

Chemical Oxidative Polymerization of Aminodiphenylamines

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The course of oxidation of 4-aminodiphenylamine with ammonium peroxydisulfate in an acidic aqueous ethanol solution as well as the properties of the oxidation products were compared with those of 2-aminodiphenylamine. Semiconducting oligomers of 4-aminodiphenylamine and nonconducting oligomers of 2-aminodiphenylamine of weight-average molecular weights 3700 and 1900, respectively, were prepared by using an oxidant to monomer molar ratio of 1.25. When this ratio was changed from 0.5 to 2.5, the highest conductivity of oxidation products of 4-aminodiphenylamine, $2.5 \times 10^{-4} \text{ S cm}^{-1}$, was reached at the molar ratio [oxidant]/[monomer] = 1.5. The mechanism of the oxidative polymerization of aminodiphenylamines has been theoretically studied by the AM1 and MNDO-PM3 semiempirical quantum chemical methods combined with the MM2 molecular mechanics force-field method and conductor-like screening model of solvation. Molecular orbital calculations revealed the prevalence of $N_{\text{prim}}\text{--C10}$ coupling reaction of 4-aminodiphenylamine, while $N_{\text{prim}}\text{--C5}$ is the main coupling mode between 2-aminodiphenylamine units. FTIR and Raman spectroscopic studies confirm the prevalent formation of linear $N_{\text{prim}}\text{--C10}$ coupled oligomers of 4-aminodiphenylamine and suggest branching and formation of phenazine structural units in the oligomers of 2-aminodiphenylamine. The results are discussed with respect to the oxidation of aniline with ammonium peroxydisulfate, leading to polyaniline, in which 4-aminodiphenylamine is the major dimer and 2-aminodiphenylamine is the most important dimeric intermediate byproduct.

Introduction

Aromatic diamine polymers have been extensively studied during the past decade^{1,2} because they have many novel and advanced functions in comparison with the polyaniline (PANI) and other similar conducting polymers of aromatic monoamines. Aminodiphenylamines, the most important dimeric intermediates of the oxidative polymerization of aniline,³ are aromatic diamine monomers of great theoretical interest. Mechanistic studies of various pathways of aniline polymerization are of fundamental importance for the understanding and control of PANI properties.⁴ Virtually all proposed mechanisms of the oxidative polymerization of aniline are based on the fact that 4-amino-diphenylamine (4-ADPA, *p*-semidine, Scheme 1) is the major dimeric product. These mechanisms differ only in the assumption whether the formation of 4-ADPA involves the radical recombination reactions between aniline cation radicals or the electrophilic aromatic substitution reactions of aniline nitrenium cations with neutral aniline molecules. Whether the oxidation of 4-ADPA would lead to PANI, similar to the oxidation of aniline, is thus the question of fundamental interest. Despite several studies on this topic, especially the electrochemical oxidation of 4-ADPA,^{5–11} the unambiguous answer is not known. To the best of our knowledge, only a few studies of the chemical oxidative polymerization of 4-ADPA have been performed.^{12,13} The probable first synthesis of 4-ADPA oligomers dates back to 1930 when Yoffe et al.¹² synthesized various

oligoaminodiphenylamines by the oxidation of 4-ADPA with ferric chloride followed by reduction with phenylhydrazine. Ding et al.¹³ performed polymerization of 4-ADPA with ammonium peroxydisulfate (APS), using [APS]/[4-ADPA] molar ratio of ~ 2.8 . In the present contribution, we investigate the oxidation of 4-ADPA with APS, as well as conductivity and structure of oxidation products, including the dependence on the oxidant-to-monomer molar ratio.

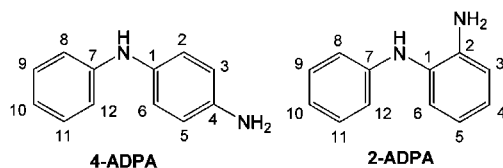
The N–C para-linked aniline molecules are assumed to constitute typical PANI chains. Only a few reports on the oxidative polymerization of aniline consider also the possibility of the N–C ortho-coupling of aniline molecules in the dimerization step, and its potential role in the further growth of PANI chains.^{3,14–17} It has recently been revealed that both types of aminodiphenylamines, i.e., 4-ADPA formed by N–C para-coupling and 2-aminodiphenylamine (2-ADPA; *o*-semidine, Scheme 1) produced by N–C ortho-coupling of aniline molecules, are generated in the course of aniline oxidation with APS in water without added acid.³ It was proved that the formation of 4-ADPA is significantly preferred over the formation of 2-ADPA, which was further shown to be a much more important byproduct than benzidine and hydrazobenzene. That is why, we have decided to compare the oxidations of 4-ADPA and 2-ADPA, leading to poly(4-aminodiphenylamine) (P(4-ADPA)) and poly(2-aminodiphenylamine) (P(2-ADPA)), respectively, under the conditions that are currently used in the preparation of PANI.¹⁸ As in the case of P(4-ADPA) and other polymers of aromatic diamines, only a deeper insight into the electrochemical oxidation of 2-ADPA was reported.^{19,20} There is no study devoted to the chemical oxidative polymerization of 2-ADPA.

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SCHEME 1: 4-Aminodiphenylamine and 2-Aminodiphenylamine



P(4-ADPA) and P(2-ADPA) were characterized by gel permeation chromatography, conductivity measurements, and with FTIR and Raman spectroscopies. For the first time, the mechanism of the oxidative polymerization of aminodiphenylamines is computationally modeled. Semiempirical quantum chemical computational methods are seen to be well balanced; they are accurate enough to have useful predictive powers and yet fast enough to allow large systems such as aniline oligomers to be studied. The semiempirical modified neglect of diatomic overlap-parametric method 3 (MNDO-PM3) quantum chemical computational method 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.^{21,22} 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. suggest that the AM1 method is preferred over the PM3 for ring-structured oligomeric chains in the gas phase.²³ Therefore, we performed comparative MNDO-PM3/AM1 study for dimeric hydrated intermediate species. The AM1 and MNDO-PM3 semiempirical quantum chemical methods, proved to be reliable tools when applied to oligomers of aromatic amines,^{2,3,23–31} have been combined with MM2 molecular mechanics force-field method³² and conductor-like screening model³³ of solvation (COSMO) in the present computational study of the early stages of the chemical oxidative polymerization of aminodiphenylamines in aqueous ethanol solution. The results of quantum mechanical calculations are confronted with the experimental analysis of molecular structure of oxidation products based on FTIR and Raman spectra. The observed differences in molecular weights, conductivities, and molecular structures of P(4-ADPA) and P(2-ADPA) in comparison with PANI are explained on the basis of substantial differences in polymerization mechanism of aminodiphenylamines vs aniline.

Experimental Section

Oxidation of Aminodiphenylamines. The comparative oxidations of 4-ADPA and 2-ADPA (0.2 M, Fluka, Switzerland) have been carried out with APS (Lach-Ner, Czech Republic) at an oxidant-to-monomer molar ratio of 1.25 in aqueous ethanol (50 vol %) solution of 0.1 M sulfuric acid at room temperature, ~20 °C. The oxidations were started by mixing the 0.4 M solution of 4-ADPA or 2-ADPA in ethanol with equal volume of the aqueous solution of APS in 0.2 M sulfuric acid. Temperature of reaction mixture was monitored to follow the progress of this exothermic reaction. The precipitates were collected after 24 h on the filter, rinsed with 0.1 M sulfuric acid, and dried in air. 4-ADPA was also oxidized at various molar ratios of the oxidant to monomer, 0.5–2.5. The products were treated as above.

Characterization of oxidation products. Molecular weights were assessed with a gel permeation chromatography (GPC)/SEC apparatus using a 8 × 600 mm PLMixedB column (Polymer Laboratories, UK) operating with *N*-methylpyrrolidone and calibrated by polystyrene standards using a spectrophotometric

detection at the wavelength of 546 nm. The samples were dissolved in *N*-methylpyrrolidone containing 0.025 g cm⁻³ triethylamine, for deprotonation of samples, and 0.005 g cm⁻³ lithium bromide, to prevent potential aggregation.

Infrared spectra of the samples dispersed in potassium bromide were recorded at 2 cm⁻¹ resolution with a Thermo Nicolet NEXUS 870 FTIR spectrometer with a DTGS TEC detector. Raman spectra with HeNe 633 nm laser excitation were collected on the Renishaw inVia Reflex Raman microscope using a 50× objective and 10 s accumulation times.

Conductivity of polymers was measured with a four-point van der Pauw method on pellets compressed at 700 MPa with a manual hydraulic press using a current source SMU Keithley 237 and a multimeter Keithley 2010 Vmeter with a 2000 SCAN 10-channel scanner card. Density was determined with a Sartorius R160P balance by weighing the pellets in air and immersed in decane. A scanning electron microscope (SEM) JEOL 6400 has been used to characterize the morphology of the samples.

