

# CHEMICAL SYNTHESIS AND CHARACTERIZATION OF POLYANILINE DERIVATIVES. SUBSTITUENT EFFECT ON SOLUBILITY AND CONDUCTIVITY

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## ABSTRACT

Polyanilines have different macroscopic properties according to the substituent incorporated into their monomers. Being conducting polymers, one of these properties is conductivity, which may increase or decrease depending on the substituent and its position in the chain. This work is focused on the modification of aniline monomers, which characteristics will vary, enabling thus the effect of the substituent on the respective polymer to be studied. For this purpose monomers substituted with methoxy and bromine, which are commercially available, and thiophenes were prepared using Suzuki and Ullman reactions. It was found that all polymers have conductivities of the order of  $10^{-6}$  S·cm<sup>-1</sup> or less. This demonstrated the performed substitutions had a negative effect on conductivity (although would facilitate their use in solar cells) as compared to aniline (PANI). These modifications also improve the solubility of the respective polymers, as most were more soluble than PANI.

**Keywords:** polyaniline, conducting polymers, conductivity, solubility.

## INTRODUCTION

The discovery of conducting polymers was another significant event regarding the use of materials known as synthetic metals. The main feature of these materials is the high p bond conjugation of their structures that facilitates the intracatenary charge transport or electron flow. In the case of PANI, this occurs when is in its emeraldine oxidation state (Figure 1). However, conductive emeraldine must be doped, *i.e.* is in ionic form bearing positively charged nitrogens, enabling thus charge mobility<sup>1</sup>.

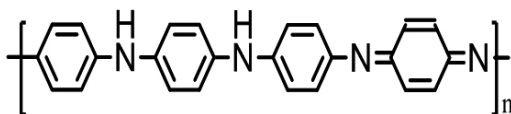


Figure 1. Structural formula of PANI emeraldine form.

On the other hand, PANI applications are often limited by its solubility problem, consequently, structural modifications are proposed to improve this property<sup>2</sup>. Nevertheless, this may change its macroscopic properties. In the current work, modifications to PANI will be intended aimed at increasing its solubility, measuring at the same time its conductivity, to check if changes of this property are promoted, while the effect on solubility is assessed. Solubility improvement would allow evaluating the use of these compounds, for instance, in the development of electronic devices<sup>3,4</sup>.

Therefore, herein the synthesis and characterization of aniline modified analogues, depicted in Figure 2, and the respective polymers to be described below, is proposed.

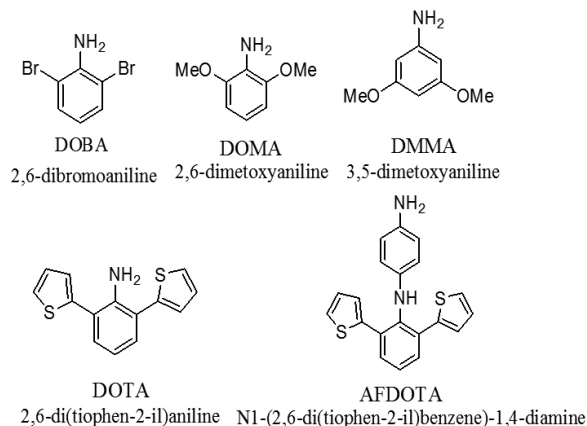


Figure 2. Structural formula of the synthesized monomers.

To carry on modifications of the structural units, differences in the monomer units must be accomplished. To this end, a wide range of reactions are available<sup>5</sup>. In this case, Suzuki and Ullman reactions were utilized and the products were structurally, optically and electronically characterized. Polymer synthesis by oxidation of the five monomers in Figure 2 permits generating eight types of polymers that are characterized according to their conductivity and solubility properties.

## EXPERIMENTAL

### Instrumentation, materials and reagents

SMP3, Stuart Scientific Melting Point Apparatus; Precision UV-vis, SPECORD, Analytik Jena Spectrophotometer (2 mg of polymer solution measured in 15 mL dimethyl sulfoxide, DMSO); Soxhlet extractor for cuprous iodide purification; PV35 vacuum pump; silica gel (0.040-0.063 mm) for chromatographic columns, Merck; Celite 545, particle size 0.02 - 0.01 mm, Merck.

Conductivity of the eight synthesized polymers in their doped and undoped state was determined by the method of the four-points-probes on an EDT Instruments Conductivity Meter. Samples were prepared by pressing 0.75 g of the respective polymer on a Carver hydraulic press.

