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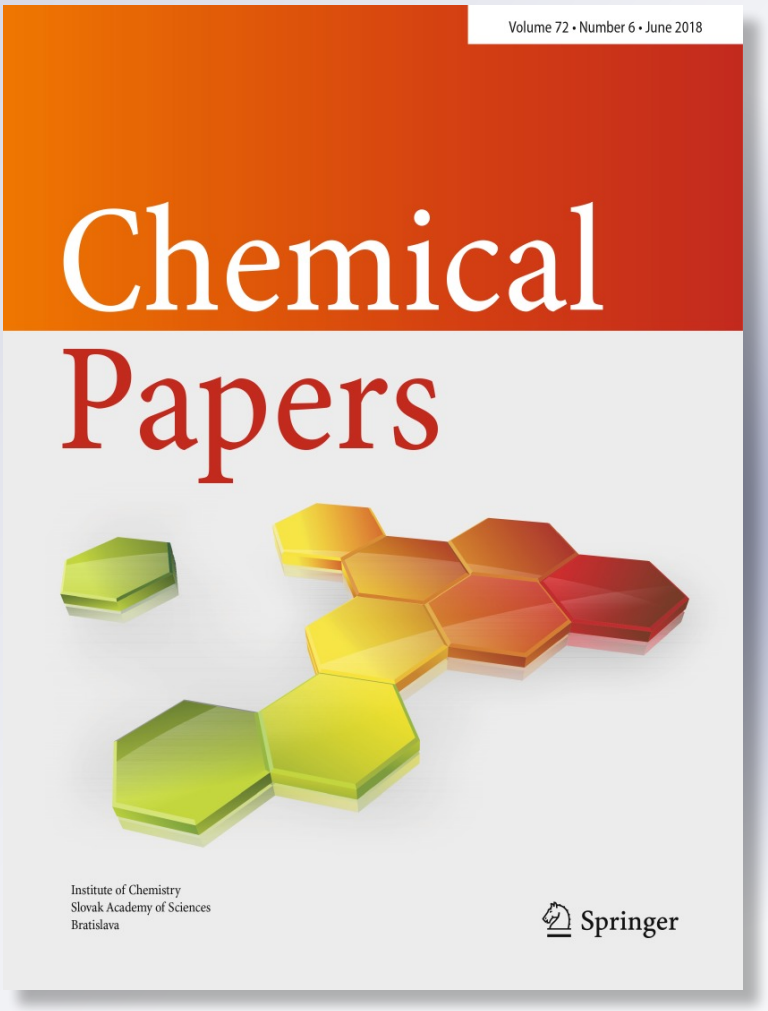

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ORIGINAL PAPER

Synthesis and investigation of poly(p-phenylenediamine)–poly(1,4-benzoquinonediimine-*N,N*-diyl-1,4-phenylene)

Nagharsh A. Miraqyan[1] · Rima H. Arakelyan[1] · Narine A. Durgaryan[1] · Angelo H. Durgaryan[1]

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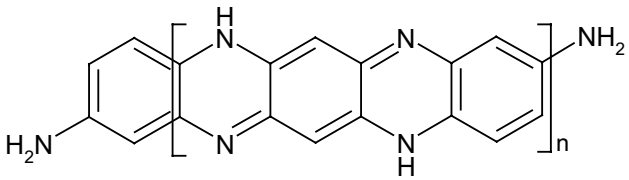
Abstract
Poly(1,4-benzoquinonediimine-N,N-diyl-1,4-phenylene) having similar structure to pernigraniline was synthesized by chemical oxidative polymerization of p-phenylenediamine and its salt using potassium peroxydisulfate as an oxidant in molar ratio 1:0.8, in acetic acid, at 278 K. Acetylation of amino end groups of polymers were carried out aiming to prevent self-condensation of amino groups with 1,4-benzoquinone diimine groups by 1,4-addition. Attempting to carry out the reduction of obtained polymer with hydrazine hydrate, it was shown that 1,4-addition of hydrazine to quinonediimine groups occurs instead of expected reduction reaction. When doping obtained polymers with iodine, the electrical conductivity increases up to 10^{-4} S/cm.

Keywords P-Phenylenediamine · Oxidative polycondensation · 1,4-addition · Conductivity · Pernigraniline

Introduction

There are extensive studies in literature concerning the oxidative polymerization and copolymerization of P-phenylenediamine (1) (Li et al. 2002; Janoševic et al. 2013; Stejskal 2015). It should be noted that acidic aqueous solutions were the most frequently applied polymerization media. There were several proposals for the molecular structure of poly(p-phenylenediamine) obtained by oxidative polymerization of (1) in hydrochloric acid medium, i.e., in (Cataldo 1996) the author mentioned that obtained polymer had similar structure to pernigraniline and the ladder structure with phenazine rings had been proposed.

