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Oxidative Polymerization of 4-Aminoazobenzene under the Action of Iodine

A. A. Durgaryan, R. A. Arakelyan, and N. A. Durgaryan

Yerevan State University,
ul. A. Manukyana 1; Yerevan, 375025 Armenia
E-mail: durgaryan@ysu.am

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Abstract—Chemical oxidative polymerization of 4-aminoazobenzene under the action of iodine was studied for the first time. Samples of poly(4-aminoazobenzene) with different molecular mass depending on the reaction conditions were obtained. Their structures were studied by means of the IR and ^{1}H NMR spectroscopy and viscometry. The polymers obtained contain mainly imino-1,4-phenylenazo-1,4-phenylene units. Together with the polymers, 3-iodo-4-aminoazobenzene is also formed.

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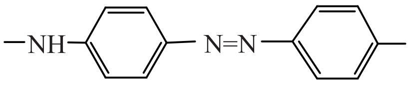
Polyaniline occupies special place among the electroactive polyconjugated polymers due to its stability to the action of the environmental conditions, and because of the easy and cheap method of its synthesis and the unique properties [1, 2]. It has a broad spectrum of probable use as the anticorrosion covering [3, 4], in the accumulator batteries [5–7], for the separation of gases and hardly separable liquids [8–10], as bio- and chemosensor [11–13], etc. [14–16].

In the series of polyconjugated electroactive polymers the substances containing aromatic azo-groups in the main chain and in the side groups [17] are studied rather scarcely. Such polymers present certain interest in connection with the possibility of their use in optical devices, in optical computers, for writing information on the polymer films [18], for conversion of the light wavelength, as the electrode for the light-emitting diode [19], etc. [20–22].

Synthesis of electroconducting polymer containing the amino and the azo-groups in the main polymer chain is actual because the polymers obtained combine specific features of polyaniline and polyazo-arylenes and may exhibit new valuable properties. With the purpose of obtaining such polymers we for the first time studied chemical oxidative polymerize-tion of 4-aminoazobenzene under the action of iodine. Electrochemical polymerization of aminoazobenzene was studied previously, and on the basis of the IR and Raman spectral data the structure of polymer consisting mainly of the repeating structural units **I** was offered [23–25].



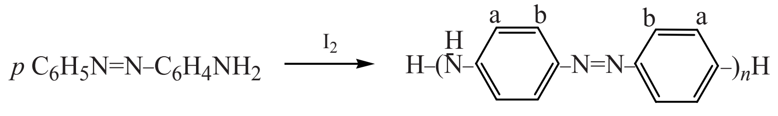
I

Oxidative polymerization of aminoazobenzene under the action of iodine was carried out in boiling ethanol at the equimolar reagent ratio. Basing on the solubility in petroleum ether the reaction products were separated to give two fractions. The soluble fraction consisted of low molecular weight compounds, while the insoluble one, PAAB-1, is a polymer partially soluble in DMF and DMSO (characteristic viscosity 0.11 dl g^{-1} in DMF at 298 K). Acidity of the reaction mixture alters in the course of the reaction due to formation of hydrogen iodide. With the purpose of establishing the dependence of the yield and the molecular mass of polymer on the acidity of the medium oxidative polymerization of aminoazobenzene was studied in presence of potassium hydrocarbonate at the aminoazobenzene:I$_2$ 1:1 and 1:1.5 molar ratio, and also in the presence of calcium carbonate at the aminoazoben-zene:I$_2$ 1:1 molar ratio to give the polymers PAAB(K-1), PAAB (K-1.5), and PAAB(Ca) respectively. Experimental data show that in all the cases presence of salts decreases the conversion of monomer to polymer. In the case of PAAB-1 it is 87%, PAAB(K-1.5) 73.3%, PAAB(K-1) 53.3%, PAAB(Ca) 40%. These polymers completely dissolve in DMF, but their molecular mass is low as compared to PAAB-1. For PAAB(K-1) and PAAB(K-1.5) [η] is 0.1 dl g^{-1}, and for PAAB(Ca) [η] is 0.08 dl g^{-1} at 298 K.

