

# Influence of Dibenzoyl Tartaric Acid on the Electrical Performances of the Polyaniline

By Nacera NAAR,<sup>1,\*</sup> Saad LAMOURI,<sup>1,\*</sup> Belkacem BELAABED,<sup>1</sup>  
Toufik KOUROUHLI,<sup>1</sup> and Nourine GABOUZE<sup>2</sup>

In this study, the dibenzoyl-L-tartaric acid (DBTA) was used as doping agent to synthesis polyaniline (PANI) by direct oxidative polymerization of a chiral aniline monomer repeat unit. The influence of DBTA on the electrical performances of the polyaniline was studied with the synthesis conditions, particularly the molar ratio of DBTA to aniline and the presence of methanol. The spectral characterization (FT-IR and UV-visible-NIR), the thermal (TGA), electrical properties at macroscopic scale (I-V, C-V curves and the gap) and the morphology of the PANI have been investigated. From the results it's found that synthetic conditions have a great influence on the electrical properties of PANI-DBTA. In addition polyaniline micro-fibres can be obtained when using methanol as a solvent of DBTA.

KEY WORDS: Polyaniline / Dibenzoyl Tartaric Acid (DBTA) / Doping / Electrical Properties /

In several chiral conducting polymers, such as polyaniline (PANI),<sup>1</sup> polyacetylene,<sup>2</sup> polypyrrole,<sup>3</sup> polythiophene,<sup>4</sup> polytoluidine,<sup>5</sup> polydiacetylene,<sup>6</sup> polyisocyanide<sup>7</sup> and poly(phenylenevinylene)<sup>8</sup> are well described in the literature that are for great interest due to their potential applications, such chiral separation,<sup>9</sup> asymmetric electrochemical synthesis,<sup>10</sup> chemical and biological sensor<sup>11–15</sup> and circular polarized electroluminescence (CPEL).<sup>16–18</sup> This kind of polymer had the easier ability to give oxidizing and reducing states with colour changes, and the possibility to exchange the physicochemical characteristics with the temperature, pH, and the electric potential. Currently, chiral polyaniline is studied in the literature by different methods like the enantio-selective electropolymerisation of aniline in the presence of (1S)-(+)- or (1R)-(-)-10-CSA,<sup>1</sup> by the acid doping of the emeraldine base with optical isomers of CSA,<sup>19</sup> by using chemical oxidative polymerization of aniline in the presence of (1S)-(+)- or (1R)-(-)-10-CSA,<sup>20</sup> by the template synthesis of polyaniline in the presence of optically active compounds,<sup>21</sup> by direct oxidative polymerization of a chiral unit of aniline monomer<sup>22</sup> and by an enzymatic method for production of optically active polyaniline.<sup>23</sup> In the literature it's confirmed that the electronic properties of PANI depends on the degree of protonation and the method of synthesis.<sup>24</sup> Moreover, the work carried out on polyaniline doped by DBTA is based only on the optical properties,<sup>25,26</sup> where the majority of works gave the electric properties of the chiral polyaniline by using an acid containing a sulphonic function and according to Zhang *et al.*,<sup>27</sup> it was reported that the variation of the concentration of the doping agent influences the electric and optical properties of the polyaniline.

The aim of this work is to study the electrical behaviour of the polyaniline doped by a chiral acid containing a carboxylic function. The polyaniline was synthesised by direct oxidative

polymerization of aniline monomer repeat unit using dibenzoyl tartaric acid (DBTA) as a dopant. The morphology, thermal, spectroscopic and electrical properties of PANI-DBTA were investigated.

The DBTA has been chosen here because it has two asymmetrical carbons which confer an optical activity of the polarization plan for the monochromatic light. The optical rotation of DBTA measured in our laboratory at 20 °C is  $-107^\circ$  to  $-113^\circ$  in methanol.

## EXPERIMENTAL

### Products

The products used in this work such as Methanol 99.8%, Aniline 99%, DBTA 99%, ethanol 96%, chloroform 99% are from FLUKA and ammonium peroxydisulfate 99% is from PROLABO. They were all used without purification.