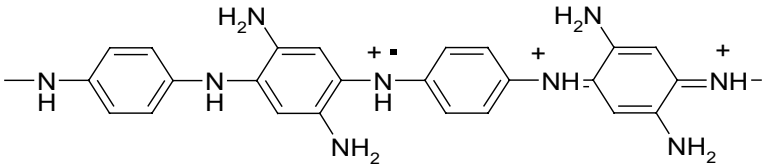


After careful investigation of poly(p-phenylenediamine) structure obtained by oxidative polymerization of (1) by persulfate in hydrochloric acid medium, authors came to the conclusion that obtained polymer had similar to polyaniline

✉ Angelo H. Durgaryan
durgaran@ysu.am

[1] Yerevan State University, Alex Manoogian 1, 025 Yerevan, Armenia

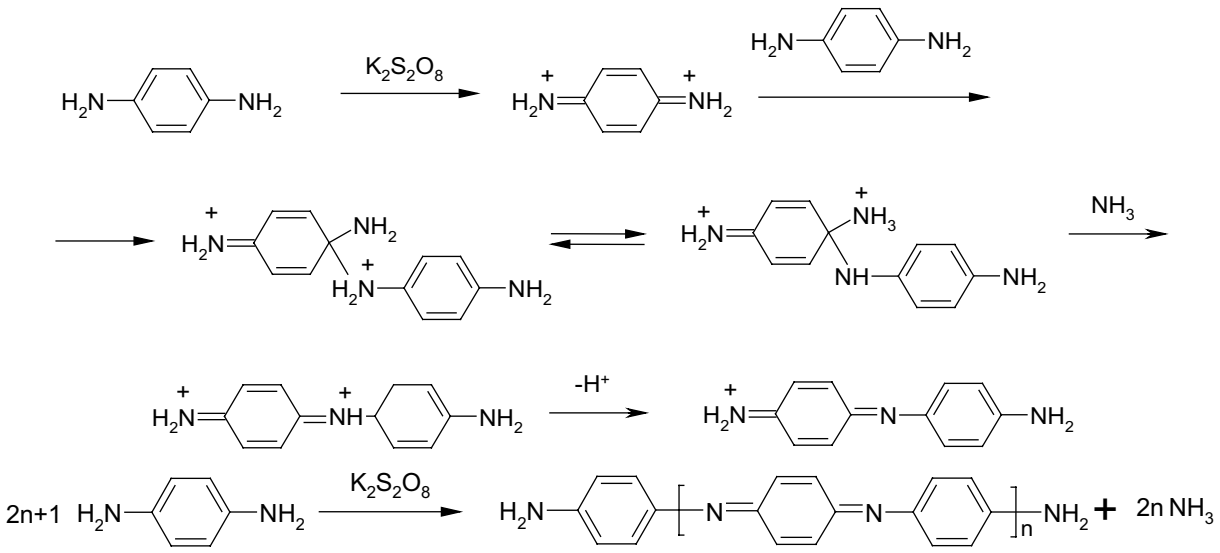
structure and iminoquinonoid base-like structure was proposed for the polymer (Sestrem et al. 2009).



The same structure has been proposed for the polymer obtained by oxidative polymerization of (1) with silver nitrate (Ciric-Marjanovic et al. 2011). According to other results, the oxidation of (1) with ammonium peroxydisulfate in 1 M HCl gives polymer containing azo and hydrazo groups (Rawat et al. 1991).When considering the theoretical (ab initio) electrochemical polymerization of (1), leucoaniline, i.e. poly(imino-1,4-phenylene) structure was established for the obtained polymer (Lakard et al. 2003). (1) was polymerized using hydrogen peroxide as an oxidant and horseradish peroxidase as a catalyst in mixed solvents of 1,4-dioxane and water. It was considered that polymers retain disubstituted benzene nuclei, which suggests that the polymerization proceeded mainly via N–N coupling, then as a result of further oxidation azo and benzoquinonediimine units were formed (Ichinohe et al. 1998). Poly(azo–p-phenylene) was obtained by oxidation of (1) with oxygen in the presence of iron (III) chelate (Tsuchida et al. 1970), as well as by oxidation with hydrogen peroxide in the presence of catalysts of copper (II) and cobalt (II) (Puzari et al. 2001). Other references to the subject of oxidative polymerization of (1) give support to one of the above-mentioned versions (Li et al. 2002; Stejskal 2015).

Based on the literature and our experimental data, we concluded that the oxidative polymerization of (1) with potassium persulfate in hydrochloric acid medium proceeds according to the following scheme (Durgaryan et al. 2014) (Scheme 1).

