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Oxidative Polymerization of *p*-Phenylenediamine

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Abstract—Oxidative polymerization of *p*-phenylenediamine in a hydrochloric acid solution yields not a polyquinoxaline polymer as described in the literature but a modified poly(1,4-benzoquinonediimine-*N,N'*-diyl-1,4-phenylene) analogous to polyaniline known as pernigraniline. A new scheme of oxidative polymerization of *p*-phenylenediamine was suggested.

Keywords: oxidative polymerization, *p*-phenylenediamine, polyquinoxaline, polyaniline, pernigraniline, 1,4-benzquinonediimine

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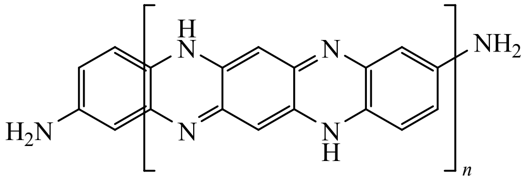
Polymers derived from aromatic amines have attracted considerable interest due to their easy preparation and suitability for various technical applications [1–4]. In particular, much research has been done on oxidative polymerization and copolymerization of *p*-phenylenediamine, but there are still widely differing views on the structure of the resulting polymer. Cataldo [5] assumed that the polymer has a structure analogous to that of polyaniline known as pernigraniline (fully oxidized polyaniline) and assigned structure **I** to the resulting poly(*p*-phenylenediamine). The same structure was reported for this polymer by Li et al. [6].

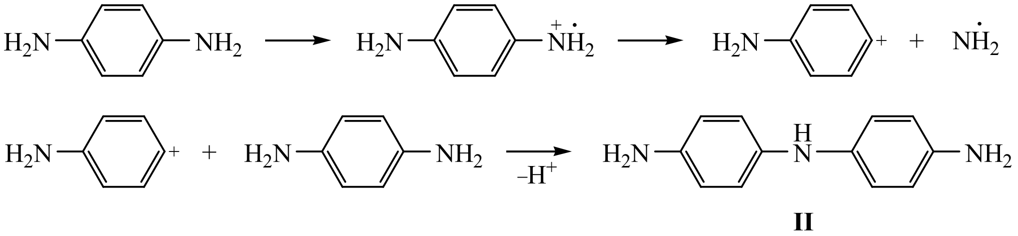

I

Lakard et al. [7] carried out an ab initio study of electrochemical polymerization of *p*-phenylenediamine and suggested the following polymerization mechanism: The oxidation of *p*-phenylenediamine leads to formation of a cation radical, followed by cleavage of the C–N bond to produce a *p*-aminophenyl carbocation which attacks another *p*-phenylenediamine molecule to form 4,4'-diaminodiphenylamine **II** (Scheme 1), with leucopolyaniline, i.e., poly(imino-*p*-phenylene) being the end product of oxidative polymerization of *p*-phenylenediamine.

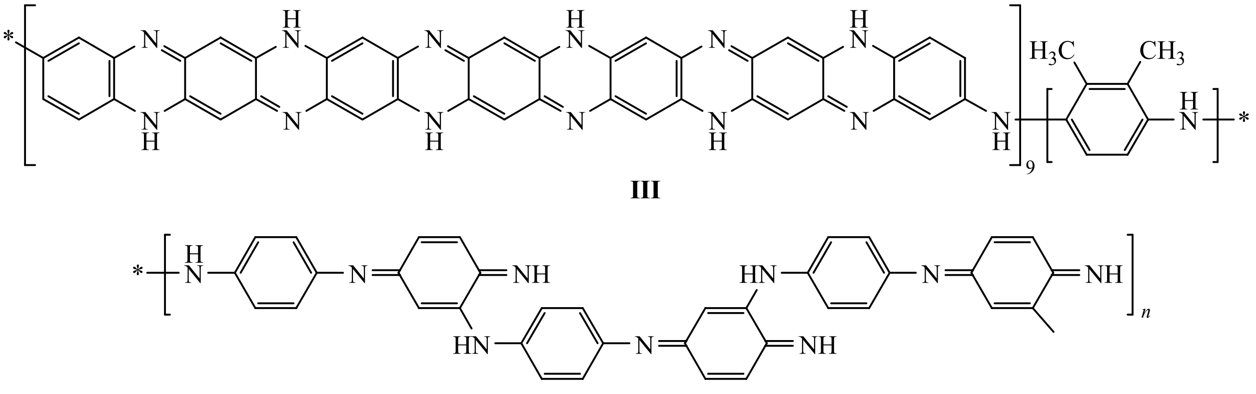
The oxidative copolymerization of *o*-xylidine with *p*-phenylenediamine yields copolymer **III** [6], and its copolymerization with aniline, copolymer **IV** [8] (Scheme 2).

