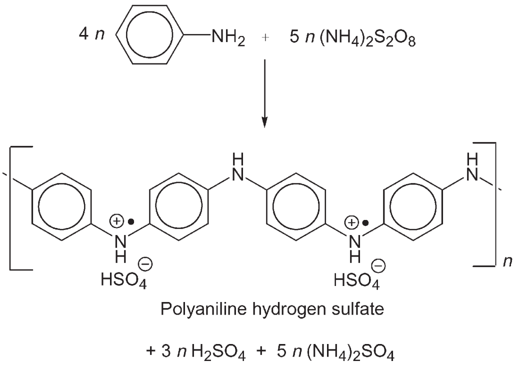


FIG. 1
The oxidation of aniline with ammonium peroxydisulfate in water yields polyaniline hydrogen sulfate. Sulfuric acid and ammonium sulfate are by-products

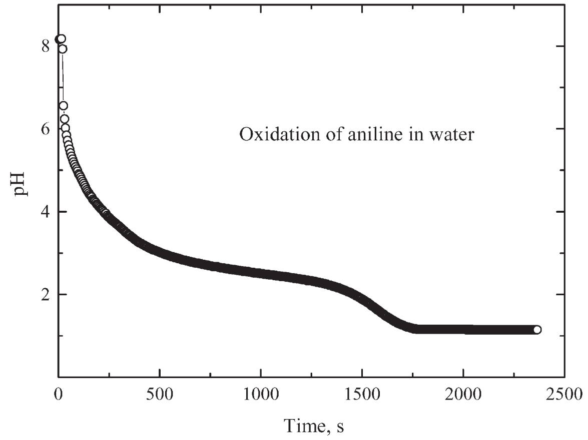


FIG. 2
Acidity profile during the oxidation of 0.2 M aniline with 0.25 M ammonium peroxydisulfate in water beginning at room temperature. Data are taken from ref.[2]

reaction of aniline and hydrolysis of ammonium ions. In this pH region, aniline base prevails over an anilinium cation; the pK_a of aniline is[35] 4.9. This is easily proved by recording the UV spectra (Fig. 3): aniline in water displays absorption maxima at 229 and 279 nm, and the peak at 254 nm typical of the anilinium cation observed in acid media, is missing in water. Gospodinova et al.[5] reported that the electrochemical potential of the system in which aniline polymerization takes place is about 0.9 V in strongly acidic media and drops on increasing the pH of the medium. Thus, the most favorable conditions for initiation of the oxidative polymerization of aniline exist in neutral or even alkaline media, rather than in strongly acidic media. Semi-empirical quantum chemical MNDO-PM3 calculations confirm these experimental findings, showing a lower value for the ionization energy, i.e. increased oxidizability, of the neutral aniline molecule (E_i = 9.03 eV) in aqueous solution, compared with a hydrated anilinium cation (E_i = 10.25 eV) in acid solutions.

To resolve the nature of the first generated reactive species obtained by aniline oxidation under such reaction conditions, we have performed an MNDO-PM3 and AM1 comparative study of the redox properties of the aniline cation radical and the neutral radical in aqueous solution. In accordance with Geniès and Lapkowski's electrochemical experiments[7], and contrary to those of Kovalchuk et al.[8], our calculations suggest a considerable decrease in ionization energies of the generated aniline cation radical

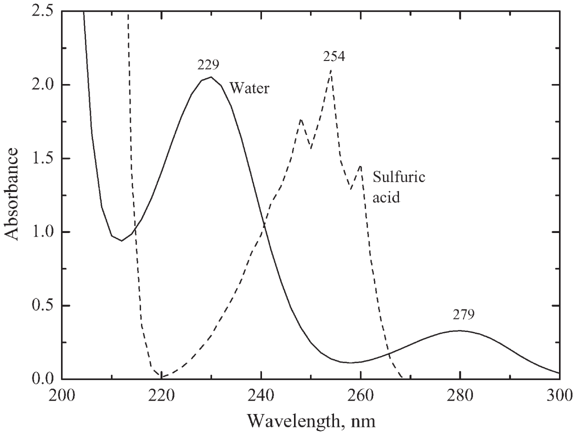


FIG. 3
UV spectra of aniline in water (full line) and anilinium cation in 0.1 M sulfuric acid (dashed line)

($E_{i(PM3)}$ = 5.66 eV) and neutral radical ($E_{i(PM3)}$ = 5.40 eV) compared with parent aniline molecule and anilinium cation (Table I). The disagreement with Kovalchuk et al.[8] is due to their unjustified neglect of solvation effects. We have confirmed their quantum chemical calculation results for species in vacuum by demonstrating that the energy of the highest occupied molecular orbital (E_{HOMO}) decreases from aniline to the cation radical, so that the oxidation of molecules becomes more difficult as their oxidation level increases. A dramatic change in oxidizability, however, is observed after taking into account the hydration of reactive species in MNDO-PM3 and AM1 calculations (Table I). Hence, the generation of the hydrated aniline cation radical as a stronger reductant compared with aniline, and the sulfate radical anion as a stronger oxidant (2.5–3.1 V vs NHE)[36], compared with the peroxydisulfate anion (2.0–2.1 V vs NHE)[35], seems to be the less favored initiation reaction:

$$C_6H_5NH_2(aq) + S_2O_8^{2-}(aq) \rightarrow C_6H_5NH_2^{+\bullet}(aq) + SO_4^{-\bullet}(aq) + SO_4^{2-}(aq) \qquad (R1)$$