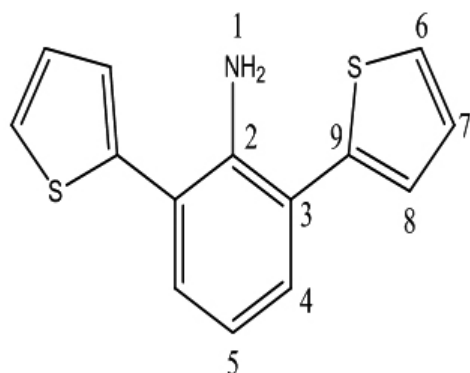
Aniline p.a. Merck, 3,5-dimethoxyaniline (98.0%) Sigma Aldrich, 2,5-dimethoxyaniline for synthesis, Merck, 2,5-dibromoaniline (97%) Sigma Aldrich, 1-iodo-4-nitrobenzene, Sigma Aldrich; bis (triphenylphosphine) palladium (II) (15.2% Pd), for synthesis, Merck, 2-thienylboronic acid, Sigma Aldrich, L-proline, Merck, sodium hydroxide, p.a. Merck; metallic iron 150 mm particle size, Merck, hydrochloric acid, p.a. Merck, ammonium hydroxide, EM Science, activated carbon, p.a. Merck, calcium hydride, particle size 10 mm, for synthesis, Merck utilized as received. Copper iodide(I), for synthesis, Merck, was purified by placing 0.5 g of the material in the thimble of a Soxhlet apparatus and then extracted with tetrahydrofuran for 20 min, and DMSO was distilled from a heterogeneous solution of 1.0 g of calcium hydride and 30 mL of DMSO.

### Synthesis of 2,6-di (thiophen-2-yl) aniline (DOTA, Figure 3)<sup>6</sup>

A mixture made of 0.502 g (2 mmol) 2,6-dibromoaniline, 0.768 g (6 mmol) thiophene-2-ylboronic acid, 0.210 g (0.3 mmol, 15%) bis (triphenylphosphine) palladium(II) chloride and 20 mL of dioxane was stirred under argon for 30 min at room temperature. 8 mL of aqueous 1 mol·L<sup>-1</sup> potassium carbonate was added and the mixture was heated for 72 h at 90 °C. After cooling and adding water, the mixture is extracted with ethyl acetate, dried with anhydrous sodium sulfate and vacuum filtered. After separating the compound by elution of the sample with a 95 % n-hexane and 5 % ethyl acetate mixture, 0.449 g (yield: 87.3 %) of light yellow oil was afforded. After recrystallization a pale yellow solid was obtained. IR 3483.44 (N-H), 1449.93 cm<sup>-1</sup> (C-S).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>), δ 7.48 (m, 4H, H<sup>4</sup>-H<sup>6</sup>), 7.42 (dd, 2H, H<sup>8</sup>), 7.28 (dd, 2H, H<sup>7</sup>), 7.00 (t, 1H, H<sup>5</sup>), 4.55 (s, 2H, H<sup>1</sup>) ppm, <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>), δ 142.84(C<sup>2</sup>), 141.60(C<sup>6</sup>), 131.66(C<sup>6</sup>), 128.30(C<sup>4</sup>), 126.92(C<sup>7</sup>),

126.21(C<sup>8</sup>), 121.03(C<sup>5</sup>), 118.58(C<sup>3</sup>) ppm.

