



# Study of the reaction of 1,4-benzoquinone with aniline oligomers and benzidine

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## Abstract

Polymers and oligomers containing fragments of aniline oligomers and benzidine connected with p-benzoquinone have been synthesized. The UV, NMR and IR spectral data, as well as thermal stabilities, of obtained compounds were studied. Some of obtained compounds were oxidized by  $K_2S_2O_8$  using different molar ratio. Electrical conductivities and conductivity activation energies of iodine and hydrochloric acid doped polymers were determined.

**Keywords** Oligomers · 1,4-benzoquinone · Conductivity · Polyaniline

## Introduction

Recently quinone containing polymers have been intensively studied due to their interesting electrochemical [1] and photoconducting [2] properties. Some biological processes have been understood due to this compounds [3–8]. These polymers are also used for preparation of magnetic [6] and electrode [7] materials. It was shown that polymers containing 1,4-benzoquinoneamine groups exhibit good adhesion to wet or rusty steel and can be used for surface drying [8].

Benzoquinone compounds were also of interest as they could be formed as by product during oxidative polymerization of aniline, some studies were dedicated to the reaction of p-benzoquinone (BQ) with aniline and p-phenylenediamine as well [9, 10]. The reaction of benzoquinone with amines processed by Michael addition reaction resulting firstly 2,5-disubstituted hydroquinone and then after in situ simultaneously oxidation by excess of 1,4-benzoquinone, 2,5-disubstituted-1,4-benzoquinone compounds were formed. Recently it has been shown, that this reaction gives opportunity to synthesize conductive polymers containing oligoaniline and aromatic diamine fragments, connected with benzoquinone linkages on the base of cheap and available monomers using industrially available methods. It has been assumed that obtained

polymers could combine the properties of polyaniline and p-benzoquinone groups significantly expanding the range of polyaniline (PANi) applications.

Continuing the study where the first members of the row of polymers having structure depicted on Scheme 1 have been synthesized, the presented work has been done in two directions: firstly to synthesize the next members of the row containing three, four and five aniline units, and since it is well known, that high conductivity of PANi is considerably caused by the sequence of quinonediamine and phenylenediamine groups, to synthesize polymers that additionally contain 1,4-benzoquinone diimine groups and study the relations between polymer structure and electrical properties.

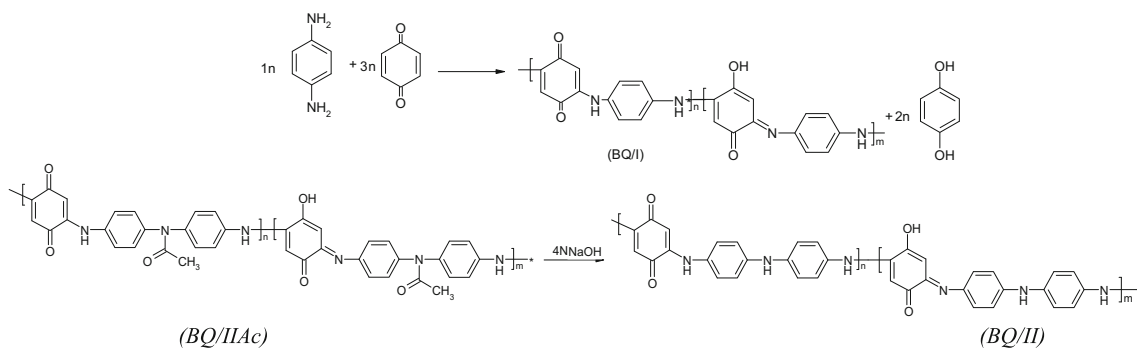
## Results and discussion

### Synthesis and structural elucidation

It has already been established that by the reaction of benzoquinone with aromatic diamines conducting polymers could be synthesized [9–11]. The general method developed for the synthesis of these polymers was easy to perform and requires mixing of reactants in boiling ethanol without any additional catalyst system. Spectral elucidations of both polymers and model compound 2,5-bis[4-aminophenylamino]-1,4-benzoquinone showed that polymers structure composed linear chains that were formed by 1,4-Michael addition reaction. Synthesized polymers are the first members in the row of the structures depicted in Scheme 1 and contain, correspondingly,

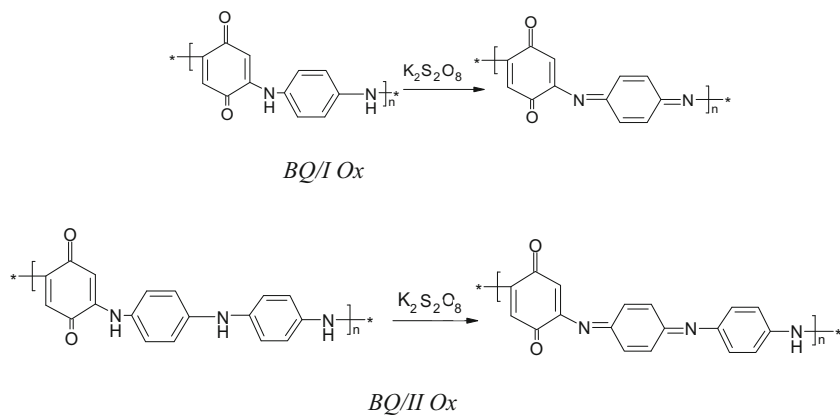
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**Scheme 1** Synthesis of *BQ/I* and synthetic route for *BQ/II*

