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Review

REVIEW

## Progress in conducting/semiconducting and redox-active oligomers and polymers of arylamines

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**Abstract:** Recent advances in synthesis, characterization and application of the selected conducting/semiconducting and redox-active oligomers and polymers of arylamines are reviewed. A brief historical background of the selected topics is given. The overview of the preparation, structure and properties of polyaniline, substituted polyanilines, especially those obtained by the oxidative polymerization of *p*-substituted anilines, poly(1-aminonaphthalene) and its derivatives, carbocyclic and heterocyclic polyaryldiamines such as poly(*p*-phenylenediamine) and polydiaminoacridines, is presented. The mechanism of formation of polyaniline nanostructures is discussed. Recent approaches to the preparation of one-dimensional polyaniline nanostructures are concisely reviewed, with special attention paid to the template-free falling-pH method. Current and potential future applications of oligo/polyarylamines are briefly discussed.

**Keywords:** polymer, oligomer, oxidative polymerization, arylamine, polyaniline, nanostructure.

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5.1.1. Oxidative polymerization of *p*-phenylenediamine

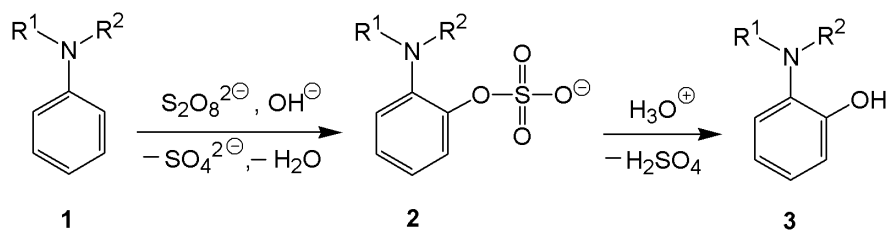
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## 6. CONCLUSIONS AND OUTLOOK

1. OXIDATION *VERSUS* OXIDATIVE POLYMERIZATION OF ARYLAMINES

Chemical oxidations of arylamines can proceed in two different ways.<sup>1</sup> Oxidants with a relatively high oxidation potential, which do not contain a reactive oxygen atom, can remove electron(s)/hydrogen from the arylamine molecule. The *in situ* formed reactive species, *e.g.*, arylamine cation radicals, arylnitrenium cations, *etc.*, undergo further reaction with the parent arylamine molecules leading to the formation of arylamine dimers (N–N, N–C, or C–C coupled dimers in the reduced and/or oxidized form), oxidatively cyclized diarylamine products, such as substituted phenazines, and higher linear/branched oligo/polyarylamines.<sup>1</sup> Oxidants that contain a reactive oxygen atom can either donate an oxygen to the arylamine molecule, thus leading to oxygen-containing products of arylamine oxidation (arylhdroxylamine, nitrozoarene, nitroarene, substituted amino-phenols and aminonaphthols, substituted benzoquinones and naphthoquinones, *o*-aminoaryl sulfate, *etc.*), and/or remove electron(s)/hydrogen from the arylamine molecule.<sup>1</sup> Perphosphoric acid, peroxomonosulfuric acid, and percarboxylic acids are well-known efficient oxygen donors, while Fe(III), Ce(IV), Cu(II), Au(III), Pt(IV), Pd(II) and Ag(I) compounds are frequently used electron acceptors. Oxidants such as H<sub>2</sub>O<sub>2</sub> and peroxydisulfate salts behave as both oxygen donors as well as electron acceptors. High temperatures and alkaline conditions are favorable for the oxygen donor mechanism, whereas low temperatures and acidic conditions are favorable for the electron acceptor mode of action of oxidants such as H<sub>2</sub>O<sub>2</sub> and peroxydisulfate. The electrochemical oxidation of arylamines can also lead, depending on the reaction conditions (electrode type, anodic potential, current density, electrolyte, solvent, pH, temperature, arylamine concentration, *etc.*) to oxygen-containing monomeric/dimeric products and/or oligo/polyarylamines.<sup>1</sup> Depending on the arylamine concentration, the oxidation of the arylamine can lead to its degradation or polymerization.<sup>1</sup>

Boyland and Sims reported in the 1950s the extension of Elbs peroxydisulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) oxidation of phenols in alkaline solution, leading to the prevalent formation of *p*-hydroxyaryl sulfates, to the oxidation of arylamines in alkaline solution with S<sub>2</sub>O<sub>8</sub><sup>2-</sup>.<sup>2-6</sup> Arylamines (Scheme 1, **1**) were found to be prevalently converted to the corresponding soluble *o*-aminoaryl sulfate (Scheme 1, **2**) under conditions similar to those used for the Elbs oxidation: room temperature or below, aqueous alkali media, and equimolar quantities of arylamine and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>.<sup>2-12</sup> Subsequent hydrolysis in highly acidic aqueous solutions leads to corresponding *o*-aminophenols (Scheme 1, **3**).



Scheme 1. Boyland-Sims oxidation of aniline ( $R^1=R^2=H$ ) and its *N*-alkyl/aryl-substituted derivatives with  $S_2O_8^{2-}$ .

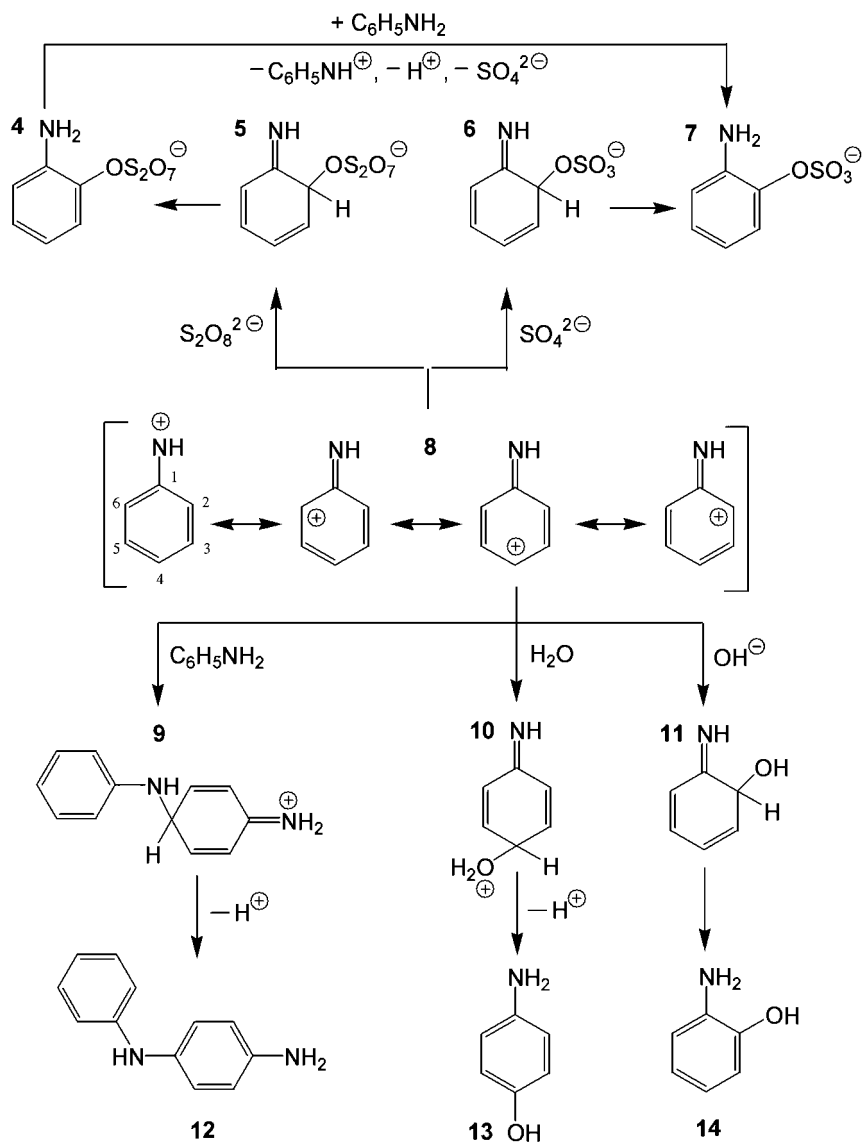
The involvement of free radical arylamine species (cation radicals and neutral radicals), as highly reactive products of single-electron oxidation of arylamines, in the formation of the *o*-aminoaryl sulfates was excluded because radical traps had no effect on the formation of the *o*-aminoaryl sulfates.<sup>7</sup> Arylnitrenium cations, as initial reactive products of two-electron oxidation of primary/secondary arylamines in acidic as well as alkaline solutions, have not been considered as reactive species involved in the formation of *o*-aminoaryl sulfates because the knowledge about aryl nitrenium cation chemistry became well established more than four decades after the discovery of the Boyland-Sims oxidation.<sup>13</sup> Behrman noted that “a nitrene mechanism is not consistent with the fact that tertiary anilines behave in a similar manner to primary anilines”.<sup>11</sup> Based on the fact that electron-releasing substituents at the aromatic ring accelerate the oxidation of arylamines with  $S_2O_8^{2-}$ ,<sup>7</sup> and taking into account some other experimental findings,<sup>11</sup> Behrman proposed that the nucleophilic  $S_N2$  displacement by the arylamine nitrogen on the peroxide oxygen of  $S_2O_8^{2-}$  represents the rate-determining step of the Boyland-Sims oxidation which leads to the formation of arylhydroxylamine-*O*-sulfonate intermediates.<sup>11</sup> This classic mechanism did not explain the regioselectivity of the Boyland-Sims oxidation and the fact that some arylamines, such as benzidine, cannot be transformed to the corresponding aminoaryl sulfates by Boyland-Sims oxidation,<sup>2</sup> but rather give iminoquinonoid compounds upon two-electron oxidation with  $S_2O_8^{2-}$ .