### Synthesis of PANI-DBTA

The PANI was synthesized by chemical oxidation of aniline, with the ammonium persulfate  $\{(NH_4)_2S_2O_8\}$  as oxidant and the (2, 3) di-benzoyl-L-tartarique acid (DBTA) as dopant.

In a glass reactor with double walls, 4.9 mL of aniline in 75 mL distilled water was mixed with the addition of DBTA in excess dissolved in methanol. The concentration of the DBTA ranged from 0.4 M to 1.2 M with an increment of 0.1 M. Using the cooling system, when the temperature solution is reached at  $-12^\circ C$ , we introduced drop by drop the oxidizing solution of ammonium persulfate  $((NH_4)_2S_2O_8)$  prepared into a ratio of concentration  $[oxidant]/[aniline]$  equal to 1.15 under continuous mechanical stirring. After four hours, the formation of a white powder transformed to a dark green precipitate was observed. The PANI-DBTA was filtered by vacuum filtration and washed several times by distilled water and ethanol, and

<sup>1</sup>Laboratoire de Chimie Macromoléculaire, BP 17, E.M.P-BEB-Alger

<sup>2</sup>Unité de Développement et de la Technologie de Silicium, 2, Bd, Franz Fanon, Alger

\*To whom correspondence should be addressed (E-mail: nacera.naar@laposte.net; lamourisaad@gmail.com).

**Table I.** Concentration of the DBTA, conductivity and the energy band gap

Concentration of DBTA (M)	Bands of UV-vis-NIR		Conductivity (S/cm)	Energy band Gap (eV)
	Band 1 (nm)	Band 2 (nm)		
0.4	407	559	$9.36 \cdot 10^{-5}$	1.43
0.5	404	546	$4.01 \cdot 10^{-4}$	1.40
0.6	388	562	$5.48 \cdot 10^{-4}$	1.37
0.7	401	608	$1.10 \cdot 10^{-3}$	1.33
0.8	331	645	$2.14 \cdot 10^{-3}$	1.31
0.9	376	599	$2.77 \cdot 10^{-3}$	1.30
1.0	384	640	$3.54 \cdot 10^{-3}$	1.25
1.1	370	645	$7.25 \cdot 10^{-3}$	1.24
1.2	372	662	$4.54 \cdot 10^{-2}$	1.23

then the powder was dried in vacuum for 48 h at 60 °C. The operating conditions are summarized in Table I.