A careful comparison of data reported in [5, 6] revealed some inconsistencies with the supposed quinoxaline structure of the resulting polymer. The IR spectrum of the polymer contains an absorption band at 830 cm^{-1}, which corresponds to para-disubstituted,

Scheme 1.


II

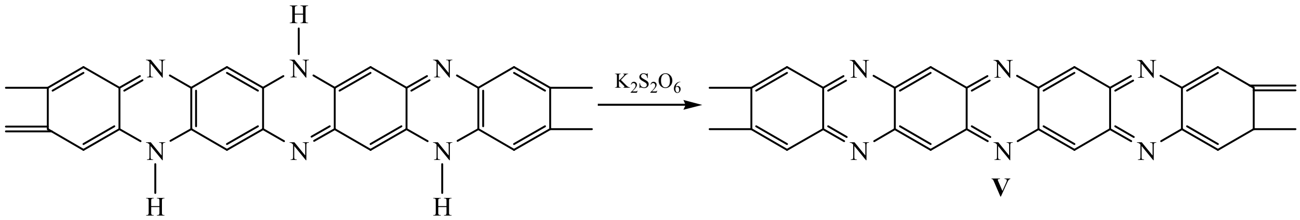
Scheme 2.



III

IV

Scheme 3.



V

rather than to 1,2,4,5-tetrasubstituted benzene ring. According to published data [9], the bands characteristic of two and one C–H bonds are those at 800–860 and 860–900 cm^{-1}, respectively (830 and 880 cm^{-1}, on the average, respectively [10]). For example, absorption bands are observed for leucopolyaniline at 816, for emeraldine at 834 [11], and for pernigraniline at 830 cm^{-1} [12]. Poly(diphenylamine) exhibits absorption at 803 cm^{-1} characteristic of *p*-phenylene compounds [13]. In the IR spectrum of the quinoxaline polymer obtained by oxidative polymerization of *o*-phenylenediamine there are absorption bands of 1,2,4,5-tetrasubstituted benzene ring at 858–868 cm^{-1} [14], and no band is observed in the 800–835 cm^{-1} region. These data confirm that the oxidative polymerization of *p*-phenylenediamine does not yield a polymer having a quinoxaline structure.