This indicates that aniline oxidation in aqueous solution with two-electron oxidants, like ammonium peroxydisulfate, leads rather to the nitrenium cation as a reactive electrophilic species in the initiation phase:

$$C_6H_5NH_2(aq) + S_2O_8^{2-}(aq) \rightarrow C_6H_5NH^{+}(aq) + H^{+}(aq) + 2\ SO_4^{2-}(aq) \qquad (R2)$$

Table I

Ionization energy, E_i, calculated by MNDO-PM3 and AM1 methods for aniline and its reactive species, cation radical and neutral radical, in vacuum and water

Species	PM3		AM1	
	E_i, eV vacuum	E_i, eV water	E_i, eV vacuum	E_i, eV water
Aniline	8.61	9.03	8.52	8.98
Aniline cation radical	10.72	5.66	10.68	5.99
Aniline neutral radical	9.25	5.40	9.29	5.28

Aniline Dimerization

Once formed, aniline nitrenium cations further react with non-transformed aniline molecules (Fig. 4). The computation of rates for the dimerization of aniline and its salts depends strongly on the interatomic distance between the two atoms involved in the coupling, which remains an unknown parameter in the frontier orbital method[37]. This is further complicated by hydration of reactive species and especially by the influence of the relative positions of the ions present with respect to the transition complex (i.e. ammonium and sulfate in the case of APS oxidation). However, the enthalpy of reaction between aniline and its nitrenium cation can be calculated exactly by MNDO-PM3. The decrease in entropy can be assumed to be equal for all aniline dimerization reactions leading to aniline dimer cation intermediates. The reaction enthalpy values combined with charge distribution in aniline molecule and its nitrenium cation then reveal the dominant coupling reactions.

The reaction of the aniline nitrenium cation with an aniline molecule is a well-known electrophilic aromatic substitution reaction. In the first rate-determining step of this reaction, the electrophile forms a σ-bond to the benzene ring, generating a positively charged benzenonium intermediate. In the second fast step, the proton is released from this intermediate, yielding a substituted benzene ring. The protons are responsible for the growing

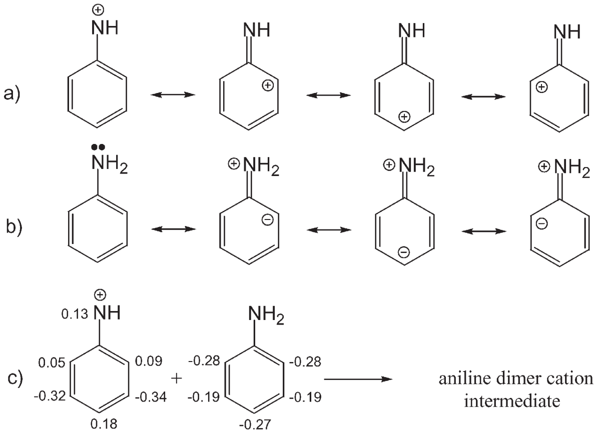


FIG. 4

a Resonance canonical forms of aniline nitrenium cation; b resonance canonical forms of aniline; c MNDO-PM3 semi-empirical quantum chemical calculation of hydrated aniline molecule and its nitrenium cation charge distribution acidity of the reaction medium (Fig. 2). The amino group in aniline determines the *ortho* or *para* substitution pattern in the reactions with electrophilic species, caused by the resonance stabilization of the lone electron pair on nitrogen (Fig. 4b). The increase in negative charge in the *ortho* and *para* positions of aniline, proved by MNDO-PM3 (Fig. 4c), implies a very low reaction rate for *meta* electrophilic aromatic substitution reactions. We have therefore focused only on the *ortho* and *para* substitution ratio. The positive charge distribution on the nitrenium cation, represented by its resonance hybrid (Fig. 4a) and calculated by MNDO-PM3 (Fig. 4c), clearly shows that C4 and N are the main nitrenium cation reactive centers for electrophilic attack on the neutral aniline molecule. The heat of the coupling reaction of the aniline nitrenium cation with an aniline molecule, $\Delta H_{\text{r(nitrenium cation+aniline)}}$, leading to the formation of the aniline dimer cation intermediate (Table II), has been calculated as the difference between the heat of formation, ΔH_f, of the hydrated dimer cation intermediate and the sum of ΔH_f values of hydrated aniline and nitrenium cation as reactive species, by the following equation:

$$\Delta H_{\text{r(nitrenium cation+aniline)}} = \Delta H_{\text{f(aniline dimer cation intermediate)}} - \\ - [\Delta H_{\text{f(aniline)}} + \Delta H_{\text{f(nitrenium cation)}}] \qquad (1)$$