The yields of aminoaryl sulfates in Boyland Sims oxidation are significantly lower than those of hydroxyaryl sulfates in the Elbs oxidation, especially in the case of primary and secondary arylamines, due to the competitive oxidative polymerizations of arylamines leading to the formation of insoluble materials,<sup>2-12</sup> which were described in many papers as humic acid-like polymers. Synthetic organic chemists paid no attention to their structural characterization since these precipitates were considered as undesirable by-products in the Boyland-Sims oxidation,<sup>2-12</sup> whereas scientists working in the field of conducting polymers became interested in the elucidation of the molecular structure and the mechanism of formation of these oligoarylamines, *e.g.*, oligoanilines,<sup>14-18</sup> because recent studies had revealed the crucial template function of *in situ* formed oligo-

anilines in the synthesis of polyaniline nanostructures by the oxidative polymerization of aniline with ammonium peroxydisulfate (APS) under falling pH conditions.<sup>14,19–21</sup>

Marjanović *et al.*<sup>22</sup> recently proposed a revised mechanism of the Boyland–Sims oxidation of arylamines based on the unique role of arylnitrenium cations in the case of primary and secondary arylamines, and arylamine dications and/or immonium cations in the case of tertiary arylamines. The revised mechanism comprehensively explained the formation of soluble aminoaryl sulfates and insoluble oligoarylamines in a manner more consistent with the experimental evidence than previous mechanistic schemes. It was revealed that the two-electron transfer between arylamine and peroxydisulfate, accompanied by the deprotonation, leading to the formation of arylnitrenium cations/arylamine dications/immonium cations and sulfate anions, represents the rate-determining step, while the subsequent reaction between arylnitrenium cations/arylamine dications/immonium cations and sulfate anions represents a regioselectivity-determining step (Scheme 2).<sup>22</sup> In accordance with the experimental findings of Boyland and Sims, it was computationally confirmed by both the AM1 and RM1 semi-empirical quantum chemical methods that the reactions of arylnitrenium cations or arylamine dications/immonium cations with sulfate anions lead to the prevalent formation of *o*-aminoaryl sulfates.<sup>22</sup> The C6–O–SO<sub>3</sub> rather than C2–O–SO<sub>3</sub> coupled aminoaryl sulfates were also computationally confirmed to be the major products of Boyland–Sims oxidation in the case of *meta*-substituted anilines that have unsymmetrical *ortho* positions. Moreover, the computations confirmed the known experimental findings that *para* substitution occurs if both *ortho* positions are blocked by substituents. The reactions between arylnitrenium cations and peroxydisulfate in an aqueous solution were found to have regioselectivities quite similar to those of the reactions between arylnitrenium cations and sulfate; *i.e.*, they lead to the prevalent formation of *o*-aminoaryl peroxydisulfates, which undergo rapid reduction to the corresponding *o*-aminoaryl sulfates (Scheme 2).<sup>22</sup>

The formation of insoluble precipitates during the Boyland–Sims oxidation of arylamines was explained by the oxidative oligomerization of arylamines, in which the dimerization phase is the reaction of arylamines with arylnitrenium cations (Scheme 2),<sup>22</sup> and by the oxidative co-oligomerizations of arylamines with aminoaryl sulfates and aminophenols, formed in the reaction of arylnitrenium cations/arylamine dications/immonium cations with both hydroxide anions in highly alkaline solution and water molecules in highly dilute aqueous solutions.<sup>22</sup> Fully oxidized branched oligoarylamines, containing mainly substituted phenazine and iminoquinonoid units with the presence of iminoquinone/phenoxazine segments, were proposed to constitute the insoluble precipitates in Boyland–Sims oxidations.<sup>22</sup>



Scheme 2. Formation of prevalent products (4, 7, 12–14), through the most stable intermediates (5, 6, 9–11), in reactions of the aniline nitrenium cation (8) with  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_8^{2-}$ , aniline,  $\text{OH}^-$  and  $\text{H}_2\text{O}$ . Reprinted<sup>22</sup> with permission. Copyright (2011) American Chemical Society.

## 2. OXIDATIVE POLYMERIZATION OF ANILINE

Polyaniline (PANI) has been the most extensively studied polyarylamine during the past three decades because of its high electrical conductivity, pronounced redox-activity, good environmental stability, simple acid–base doping–

–dedoping, ease of preparation by chemical and electrochemical oxidative polymerization of aniline and its salts, and versatile applicability in various areas of modern technologies, such as rechargeable batteries, sensors and indicators, catalysts, shielding of electromagnetic interference, microwave and radar absorbing materials, non-linear optical and light-emitting devices, electron field emitters, field-effect transistors, Schottky diodes, erasable optical information storage, digital memory devices, asymmetric films, membranes, electrochemical capacitors (supercapacitors), electrochromic devices, electromechanical actuators, electrorheological (ER) fluids, antistatic and anticorrosion coatings, and fuel and solar cells.<sup>1,23</sup> PANI has a variety of redox and acid–base forms<sup>24</sup> with quite different optical, magnetic, electrical and other properties. The most important form of PANI is the green emeraldine salt, which attains a conductivity of about  $1\text{--}10\text{ S cm}^{-1}$  for granular PANI powders,<sup>25</sup>  $\approx 10^2\text{ S cm}^{-1}$  for PANI powders with nanospherical morphology<sup>26</sup> and  $\approx 10^3\text{ S cm}^{-1}$  for PANI films.<sup>27</sup> Emeraldine salt contains, depending on the preparation method and isolation procedure, various proportions of diamagnetic  $[(-\text{B}-\text{NH}^+=\text{Q}=\text{NH}^+-\text{B}-\text{NH}-\text{B}-\text{NH}-)_n](\text{A}^-)_{2n}$  and paramagnetic  $[(-\text{B}-\text{NH}^{\bullet}-\text{B}-\text{NH}-)_n](\text{A}^-)_n$  units; in the preceding formulae B, Q, and A denote a benzenoid ring, a quinonoid ring, and a dopant anion, respectively. Chemical/electrochemical oxidative polymerization of aniline in aqueous solutions of strong acids ( $\text{pH} < 2.0$ ) at room temperature is a typical method for the preparation of conducting PANI emeraldine salt.<sup>1,25</sup> Besides APS and Fe(III) compounds as the most frequently used oxidants in PANI syntheses, various other oxidants were recently used, *e.g.*, transition metal compounds such as Mn(III), Mn(IV), Mn(VII), Cr(VI), Ce(IV), V(V) and Cu(II) compounds,  $\text{KIO}_3$ ,  $\text{H}_2\text{O}_2$ , and benzoyl peroxide,<sup>1</sup> as well as noble metal compounds such as Au(III), Pt(IV), Pd(II) and Ag(I) compounds.<sup>28</sup> Mixtures of oxidants were also used, *e.g.*,  $\text{FeCl}_3/\text{H}_2\text{O}_2$  and  $\text{KIO}_3/\text{NaClO}$ .<sup>1</sup>

