

# COPOLYMERIZATION OF ANILINE WITH *P*-PHENYLENEDIAMINE IN AN ACETIC ACID MEDIUM

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## Abstract

The oxidative copolymerization of aniline with *p*-phenylenediamine in an acetic acid medium has been investigated for the first time. It has been determined that as a result of copolymerization, a polymer having a structure analogous to the polyaniline called emeraldine is formed. The obtained copolymer doped with 3N hydrochloric acid has an electrical conductivity five times higher than that of polyaniline prepared by the usual method. Aniline polymerization proceeds more slowly at 273 K under the same copolymerization conditions and the obtained polymer has low conductivity. However, in a mixture of acetic acid-methanol, the reaction proceeds faster and the obtained polymer has a conductivity almost equal to that of emeraldine. It has been observed that the conductivity of polymers doped with formic acid is lower than that of polymers obtained by doping with hydrochloric acid by 2 orders of magnitude.

Keywords : conjugated polymer, copolymerization, polyaniline, emeraldine, aniline, *p*-phenylenediamine, conductivity.

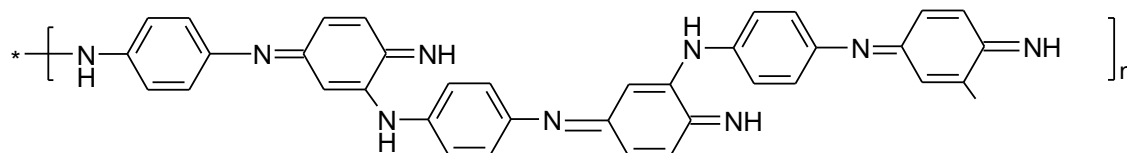
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## Introduction

Among the electroactive polymers, the emeraldine form of polyaniline (PANI) attracts intense interest [1,2]. PANI occupies a particular place among the electroactive conjugated polymers owing to its environmental stability, easy and cheap method of preparation and its unique properties. It is extensively used in various fields of technology [3-14]. To improve the properties of PANI, studies of aniline copolymerization with different monomers have been conducted [12-19]; however, the conductivity of the obtained copolymers is inferior to that of PANI in spite of high solubility.

According to the literature data, copolymer I [20] is formed during the copolymerization of *p*-phenylenediamine (PPDA) with aniline.

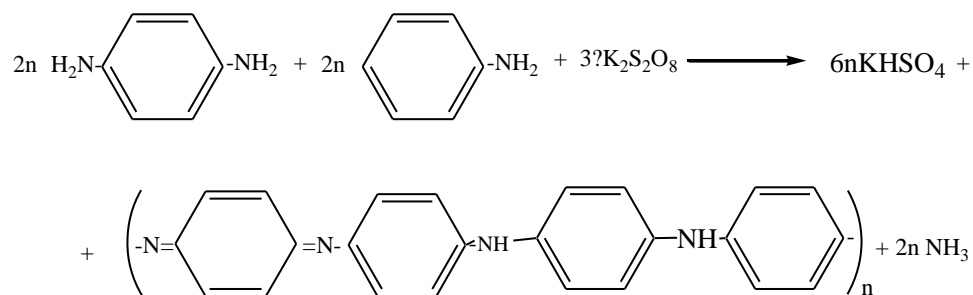


### Copolymer I

In the formation of copolymer I, for 1 mole each of aniline and PPDA, 3 moles of peroxydisulphate (PDS) are required [20] because when using 1 mole of PDS for 1 mole of aniline, the calculated yield for aniline cannot be higher than 33%, while a yield of 62% to 75% was actually obtained [20]. It may be concluded from these data that the reaction does not proceed according to Fig.4 given in the literature [20].

According to other literature data, in the case of a molar ratio of aniline/PPDA of 50:1, the presence of PPDA greatly increases the rate of polymerization and does not affect the structure and crystallinity of PANI [21].

These data strengthen our opinion that the reaction mechanism differs from that described in the literature [20], and considering the scheme for the oxidative polymerization of PPDA [22], we have proposed that it proceeds with a mechanism similar to that depicted in Scheme 1 [23].



