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## Preparation and characterization of a new polyaniline salt with good conductivity and great solubility in dimethyl sulphoxide

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**Abstract:** In this study, a novel conducting and soluble polyaniline salt prepared by chemical polymerization in the presence of a new doping agent (IAs) is proposed. This doping agent was prepared by the sulphonation of itaconic acid (IA) with concentrated sulphuric acid in tetrahydrofuran (THF). The obtained doped polyaniline (PANI–IAs) was extremely soluble in dimethyl sulphoxide (DMSO) at room temperature, in which the solubility reached 44 mg mL<sup>-1</sup>. The conductivity measurement of doped polyaniline powder precipitated in THF as dispersing medium gave a value of 0.13 S cm<sup>-1</sup> when the emeraldine base form of polyaniline was fully protonated. The polyaniline salt sample was characterized by thermogravimetry (TG), differential scanning calorimetry (DSC), X-ray diffraction and UV–Vis and FTIR spectroscopy.

**Keywords:** conducting polymer; PANI; itaconic acid; sulphonation; solubility.

### INTRODUCTION

Intrinsically conducting polymers (ICPs) have attracted important attention in many advanced applications. Among ICPs, polyaniline (PANI) is one of the essential conductive polymer for its wide use in many domains, such as organic lightweight batteries,<sup>1</sup> electro-chromic display devices,<sup>2,3</sup> photo-electronic devices,<sup>4</sup> chemical sensors<sup>5,6</sup> and hydrogen storage.<sup>7</sup> Polyaniline has been considered as one of the most promising electrode materials due to its simple synthesis, environmental stability, unique electronic properties, and simple acid–base doping/dedoping chemistry.<sup>8,9</sup> On the other hand, the intractable solubility of PANI in common organic solvents has limited its practical applications in many fields. It is therefore a very important challenge to design doped polyaniline and its derivatives in forms that are easily processable and applicable. In

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recent years, a number of studies were focused on the improvement of PANI solubility, a variety of methods were proposed that consisted in doping PANI emeraldine base (PANI-EB) by extended organic alkyls of sulphonic acids (DBSA and CSA)<sup>10–12</sup> or with polymeric acids.<sup>13–16</sup>

In 2009, Peng studied an emulsion polymerization process that had been developed for the direct synthesis of organo-soluble polyaniline (PANI) with oleic acid (OA) as a surfactant and dopant.<sup>17</sup> Gribkova *et al.*, reported the chemical synthesis of polyaniline in the presence of polymeric acids (such as poly-(amidosulphonic acids)), which contain sulphonic groups in the chemical structure. They found that the matrix polymerization of aniline resulted in the formation of water-soluble interpolymer complexes of PANI with polyacid.<sup>18</sup> In 2015, Zeghioud *et al.* prepared soluble polyaniline salts doped with poly (itaconic acid); they found that the solubility reaches 4 mg mL<sup>-1</sup> in an optimized mixture of THF/water at room temperature.<sup>19</sup>

Wang *et al.* prepared polyaniline nanorods by chemical oxidation polymerization using itaconic acid as dopant. The obtained polyaniline salt, compared to the undoped form, possesses high productivity, conductivity and excellent solubility in organic solvents (*N*-methylpyrrolidone, NMP, tetrahydrofuran, THF, and dimethyl formamide, DMF), which reached 19 mg mL<sup>-1</sup>.<sup>20</sup>

In this work, a new and low-cost sulphonic dopant was prepared from itaconic acid (a platform chemical produced from renewable resources) by a simple chemical reaction. Therefore, the development of a new polyaniline salt with simultaneously very good solubility (in common solvents) and good electrical conductivity is a challenge and it was the aim of the present study. The structure, spectroscopic properties, thermal stability and conductivity of the obtained polyaniline were also investigated.