Both MNDO-PM3 and AM1 methods lead to the same conclusions. All coupling reactions of aniline and its nitrenium cation are exothermic (Table II). The coupling mode N–C4, leading to 4-aminodiphenylamine (4-ADPA, *p*-semidine) (Fig. 5), is dominating. The dimerization reaction N–C2, leading to 2-aminodiphenylamine (2-ADPA, *o*-semidine) (Fig. 5), is also important. It should be noted that the N–N and C4–C4 couplings

TABLE II

Heat of reaction of the aniline dimer cation intermediate formation, $\Delta H_{\text{r(nitrenium cation + aniline)}}$, calculated by MNDO-PM3 and AM1 methods for various coupling reactions of aniline and its nitrenium cation in aqueous solution

Coupling mode (nitrenium cation + aniline)	N–N	N–C2	N–C4	C2–N	C2–C2	C2–C4	C4–N	C4–C2	C4–C4
ΔH_r, kcal mol^{-1} PM3	–15.6	–39.3	–42.3	–22.1	–19.1	–23.2	–28.4	–21.1	–26.4
ΔH_r, kcal mol^{-1} AM1	–13.7	–35.1	–37.1	–19.3	–21.0	–23.7	–22.1	–20.5	–25.3

yielding hydrazobenzene and benzidine, respectively, are much less probable. In the study of further growth to aniline trimers, we have thus focused on the reactions involving 4-ADPA and 2-ADPA.

Aniline Dimers and Their Redox and Acid-Base Properties

The aniline dimer, 4-ADPA, shows complex redox and acid-base behaviour. The calculations of the heat of formation confirm that the aromatic primary amino group in 4-ADPA is a stronger base[38] (pK_a = 5.20) than its secondary amino group[35] (diphenylamine, pK_a = 0.79) (Fig. 6). This finding is in accordance with the well-known lower basicity of secondary aromatic amines in comparison with primary aromatic amines[39] due to the more pronounced delocalization of nitrogen lone electron pair in secondary aromatic amines. It has to be noted that opposite theoretical conclusions concerning acid-base properties of 4-ADPA have recently been published by Can et al.[40], and are a consequence of the unjustified neglect of hydration effects. We confirm the results calculated for 4-ADPA in vacuum; the conclusions, however, are not valid for 4-ADPA in aqueous solution.

4-ADPA has a considerably lower electrochemical potential compared with aniline[41], in accordance with our results for the ionization energy

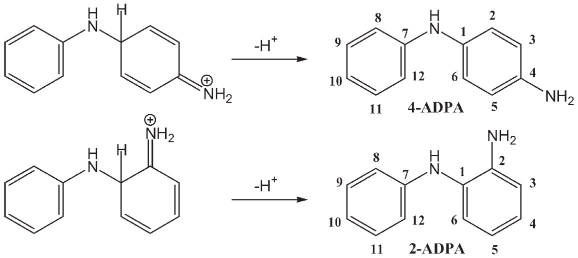


FIG. 5
Formation of 4-ADPA and 2-ADPA by deprotonation of the most stable aniline dimer cation intermediates

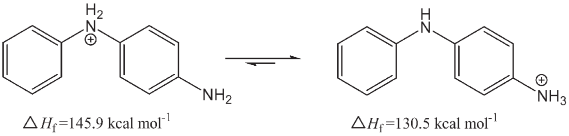


FIG. 6
Monoprotonated forms of 4-ADPA and the corresponding heats of formation in water, calculated by the MNDO-PM3

($E_{i(4\text{-ADPA})}$ = 8.70 eV). This is the reason for the instantaneous oxidation of 4-ADPA. The oxidizability of 4-ADPA depends on pH; the fully protonated form of 4-ADPA being even harder to oxidize (E_i = 10.34 eV) than the anilinium cation. 2-ADPA shows very similar redox and acid-base behaviour to that of 4-ADPA. The 2-ADPA base form is slightly more oxidizable (E_i = 8.85 eV) than aniline, but less oxidizable than 4-ADPA. Ionization energy calculations for monoprotonated 2-ADPA (E_i = 9.17 eV) and diprotonated 2-ADPA (E_i = 10.39 eV) show a decrease in 2-ADPA oxidizability with decreasing pH.