Scheme 1

If the reaction occurs according to Scheme 1, the maximum yield calculated for aniline will be 67%, while in the case of a ratio of PPDA-aniline in the copolymer of more than 1, the yield will be above 67%.

The purpose of the present work is to verify the possibility that the reaction proceeds according to Scheme 1.

## 2. Experimental

### 2.1 Measurements

The inherent viscosity of DMSO solution was determined at 25°C, using Ubbelohde viscometer.

The UV/vis spectra of the polymer samples were recorded in 1 cm quartz cuvettes with Specord 65 spectrometer. FT IR Nicolet Nexus spectrometer was served for obtaining FT-IR spectra in the range of 5000-600 cm<sup>-1</sup> (KBr pellets). <sup>1</sup>H- NMR spectra were obtained in deuterated dimethylsulfoxide using Mercury 300 Varian NMR spectrometer.

Electrical conductivity was measured on the preliminarily prepared pellets by two-probe method using Teraohmmeter E6-137.

### 2.2 Materials

PPDA was purified by sublimation (mp 416-418 K) and PPDA sulfate was recrystallized from water. Aniline was used after double-distillation. All other chemicals were of analytical grade and were used as received without any further purification.

### 2.3. Oxidative copolymerization of PPhDA with aniline by potassium peroxydisulphate

### 2.3.1. In the hydrochloric acid medium [20]

To 1.08g (10mmol) of PPhDA and 0.91ml(10mmol) of aniline in 100ml (0.1N) of hydrochloric acid, solution of 2.7g (10mmol) potassium peroxydisulphate in 190ml (0.1N) of hydrochloric acid has been added within 3 hours under continuous magnetic stirring at (273-275K). The solution was kept in refrigerator (270 K) at night. Then, the solution was filtered and the precipitate was washed with distilled water until neutral pH. 190 ml of 0.1 N solution of ammonium hydroxide was added on the precipitate and the mixture was filtered after 13 hour stirring. The precipitate was washed with distilled water until neutral pH and absence of  $\text{SO}_4^{-2}$  ions, dried in vacuo (323K /2 kPa) and stored in a desiccator over phosphorus pentoxide.

The yield is 1.02g (60%).

After getting rid of water from the filtrate the ammonia was determined.

### 2.3.2 In the glacial acetic acid medium

#### a. copolymer (serie C -I)

To a solution of 0.43 g (4.6mmol) aniline, 0.93g (4.3 mmol) PPDA sulfate in 8 ml acetic acid. 1.44g (6.45 mmol) potassium persulfate was added under continuous magnetic stirring at 27 K, the mixture was stirred for 3.3 h. After that, the reaction mixture was kept in refrigerator at 270 K. Then the cooled water was added into the mixture. Subsequent procedure was similar to the mentioned above.

The yield is 0,42g (51%).

#### b. copolymer (serie C-II)

The oxydative copolymerization was carried out by the above-mentioned procedure with the difference in the duration of the reaction (See Table ).

#### c. copolymer (serie C- III)

The oxydative copolymerization was carried out by the above-mentioned procedure using acetic acid (8 ml) -methanol (0.8 ml) medium (Table).

### 2.3.3. *Semi-quantitative determination of ammonia*

Ammonia was determined using distillation apparatus equipped with liquid trap, receiver filled with 120 ml 0.1N hydrochloric acid for ammonia absorption and Tishchenko bottle filled with water.

On a dry precipitate obtained after evaporation of the liquid from the filtrate, solution of 2.4 g of KOH in 6 ml of water was added through the dropping funnel. Heating was carried out so, that liquid distillation didn't proceed. The ammonia content was determined by titration of hydrochloric acid with alkali and was found to be 8.96 mmol.

### 2.2.4. *Oxidative polymerization of aniline*

#### 2.2.4.1. *in acetic acid medium*

4.01g (15mmol) of potassium peroxodisulfate was added to the mixture of 1.04g (11.16 mmol) of aniline, 0.483g (3.72 mmol) of aniline hydrochloride in 5 ml of acetic acid under continuous magnetic stirring 15 hour within 5 days, at 273-275K. Every time when stirring was interrupted, the reaction mixture was kept in refrigerator at 270 K. Subsequent procedure was similar to the mentioned above.