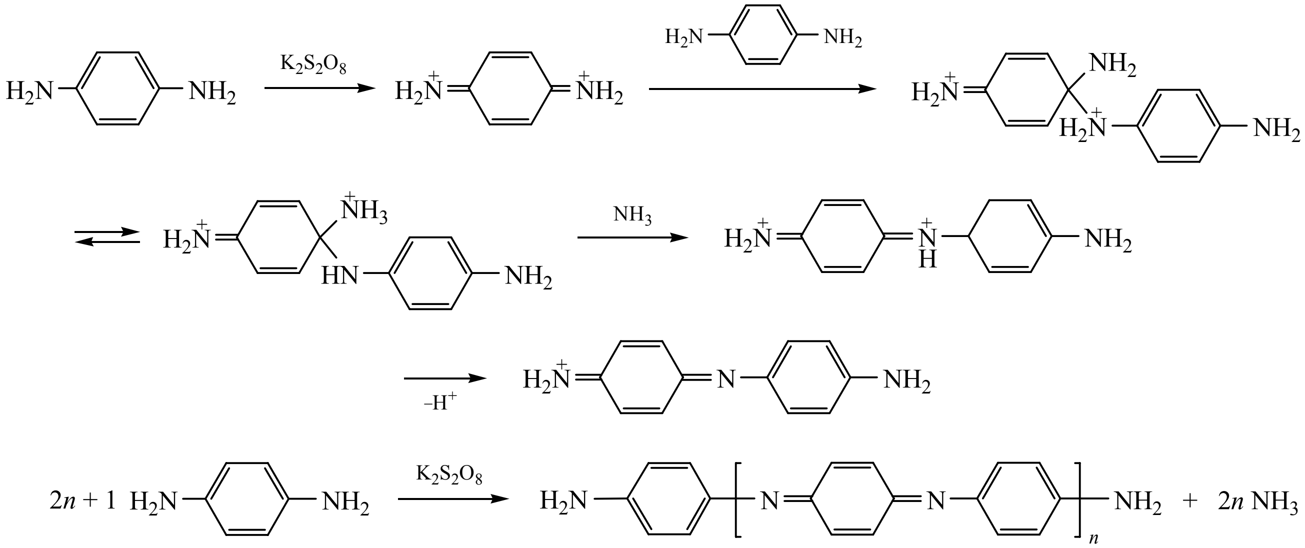
The ^{1}H NMR spectra presented in [5, 6] possess fairly strong differences. The reason is that, in [5], a salt form, and in [6], a base form of the polymer was obtained, and the signal at 4.5 ppm, which was attributed to the NH and NH_2 protons [5], actually corresponds to the water protons from DMSO. The intensity of this signal strongly exceeds the sum of the intensities of the signals from the remaining protons, which contradicts the polymer structure proposed in [5].

In the ^{1}H NMR spectrum of the polymer presented in [6] the signal at 4.5 ppm is lacking, but there is a signal in the upfield region at 3.4 ppm. The assignment of the broadened signal at 5.84 and four doublets at 6.60, 6.82, 7.10, and 7.16 ppm to the protons of the amine groups [6] is questionable for two reasons. Firstly, these signals are more intense than those from aromatic protons, but the proposed structure of the polymer has twice as many aromatic protons as the protons in the NH groups. Secondly, the signals from the NH protons appear as broadened singlets and triplets with coupling constants J of 49–60 Hz [15]. The doublet signals with J of 7.0–9.2 Hz presumably belong to the nonequivalent ortho protons of the benzene ring [15] (Scheme 2, structure **III**).

The structure suggested in [5] does not correspond to the fully oxidized state of the polymer. However, the fully oxidized form **V** of polymer **I** results from subsequent oxidation, like in the case of oxidative polymerization of *o*-phenylenediamine [14] (Scheme 3).

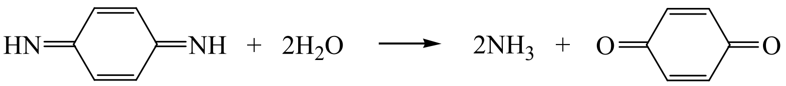
Theoretically, the formation of the polymer with structure **I** requires the use of 2.5 mol of persulfate per

Scheme 4.

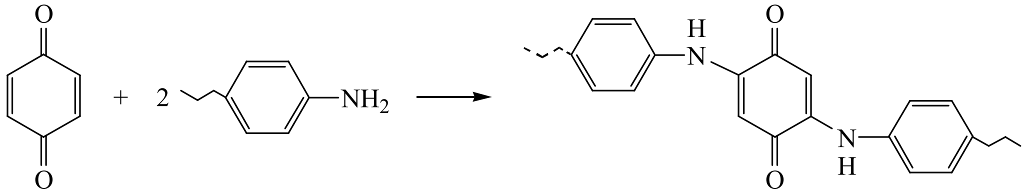


VI

Scheme 5.