According to proposed scheme, poly(1,4-benzoquinonediimine-N,N'-diyl-1,4-phenylene) (2)—polymer with analogous to pernigraniline structure—would be formed. However, as we showed previously, side reactions had occurred if the reaction was performed at the temperature of 295–298 K and in the hydrochloric acid medium due to high reactivity of quinonediiminic groups (Durgaryan et al. 2014). According to the literature, pernigraniline could be synthesized by oxidation of emeraldine solution in NMP with an acetic acid solution of *m*-chloroperbenzoic acid (MacDiarmid et al. 1991) and by oxidation of emeraldine film with ammonium persulfate (Cao 1990). Kang et al. (1993) reported that in the polymers obtained by (MacDiarmid et al. 1991), content of 1,4-benzoquinonediimine-*N,N*'-diyl-1,4-phenylene groups is only 75%. Concerning this, it could be mentioned that the synthesis of (2) due to the interaction of N,N'-dichloro-1,4-benzoquinonediimine with 1,4-phenylenedimagnesium



Scheme 1 Mechanism of oxidative polymerization of p-phenylenediamine (1)

bromide becomes impossible because of in situ reduction of polymer (Yamamoto et al. 1999).

To decrease side reactions, the reaction conditions had been worked out in glacial acetic acid medium, at reaction temperature 288 K and the model compound—N,N'–bis(4′-aminophenyl)-1,4-benzoquinonediimine (3) was obtained using molar ratio of (1)/$K_2S_2O_8$ equal to 1:0.25. This additionally provides the evidence of proposed mechanism, shows that the reaction actually proceeds by step-growth mechanism and shows that undesired side reactions are suppressed under these conditions (Durgaryan et al. 2017).

The aim of the presented work is to use the worked out method for synthesis of (2) using (1)/oxidant molar ratio equals to 1.25:1. (2) is a polymer with structure similar to pernigraniline.

Experimental

Materials

(1) was purified by sublimation (m.p. 416−418 K), and its sulfate was purified by recrystallization from water. All other chemicals were of analytical grade and were used as received without any further purification. Vacuum (0.2 kPa) desiccator with P_2O_5 was used for drying the obtained compounds. UV/Vis spectra of the polymer samples were recorded in 1-cm quartz cuvettes with Specord 65 spectrometer. FT-IR Nicolet Nexus spectrometer was served for obtaining FT-IR spectra (KBr pellets). ^{1}H NMR spectra were obtained in deuterated dimethylsulfoxide using Mercury 300 Varian NMR spectrometer. Intrinsic viscosity was measured using an Ubbelohde capillary type viscometer (solvent formic acid, at 298 K). For conductivity measurements, polymer powders were pressed into tablets under the pressure (30 kg/cm^2). The electrical conductivities were measured using AT512 precision resistance meter.

Chemicals

(2): To a solution of 2.0 g (19 mmol) (1) and 1.25 g (6.1 mmol) of its sulfate in 24 mL glacial acetic acid 5.31 g (19.7 mmol) of potassium peroxydisulfate was added slowly during 2 h with continuous stirring at 288 K. After complete addition of the oxidizing agent, the reaction mixture was kept under constant stirring for 24 h at the same temperature. The reaction mixture was kept in refrigerator at 279 K every time when the stirring was interrupted. Reaction mixture was treated with 10% Na_2CO_3 solution at 275 K up to pH 9 under vigorous stirring for 4 h. The precipitated powder was collected by filtration at 275 K and washed with distilled water until neutral pH and to the absence of SO_4^{2-} ions in washings. Obtained solid powder was dried on air, extracted with methanol at 288–289 K and after filtration remained polymer was vacuum-dried at 288 kPa to constant weight. The yield is 1.7 g (76%).

(3): (Durgaryan et al. 2017): 0.75 g (7 mmol) of PPDA and 0.476 g (2.3 mmol) PPDA sulfate were dissolved in 6 mL of acetic acid in a flask equipped with a magnetic stirrer. The reaction mixture was stirred at temperature 288 K to dissolve PPD and then, under the continuous stirring, 0.62 g (2.3 mmol) of potassium peroxy disulphate was added and continued to stir for 21 h at 288 K. The reaction mixture had been kept in refrigerator at 279 K every time if the stirring was interrupted. Reaction mixture was treated by 10% Na_2CO_3 solution at 275 K up to pH 9 under vigorous stirring for 4 h. The precipitated powder was collected by filtration, washed with cold distilled water till neutral reaction and absence of sulfate ions and dried in air. The air-dried precipitate was extracted by methanol at 288–289 K. After solvent evaporation residue was treated by diethyl ether and dried in vacuo (323 K/2 kPa) desiccator over phosphorous pentoxide. 0.50 g (yield 75%) m.p530–531 K 0.11 g (yield 20%) insoluble fraction.