In numerous performed oxidative polymerization experiments with “equimolar” quantities of commercially available aniline and the corresponding acid (which serves as a dopant, enabling the high conductivity of the final PANI emeraldine salt), there was up to a few percent surplus of aniline or acid because researchers assumed incorrectly that used aniline and acid were 100 % pure despite the fact that commercially available aniline is most frequently  $\geq 99.0\text{--}99.5\%$  pure while the majority of employed acids (especially organics, *e.g.*, camphorsulfonic acid) are  $\geq 98\%$  pure. These subtle differences in the initial aniline/acid molar ratio led to significant differences in the initial pH of the oxidative polymerization process, known to have a crucial impact on the polymerization mechanism and molecular/supramolecular structure of PANI.<sup>14,15,19–21,29–35</sup> Since the initial pH of the reaction mixture was usually not recorded, this variation in the initial pH could be the major reason for the pronounced irreproducibility of most of the previously published results in the

field of PANI research noticed by MacDiarmid *et al.*<sup>36</sup> who made the well known statement – “there are as many different types of polyaniline as there are people who make it!” Therefore, it could reasonably be expected that the polymerization of purified aniline salts would provide much more reproducible results. Furthermore, it should be noted that the handling of solid aniline salts is much less hazardous than the handling of liquid aniline. Finally, because the anilinium cation is much less oxidizable than the non-protonated aniline molecule,<sup>29</sup> crystalline aniline salts are much more resistant in comparison with liquid aniline against oxidative degradation by atmospheric oxygen during storage. However, the performed oxidative chemical polymerizations of commercially available aniline salts, such as hydrochloride and sulfate, gave PANI salts that were almost insoluble in common solvents. This lack of solubility limits the processability of ordinary PANI emeraldine salts (chlorides/sulfates), which must be transformed by a dedoping–redoping procedure to a more processable PANI doped with functionalized acids. Many attempts to synthesize processable PANI salts by the oxidation of aniline with  $S_2O_8^{2-}$  in the presence of various functionalized acids failed because hydrogen sulfate, formed as a by-product during the polymerization ( $nC_6H_5NH_2 + nS_2O_8^{2-} \rightarrow (-C_6H_4NH-)_n + 2nH_2SO_4$ ), was incorporated into the PANI structure instead of a functionalized dopant anion, especially in the cases of salts of aniline and weak acids.<sup>37</sup> Therefore the quest for an aniline salt with functionalized acid which could be directly oxidized with APS or other oxidants to the processable conducting PANI emeraldine salt presents a challenge up to the present time.

It was reported that PANI solubility, crystallinity, thermal and electrochemical stability, and anticorrosive properties were improved using 5-sulfosalicylic acid (SSA) as the dopant.<sup>38–41</sup> Conducting PANI–5-sulfosalicylate (PANI–SSA) was successfully prepared by chemical and electrochemical oxidation of aniline in the presence of SSA using a mole ratio [SSA]/[aniline] in the broad range from 0.25 to 10.0.<sup>19,30,38,39,41</sup> It was observed that PANI–SSA nanotubes and nanorods were formed using the ratio [SSA]/[aniline] = 0.25, while granular PANI–SSA was obtained at [SSA]/[aniline]  $\geq$  0.5.<sup>19</sup> Anilinium 5-sulfosalicylate was recently prepared, recrystallized, and polymerized to processable conducting PANI–SSA,<sup>42</sup> which had mass-average molar mass and polydispersity index of 22,900 g mol<sup>-1</sup> and 2.7, respectively, and exhibited high thermal stability. An elemental analysis and FTIR spectroscopic study of PANI–SSA revealed the doping level and the oxidation state between the emeraldine and protoemeraldine salt, while corresponding studies of the PANI base indicated a small extent of covalent bonding of SSA anions to the PANI chains.<sup>42</sup>



### 2.1. Polyaniline nanostructures

Interest in the study of PANI nanostructures has dramatically increased during the last decade due to the significantly enhanced dispersibility and processibility as well as substantially improved performance of nanostructured PANI materials in many applications, *e.g.*, sensors, catalysts, electron field emitters, field-effect transistors, corrosion protection, data storage, actuators, membranes, solar cell devices, rechargeable batteries, fuel cells, ER fluids, Schottky diodes, supercapacitors, electromagnetic interference shielding, microwave absorption and antistatic coatings, in comparison with ordinary granular PANI materials.<sup>1,43</sup> PANI nanostructures have also been successfully used as precursors in the process of carbonization leading to the formation of nitrogen-containing carbon nanomaterials that have versatile applicability.<sup>44–57</sup> The formation, molecular structure, properties and applications of PANI nanostructures were reviewed during the last several years.<sup>1,43,58–67</sup> PANI nanostructures were also reviewed within the frame of review articles devoted to nanostructured conducting polymers.<sup>68–75</sup>

Colloidal PANI nanoparticles (NPs) can be simply prepared by dispersion polymerization of aniline in the presence of various colloidal stabilizers.<sup>76</sup> Several physical methods for the fabrication of PANI nanofibers (NFs) and/or nanorods (NRs) from granular PANI are known, *e.g.*, electrospinning, ultrasonication, spin coating, and irradiation of the freestanding PANI film with a pulsed electron beam.<sup>1,43</sup> Various template methods for the preparation of 1-D PANI nanostructures (NFs, nanowires (NWs), NRs or nanotubes (NTs)) *via* the oxidative polymerization of aniline, *e.g.*, hard template methods (nanoporous template, nanostructured seed template and the reactive template method) and soft template methods (oligomer-, polymer-, surfactant- and amphiphilic acid-assisted syntheses) were developed during the last two decades.<sup>1,43</sup> Template-free methods, *e.g.*, not-shaken/not-stirred, aqueous/organic interfacial, rapid-mixing and dilute polymerizations; photo-assisted, radiolytic, sonochemical, solid-state mechanochemical and electrochemical syntheses (voltammetric, potentiostatic, galvanostatic, *etc.*), as well dopant-free, falling-pH, “pH-stat” and hydrophobic surface methods for the synthesis of 1-D PANI nanostructures were also reported in the last decade.<sup>1,43</sup> The falling-pH method was the most frequently used template-free method for the preparation of PANI–NTs accompanied with PANI–NRs,<sup>19,77</sup> while in some cases, PANI–NRs were prevalently obtained (Fig. 1).<sup>78,79</sup> Special attention was paid to the oxidative polymerization of aniline in water without any added acid as the simplest falling-pH method for the preparation of 1-D nanostructured PANI (Fig. 2).<sup>14,15,20,21,33,80–89</sup>



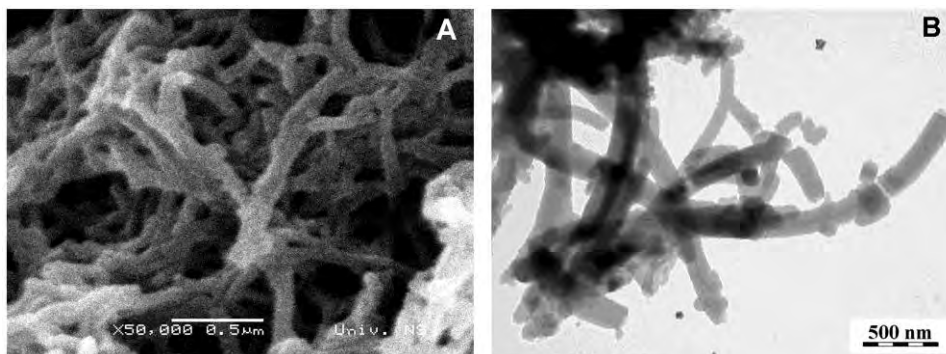


Fig. 1. SEM (A) and TEM (B) images of PANI 3,5-dinitrosalicylate NRs prepared by the chemical oxidative polymerization of aniline with APS at mole ratios [3,5-dinitrosalicylic acid]/[aniline] = 0.5 and [APS]/[aniline] = 1.25. Adapted<sup>51</sup> with permission. Copyright (2012) Elsevier.