**Scheme 2** Oxidation of aniline fragments of polymers *BQ/I* and *BQ/II*



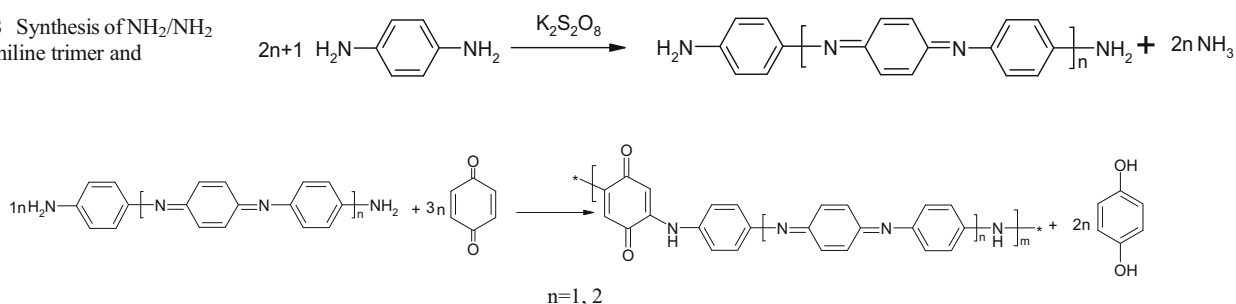
**Table 1** Values of UV-vis spectra of obtained compounds

Compound	nm	$Y_2/Y_1$ $Y_3/Y_1$
BQ/I	$X_1 = 278$	0,54
	$X_2 = 374$	0,59
BQ/I Ox-0,65	$X_1 = 278$	0,42
	$X_2 = 374$	0,57
	$X_3 = 451$	
BQ/I Ox-1,3	$X_1 = 278$	0,49
	$X_2 = 374$	0,51
	$X_3 = 451$	
BQ/II	$X_1 = 300$	0,35
	$X_2 = 394$	0,35
	$X_3 = 454$	
BQ/II Ox-0,5	$X_1 = 300$	0,38
	$X_2 = 395$	0,33
	$X_3 = 454$	
BQ/II Ox-1	$X_1 = 300$	0,42
	$X_2 = 395$	0,37
	$X_3 = 454$	
III	$X_1 = 261$	1,02
	$X_2 = 339$	0,65
	$X_3 = 496$	
BQ/III	$X_1 = 262$	0,380
	$X_2 = 420$	0,33
	$X_3 = 497$	
IV	$X_1 = 263$	0,77
	$X_2 = 302$	0,28
	$X_3 = 420$	
BQ/IV	$X_1 = 278$	0,63
	$X_2 = 356$	0,31
	$X_3 = 502$	
BQ/Bz	$X_1 = 317$	0,34
	$X_2 = 420$	

one (refers as *BQ/I*) and two (refers as *BQ/II*) phenylenediamine units connected with benzoquinone groups. Polymers' conductivities were increased on more than 4 order and achieved to maximum  $10^{-6}$  S/cm. The major idea in order to improve conductivity was to incorporate benzoquinonediimine units into polymer structure by oxidation of obtained polymers with potassium peroxydisulphate. This approach is based on the fact, that the formation of mobile charge carriers in polyaniline like structures depends on the sequence of quinonediimine and phenylenediamine groups in polymer. For this purpose, polymer to oxidant two different molar ratios have been used for each polymer: for *BQ/I*-1:0,65 (*BQ/I Ox*-0,65) and 1:1,3 (*BQ/I Ox*-1,3), for *BQ/II*-1:0,5 (*BQ/II Ox*-0,5) and 1:1 (*BQ/II Ox*-1) (Scheme 2).

Comparison of UV-vis spectra of obtained polymers with different oxidation degrees with initial polymers shows change in relative intensities of 1,4-disubstituted phenylenes ( $n-\pi^*$  transition at 300 nm) to 1,4-benzoquinone groups ( $\pi-\pi^*$  transition at 424 nm) and formation of new band which appears as shoulder at approximately 418 nm (Table 1).

