A dependence of electrical conductivity and some properties of paramagnetic centers on the doping level of poly(4-aminoazobenzene) with iodine

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The dependences of the electrical conductivity, ESR spectral linewidths, spin concentrations, and *g*-factor on the level of iodine doping of poly(4-aminoazobenzene), synthesized by the oxidative polymerization of 4-aminoazobenzene with iodine, were studied for the first time. The polymers were studied by ESR and UV spectroscopy. With an increase in the level of iodine doping, the electrical conductivity of the polymers increases from $3 \cdot 10^{-10}$ to $4 \cdot 10^{-1}$ S m^{-1}, the ESR linewidth increases from 0.96 to 1.94 mT, and the *g*-factor increases from 2.004 to 2.007. The spin concentration changes ambiguously, depending on the doping level. In the iodine-doped polymers, spins are mainly localized on two nitrogen atoms of the azo groups.

Key words: poly(4-aminoazobenzene), doping, electrical conductivity, ESR spectroscopy, UV spectroscopy.

Polyaniline (PANI) evokes great interest as an electroactive polymer due to its unique properties.[1,2] PANI is used as an anticorrosion agent,[3,4] in accumulator batteries,[5—7] for separation of gases and poorly separable liquids,[8—10] as bio- and chemosensors,[11—13] *etc*.[14—16]

Polymers containing azobenzene groups are studied with the purpose of using in optical devices, in particular, for data detection, conversion of the length of light waves, in optical computational technique, and in other areas.[17—22]

Since the polymers containing amino and azo groups in the main polymer chain combine the properties of PANI and polyazoarylenes and can possess new important properties, it was of interest to study poly(4-aminoazobenzene) synthesized using the electrochemical techniques[23—25] and the chemical method.[26]

In the present work, we studied the electrical properties of poly(4-aminoazobenzene) synthesized by the oxidative polymerization of 4-aminoazobenzene (AAB) with iodine in an ethanolic solution. The results obtained were compared with the known literature data.

Experimental

A sample of AAB was synthesized using a known procedure[27] and purified by recrystallization from ethanol, m.p. 397—399 K.

The electrical conductivity of the samples as pressed pellets was measured on a Teraommetr E6-137 instrument using the two-contact method. ESR spectra were recorded on an SE/X-2543 instrument (Radiopan) (microwave bridge, X range (9 GHz), power to 300 mW, ambient temperature of measurements). Optical spectra were measured using a Specord-50 spectrometer.

Synthesis of polyaminoazobenzene (PAAB).[26] A mixture of AAB (3.0 g), EtOH (33 mL), and iodine (3.87 g) was refluxed with stirring in a water bath for 63 h. Then a saturated aqueous solution of sodium hydrocarbonate (3.0 g) was added, and the mixture was kept for 3 days. The precipitate was filtered off and washed with water until I^- ions disappeared and the neutral pH was achieved. The precipitate was dried in air, extracted with petroleum ether, and separated into two fractions. The fraction soluble in petroleum ether was obtained in a yield of 0.42 g and 2.6 g of the insoluble fraction was obtained. The fraction insoluble in petroleum ether was purified by reprecipitation from a DMF solution with water. Of 2.6 g of the fraction insoluble in petroleum ether, 1.8 g are dissolved and 0.8 g is not dissolved in DMF and DMSO. The yield of the polymer was 2.6 g (87 %).

Polyaminoazobenzene [PAAB(K-1)] was obtained similarly to PAAB. A mixture of AAB (3.0 g), EtOH (33 mL), iodine (3.85 g), and potassium hydrocarbonate (3.04 g) was refluxed for 23 h and then water (60 mL) was added. The fraction soluble in petroleum ether was obtained in a yield of 1.9 g and 1.6 g of the insoluble fraction were obtained. The conversion to polymer was 53.3%.

Polyaminoazobenzene [PAAB(K-1.5)] was synthesized similarly to PAAB(K-1). A mixture of AAB (1.5 g), EtOH (17 mL), iodine (2.9 g), and potassium hydrocarbonate (2.28 g) was heated for 40 h to obtain 0.38 g of the fraction soluble in petroleum ether and 1.1 g of the insoluble fraction. The conversion to polymer 73.3%.

Polyaminoazobenzene [PAAB(Ca)] was synthesized similarly to PAAB. A mixture of aminoazobenzene (1.01 g), EtOH (12 mL), iodine (1.3 g), and calcium carbonate (0.51 g) was heated for 110 h to obtain 0.69 g of the fraction soluble in petroleum ether and 0.4 g of the insoluble fraction. According to the data of ^{1}H NMR spectroscopy, 0.22 g of unreacted AAB was obtained and the conversion was 78%. The yield of polymer was 0.40 g (40%).