(4): a) 0.10200 g (0.2 mmol) of (2) was dissolved in 3 mL glacial acetic acid and then 0.1 mL of 93 % acetic anhydride was added. The reaction mixture was stirred for 6 h at 288 K. Obtained polymer was precipitated by ice water, collected by filtration and then treated with 10% Na_2CO_3 solution at 275 K up to pH 9 and continued stirring for 8.5 h. The powder was collected by filtration, washed first with icy distilled water till neutral reaction, then with methanol and dried on air. Then, the polymer was dried in vacuo desiccator over phosphorous pentoxide (288 K/2 kPa). The yield is 0.10 g.

b) To a solution of 2.08 g (19.2 mmol) (1) and 1.32 g (6.4 mmol) of its sulfate in 25 mL glacial acetic acid 288 K 5.53 g (20 mmol) of potassium peroxy disulphate was added slowly during 2 h with continuous stirring at 288 K. Afterwards, 2.6 ml (35 mmol) of 93 % acetic anhydride was added and the reaction mixture was kept under constant stirring for 7 h at the same temperature. Obtained polymer was precipitated by ice water, collected by filtration, then treated by 10% Na_2CO_3 solution at 275 K up to pH 9 and continued stirring for 8.5 h. The powder was collected by filtration, washed with icy distilled water till neutral reaction. After the extraction with methanol, the residue was extracted with ethylene glycol and dried, firstly in air, then in vacuo desiccator over phosphorous pentoxide (288 K/2 kPa). The yield is 1.82 g (79%).

(5): 0.1991 g (1.1 mmol) of (2) was added to an Erlenmeyer flask containing 4 mL (44 mmol) of hydrazine (35% aqueous solution) and kept at room temperature 293–295 K for 4 days. The product was precipitated by aqueous saturated solution of sodium chloride and kept in refrigerator.

Next day, the product was filtrated, washed with distilled water till neutral and dried under vacuum. The yield is 0.096 g.

(6): 0.05 g (0. 274 mmol) of compound **(5)** was added to an Erlenmeyer flask containing 1.2 mL of acetic acid and under continuous stirring at 288 K was added 0.0376 g (0.139 mmol) of $K_2S_2O_8$ as an oxidant. The mixture was stirred 9 h during 2 days. Reaction mixture was treated by 10% Na_2CO_3 solution at 275 K up to pH 9. Then, the product was filtered and washed with distilled water till neutral and absence of SO_4^{2-} then dried under vacuum. The yield is 0.05 g.

(**7**): 0.05595 g of compound (3) was added to an Erlenmeyer flask containing 1 mL (11 mmol) of hydrazine (35% aqueous solution) and was stirred for 6 h during 2 days at room temperature. The product was precipitated by aqueous saturated solution of sodium chloride and kept in refrigerator. Next day, the product was filtered and washed with distilled water till neutral and dried under vacuum. The yield is 0.03840 g (55.5%).

Doping by iodine

Different amounts of 0.18 N iodine solution in CCl_4 were added to polymer powder with determined weight and kept at room temperature. After 3 days, polymer was filtered, washed with small amounts of CCl_4 and dried under vacuum (0.2 kPa) in a desiccator with P_2O_5. Iodine content in polymers was determined via filtrate titration with $Na_2S_2O_3$ 0.1 N solution and by polymers' weight increase.

The doping level was calculated by formula:

Y = mole of iodine/(mole of repeating structural units).

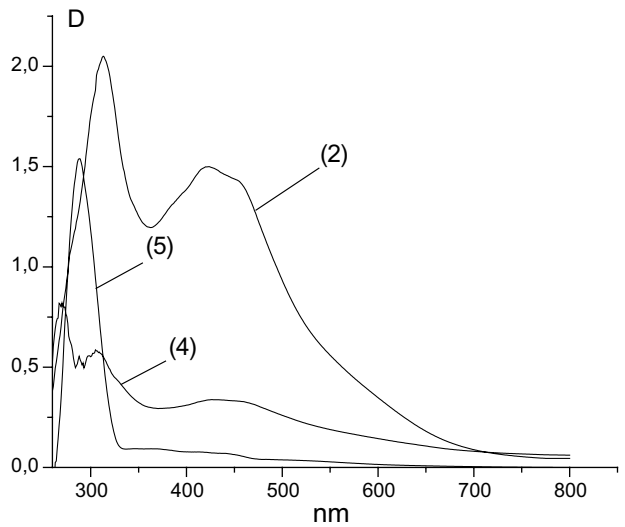


Fig. 1 UV–Vis spectrum (solvent NMP, λ, nm) of compounds (2) (λ_{max} = 311, y = 2.155; λ_{max} = 424–452; y = 1.50), (4) (λ_{max} = 292; y = 0.606; λ_{max} = 418–434; y = 0.323) and (5) (λ_{max} = 280 nm)