Computational Methods. The semiempirical AM1 and MNDO-PM3 models^{21,22} (included in molecular orbital package³⁴ MOPAC 97, part of the Chem3D Pro 5.0 package, CambridgeSoft Corporation), with full geometry optimization by the EigenFollowing procedure^{35,36} were used to obtain the molecular orbitals, ionization energy (E_i), heat of formation (ΔH_f), and spin density of individual species. The conformational analysis of aminodiphenylamines and their dimeric intermediates was performed. Input files for the semiempirical computations were the most stable conformers of the investigated molecular structures with minimized steric energy using the MM2 molecular mechanics force-field method.³² The COSMO technique has been applied during the geometry optimization to approximate the effect of a solvent surrounding the molecule.³³ Dielectric constant in COSMO calculations (EPS), for the experimentally used water–ethanol mixture, was taken into account (EPS = 53.5).³⁷ The restricted Hartree–Fock method was used for the molecular structures, and the unrestricted Hartree–Fock method was used for radical species.

Results and Discussion

Comparative Oxidation of 4-ADPA and 2-ADPA. The solubility of aminodiphenylamines in water is low (3.3×10^{-3} mol dm⁻³ at 20 °C for 4-ADPA), and under the conditions comparable with the aniline oxidation, the monomer is not completely soluble in the reaction medium. That is why, the oxidations of 4-ADPA and 2-ADPA with APS have been carried out in the aqueous ethanol (50 vol %) solution of 0.1 M sulfuric acid, where both the monomers and oxidant were completely dissolved. We have compared the oxidations of 4-ADPA and 2-ADPA at the same [APS]/[monomer] molar ratio of 1.25, which is used in the “standard” preparation of PANI.¹⁸ The progress of the exothermic reaction was monitored by recording the temperature of the medium (Figure 1). In both oxidations, there was no induction period, which is typical for the oxidation of aniline in acidic media where anilinium cations are significantly prevalent over neutral aniline molecules.^{18,38} This is due to the considerably lower ionization energy of solvated monoprotonated forms of 4-ADPA ($E_{i \text{ AM1}} = 8.88$ eV) and 2-ADPA ($E_{i \text{ AM1}} = 8.97$ eV) in comparison with solvated anilinium cation ($E_{i \text{ AM1}} = 10.22$ eV) in an aqueous ethanol solution. This is in accordance with the observation that the induction period of the oxidative polymerization of aniline in an acidic aqueous solution was found to be significantly reduced when small amounts of 4-ADPA were added to the reaction mixture.³⁹ The

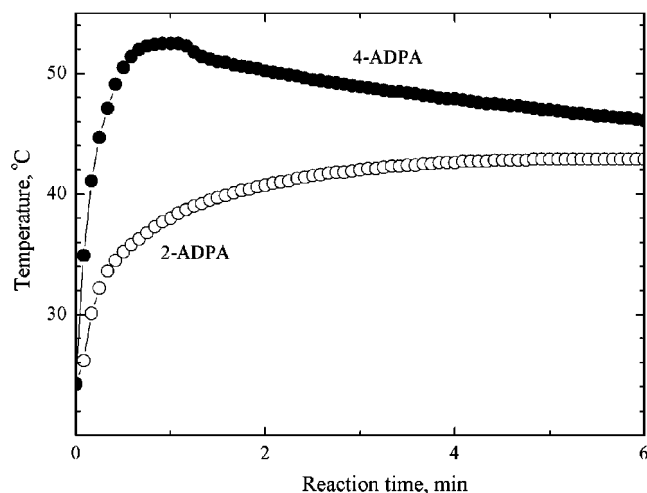


Figure 1. The temperature of the reaction mixture during the oxidation of 4-ADPA and 2-ADPA.

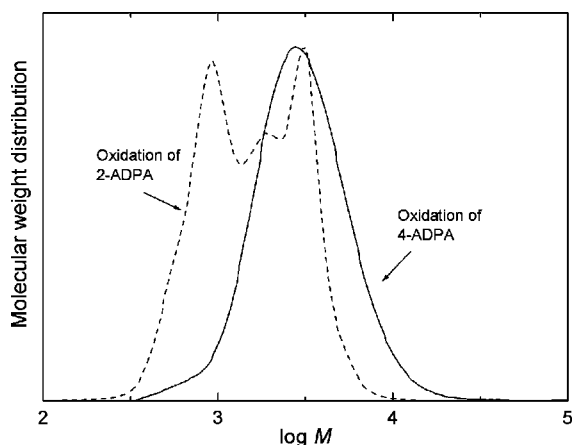


Figure 2. Molecular weight distributions of the oxidation products of 4-ADPA (full line) and 2-ADPA determined by gel permeation chromatography in *N*-methylpyrrolidone.

oxidation of both aminodiphenylamines starts immediately and is completed in a few minutes, the process being faster for 4-ADPA than for 2-ADPA (Figure 1). A small ionization energy difference of ~ 0.1 eV between monoprotonated 4-ADPA and 2-ADPA, i.e., a small difference in initiation rate cannot alone explain the significant differences in the overall oxidation rate of both aminodiphenylamines. The considerably higher rate of the oxidative polymerization of protonated 4-ADPA in comparison with 2-ADPA (Figure 1) is mainly due to the differences in the propagation rate. This is an indication of the lower content of oligoaminodiphenylamines with oxidant power (pernigraniline-like oligomers) in the propagation phase of 2-ADPA polymerization. The heat evolution during the oxidation, proportional to the peak temperature, is higher for 4-ADPA than for 2-ADPA; the maximum temperature reached during the oxidation of aniline under similar conditions falls between those found for 4-ADPA and 2-ADPA.¹⁸

Properties of P(4-ADPA) and P(2-ADPA). The present GPC results demonstrate that P(4-ADPA) shows unimodal molecular-weight distribution while P(2-ADPA) has three components with peak molecular weights $M_{p1} = 930$, $M_{p2} = 1860$, and $M_{p3} = 3160$ (Figure 2). In both cases the molecular weights are of the order of thousands (Table 1) and the oxidation products have to be regarded as higher oligomers, although for the purpose of present discussion, they are referred to as polymers, P(4-ADPA) and P(2-ADPA). It should be noted that

TABLE 1: Properties of the Oxidation Products of 4-Aminodiphenylamine and 2-Aminodiphenylamine

property	oxidation product ^a of	
	4-ADPA	2-ADPA
yield, %	96.8	49.0
conductivity, S cm ⁻¹	7.1×10^{-5b}	$<10^{-10c}$
density, ^d g cm ⁻³	1.34	N/A
molecular weight, ^e M_w	3700	1900
polydispersity, ^e M_w/M_n	1.3	1.5

^a The monomers (0.2 M) were oxidized with APS (0.25 M) in the aqueous ethanol (50 vol.%) solution of 0.1 M sulfuric acid. ^b By four-point method. ^c The samples could not be compressed to pellets; the conductivity was estimated on powder placed between two pistons. ^d By Archimedes method, i.e., by weighing the samples in air and immersed in decane. ^e M_w and M_n are the weight- and number-average of molecular weights, respectively, obtained by gel permeation chromatography in *N*-methylpyrrolidone.

the weight-average molecular weights of P(4-ADPA), $M_w = 3700$, and P(2-ADPA), 1900, are somewhat higher than molecular weights of electrochemically synthesized P(4-ADPA)^{5,6} and P(2-ADPA),²⁰ $M_w = 2800$ and 830, respectively. Based on the known comparative GPC and light scattering studies of molecular weights of polyanilines,⁴⁰ the substantial overestimation ($\sim 30\%$) of molecular weights of P(4-ADPA) and P(2-ADPA) obtained by GPC using polystyrene standards, in comparison with absolute molecular weights measured by light scattering, could be expected. The molecular weight of PANI prepared under similar conditions is about ten times higher.⁴⁰ It is open to discussion why aminodiphenylamines do not become high molecular weight polymers. Our recent MNDO-PM3 study of the early stages of the chemical oxidative polymerization of aniline in aqueous solution³ has proved that the two-electron oxidations of 4-ADPA (the major aniline dimer) and 2-ADPA (the most important byproduct of aniline dimerization) with peroxydisulfate lead to the formation of *N*-phenyl-1,4-benzoquinonediimine (PBQI) and *N*-phenyl-1,2-benzoquinonediimine (OBQI), respectively. The absence of aminodiphenylamine cation radicals and nitrenium cations in the initiation phase, as well as the absence of highly reactive fully oxidized oligomeric species with an odd number of aniline units in propagation phase, proposed recently to be crucial for efficient PANI growth,³ could be the main reason for much lower molecular weights of P(4-ADPA) and P(2-ADPA) in comparison with PANI.

P(4-ADPA) has a conductivity on the semiconductor level of the order of 10^{-4} S cm⁻¹, more than 6 orders of magnitude higher than that of P(2-ADPA), which is $<10^{-10}$ S cm⁻¹ (Table 1). The maximum conductivity of the oxidation product of 4-ADPA was 2.5×10^{-4} S cm⁻¹ at $[APS]/[4-ADPA] = 1.5$ (Figure 3). This result is in agreement with theoretically predicted optimum ratio, since 1 mol of two-electron oxidant, APS, is theoretically needed for 1 mol of 4-ADPA molecules to be incorporated into the polymer chain and the additional 0.5 mol of APS provides transformation of the thus obtained leucoemeraldine-like form to emeraldine-like P(4-ADPA) (Figure 4). The four orders of magnitude lower conductivity of P(4-ADPA) in comparison with ordinary PANI ($\sim 10^0$ S cm⁻¹), synthesized under similar reaction conditions,^{18,41,42} is an indication of the presence of nonconducting structural units besides conducting PANI-like segments in P(4-ADPA). The absence of PANI-like units in P(2-ADPA) is indicated by its nonconducting nature.

