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Investigation of addition reaction of sodium thiosulfate pentahydrate to quinonediimine groups

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Abstract

It was established that the reaction of sodium thiosulfate with poly(p-phenylenediamine)—poly(1,4-benzoquinonediimine-*N,N′*-diyl-1,4-phenylene) and its derivative with acetylated end amino groups results in 1,4-addition of thiosulfate to quinonediimine groups. The same reaction was investigated with its model compound *N,N′*-di(4-acetaminophenyl)-1,4-benzoquinonediimine. The reaction conditions for high conversion of quinonediimine groups were worked out. Electrical conductivity of obtained polymers was less than 10^{-10} S/cm and was increased with doping level increase up to 2.8×10^{-6} S/cm when doping with iodine.

Keywords 1,4-Addition · Conductivity · Polyaniline · Pernigraniline · Thiosulfate

Introduction

Electroactive polymers synthesized by oxidative polymerization technique from aromatic amines are of huge interest due to the easy method of preparation, stability and possibilities of application in different areas of industry [1–3]. Among these polymers, polyaniline (*PANI*) is most attractive and promising [1–4]. Aiming to obtain *PANI* with improved mechanical properties and processability, huge work has been done on the synthesis of substituted *PANI* using copolymerization method [5–7].

It is well known that *PANI* exists in three states that differ from each other by oxidation degrees: Pernigraniline is fully oxidized, emeraldine half oxidized and leucoemeraldine fully reduced state of polymer. Emeraldine state of polymer is most stable, and in salt form, it exhibits increase in conductivity of almost 6 order. Commonly used method to synthesize other two states of *PANI* is reduction/oxidation of emeraldine form.

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Recently, polymer having similar structure to pernigraniline, poly(1,4-benzoquinonediimine-*N,N′*-diyl-1,4-phenylene) compound (*1*) [8] and *N,N′*-di(4-aminophenyl)-1,4-benzoquinonediimine [9] has been synthesized on the base of p-phenylenediamine(PPDA) by one-step method in organic medium (Scheme 1).

This new method of synthesis of the polymer with pernigraniline structure has stimulated the interest to obtain polymer analogues to emeraldine base by reduction in half part of quinonediimine groups in the polymer chain. For reduction of emeraldine hydrazine [10], sodium thiosulfate [11] and *N,N*-diethylhydroxylamine, sodium tetrahydroborate, sodium dithionite [12] were used as reductants. Pernigraniline is highly reactive due to the presence of quinonediimine groups connected via phenylene rings and, as it had been proved previously, could not be reduced to other form of *PANI* by hydrazine hydrate being commonly used reducing agent for emeraldine [8]. 1,4-Addition reaction of hydrazine to quinonediimine groups of compound 1 results in substituted *PANI*. Despite futile efforts to obtain half and totally reduced forms of *PANI* from compound 1, which has pernigraniline like structure, the reaction with hydrazine shows the opportunity to obtain substituted *PANI* with regular structure in case of 100% conversion. The latter has been difficult to implement by other methods.

In this paper, we continue the investigation of the reaction of pernigraniline-type compounds: compound *1*, *1* with acetylated end amino groups (compound *2*) and model compound *N,N′*-di(4-acetylaminophenyl)-1,4-benzoquinonediimine (compound *3*) with sodium thiosulfate, the reagent which has been used for reducing emeraldine [11].

Experimental

Measurements and materials

p-Phenylenediamine 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. Compounds *1*, *2*, *3* were synthesized by the known methods [5 and 6]. IR spectra (KBr pellets) were recorded by FTIR Nicolet Nexus. ^{1}H NMR spectra were obtained in deuterated DMSO using a Mercury 300 Varian NMR and TMS as internal reference. Spectra
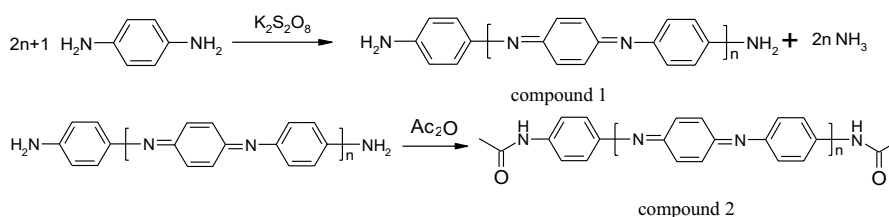
Scheme 1 Oxidative polycondensation of p-phenylenediamine and acetylation of terminal amino groups of obtained polymer