It was notable, that as a result of oxidation, electrical conductivity of obtained as-synthesized polymer *BQ/I Ox*-0,65 was only one order lower than the conductivity of doped with iodine examples of initial polymer with doping level equal to 0,89 (Table 3). This could coincide with the fact, that at lower doping levels oxidation of polymers with dopant takes place, similar to that done by potassium peroxydisulfate and the

**Scheme 3** Synthesis of  $\text{NH}_2/\text{NH}_2$  capped aniline trimer and pentamer**Scheme 4** Synthesis of aniline fragment and benzoquinone group containing polymers

major role in the increase of conductivity is surely caused by the presence of quinonediimine groups in polymer. Room temperature conductivity of the sample *BQ/I Ox-1,3* shows interesting non-constant behavior upon time: it is changed in value in the range of  $5,6 \times 10^{-8} - 1,6 \times 10^{-9}$  S/cm during three hours. This phenomenon, to our knowledge, was noticed for the first time.

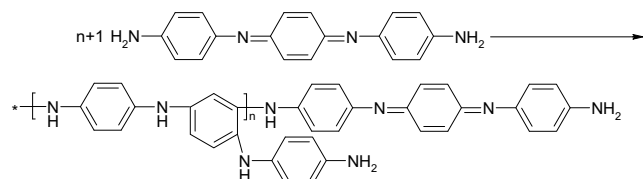
Syntheses of the next members of the row containing in their structure three and five aniline units with oxidized 1,4-benzoquinonediimine groups have been done using as aromatic amines  $\text{NH}_2/\text{NH}_2$  capped aniline trimer and pentamer [11–13]. The latter compounds were synthesized by oxidative condensation of p-phenylenediamine by potassium peroxydisulfate peroxide in acetic acid medium by the known method [12] (Scheme 3).

Tetramer of aniline which corresponds to structural unit of PANi in totally reduced leucoemeraldine form was synthesized by oxidative condensation of acetanilide and 4,4-diamino-N-acetyldiphenylamine with potassium peroxydisulfate and subsequent hydrolysis of the product [13].

Exactly the presence of end amino groups in oligomers structure makes these compounds useful for aimed purposes. Schematically, all implemented syntheses were provided on Scheme 4.

As it turned out, boiling alcohol medium could not be applied for the synthesis involving quinonediimine group containing monomers because of self-condensation reaction, which simultaneously processed at the end point of dropping funnel during the dropwise addition of amine [12] (Scheme 5).

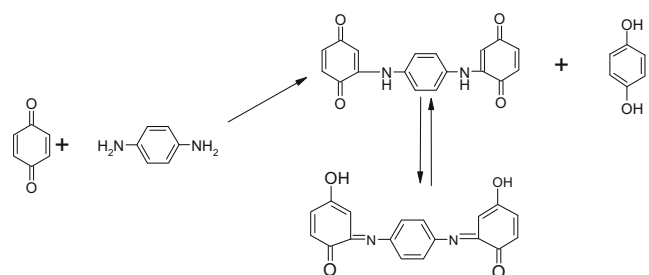
For this reason the reaction was carried out at 20 °C and as a result partially soluble in dimethylformamide (DMFA) and DMSO polymer was synthesized (Scheme 4,  $n=1$ , BQ/III \_).

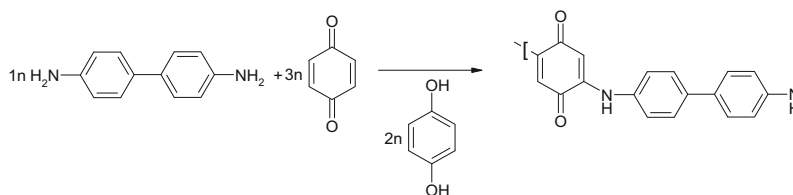
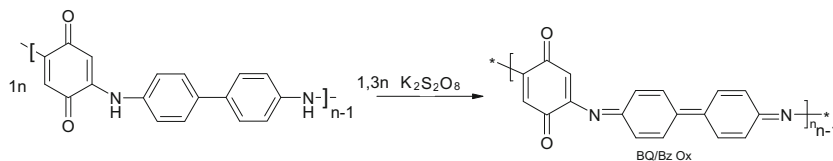
**Scheme 5** Selfcondensation of  $\text{NH}_2/\text{NH}_2$  capped aniline trimer

Additionally in  $^1\text{H}$  NMR spectrum ( $(\text{CD}_3)_2\text{SO}$ ,  $\delta$ , nm) of obtained compound *BQ/III* the integral intensity of NH (OH) groups (8,5–10 ppm (1,76);  $0,87 \times 2 = 1,74$ ) compared with relative intensities of quinone and benzene groups (4,5–8,5 ppm (integral intensity 12,2;  $12,2/14 = 0,87$ )) was lower than expected. This could be caused by oxidation of phenylenediamine groups with 1,4-benzoquinone.