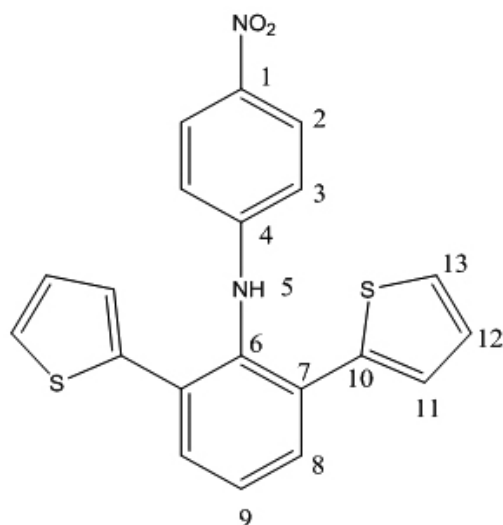


**Figure 3.** 2,6-di (thiophene-2-yl) aniline (DOTA).

**Synthesis of N-(4-nitrophenyl)-2,6-di(thiophen-2-yl)aniline (NFDOTA, Figure 4)**<sup>7</sup>

A mixture of 0.515 g (2 mmol) of 2,6-di (thiophen-2-yl) aniline, 0.623 g (2.5 mmol) of p-iodonitrobenzene, 0.038 g (0.2 mmol) copper(I) iodide, 0.046 g (0.4 mmol) L-proline, 0.553 g (4 mmol) anhydrous potassium carbonate in 5 mL of anhydrous DMSO was sonicated for 20 min under argon. After this time, the mixture was stirred for 48 h at 90 °C. Subsequently, water was added and the mixture extracted with ethyl acetate. The organic phase was dried with sodium sulfate and eluted using a hexane/ethyl acetate mixture, in polarity gradient, from 95:5 to 8:1, obtaining 0.151 g (Yield: 20.0%) of a yellow solid, melting point between 120 and 122 °C. IR 3370.57 cm<sup>-1</sup> (N-H), 1424.64 cm<sup>-1</sup> (C-S), 1516.08, 1342.49 cm<sup>-1</sup> (N-O), 1317.25 cm<sup>-1</sup> (C-N).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>), δ 8.21 (dd, 2H, H<sup>2</sup>), 7.91 (dd, 2H, H<sup>3</sup>), 7.80 (d, 2H, H<sup>11</sup>), 7.61 (d, 2H, H<sup>8</sup>), 7.38 (t, 1H, H<sup>9</sup>), 7.27 (dd, 2H, H<sup>13</sup>), 6.87 (dd, 2H, H<sup>12</sup>), 6.45 (s, 1H, H<sup>5</sup>) ppm, <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>), δ 146.21(C<sup>4</sup>), 140.68(C<sup>6</sup>), 139.70(C<sup>10</sup>), 136.14(C<sup>1</sup>), 130.83(C<sup>8</sup>), 129.96(C<sup>13</sup>), 129.50(C<sup>12</sup>), 128.21(C<sup>11</sup>), 127.45(C<sup>7</sup>), 126.94(C<sup>2</sup>), 125.45(C<sup>3</sup>), 120.93(C<sup>9</sup>) ppm.



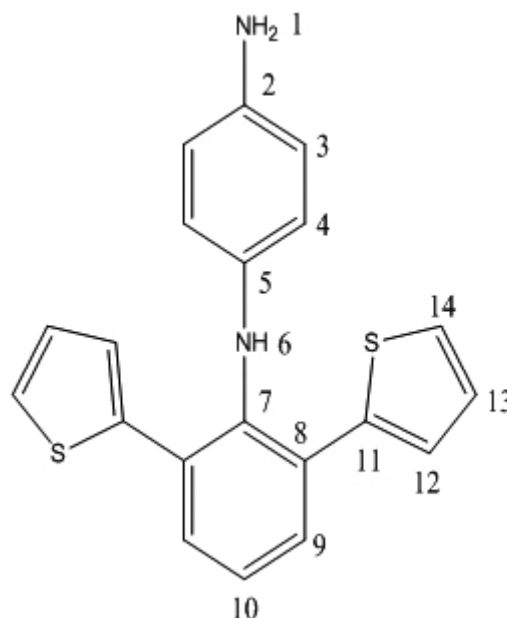
**Figure 4.** N-(4-nitrophenyl) -2,6-di (thiophen-2-yl) aniline (NFDOTA).

**Synthesis of N<sup>1</sup>-(2,6-di (thiophenyl-2-yl)phenyl)benzene-1,4-diamine (AFDOTA, Fig. 5)**<sup>8</sup>

A suspension made of 50 mg (0.13 mmol) of N-(4-nitrophenyl) -2,6-di (thiophen-2-yl) aniline (NFDOTA), 271 mL of acetic acid and 271 mL ethanol in 136 mL distilled water and 0.038 mg (0.625mmol) of metallic iron was sonicated for 180 min, at 90 °C. Iron excess was then remove by vacuum filtration. To the filtrate 2 mol·L<sup>-1</sup> KOH solution was added and then extracted

with ethyl ether. The extract was dried with anhydrous MgSO<sub>4</sub> and finally reaction mixture was concentrated and eluted with n-hexane/ethyl acetate (2:1). 0.0385 g (85.0% yield) of a dark yellow solid was obtained, melting between 140 and 142 °C. IR 3459.21, 3368.29 cm<sup>-1</sup> (N-H), 1312.49 cm<sup>-1</sup> (C-S), 1516.08, 1342.49 cm<sup>-1</sup> (N-O), 1080.95 cm<sup>-1</sup> (C-N).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>), δ 7.44 (d, 2H, H<sup>14</sup>), 7.14 (m, 4H, H<sup>9</sup>-H<sup>12</sup>), 7.05 (m, 2H, H<sup>1</sup>), 6.86 (t, 3H, H<sup>10</sup>-H<sup>13</sup>), 6.37 (d, 2H, H<sup>4</sup>), 6.32 (d, 2H, H<sup>3</sup>), 5.28 (s, 1H, H<sup>6</sup>), <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>), δ 139.47 (C<sup>7</sup>), 138.20 (C<sup>11</sup>), 137.48 (C<sup>2</sup>), 136.08 (C<sup>5</sup>), 130.45 (C<sup>14</sup>), 129.08 (C<sup>9</sup>), 125.79 (C<sup>13</sup>), 125.25 (C<sup>12</sup>), 124.95 (C<sup>8</sup>), 123.54 (C<sup>4</sup>), 116.01 (C<sup>10</sup>), 115.33 (C<sup>3</sup>) ppm.