In the IR spectra of obtained polymers PAAB-1, PAAB(K-1), PAAB(Ca), and PAAB(K-1.5) absorption bands of primary amino groups of the aminoazobenzene at 3400, 3450, and 1615 cm^{-1} are absent, and the absorption bands of secondary amino groups at 3199–3380 cm^{-1} are observed. Hence, in the course of the reaction primary amino groups are converted to secondary ones, while azo groups remain intact (absorption at 1405 cm^{-1}, see the table). Presence of absorption band at 830–836 cm^{-1} (*p*-disubstituted benzene ring 2H), and practically absence of absorption at 880 cm^{-1} (1H) shows that the amino group occupies mainly *para*-position respectively to the azo group.

According to these data the oxidative polymerizetion of aminoazobenzene as well as its electrochemical polymerization [23, 24] can be described by following reaction.

Scheme 1.



In the ^{1}H NMR spectra of all the polymers the signals of protons in DMSO are broadened (δ, ppm in DMSO). Considering that the signals of protons of *p*-diphenylenamine units in poly(diphenylamin-4,4'-diyl) in trifluoroacetic acid are observed at 7.52 ppm [26], and of $[C_6H_4(BOC)NC_6H_4NH–]_n$ in THF at 7 ppm as two doublets [27], and also that the signals of protons in *o*-position in relation to azo group are observed in the monomer at 7.6–7.8 ppm, while in 7-(4-*N,N*-dihydroxyethylaminophenylazo)-2-nitro-9-fluorene *ortho*-proton of azophenyl group gives a signal at 8.01 ppm [28], following assinment of the signals can be made. The signals at 7.34–7.66 ppm belong to the *ortho*-protons in relation to amino groups and the amino group protons, while the signals at 7.66–8.10 ppm belong to the *ortho*-protons in relation to azo group. Integral intensity of the latter is smaller as compared to the signal at 7.34–7.66 ppm that is explained by the presence of terminal groups in the polymer (Scheme 1).

To improve resolution in the ^{1}H NMR spectrum of PAAB-1 it was taken at different temperatures (Fig. 1)

Absorption bands in the IR spectra of polymers and the 4-aminoazobenzene monomer

PAAB(K-1)	PAAB(Ca)	PAAB(K-1.5)	PAAB-1	AAB
3380, 3310	3334, 3199	3300	3220; NH	3400; 3450, NH
3057	3059	3060	3050	3050; 1613, NH
1588	1593	1586	1590	1587, benzene ring
1504	1497	1500	1502; 1475	1504, benzene ring
1462		1460	1460	1460, N=N
1436		1420	1420	
1409			1409	1408, N=N
1298	1302	1300	1302	1299; =N–Ar
1230			1220–1240	1235; =N–Ar
1175	1180	1180; 1150	1180; 1150	
1138	1130	1136	1138	1136, C–N=
1070	1070	1070	1100; 1070	1111, –C–N, N–N
1018	1015	1015	1013	–C–N, N–N
925		930	950	
833	831	834	830	833 (2H)
765	766	766	766	769 (5H)
686	689	686	687	690 (5H)