in UV and visual diapason were recorded on Specord 50 in DMSO and N-methyl-2-pyrrolidone (NMP) solutions. Electrical conductivity was measured by the four-probe method using model high-precision ohmmeter AT512.

Chemicals

Synthesis of compound *1* [8]

To a solution of 2.0 g (19 mmol) of p-phenylenediamine 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% of 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^{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%).

Synthesis of compound *2* [8]

0.10200 g (0.2 mmol) of compound 1 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 iced distilled water till neutral reaction and then with methanol and dried on air. Then, the polymer was dried in vacuo desiccator over phosphorous pentoxide (288 K/2 kPa). The yield was 0.10 g.

Synthesis of compound *3* [9]

Potassium peroxodisulfate 0.62 g (2.3 mmol) was added to a solution of 0.75 g (7 mmol) of *p*-phenylenediamine and 0.476 g (2.3 mmol) of *p*-phenylenediammonium sulfate in 6 mL of glacial acetic acid at 15–16 °C, and the mixture was stirred for 21 h. The mixture was kept in a refrigerator at 6 °C each time when the stirring was interrupted. It was then treated with 10% aqueous sodium carbonate to pH 9 and stirred for 4 h at 2 °C. The precipitate was filtered off, washed on a filter with cold water until neutral washings and the absence of sulfate ions therein, dried in air, treated first with methanol at 15–16 °C and then with diethyl ether and dried under reduced pressure over P_2O_5 (0.2 kPa).

A solution of 0.05005 g (0.174 mmol) of methanol soluble fraction in a mixture of 2 mL of acetic acid and 0.08 mL(0.787 mmol) of 93% acetic anhydride was

stirred for 7 h at 15 °C. The mixture was treated with 10% aqueous sodium carbonate to pH 9 and stirred for 4 h at 2 °C. The precipitate was filtered off, washed on a filter with ice water until neutral washings, dried in air, treated with methanol at 15 °C and dried in a vacuum desiccator over P_2O_5 (0.2 kPa). The yield was 0.05 g (77%), $mp > 290$ °C. IR spectrum, ν, cm^{-1}: 3431, 3249(N–H), 3034 (C–H arom), 2925, 2848 (C–Haliph), 1631(C=O), 1605 (C=C arom), 1564 (C=N), 1500 (C=C, quinone), 1384, 1306 (=N–C), 1213 (N–C), 1096, 1024 (C–Harom), 815 (δ C–Harom). ^{1}H NMR spectrum, δ, ppm: 2.00s (6H, CH3), 5.40s, 6.15s (4H, quinone), 6.65d and 7.50d (4H each, H arom), 9.80s (2H, NH). Found, %: C 70.85; H 5.50; N 14.93. $C_{22}H_{20}N_4O_2$. Calculated, %: C 70.97; H 5.38; N 15.05.

The reaction of compounds *2* and *3* with sodium thiosulfate pentahydrate (Table 1)

To the solution of formic acid and compound 1, 2 and 3 was added sodium thiosulfate pentahydrate. The reaction proceeded under continuous stirring at 288 K. Every time after stirring, the reaction mixture was kept in refrigerator at 278 K. Then, the reaction mixture was treated by an aqueous solution of sodium carbonate 10 hydrate under continuous stirring during 6 h up to pH 9 at 273–278 K. The product was collected by filtration and rinsed by distilled water until neutral pH and to the absence of $S_2O_3^{2-}$ ions in the precipitation. The product was vacuum-dried at 288 kPa to constant weight.