Scheme 6.



1 mol of *p*-phenylenediamine; in [5, 6], there was 1 mol of persulfate. Consequently, the maximum yield as calculated with respect to *p*-phenylenediamine may be 40%, whereas the experimental yield of the polymer prepared in [5] was 85%.

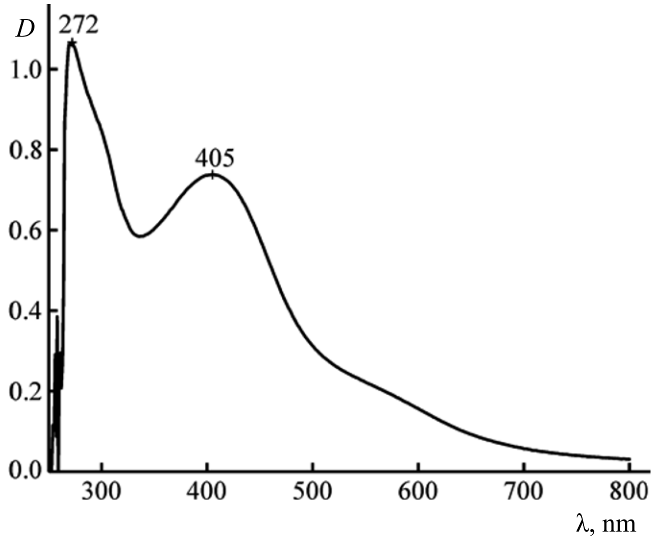
Based on published data [5, 6], we concluded that oxidative polymerization of p-phenylenediamine yields not a polyquinoxaline polymer but poly(1,4-benzoquinonediimine-*N,N*'-diyl-1,4-phenylene) **VI** analogous to polyaniline known as pernigraniline [16] (Scheme 4).

The comparison of the formation schemes for compounds **VI** and **I** [5] shows that, if oxidative polymerization of *p*-phenylenediamine proceeds by Scheme 4, ammonia should be eliminated during the reaction. To test this assumption, we reproduced the experiment described in [5] and detected ammonia in the filtrate. In polymerization of 9 mmol of *p*-phenylenediamine, 8.96 mmol of ammonia was found. However, ammonia can be formed via hydrolysis of quinonediimine as well (Scheme 5).

To check this possibility, we carried out extraction of benzoquinone from the resulting substance with diethyl ether. After evaporation of the solvent, an insignificant amount of residue was left.

If the reaction leads to formation of benzoquinone, there exists a possibility that the latter will react with the terminal amino groups of the oligomers to form a polymer containing benzoquinone moieties [17, 18] (Scheme 6).

In the IR spectrum of the resulting polymer, however, there are no absorption bands of benzoquinone carbonyl groups at 1630–1670 cm^{-1}. Thus, the above-mentioned findings suggest that hydrolysis of benzoquinonediimine proceeds to insignificant extent and, therefore, ammonia is formed mainly by Scheme 4.



UV spectrum (DMSO) of the polymer obtained at a 1 : 1 molar ratio of *p*-phenylenediamine to $K_2S_2O_8$.

According to Scheme 4, oxidative polymerization of 1 mol of *p*-phenylenediamine requires 0.5 mol of persulfate. Our studies showed that, at the 1 : 0.55 and 1 : 1 molar ratios of p-phenylenediamine to persulfate, the reaction yields were identical.

As indicated in [5], the UV spectra of the HCl salt of the polymer prepared from *p*-phenylenediamine in DMF and in water are similar to those of pernigraniline. In the UV spectrum of the polymer in DMSO (see figure) the absorption at 405 nm is lower than that reported in the literature for pernigraniline [12, 19, 20].