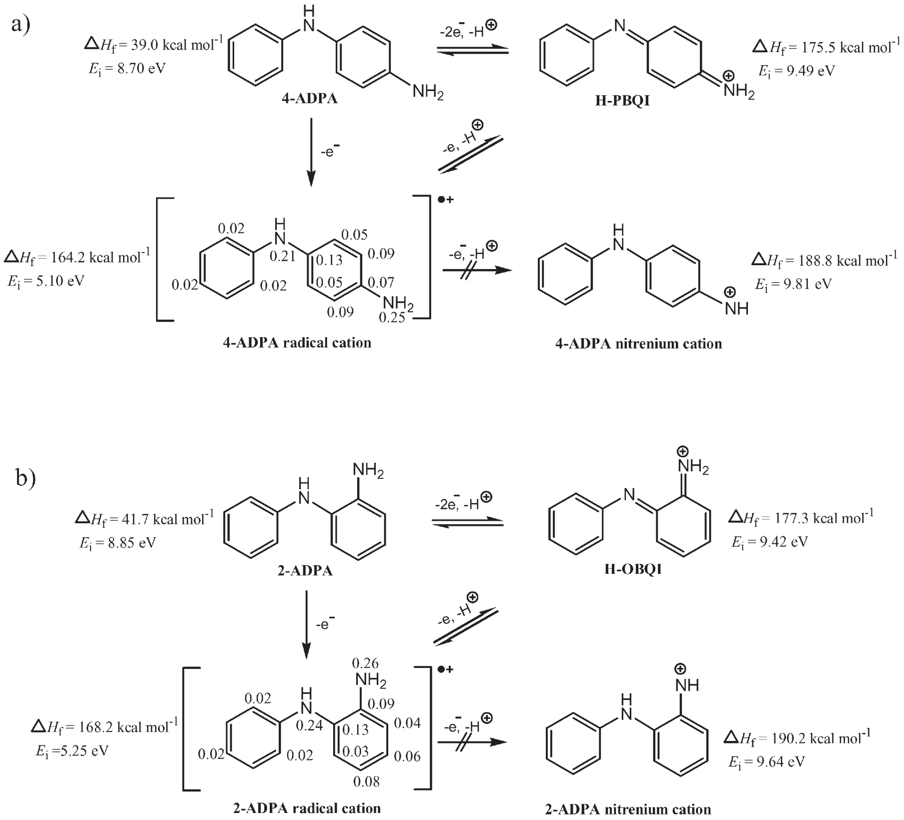


FIG. 7

MNDO-PM3-calculated heat of formation of 4-ADPA, 2-ADPA, and species obtained by their oxidation in water: a 4-ADPA cation radical, 4-ADPA nitrenium cation, H-PBQI; b 2-ADPA cation radical, 2-ADPA nitrenium cation, H-OBQI. Spin density of 4-ADPA and 2-ADPA cation radicals is also shown

The oxidized form of 4-ADPA, PBQI, has been identified at the initial stage of the aniline oxidative polymerization by using electronic absorption spectroscopy[41]. In some papers, the nitrenium cation of 4-ADPA is mentioned as a reactive species[42]. The heat of formation and the ionization energies calculated by MNDO-PM3 suggest that a two-electron oxidation of both 4-ADPA and 2-ADPA with APS leads to PBQI and *N*-phenyl-1,2-benzoquinonediimine (OBQI) species, and not to the 4-ADPA and 2-ADPA cation radicals or nitrenium cations (Fig. 7). It must be noted that the nitrenium cation of 4-ADPA, proposed by Wei et al.[42], is in fact the resonance canonical form of less stable monoprotonated PBQI (Figs 8 and 9). A higher protonation level in both PBQI and OBQI causes the increase in their oxidant power (decrease in E_{LUMO}, Table III).

Aniline Trimerization

It is known that redox interaction is feasible under the constraint[8]

$$|E_{\mathrm{HOMO(D)}} - E_{\mathrm{LUMO(A)}}| < |E_{\mathrm{HOMO(A)}} - E_{\mathrm{LUMO(D)}}| \qquad (2)$$

where D represents an electron donor (reductant) and A stands for an electron acceptor (oxidant)[8]. Based on this constraint, it can be calculated that PBQI and OBQI (A) in all acid-base forms can oxidize aniline (D) (Fig. 10).

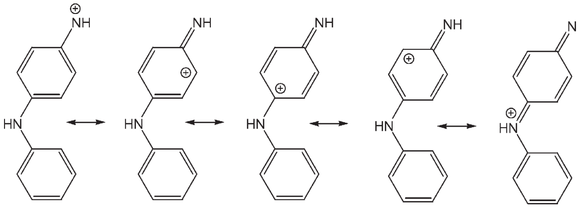


FIG. 8
Resonance canonical forms of the less stable monoprotonated PBQI form

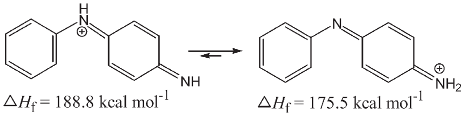


FIG. 9
Monoprotonated forms of PBQI and the corresponding heat of formation in water, calculated by the MNDO-PM3

Thus the formed cation radicals of 4-ADPA (or 2-ADPA) and aniline instantaneously react via radical recombination to aniline trimer dication intermediates, which further are transformed to aniline trimers by releasing protons (Figs 10 and 11).

Analogous oxidation of the anilinium cation, however, is considerably slower; this was proved by the constraint (*2*). Consequently, as pH decreases below 3.5 (Fig. 2), the anilinium cation predominates over aniline, and the reaction rate for the coupling of aniline and oxidized dimers of aniline significantly decreases.