Doping by iodine

Different amounts of 0.18 N iodine solution in CCl_4 were added to polymer powder with certain weight and kept at room temperature. After 3 days, polymer was filtered, washed with small amount of CCl_4 and dried in 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 the formula $Y =$ mole of iodine/(mole of 1.4-benzoquinonediimine-*N,N′*-diyl-1,4-phenylene units).

Results and discussion

The reaction was carried out in formic acid at 288 K with sodium thiosulfate: compound 2 molar ratio of 1:1.3. The reaction mixture was kept in refrigerator at 278 K every time when the stirring was interrupted. The choice of compound 2 as the starting point of investigation intends to exclude the other possible 1,4-addition reaction of amino end groups to quinonediimine structural units proved by us earlier [9].

Spectroscopic measurements have been provided by information on the electronic structure of all forms of *PANI*. UV spectroscopy was the most expedient method to evaluate the conversion of quinonediimine groups by changing relative intensities of absorption peaks at 418 nm to 268 nm [13]. Comparison of UV–Vis spectra of obtained compound *4a* with initial compound *2* coincides with the fact that quinonediimine groups were partially conversed into amino phenylenes

Table 1 Data of reaction of compounds 2 and 3 with sodium thiosulfate pentahydrate

Obtained compound	Reactant			$Na_2S_2O_3 \cdot 5H_2O$		Formic acid ml	Reaction duration		Yield		Conversion
	Initial compound	g	mmol	g	mmol		Hour	Day	%	g	%
4a	2	0.14940	0.83	0.26759	1.07	7.2	19	10	41.5	0.092	51
4b		0.2368	1.315	0.65300	2.633	16	7	10	36.7	0.165	94
4c		0.2089	1.16	0.57575	2.32	14.5	74	13	59	0.235	96
5a	3	0.0503	0.135	0.04360	0.175	1.68	35	10	83	0.0496	38
5b		0.0984	0.264	0.13140	5.29	5.2	74	14	52	0.075	–

Fig. 1 UV-Vis spectra of polymers **2**, **4a** and **4c** (DMSO, λ, nm). Spectrum of polymer 2 was conducted in N-methyl pyrrolidone (NMP) [8]
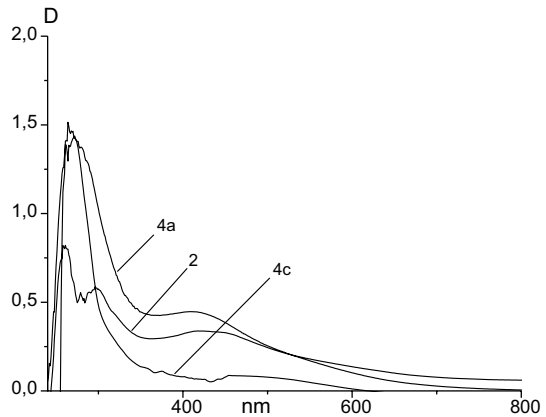

(Fig. 1): Relative intensities of quinonediimine (418 nm) to amino phenylene groups (268 nm) lowered as a result of conversion [8].

Having in mind the possibility of 1,4-addition reaction instead of reduction and the fact that according to the literary data [13] both partially reduced emeraldine and emeraldine itself have an absorption at 600–630 nm instead of absorption at 417 nm for compound **4a**, the presence of thiosulfate group in polymer structure was identified by different methods (Scheme 2).

The qualitative analysis was carried out by boiling the solution of compound **4a** in 10% potassium hydroxide and subsequent precipitation of sulfate ions with barium chloride. The conversion was quantitatively determined by the method of Carius and was equal to 51%. According to elemental analysis data, C, H, N and S average value of conversion is equal to 54%, if compound **4a** contains two crystal hydrates. To determine the amount of crystal hydrate, all obtained compounds were heated in 170 °C till constant weight. Afterward, using gravimetric method, it was found that all obtained thiosulfates contain two molecules of water.