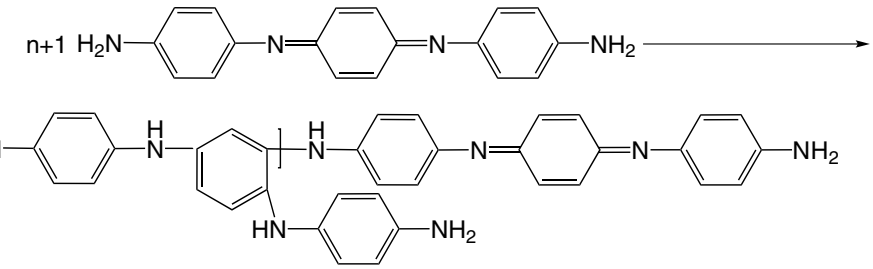
Results and discussion

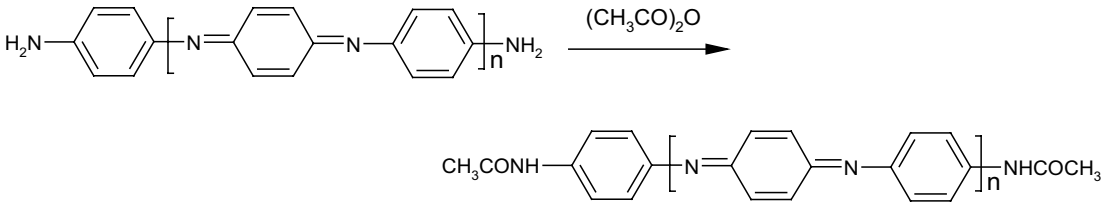
Oxidative polymerization of (1) and its sulfate has been carried out in glacial acidic acid medium, at 288 K, as in the case of synthesis of (3), using (1)/oxidant molar ratio equal to of 1:0.8. The reaction was carried out using mixture of (1) and its sulfate, but the reaction could proceed with slower rate without the latter compound. This could be caused by the catalytic effect of sulphuric acid of the substitution reaction, as a result of which ammonia was formed. Sulphuric acid generated during the reaction of (1) with persulfate when the reaction occurs without p-phenylenediamine sulfate. The obtained polymer (2) has intrinsic viscosity equal to $[\eta] = 0.22$ dL/g (298 K, in formic acid). But it should be mentioned that as the reaction occurs by step-growth mechanism (Durgaryan et al. 2017), the yield and the molecular weight of polymers are highly dependent on the reaction time.

UV–Vis spectrum of (2) consists of bands at 311 and 424–452 nm (Fig. 1). The absorptions at 424–450 nm are attributed to π–π* transitions centered on the quinoid rings in 1,4-disubstituted quinone diimine groups, the energy of which would be lower than π–π* transitions centered on the benzenoid rings at 311 nm. Absorption at 424–450 nm is slightly long-wave shifted than that reported for the poly(p-phenylenediamine) obtained in hydrochloric acid medium (405 nm, DMSO) (Durgaryan et al. 2014). According to the literature, pernigraniline obtained by oxidation of emeraldine solution in NMP with an acetic acid solution of *m*-chloroperbenzoic acid has an absorption band at ~ 520 nm (MacDiarmid et al. 1991), pernigraniline prepared by oxidation of emeraldine film with ammonium persulfate has an absorption band at 564 nm (Cao 1990). These differences may be due to several factors: Kang et al. (1993) reported that in the polymers obtained by (MacDiarmid et al. 1991), content of 1,4-benzoquinonediimine-*N,N*'-diyl-1,4-phenylene groups is only 75% (in Cao 1990 percent of oxidation of polyaniline is not defined). Additionally, obtained compounds were not treated by alkaline, and so there were in partial salt forms [partial salt of ammonium bisulfate (Cao 1990] and partial salt of acetic acid (MacDiarmid et al. 1991). UV spectra of model compounds exhibit the following absorption bands: (3) (in DMSO, nm) at 260, 341, 496 (Durgaryan et al. 2017); *N,N*'-bis(p-tolyl)-2,5–dimethyl-1,4-benzoquinonediimine (in DMF, nm) at 310; 457 and *N,N*'-bis(p-tosyl)-1,4-benzoquinonediimine (in DMF) 484 nm (Yamamoto et al. 2001).

IR spectrum (KBr tablets, cm^{-1}) of (2) clearly exhibits bands at 3211, 3326, 3420, which have been assigned to υ (N–H) stretches in primary NH_2 end groups. The assignment has been done based on the existence of the same bands in the corresponding spectrum of model compound (3) (Durgaryan et al. 2017). Some lowering of the value of band at

Scheme 2 Self-condensation of N,N'–bis(4′-aminophenyl)-1,4-benzoquinonediimine (3)





Scheme 3 Acetylation of terminal amino groups

3211 from the region assigned to secondary and primary amines (3500–3300) could be caused by hydrogen bonding as a result of interaction between amino and quinonediimine groups (Trchova and Stejskal 2011; Bellamy 1958). Band at 3031 is attributed to aromatic C–H stretching. Absorptions with maxima at 1604, 1552, 1509, 1448 could be assigned to aromatic C=C stretching mixed with N–H scissoring of primary aromatic amine (Stejskal 2015; Kang et al. 1993), C=N stretching (Bellamy 1958) and different types of C–H bending vibrations (Vuillard et al. 1994), at 1285, 1384 –to C–N stretching, at 1170 and 1130 –to C–H in plane deformation, at 829 cm^{-1}– to out-of-plane vibrations of C–H in 1,4-disubstituted aromatic compounds (Bellamy 1958).

