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Synthesis of Polymers Containing Azo Groups in the Main Chain from *m*-Phenylenediamine: Study of Doping

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Abstract—Synthesic approach to polymers containing azo groups was developed on the basis of diazotization and azo-coupling reaction of *m*-phenylenediamine (*m*-PDA) with various ratio *m*-phenylenediamine–sodium nitrite. Doping of poly(azoaminophenylenes) with iodine, perchloric and hydrochloric acids was examined. Electroconductivity increases in the case of iodine to 0.2 S mol^{-1}, of perchloric acid, to 7×10^{-3} S mol^{-1}, and at the action of hydrogen chloride it is virtually unaffected. According to the ESR spectra, at the doping with iodine and perchloric acid electroconductivity enhances generally due to the mobility increase of the charge carriers (polarons).

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The policonjugated electroconductive polymers are used and can be used in many industrial fields [1]. Among the polyconjugated electrically active polymers the compounds containing aromatic azo groups are relatively poorly investigated. The latter are of certain interest as electrodes for emitting diode [2]. They can show photoconductivity in the wavelength region of 300–550 nm [3]. The polymer films doped with non-linear organic azo compounds and also polymers, containing azo benzene groups in the main chain and as side groups, are studied, aiming at their use in optic instruments for data recording, conversion of the light wave lengths etc. [4–10].

First the poly(azoarylenes) were obtained from aromatic diamines by the action of oxygen in the presence of copper(I) chloride in pyridine. The obtained polymers contained a low number of azoxy groups [11–13]. Poly(azo-*p*-phenylene) [14, 15], poly-(oxy-*p*-phenyleneazo-*p*-phenylene), poly(thio-*p*-phenyl-eneazo-*p*-phenylene), poly(azo-2-methyl-1,4-phenylene-3-methyl-1,4-phenylene) and their copolymers were produced by this method [15]. It was found that on doping with iodine [14, 15] and sodium naphthalide [15] their electroconductivity amounts to 10^{-2}–10^{-3} S mol^{-1} [14, 15]. Polymers containing telluro-, *p*-arylene and azo groups were also synthesized using different methods; their doping with bromine was examined [16].

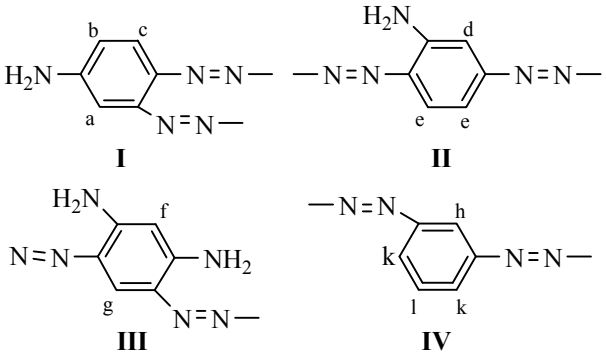
This work deals with the synthesis of polymers containing aromatic azo groups and with the study of the dependence of their electroconductivity, paramagnetic centers concentration (PMC) and PMC characteristics from the dopant nature and concentration, and also from molecular mass of the obtained polymer.

Vesuvin dye is known to be obtained by the reaction of *m*-phenylenediamine with excess amount of sodium nitrite [17]. As a result the cross-linked insoluble polymer forms. We chose this available method to obtain polyazo-compounds. Since this is a polycondensation reaction, it would be expected that the molecular mass of the obtained polymer can be regulated by changing of the ratio *m*-phenylenediamine–sodium nitrite. Evidently, the ratio between azo and amino groups increases as sodium nitrite amount enhances.

Reactions of *m*-phenylenediamine with sodium nitrite were carried out using molar ratio 1:0.9; 1:1; 1:1.3 and 1:2. The obtained polymers are labeled as P-0.9; P-1; P-1.3 and P-2 respectively (Table 1). Diazotization and azo coupling reactions proceed simultaneously.

According to the ^{1}H NMR spectra (Fig. 1) P-0.9 contains generally the following structural units:

Compound **I**: 41 mol %; (a) 5.88 d, J_{ab} 2.3 Hz; (b) 6.05 d.d, J_{bc} 8.8 Hz, J_{ba} 2.3 Hz; (c) 7.40 d, J_{cb} 8.8 Hz. Compound **II**: 18 mol %; (d) 5.93 s; (e) 8.11 s. Compound **III**: 14 mol %; (f) 5.93 s; (g) 7.98 s . Compound **IV**: 14 mol %; (h) 7.94 t, J_{hk} 2.1 Hz; (k) 7.59 d.d, J_{kl} 7.2 Hz, J_{kh} 2.1 Hz; (l) 7.47 t, J_{kl} 7.2 Hz and about 13 mol % other structural units.