To obtain more detailed information about the structure of obtained compound, the reaction of thiosulfate was carried out with model compound of polymer—compound **3**, using the same molar ratio of reagents 1:1.3 as was taken for polymer. According to elemental analysis data 1,4-addition of thiosulfate groups to quinonediimine was processed on 38% with the formation of compound **5**.
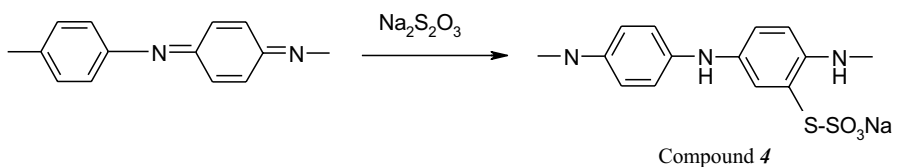
Compound **4**

Scheme 2 The reaction of quinonediimine groups with sodium thiosulphate
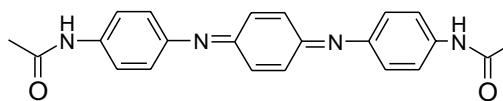
compound **3**
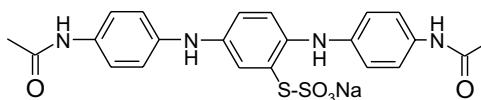
compound **5**

^{1}H NMR (D$_6$C$_2$SO, δ, ppm) (Fig. 2) spectrum of obtained compound **5a** was characterized by shifts at 2 ppm with intensity of one proton $2/6 = 0.33$ (CH$_3$) and 10.4 ppm with intensity of one proton $0.6/2 = 0.3$ NH amide groups. Chemical shifts of the rest protons were characterized at 6-9 ppm with intensity equal to 4.1, and as average integral intensity for one proton was 0.315, the number of the rest protons was equal to 13.9 ($4.1/0.315 = 13.9$); the percent of conversion could be calculated equal to 38% if thiosulfate contains two molecules of crystal water ($12(1-x) + 17x = 13.9$, $x = 1.9/5 = 0.38$).

Pure compound **5** was isolated by reprecipitation from ethylene glycol solution of compound **5b** (see discussion below) by methanol. UV–Vis spectra of obtained compound were characterized with only one absorption band of benzene ring π–π* transition at 296 nm (Fig. 3). UV spectra of **5** and **5b** compounds differ slightly which shows that the percent of conversion is high.
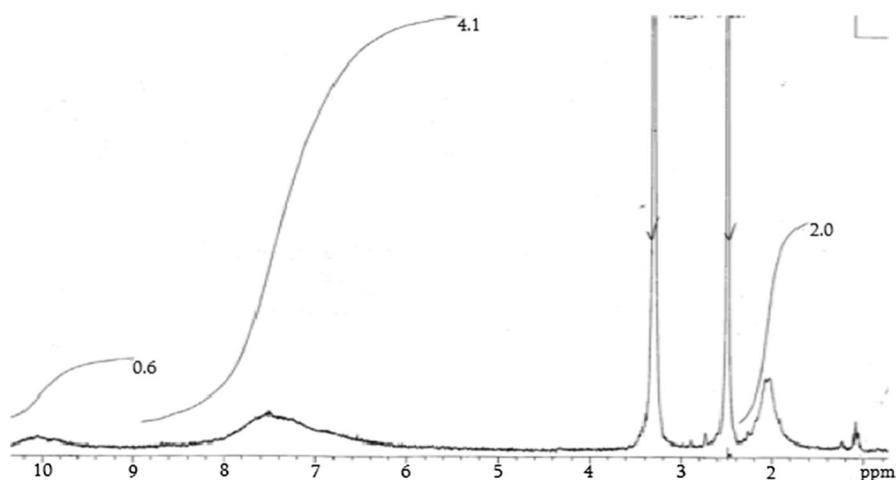