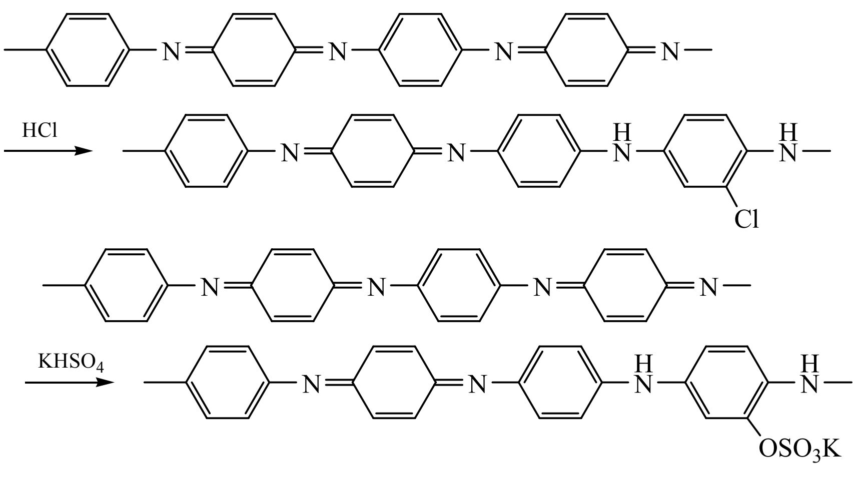
These differences may be due to several factors. Kang et al. [21] reported that in the polymers obtained by the above-described techniques the content of 1,4-benzoquinonediimine-*N,N'*-diyl-1,4-phenylene groups is only 75%. Cao [12] and Albuquerque et al. [19] prepared pernigraniline by oxidation of emeraldine, base form of polyaniline with ammonium persulfate and the spectra presented in those studies obviously correspond to ammonium bisulfate partial salt. MacDiarmid et al. [20] obtained pernigraniline by oxidation of free emeraldine with an acetic acid solution of *m*-chloroperbenzoic acid. Consequently, the compound involved in oxidation was a partial salt of acetic acid. As to the compound obtained by us, this is a modified poly(1,4-benzoquinonediimine-*N,N'*-diyl-1,4-phenylene).

The ^{1}H NMR spectrum of the polymer in DMSO-d_6 fully coincides with that presented in [6]. It contains signals from the protons of the terminal NH_2 groups (5.1–5.9 ppm) and those from the phenylene and quinonediimine protons (6.4–8.0 ppm). The signals at 8.8–10.0 ppm are probably associated with the protons of water coordinated to the sulfonate groups, which were revealed by subsequent analysis of the polymer that we obtained.

The quinonediimine groups are responsible for reactivity of pernigraniline. It is known [20] that the reaction of pernigraniline with hydrochloric acid proceeds via 1,4-addition followed by ring aromatization. Pernigraniline reacts in a similar way with sulfuric acid, or with potassium bisulfate which is formed from potassium persulfate during polymerization (Scheme 7).

To prove the presence of sulfonate groups, the polymer was heated for 5 h on a water bath with a 5%

Scheme 7.



KOH solution, the sulfate ions were precipitated by barium chloride, and sulfonate groups were determined semiquantitatively (7.17 %). The sulfonate groups in the polymer can affect its UV spectrum.

For obtain more data, the reaction was carried out at a 1:0.25 molar ratio of the monomer to potassium persulfate under the conditions of oxidative polymerization of *p*-phenylenediamine.