Structure of the compounds obtained was proved also by the IR and UV spectroscopic data. The IR spectrum contains absorption bands at 3213, 3346, 3450, 1617, 801 (NH_2), 3060, 1600, 890 (1H, arom.), 824 (2H, arom.), 1480, 1345 (N=N–), 1247 (=N–C), 1132 cm^{-1} (N–C).

In the UV spectrum (Fig. 2) there are absorption bands at 483 and 397 nm (probably, *o*-diazo and other azo groups respectively) and 283 nm (aromatic amino group). This assignment was made considering that 4-phenylazoaniline had absorption bands at 395 and 250 nm. From the IR spectral data follows that amino groups are diazotizated incompletely if the ratio between *m*-PDA and sodium nitrite is 1:2. Expectably, the molar mass of the obtained polymers increases as the molar ratio sodium nitrite–*m*-PDA enhances: P-0.9 and P-1 are completely soluble in DMF, DMSO and alcohol (for P-0.9 [η] = 0.18 dl g^{-1} at 298 K in DMF; for P-1 [η] = 0.22 dl g^{-1} at 298K in DMF and alcohol); P-1.3 is soluble in DMF only partially (58%), and P-2 is fully cross-linked polymer.

Table 1. Data on the syntheses of polymers P-0.9, P-1, P-1.3, and P-2

Starting materials		Yield, g (%)
m-PDA, g (mmol)	$NaNO_2$, g (mmol)	
1.0 (9.26)	0.58 (8.33)	0.97 (89)
1.0 (9.26)	0.64 (9.26)	0.85 (78)
2.0 (18.52)	1.66 (24.1)	1.92 (85)
2.0 (18.52)	2.55 (37)	2.2 (90)

The synthesized polymers were doped with iodine, hydrochloric, and perchloric acids. Electroconductivity, spin concentration, ESR lines width (ΔBpp), and the *g*-factor for the obtained doped and undoped polymers were determined. Electroconductivity for the undoped polymers decreases from 2×10^{-8} to 7×10^{-10} S mol^{-1} as the molar mass and the ratio between azo and amino groups increases (Fig. 3). In keeping with the phblished data for polyazoarenes electroconductivity equals 10^{-8}–10^{-36} S mol^{-1} [12], and lines width (ΔBpp) (Fig. 4), spin concentration (Fig. 5), and *g*-factors are approximately identical. The exception is the cross-linked polymer P-2, a spin concentration of which is approximately five times more than that of the others, but its electroconductivity is minimal 7×10^{-10} S mol^{-1} (Figs. 3, 5).

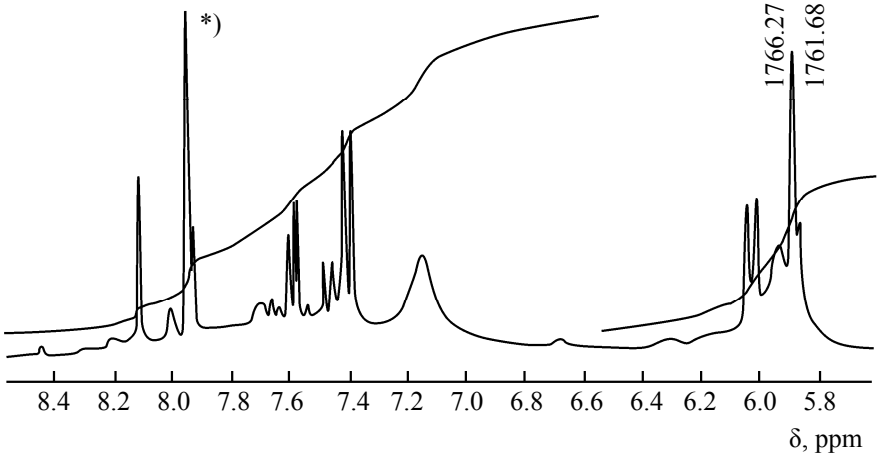


Fig. 1. The ^{1}H NMR spectrum of P-0.9 in $(D_3C)_2SO$, (δ, ppm); *) DMF.