Taking into account the spin density of the aniline cation radical and 4-ADPA (2-ADPA) cation radicals (Figs 7 and 10), both MNDO-PM3 and AM1 enthalpy calculations of trimerization reactions (Table IV) revealed the prevalence of $N_{prim,4\text{-}ADPA}$–$C_{para(aniline)}$, $N_{prim,2\text{-}ADPA}$–$C_{para(aniline)}$, and $N_{aniline}$–$C5_{(2\text{-}ADPA)}$ couplings, leading to aniline trimers with a newly-formed N–C4 bond (Fig. 11), i.e., 1,4- and 1,2,4-substitution patterns (here, N_{prim}

TABLE III

Ionization energy, E_i, and energy of the lowest unoccupied molecular orbital, E_{LUMO}, calculated by the MNDO-PM3 method for *N*-phenyl-1,4-benzoquinonediimine (PBQI) and *N*-phenyl-1,2-benzoquinonediimine (OBQI) and their protonated forms in aqueous solution

Energy, eV	PBQI	HPBQI	H_2PBQI	OBQI	HOBQI	H_2OBQI
E_i	9.38	9.49	9.74	9.32	9.42	9.69
E_{LUMO}	–1.58	–1.86	–2.43	–1.51	–1.85	–2.53

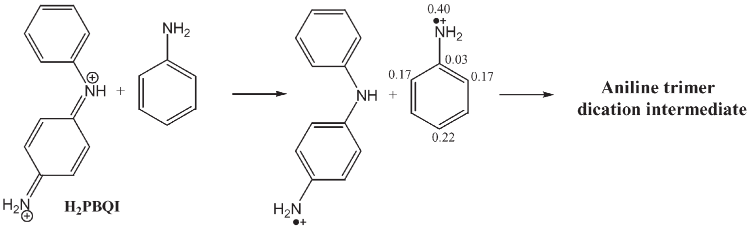
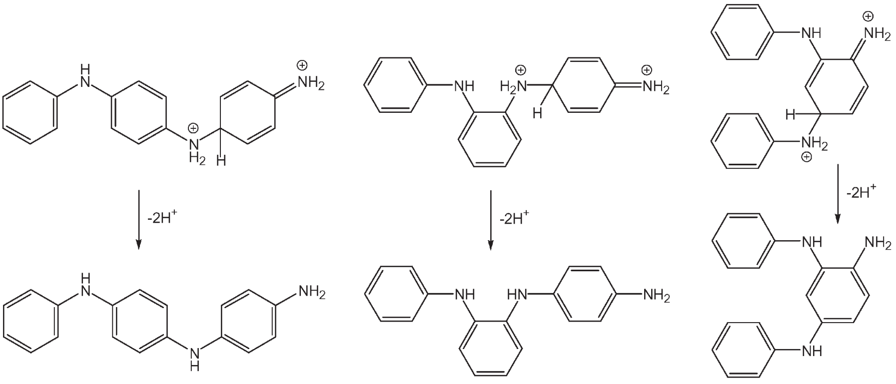


FIG. 10

Oxidation of aniline with the diprotonated form of *N*-phenyl-1,4-benzoquinonediimine, H_2PBQI. Spin density of the hydrated aniline cation radical, calculated by the MNDO-PM3, is shown in the formulae

TABLE IV
Heat of reaction of the aniline trimer dication intermediate formation, $\Delta H_{\mathrm{r(aniline^{+\bullet} + 4\text{-}ADPA^{+\bullet})}}$ ($\Delta H_{\mathrm{r(aniline^{+\bullet} + 2\text{-}ADPA^{+\bullet})}}$), calculated by MNDO-PM3 and AM1 methods for various coupling reactions of 4-aminodiphenylamine or 2-aminodiphenylamine cation radicals and aniline cation radical in aqueous solution

Aniline trimer dication coupling mode	ΔH_r, kcal mol^{-1} aniline$^{+\bullet}$ + 4-ADPA$^{+\bullet}$ (aniline$^{+\bullet}$ + 2-ADPA$^{+\bullet}$)		Aniline trimer dication coupling mode	ΔH_r, kcal mol^{-1} aniline$^{+\bullet}$ + 4-ADPA$^{+\bullet}$ (aniline$^{+\bullet}$ + 2-ADPA$^{+\bullet}$)	
	AM1	PM3		AM1	PM3
$N_{prim(4\text{-}ADPA)}–C_{ortho(aniline)}$	–4.8	–10.0	$N_{(aniline)}$–C2 (C6)$_{(4\text{-}ADPA)}$	4.1	3.1
$N_{prim(4\text{-}ADPA)}–C_{para(aniline)}$	–13.5	–20.0	$N_{(aniline)}$–C8 (C12)$_{(4\text{-}ADPA)}$	3.7	2.0
$N_{sec(4\text{-}ADPA)}–C_{ortho(aniline)}$	12.2	2.4	$N_{(aniline)}$–C10$_{(4\text{-}ADPA)}$	–5.8	–5.5
$N_{sec(4\text{-}ADPA)}–C_{para(aniline)}$	1.7	–8.1	$N_{(aniline)}$–C3$_{(2\text{-}ADPA)}$	–4.4	0.7
$N_{prim(2\text{-}ADPA)}–C_{ortho(aniline)}$	–5.6	–10.0	$N_{(aniline)}$–C4$_{(2\text{-}ADPA)}$	–5.8	–6.7
$N_{prim(2\text{-}ADPA)}–C_{para(aniline)}$	–14.2	–17.7	$N_{(aniline)}$–C6$_{(2\text{-}ADPA)}$	5.0	3.2
$N_{sec(2\text{-}ADPA)}–C_{ortho(aniline)}$	12.4	3.8	$N_{(aniline)}$–C5$_{(2\text{-}ADPA)}$	–13.0	–16.7
$N_{sec(2\text{-}ADPA)}–C_{para(aniline)}$	2.0	–6.3	$N_{(aniline)}$–C8 (C12)$_{(2\text{-}ADPA)}$	0.1	–0.7
$N_{(aniline)}$–C3 (C5)$_{(4\text{-}ADPA)}$	–2.6	–9.2	$N_{(aniline)}$–C10$_{(2\text{-}ADPA)}$	–9.7	–9.0