According to the ^{1}H NMR spectrum, the reaction gives *N,N'*-bis(4-aminophenyl)-1,4-benzoqiunonediimine (Scheme 4, *n* = 1) which subsequently reacts with potassium bisulfate to form 1,4-di(4-aminoanilino)benzene-2-sulfonate. The ^{1}H NMR spectrum (DMSO-d_6) contains signals from the NH_2 protons at 5.2–6.0 ppm and those from the aromatic protons and NH protons at 6.4–8.0 ppm [6.6 d, 6.9 d (6H); 6.75 d, 7.1 d (4H), 7.3–8.2 ppm (3H)]. The signals at 9–10.4 ppm are apparently due to the protons of water coordinated to the sulfonate groups. At a 1 : 0.25 molar ratio in glacial acetic acid the reaction of *p*-phenylenediamine with persulfate gives *N,N'*-bis(4-aminophenyl)-1,4-benzquinonediimine [22].

Thus, the above data confirm that oxidative polymerization of *p*-phenylenediamine proceeds by Scheme 4, and the structure of the resulting polymer is analogous to that of pernigraniline which, under the reaction conditions, undergoes certain transformations.

EXPERIMENTAL

In our experiments, *p*-phenylenediamine was purified by sublimation (mp 143–145°C), and analytically pure grade potassium persulfate was used. The IR spectra were recorded on a Nicolet/Nexus FT-IR spectrometer, the electronic spectra, on a Specord 65 spectrometer, and the ^{1}H NMR spectra, on a Mercury 300 Varian NMR spectrometer.

Oxidative polymerization of *p*-phenylenediamine under the action of potassium persulfate [5]. *a.* Molar ratio 1 : 1. To a solution of 1.00 g (9.3 mmol) of *p*-phenylenediamine in 102 mL (0.15 mol) of HCl, a solution of 2.51 g (9.3 mmol) of potassium persulfate in 47 mL of distilled water was added within 5–6 min, and the resulting mixture was stirred for 16 h at room temperature. Next, the solution was filtered, and the precipitate was air-dried. The filtrate after alkalization with concentrated KOH was distilled on an apparatus equipped with a liquid trap, a receiver filled with water for ammonia absorption, and a Tishchenko flask with water. The distillate and the Tishchenko flask contents were titrated with 0.1 N HCl. Found: 8.96 mmol of ammonia. After distillation, the contents of the distillation flask were filtered, and the precipitate was washed with distilled water until neutral pH and then treated with ether, the result being that 0.003 g of the substance was dissolved in ether. To the air-dried precipitate, a 10% $KHCO_3$ solution was added (to pH 10), and the mixture was stirred for 8 h. The resulting precipitate was filtered off, washed with distilled water until neutral pH and to the absence of SO_4^{2-} ions in washings. The resulting polymers were vacuum-dried at 60°C (2 kPa) to constant weight. Yield 0.72 g (86%).

b. Molar ratio 1 : 0.55. The reaction was carried out in a similar way. In 105 mL (0.15 mol) of HCl, 1.00 g (9.3 mmol) of *p*-phenylenediamine was dissolved. Next, 1.38 g (5.1 mmol) of potassium persulfate was dissolved in 26 mL of distilled water, and the resulting solution was added dropwise within 5–6 min into the solution of *p*-phenylenediamine. In the distillate, 6.4 mmol of ammonia was found. Yield 0.74 g (88%).

c. Molar ratio 1 : 0.25. In a flat-bottomed flask, 1.00 g (9.3 mmol) of *p*-phenylenediamine was placed, and 105 mL (0.15 mol) of HCl was added, after which the content of the flask was stirred until dissolution of *p*-phenylenediamine. Next, a con-centrated solution of 0.63 g (2.65 mmol) of potassium persulfate in 12 mL of water was added at 20°C under permanent stirring within 5 min. The reaction mixture was stirred for 14 h, and the resulting precipitate was filtered off, air-dried, and treated with a 10% aqueous $KHCO_3$ solution (to pH 10), after which the mixture was stirred for 8 h. The resulting precipitate was filtered off, washed with water until neutral pH and to the absence of SO_4^{2-} ions in washings. Yield 0.11 g (10%).

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