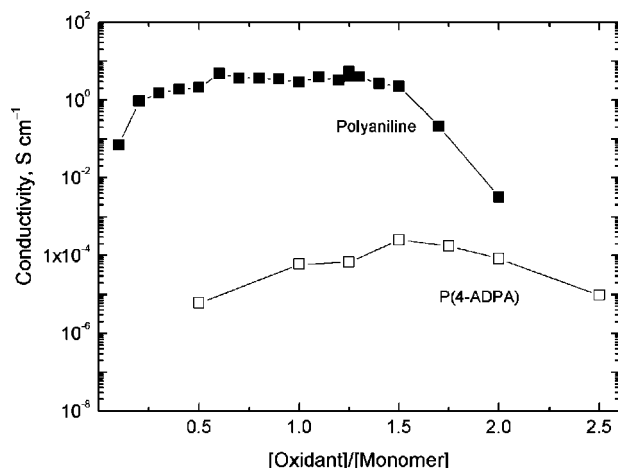


Figure 3. The dependence of the conductivity of the oxidation products of aniline hydrochloride in water⁴² (■) and 4-ADPA in aqueous ethanol (50 vol %) solution of 0.1 M sulfuric acid (□) on the [oxidant]/[monomer] molar ratio.

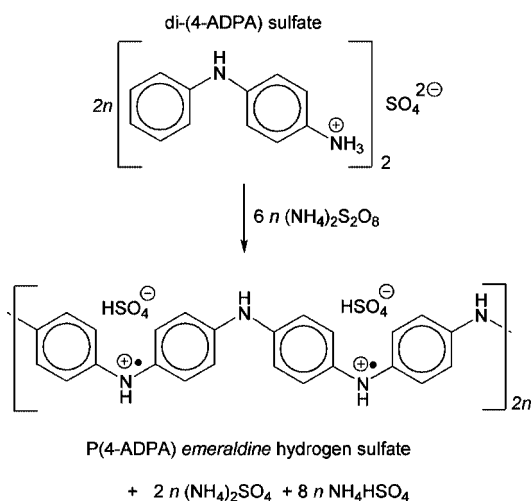


Figure 4. The formation of P(4-ADPA) hydrogen sulfate in the emeraldine-like form.

Theoretical Study of the Oxidative Polymerization of Aminodiphenylamines with Peroxydisulfate. The formation of monoprotonated aminodiphenylamines is analyzed. AM1 and MNDO-PM3 calculations of the heat of formation of monoprotonated aminodiphenylamines in aqueous ethanol (50 vol %) solution (Table 2) have proved that primary amino groups in solvated 4-ADPA and 2-ADPA are protonated rather than their secondary amino groups. This is consistent with well-known higher basicity of primary aromatic amines in comparison with secondary aromatic amines.⁴³ It should be noted that, as a consequence of the unjustified neglect of solvation effects, opposite computational results concerning basicity of 4-ADPA have recently been reported by Can et al.⁴⁴ We have confirmed Can's computational finding that the secondary amino group of 4-ADPA is more basic than its primary amino group in gas phase (Table 2). However, this is not valid for solvated 4-ADPA in aqueous ethanol solution. The present results are well correlated with our previous semiempirical quantum chemical study³, which has clearly shown the crucial influence of solvation on the acid–base and redox properties of aniline, its reactive species, and oligoanilines. It is interesting to note that the primary amino group of 2-ADPA is a stronger base than its secondary amino group in both gas phase and aqueous ethanol.

Similar to the recent theoretical study of aniline oxidation with APS in water,³ it is proposed that in the first phase of the

TABLE 2: Heat of Formation, ΔH_f , Calculated by AM1 and MNDO-PM3, for Monoprotonated 4-ADPA and 2-ADPA in Gas Phase and Aqueous Ethanol (50 vol %)

4-ADPA and 2-ADPA monoprotonated forms	AM1		MNDO-PM3	
	ΔH_f (kcal) (gas phase)	ΔH_f (kcal) (water-EtOH)	ΔH_f (kcal) (gas phase)	ΔH_f (kcal) (water-EtOH)
	201.9	147.7	194.3	145.4
	204.3	134.4	196.0	131.2
	204.3	149.6	198.1	147.1
	202.7	137.8	197.6	137.0

oxidative polymerization of monoprotonated aminodiphenylamines with a two-electron oxidant, APS, the protonated forms of *N*-phenyl-1,4-benzoquinonediimine (H_2 -PBQI) and *N*-phenyl-1,2-benzoquinonediimine (H_2 -OBQI) are generated (Figure 5). In the accordance with mechanistic concepts of Male and Allendoerfer,⁸ Petr and Dunsch,⁹ and Zimmermann et al.,¹⁰ which have been applied in the cases of electrochemical oxidation of 4-ADPA, the one-electron comproportionation redox dimerization reaction has been considered. This is the one-electron oxidation of monoprotonated 4-ADPA (1) with diprotonated PBQI and the one-electron oxidation of monoprotonated 2-ADPA (2) with diprotonated OBQI, which lead to the formation of the corresponding aminodiphenylamine cation radicals (Figure 5). We have proved the feasibility of these redox interactions on the basis of the known constraint⁴⁵ $|E_{HOMO}(\text{reductant}) - E_{LUMO}(\text{oxidant})| < |E_{HOMO}(\text{oxidant}) - E_{LUMO}(\text{reductant})|$. It can be calculated by the AM1/COSMO method that H_2 -PBQI ($E_{HOMO} = -10.03$ eV, $E_{LUMO} = -2.82$ eV) and H_2 -OBQI ($E_{HOMO} = -10.14$ eV, $E_{LUMO} = -2.94$ eV) can oxidize monoprotonated 4-ADPA ($E_{HOMO} = -8.88$ eV, $E_{LUMO} = -0.47$ eV) and monoprotonated 2-ADPA ($E_{HOMO} = -8.97$ eV, $E_{LUMO} = -0.48$ eV), respectively, in aqueous ethanol solution.

The generated cation radicals of aminodiphenylamines instantaneously react among themselves via radical recombination route (Figure 5). According to the Hammond postulate,⁴⁶ the regioselectivity of recombination reactions of 4-ADPA and 2-ADPA cation radicals is governed by the stability of formed dimeric dication intermediates (Table 3), resembling structurally the corresponding transition states. That is why the quest for the most stable dimeric aminodiphenylamine dication intermediates is performed. The deprotonation of the most stable intermediates (3 and 5, Figure 5), which have the lowest heat of formation (Table 3), leads to the major linear $N_{\text{prim}}-C10$ coupled 4-ADPA dimer (4, Figure 5) and to the major branched $N_{\text{prim}}-C5$ coupled 2-ADPA dimer (6, Figure 5) in monoprotonated form.

In accordance with our recent semiempirical quantum chemical study of redox properties of aniline and its dimers and trimers in water,³ we have found that aminodiphenylamine dimers in monoprotonated form are more oxidizable than parent monoprotonated aminodiphenylamines themselves (cf. E_i in Figure 5). The monoprotonated aminodiphenylamine dimers (4, 6)