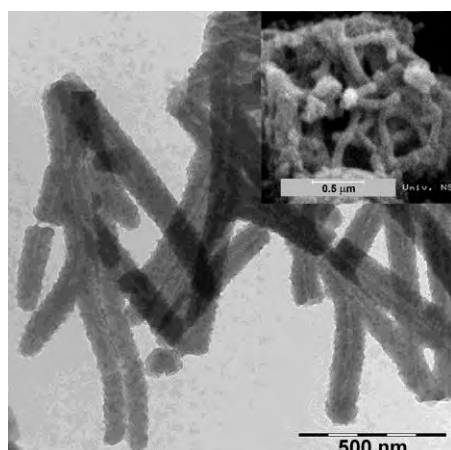


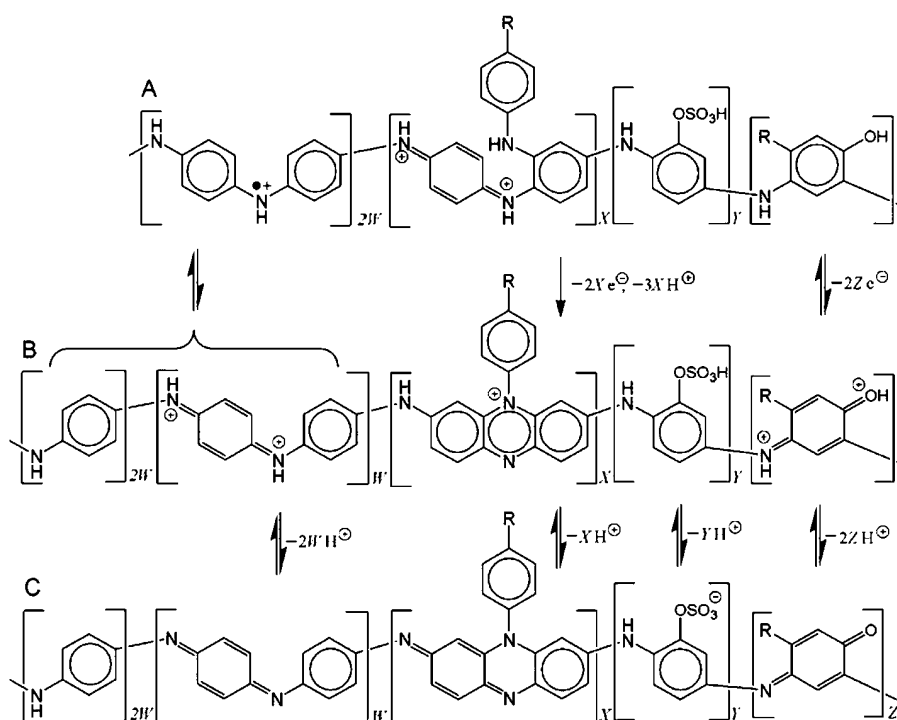
Fig. 2. TEM image of PANI hydrogensulfate/sulfate NTs prepared by the chemical oxidative polymerization of aniline with APS in water without any added acid. The corresponding SEM image is shown in the inset. Adapted<sup>85</sup> with permission. Copyright (2011) Elsevier.

The molecular structure of nanostructured PANIs obtained by the falling-pH method (starting from slightly acidic or neutral media) is much more complex than that of ordinary PANIs prepared in strongly acidic media (Scheme 3),<sup>85</sup> as was predicted by semi-empirical quantum chemical computations<sup>29,31,32</sup> and confirmed by spectroscopic data (Fig. 3).<sup>14,15,19,78,85</sup>

The redox-activity and paramagnetic behavior of nanostructured PANI was frequently confirmed, *e.g.*, in the case of PANI-NRs prepared in the presence of tannic acid (Fig. 4).<sup>79</sup>

Substantial efforts have been made in order to understand the mechanisms of formation of PANI nanostructures during aniline oxidative polymerization.<sup>1,43,64,65</sup> It was found that PANI-NFs/NWs/NRs are naturally formed during the chemical oxidative polymerization of aniline in acidic aqueous solutions,<sup>1,43</sup> whereas PANI-NTs/NFs/NWs/NRs and/or PANI nanosheets are formed by self-

assembly under falling-pH conditions.<sup>1,43</sup> The theoretical approach of Stejskal *et al.* to the genesis of PANI nanostructures under falling-pH conditions was based on the oligoaniline-guided self-assembly process,<sup>65</sup> while an expanded PANI nanostructure self-assembly model, based on a multi-layered approach incorporating intrinsic PANI morphologies (NFs, nanosheets and NPs) was proposed by Travas-Sejdic *et al.*<sup>64</sup>



Scheme 3. Acid–base and redox equilibria between protonated (A and B) and deprotonated (C) oligoaniline/PANI backbones that contain *N*-phenylphenazine (R=H), substituted *N*-phenylphenazine (R = oligoaniline), *ortho*-aminophenyl sulfate, and iminoquinone/4-aminophenol units (R = H and/or R = oligoaniline), besides the classic aminophenyl and *N*-phenyl-1,4-benzoquinonediimine units. Reprinted<sup>85</sup> with permission.

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### 3. OXIDATIVE POLYMERIZATION OF SUBSTITUTED ANILINES

Oxidative polymerization of ring/*N*-substituted anilines was extensively studied during the past three decades. Investigations were focused on the oxidation of *ortho/meta*- and *N*-substituted anilines<sup>90–98</sup> because it was expected that these monomers could give prevalently N–C4 coupled oligomers/polymers upon oxidation, similarly to aniline. Considerable attention was also paid to the oxidative polymerization of *para*-substituted anilines.<sup>99–178</sup>

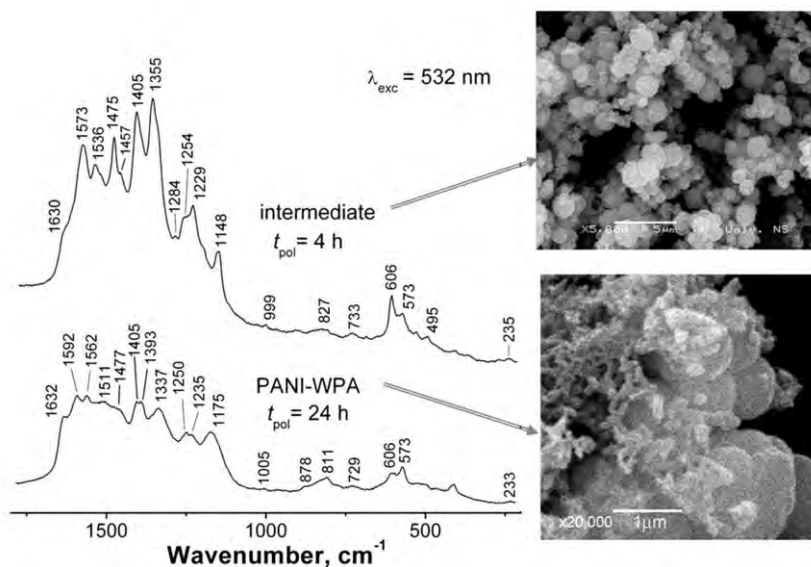


Fig. 3. Raman spectra of oligoaniline intermediate (submicro- and microspheres) and PANI-WPA (submicro- and microspheres / nanorods) produced in the presence of 12-tungstophosphoric acid (WPA) at an initial pH 5.7 (weight ratio WPA/aniline = 0.5) with the corresponding SEM images. Bands attributed to phenazine-like segments are seen at 1405 and  $\approx 1630$   $\text{cm}^{-1}$ . Adapted<sup>77</sup> with permission. Copyright (2010) Elsevier.