4-ADPA-(N_{prim}-C4)-aniline **2-ADPA-(N_{prim}-C4)-aniline** **aniline-(N-C5)-2-ADPA**

FIG. 11
Formation of the main aniline trimers by deprotonation of the most stable aniline trimer dication intermediates

and N_{sec} denote nitrogen atoms in primary and secondary amino groups). The heat of the coupling reaction of the aniline cation radical with a 4-ADPA (2-ADPA) cation radical, $\Delta H_{r(aniline^{+\cdot}+4\text{-}ADPA^{+\cdot})}$ ($\Delta H_{r(aniline^{+\cdot}+2\text{-}ADPA^{+\cdot})}$), leading to the formation of the aniline trimer dication intermediate (Table IV) is calculated as the difference between the heat of formation ΔH_f of hydrated trimer dication intermediate and the sum of ΔH_f values of hydrated aniline cation radical and 4-ADPA (2-ADPA) cation radical as reactive species, by following equations:

$$\Delta H_{r(aniline^{+\cdot}+4\text{-}ADPA^{+\cdot})} = \Delta H_{f(aniline\ trimer\ dication\ intermediate)} - [\Delta H_{f(aniline^{+\cdot})} + \Delta H_{f(4\text{-}ADPA^{+\cdot})}] \quad (3)$$

$$\Delta H_{r(aniline^{+\cdot}+2\text{-}ADPA^{+\cdot})} = \Delta H_{f(aniline\ trimer\ dication\ intermediate)} - [\Delta H_{f(aniline^{+\cdot})} + \Delta H_{f(2\text{-}ADPA^{+\cdot})}] \quad (4)$$

Aniline trimers can also be formed by the electrophilic aromatic substitution reaction of the aniline nitrenium cation $C_6H_5NH^+$ with 4-ADPA and 2-ADPA. Taking in account the charge distribution in the nitrenium cation (Fig. 4) and 4-ADPA (2-ADPA) (Fig. 12), MNDO-PM3 enthalpy calculations of these trimerization reactions (Table V) show that the predominating aniline trimer is unique for both 4-ADPA and 2-ADPA reactions with the aniline nitrenium cation (Fig. 12). This trimer has the same structure as the branched aniline trimer obtained by the reaction of OBQI with aniline (Fig. 11) and includes a newly-formed 1,2,4-trisubstitution pattern. The

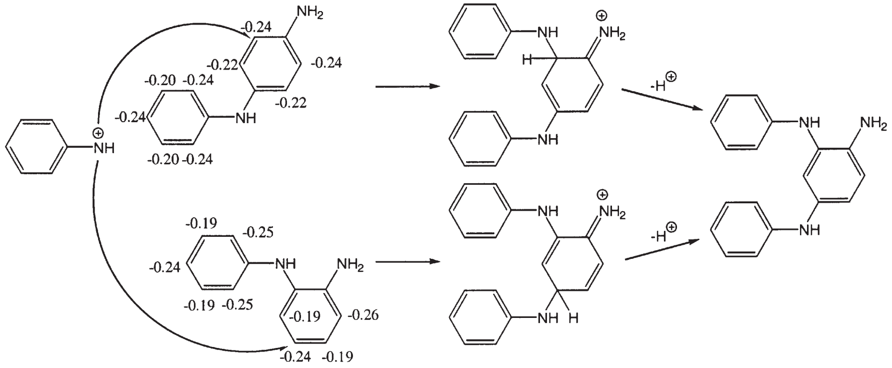


FIG. 12
Reactions of the aniline nitrenium cation with 4-ADPA and 2-ADPA lead to the unique predominating trimer. Charge distributions of hydrated 4-ADPA and 2-ADPA, calculated by the MNDO-PM3, are shown in the formulae

heat of the coupling reaction of the aniline nitrenium cation with a 4-ADPA (2-ADPA), $\Delta H_{\text{r(aniline nitrenium}^{+}+4\text{-ADPA)}}$ ($\Delta H_{\text{r(aniline nitrenium}^{+}+2\text{-ADPA)}}$), leading to the formation of aniline trimer cation intermediate (Table V), has been calculated as the difference between heat of formation, ΔH_f, of hydrated trimer cation intermediate and the sum of ΔH_f values of hydrated aniline nitrenium cation and 4-ADPA (2-ADPA) molecule, similarly as above:

$$\Delta H_{\text{r(aniline nitrenium}^{+}+4\text{-ADPA)}} = \Delta H_{\text{f(aniline trimer cation intermediate)}} - [\Delta H_{\text{f(aniline nitrenium}^{+})} + \Delta H_{\text{f(4-ADPA)}}] \quad (5)$$

$$\Delta H_{\text{r(aniline nitrenium}^{+}+2\text{-ADPA)}} = \Delta H_{\text{f(aniline trimer cation intermediate)}} - [\Delta H_{\text{f(aniline nitrenium}^{+})} + \Delta H_{\text{f(2-ADPA)}}] \quad (6)$$