To investigate the possibility of occurrence of parallel reactions, model compound was synthesized by the reaction of (*I*) and *BQ* using 1:6 M ratio of the reagents in boiling ethanol.  $^1\text{H}$  NMR spectrum of obtained model compound in DMSO  $d_6$  (Fig. 1) showed signals of two different groups of protons at 8.5–10 (3,98, integral intensity  $3,98/2 = 1,99$ ) ppm (assigned to N-H and OH protons), 5–8,5 (21,04;  $21,4/10 = 2,14$ ) ppm (assigned to aromatic protons of quinone and phenylene groups). From the ratio of integral intensities of signals of aromatic protons to amino protons 1 to 5, it can be concluded that N,N'-di(1,4-benzoquinone-2-yl)-1,4-phenylenediamine (*BQ/I-6:1*) was obtained (Scheme 6). The down-field shift of amino groups can be explained by the existence of hydrogen bonding of O-H-N type and existence of tautomer forms [11] which make this protons more label. This fact was found its proof in IR spectrum by intense absorbance band at 1135, 1124  $\text{cm}^{-1}$ , 1095  $\text{cm}^{-1}$  and 468  $\text{cm}^{-1}$  (discussed later).

The synthesis of four and five aniline unit containing polymers was carried out by the same method, only aiming to improve the solubility of oligomers, DMSO was used as a solvent. Solubility of obtained polymers decreased with the increase of oligoaniline fragments length, i.e. the trimer and tetramer fragments containing polymers were still partially

**Scheme 6** Oxidation of phenylenediamine groups with 1,4-benzoquinone

**Scheme 7** Synthesis of *BQ/Bz***Scheme 8** Oxidation of benzidine units of polymer *BQ/Bz*

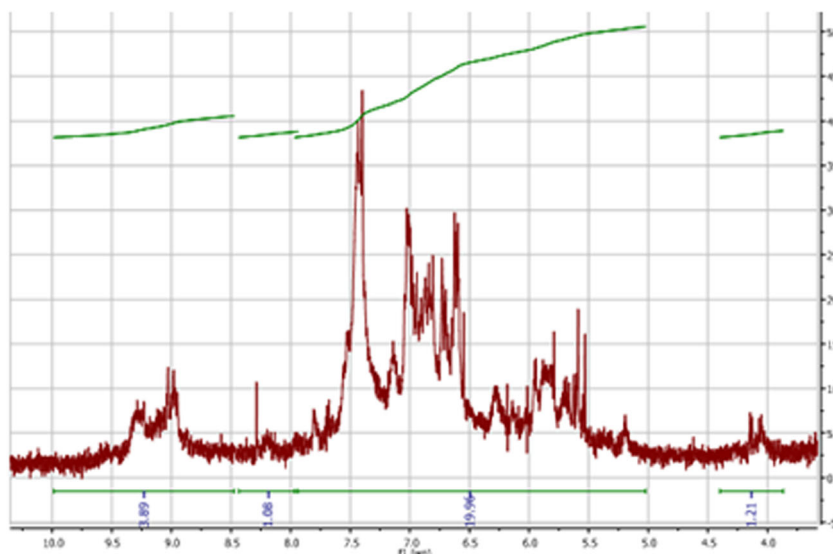
soluble in DMFA and DMSO, pentamer fragment containing polymer was completely insoluble in all applied solvents (chloroform, alcohols, acetonitrile, NMP, DMFA, DMSO). Furthermore, the model compound synthesized by the reaction of (*V*) and *BQ* using 1:6 M ratio of the reagents in DMSO was also insoluble. As it was also interesting to study the structural dependence of conductivities from the alternation of phenylene and amine groups, the reaction of quinone with benzidine (*Bz*) in boiling ethanol medium was carried out (*BQ/Bz*):-(Scheme 7).

The obtained polymer was oxidized by  $K_2S_2O_8$  in 1:1,3 M ratio in formic acid (*BQ/BzOx*) (Scheme 8). UV spectrum of obtained polymer showed absorption in visible range at 420 nm with broad shoulder which includes rather large visible range with maximum at 560 nm.

UV, IR methods were used for the identification of the structure of obtained polymers (exception: only for *BQ/V* and its model compound only IR). All obtained data were compared in Tables 1 and 2. UV spectra of all obtained

polymers contain absorption bands of initial monomers and thus proved the structure of obtained compounds.

Comparison of all IR spectroscopy data (Fig. 2) of newly synthesized polymers and oligomers with already synthesized *BQ/I*, *BQ/III* have been done in Table 2. First of all, it can be mentioned the similarities of proposed data and, then the fact, that the spectra of obtained polymers contain the bands characteristic of corresponding monomers. However some differences have also been noticed. It is known, that the N-H stretching absorption is less sensitive to hydrogen bonding than are O-H absorptions. This and the fact of existence of terminal primary amino groups in polymers (proved also by  $^1H$  NMR spectra) caused only little changes in appearance of new band at 3444 with middle intensity of secondary amino groups for polymers containing quinonediimine groups (*BQ/III*) and the change of intensities of absorptions at 3420, 3342 for *BQ/IV*. Broadening of this region (to  $-3700\text{ cm}^{-1}$ ) (*BQ/V*, *BQ/IV*) and bands at  $3605\text{ cm}^{-1}$  and  $3613\text{ cm}^{-1}$  (*BQ/III* 25 °C and boiling ethanol) appeared as a result of tautomeric OH