**Figure 5.** N<sup>1</sup>-(2,6-di (thiophenyl-2-yl) phenyl) benzene-1,4-diamine (AFDOTA).

**Polymers Synthesis**

Polymers preparation in acidic aqueous solution. Poly-3,5-dimethoxyaniline (PDMMA), poly-2,6-dimethoxyaniline (PDOMA) and poly-aniline/2,6-dimethoxyaniline (1:1) (CAD1) synthesis<sup>9</sup>

A mixture of 1.1 mL (5 mmol) aniline, 0.766 g (5 mmol) 2,6-dimethoxyaniline) or (10 mmol of the monomer), were dissolved in 100 mL of 1 mol·L<sup>-1</sup> HCl. 5.7 g (10 mmol) of ammonium persulfate was slowly added and then stirred for 24 h at ca. 1 °C. The obtained precipitate (saline form) was vacuum-filtered and washed with water until the filtrate is decolorized. Then, the solid was washed with methanol and acetone. Finally, the obtained product was vacuum-dried during 30 h. The base form was prepared by adding 1.0 g of the obtained polymer to 250 mL of 0.05 mol·L<sup>-1</sup> aqueous ammonia, stirring for 12 h, and finally vacuum-filtered, washed with water and allowed vacuum-drying for 30 h.

Preparation of polymers in organic medium: synthesis of poly-2,6-di (thiophen-2-yl)aniline (PDOTA), poly-aniline/2,6-di-(thiophen-2-yl)aniline (1:1) (CAD2), poly-2,5-dimethoxyaniline/2,6-di(thiophen-2-yl)aniline (1:1) (COO), poly-N<sup>1</sup>-(2,6-di(thiophen-2-yl)phenyl)benzene-1,4-diamina (PAFDOTA) and 2,6-dibromoaniline (PDOBA)<sup>10</sup>

To a 100 mL round-bottom flask, 0.63 mL (0.011 mmol) perchloric acid, 0.192 g (1 mmol) periodic acid, 7 mmol of the respective monomer and 25 mL of dry THF as solvent was added. The mixture was stirred for 24 h at room temperature. Next, THF was evaporated in a rotary evaporator, to then add water and stir for 3 h. After this time, the solution was vacuum filtered and the residue, both in the flask and on the filter paper, was redissolved using 40 mL THF. Then, the dissolution was transferred to a beaker and evaporated with stirring at about 60 °C.

## RESULTS AND DISCUSSION

One of the proposed polymers, PAFDBD, failed to be prepared following the intended route due to problems in the obtention of its monomer. Nevertheless, an analogous molecule, PAFDOTA, a polymer from an aniline dimer, was designed that enabled determining from its structural differences, the differences in the properties we were seeking to achieve. Furthermore, DOTA, AFDOTA, and NFDOTA species were synthesized and characterized with approx. 15 % yield, being Ullman reaction the critical step, owing to the low DOTA reactivity. In addition, other polymers were obtained, that allow the conductivity change to be compared, following the effect of the substituent on the monomers (Table 1).

DOTA structure was corroborated by NMR, IR, and UV-Vis spectroscopy. NFDOTA intermediate, product of the Ullman reaction, gave a low yield, chiefly because the nitrogen of the aniline ring is not sufficiently activated. Resonance and conjugation of thiophenes cause decreased basicity, a necessary prerequisite for NC Ullman coupling, and this in turn leads to a weak interaction between aniline and copper catalyst<sup>7</sup>.

Another important aspect in this kind of reaction is that the presence of a small amount of water in the reaction medium, either in the environment or in the solution, makes the yield to decrease due to the competition of the oxygen electron pair with nitrogen electrons. The final product, N<sup>1</sup>-(2,6-di(thiophenyl-2-yl)phenyl benzene-1,4-diamine) (AFDOTA) was characterized by NMR, IR, and UV-Vis as well.

It is noteworthy that the structures of all intermediates were properly corroborated.