TABLE V

Heat of reaction of the aniline trimer cation intermediate formation, $\Delta H_{\text{r(aniline nitrenium}^{+}+4\text{-ADPA)}}$ ($\Delta H_{\text{r(aniline nitrenium}^{+}+2\text{-ADPA)}}$), calculated by the MNDO-PM3 method for various coupling modes of 4-ADPA or 2-ADPA and aniline nitrenium cation, $C_6H_5NH^+$, in water

Aniline trimer cation coupling mode	ΔH_r, kcal mol^{-1} aniline nitrenium$^+$ + 4-ADPA (aniline nitrenium$^+$ + 2-ADPA)	Aniline trimer cation coupling mode	ΔH_r, kcal mol^{-1} aniline nitrenium$^+$ + 4-ADPA (aniline nitrenium$^+$ + 2-ADPA)
$N_{\text{(aniline)}}$–C3 (C5)$_{\text{(4-ADPA)}}$	–38.9	$C4_{\text{(aniline)}}$–C3 (C5)$_{\text{(4-ADPA)}}$	–21.4
$N_{\text{(aniline)}}$–C2 (C6)$_{\text{(4-ADPA)}}$	–32.2	$C4_{\text{(aniline)}}$–C2 (C6)$_{\text{(4-ADPA)}}$	–13.6
$N_{\text{(aniline)}}$–C8 (C12)$_{\text{(4-ADPA)}}$	–34.1	$C4_{\text{(aniline)}}$–C8 (C12)$_{\text{(4-ADPA)}}$	–12.3
$N_{\text{(aniline)}}$–$C10_{\text{(4-ADPA)}}$	–34.9	$C4_{\text{(aniline)}}$–$C10_{\text{(4-ADPA)}}$	–21.3
$N_{\text{(aniline)}}$–$C3_{\text{(2-ADPA)}}$	–40.0	$C4_{\text{(aniline)}}$–$N_{\text{prim(2-ADPA)}}$	–26.9
$N_{\text{(aniline)}}$–$C4_{\text{(2-ADPA)}}$	–33.1	$C4_{\text{(aniline)}}$–$N_{\text{sec(2-ADPA)}}$	–15.8
$N_{\text{(aniline)}}$–$C6_{\text{(2-ADPA)}}$	–28.3	$C4_{\text{(aniline)}}$–$C3_{\text{(2-ADPA)}}$	–19.1
$N_{\text{(aniline)}}$–$C5_{\text{(2-ADPA)}}$	–42.5	$C4_{\text{(aniline)}}$–$C4_{\text{(2-ADPA)}}$	–14.1
$N_{\text{(aniline)}}$–C8 (C12)$_{\text{(2-ADPA)}}$	–31.8	$C4_{\text{(aniline)}}$–$C5_{\text{(2-ADPA)}}$	–24.6
$N_{\text{(aniline)}}$–$C10_{\text{(2-ADPA)}}$	–33.2	$C4_{\text{(aniline)}}$–C8 (C12)$_{\text{(2-ADPA)}}$	–7.8
$C4_{\text{(aniline)}}$–$N_{\text{prim(4-ADPA)}}$	–30.9	$C4_{\text{(aniline)}}$–$C10_{\text{(2-ADPA)}}$	–17.2
$C4_{\text{(aniline)}}$–$N_{\text{sec(4-ADPA)}}$	–20.5		

Aniline Trimers and Their Redox Properties

The main aniline trimers, generated by both proposed trimerization mechanisms, contain newly-formed 1,4- and 1,2,4-substitution patterns. Aniline trimers, being more oxidizable than aniline and aniline dimers, undergo fast two-electron oxidation with peroxydisulfate. MNDO-PM3 charge-distribution calculations show that the most stable half-oxidized aniline

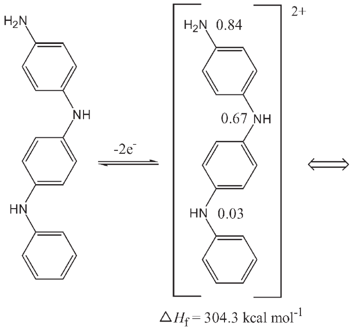


FIG.13
Two-electron oxidation of the aniline trimer produces the half-oxidized trimer dication bearing the oxidized head in quinonoid form, as can be seen from the shown charge distribution, calculated by the MNDO-PM3 method