^{1}H NMR investigation of the structure of obtained (2) is complicated due to the poor spectral resolution. The spectrum ($(CD)_3$ SO, δ, ppm) contains only two broaden signals: protons of the terminal NH_2 groups at 5.5 ppm with 4H, (intensity of one proton 0.4/4 = 0.1), of aromatic and benzoquinone diimine groups at 6.0–8.6 ppm (intensity of one proton 13.4/8 = 1.65); so the average degree of polymerization is equal to 1.65/0.1 = 16.5.

As previously, it has been shown that the heating of (3) causes self-condensation of terminal amino groups with quinonediimine groups by 1,4-addition reaction (Durgaryan et al. 2017) (Scheme 2), so, acetylation of terminal amino groups by acetic anhydride was carried out to prevent the occurrence of above-mentioned reaction (Scheme 3).

The reaction of acetylation of amino end groups in (2) was conducted in two ways: (a) acetylation of the pure polymer using the same reaction condition as described for the acetylation of (3) (Durgaryan et al. 2017); (b) in situ acetylation, i.e. at the end of the polymerization acetic anhydride was added directly to the reaction mixture causing the acetylation of all amino groups including amino groups of the unreacted monomer (1). Later, solid residue was consecutively extracted with methanol and the mixture of ethanol—glycol, aiming to remove the acetylated (1) and unreacted (3) compounds. IR spectra (KBr tablet, cm^{-1}) of the acetylated polymers obtained by two different methods were identical and were basically similar to initial polymers' spectrum with some differences in the range of 3200–3400 cm^{-1} and with appearance of new bands at 2924 and 2853 cm^{-1} (stretching vibration in CH_3).

In UV spectrum of acetylated polymer (Fig. 1), absorption bands were blue shifted to lower wavelength compared with those of initial polymer.

It is well known that three forms of polyaniline differ from each other by oxidation degree and two forms—pernigraniline (fully oxidized form) as well as leucoemeraldine (fully reduced form) could be synthesized from emeraldine (half oxidized form). Aiming to obtain other forms of polyaniline—leucoemeraldine and emeraldine, reduction of (2) was carried out by hydrazine hydrate being the commonly used reducing agent for the reduction of emeraldine (Zeng et al. 1998). As it is well known that the UV–Visible spectrum of polyaniline is sensitive to oxidation state and transitions between oxidation states (de Albuquerque et al. 2004); hence, absorbance parameters of the polymer can be used to estimate the occurrence of the reaction. According to UV–Visible spectrum, data absorption band centered on 424–452 nm of quinone diimine groups disappeared, so all quinone diimine groups were converted to aminophenylene aniline groups under the influence of hydrazine hydrate (Fig. 1).

Obtained polymer (5) was oxidized aiming to synthesize polymer with analogous to emeraldine structure. However,

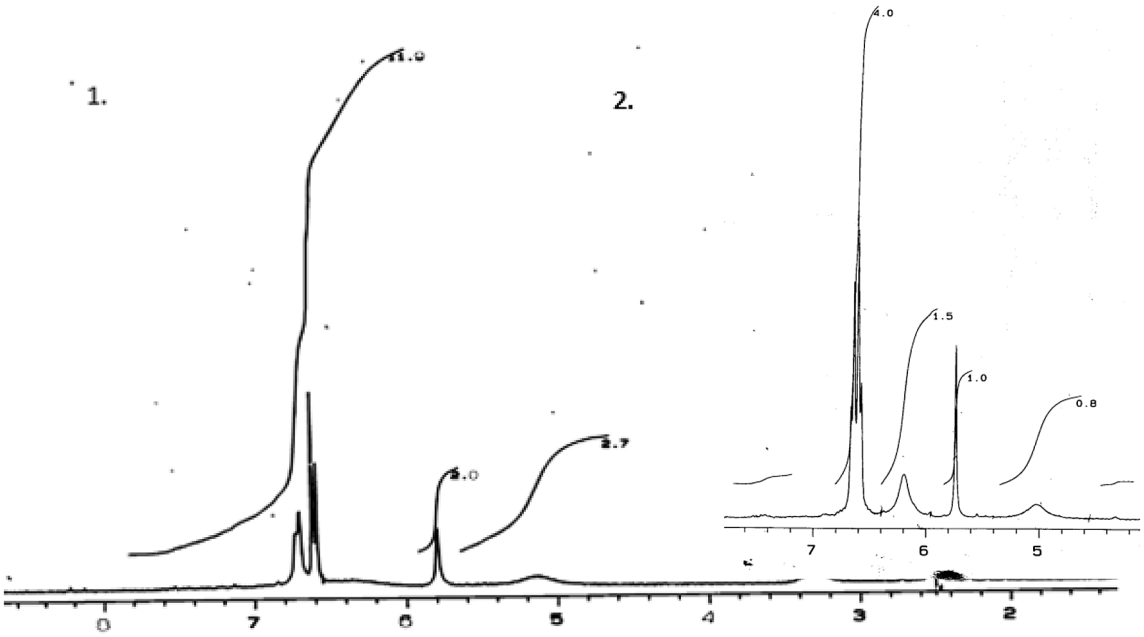
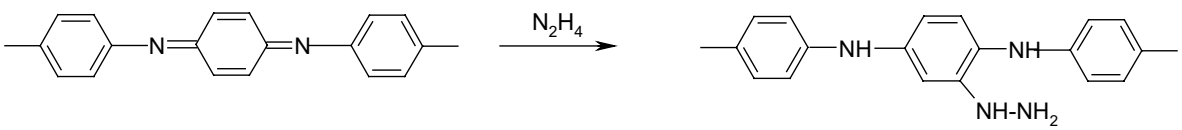