**Fig. 1**  $^1H$  NMR spectrum ( $(CD_3)_2SO$ ,  $\delta$ , ppm) of compound *BQ/I* 6:1

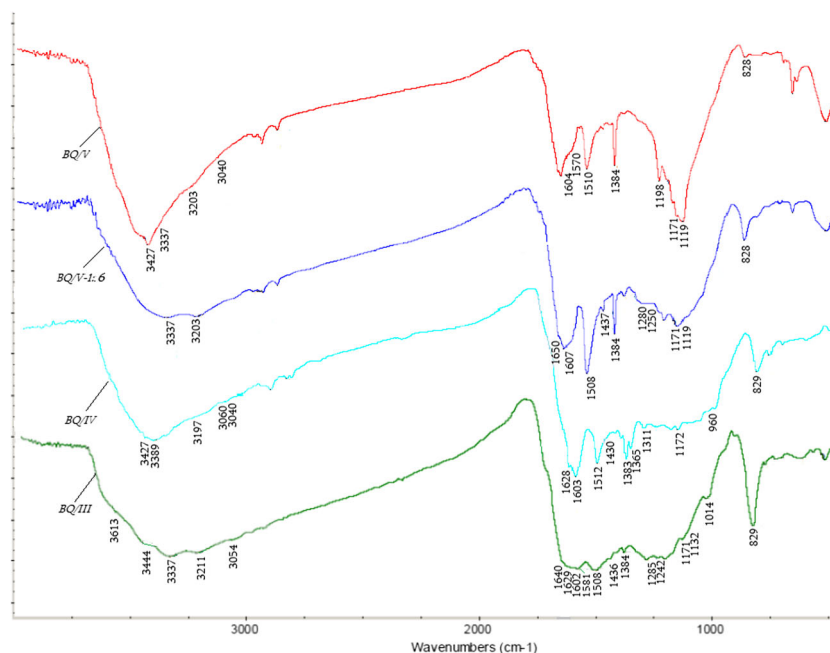
**Table 2** IR spectral data of obtained compounds [15, 16]

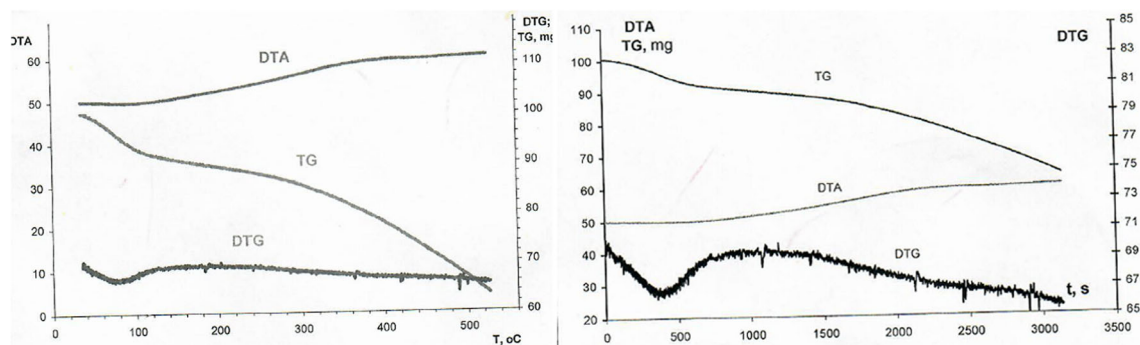
Groups	Compounds							
	BQ/I	II	BQ/II	BQ/III	BQ/III (b)	BQ/IV	BQ/V	BQ/V 1:5
$\nu$ (Capped NH <sub>2</sub> , NH) hydrogen bonded	3441sh	3347w; 3449	3433	3444 s 3613w.sh 3337 s	3427 s 3605w 3341 s	3422 3389	3427 3337 s	3337
$\nu$ (Secondary NH)	3219;	3223 v.w	3271	3211 s	3211	3197	3203 s	3203
$\nu$ (Ar-H)	3060 sh.	3041 w, 3013 w		3054sh	3040w	3040w 3060w	3040w	
$\nu$ quinone (C=O)	1641;	1633 w	1650	1629s 1640sh	1640sh	1628		1650
Skeleton aromatic, NH, Quinonediiimine	1511; 1416; 1385;	1557, 1517 v.w 1434 m; 1483 v.w	1573; 1508; 1468	1602s 1581 1508vs 1436	1605, 1579, 1512	1603 1512 1430	1604s 1570	1607, 1508, 1437
$\nu$ (C-N)	1347; 1283	1359, 1278	1374 1285	1384	1384	1383s 1365 1311		1384
(C-N)	1232; 1206		1285	1285,1242	1278,1241			1280, 1250
Ar-H out of plane	1187' 1132;1101; 1016	1191 v.w	1141; 1179	1132 1171 1014	1174, 1134 1013	1172	1171 1119	1171, 1119
(1C-H) out of plane	961; 899;	689;733	670			960,775		
(1,4-phenylene) out of plane	822	829	826	829	832	829	826	826

groups formation, as a result of interaction of carbonyl with imino group in ortho position. The stretching vibration of C=O of quinone is observed as  $1604\text{ cm}^{-1}$  peak enlargement to approximately  $1650\text{ cm}^{-1}$ . This can also be explained by coordination of oxygen of carbonyl with hydrogen of amino groups by formation of tautomer forms. However, several other peaks with peak positions at  $1135$ ,  $1124\text{ cm}^{-1}$ ,  $1095\text{ cm}^{-1}$  and  $468\text{ cm}^{-1}$  are left unassigned. The intensities of these bands