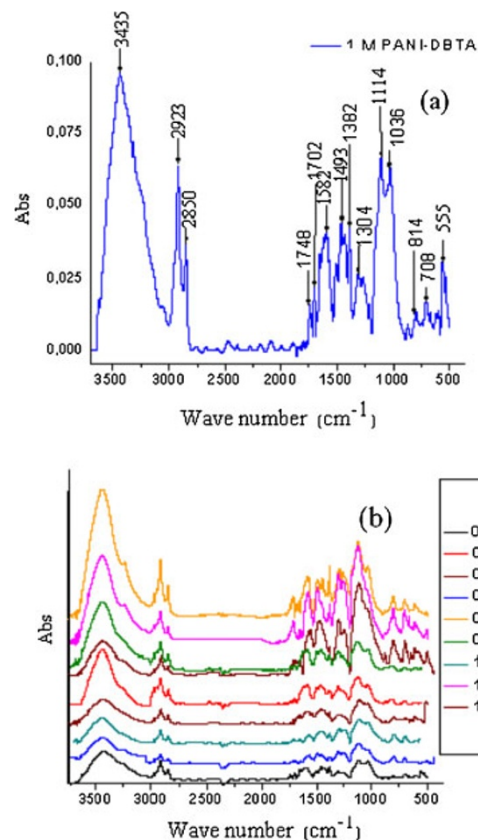
### Measurements

The FT-IR spectra of polyaniline-KBr pellets were obtained by using Shimadzu FT-IR 84005 Spectrometer in the range from 4000 to 400  $\text{cm}^{-1}$  at resolution of 1  $\text{cm}^{-1}$ . UV-vis-NIR spectra were obtained by using a Varian UV model Cary 500 Spectrometer. The Thermogravimetry (TGA) measurements were effectuated by Setaram MTB with “ $10^{-8}$ ” sensitivity, under continued purge nitrogen ( $\text{N}_2$ ) with a flow rate of 15 mL/min and a heating rate of 10 K/min until 500 °C. Morphological analysis powder (PANI-DBTA) was investigated by the scanning electronic microscope SEM 515 PHILIPS. The electrical conductivity at room temperature of different films of PANI-DBTA were measured by the standard four probe method by CMT-SR 2000N Resistivimeter instrument and LCR Databridge 9341 for mixtures having low conductivity. The I-V and C-V curves were plotted using a potentiostat SR 830.

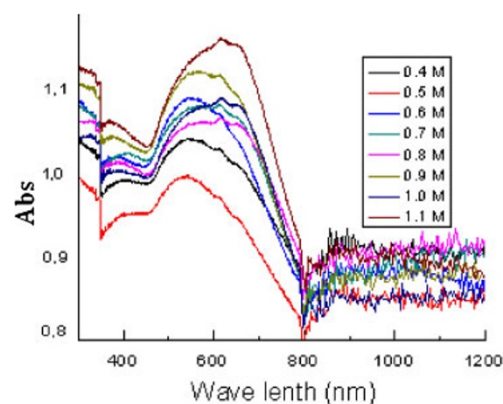
## RESULTS AND DISCUSSION

### Infrared Spectroscopy

The assigned infrared spectra of PANI-DBTA (0.1 M) and the superposition of the various spectra obtained are shown in Figure 1 (a, b). An intense band located around 3450  $\text{cm}^{-1}$  corresponds to the N-H elongation was noted, another band located between 2850  $\text{cm}^{-1}$  and 2923  $\text{cm}^{-1}$  is associated to C-H elongation, two bands at 1491 and 1582  $\text{cm}^{-1}$  are associated to C-C vibrations of (N=Quinoid=N) system and (N-Benzoïd-N) system.<sup>28</sup> The appearance of the bands around 1036  $\text{cm}^{-1}$ , 1382  $\text{cm}^{-1}$ , 1602  $\text{cm}^{-1}$ , 1702  $\text{cm}^{-1}$  and 1748  $\text{cm}^{-1}$  are due to the vibrations CO, RCOO- and RCOOH of the carboxylate function. In addition, the two bands at 1302 and 1114  $\text{cm}^{-1}$ , are attributed to the C-N vibration of the (N-B-N) system, and C=N vibration of the (N=Q=N) system respectively, which confirms the delocalization and the protonation of the obtained polymer. Finally, the existence of the bands towards 814  $\text{cm}^{-1}$ , 708  $\text{cm}^{-1}$  and 555  $\text{cm}^{-1}$  which correspond respectively to the deformation of C-H of benzene 1,4 disubstituted and the benzene mono substituted were observed. According to the FT-IR spectrum, it can be noted a slight



**Figure 1.** FT-IR Spectra (a) PANI-DBTA 1 M and (b) PANI-DBTA at different concentration.



**Figure 2.** UV-visible-NIR absorption spectra of different concentration of PANI-DBTA.

difference between the bands of the polyaniline synthesized in methanol and the bands of the polyaniline reported in the literature.<sup>28</sup> This can be explained by the existence of the hydrogen band between the polyaniline and methanol.

### UV-visible-NIR Analysis

The UV-vis-NIR analysis carried out for PANI doped with DBTA is shown in Figure 2. The UV-visible-NIR spectrum of polyaniline doped by DBTA justifies the presence of the