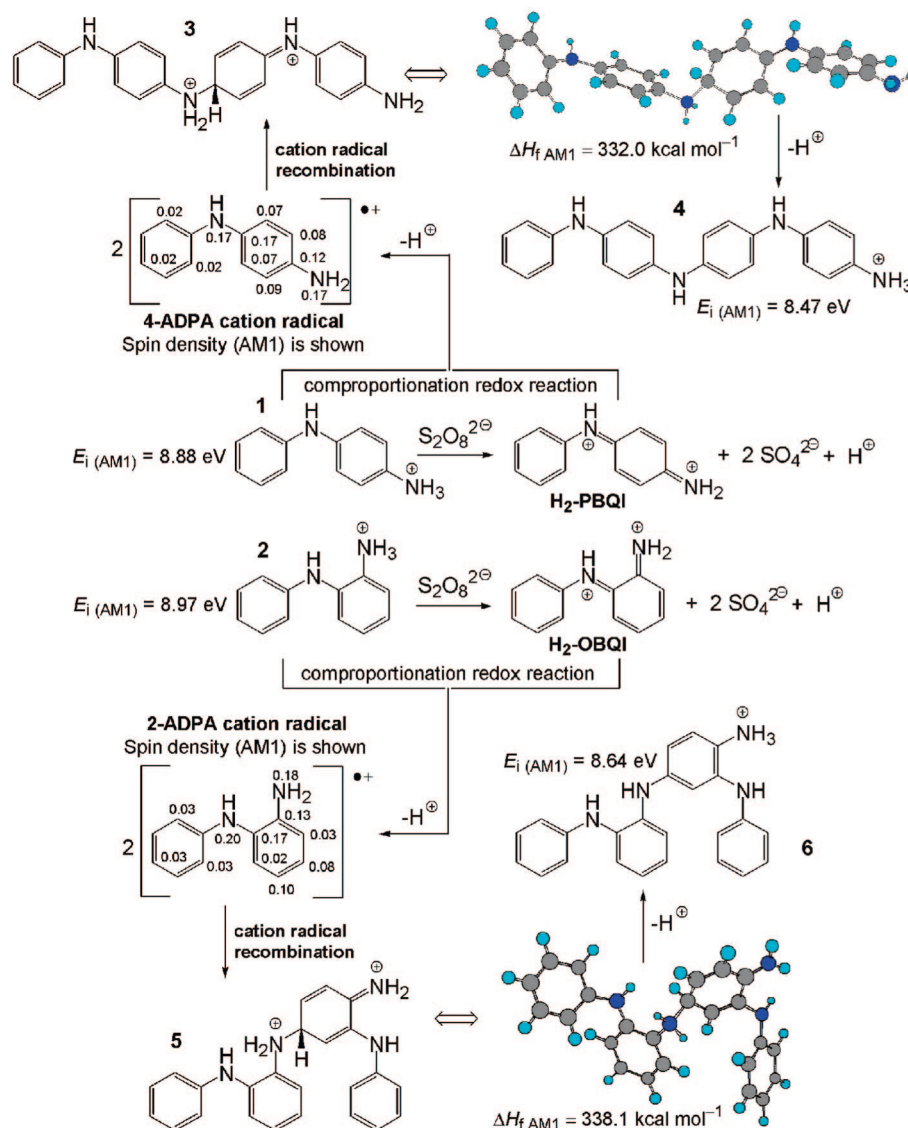


Figure 5. The mechanism of the oxidative dimerization of monoprotonated 4-ADPA (1) and 2-ADPA (2) with peroxydisulfate in aqueous ethanol (50 vol%) solution of 0.1 M sulfuric acid.

TABLE 3: The Heat of Formation, ΔH_f , of Diaminodiphenylamine Dication Intermediates, Generated by Various Coupling Reactions of Cation Radicals of 4-ADPA and 2-ADPA, respectively, in Aqueous Ethanol (50 vol %) Solution

coupling mode 4-ADPA ⁺⁺ + 4-ADPA ⁺⁺	ΔH_f (kcal mol ⁻¹)		coupling mode 2-ADPA ⁺⁺ + 2-ADPA ⁺⁺	ΔH_f (kcal mol ⁻¹)	
	AM1	PM3		AM1	PM3
N _{prim} -C3 (C5)	335.9	322.3	N _{prim} -C3	348.5	335.9
N _{prim} -C2 (C6)	343.2	334.1	N _{prim} -C4	342.0	332.5
N _{prim} -C8 (C12)	342.4	333.7	N _{prim} -C5	338.1	326.1
N _{prim} -C10	332.0	320.9	N _{prim} -C6	356.5	350.0
N _{prim} -N _{prim}	372.5	360.1	N _{prim} -C8 (C12)	351.5	346.7
N _{prim} -N _{sec}	387.5	379.6	N _{prim} -C10	341.3	335.6
N _{sec} -C3 (C5)	351.8	335.4	N _{prim} -N _{prim}	388.0	376.1
N _{sec} -C2 (C6)	359.9	350.3	N _{sec} -C3	363.4	353.9
N _{sec} -C8 (C12)	358.1	345.1	N _{sec} -C4	357.6	344.8
N _{sec} -C10	346.9	332.8	N _{sec} -C5	352.8	336.4
N _{sec} -N _{sec}	404.1	391.4	N _{sec} -C8 (C12)	370.6	360.8
C3 (C5)-C3 (C5)	339.7	336.4	N _{sec} -C10	356.5	348.3

undergo a fast two-electron oxidation with the remaining peroxydisulfate to the most stable half-oxidized dimeric aminodiphenylamines (7, 10; Figures 6 and 7). In the pH region where monovalent hydrogen sulfate anions prevailed over divalent sulfates (pH < 2.0), the charge separation leads to the polaronic structures of aminodiphenylamine dimers (8, Figure

6). The four-electron oxidation of noncyclized aminodiphenylamine dimers results in pernigraniline-like structures (9, 11; Figures 6 and 7).

Two-electron and four-electron oxidations of aminodiphenylamine dimers containing 1,2- or 1,2,4-substituted benzene rings or both, combined with the intramolecular cyclization, lead

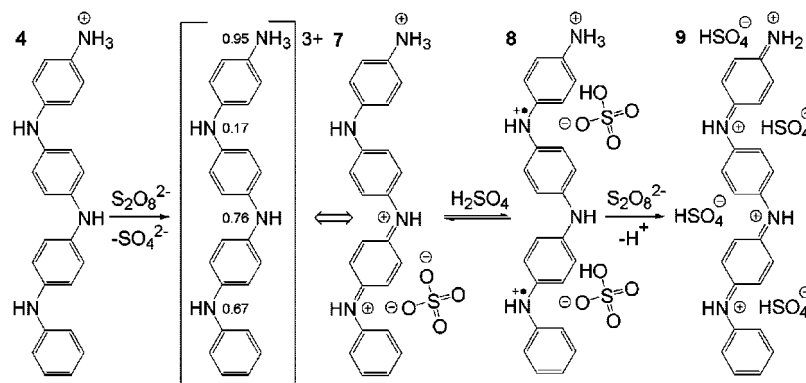


Figure 6. The oxidation of the main linear, N_{prim} -C10 coupled, monoprotonated 4-ADPA dimer (**4**) with the peroxydisulfate. The positive charge distribution over nitrogen atoms in solvated emeraldine salt form of monoprotonated 4-ADPA dimer (**7**), calculated by MNDO-PM3/COSMO, is shown.

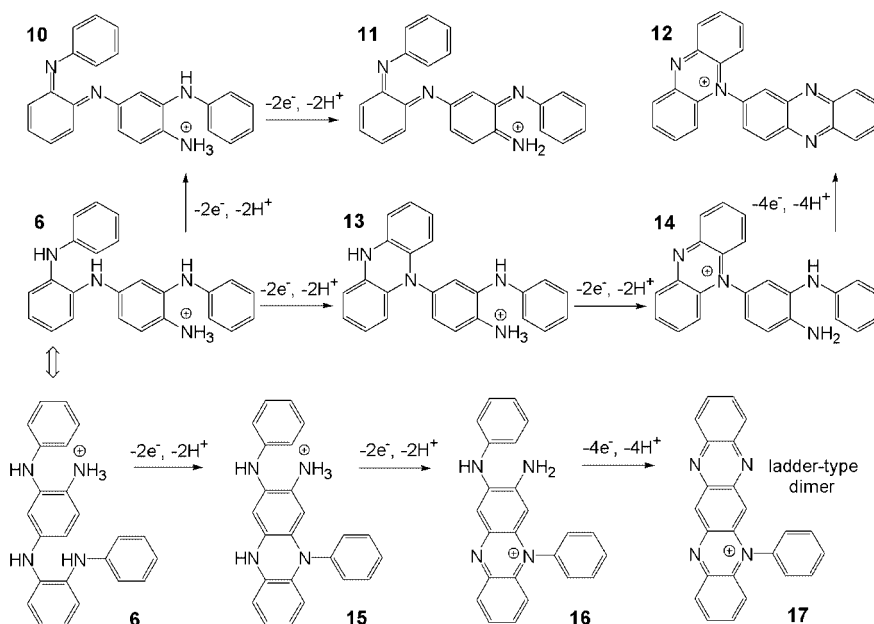


Figure 7. The oxidation of the main, N_{prim} -C5 coupled, monoprotonated 2-ADPA dimer (**6**) with the two-electron oxidant.

to the substituted dihydrophenazines (**13**, **15**) that are readily oxidized to substituted phenazines (**12**, **14**, **16**), Figure 7. MM2/MNDO-PM3/COSMO results suggest that the oxidative intramolecular cyclization of the major monoprotonated 2-ADPA dimer (**6**) in aqueous ethanol solution is thermodynamically favorable, because it leads to the formation of more stable dihydrophenazine-containing dimers [$\Delta H_f = 193.0$ and 189.7 kcal mol $^{-1}$ (**13** and **15**, respectively)] than the corresponding noncyclized *ortho*-iminoquinonoid dimer [$\Delta H_f = 224.2$ kcal mol $^{-1}$ (**10**, Figure 7)], all compared species bearing the same oxidation state. The formation of ladder structured oligomers (**17**, Figure 7) during the course of oxidative polymerization of aminodiphenylamines, characteristic of a number of aromatic diamine polymers growth mechanisms,¹ is also possible. The ratio of phenazine to noncyclized constitutional units follows the ratio of branched to linear structural units and increases from P(4-ADPA) to P(2-ADPA).

Because H_2 -PBQI and H_2 -OBQI have significantly lower oxidation power than peroxydisulfate, the reaction rates of the comproportionation redox processes of H_2 -PBQI (or H_2 -OBQI) and monoprotonated 4-ADPA (or 2-ADPA) could be postulated to be substantially lower than the rates of initial oxidation of monoprotonated aminodiphenylamines by peroxydisulfate. Consequently, the accumulation of H_2 -PBQI and H_2 -OBQI in the

early stages of the oxidation of aminodiphenylamines is expected. We propose that further growth of P(4-ADPA) [or P(2-ADPA)] occurs mainly by the redox reaction of accumulated H_2 -PBQI (or H_2 -OBQI) with formed aminodiphenylamine oligomers in lower oxidation states as well as by the oxidation of remaining monoprotonated 4-ADPA (or 2-ADPA) with fully oxidized pernigraniline-like oligoaminodiphenylamines.