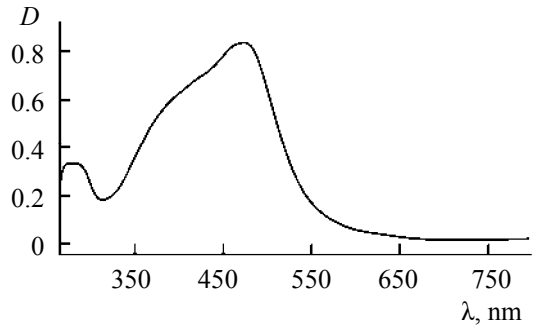


Fig. 2. The UV spectrum of P-0.9 in DMSO.

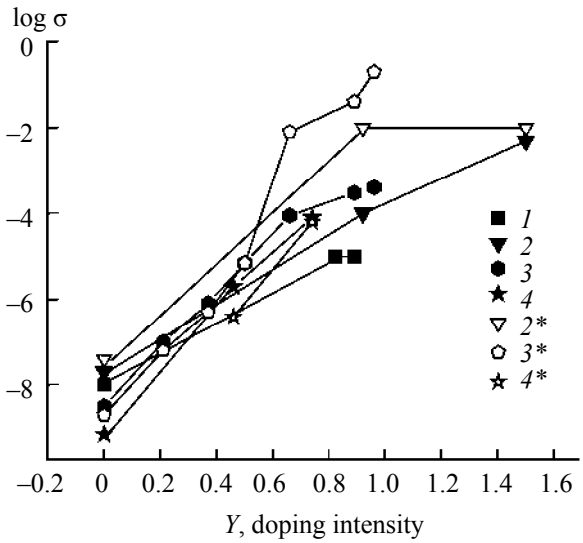


Fig. 3. Dependence (log σ) of electroconductivity (S mol^{-1}) on doping intensity (*Y*): (*1*) P-0.9; (*2*) P-1; (*3*) P-1.3; (*4*) P-2; (*1–4*) are first determinations of electroconductivity; (*2*–4**) are repeated determination of electroconductivity after heating to 343 K; electroconductivity was determined at 293±3 K.

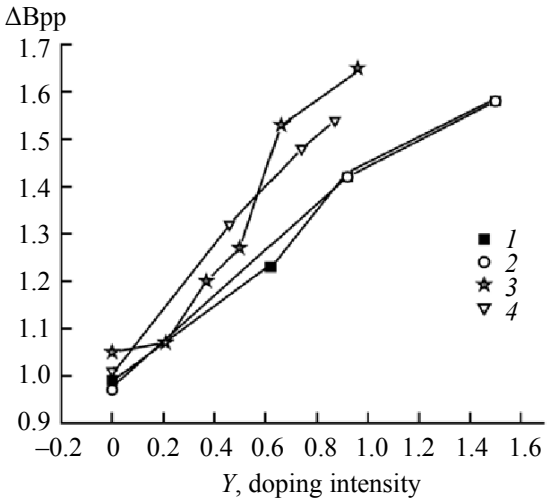


Fig. 4. ESR lines width dependence (ΔBpp, mT) on doping intensity (*Y*): (*1*) P-0.9; (*2*) P-1; (*3*) P-1.3; (*4*) P-2.

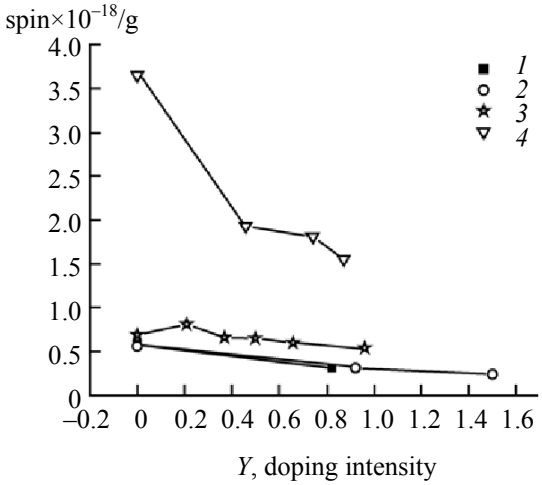


Fig. 5. Spin concentration dependence (spin/g) on doping intensity (*Y*): (*1*) P-0.9; (*2*) P-1; (*3*) P-1.3; (*4*) P-2.