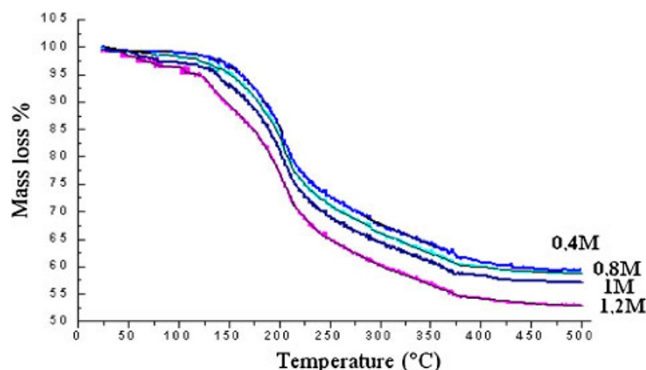


Figure 3. TGA thermograms of different concentration of PANI-DBTA.

emeraldine salt shape. Indeed, the spectra include two bands of absorption (band 1, band 2). The first one (Table I) is associated to  $\pi \rightarrow \pi^*$  electronic transition in the benzenoid rings,<sup>29</sup> while the second band is due to the transition from the  $\pi$  electrons between orbital HOMO of benzenoid system and orbital LUMO of the quinoid system of the PANI. The absorption peaks are about 350 nm from  $\pi \rightarrow \pi^*$  transition and about 450 nm of polaron  $-\pi^*$  bands. In the present work, the peak due to  $\pi$ -polaron transition of the PANI-DBTA films obtained with methanol shifts to 665 nm. Mainly this shifting of the polaron-transition can be influenced by the presence of the methanol in the synthesis process of polyaniline.

### Thermogravimetry Analysis (TGA)

Thermograms of the PANI-DBTA at different concentration were shown in Figure 3. Initially, a weak loss of gradual mass less than 10% between 80 and 140 °C was observed which corresponds to the physical absorbed water.<sup>30</sup> On the other hand, there is an important fall of the mass of approximately 40% for temperatures between 140 and 420 °C. This can be due to the detachment of oligomers and doping agent from the PANI-DBTA. It is remarkable that more than 50% of the initial mass is preserved for temperatures up to 500 °C. This residual mass corresponds to the presence of reticule polymer which is formed at high temperatures.<sup>31</sup>

### PANI-DBTA Morphology Analyses

The PANI-DBTA image obtained by scanning electron microscopy (SEM) is illustrated in Figure 4. The existence of the micro-fibres form in the structure of the PANI doped by DBTA is observed. The alcohol is an amphipathic molecule; it may play the role of a surfactant molecule. It's reported that the interaction between PANI chains and alcohol molecules may be much higher than the interaction between PANI chains and water molecules.<sup>32</sup>

### Conductivity Measurements

The conductivity of thin film of PANI-DBTA (Table I), was measured at room temperature by four probes method. The samples of PANI-DBTA in the powder form were compacted in order to obtain films with a thickness of 0.5 mm. The curve

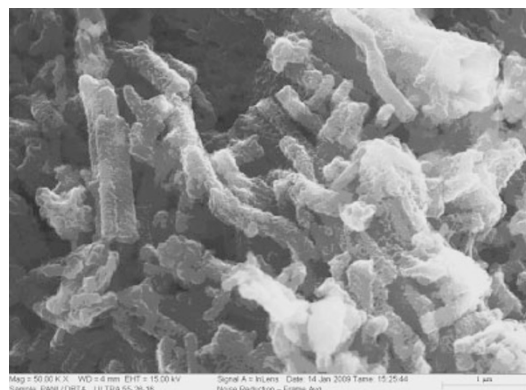


Figure 4. SEM image of PANI-DBTA.

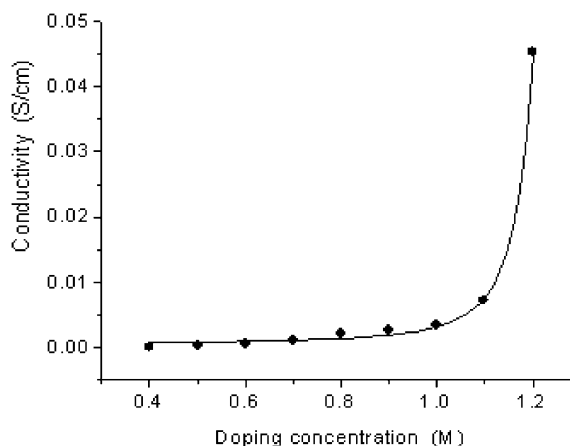


Figure 5. Relationship between the electrical conductivity and doping concentration.