Fig. 2 ^{1}H NMR spectrum ($(CD_3)_2SO$, δ, ppm) of the reaction product of **1.** (3) with hydrazine hydrate–(7), **2.** (3)



Scheme 4 Reaction of quinonediimine groups with hydrazine

the conductivity of obtained polymer after the doping with 3 N hydrochloric acid was only 1.3×10^{-7} S/cm, instead of expected at least 10^{-1} S/cm, which is the typical value of the conductivity of emeraldine salt obtained by doping with the same method. Therefore, polymer (5) does not have leucoemeraldine structure. To elucidate the causes of obtained data, the reaction of model compound (3) with hydrazine hydrate was investigated, as well. According to ^{1}H NMR data, 1,4-addition of hydrazine to quinonediimine groups occurs rather than reduction.

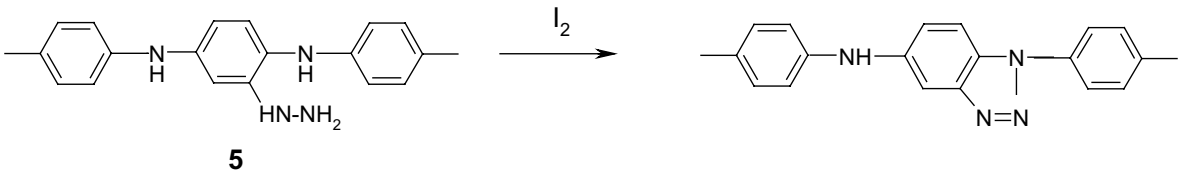
^{1}H NMR spectrum ($(CD_3)_2SO$, δ, ppm) of the reaction product of (3) with hydrazine hydrate -*N,N*'-di(4-aminophenyl)-2-hydrazyl-1,4-phenylenediamine (7) featured the following signals (Fig. 2): NH_2 protons $\delta = 5.0$–4.3 ppm with 4H (the intensity of one proton 2.7/4 = 0.675), N_2H_3 protons $\delta = 5{,}8$ ppm with 3H the intensity of one proton 2.0/3 = 0.637), protons of aromatic, NH and $2H_2O$ groups at $\delta = 6$–7.7 ppm with 17H (the intensity of one proton 11.9/17 = 0.7) the total average intensity of one proton was equal to 0.69 (11.9 + 4.7 = 16.6/24 = 0.69). Comparison of ^{1}H NMR spectra [$(CD)_3SO$, δ, ppm) of the initial compound (3) (in Fig. 4; (b) NH_2 protons $\delta = 5.00$ and 5.75 ppm with 4H (1.8/4 = 0.45), protons of aromatic and benzoquinone diimine groups at 6.20 ppm, 6.60 ppm, $J = 8$ Hz, 6.65 ppm, J = 8 Hz. 12H (5.5/12 = 0.46), by integration (intensity of one proton 5.5/12 = 0.46) (Durgaryan et al. 2017)] with the reaction product (7) shows the lowering in relative intensity of the signal at 6.20 ppm and the increase of relative intensity of NH and aromatic groups which could be due

Table 1 Dependence of conductivities on doping level (*Y*) of compounds (2) and (5)

Doping level (*Y*)		Conductivities σ; S/см	
(2)	(5)	(2)	(5)
0		$< 10^{-10}$	$< 10^{-10}$
0.5		4×10^{-8}	
0.96	1.62	1.4×10^{-6}	1.2×10^{-6} [a]
1.45	2.5	4.9×10^{-5}	2.2×10^{-5} [b]
1.5	2.67	5×10^{-5}	1×10^{-4} [c]