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Doping with iodine. The calculated amount of a 0.18 *M* solution of I_2 in CCl_4 was added to a certain amount of the powdered polymer. After 3 days the precipitate was filtered off and washed with a small amount of CCl_4.

To determine the amount of absorbed iodine, the filtrate was titrated with a 0.1 *M* solution of sodium thiosulfate and the polymer was dried *in vacuo* (0.2 kPa/P_2O_5) to a constant weight.

The doping level (*Y*) was calculated from the data of iodine titration and a change in the polymer weight upon doping by the formula

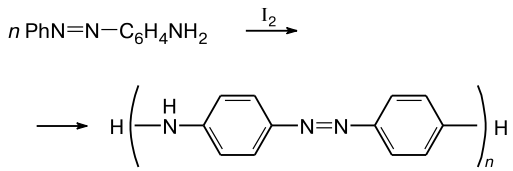
$$Y = N_d/N_m,$$

where N_d and N_m are the number of moles of the dopant and monomeric units of PAAB, respectively.

Results and Discussion

Polymers were obtained from AAB by the oxidative polymerization with iodine in an ethanol solution in the presence of potassium hydrocarbonate at the molar ratio of AAB and iodine equal to 1 : 1 (PAAB(K-1)) and 1 : 1.5 (PAAB(K-1.5)), as well as in the presence of calcium carbonate (PAAB(Ca)) and in the absence of salts (PAAB). The reaction follows Scheme 1.[26]

Scheme 1



The dependences of the electrical conductivity, concentrations of paramagnetic centers (PC), ESR spectral linewidths, and *g*-factor on the level of iodine doping of the synthesized polymers were studied. The electrical conductivity of the undoped polymers varies from $3 \cdot 10^{-10}$ to 10^{-8} S m^{-1} and increases to $4 \cdot 10^{-1}$ S m^{-1} with an increase in the doping level to 1.0 (Fig. 1), which is not inferior to the electrical conductivity of iodine-doped PANI in the oxidation state of emeraldin ($1.83 \cdot 10^{-1}$ S m^{-1})[28] and exceeds that of poly(azo-*p*-phenylene) (10^{-2} S m^{-1}).[29]

According to the published data, when PANI is doped with iodine vapor, a polymer with an I_3^- content of 8.2 mol.% and electrical conductivity to 50 S m^{-1} is formed. The authors of Ref. 30 believe that hydrogen iodide formed during doping also participates in the doping process. It should be mentioned that the conductivity of PANI doped with hydrochloric acid with the dopant content ~8 mol.% is only ~10^{-2} S m^{-1}.[31]

It is known[28] that the dependence of the conductivity of PANI on the level of doping with an ethanolic solution of iodine passes through a maximum at a molar ratio I : N of 1. In the case of poly(azo-*p*-phenylene) doped with iodine vapor at 390 or 320 K, the conductivity maximum is observed in $8 \cdot 10^3$ min or is not achieved even for $9 \cdot 10^4$ min, respectively, depending on the doping duration.

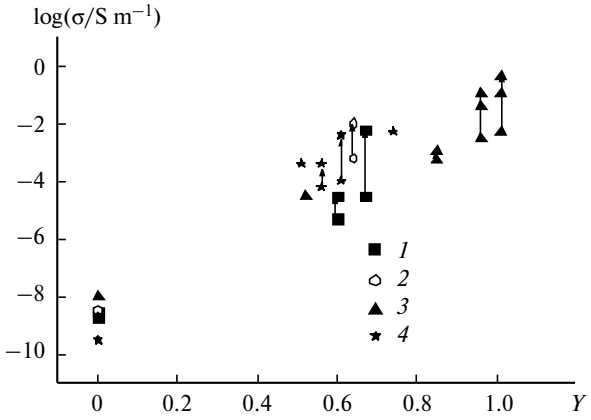


Fig. 1. Electrical conductivity (σ) at 290—298 K *vs* level of iodine doping (*Y*) for the samples PAAB(K-1) (*1*); PAAB(Ca) (*2*), PAAB (*3*), and PAAB(K-1.5) (*4*). Arrows show the change in the electrical conductivity after heating of the sample to 343 K.

In the case of poly(4-aminoazobenzene) synthesized by the oxidative polymerization of AAB with iodine, the conductivity increases and does not pass a maximum with an increase in the doping level to $Y = 1$. Therefore, a higher electrical conductivity at greater doping levels is possible in this case.