## EXPERIMENTAL

### *Materials*

Aniline (ANI, 99b% pure) was purchased from Fluka. The other employed materials were hydrochloric acid (35.37 %) from Organics Stinnes Chemicals, methanol (99.5 %) and ammonium peroxodisulphate (APS, 99 %) from Prolabo, acetone (99 %) from Acros Organics. While ammonia (25 % solution), *N*-methylpyrrolidone (NMP, 99.5 %) and tetrahydrofuran (99 %) were from Merck. Itaconic acid (IA, 99 %) was from Aldrich, dimethyl sulphoxide (DMSO, 100 %) and dimethyl formamide (DMF, 100 %) from Sigma-Aldrich. All these products were used without further purification.

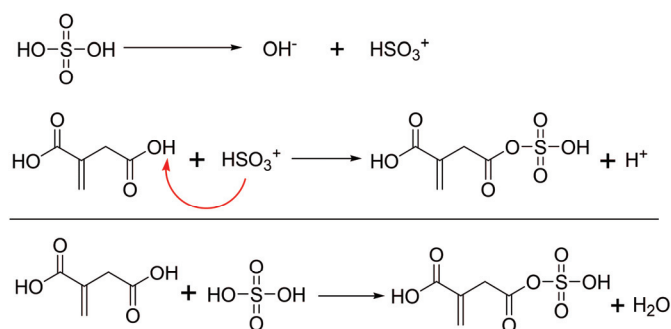
### *Synthesis of PANI*

Polyaniline powder in the emeraldine salt form was synthesized as follows: 4.8 g of aniline (4.75 mL) and 15 mL of HCl were dispersed in 50 mL of deionised water under vigorous stirring at room temperature for 2 h, to obtain a uniform solution. An aqueous solution of APS (11.8 g of APS + 50 mL of deionised water) was slowly added to the above mixture with mole ratio equal to one (APS/ANI = 1). The resulting solution was stirred for 30 min to ensure complete mixing. Then, the reaction was followed by continuous stirring at 2 °C

for about 4 h. Finally, the formed precipitate was filtered, washed successively with distilled water followed by methanol (to remove oligomers and other by-products) until the filtrate was colourless, and then dried at 60 °C for 48 h. The polyaniline salt (PANI–HCl) was converted to base form (PANI–EB) by treatment with aqueous NH<sub>4</sub>OH solution for 72 h, followed by washing with distilled water and methanol; the base form of PANI was obtained as a blue powder. The polymerization yield was 80 %.

#### Synthesis of the dopant

Itaconic acid sulphonated (IAs) was prepared by chemical reaction between itaconic acid (IA) and a concentrated sulfuric acid as follows: 3 g of IA was dissolved in 10 ml of THF under continuous stirring in round-bottom flask (triple-neck type); the system was placed in a thermostatic bath at 40 °C. A small quantity of sulfuric acid was added drop by drop to the above solution with the help of dropping funnel to a mole ratio equal to one. The solution was left under constant stirring for 3 days. Subsequently, the product (IAs) was separated by drying for 5 days at 70 °C. The possible reaction mechanism is presented in Scheme 1.



Scheme 1. Plausible mechanism of the sulphonation reaction.