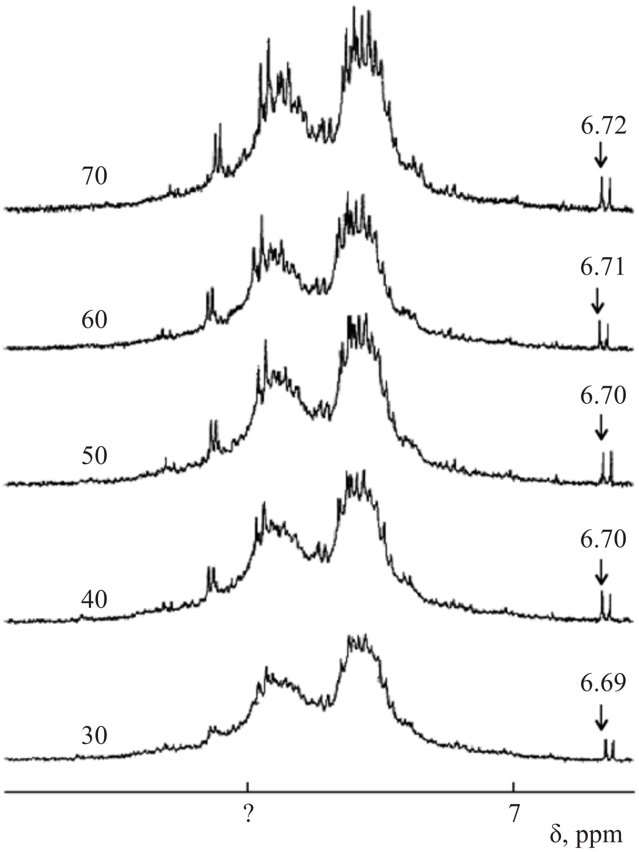


Fig. 1. ^{1}H NMR spectrum of PAAB-1 polymer (δ, ppm in DMSO-d_6). Registration temperature, °C, is given above each spectrum.

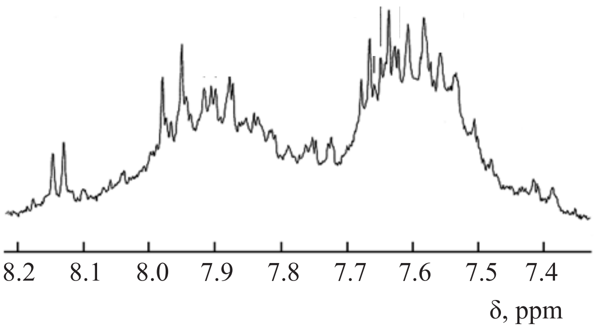


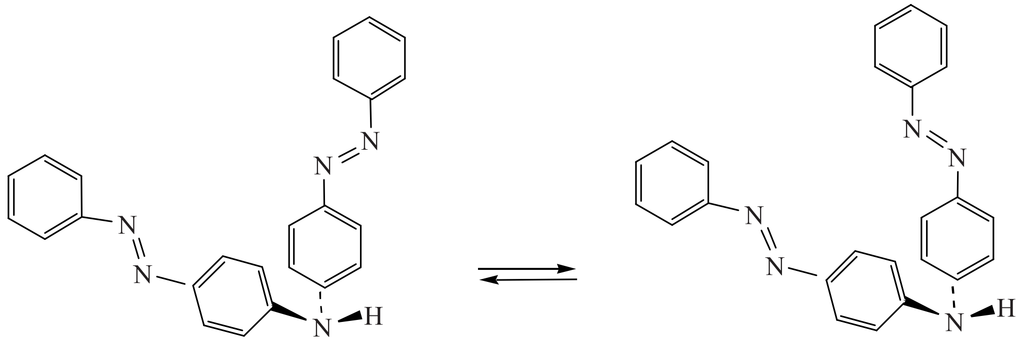
Fig. 2. ^{1}H NMR spectrum of PAAB-1 polymer [δ, ppm in $(D_3C)_2SO$] at 70°C.

in the range 30–70°C. Increase in temperature improves the resolution, and for the spectrum obtained at 70°C (Fig. 2) the following assignment can be made: the protons a at 7.63 ppm, d, *J* 8.73 Hz; 7.64 ppm, d, *J* 8.73 Hz; 7.67 ppm, d, *J* 8.7 Hz; 7.62 ppm, d, *J* 8.33 Hz; 7.66 ppm, d, *J* 4.76 Hz; protons *b* 7.97 ppm, d, *J* 8.73 Hz; 7.89 ppm, d, *J* 8.33 Hz; 8.13 ppm, d, *J* 4.76 Hz; protons a and b of terminal groups: 6.69 ppm, d, and 7.73 ppm, d, *J* 8.73 Hz respectively. Presence of a large number of signals can be explained by slow interconversion of monomers due to rotation about N–C bond, for example as is shown in Scheme 2.