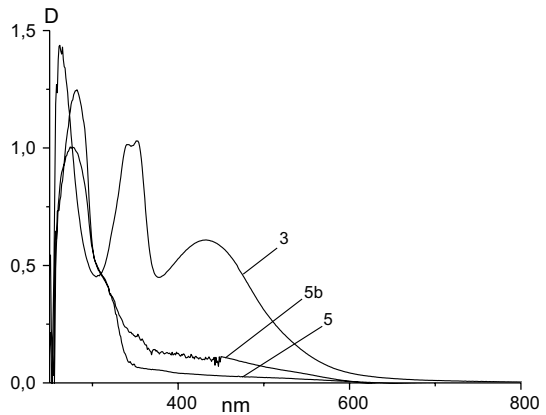**Fig. 2** ^{1}H NMR spectrum of (D$_6$C$_2$SO, δ, ppm) compound **5a**

Fig. 3 UV-Vis spectra (DMSO, λ, nm) of compounds *3*, *5b* and *5*

^{1}H NMR spectrum confirms the identity of synthesized sodium salt of pure 1,4-bis(4-acetamino anilino)-3-sulfthiobenzene (compound *5*). The spectrum shows chemical shifts of amidic NH at 10.2 ppm (intensity of one proton 1.7/2 = 0.85), *sec*-amino groups at 8.6 ppm (intensity of one proton 1,6/2 = 0.8), benzene rings at 7.4–8.2 ppm (intensity of one proton 9.7/11 = 0.88) and aliphatic protons at 2.1 (intensity of one proton 6. 0/6 = 1) (Fig. 4).

In this way, thiosulfate group-substituted polyanilines have been synthesized for the first time. Despite the fact that addition of thiosulfate to 1,4-benzoquinones was well investigated [14], the reaction with quinonediimines has been observed for the first time. Introduction of thiosulfate groups into the polymer structure will increase its solubility in water. Aiming to increase solubility of polystyrene in water, thiosulfate group containing polymer has been synthesized [15], and for the same purpose, many publications were devoted to sulfonation of *PANI* [16–19]. Molar ratio
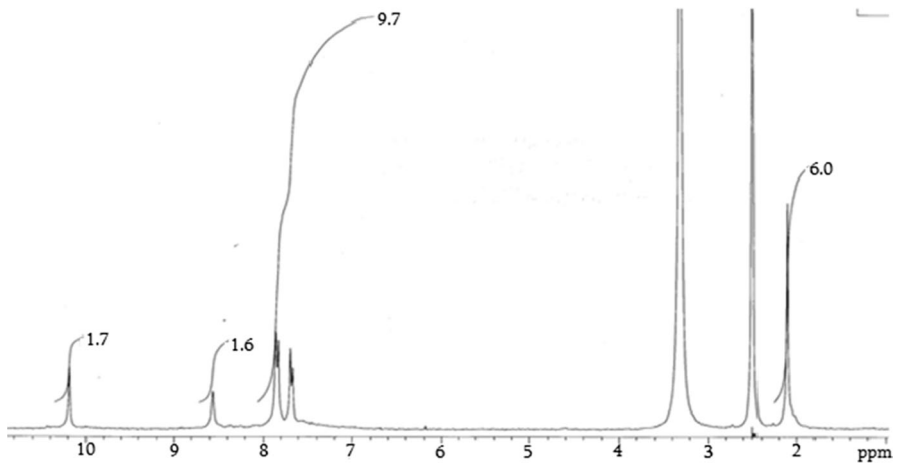
Fig. 4 ^{1}H NMR spectrum (D$_6$C$_2$SO, δ, ppm) of compound *5*

of reagents, temperature and reaction time is the most significant factors that can affect the conversion yield. Temperature increase can give rise to side reaction due to high reaction ability of quinonediimine groups. To increase the amount of thiosulfate groups, the reaction of initial compounds *2*, *3* with sodium thiosulfate was carried out using molar ratio of quinonediimine groups of polymer to sodium thiosulfate 1:2 and different reaction durations. The obtained results are shown in Table 1. From Table 1, it is clear that conversion increased with reaction time increase and achieved up to 96% conversion (compound *4c*, reaction time 75 h within 13 days). Solubility tests for polymer *4c* show solubility of 0.26 g/L (0.74 mmol/L) in water and 0.952 g/L (2.7 mmol/L) in concentric HCl.