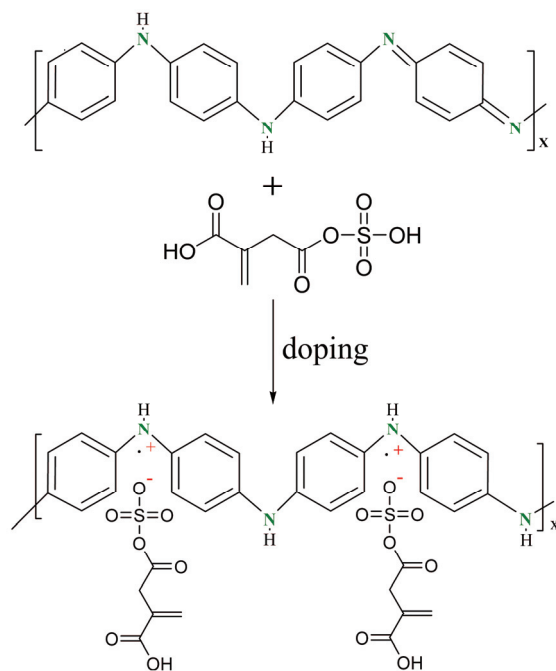
#### Doping

For the preparation of sulphonated acid doped polyaniline, undoped PANI solution in THF (or another organic solvent) was mixed with IAs in mole ratio equal to two between IAs and tetrameric repeat unit of PANI–EB. The mixture was transferred to an ultrasound bath for 2 h, followed by constant agitation for 6 h. A dark green colour was obtained. The PANI–IAs dispersion (in THF or NMP) was filtered using polytetrafluoroethylene (PTFE) filters, washed and dried at 60 °C for 24 h. The reaction mechanism is shown in Scheme 2. The obtained apparent viscometric average molar mass of the sulphonated itaconic acid-doped polyaniline (PANI–IAs) was  $\bar{M}_v = 4430 \text{ g mol}^{-1}$ .

#### Characterization

Fourier transform infrared (FTIR) spectra were recorded between 400 and 4000 cm<sup>-1</sup> from KBr pellets on an infrared Fourier transform spectrometer (Shimadzu type 8400 S). UV–Vis spectra of all samples dissolved in different solvents were recorded using a Shimadzu UV-2401PC UV–Vis spectrometer with a resolution of 2 nm, in the wavelength range of 300–900 nm. X-Ray powder diffraction patterns were recorded on a PANalytical X'Pert PRO diffractometer fitted with CuK<sub>α</sub> radiation ( $\lambda = 1.5404 \text{ nm}$ ) at 40 kV and 40 mA in the 4–60° 2 $\theta$  region. Thermogravimetry (TG) was performed using Setaram an MTB thermogravimetric instrument at a sensitivity of “10<sup>-8</sup>”, operating at a heating rate of 10 °C min<sup>-1</sup>, from room

temperature up to 450 °C under an air atmosphere. The sample mass ranged between 3 and 6 mg. The differential scanning calorimetry (DSC) measurements were realised on a Netzsch DSC 204 F1 at a scanning rate of 10 °C min<sup>-1</sup> from room temperature up to 400 °C under an inert atmosphere.



Scheme 2. Mechanism of PANI doping with IAs.

## RESULTS AND DISCUSSION

### *Conductivity measurements*

The conductivity measurements on compressed pellets of various forms of PANI powder prepared by chemical polymerization were made by the conventional four-point probe technique at room temperature. For IAs-doped polyaniline, the powder was obtained by filtration and drying of the precipitate formed in the dispersion of THF and NMP.

The band gap in eV was calculated by the equation:<sup>21</sup>

$$E_g = \frac{1237.5}{\lambda} \quad (1)$$

where  $\lambda$  represents the maximum wavelength (nm) in the band attributed to  $\pi$ - $\pi^*$  (Band 1) transitions. The measured values of conductivity are given in Table I; PANI-HCl has better conductivity (4.6 S cm<sup>-1</sup>) than PANI-IAs. This was confirmed by the smaller band gap of PANI-HCl, around 3.2 eV, compared with that of PANI-IAs (3.62 eV). However, the conductivity value of the latter depended

strongly on the dispersion medium during synthesis, whereby the highest value ( $0.13 \text{ S cm}^{-1}$ ) was obtained in THF.

TABLE I. Conductivities and energy band gap of different forms of PANI

Sample (dispersion medium)	UV-Vis band, nm		Conductivity $\text{S cm}^{-1}$	Band gap energy eV
	1	2		
PANI-HCl	387	467	4.60	3.20
PANI-EB	331	626	$8.14 \times 10^{-10}$	–
PANI-IAs (THF)	–	–	0.13	3.62
PANI-IAs (NMP)	–	–	0.01	–
PANI-IAs (DMSO)	342	417	–	–

#### UV-Vis spectroscopy

The UV-Vis spectrum of undoped polyaniline included two absorption bands at 331 and 626 nm due to the excitation of the benzoid and quinoid segments in the polyaniline chain, respectively,<sup>22</sup> (Fig. 1, curve (a)).