Yield is 0.11g(8.6%)

#### 2.2.4.2. *in the mixture of acetic acid-methanol*

3.64g (0.012 mol) of ammonium peroxodisulfate was added to a solution of 1.11g (0.012 mol) aniline, 0.523g (0.004 mol) of aniline hydrochloride in 17 ml of acetic acid and 1.7 ml of methanol under continuous magnetic stirring 36 hour within 8 days, at 273-275K. Every time when stirring was interrupted, the reaction mixture was kept in freezer at 1-2<sup>0</sup>C. Further procedure was carried out as described above.

Yield is 0.82g (57%).

### 2.2.5. Procedure for doping

#### 2.2.5.1. with hydrochloric acid.

1.9 ml of 3N hydrochloric acid was added on the fine powder of polymer and left 7 days at room temperature. Then the precipitate was filtered and washed twice with a small amount of ethanol. The precipitate was dried until constant weight under vacuo in a desiccator over phosphorus pentoxide (0,2kPa).

#### 2.2.5.2. Doping with formic acid.

0.05g of fine powder of polymer was dissolved in 5 ml of formic acid at room temperature. The solvent was removed at room temperature and the remained powder was dried until constant weight under vacuo in a desiccator over phosphorus pentoxide (0,2 kPa).

## 3. Results and Discussion

During the course of the reaction according to Scheme , ammonia is formed as a result. For the purpose of checking these data, we have repeated the experiment described in the literature [20] and we have semiquantitatively determined the resulting ammonia content and found that 1.43 mmol of ammonia were formed from 10 mmol of PPDA.

If the reaction proceeds according to Scheme 1, a polymer analogous to that of emeraldine would be formed. However, the conductivity of the obtained chloride salt form of the polymer is equal to  $2.719 \times 10^{-5}$  S/cm [20], which is much lower than that of emeraldine. Because the mentioned value is related to the conductivity of the as-synthesised salt form of the polymer, and consequently, there are no data about doping levels, the as-synthesised polymer was converted to its base form and doped with 3 N hydrochloric acid to reveal a conductivity of  $2.9 \times 10^{-7}$  S/cm, which is, as mentioned above, far inferior to that of emeraldine.

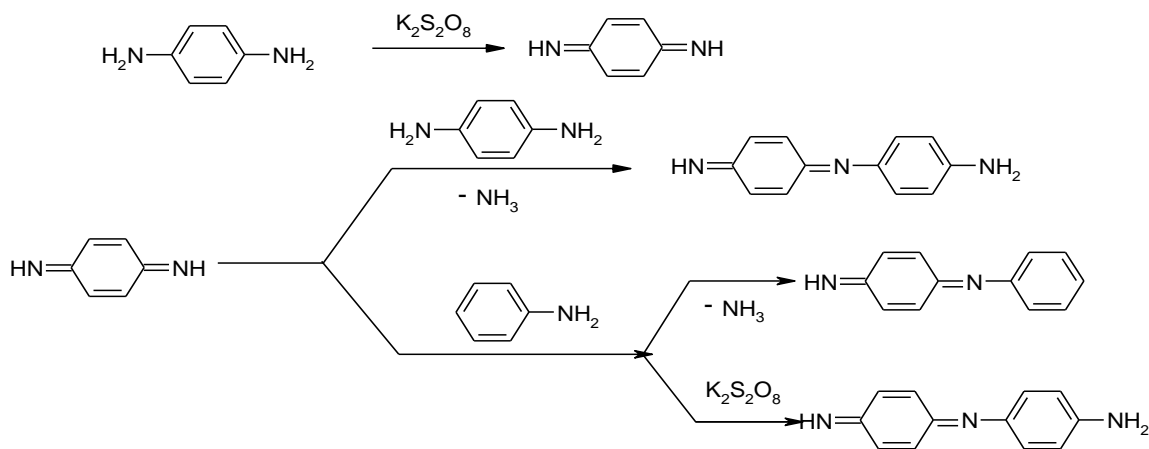
Moreover, PPDA-aniline copolymer solutions in methanol and DMSO exhibit absorption bands at 308 and 549 nm [20], and 320 and 585 nm (Fig.1), respectively. The emeraldine base in *N*-methylpyrrolidinone (NMP) is characterised by two absorption bands at 320 and 634 nm [24], and the film shows absorption bands at 326 and 630 nm [25].