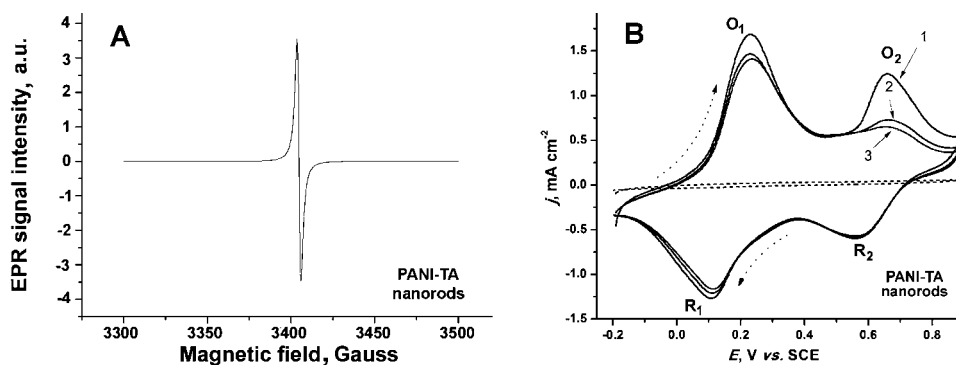


Fig. 4. A) EPR spectrum of PANI-NRs and B) first three consecutive cyclic voltammograms of PANI-NRs deposited on a glassy carbon electrode, recorded in 0.1 M aqueous  $\text{H}_2\text{SO}_4$  solution at a sweep rate of  $50 \text{ mV s}^{-1}$ . PANI-NRs were prepared by the oxidative polymerization of aniline with APS in the presence of tannic acid, at mole ratios  $[\text{tannic acid}]/[\text{aniline}] = 0.01$ ,  $[\text{APS}]/[\text{aniline}] = 1$ . Adapted<sup>79</sup> with permission. Copyright (2012) Elsevier.

### 3.1. Oxidative polymerization of para-substituted anilines

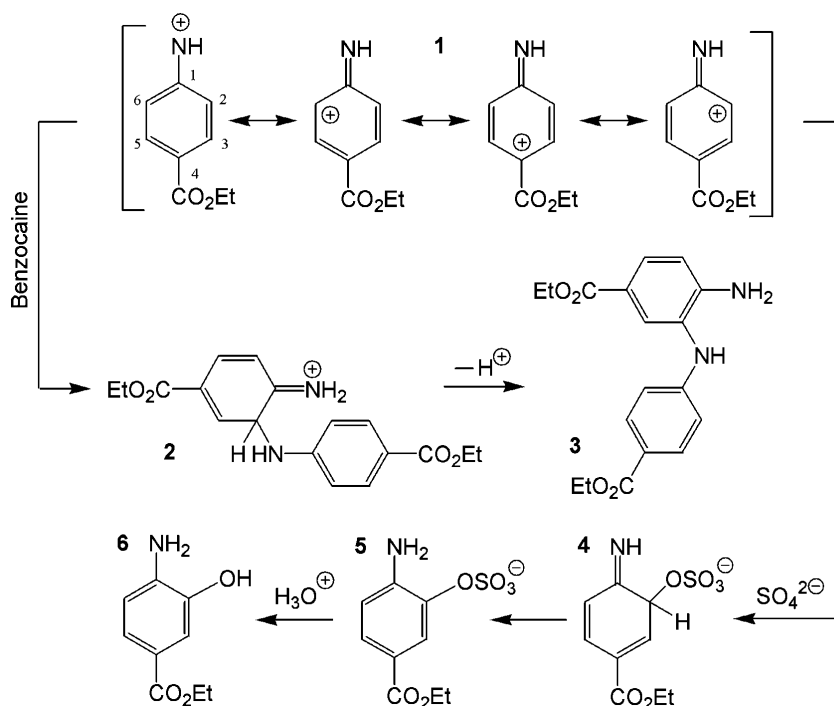
The oxidative polymerization of *para*-substituted anilines,<sup>99–178</sup> e.g.,  $\text{CH}_3-$  (*p*-toluidine),<sup>99–102</sup>  $\text{CH}_3\text{CH}_2-$ ,<sup>103</sup>  $(\text{CH}_3)_3\text{C}-$ ,<sup>104</sup>  $\text{C}_6\text{H}_5-$ ,<sup>105</sup>  $\text{H}_2\text{N}-\text{C}_6\text{H}_4-$

–(benzidine),<sup>106–114</sup>  $\text{N}\equiv\text{C}$ –,<sup>104,115</sup>  $\text{HOOC}$ – (4-aminobenzoic acid),<sup>115–119</sup>  $\text{F}$ –,<sup>104,120–122</sup>  $\text{Cl}$ –,<sup>102–104,115,121,123,124</sup>  $\text{Br}$ –,<sup>104,115,121,124</sup>  $\text{I}$ –,<sup>124</sup>  $\text{H}_2\text{N}$ – (*p*-phenylenediamine),<sup>107,112,125–151</sup>  $\text{C}_6\text{H}_5\text{–NH}$ – (4-aminodiphenylamine),<sup>152–163</sup>  $\text{H}_2\text{N–C}_6\text{H}_4(\text{CH}_3)$ – (*o*-tolidine),<sup>164</sup>  $\text{O}_2\text{N}$ –,<sup>104,115,165</sup>  $\text{HO}$ – (4-aminophenol),<sup>166–173</sup>  $\text{CH}_3\text{O}$ – (*p*-anisidine),<sup>115</sup>  $\text{CH}_3\text{CH}_2\text{O}$ – (*p*-phenetidine),<sup>115</sup>  $\text{HO}_3\text{S}$ – (sulfanilic acid)<sup>116,174–176</sup> and  $\text{H}_2\text{NO}_2\text{S}$ –substituted aniline (sulfanilamide),<sup>177</sup> was reported. Peroxydisulfates were most frequently used as oxidants.<sup>102,103,112–114,122,124,129,140–145,153–156,164,165,173</sup> Bromine,<sup>126</sup> iodine,<sup>140</sup> Fe(III) compounds,<sup>103,139,152</sup> metal chelate/ $\text{O}_2$ ,<sup>138</sup> tetrachloroauric acid,<sup>150</sup>  $\text{H}_2\text{O}_2$  without catalyst<sup>146</sup> and with horseradish peroxidase,<sup>147,166</sup> *cis*-bisglycinato-Cu(II)-monohydrate/Co(II)-dionemoxime,<sup>149</sup> silver nitrate<sup>151</sup> and sodium dichromate<sup>177</sup> were occasionally employed. The enzyme-catalyzed oxidative polymerization of *p*-substituted anilines was also studied.<sup>123,147,148,166</sup> Electrochemical oxidative polymerizations were also widely used for the synthesis of poly(*p*-substituted anilines).<sup>99–101,104–111,115–121,127–137,157–163,167–172,174–176</sup> Molar mass distribution measurements revealed that the products of oxidative polymerization of *p*-substituted anilines were low- to high-molar-mass oligomers rather than polymers.

Spectroscopic methods for structural characterization combined with semi-empirical quantum chemical studies of the polymerization mechanisms were proved to be powerful tools in the elucidation of the molecular structures of oligo/poly(substituted anilines).<sup>155,178</sup> The course of the oxidation of 4-aminodiphenylamine (4-ADPA) with APS in acidic aqueous ethanol solution as well as the properties of the oxidation products were compared with those of 2-aminodiphenylamine (2-ADPA) oxidation.<sup>155</sup> Semiconducting oligomers of 4-ADPA and non-conducting oligomers of 2-ADPA of mass-average molar masses of 3,700 and 1,900  $\text{g mol}^{-1}$ , respectively, were prepared using an oxidant to monomer mole ratio of 1.25. Molecular orbital calculations revealed the prevalence of  $\text{N}_{\text{prim}}\text{–C}_{10}$  coupling reaction of 4-ADPA, while  $\text{N}_{\text{prim}}\text{–C}_5$  was found to be the main coupling mode between 2-ADPA units. FTIR and Raman spectroscopic studies confirmed the prevalent formation of linear  $\text{N}_{\text{prim}}\text{–C}_{10}$  coupled oligomers of 4-ADPA and suggested chain branching and formation of phenazine structural units in the oligomers of 2-ADPA.