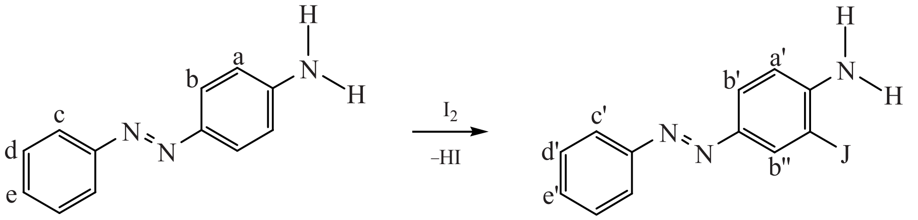
The fraction with low molecular mass soluble in petroleum ether was also studied by means of ^{1}H NMR spectroscopy in DMSO-d_6 (Fig. 3). The sample under investigation was obtained parallel to PAAB-1 polymer. It was found that it is an equimolar mixture of two compounds, aminoazobenzene and 3-iodo-4-aminoazobenzene. The elemental analysis data show that nitrogen content in the obtained low molecular fraction is 16.11; 15.93% that corresponds to the calculated value 16.15% for the equimolar mixture of compounds. It permits to conclude that in parallel to polymerization, the substitution of hydrogen with iodine in the monomer slowly proceeds (Scheme 3).

^{1}H NMR and the elemental analysis data for the soluble fraction obtained in the course of oxidative polymerization of aminoazobenzene in presence of potassium carbonate was considered analogously. Composition of the obtained mixture of low molecular compounds is presented in the Experimental. Performing the reaction of aminoazobenzene with iodine in the presence of calcium carbonate leads to increase in the

Scheme 2.



Scheme 3.



yield of the iodine derivative that can be explained by the fact that CaI_2 obtained in the course of the reaction acts as a Friedel–Krafts catalysts to favor the substitution with iodine. This effect may be used for the preparing the iodine-substituted aminoazobenzene.

IR spectra of all low molecular fractions contain the absorption bands common to aminoazobenzene as well as to iodoaminoazobenzene, and also the absorption bands of the 1,2,4-substituted benzene ring [δ_{C-H} 890 cm^{-1} (1H)]. The bands at 680 and 650 cm^{-1} belong evidently to C–I bond and are characteristic only of the iodine derivative.

Hence, a procedure for preparing PAAB by means of chemical oxidative polymerization of the aminoazobenzene is developed for the first time. The structure of the polymers obtained is established. It is shown that substitution with iodine in the molecule of monomer leading to the iodine derivative proceeds simultaneously.

EXPERIMENTAL

Aminoazobenzene was prepared according to the established procedure and purified by crystallization from ethanol, mp 124–126°C [29]. IR spectra were registered on a FT IR Nicolet Nexus spectrometer in KBr pellets and by means of ATR technique on the ZnSe crystal. ^{1}H NMR spectra were taken on a Varian Mercury 300 spectrometer in DMSO-d_6.

Synthesis of polyaminoazobenzene [PAAB-1]. A mixture of 3.0 g of aminoazobenzene, 33 ml of ethanol, and 3.87 g of iodine was refluxed with stirring on a water bath for 63 h. The mixture obtained was treated with a saturated water solution of 3.0 g of sodium hydrocarbonate and left for 3 days. After that reaction mixture was filtered, washed with water until the disappearance of iodide anions and the neutral reaction of the medium. Precipitate obtained was dried in air, extracted with petroleum ether, and two frac-