describing the evolution of the electric conductivity ( $\sigma$ ) according to the doping concentration follows an exponential form (Figure 5). Indeed, the electrical conductivity order values are found of “ $10^{-4}$ ” and “ $10^{-3}$ ” for concentrations of doping of 0.4 and 1 M respectively. Note that each value in Figure 5 is an average of six measurements. It is clearly shown that the electrical conductivity obtained with a dopant concentration of 1.2 M is 500 times greater than that found with 0.4 M. This result is in the agreement with the work of S. Palaniappan,<sup>33</sup> which proves that the conductivity increases with the increase in the concentration of the tartaric acid.

### Characterization Current-Voltage

The current-voltage characteristic for the four polyaniline samples (films with 1.12 mm as thickness and 13 mm of diameter) doped with DBTA at concentrations of 0.4, 0.7, 0.9, and 1.1 M, shows (Figure 6) that the shape of the I-V curves is similar to that obtained with the traditional inorganic semiconductors. The obtained curves show a zone tension where the variation of the conductance along the polymeric chain is negligible; it corresponds to the minimal energy necessary to

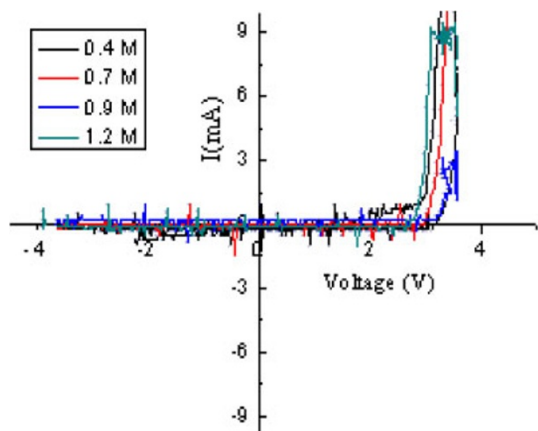


Figure 6. Current-voltage characteristic of the PANI-DBTA.

the passage of the current. The other zone of positive potentials corresponds to the oxidation of polymer (*i.e.*, the extraction of the electrons injected into the polymeric chains). This confirms a p-type doping of a semiconductor.<sup>34</sup> The threshold tension of the PANI-DBTA samples is around +0.6–0.7 volt.

#### Characterization Capacitance–Voltage

The evolution of the capacitance-voltage according to Figure 7 follows a parabolic law. The minimum of the capacitance is recorded with a zero value of potential, this minimum is found of 17.87 nF for the PANI-DBTA 0.5 M and of 15.87 for the PANI-DBTA 1.2 M. The capacity has a tendency to increase with the increase of polarization potential for the two regions. The characteristic C-V is done in the range of potential where the polymer is current rectifying, which justifies the region of selected tension. The variation of the capacitance-voltage are classically described by the following equation:  $C(V) = C_0 + C_1V + C_2V^2$ .

In which the coefficient  $C_0$  is the value of the capacity measured at a fixed temperature and frequency, for an applied voltage of zero ( $V = 0V$ ); The  $C_1$  is the linear coefficient and the  $C_2$  is the quadratic coefficient of the characteristic C-V. From Figure 7, the treatment of the characteristics C-V by a simple parabolic law gives the equations for the two samples of PANI-DBTA:

$$\text{PANI-DBTA } 0,5\text{ M: } C(V) = 17.87 + 11.35V + 38.48V^2$$

$$\text{PANI-DBTA } 1,2\text{ M: } C(V) = 15.87 - 0.45V + 1.28V^2.$$

#### Optical Gap

The polyaniline is described by a model of bands similar to that of the traditional semiconductors (inorganic). It has the characteristic to have a band either partially empty or partially filled with gap varying from 1.7 to 2.4 eV. According to Pankove's relation,  $\alpha(h\nu) = A(h\nu - E_g)^{1/2}$ ,<sup>35</sup> the optical gap values (Table I and Figure 8) obtained by extrapolation of the curves to the energy ( $h\nu$ ) axis are found between 1.23 and 1.40 eV for PANI-DBTA with different doping agent concentration.