The protonated pernigraniline-like oligoanilines are susceptible to hydrolysis.⁴ The quinonoid products of hydrolytic side reactions of H_2 -PBQI, H_2 -OBQI (**18**–**21**), and other pernigraniline-like oligoaminodiphenylamines are redox active and can be incorporated into the growing P(4-ADPA) and P(2-ADPA) chains, respectively (Figure 8). The one-electron oxidation of monoprotonated 2-ADPA with the major hydrolytic product (**20**) of H_2 -OBQI is analyzed. The generated cation-radicals of 2-ADPA and 2-hydroxydiphenylamine instantaneously react via radical recombination, leading to the formation of the most stable N_{prim} -C4 coupled intermediate (**22**, $\Delta H_f = 288.4$ kcal mol $^{-1}$, computed by the MM2/MNDO-PM3/COSMO method). The major oligoaminophenol (**23**), formed by the deprotonation of the intermediate (**22**), can be transformed to substituted phenoxazine (**24**) by the oxidative intramolecular cyclization of substituted *ortho*-aminophenol segment.

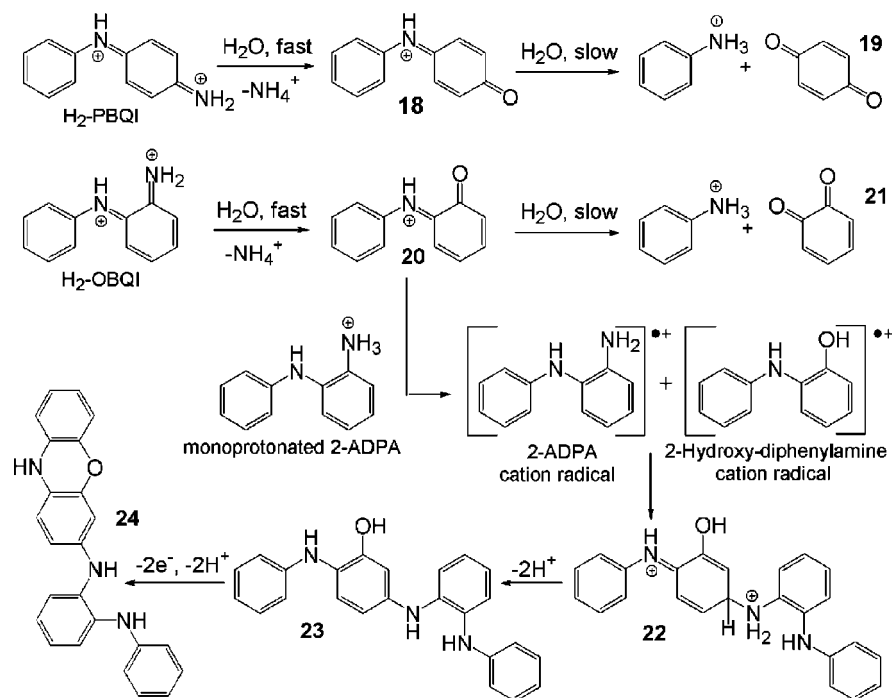


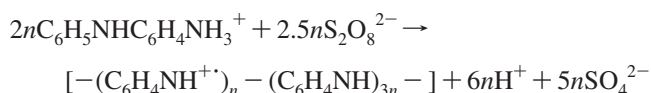
Figure 8. The hydrolysis of H₂-PBQI and H₂-OBQI. The incorporation of the major hydrolytic product (20) of H₂-OBQI into the growing P(2-ADPA) chains, leading to the formation of oligoaminophenols (23) and substituted phenoxazines (24), is also shown.

FTIR Spectra of the Oxidation Products of 4-Aminodiphenylamine. The FTIR spectrum of P(4-ADPA), synthesized using the molar ratio [APS]/[4-ADPA] = 1.25, differs significantly from the spectrum of 4-ADPA especially in the high frequency region (Figure 9a). The monomer spectrum exhibits two peaks at 3459 and 3371/3384 cm⁻¹ (doublet) corresponding to the free N–H stretching vibrations of primary and secondary amino groups.⁴⁷ Instead of these two bands, a single sharp peak appears at about 3411 cm⁻¹ in the spectrum of P(4-ADPA), which corresponds most probably to the N–H stretching of secondary amino groups. A new strong and a broad band with the maxima observed at about 3200, 3054, 2970, and 2857 cm⁻¹ in the spectrum of P(4-ADPA) is attributed to the different types of intra- and intermolecular hydrogen-bonded N–H stretching vibrations.^{30,47–49} The contribution of various aromatic C–H stretching modes at about 3050 cm⁻¹ is also possible.

The intensity of the absorption tail in the spectral region above 1700 cm⁻¹ is lower than that observed in the spectra of standard PANI (Figure 9a,b). This FTIR finding is in accordance with the observed lower conductivity of P(4-ADPA) in comparison with conducting PANI.

The FTIR spectrum of P(4-ADPA) (Figure 9b) exhibits the new peak at 1587 cm⁻¹, which corresponds to the quinonoid (Q) ring stretching vibration of –N=Q=N– structural unit.¹⁷ The strong monomer peaks due to the benzenoid (B) ring stretching vibrations at 1514, 1500, and 1489 cm⁻¹ are blue-shifted to 1524, 1506, and 1496 cm⁻¹ in the spectrum of P(4-ADPA). The bands present in the spectrum of 4-ADPA at 1624 and 1282 cm⁻¹, due to the N–H deformation vibration⁴⁷ and C–N stretching⁴⁸ of primary amino group, respectively, are not observed in the spectrum of P(4-ADPA), confirming the oxidative transformation of primary amino groups during the polymerization into the secondary amino groups and terminal imino groups. The band observed at 1315 cm⁻¹ with the shoulder at 1340 cm⁻¹ corresponds to the C–N stretching of secondary aromatic amine in P(4-ADPA).^{47,50} It is important to note that the broad band at ~1240 cm⁻¹, which has been

usually interpreted as C–N⁺ stretching vibration²⁰ of the polaron lattice of PANI,⁵⁰ is not observed in the spectrum of P(4-ADPA) (Figure 9b). The absence of emeraldine-like conducting polaron lattice (–C₆H₄NH⁺–C₆H₄NH–)_n in P(4-ADPA) is well correlated with the theoretically predicted formation of protoemeraldine-like form [–(C₆H₄NH⁺)_n–(C₆H₄NH)_{3n}–] of P(4-ADPA) by using the oxidant to monomer ratio [APS]/[4-ADPA] = 1.25 as follows:



The most prominent band in the FTIR spectrum of P(4-ADPA) is observed at 1146 cm⁻¹ (Figure 9b). The band located at similar position in the spectra of PANI has been assigned to the vibration mode of the –NH⁺= structure and is associated with the vibrations of the charged polymer units Q=NH⁺–B or B–NH⁺–B.^{50–52} This band has been related to the high degree of electron delocalization in PANI⁵¹ as well as to a strong interchain NH⁺⋯N hydrogen bonding.⁵³ The asymmetric SO₃ stretching vibration in hydrogen sulfate anion, as a dopant,⁴⁷ can also contribute to this band. Hydrogen sulfate counterion is additionally evidenced by the band at 1030 cm⁻¹, attributed to the symmetric SO₃ stretching.⁴⁷

The band at ~815 cm⁻¹ in the FTIR spectrum of 4-ADPA, due to C–H out-of-plane bending vibrations, γ(C–H), of two adjacent hydrogen atoms on 1,4-disubstituted benzene ring^{47,48,54} remains to be the most pronounced one in the substitution region 900–650 cm⁻¹ in the spectrum of P(4-ADPA) (Figure 9b). This spectroscopic finding confirms computationally predicted prevalence of N_{prim}–C10 coupling between monomeric units, i.e., linear polymerization products of 4-ADPA. The presence of the weaker band at 878 cm⁻¹, assigned to γ(C–H) vibration,^{47,48} indicates the relatively low content of 1,2,4-trisubstituted rings and the branching of the polymerization products of 4-ADPA as a side reaction.