For structural elucidation, it is worth to mention that this kind of compounds is called Bunte salts, and according to the literary data, thiosulfate group attacks double bond by sulfur [14, 15].

IR spectra of all obtained products are given in comparison with starting compounds in Fig. 5. All samples were recorded having approximately the same concentration in KBr pellets.

It should be noted that new absorption bands were observed at

- 1211, 1235, 1256 cm^{-1} (compound *4c*); 1230, 1260 cm^{-1} (compound *5*), due to presence of thiosulfate groups [20],
- 962, 1017, 1117 cm^{-1} (compound *4c*); 970,1021, 1119 cm^{-1} (compound *5*), due to presence of 1,2,4-substituted aromatic rings,
  and at
- 3171, 1572 cm^{-1} (compound *4c*); 3131,1584 cm^{-1} (compound *5*), due to presence of secondary amino groups (N–H) [21].

Intensities of quinoid absorption bands at 1604, 1113, 1309 and 1384 cm^{-1} of compound *2* and at 1606, 1094, 1306 and 1367 cm^{-1} of compound *3* correspondingly decreased compared to that appeared in IR spectra of compounds *4c* and *5* [22].

Electrical conductivities of compounds *4b*, *4c* upon doping level with iodine have been investigated (Table 2). On all cases, as doping level was increased, the increase in conductivities was observed from $< 10^{-10}$ to 10^{-6} S/cm. The conductivities of obtained substituted products were approximately of the same order and were one order lower than for the initial polymer *1*. There are only a few reports on the reaction of PANI with iodine, and there is a considerable variation in the experimental results and their interpretation [23]. Polymers *4a–c* have the structure of substituted PANI in leucoemeraldine form with sequence of substituted and unsubstituted phenylenediamines structural units. According to the literature, treatment of leucoemeraldine base form with I_2 in n-heptane solution results in more highly oxidized forms of the polymer due to oxidation of benzene diamine units into quinonediimine units, resulting in non-conductive product [24]. In contrast to this, Zeng and Ko [25] found that reaction of EB-PANI with I_2 in ethanol solution resulted in an eight orders of magnitude increase in conductivity. These authors proposed a reaction mechanism involving oxidative attack of iodine on the nitrogen atoms of the quinonediimine units, rather than the benzene
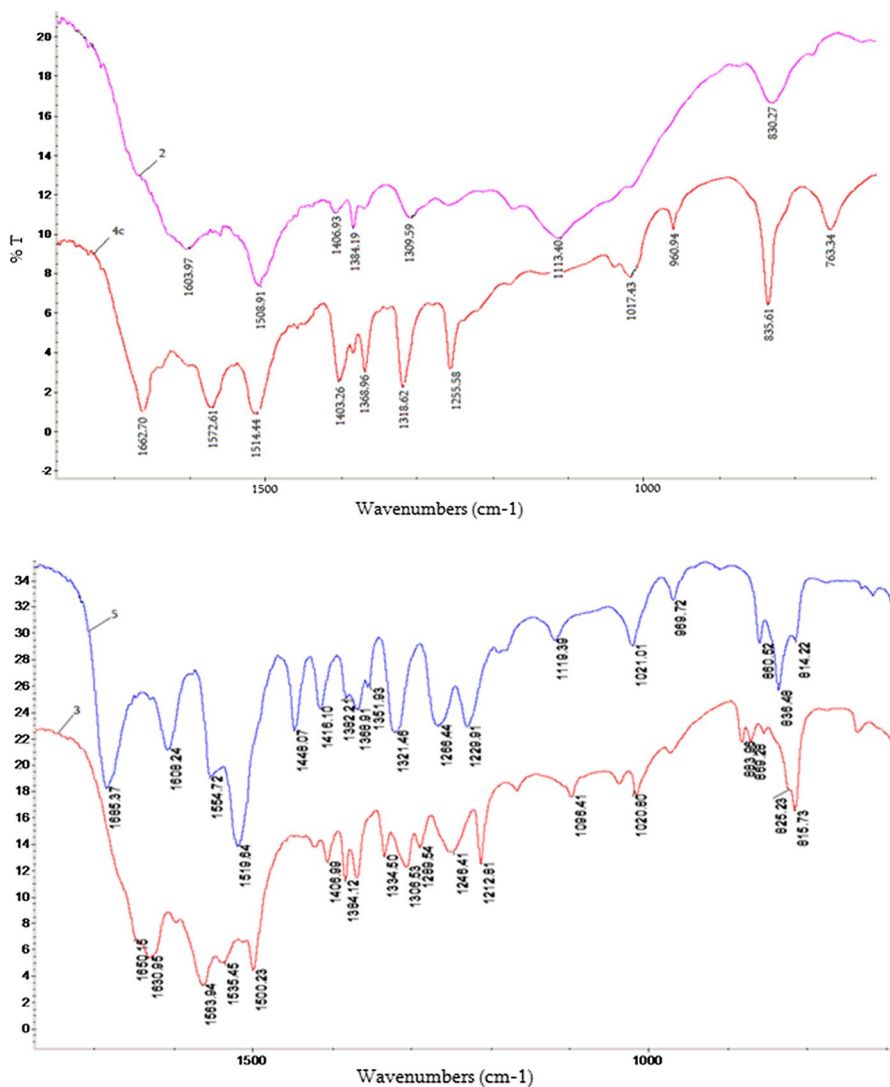
Fig. 5 Comparison of IR spectra (KBr) of compounds *2* and *4c*; *3* and *5*