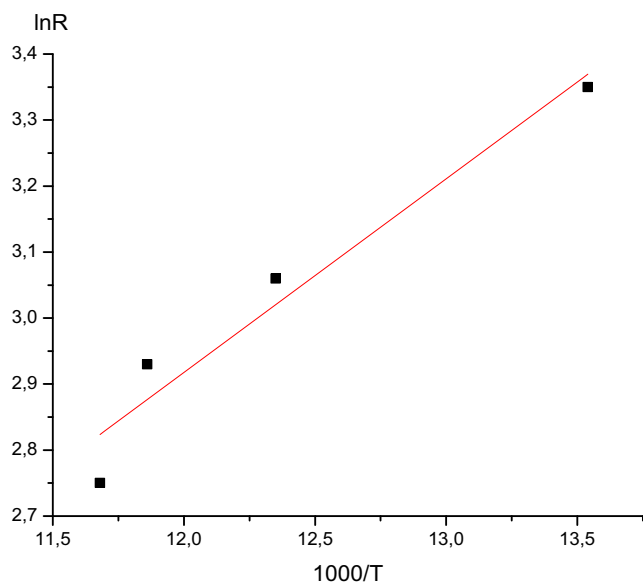
increase with the increase of the number of quinonediiimine units in aniline oligomers and may correspond or may even originate from interaction between two molecules with complex formation resulting tautomeric hydroquinonic forms [14].

Based on the similarity of IR spectra of the soluble and insoluble fractions, it can be concluded, that the observed difference in solubility stems from the differences in molecular weight of polymers.

**Fig. 2** Comparison of IR spectra ( $\nu$ ,  $\text{cm}^{-1}$ ) of compounds BQ/I; BQ/II; BQ/III; BQ/IV; BQ/V; BQ/V-1:5



**Fig. 3** TG,DTG and TG curves of *BQ/V* at a heating rate 10 °C/min



**Fig. 4** Activation energy of *BQ/II Ox-0,5*

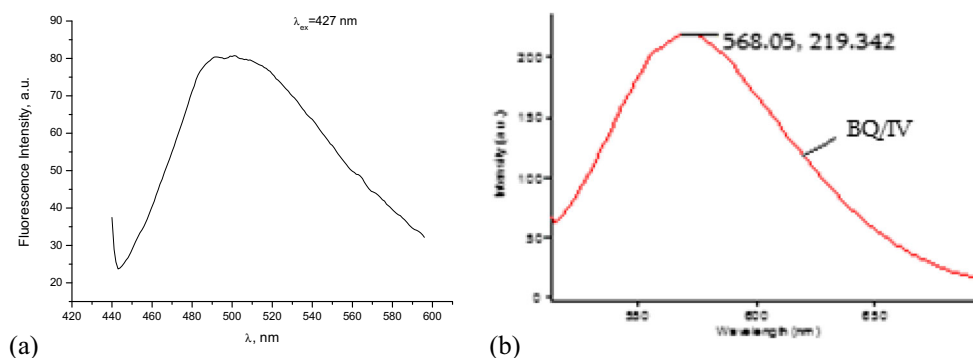
### TGA analysis

TGA analyses of *BQ/V* show three stages of weight loss (Fig. 3). As can be seen from the thermogram, the polymer has significantly different TG (Thermogravimetric), DTA (Differential Thermal Analysis), DTG (Derivative Thermogravimetry) curves for that of the emeraldine base and pernigraniline. The polymer shows a three-step decomposition. The first step ( $T$  lower than 100 °C) corresponds to the desorption of water, solvent residues (10%). The second step corresponds to the very low with only 8% weight loss till 300 °C. For emeraldine base T1/2d, defined as the temperature at which the loss of weight during pyrolysis reaches 50% of its final value, as referred in literature, equals to 540 °C. Under this temperature considered polymer lost only 38% of its initial weight (Fig. 4).