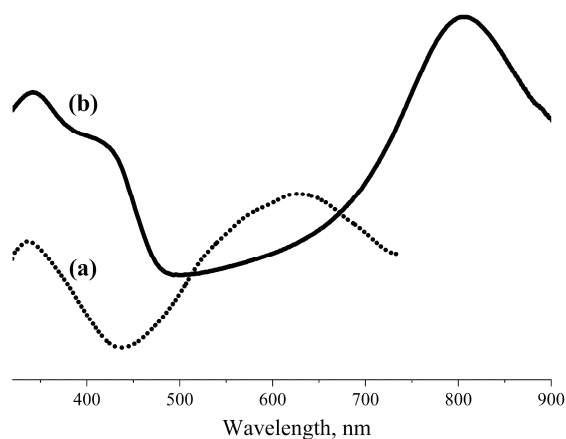


Fig. 1. UV-Vis spectra of: a) PANI-EB and b) PANI-IAs recorded in DMSO solvent.

Curve (b) in Fig. 1 illustrates the UV-Vis spectrum after IAs had been added to the DMSO containing PANI-EB. Thus, the absorption band at 626 nm disappeared. However, the characteristic polaron band would appear at 807 nm. The characteristic absorption bands in the spectrum of PANI-IAs are clearly observed at about 807 and 417 nm, which are attributed to the transitions from the  $\pi$  band to the polaron band and from the polaron band to the  $\pi^*$  band of the alternating benzoid-quinoid structures, respectively.<sup>23</sup> The band around 342 nm is referred to the transition from the  $\pi$  band to the  $\pi^*$  band centred on the benzoid rings associated with the extended  $\pi$  orbitals on polymer backbone (band gap excitation).<sup>24</sup>

### Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of IA and IAs samples are shown in Fig. 2. The spectrum of IA and IAs presented a broad band centred at  $2926\text{ cm}^{-1}$ , which is attributed to O–H stretching vibrations. The spectrum of IA (curve a) showed peaks around  $1718$ ,  $1430$ , and  $1190\text{ cm}^{-1}$ , indicating the stretching C=O (carboxylic acid), C–O–H in the plane and C–O, respectively.<sup>25,26</sup>

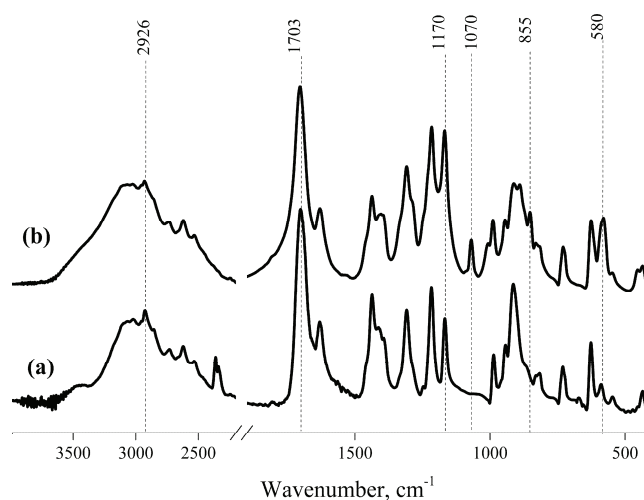


Fig. 2. FTIR spectra of: a) IA and b) IAs.

The spectrum of IA obtained after sulphonation (curve b) showed the characteristic absorption band for the acid carbonylic groups at  $1703\text{ cm}^{-1}$ .<sup>27</sup> The peaks around  $1400$  and  $1170\text{ cm}^{-1}$  were assigned to the stretching vibrations of C–O–H of carboxylic acid and asymmetrical stretching of  $\text{SO}_2$ , respectively. New peaks appeared at  $1070$  and  $855\text{ cm}^{-1}$ , which are attributed to the stretching vibration of symmetrical  $\text{SO}_2$  and the bending of O–S, respectively.<sup>27–29</sup> The non-disappearance of the C=C peak at  $1629\text{ cm}^{-1}$  confirmed the sulphonation of IA by sulphuric acid according to the mechanism proposed in the Scheme 1.