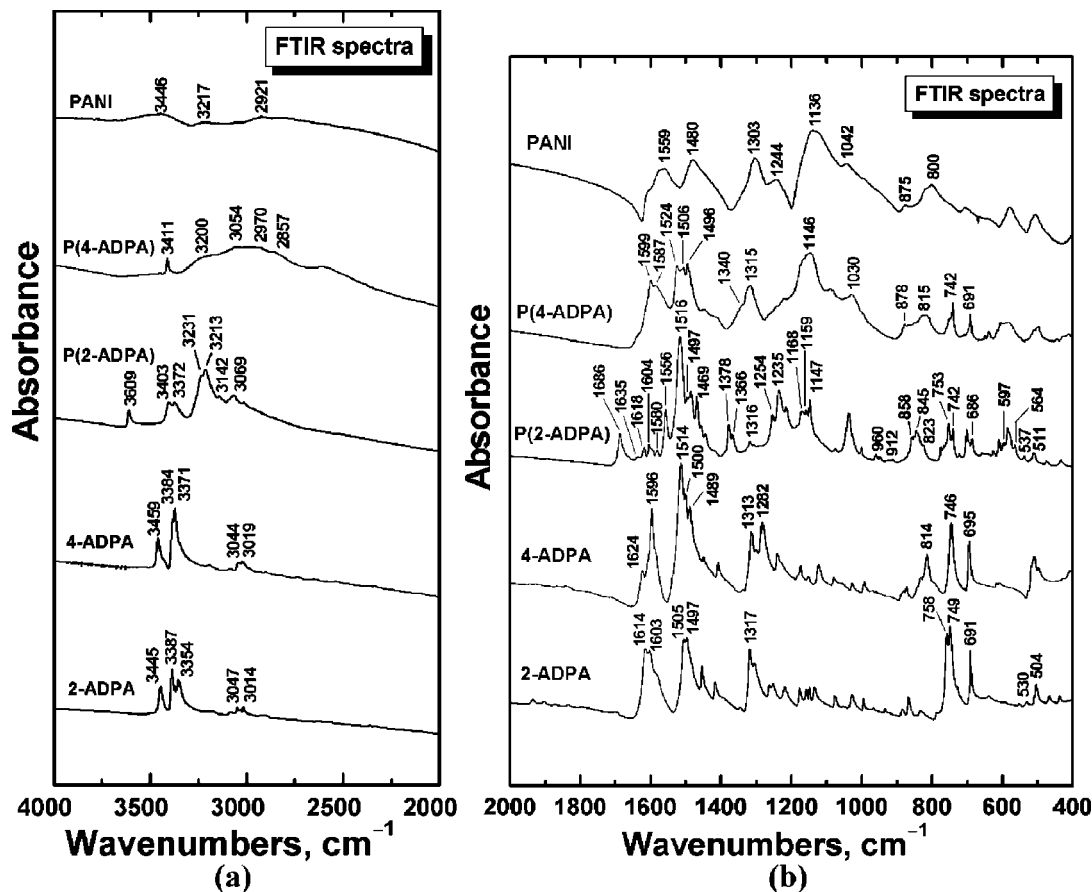


Figure 9. FTIR spectra of P(4-ADPA) and P(2-ADPA) prepared at the [oxidant]/[monomer] molar ratio of 1.25 in the wavenumber regions (a) 4000–2000 cm^{-1} and (b) 2000–400 cm^{-1} . FTIR spectra of standard PANI, prepared under the same polymerization conditions,⁴² and of the corresponding monomers are shown for comparison.

The FTIR spectra of P(4-ADPA) samples prepared at various molar ratios of the oxidant to monomer, 0.5–2.5 (Figure 10), can be divided into two groups. The spectra of the first group (I), corresponding to molar ratios $[\text{APS}]/[\text{4-ADPA}] \leq 1.25$, are more complex and contain some characteristics of the 4-ADPA spectrum, while the spectra from the second group (II), for $[\text{APS}]/[\text{4-ADPA}] \geq 1.5$, are closer to the spectrum of conventional PANI. The oligomeric nature of all studied P(4-ADPA) samples is confirmed by the presence of two bands at ~ 690 and $740\text{--}760\text{ cm}^{-1}$, assigned to the out-of-plane ring bending and $\gamma(\text{C-H})$ vibration of monosubstituted benzene rings, respectively.^{38,47} These bands are of medium-to-strong intensity in the spectra of the group I and of medium intensity in the spectra of the group II. The increase in P(4-ADPA) chain length with the increase of oxidant to monomer ratio is indicated by the disappearance of some bands in the second group of P(4-ADPA) spectra which correspond to the vibrations of terminal units. Thus, the band observed at 1525 cm^{-1} in the spectra of the group I, attributed to the stretching vibration of terminal monosubstituted benzene ring,⁵⁵ is absent in the spectra of the group II.

The spectrum of the most conducting P(4-ADPA), corresponding to $[\text{APS}]/[\text{4-ADPA}] = 1.5$ (Figure 10), is the most similar to the spectrum of a standard PANI emeraldine salt (Figures 9a,b). For this molar ratio, the peaks assigned to the Q and B ring stretching vibrations as well as the broad peak corresponding to the C-N^+ stretching vibration of the polaron lattice ($-\text{C}_6\text{H}_4\text{NH}^+-\text{C}_6\text{H}_4\text{NH}-$)_n are developed, with the shape and wavenumbers close to those observed in the spectra of PANI in emeraldine form, at 1574, 1506/1494 (doublet), and 1246

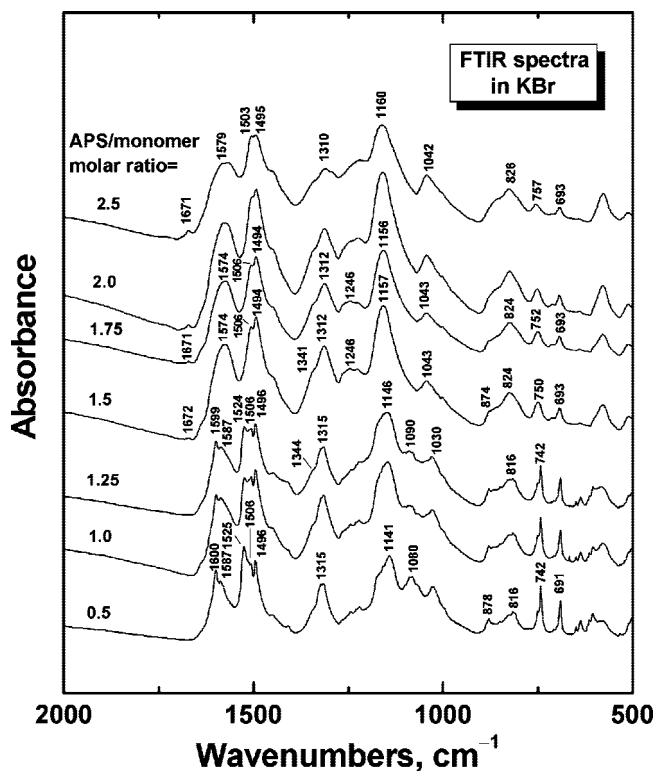


Figure 10. FTIR spectra of the oxidation products of 4-ADPA prepared at various [oxidant]/[monomer] molar ratios.

cm^{-1} , respectively.^{34,40,47,55,56} However, it should be stressed that the presence of characteristic bands of the monosubstituted (750 and 693 cm^{-1}) and 1,2,4-trisubstituted benzene rings (874 cm^{-1}) indicates substantially shorter and more branched P(4-ADPA) chains compared with PANI. It is also important to note that the appearance of the weak band at 1672 cm^{-1} , assigned to the stretching of quinonoid C=O groups,⁴⁷ is an indication of the hydrolysis of iminoquinonoid C=N bonds in the most conducting P(4-ADPA). This hydrolytic degradation is expected to be favored by the oxidation state of the polymer higher than that of emeraldine-like.⁵⁷ Finally, it is noteworthy that the band due to the vibration mode of the $-\text{NH}^+=$ structure is significantly blue-shifted to 1157 cm^{-1} in the spectrum of the most conducting P(4-ADPA) (Figure 10) in relation to the position at 1136 cm^{-1} in the PANI spectrum (Figure 9b).

The increase of the ratio [APS]/[4-ADPA] above 1.75 leads to the disappearance of the polaron lattice band at $\sim 1240\text{ cm}^{-1}$ (Figure 10). This can be explained by the oxidation of linearemeraldine-like segments of the P(4-ADPA) to nigraniline-like $[-(\text{C}_6\text{H}_4\text{NH}^+)_{3n}-(\text{C}_6\text{H}_4\text{NH})_n-]$ and pernigraniline-like $[-(\text{C}_6\text{H}_4\text{NH}^+)_{n-}]$ segments. The overoxidation of P(4-ADPA) chains is accompanied with their increased hydrolysis, detected in the FTIR spectra as the increase in the intensity of the band at $\sim 1670\text{ cm}^{-1}$ attributed to quinonoid C=O group.