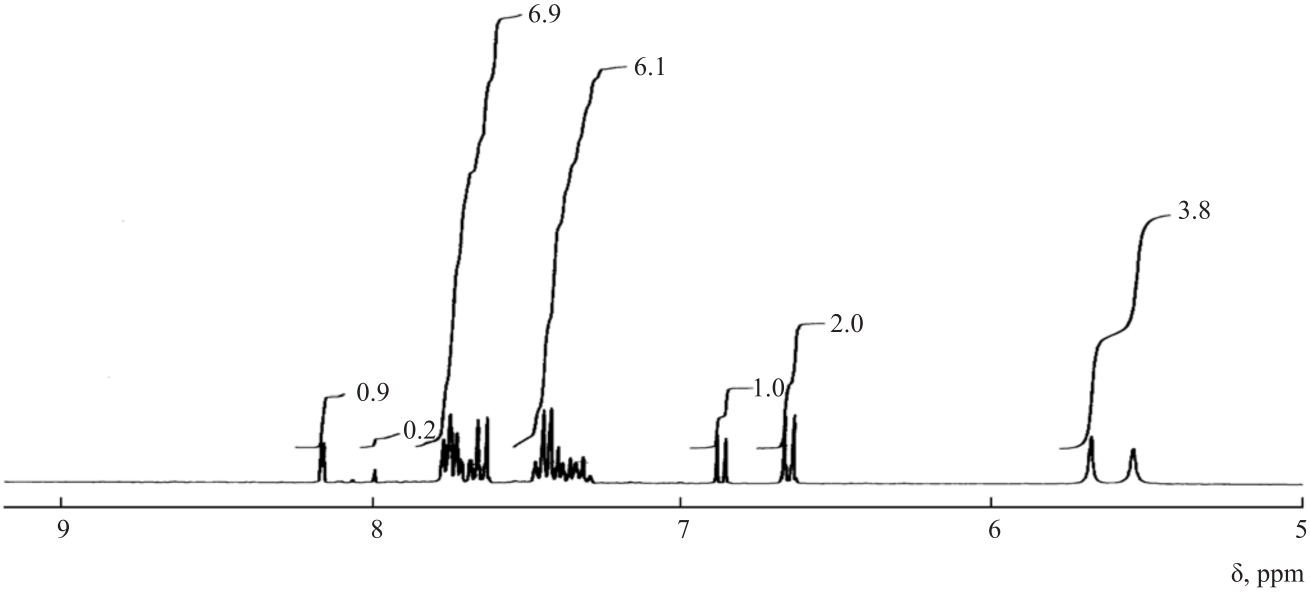


Fig. 3. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, of low molecular fraction formed with PAAB-1.

tions were separated. One of them, 0.42 g, was soluble in petroleum ether, while another one, 2.6 g, was insoluble. The last fraction is partially soluble in DMF and DMSO (1.8 g), while 0.8 g remains undissolved. According to ^{1}H NMR data from 3 g of aminozobenzene 2.6 g (87%) converts to a polymer, 0.16 g (5.3%) converts to 3-iodo-4-aminoazobenzene, and 0.16 g (5.3%) remains unreacted. The fraction insoluble in petroleum ether was purified by precipitation from DMF solution with water. ^{1}H NMR spectrum, δ, ppm (J, Hz): aminoazobenzene: 5.52 s (NH_2), 6.64 d ($2H^a$, J_{ab} 8.73 Hz), 7.65 d ($2H^b$, J_{ab} 8.73 Hz); 3-iodo-4-aminoazobenzene: 5.68 s (NH_2), 6.87 d ($1H^{a'}$, $J_{ab'bd'}$ 8.73 Hz), 7.70 d ($1H^{b'}$, $J_{ab'bd'}$ 8.73 Hz, $J_{b'b''}$ 2.37 Hz), 8.19 d ($1H^{b''}$, $J_{b'b''}$ 2.37 Hz), 7.74-7.78 m ($4H^{c},{}^{c'}$), 7.29–7.47 m ($6H^{d,d',e,e'}$).

Synthesis of polyaminoazobenzene [PAAB(K-1)] was carried out analogously to PAAB-1. A mixture of 3.0 g of aminoazobenzene, 33 ml of ethanol, 3.85 g of iodine, and 3.04 g of potassium hydrocarbonate was refluxed for 23 h. After that reaction mixture was treated with 60 ml of water to give 1.9 g of the fraction soluble in petroleum ether and 1.6 g of the insoluble one. Conversion to polymer 53.3%.

Synthesis of polyaminoazobenzene [PAAB(K-1.5)] was carried out analogously. A mixture of 1.5 g of aminoazobenzene, 17 ml of ethanol, 2.9 g of iodine, and 2.28 g of potassium hydrocarbonate was refluxed for 40 h to give 0.38 g of the fraction soluble in petroleum ether and 1.1 g of the insoluble one. Conversion to polymer 73.3%.

Synthesis of polyaminoazobenzene [PAAB(Ca)] was carried out analogously to PAAB-1. A mixture of 1.01 g of aminoazobenzene, 12 ml of ethanol, 1.3 g of iodine, and 0.51 g of calcium carbonate was refluxed for 110 h to give 0.69 g of the fraction soluble in petroleum ether, and 0.4 g of the insoluble fraction. According to ^{1}H NMR data recovery of aminoazobenzene 0.22 g (conversion 78%). Yield of the polymer 0.40 g (40%), and of 3-iodo-4- aminoazobenzene 0.47 g (36%).

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