Figure 3 shows the FTIR spectra of PANI–EB and PANI–IAs. In the spectrum of PANI–EB (curve a), the characteristic absorption peaks at  $1583$ <sup>30</sup> and  $1494$ <sup>31</sup>  $\text{cm}^{-1}$  could be assigned to the C=C stretching mode for the quinoid rings and the C=C stretching mode for the benzoid rings, respectively. The absorption peak at  $1303\text{ cm}^{-1}$  corresponds to the C–N stretching mode. The in-plane bending of C–H is reflected in the  $1160\text{ cm}^{-1}$  peak, and the out-of-plane bending vibration of C–H occurred at  $508\text{ cm}^{-1}$ .<sup>31–33</sup> In the spectrum of PANI–IAs (curve c), the characteristic peaks at  $1562$ <sup>27</sup> and  $1470$ <sup>28</sup>  $\text{cm}^{-1}$  could be assigned to the C=C stretching mode for the quinoid rings and the C=C stretching mode for the benzoid rings, respectively. Two absorption peaks at  $1303$  and  $1240\text{ cm}^{-1}$  corres-

pond to the C–N stretching<sup>33</sup> and C–N stretching of protonated mode,<sup>30</sup> respectively. The in-plane bending of C–H was reflected in the 1121 cm<sup>-1</sup> peak, and the out-of-plane bending vibration of C–H occurred at 508 cm<sup>-1</sup>.<sup>27</sup> The shift of the characteristic peaks of PANI indicated strong interaction between PANI–EB and the dopant.

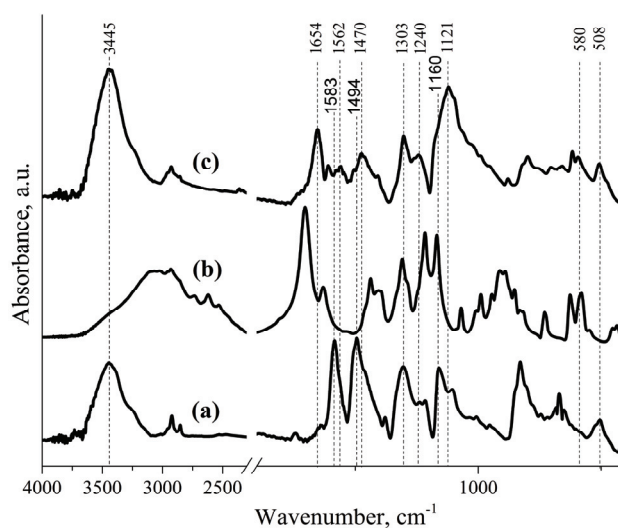


Fig. 3. FTIR spectra of: a) PANI–EB, b) IAs and c) PANI–IAs.

#### Solubility determination

The PANI–IAs was synthesized in different polar solvents, such as NMP, DMSO, THF and DMF (Fig. 4). The obtained dispersions (in THF and NMP) were filtered using 0.45- $\mu$ m PTFE filters, washed and dried to recover the PANI–IAs powder.

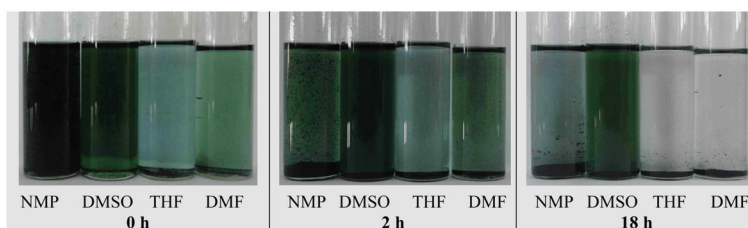


Fig. 4. PANI–IAs dispersions in different solvents.