FTIR Spectra of the Oxidation Products of 2-Aminodiphenylamine. The FTIR spectrum of P(2-ADPA), synthesized using the molar ratio [APS]/[2-ADPA] = 1.25, shows considerably increased number of bands in comparison with spectra of P(4-ADPA) and PANI prepared under similar reaction conditions and a much more complex spectrum compared with the spectrum of the parent monomer, 2-ADPA (Figure 9a,b). This is caused mainly by the fact that the P(2-ADPA) is a mixture of three different oligomeric products, as revealed by GPC, with very complex structure. The monomer spectrum displays bands at 3445 , 3387 , and 3354 cm^{-1} (Figure 9a), corresponding to the free N–H stretching vibrations of primary and secondary amino groups,⁴⁷ and the band at 1614 cm^{-1} (Figure 9b) due to the N–H scissoring vibration of a primary aromatic amine.^{47,54} In accordance with GPC data, two bands observed at 3403 and 3372 cm^{-1} as well as the band at 1618 cm^{-1} in the spectrum of P(2-ADPA) indicate the significant content of terminal primary amino groups besides secondary amino groups, i.e., the short chain length of P(2-ADPA). The pronounced hydrogen bonding in P(2-ADPA) is reflected by the three peaks at 3213 (with a shoulder at 3231 cm^{-1}), 3142 , and 3069 cm^{-1} due to the H-bonded N–H stretching vibrations, with a contribution from aromatic C–H stretching to the band at $\sim 3069\text{ cm}^{-1}$.^{30,47–49} A new sharp peak observed at 3609 cm^{-1} is connected with the phenolic O–H stretching vibration.^{47,54} In accordance with theoretical predictions, the phenolic OH group in P(2-ADPA) is most probably formed by the reduction of quinonoid C=O group of hydrolyzed OBQI and fully oxidized 2-ADPA oligomers with 2-ADPA and its oligomers in reduced form (Figure 8). This transformation of the primary amino group at the head of P(2-ADPA) oligomeric chains into the phenolic hydroxy group could be an additional reason for inefficient oxidative polymerization of 2-ADPA, since it causes the termination of the regular chain growth of P(2-ADPA). It should be noted that the absence of band corresponding to the vibration of the phenolic OH group in the spectra of PANI and P(4-ADPA) indicates significantly lower extent of their hydrolytic degradation and subsequent incorporation of hydrolytic products into the growing PANI and P(4-ADPA) chains, respectively, in

comparison with P(2-ADPA). This conclusion is also supported by the fact that the band of medium intensity at 1686 cm^{-1} observed in the spectrum of P(2-ADPA), attributed to quinonoid C=O group, is absent in the spectra of PANI and P(4-ADPA), Figure 9b.

Computationally predicted formation of various substituted and fused phenazine segments in P(2-ADPA) is proved by the appearance of many new bands in the spectrum of P(2-ADPA) at almost identical wavenumbers (1635 , 1556 , 1516 , 1469 , 1378 , 1366 , 960 , 912 , 858 , 823 , and 597 cm^{-1}) with respect to those present in the phenazine spectrum itself.^{58,59} The relative intensities of characteristic phenazine bands are not the same in the FTIR spectra of P(2-ADPA) and phenazine, mainly because of the effects of substituents on the vibrations of phenazine rings in P(2-ADPA). The bands at 1635 , 1378 , and 1366 cm^{-1} are attributable also to safranine-like (substituted *N*-phenyl-phenazine-like) segments.⁶⁰ The contribution of the vibrations of phenoxazine units to the bands at 1635 , 1556 , and 1516 cm^{-1} is also possible.⁶¹

A new weak band observed at 1580 cm^{-1} in the spectrum of P(2-ADPA) is attributed to the Q ring stretching vibration of $-\text{N}=\text{Q}=\text{N}-$ structural unit. This is the important difference from the spectrum of P(4-ADPA), which shows strong “quinonoid band” at 1587 cm^{-1} . The band at 1516 cm^{-1} due to benzene ring stretching, mixed with fused benzene ring stretching in phenazine-like units,^{58,59} is the dominating band in the spectrum of P(2-ADPA). This feature could result from increased content of newly formed heterocyclic segments of phenazine or safranine type on account of decreased content of quinonoid units in polymerization products of 2-ADPA. New strong band observed at 1469 cm^{-1} is assigned to phenazine-ring stretching.

In the region of C–N bonds vibrations, the weak band due to the C–N stretching of secondary aromatic amine is observed at 1316 cm^{-1} in the spectrum of P(2-ADPA). Bearing in mind that the spectrum of 2-ADPA shows a strong band at 1317 cm^{-1} , the observed feature reveals the pronounced transformation of secondary aromatic amine C–N bond of the monomer to other types of bonds in polymerization products of 2-ADPA. Two new bands appeared in the spectrum of P(2-ADPA) at 1366 and 1378 cm^{-1} that are not observed in the FTIR spectra of P(4-ADPA), 4-ADPA, or 2-ADPA. The former band has been attributed to the ring stretching of phenazine,^{58,59} while the latter could be correlated with the strong band at $\sim 1380\text{ cm}^{-1}$ present in the spectra of safranines.⁶⁰ The band at 1254 cm^{-1} , due to the C–N stretching vibration of primary aromatic amine,⁴⁸ additionally indicates the oligomeric nature of the oxidation products of 2-ADPA. In the spectrum of 2-ADPA, this band is seen as a doublet at 1262 and 1253 cm^{-1} . A new strong and sharp band appears at 1235 cm^{-1} in the spectrum of P(2-ADPA), in comparison with the spectrum of 2-ADPA, which is attributable to phenolic out-of-phase C–C–O stretching.⁵⁴ The absence of the so-called “free-carrier absorption” in the 4000 – 1700 cm^{-1} region indicates that P(2-ADPA) does not contain delocalized polaron lattice. Indeed, P(2-ADPA) is nonconducting (Table 1). As an important difference in comparison with P(4-ADPA), the FTIR spectrum of P(2-ADPA) shows three peaks around 1150 cm^{-1} (at 1168 , 1159 , and 1147 cm^{-1}). These bands correspond to C–H in-plane deformation vibrations of 1,2- and 1,2,4-substituted benzene rings, with contribution of hydrogen sulfate ion vibration rather than the vibration of $-\text{NH}^+=$ structure, which manifests itself by a single strong and a broad band.

A doublet of very strong bands at 758 and 749 cm^{-1} , which is present in the spectrum of 2-ADPA and assigned to $\gamma(\text{C–H})$ vibrations of mono- and 1,2-disubstituted benzene rings,⁴⁷ is

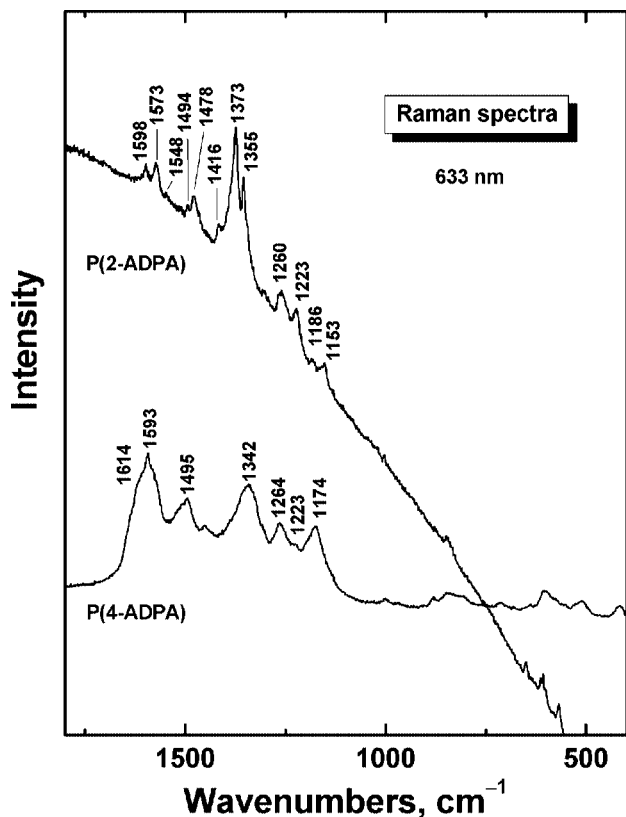


Figure 11. Raman spectra of P(4-ADPA) and P(2-ADPA), prepared at the [oxidant]/[monomer] molar ratio of 1.25, at excitation wavelength 633 nm.

transformed to bands of medium intensity positioned at 753 and 742 cm^{-1} in the spectrum of P(2-ADPA). This feature indicates measurable content of mono- and/or 1,2-disubstituted rings in P(2-ADPA) because of low polymerization degree. The latter band may also be correlated with unsubstituted fused benzene rings in phenazine- and phenoxazine-like segments at the ends of P(2-ADPA) chains. Short oligomeric chains are also recognized by the bands at 686 cm^{-1} , due to the out-of-plane ring bending vibration, and at 537 and 511 cm^{-1} , due to in-plane deformation of monosubstituted rings, which are present in the corresponding spectrum of the monomer at 691, 530, and 504 cm^{-1} , respectively.

The presence of 1,2,4-trisubstituted benzene rings in P(2-ADPA) is indicated by $\gamma(\text{C-H})$ bands at 845 and 858 cm^{-1} as well as by the band at 564 cm^{-1} , due to the aromatic-ring-deformation vibrations, which are not present in the spectrum of the parent monomer.^{47,48,54} The bands at 912 and 858 cm^{-1} are also indicative of phenazine-like units and possibly of 1,2,4,5-tetrasubstituted rings, which could be found in the ladder type of structural units^{47,48,54} (17, Figure 7).