Electroactive paramagnetic *ortho*-coupled aniline oligomers functionalized with ethyl ester groups were recently synthesized by the oxidation of 4-(ethoxycarbonyl)aniline, the well known anesthetic benzocaine, with APS in an acidic aqueous medium at room temperature.<sup>178</sup> Molecular orbital AM1 and RM1 computations, combined with the MM2 molecular mechanics force-field method and the conductor-like screening model (COSMO) of solvation, indicated that oligobenzocaines contain  $\text{N–C}_2$  coupled dibenzocaine units as the major structural segments, which can exist in both the reduced (aminobenzenoid) and the ox-

dized (iminoquinonoid) form (Scheme 4). Quantum chemical prediction of benzocaine oligomerization pathway was consistent with the results from FTIR spectroscopic analysis, which confirmed the transformation of the 1,4-disubstituted benzene ring of the monomer to 1,2,4-trisubstituted and 1,2,3,5-tetrasubstituted rings in oligobenzocaines containing unchanged ethoxycarbonyl ester groups (Fig. 5). The FTIR and Raman spectra also proved the presence of phenazine-like units in the benzocaine oligomers, while paramagnetism, caused by the existence of cation radical dibenzocaine structural segments, and electroactivity of the oligobenzocaines were proved by EPR and cyclic voltammetry, respectively.



Scheme 4. Formation of prevalent products (**3** and **5**) in reactions of benzocaine nitrenium cation (**1**) with benzocaine and the sulfate anion. Reprinted<sup>178</sup> with permission. Copyright (2011) Elsevier.

#### 4. OXIDATIVE POLYMERIZATION OF 1-AMINONAPHTHALENE AND ITS DERIVATIVES

Oligomers and polymers of 1-aminonaphthalene<sup>179–186</sup> and its derivatives, such as *N*-phenyl-1-aminonaphthalene,<sup>187,188</sup> 2-methyl-1-aminonaphthalene,<sup>189–191</sup> 1,5-diaminonaphthalene,<sup>192–194</sup> 1,8-diaminonaphthalene,<sup>195</sup> 5-amino-1-naphthol,<sup>196–205</sup> 5-amino-2-naphthol,<sup>206</sup> 5-amino-1,4-naphthoquinone,<sup>207</sup> 2-methyl-5-amino-1,4-naphthoquinone,<sup>208,209</sup> 2-(5-amino-1-naphthoxy)acetic acid,<sup>210</sup>

2-(5-amino-1-naphthoxy)-2,2-difluoroacetic acid,<sup>210</sup> 3-(5-amino-1-*n*-naphthyl-oxy)-1-propanesulfonic acid<sup>210</sup> and sodium 4-amino-3-hydroxynaphthalene-1-sulfonate,<sup>211</sup> have received increased attention in the past two decades. These oligomeric/polymeric materials were suggested for application in corrosion protection,<sup>204,212,213</sup> sensors,<sup>181,182,214–216</sup> electrocatalysts,<sup>194,202</sup> adsorbents<sup>179</sup> and electrochromic devices.<sup>184,196,198</sup>

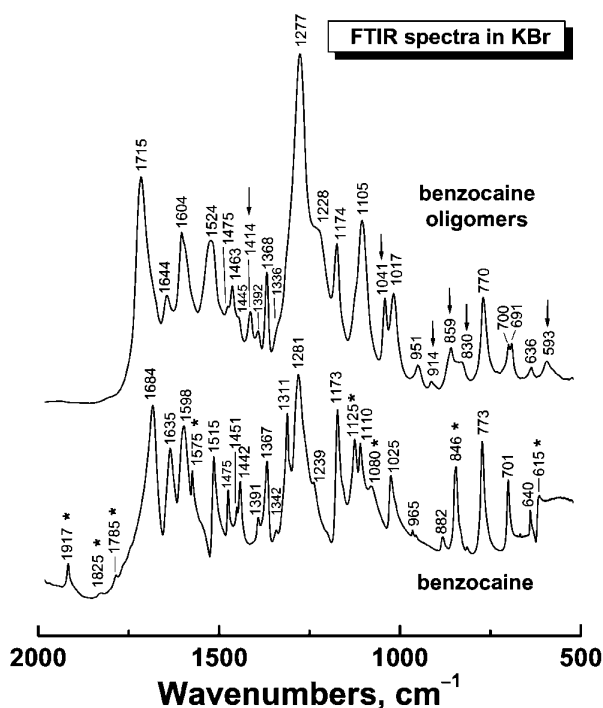


Fig. 5. FTIR spectra of benzocaine and its oligomers produced by chemical oxidative polymerization. The new bands that appeared in the spectrum of the oligomers are marked by arrows; the bands of monomer that disappeared in the spectrum of the oligomers are marked by asterisks. Reprinted<sup>178</sup> with permission. Copyright (2011) Elsevier.

Semiconducting electroactive polymeric materials that were water soluble, were synthesized by the electrochemical polymerization of sodium 4-amino-3-hydroxynaphthalene-1-sulfonate (AHNSA–Na) in aqueous solution.<sup>211</sup> Gel-permeable chromatography (GPC) proved the presence of oligomeric chains with molar masses up to  $\approx 6,300 \text{ g mol}^{-1}$  and showed that octamers to dodecamers were the dominant oligomeric species. FTIR and NMR (<sup>1</sup>H and <sup>13</sup>C) spectroscopic findings, which indicated the formation of new covalent bonds on the naphthalene ring in poly(AHNSA–Na), were correlated with the prevalent coupling modes of monomeric units determined by PM3 semi-empirical quantum-chemi-

cal computations. It was found that poly(AHNSA–Na) contained mainly N–C6 and N–C8 coupled dimer units. The paramagnetic nature of poly(AHNSA–Na) was proved by EPR spectroscopy, while the redox activity was confirmed by cyclic voltammetry. The ratio of the intensity of the two newly formed bands in the UV–vis spectrum, attributed to the polaron (delocalized poly(cation-radical)) and bipolaron form of poly(AHNSA–Na), as well as the presence of naphthoiminoquinonoid and benzenoid segments detected by FTIR and Raman spectroscopies, indicated that partly and fully oxidized bipolaron forms of poly(AHNSA–Na) prevailed. Homopolymers of AHNSA and its salts AHNSA–HCl, AHNSA–Na and AHNSA–Na<sub>2</sub>, soluble in polar solvents, were also obtained by the standard chemical oxidative polymerization route.<sup>217</sup> It was shown that the use of AHNSA salts, instead of AHNSA, leads to polymeric materials with higher  $w_p$ ,  $PDI$  values. The conductivity of the AHNSA polymers was in the range of  $10^{-5}$ – $10^{-7}$  S cm<sup>-1</sup>, poly(AHNSA–HCl) showing the highest value of  $1.3 \times 10^{-5}$  S cm<sup>-1</sup>. The IR spectra and elemental analysis combined with MNDO-PM3 quantum chemical calculations revealed that the polymerization proceeded mainly through the oxidation of the amino group in the studied pH range, accompanied by considerable elimination of sulfonic groups. The resulting functional polymers represent polynaphthylamine-like structures with naphtho-iminoquinonoid and benzenoid N–C1, N–C5 N–C6, N–C7, and N–C8 dimer units, bearing free OH and sulfonic groups in the chains.