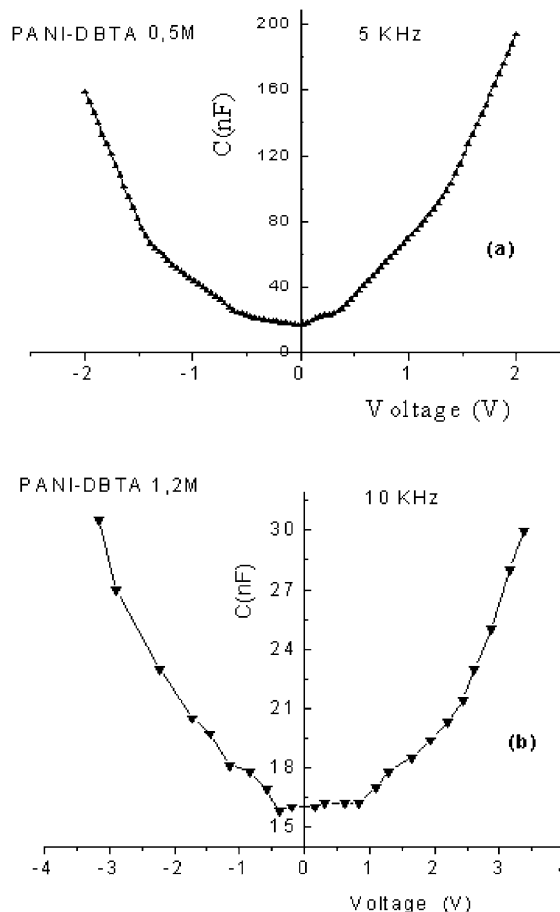


Figure 7. Capacitance-voltage characteristic (a) PANI-DBTA 0.5 M and (b) PANI-DBTA 1.2 M.

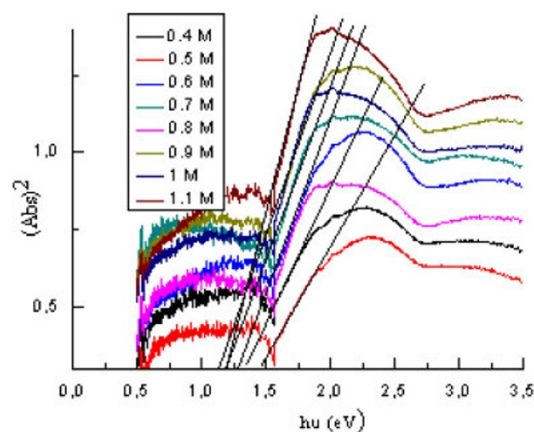


Figure 8. Optical gap of different samples of the PANI-DBTA.

#### CONCLUSION

The examination of FT-IR and UV-vis-NIR spectra, showed various absorption bands which confirmed a protonation of the polyaniline by the used dopant. The thermal analysis by TGA of the synthesized PANI-DBTA reveals a thermal stability until 500 °C, with a preserved mass of about 55%. SEM morpho-



logical study of the elaborated samples showed the existence of micro-fibres in the structure. In addition, the samples of PANI-DBTA exhibited a good electrical conductivity, although the dibenzoyl tartaric acid is a carboxylic acid with a very low constant of acidity. The electrical conductivity is proportional to the concentration of the doping agent (DBTA). The values of the band gap of the PANI-DBTA measured for various concentrations of the doping agent confirm its protonation; indeed, they are all in the range of that obtained with semiconductor materials. The characteristic current-voltage indicated the doping type of PANI-DBTA and the capacitance-voltage curve confirmed a model similar to that of the traditional semiconductors (inorganic). The observation of PANI-DBTA at a macroscopic and microscopic scale shows that using methanol as organic solvent to dissolve the dopant in the synthesis of polyaniline improved its morphological and electrical properties.

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