Raman Spectra of the Oxidation Products of 4-Aminodiphenylamine. The most intense bands in the Raman spectrum of P(4-ADPA) (Figure 11) are associated with the vibrations of oxidized segments. The strong band at 1593 cm^{-1} is due to the $\text{C}=\text{C}$ stretching vibration of the Q rings and $\text{C}\sim\text{C}$ stretching of the semiquinonoid rings, with the shoulder at 1614 cm^{-1} corresponding to $\text{C}\sim\text{C}$ stretching of the B rings^{62–66} (where \sim denotes the bond intermediate between the single and double bonds). The strong band observed at 1495 cm^{-1} corresponds to $\text{C}=\text{N}$ stretching vibration of $-\text{N}=\text{Q}=\text{N}-$ units, with the possible contribution of the N-H bending vibration.^{62–64,67,68} The intensive band

appears at 1342 cm^{-1} . The bands observed at similar positions in PANI spectra are characteristic of its conducting form and have been assigned to the $\text{C}\sim\text{N}^{+}$ stretching vibration of polaron lattice.^{63,65–67,69,70} In the spectrum of P(4-ADPA), this band is blue-shifted from the positions found in PANI spectra.^{70,71} This shift is associated with a lower degree of the polaron delocalization along the P(4-ADPA) chain compared with PANI.⁶³ The band due to C-N stretching in B units is observed at 1223 cm^{-1} .^{62,65,66,68} The strong band at 1174 cm^{-1} corresponds to the C-H bending in-plane vibrations of the semiquinonoid rings (a cation radical segments).⁶³

Raman Spectra of the Oxidation Products of 2-Aminodiphenylamine. In the Raman spectrum of P(2-ADPA) (Figure 11), the band observed at 1598 cm^{-1} due to the $\text{C}=\text{C}$ stretching vibration of the quinonoid ring is blue-shifted with respect to its position in the spectrum of P(4-ADPA). The bands corresponding to the $\text{C}=\text{N}$ stretching vibration in $-\text{N}=\text{Q}=\text{N}-$ units have been observed at 1494 and 1478 cm^{-1} , indicating the existence of two types of quinonoid rings in P(2-ADPA). The phenazine-like segments can be associated with the latter band.⁵⁸

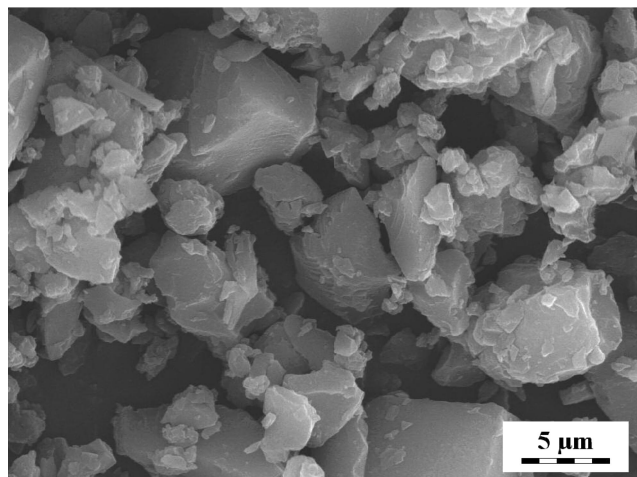
The most important spectral differences in the Raman spectrum of P(2-ADPA) with respect to the spectrum of P(4-ADPA) are observed in the 1300–1400 cm^{-1} region. The band at 1373 cm^{-1} becomes the most prominent band in the spectrum of P(2-ADPA), and the intensive band is observed at 1355 cm^{-1} . These bands are attributable to the ring stretching vibrations of phenazine-like and safranin-like segments.^{58–60} The band observed at 1548 cm^{-1} is also associated with phenazine-like and safranin-like units in P(2-ADPA). In the spectra of phenazine, phenosafranin, and safranin, the bands at similar positions 1550, 1542, and 1546 cm^{-1} are observed, respectively (at excitation wavelength 633 nm).^{58,60} The bands observed in the spectrum of P(2-ADPA) at 1573 and 1416 cm^{-1} are also indicative for phenazine-like structural segments in P(2-ADPA).^{58,67,72}

Instead of the single band at $\sim 1174 \text{ cm}^{-1}$, which was observed in the spectrum of P(4-ADPA), the spectrum of P(2-ADPA) shows two bands at 1186 and 1153 cm^{-1} , assigned to the C-H in-plane bending vibrations of benzenoid and quinonoid rings, respectively.^{66,73} This Raman feature proves the absence of semiquinonoid segments in P(2-ADPA).

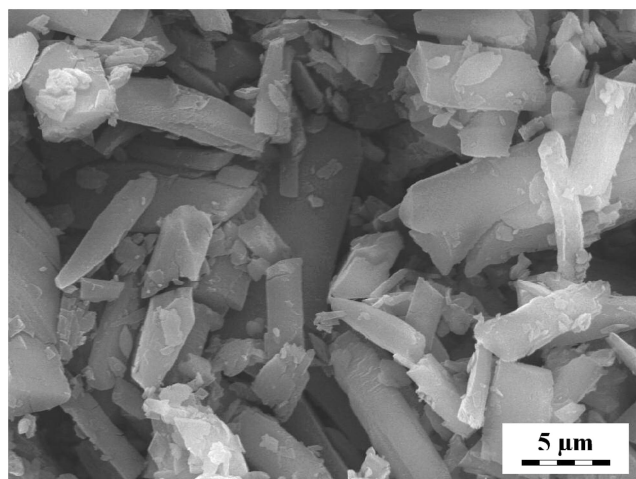
Morphology. The oligomeric oxidation products of both 4-aminodiphenylamine and 2-aminodiphenylamine have fragmental morphology (Figure 12), resembling rather the morphology of the oligosafranines [2] than the granular morphology of PANI [38] obtained under similar reaction conditions.

Conclusions

Oxidative polymerizations of 4-aminodiphenylamine and 2-aminodiphenylamine with ammonium peroxydisulfate, using the ratio [oxidant]/[monomer] = 1.25, in acidic aqueous ethanol solution proceed without induction period, the process being faster for 4-ADPA than for 2-ADPA. The gel permeation chromatography revealed that the oligomeric oxidation product of 4-ADPA has unimodal molecular-weight distribution with a weight-average molecular weight of 3700, while the oxidation product of 2-ADPA has three shorter oligomeric components with peak molecular weights 930, 1860, and 3160. P(4-ADPA) has a conductivity of $\sim 10^{-4} \text{ S cm}^{-1}$, 4 orders of magnitude lower than conducting polyaniline prepared under the same polymerization conditions but more than 6 orders of magnitude higher than nonconducting P(2-ADPA). P(4-ADPA) had the highest conductivity $2.5 \times 10^{-4} \text{ S cm}^{-1}$ when the molar ratio [APS]/[4-ADPA] = 1.5.



(a)



(b)

Figure 12. Scanning electron micrographs of (a) P(4-ADPA) and (b) P(2-ADPA), prepared at the [oxidant]/[monomer] molar ratio of 1.25.

According to the semiempirical quantum chemical study of the mechanism of the oxidative polymerization of monoprotonated 4-ADPA and 2-ADPA with two-electron oxidant, peroxydisulfate, in an acidic aqueous ethanol solution, the protonated forms of *N*-phenyl-1,4-benzoquinonediimine, and *N*-phenyl-1,2-benzoquinonediimine are formed in the initiation phase, respectively. They react further with parent monoprotonated aminodiphenylamines via one-electron disproportionation redox process, generating corresponding aminodiphenylamine cation radicals. 4-ADPA and 2-ADPA cation radicals react instantaneously via radical recombination route, leading to the formation of 4-ADPA and 2-ADPA dimer dication intermediates, respectively. Molecular orbital AM1 and MNDO-PM3 calculations, combined with MM2 molecular mechanics force-field method and conductor-like screening model of solvation, revealed the prevalence of linear $N_{\text{prim}}\text{--C10}$ coupled 4-ADPA dimer and branched $N_{\text{prim}}\text{--C5}$ coupled 2-ADPA dimer, formed by deprotonation of the most stable corresponding dimer dication intermediates. The absence of highly reactive species (cation radicals and nitrenium cations) in the initiation phase, as well as the absence of highly reactive fully oxidized oligomeric species with an odd number of aniline units in the propagation phase, seems to be the main reasons for much less efficient oxidative

polymerization of 4-ADPA and 2-ADPA in comparison with aniline. The further oxidation of linear 4-ADPA oligomers leads to the formation of emeraldine-like and pernigraniline-like products, while the oxidation of branched 2-ADPA oligomers leads to partly and fully oxidized open-ring structure and phenazine-like and ladder products. The incorporation of quinonoid hydrolytic products into the oligoaminodiphenylamine chains, as a side reaction, leads to the formation of oligoaminophenols and phenoxazines in the overoxidized products.

Quantum chemical prediction of polymerization pathways is consistent with the results from FTIR spectroscopic analysis, which have shown that the chains of P(4-ADPA) contain mainly N--C para-coupled aniline units, while the branching of the chains is much more pronounced in P(2-ADPA). The formation of relatively shorter oligomeric chains in P(2-ADPA), in comparison with P(4-ADPA), is confirmed by the presence of characteristic vibrational bands of monosubstituted benzene rings and terminal primary amino groups. The FTIR spectral features commonly associated with polyaniline conductivity are observed only in the spectrum of P(4-ADPA). The FTIR spectroscopy proved the presence of phenazine-like units in P(2-ADPA), besides the open-ring segments, and suggested the presence of some quantities of quinonoid C=O group and phenolic OH group. Raman spectra of P(4-ADPA) and P(2-ADPA) have additionally proved the existence of delocalized polarons in P(4-ADPA) and phenazine-like segments in P(2-ADPA).

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