##### 5. OXIDATIVE POLYMERIZATION OF ARYLDIAMINES

Oligomers and polymers of carbocyclic aryldiamines (phenylenediamines,<sup>107,112,125–151,218</sup> aminodiphenylamines,<sup>152–163</sup> diamionaphthalenes,<sup>192–195,219–223</sup> diaminoanthraquinones,<sup>224–228</sup> benzidine,<sup>106–114</sup> substituted benzidines<sup>164</sup> and naphthidines<sup>229</sup>) and heterocyclic aryldiamines (diaminopyridines,<sup>230,231</sup> diaminophenazines,<sup>232</sup> diaminoacridines<sup>233</sup> and diaminocarbazoles<sup>234</sup>) have received increasing attention during the last two decades.<sup>235</sup> Molar mass distribution measurements revealed that the products of oxidative polymerization of aryldiamines are low- to high-molar-mass oligomers rather than polymers. Aryldiamines are susceptible to oxidative polymerization *via* oxidation of one or both amino groups to give linear poly(aminoarylamines), polymers/oligomers containing phenazine units and ladder polyphenazines. Oligo/polyaryldiamines have shown tunable electroactivity,<sup>236</sup> high permselectivity to various electroactive species,<sup>237,238</sup> unique electrochromism,<sup>239</sup> linear sensitivity of the conductivity to moisture,<sup>240</sup> controlled variation of the conductivity with temperature<sup>241</sup> and an external electric field,<sup>242</sup> high sensibilities of polymer-modified electrodes to biosubstances at an extremely low concentration,<sup>243,244</sup> good ability in detecting electro-inactive anions,<sup>245</sup> pronounced electrocatalytic pro-



erties,<sup>246,247</sup> effective adsorption of heavy-metal ions,<sup>248–252</sup> strong adhesion to metals,<sup>253</sup> anticorrosion ability<sup>213</sup> and high capacitance.<sup>254,255</sup>

### 5.1. Oxidative polymerization of phenylenediamines

Polyphenylenediamines are the most frequently studied polyaryldiamines.<sup>107,112,125–151,218</sup> Phenylenediamines are very susceptible to oxidative polymerization *via* the oxidation of one or both amino groups to give linear azopolymers, polyaminoanilines, ladder polyphenazines and phenazine/iminoquinonoid-unit-containing polymers. Molar mass distribution measurements revealed that polyphenylenediamines are low- to high-molar-mass oligomers rather than polymers, their molar mass being below 10,000 g mol<sup>-1</sup>. Due to their complex molecular structure, oligo/polyphenylenediamines showed the unique characteristics of redox oligomers and versatile applicability in electrocatalysis, sensors and heavy metal ion removal. Mechanisms of the formation of oligo/polyphenylenediamines and their structures are still under debate.

#### 5.1.1. Oxidative polymerization of *p*-phenylenediamine

A century ago, it was predicted that the products of a single-electron oxidation of *p*-phenylenediamine (PDA) are free radicals (Wurster dyes/salts) that may polymerize in a sufficiently concentrated solution at low temperature or in the solid state.<sup>125</sup> Chemical<sup>112,126,129,138–146,148,150,151</sup> and electrochemical<sup>107,127–137</sup> oxidative polymerizations have been widely used for the synthesis of poly(*p*-phenylenediamine) (PPDA), whereas enzyme-catalyzed oxidative polymerization has been rarely used.<sup>148,149</sup> Acidic aqueous solutions were the most frequently applied polymerization media. It should be noted that dissolved aerial oxygen without any catalyst and/or co-oxidant is sufficient for the chemical oxidative polymerization of PDA. For example, PDA can polymerize in boiling aqueous acetic acid solution to semiconducting PPDA.<sup>140</sup> Depending on the synthetic route, there were several proposals for the molecular structure of PPDA, *i.e.*, a ladder structure with phenazine rings,<sup>129</sup> an iminoquinonoid Bandrowski base-like structure,<sup>145</sup> a linear structure with hydrazo<sup>148</sup> and azo bonds,<sup>138</sup> and an emeraldine-salt form of PANI.<sup>132</sup>

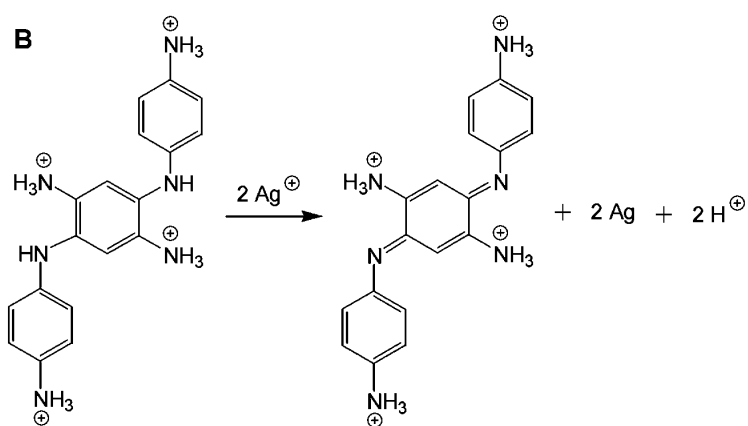
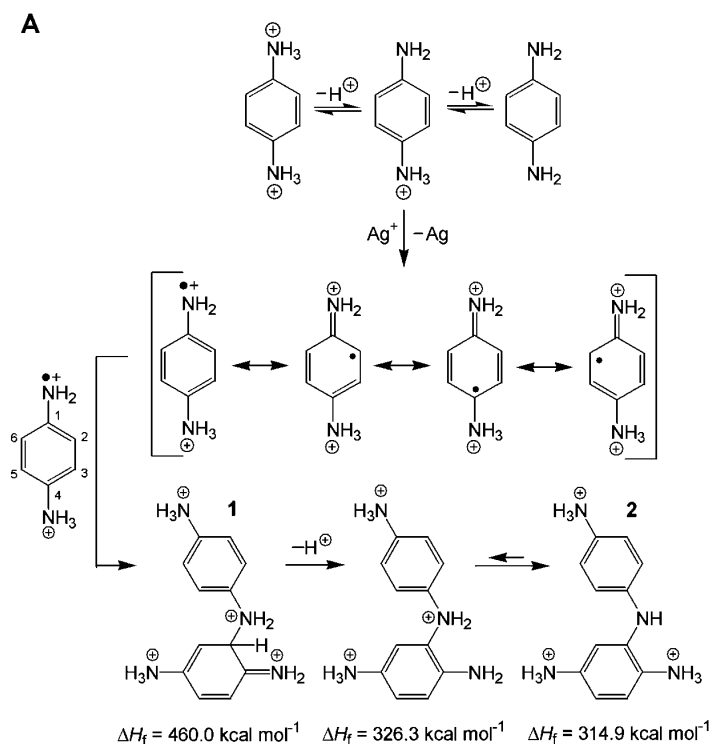
The oxidation of PDA with silver nitrate in aqueous solutions of both acetic and nitric acids, using an initial concentration [PDA] = 0.2 M and various [AgNO<sub>3</sub>]/[PDA] mole ratios in the range from 2.5 to 7.5 was recently found to lead to the formation of highly conducting micro/nanostructured poly(*p*-phenylenediamine)–silver composites (PPDA–Ag), which significantly exceeded the conductivities of PANI–Ag analogs and commercial silver–polymer composites.<sup>256</sup> The conductivity of PPDA–Ag composites synthesized in acetic acid were generally much higher than that of composites prepared in nitric acid. The highest conducting PPDA–Ag composite ( $\sigma = 13,200$  S/cm) containing PPDA in

salt form was prepared in 1 M acetic acid using the mole ratio  $[\text{AgNO}_3]/[\text{PDA}] = 3.75$ , whereas the most conducting PPDA–Ag composite ( $\sigma = 31,700 \text{ S/cm}$ ) containing PPDA in base form was prepared using the mole ratio  $[\text{AgNO}_3]/[\text{PDA}] = 7.5$ .<sup>256</sup> The organic component was composed of oligomeric and polymeric fractions, their proportions varying depending on the employed concentration of  $\text{AgNO}_3$ . In 1 M acetic acid, the formation of a true polymer fraction is marked. Molecular orbital AM1 computations, combined with the MM2 molecular mechanics force-field method and COSMO, indicated that PPDA macromolecules contain both N–C2(6) coupled PDA dimer units and Bandrowski base-like PDA trimer segments, which can exist in both the reduced (aminobenzenoid) and oxidized (iminoquinonoid) forms (Scheme 5).<sup>256</sup> The quantum chemical prediction of the PDA oligomerization pathway was consistent with the results from FTIR spectroscopic analysis of the samples, which confirmed the partial transformation of 1,4-disubstituted benzene ring of monomer to 1,2,4-trisubstituted, 1,2,3,5-tetrasubstituted, and 1,2,4,5-tetrasubstituted rings in positively charged PPDA chains containing nitrate counter-ions.<sup>256</sup> The FTIR and Raman spectroscopy results also indicated the presence of phenazine-like units and cation radicals in PPDA.<sup>256</sup>