Conductivities were measured at room temperature on the next day after heating to 358 K

[a] 2.4×10^{-6}; [b] 5.1×10^{-4}; [c] 5.7×10^{-4}



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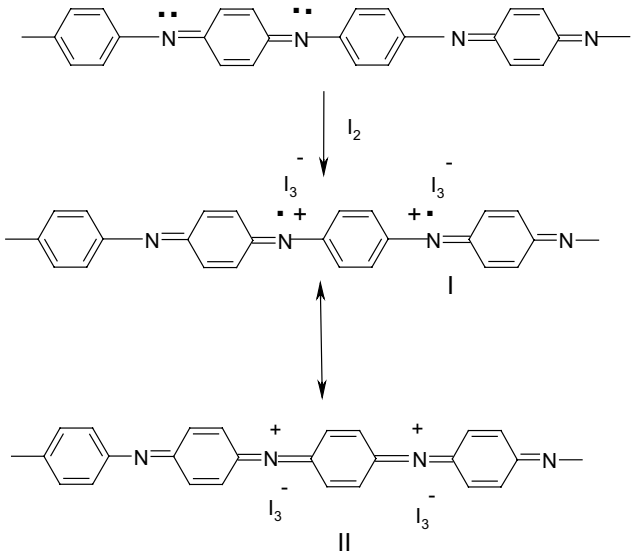
Scheme 5 Oxidation of (5) by iodine possible occured during the doping process



Scheme 6 The formation of charge-transfer complex between iodine and polymer (2)

to the conversion of quinone diimine groups and therefore, 1,4-addition occurs, but not reduction.

It is noteworthy to mention that IR spectral data for compound 5 are consistent with the results obtained for the model compound, i.e. the addition reaction of hydrazine occurred rather than reduction (Scheme 4). New strong absorbance at 3342 cm^{-1} coincides with the absorbance of phenylhydrazine (AIST Database 2018a) and hydrazine monohydrate (AIST Database 2018b), and appearance of new absorbance bands at 980, 1121, 1012 cm^{-1} proves the presence of 1,2,4 substituted aromatic rings in polymer structure. The changes in relative intensities of the bands in region 1650–1400, especially appearance of the band at 1512 cm^{-1} with high intensity, could be caused by the increase in the concentration of secondary amines and conversion of quinonediimine groups to benzenoic.

Despite futile efforts to obtain half and totally reduced forms of polyaniline (PANi) from (2), which has pernigraniline-like structure, reaction with hydrazine shows the opportunity to obtain substituted PANi with regular structure in case of 100% conversion. The later has been difficult to realize by other methods.

We studied the dependence of electrical conductivities of (2) and (5) as a function of iodine doping level (Table 1). On both cases, as doping level was increased, the increase in conductivities was observed. According to obtained data, doping level in all cases is higher for compound 5. It can be deduced that the treatment of compound 5 powder with iodine involves its oxidation according to the Scheme 5.

Conductivities of doped (5) samples measured at room temperature on the next day after heating to 358 K increase (Scheme 5).

It should be mentioned that conductivity of pernigraniline is 1.3×10^{-9}; doped with iodine with dopant content $y = 0.02–2. \times 10^{-4}$ S/cm (Cao 1990), and conductivity of emeraldine with the same dopant is 8.3×10^{-3} S/cm) (Zeng et al. 1998).

It was established that upon doping of pernigraniline, polymer with similar to (2) structure, by iodine only minor increase in magnetic susceptibility had been observed (Cao 1990). Obviously, oxidation of (2) with iodine processed by electron transfer from nitrogen atom to iodine and formation of cation—radical (I structure) (Durgaryan et al. 2010). Afterwards, the reaction among polarons takes place, leading to formation of energetically more favorable quasi-particles, i.e., of a pair of charged solitons (bipolarons). Estimation of possibilities of resonance structures obviously shows that II structure could be realized only on heavy doping levels. With doping level increase, the contribution of II resonance structure would increase (Scheme 6).

Conclusions

Proposed method on the basis of oxidative condensation of (1) is a convenient one step and unique method for the synthesis of the polymer having structure similar to that of fully oxidized state of polyaniline-pernigraniline. The structure composed of quinone diimine groups connected with phenylene rings makes it very reactive and used mild conditions—low temperature and glacial acetic acid medium, makes it possible to avoid side reactions and, on the other hand, this structural specifics makes the 1,4-addition reaction of hydrazine more favorable rather than reduction. It was the first time that hydrazine-substituted polyaniline with

regular structure has been synthesized. Electrical properties of obtained and doped with iodine polymers are close to that of obtained for pernigraniline. The fact that for similar values of conductivities of both polymers the doping level was higher for the compound 5 was explained by its oxidation with iodine.

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