**Table 3** Dependence of electrical conductivities and activation energies of as synthesized and iodine doped polymers from the length of oligoaniline fragment

Compounds	Doping level	Specific electrical conductivity S/cm	Activation energy eV
BQ/I	0,89	$9 \times 10^{-9}$ [11]	
BQ/I Ox-0,65	–	$3 \times 10^{-10}$	–
BQ/I Ox-0,65	0,63	$5 \times 10^{-8}$	0,0044
BQ/I Ox-1,3	–	$5,6 \times 10^{-8}$ - $1,3 \times 10^{-9}$	–
BQ/I Ox-1,3	1,08	$1,6 \times 10^{-8}$	0,704
BQ/II	1,47	$2,3 \times 10^{-7}$	0,9134
BQ/II	1,79	$2,7 \times 10^{-6}$ [11]	
BQ/II Ox-0,5	1,9	$1,36 \times 10^{-6}$	0,0058
BQ/II Ox-1	1,7	$1,3 \times 10^{-6}$	1101
BQ/III	2	$1,9 \times 10^{-6}$	0,724
BQ/IV	1,5	$1,9 \times 10^{-6}$	0,48
BQ/V	1,9	$1,2 \times 10^{-5}$	0,153
BQ/Bz	–	$<10^{-11}$	
BQ/Bz	1,8	$5,5 \times 10^{-6}$	0,56
BQ/Bz Ox	1,82	$6,6 \times 10^{-6}$	0,58

**Fig. 5** Photoluminescent spectrum of (a) *BQ/I Ox-1,3* (491–501 nm), (b) *BQ/IV* (DMSO, nm)



**Table 4** Dependence of conductivity of hydrochloric acid doped polymers from doping level

Compounds	N HCl	Polymer/dopant molar ratio	Doping level	Specific electrical conductivity S/cm
BQ/I	—	—	—	$<10^{-10}$
BQ/I	1	1: 6	0,58	$6 \times 10^{-9}$
BQ/I	4.12	1: 36	0,99	$1,25 \times 10^{-8}$
BQ/I Ox-0.65	4	1:36	1,52	$7 \times 10^{-9}$
BQ/I Ox-1.3	4	1:36	0,88	$1,4 \times 10^{-7}$
BQ/IIOx -0.5	4.12	1:37	0.41	$3.05 \times 10^{-10}$

**DC conductivity, conductivity activation energies, photoluminescent properties**

The variation of DC conductivity of polymers with temperature was studied and reported. The DC conductivity of doped samples were increased by almost 4 order when compared with as-synthesized polymers (Table 3). It was observed that the DC conductivity of all obtained polymers were not much affected with the length of oligoaniline units of the chain and was of  $10^{-6}$  order for doping levels equal to approximately 1,08–1,8. Only for BQ/V electrical conductivity was one order higher. All polymers except BQ/III achieve some

saturation after this value of doping level and subsequent increase in iodine/polymer molar ratio didn't have any influence on doping level. In case of BQ/III doping level was increased till 2, however, not any additional increase of conductivity was observed. Alternation of phenylene units, as well as the oxidation of later compound have low impact on conductivity (Table 3).

It is known that generally; polymers exhibit a similar electrical conductivity behavior depending on temperature to that of semiconductors (Fig. 4). This means that conductivity is increased with increasing temperature and that is because of the increasing charge carriers in the conduction band. The

**Table 5** Reaction of p-benzoquinone with aromatic diamines and oligomers

Compound	BQ g; mmol	Compound g; mmol	Solvent/ ml 1) Methanol 2) Ethanol 3) DMSO	Temp. °C;	Time Hour	Yield g, %
<b>BQ/I-6:1</b>	3; 27,7	<b>I</b> 0,5; 4,63	2)55	84	30 min.	1,096; 75
<b>BQ/I-6:1 Ox</b>	0,2025;1875	<b>BQ/I-6:1</b> 0,2; 0,625	2) 10	84	7	0,1664;84
<b>BQ/IIIa</b>	0,158;1,49	<b>III</b> 0,143; 0,496	2) 20,4	84	1	0,16; 84
<b>BQ/IIIb</b>	0,112; 1055	<b>III</b> 0,101; 0,35	1)39	40	19	0,105;77
<b>BQ/IV</b>	0,0598;0,553	<b>IV</b> 0,0675;0,184	3) 2	20–25	20	0,0745;86
<b>BQ/V</b>	0,13735; 1,29	<b>V</b> 0,19865;0,424	3) 2,3	20	3	0,2495;100
<b>BQ/V-1:5</b>	0,20555; 1,9	<b>V</b> 0,1785; 0,381	3) 1	20	17	0,2224;87,5
<b>BQ/Bz</b>	2,5558;13,89	<b>Bz</b> 4,502; 41,68	2)2	117	1	3,6825; 93