### 5.2. Oxidative polymerization of diaminoacridines

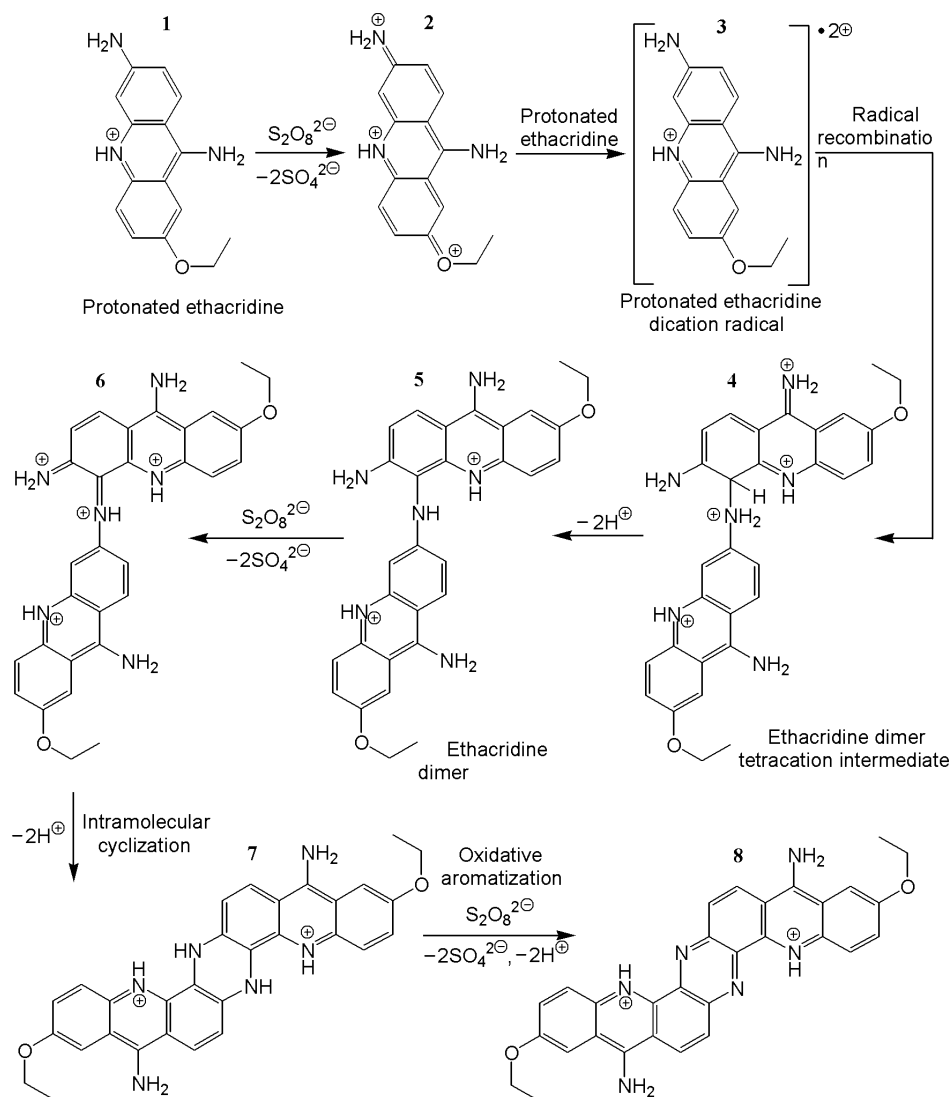
There is only one report regarding the electropolymerization of ethacridine (2-ethoxy-6,9-diaminoacridine) by potentiostatic and cyclic voltammetric methods,<sup>233</sup> however, without any structural characterization of the poly(ethacridine) film at the Pt electrode. Glucose oxidase was simultaneously incorporated into the matrixes of the thin poly(ethacridine), which was developed to fabricate a glucose sensor that exhibited good stability and fast amperometric response to glucose.<sup>233</sup>

Electro-active paramagnetic ethacridine oligomers were recently synthesized by the oxidation of ethacridine lactate with APS in acidic aqueous solution.<sup>257</sup> MALDI–TOF MS evidenced the presence of oligo-ethacridine species from dimers up to hexamers. Oligo-ethacridines protonated by both hydrochloric acid and *in situ* formed sulfuric acid, as revealed by the elemental analysis, were non-conducting ( $\approx 6.5 \times 10^{-9} \text{ S cm}^{-1}$ ) and had fragmental and submicro/micro-layered morphology. Molecular orbital RM1 computations, combined with the MM2 molecular mechanics force-field method and COSMO, indicated that oligo-ethacridines contained N(C6)–C5 coupled the diethacridine unit as the major structural segment that can exist in both the reduced (aminobenzenoid) and oxidized (iminoquinonoid) form (Scheme 6).<sup>257</sup> Quantum chemical prediction of the ethacridine oligomerization pathway was consistent with the results from FTIR spectroscopic analysis, which confirmed the oxidative transformation of the  $\text{NH}_2(\text{C6})$  group of the monomer. The formation of oligomers, as well as the presence



Scheme 5. A) The oxidation of monoprotonated PDA with  $\text{Ag}^+$  leading to the formation of  $[\text{H-PDA}]^{2+}$  cation radicals and metallic Ag, followed by the recombination of  $[\text{H-PDA}]^{2+}$  cation radicals and the formation of the prevalent PDA dimer in the most stable triprotonated form (**2**) through the deprotonation of the most stable N-C2(6) coupled dimer intermediate (**1**); B) formation of Bandrowski base PDA trimer. Adapted<sup>256</sup> with permission.

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Scheme 6. Oxidative dimerization of protonated ethacridine with peroxydisulfate. Reprinted<sup>257</sup> with permission. Copyright (2012) Elsevier.

of both reduced and oxidized structural units in the oligomers was proved by UV–Vis spectroscopy. FTIR and Raman spectroscopies also proved the presence of phenazine-like units in the ethacridine oligomers.

## 6. CONCLUSIONS AND OUTLOOK

Significant progress in conducting/semiconducting and redox-active oligomers and polymers of arylamines, including the well-known polyaniline, was

achieved in the 21<sup>st</sup> century. New important quantum-chemical insights into the mechanism of polymerization of arylamines combined with the rapid development of knowledge regarding the spectroscopic characteristics of oligo/polyarylamines allowed much better elucidation of their molecular structure recently. Considerably increased understanding of the structure-properties relationship of oligo/polyarylamines opened up quite new perspectives regarding the applicability of these macromolecules in modern technology. Advances in the controlled preparation of various micro/nanostructured oligo/polyarylamines, especially polyaniline nanostructures, give today the opportunity to design new conducting/semiconducting redox-active nanomaterials with exciting properties and enhanced applicability in the fabrication of rechargeable batteries, sensors and indicators, catalysts, microwave and radar absorbing materials, non-linear optical and light-emitting devices, electron field emitters, field-effect transistors, Schottky diodes, digital memory devices, asymmetric films, membranes, supercapacitors, electrochromic devices, electromechanical actuators, electrorheological (ER) fluids, antistatic and anticorrosion coatings, fuel and solar cells.

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#### ИЗВОД

#### НАПРЕДАК У ИСТРАЖИВАЊИМА ПРОВОДНИХ/ПОЛУПРОВОДНИХ И РЕДОКС-АКТИВНИХ ОЛИГОМЕРА И ПОЛИМЕРА АРИЛАМИНА

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и ГОРДАНА ЂИРИЋ-МАРЈАНОВИЋ<sup>3</sup>

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У овом ревијалном раду приказан је напредак остварен у последњих неколико година у синтези, карактеризацији и примени неких проводних/полупроводних и редокс-активних олигомера и полимера ариламина. Дат је кратак приказ историјског развоја појединих области. Представљени су поступци синтезе, структура и својства полианилина, супституисаних полианилина, посебно оних добијених оксидативном полимеризацијом пара-супституисаних анилина, поли(1-аминонафталена) и његових деривата, карбоцикличних и хетероцикличних полиарилдиамина, као нпр. поли(пара-фенилендиамина) и полидиаминоакридина. Дискутован је механизам формирања наноструктура полианилина. Недавно развијени синтетички поступци за добијање једнодимензионалних наноструктура полианилина су концизно приказани, а посебна пажња посвећена је методама без темплата. Приказан је и кратак преглед актуелних и потенцијалних будућих примена олиго/полиариламина.

(Примљено 9. августа 2013)

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