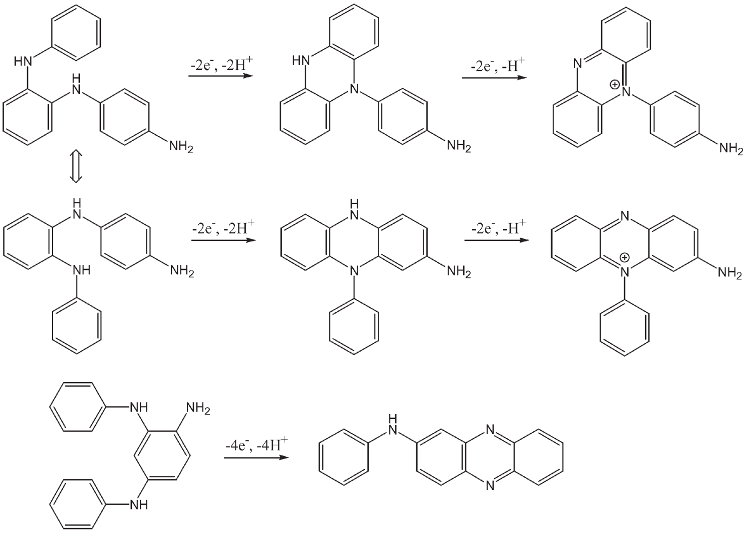


FIG. 14
Substituted phenazines formed by aniline trimer oxidation and the intramolecular cyclization route

trimer structures have an oxidized head (primary amino group) rather than a tail (secondary amino group) in quinonoid form (Fig. 13). In the case of dominant aniline trimers containing 1,2- or 1,2,4-substitution patterns, a two-electron oxidation process can also lead to the formation of dihydrophenazines, which are readily oxidized to substituted phenazines (Fig. 14).

Half-oxidized aniline trimers further undergo two-electron oxidation with APS to give the aniline trimer nitrenium trication as a reactive species (Fig. 15). This is proved by the low ionization energy, calculated by MNDO-PM3, of the hydrated aniline trimer radical trication (E_i = 6.04 eV for linear trimer). It is interesting to note that the spin density values show the SOMO localized mainly on the aniline trimer radical trication head (Fig. 15, primary amino group).

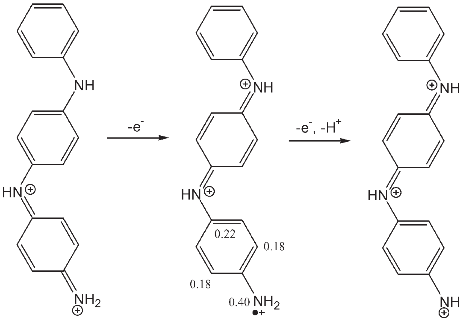


FIG. 15
Half-oxidized linear aniline trimer, aniline trimer radical trication, and fully-oxidized aniline trimer nitrenium trication. Spin density values of the hydrated aniline trimer radical trication, calculated by the MNDO-PM3, are shown in the formulae

CONCLUSIONS

The formation of reaction intermediates in the chemical oxidation of aniline in water yielding polyaniline has been analyzed. Based on the semiempirical quantum chemical MNDO-PM3 calculations, it can be proposed that, in the first phase of aniline oxidative polymerization with ammonium peroxydisulfate in aqueous solution without added acid, aniline nitrenium cations are formed. These react instantaneously with aniline leading to 4-ADPA as the main dimeric product, and 2-ADPA as the most important side dimeric product. Being more oxidizable than aniline, both aminodiphenylamines undergo a fast two-electron oxidation to *N*-phenyl-1,4-benzoquinonediimine (PBQI) and *N*-phenyl-1,2-benzoquinonediimine (OBQI), respectively. Theoretical MNDO-PM3 investigation of the proton effect on aniline polymerization clearly shows an increase in the PBQI and OBQI oxidant power and a decrease in 4-ADPA and 2-ADPA oxidizability with decreasing pH.

The trimerization process is proposed to occur via two different mechanisms:

(*1*) Redox reaction of PBQI and OBQI with aniline results in linear and branched aniline trimer structures, respectively.

(*2*) Reaction of the aniline nitrenium cation with both 4-ADPA and 2-ADPA leads to the formation of a branched aniline trimer.

The formation of a branched aniline trimer by both proposed mechanistic routes indicates a pronounced branching in further aniline oligomerization and polymerization. We can speculate that this two-dimensional PANI growth seems to be a reasonable step prior to the three-dimensional growth of PANI nanotubes.

Aniline trimers undergo further oxidation with an oxidant giving products with an oxidized primary amino group rather than an oxidized secondary amino group. These half-oxidized trimers can subsequently be fully oxidized to trimer nitrenium trications which are a new reactive species. It can be concluded that oligomeric nitrenium cations as reactive species in aniline polymerization, proposed by many authors, exist only in the cases of fully oxidized aniline oligomers with an odd number of aniline units. This feature could be the main reason for the much more efficient polymerization of aniline compared with polymerization of its dimers (4-ADPA, 2-ADPA or benzidine).

Aniline trimers with 1,2- and 1,2,4-substitution patterns can be oxidized to substituted phenazines. The importance of this intramolecular cyclization reaction pathway increases for higher 1,2,4-branched oligomers.

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