**Table 6** Oxidation of *BQ/I*, *BQ/II* and *BQ/Bz* compounds by  $K_2S_2O_8$ - $n\mu$ 

Compound	$K_2S_2O_8$ g:mmol	Compound g:mmol	Solvent/ ml 1) Formic acid 2) Acetic acid	Hour	Yield g
<b>BQ/I Ox-0,65</b>	0,09173;0,3398	<b>BQ/I</b> 0,11,433;0,5392	1) 5	24	0.1156
<b>BQ/I Ox-1,3</b>	0,2; 0,943	<b>BQ/I</b> 0,33;1226	1) 10	26	0,19
<b>BQ/II Ox-0,5</b>	0,201;0,6638	<b>BQ/II</b> 0,881;0,326	2) 10	23	0,188
<b>BQ/II Ox-1</b>	0,18755;0,619	<b>BQ/II</b> 0,16775;0,621	2) 10	34	0,185
<b>BQ/BzOx-1,3</b>	0,2438; 0,903	<b>BQ/Bz</b> 0,2; 0,6946	1) 10	28	0,216

relation between the effect of temperature and the electrical conductivity for all polymers (*BQ/II*, *BQ/II Ox1,3*, *BQ/III*, *BQ/IV* and *BQ/V*) in the pure and doped state with approximately the same doping level are shown in Table 3. The results clearly showed that there is mainly 1 order increase in the electrical conductivity (reduction in the electrical resistance) with increasing of temperature from 25 to 90 °C in a behavior similar to that of semiconductors. The variation of conductivity for doped polymers of different length of oligoaniline chain as a function of temperature shows that all sample conductivity is increased with increasing temperature characteristic of semiconductors. As conductivity vs temperature follows Arrhenius law, the slope of the graph line was multiplied by Boltzmann constant to find activation energy. Based on the obtained data the following conclusions can be drawn.

- The activation energy was decreased with the increase of the length of oligoaniline chain.
- 0.5–0.65 oxidized units have the lowest activation energy.

Oxidized samples were also doped by hydrochloric acid, but only 2–3 order of increase in conductivities was observed (Table 4).

It's well known that during past several decades there has been enormous demand for polymers with photoluminescent properties and especially polymers which combine semiconducting and photoluminescent properties [17, 18]. Hence, it's noteworthy to mention that polymers *BQ/I Ox-1,3* and *BQ/IV* exhibit blue and green emission peaking at 470–500 nm and 568 nm correspondingly (Fig. 5).

## Materials

1,4-Phenylenediamine (pure grade) was purified by sublimation (mp 143–145 °C) and 1,4-benzoquinone (pure grade) was recrystallized from ethanol. All chemicals were synthesized and recrystallized and were analytically pure. Solvents were used without further purification. *BQ/I* and *BQ/II* compounds were synthesized by known method [11].

## Measurements

IR spectra (KBr) were recorded using a Nicolet Nexus FTIR spectrometer.  $^1H$  NMR spectra were recorded using a Mercury 300 Varian NMR instrument (solution in  $(CD_3)_2SO$ , TMS as reference). UV-vis spectra were recorded using a Specord 50 spectro-photometer (solution in DMSO). For conductivity measurements, polymer powders were pressed into tablets under the pressure (30 kg/cm<sup>2</sup>). Electrical conductivity of the tablets were measured using an AT512 high-sensitivity Ohmmeter.

## Reaction of p-benzoquinone with aromatic diamines and oligomers (Table 5)

To a solution of p-benzoquinone was added corresponding diamine or oligomer solution under continuous stirring. Then the precipitation was filtered off and treated by hot ethanol (until p-hydroquinone disappearance). The product was dried under vacuum until constant weight.

## Oxidation of obtained compounds by potassium peroxydisulfate (Table 6)

To a polymer mixture was added  $K_2S_2O_8$  at 283 K temperature and under continuous stirring. After stirring the reaction mixture was treated by 10% sodium carbonate solution until pH 9 and stirring for 4 h at 273–278 K. The precipitation was filtered and washed by cold water until neutral and absence of  $SO_4^{2-}$  ions. The product was dried under vacuum until constant weight.

## Doping with iodine

A required volume of 0,19 N solution of iodine in  $CCl_4$  was added to a weighed amount of polymer. The mixture was left for 3–4 days at room temperature; the precipitate was filtered off and washed twice with a small volume of  $CCl_4$ . The filtrate



was titrated with 0,1 N solution of sodium thiosulfate and the precipitate was dried to a constant weight in a vacuum dessicator over P<sub>2</sub>O<sub>5</sub> (0.2 kPa). The amount of iodine in the polymer specimen was calculated from the iodine consumption and the gain of the polymer mass. The doping degree was calculated as the molar ratio of iodine to the repeated unit of the polymer.

## Doping with hydrochloric acid

A required volume of hydrochloric acid solution was added to a weighed amount of polymer. The mixture was left for 4–5 days at room temperature; the precipitate was filtered off and washed twice with a small volume of ethanol. The filtrate was titrated with 1 N of potassium bicarbonate, the precipitate was dried to a constant weight in a vacuum dessicator over P<sub>2</sub>O<sub>5</sub> (0.2 kPa). The doping degree was calculated as the molar ratio of hydrochloric acid to the repeated unit of the polymer. The doping level was calculated by the formula  $Y = \text{mole of dopant} / (\text{mole of repeating units of polymer})$ .

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