At doping polymers with iodine, as doping intensity enhances the electroconductivity increases to 2× 10^{-1} S mol^{-1} (Fig. 3) that is higher than electroconductivity for poly(azo-*p*-phenylene) (10^{-2} S mol^{-1}) doped with iodine [14,15] and is no worse than PANI (1.83×10^{-1} S mol^{-1}) [18]. Generally, the higher the concentration of azo groups in the polymer (and molar mass respectively), the faster electroconductivity increases as the doping intensity grows. After the heating to 345 K electroconductivity of polymer doped with iodine and containing more than 0.8 mol of iodine per one mol of azoaminophenylene units increases in some cases by 2–3 orders of magnitude (Fig. 3). Evidently, this is caused by changing of supramolecular structure of the doped polymer.

The electroconductivity (Fig. 3) and ESR signal width (Fig. 4) for the undoped polymers enhances as doping intensity increases. This relationship is observed also for poly(azo-*p*-phenylene) [14].

It may be concluded from this that the growth of the ESR signal width is connected with an increase in

Table 2. Dependence of polymer electroconductivity, PMC concentration, ΔBpp, and *g*-factor on the dopant ($HClO_4$) concentration

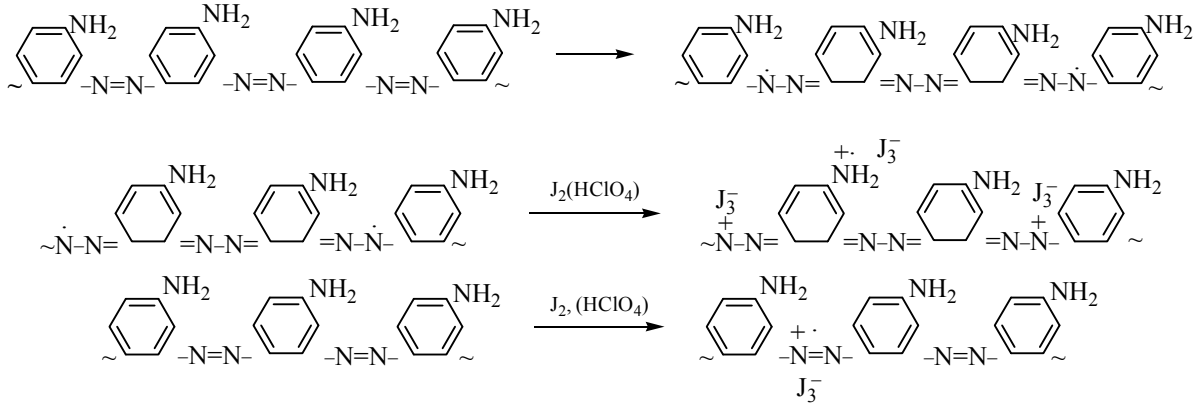
Polymer, Y	σ, S m^{-1}	E_a^*, eV	ΔBpp, mT	PMC concentration		*g*-Factor
				spin×10^{-18}/g	spin×10^{-20}/mol	
P-1.3, 0	3×10^{-9} [a]		1.05	0.68	0.83	2.005
	2×10^{-9}					
P-1.3, 0.6	2×10^{-4}					
	7×10^{-3} [a]					
P-1, 0	2×10^{-8}		0.97	0.56	0.6	2.005
	4×10^{-7} [a]					
P-1, 0.7	5×10^{-4}	1.7	1.01			2.005
	5×10^{-4} [a]	0.8				
P-1, 1.3	2×10^{-4}	0.8	1.31	0.44	1.1	2.004
	3×10^{-3} [a]					

[a] Repeated electroconductivity determination after heating to 323 K.

the collision rate of moving spins (through spin-orbital interaction-bonding), which is proportional to a mobility of the spin-carrier polaron, i.e. electroconductivity increases generally owing to polarons mobility growth [20].

In the case of polymers P-2 and P-1.3 the ESR signal width (Fig. 4) and electroconductivity (Fig. 3) are more increased than for P-1 and P-0.9 as the dopant (I_2) concentration rises. This is probably caused by the involvement of the azo groups the doping process.