It follows from the presented data that the polymer obtained by chemical oxidative copolymerization of PPDA and aniline does not have a structure similar to that of emeraldine. These data could be explained by the occurrence of side reactions that occur during the oxidative polymerization of PPDA [26].

To reduce the proportion of side reactions, we performed the copolymerization reaction of PPDA and aniline in glacial acetic acid and acetic acid-methanol media. The reaction in glacial acetic acid was conducted in three variations designed to investigate the effect of reaction time on the yields and electrical conductivities of the obtained copolymers (Table 1). An acetic acid-methanol medium was applied to decrease the melting point of acetic acid.

The semiquantitative determination of ammonia content shows that 2.3 mmol of PPhDA and 0.19 mmol of ammonia were formed.

Most likely, the reaction of PPDA with PDS takes place at first, and 1,4-benzoquinonediimine is formed, which can participate in the subsequent reaction (Scheme 2). Finally, as a result of copolymerization, poly(1,4-benzoquinonediimine-*N,N'*-diyl-1,4-phenyleneimino-1,4-phenyleneimino-1,4-phenylene), which has a structure analogous to emeraldine PANI, is formed (Scheme 1). The copolymers are soluble in formic acid, NMP and DMF, and partially soluble in DMSO.



Scheme 2

The PMR, IR and UV spectra of the obtained copolymers are in close agreement with those published in the literature for emeraldine.

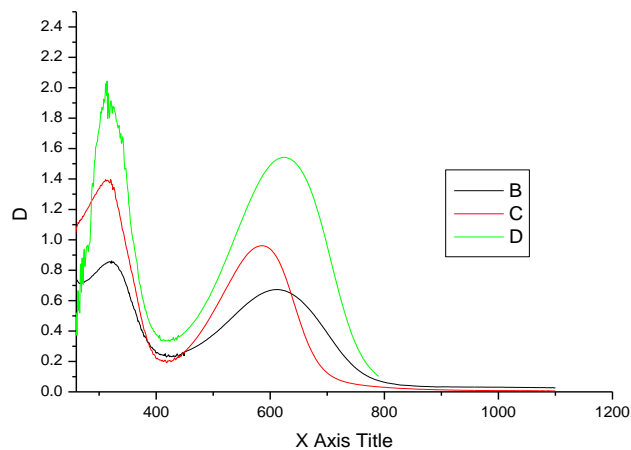


Fig.1. UV spectra ( $\lambda$ , nm) of (B) PPDA-aniline copolymer, obtained in a mixture of acetic acid-methanol, in NMP,  $\lambda_{\max}=320,611$ ; (C) PPDA-aniline copolymer, obtained in hydrochloric acid, in DMSO,  $\lambda_{\max}=320,585$ ; (D) Polyaniline, obtained in a mixture of acetic acid-methanol, in NMP,  $\lambda_{\max}=320,629$ .

The UV spectrum of the copolymer obtained in a medium of acetic acid-methanol shows absorption bands at 320 and 611 nm in NMP (Fig.1). Accordingly, as cited above, a solution of emeraldine in NMP exhibits absorption bands at 320 and 634 nm [23], while the film shows absorption bands at 326 and 630 nm [24]. Polyaniline, obtained in a mixture of acetic acid-methanol, in NMP shows absorption bands at 320 and 629 nm.

The  $^1\text{H}$  NMR spectrum of the copolymer [Fig.2] is very similar to that reported in the literature for emeraldine [27], with the difference being that there is an additional very weak chemical shift at 6.6 ppm, which may most likely be assigned to the *ortho* protons of the terminal primary amino groups.

IR spectrum: 506,696,717,831,956, 1008, 1162; 1310; 1331; 1498; 1590; 3033; 3331  $\text{cm}^{-1}$ . These data almost completely coincide with those reported in the literature for emeraldine [25].