diamine units. According to the other literature source, intrinsic oxidation state, namely the nigraniline oxidation state with approximately 72% oxidized and 28% reduced units, is obtained during the oxidation of leucoemeraldine base by iodine. Furthermore, covalently bonded iodine is observed in polymers after oxidation saturated acetonitrile solution of iodine, followed by compensation with 0.5 M NaOH [26]. Comparison of IR spectra of both doped with iodine and as synthesized polymers *4c* reveals similarities even in case of samples after heating to 70 °C to obtain activation energies. Neither eventual change in intensities

Table 2 Electrical conductivities as a function of doping level

Obtained compound	Doping level	Conductivity S/cm
1 [8]	0	10^{-10}
	0.5	4×10^{-8}
	0.96	1.4×10^{-6}
	1.45	4.9×10^{-5}
	1.5	5×10^{-5}
4b	0	$< 10^{-10}$
	0.7	2.3×10^{-7}
	1.5	2.8×10^{-6}
4c	0	$< 10^{-10}$
	0.72	1×10^{-7}
	0.91	1.8×10^{-7}

of phenylenediamine groups nor new peaks characteristic of quinonediimine units were observed in appropriate regions. The change in relative intensities of absorption peaks in the region of 1000–1200 cm^{-1} lets us assume that oxidation with iodine occurred with sulfur atom of substituent group, which is not surprisingly, taking into account the possibility of easy oxidation of thiosulfate group itself and divalent sulfur, as well, by iodine.

Conclusion

We synthesized novel thiosulfate group containing polymers and show that the reaction of polymers containing 1,4-benzoquinonediimine groups connected with 1,4-phenylene groups with sodium thiosulfate processed via 1,4-addition instead of reduction as it takes place in case of using thiosulfate for the reduction of emeraldine form of PANI. This makes it possible to obtain substituted *PANI* with regular structure in case of 100% conversion. Level of conversion could be controlled by compound 2 or 3: thiosulfate molar ratio and reaction time. Model compounds were synthesized and characterized to elucidate the polymers structure and the reaction route. It seems that UV spectral method which usually explored to estimate oxidation state of PANI could not be definitely used in case of reduction of pernigraline-like structures. The obtained thiosulfate group containing polymer has poor solubility in water and concentrated hydrochloric acid. Interesting was the fact that the obtained polymers have substituted leucoemeraldine-like structure and show moderate conductivity of 10^{-5} S/cm which was caused by the presence of sulfur atom with ability to be easily oxidized by iodine.

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