According to the ESR spectral data, if the concentration of the dopant (I_2) rises, the spin concentration per one gram of polymer decreases (Fig. 5), and per one mole of the structural units it changes insignificantly. These data can be explained with a fact that the undoped polymers contain unpaired uncharged PMC [reaction (1)] similarly to the undoped trans-transoid polyacetylenes [19], which do not increase electroconductivity. On the doping with iodine, polarons and bipolarons are obtained, whose formation significantly rises the electroconductivity [reaction (2)]:



As in the other cases [14], on doping of polymer with iodine the *g*-factor value rises with increase in iodine amount in polymer from 2.005 to 2.008. It may be concluded from the *g*-factor values that spins are localized generally on the nitrogen atoms. The increase in the *g*-factor values is caused by changing of the latter depending on the neighbouring environment of an unpaired electron.

On the doping of polymers with hydrochloric acid, electroconductivity is not practically increased, when hydrogen chloride concentration in polymer is 0.24–0.43 mol of HCl/mol of the structural units.

Doping of polymers with perchloric acid increases electroconductivity to 7×10^{-3} S mol^{-1} (Table 2). Concentration of PMC and the ESR signal width are

changed similarly to the doping with iodine. However, *g*-factor value is not enhanced, indicating that the g-factor value growth on the doping with iodine is caused by interaction between polymer and iodine. By these data, perchloric acid dopes polymer as oxidant, same as iodine. Polymers doped with perchloric acid are explosive at heating above 333 K.

Thus, soluble polymers are synthesized from the cheap *m*-phenylenediamine by accessible way. When doped with iodine and perchloric acid, they show semiconducting properties with low and medium electroconductivity.

EXPERIMENTAL

m-Phenylenediamine was purified by a vacuum distillation [bp 358–360K (0.7 kPa), mp 335.5–336 K]; sodium nitrite of "pure for analysis" grade was used without purification.

Electroconductivity of the samples as pressed pellets was measured on a Teraohmmeter E6-137 instrument by means of two-contact method. The ESR spectra were registered on a SE/X-2543 instrument (Radiopan). The IR spectra were recorded on a FT-IR Nicolet Nexus spectrometer (KBr pellets). The ^{1}H NMR spectra were taken on a Mercury 300 Varian NMR spectrometer and UV-Vis spectra, on a Specord 50 instrument.

Synthesis of polymers P-0.9, P-1, and P-2 (Table 1). To a solution of *m*-phenylenediamine in distilled water (1 g of *m*-phenylenediamine per 10 ml of water) was added a solution of 1 g of sodium nitrite in 8.5 ml of water. Then to this mixture was slowly added 2.2 mol of 34% hydrochloric acid per one mole of phenylenediamine at 297–300 K. The reaction mixture was kept for one day at room temperature and neutralized with sodium hydrogen carbonate to pH > 7. The solution was filtered off, and the residue was washed with water to neutral reaction. The polymers obtained were dried at room temperature, extracted with DMF, precipitated and reprecipitated. The polymers were dried in a vacuum at 323–343 K (2 kPa).

Doping with iodine. To a weighed sample of fine powdered polymer was added 0.3; 0.5; 1 and 2 mol of 0.19 N iodine solution in CCl_4 per one mole of the structural unit. This mixture was kept for 2–3 days at room temperature. The precipitate was filtered off and washed twice with a little amount of CCl_4. The filtrate was titrated with 0.1 N solution of sodium thiosulfate and dried to constant mass in a vacuum in a desiccator over P_2O_5 (0.2 kPa). Iodine amount in the polymer was calculated by both iodine charge and polymer weight increase.

Doping with perchloric acid. To a weighed sample of fine powdered polymer was added 1–2 mol of 0.7 N solution of perchloric acid per one mole of the structural unit. This mixture was kept for 2–3 days at room temperature. The precipitate was filtered off and washed twice with a little of ethanol. The filtrate was titrated with 0.2 N solution of NaOH and dried to constant mass in a vacuum in a desiccator over P_2O_5 (0.2 kPa). Perchloric acid amount in the polymer was calculated by both perchloric acid charge and polymer weight increase.

Doping with hydrochloric acid was carried out similarly.

The doping intensity was calculated by formula:

$$Y = \frac{n_{\text{dopant}}\ (\text{mol})}{n_{\text{repeated structural units}}\ (\text{mol})}.$$

Quantity of the structural units was calculated considering that diazotation and azo coupling reactions proceed quantitatively.

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