As for polymerization, in order to obtain high yields, the reaction medium was chosen according to monomers solubility<sup>11</sup> NMR spectral analysis revealed a 1-4 substitution for all polymers, without side ramifications. For *ortho*-substituted monomers, *para*-hydrogen triplets disappeared and doublets for *meta*-hydrogen changed to singlets. In the case of *meta*-substituted monomers, signals corresponding to *para*-hydrogens disappeared while the *ortho*-singlet remained.

In the UV-Vis spectra, the maximum absorptions between 250-650 nm

correspond to the highly conjugated structure of the main polymer backbone<sup>12</sup>. The maximum absorptions between 650 and 900 nm represent the oxidation level of the polymer (quinoid form).

As summarized in Table 1, the conductivity of polymers obtained in undoped form lies between 10<sup>-9</sup> and 10<sup>-12</sup> S·cm<sup>-1</sup> and the doped form between 10<sup>-8</sup> and 10<sup>-6</sup> S·cm<sup>-1</sup>. The following sequence was found (from low to high conductivity): PDOBA < PDOTA < COO < CAD2 < PDMMA < PDOMA < PAFDOTA < CAD1.

PAFDOTA, an aniline and DOTA (together) homopolymer, and CAD2, an aniline and DOTA copolymer, exhibit a difference in their conductivities due to the effect of the molecular ordering. Likewise, the homopolymer, having a higher degree of ordering, is a better conductor.

**Table 1.** Polymers conductivity.

Polymer	Undoped (S·cm <sup>-1</sup> )	Doped (S·cm <sup>-1</sup> )
PDOMA	8.52·10 <sup>-10</sup>	5.02·10 <sup>-6</sup>
PDMMA	7.28·10 <sup>-10</sup>	4.22·10 <sup>-6</sup>
PAFDOTA	8.60·10 <sup>-10</sup>	6.08·10 <sup>-6</sup>
COO	9.03·10 <sup>-11</sup>	8.70·10 <sup>-7</sup>
CAD1	7.21·10 <sup>-9</sup>	8.35·10 <sup>-6</sup>
CAD2	3.26·10 <sup>-10</sup>	1.23·10 <sup>-6</sup>
PDOTA	1.57·10 <sup>-11</sup>	3.01·10 <sup>-7</sup>
PDOBA	2.12·10 <sup>-12</sup>	1.52·10 <sup>-8</sup>

Finally, the following solvents were tested: dioxane, acetone, ethyl acetate, n-hexane, ethyl ether, chloroform, DMSO, EtOH, MeOH, and THF to assess polymers solubility and determine trends regarding the substituent effect, as specified in conclusions.

**Table 2.** Solubility of synthesized polymers.

Polymer/ solvent	Dioxane	Acetone	Ethyl acetate	n-hexane	Ethyl ether	Chloroform	DMSO	Ethanol	Methanol	THF
PANI	+/-	+/-	+/-	-	-	-	+	+/-	+/-	-
PDOMA	+/-	+	+/-	-	-	+	+	-	-	+/-
PDMMA	-	+/-	+/-	-	-	-	+	+/-	+/-	+/-
PAFDOTA	+/-	+/-	+/-	-	-	-	+/-	-	-	-
COO	+/-	+/-	+/-	-	-	-	+	-	-	-
CAD1	+	+/-	+/-	+/-	+/-	+/-	+	+/-	+	+/-
CAD2	+/-	+	+	-	-	+/-	+	+/-	+/-	+/-
PDOTA	+	+	+/-	-	-	+	+	-	-	+/-
PDOBA	+/-	+/-	+	-	-	-	+	+	+	+/-

## CONCLUSIONS

The obtained conductivities allow concluding that a bulky substituent, such as bromo or thiophene, decreases the conductivity as compared to that of a smaller substituent such as methoxy. In addition, PDOTA shows conductivities lower than PAFDOTA and CAD2, which leading to the conclusion that adding unsubstituted structures to the polymer, a positive effect is obtained when DOTA and aniline are orderly alternated.

Conductivity increases when unsubstituted forms are added to the polymer structures. PDOMA conductivity is higher than that of PDMMA: the substituent position effect, slightly alter conductivity. In the case of the homopolymer with methoxy substituent, polymer interactions with polar solvents tend to improve, e.g. when mixed with aniline, solubilization is accomplished in nonpolar solvents.

In the case of the thiophene substituted homopolymer, it dissolves in nonpolar solvents and, even when alternate forms with aniline exist, its

solubility in polar solvents improves.

Mixed methoxy and thiophene substituted polymers, decrease their solubility in polar solvents.

## DEDICATION

This work is dedicated to Dr. Elsa Abuin (RIP), to whom we express our admiration and respect, not only as a great scientist, but especially for her outstanding human qualities.

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