In some cases, the electrical conductivity of the iodine-doped polymers measured at room temperature after heating to 343—350 K increases to two orders of magnitude (see Fig. 1), which can be due to a change in the supermolecular structure (morphology) of the doped polymer.

With an increase in the doping level, the ESR spectral linewidth between the points of maximum steepness (Fig. 2) for the polymer samples obtained increases from 0.96—1.1

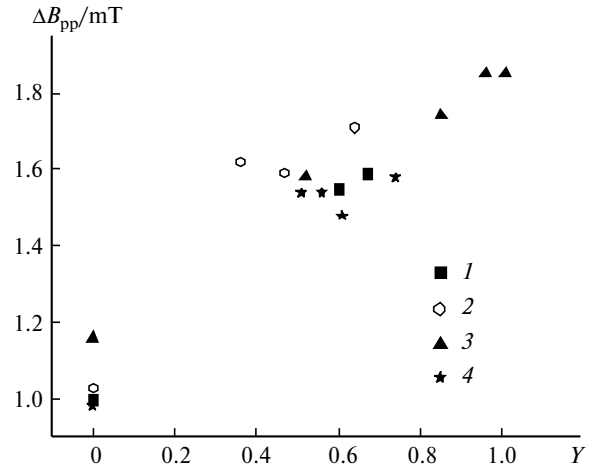


Fig. 2. ESR spectral linewidth (ΔB_{pp}) *vs* level of iodine doping (*Y*) for the samples PAAB(K-1) (*1*), PAAB(Ca) (2), PAAB (*3*), and PAAB(K-1.5) (*4*).

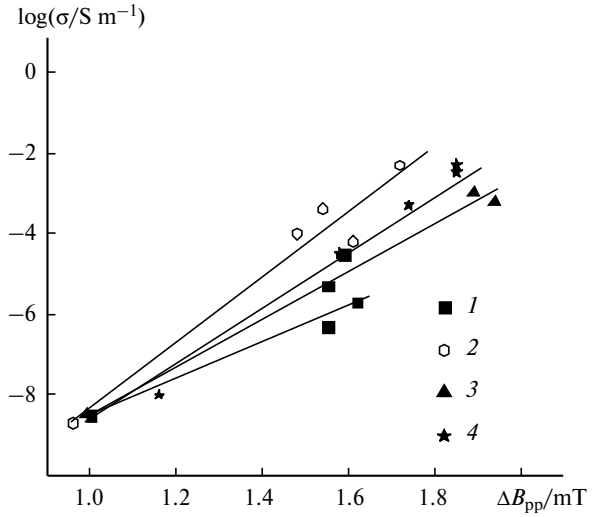


Fig. 3. Electrical conductivity (σ) *vs* ESR spectral linewidth (ΔB_{pp}) for the samples PAAB(K-1) (*1*), PAAB(K-1.5) (*2*), PAAB(Ca) (*3*), and PAAB (*4*).

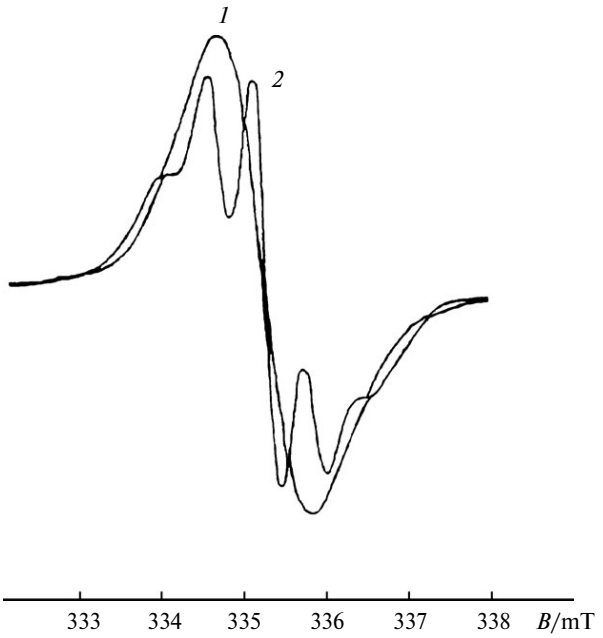


Fig. 4. ESR spectra (solutions in DMF) of PAAB(K-1) (0.13 mol L^{-1}) (*1*) and the complex of PAAB(K-1) (0.13 mol L^{-1}) with iodine (0.12 mol L^{-1}) (*2*).

to 1.58—1.85 mT. Analogously, in the case of poly(azo-*p*-phenylene), the ESR signal width increases to ~1.7 mT, *i.e.*, the lower the conductivity, the narrower the signal width.[30] An almost rectilinear dependence of the logarithm of conductivity (logσ) on the ESR linewidth (Fig. 3) is observed in our case, which can be explained from the viewpoint of the theory of electrical conductivity[32] by an increase in the rate of collisions of moving spin that is proportional to the mobility of the spin carrier (polaron). In other words, the electrical conductivity probably increases due to an increase in the mobility of polarons.