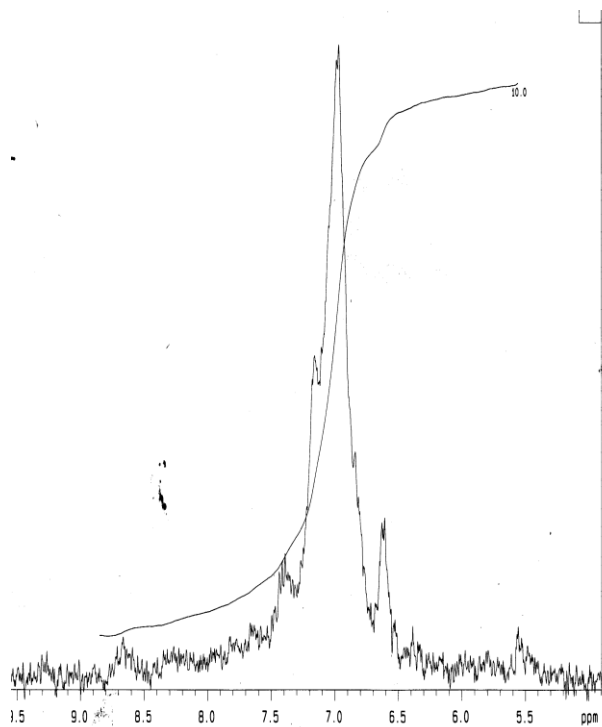


Fig.2  $^1\text{H}$  NMR spectrum ( $\text{DMSO-}d_6$ ,  $\delta$ , ppm) of the PPDA-aniline copolymer.

To make a comparison with aniline-PPDA copolymerization, the polymerization of aniline in acetic acid and in a mixture of acetic acid-methanol has been investigated. The oxidative polymerization reaction of aniline proceeds at a much slower rate compared to copolymerization, and it depends on the medium in which the reaction occurs. The specific electroconductivity of the copolymers doped with 3N hydrochloric acid changed, depending on the copolymerization conditions, from 0.1 to 0.51 S/cm. The PANI obtained in acetic acid (P-I) has an electrical conductivity of  $3.4 \times 10^{-4}$  S/cm, and that obtained in a mixture of acetic acid-methanol was 0.06 S/cm. The latter value is comparable to that obtained for the 3N hydrochloric acid-doped emeraldine PANI (0.09 S/cm) having been synthesised by the standard method (in a solution of hydrochloric acid at  $0^\circ\text{C}$ ) and to that according to the literature data (0.1 S/cm).[20].

The great difference in the conductivities of P-I and P-II could mainly be caused by the low molecular mass of the former (see Table). It should be noted that the characteristic viscosities of the copolymer(C-III) and the polymer (P-III) differ only slightly. The obtained data hereby indicate that PPDA-aniline copolymers are, in fact, analogous to emeraldine PANI structures. The fact that the conductivity of the copolymer is slightly higher than that of PANI can be caused by fewer defects in the former compound's structure.

Table

Data for yields, specific viscosities and electrical conductivities of aniline homopolymers (P) and copolymers (C) with PPDA.

Homopolymer, (P); copolymer(C)	Reaction time		Yield %	[ $\eta$ ] dl/g	$\sigma$ ; S/cm	
	Hours	Days			Dopant	
					3 N hydrochloric acid	Formic acid
C-Ia	3,3	1	51		0,1	
C-Ib	3,3	1	51		0.15	
P-I	15	4	14.3	0,074	$3.4 \times 10^{-4}$	
C-IIa	2.3	7	61		0.13	
C-IIb	2.3	7	61		0.17	
C-IIIb	9	2	54	0,20	0,56; 0,46;	$1 \times 10^{-3}$
P-III	36	8	59	0,16	0.06; 0.052;0,0459	$1.8 \times 10^{-4}$

a, b-see experimental section

According to the literature, the conductivity of PANI salts obtained in formic acid is higher than that obtained in hydrochloric acid [28]. It should be noted that, during the oxidative polymerization of aniline, ammonium or potassium bisulphate is formed from peroxydisulphate, and it also forms salts with the polymer, along with hydrochloric acid and formic acid [29].

The conductivities of both polymers and copolymers are two orders of magnitude lower in the case of doping with pure formic acid than in a 3N solution of hydrochloric acid (Table).

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