No dependence is observed between the concentration of spins of electrons and electrical conductivity, as it was observed for poly(azo-*p*-phenylene).[30] It follows from the data obtained that PC of doped and undoped polymers differ strongly. It is most likely that undoped polymers contain uncharged PC, whereas doped polymers include charged PC. The latter, unlike uncharged PC, strongly increase electrical conductivity.

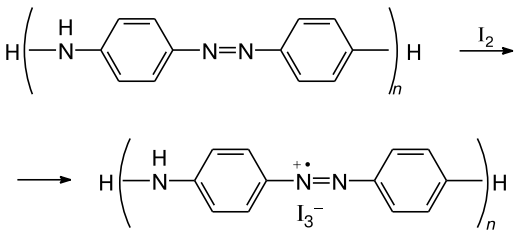
As in the described cases,[29] on doping of the polymer with iodine the value of *g*-factor increases from 2.004 to 2.007 with an increase in the iodine amount in the polymer. The *g*-factor should change depending on the nearest environment of an unpaired electron.

The ESR spectra of solutions of the undoped polymers and their complexes with iodine in DMF were recorded. In the case of the undoped polymers, no hyperfine structure is observed, while for the iodine-doped polymer the hyperfine structure appears and consists of five components (Fig. 4). These data show that, in the latter case, the unpaired electron in solution is mainly localized on two nitrogen atoms of the azo group.

The splitting constant on these nitrogen atoms is 0.67 mT, which is comparable with the data for poly(1-*p*-dimethylaminophenylimino-2-*p*-dimethylaminophenylamino-1.4-butanediyl): 0.73 mT,[33] whereas for *N*,*N*′-di-*n*-octyl-*p*-phenylenediamine and *N*,*N*′-di-*sec*-octyl-*p*-phenylenediamine the splitting constant is 0.51 and 0.62 mT (see Ref. 34).

The results obtained indicate the formation of a charge-transfer complex between iodine and the polymers (Scheme 2).

Scheme 2



This conclusion is confirmed by the data of UV spectroscopy (Fig. 5): new very intense absorption band appear at 296 and 366 nm due to the interaction of iodine with the polymer in DMSO. These absorption bands also appear in a solution of potassium iodide and iodine in DMSO (see Fig. 5) and are assigned to the absorption of ions I_3^- and I_5^-. It was shown[28] that iodine-doped PANI includes ions I_3^- and I_5^- and the relative concentration of anion I_5^- increases with an increase in the iodine concentration.

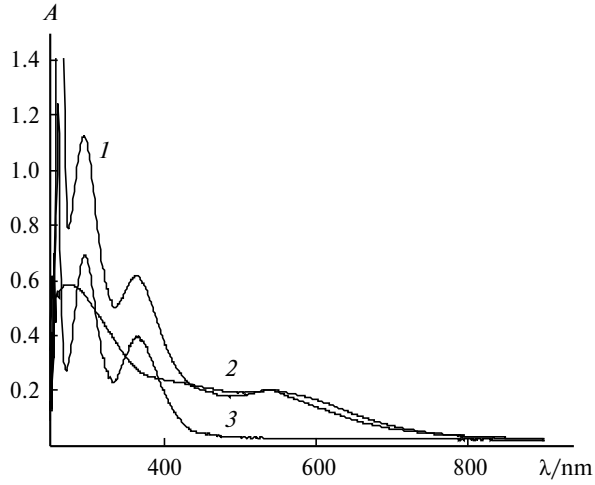


Fig. 5. Optical absorption spectra (DMSO): *1*, PAAB + I_2 ($4 \cdot 10^{-5}$ mol L^{-1}); *2*, PAAB ($4 \cdot 10^{-5}$ mol L^{-1}); *3*, potassium iodide ($7.1 \cdot 10^{-6}$ mol L^{-1}), iodine ($10.25 \cdot 10^{-6}$ mol L^{-1}).

Thus, upon doping with iodine the mainly soluble polymers obtained by the oxidative polymerization of AAB with iodine form charge-transfer complexes manifesting semiconduction properties with the medium and low electrical conductivity.

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