Figure 4 shows the very good solubility in NMP and DMSO just after doping. After 2 h, strong interactions between the polymers chains were clearly detected in all dispersion media except for the PANI–IAs/DMSO solution. After filtration and UV–Vis analysis of the resulting solutions, DMSO was found to be

the only solvent capable of dissolving the PANI-IAs chains at room temperature. The maximum solubility was determined by calculation of the difference between the densities of PANI-IAs/DMSO solution and pure DMSO; it was found that the solubility could reach  $44 \text{ mg mL}^{-1}$ . From this, it was concluded that DMSO is a very good solvent for PANI-IAs, which is confirmed by Fig. 5.



Fig. 5. Digital photos of solutions of: a) concentrated and b) dilute solution of PANI-IAs in DMSO solvent.

Polyaniline is soluble only in DMSO because the interactions between the PANI chains and DMSO are more important than the interactions between the polyaniline chains that increases the distance between the molecular chains and gives a relatively extended conformation to these chains. Thus, the solubility of polyaniline is primarily controlled by the molecular structures of the polymer chain (including the doping agent) and the solvent properties (polarity, number of carboxylic groups and molecular size).

#### *X-Ray diffraction pattern (XRD)*

The X-ray diffraction pattern of the PANI-EB and PANI-IAs powder are presented in Fig. 6. The crystalline region presented by the peak and the amorphous region presented by the remainder of diffractogramme were both integ-

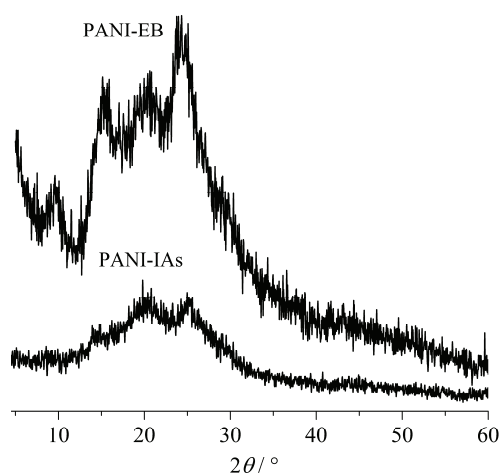


Fig. 6. XRD Patterns of PANI-EB and PANI-IAs.



rated in  $2\theta$  space. From these integrated peaks areas ( $I_c, I_a$ ), the ratio  $X_c/X_a$  can be calculated from  $X_c/X_a = 1.8(I_c/I_a)$ . A Ryland factor of 1.8 is commonly used for semi-crystalline polymers.<sup>34</sup> The percentage crystallinity  $X_c$  (%) was obtained from Eq. (2):<sup>34</sup>

$$X_c (\%) = 100 - \frac{100}{(1 + X_c / X_a)} \quad (2)$$

The XRD profile of PANI-EB showed a number of narrow sharp reflection peaks at  $2\theta$  9.54, 15.22, 20.75 and 24.29°, representing the (001), (011), (100) and (110) crystal planes, respectively (Table II). The peak centred at  $2\theta \sim 20^\circ$  may be ascribed to periodicity parallel to the polymer chain, while the peak at  $2\theta \sim 25^\circ$  may be caused by periodicity perpendicular to the polymer chain.<sup>35</sup>

TABLE II. The  $2\theta$  values, intensity and indexation ( $hkl$ ) of PANI-EB and PANI-IAs

Sample	$2\theta / ^\circ$	$d / \text{Å}$	$hkl$	Ref.	$X_c / \%$
PANI-EB	09.57	09.23	001	36	9.64
	15.22	05.82	011	27	
	20.75	04.28	100	37	
	24.29	03.66	110	38	
PANI-IAs	08.63	10.23	001	37	8.70
	14.20	06.23	011	39	
	19.73	04.49	100	36	
	25.19	03.54	110	38	

After conversion of PANI-EB into PANI-IAs, broad diffuse peaks centred at  $2\theta$  8.63 (001) and 14.2° (011) appeared, and two small peaks at  $2\theta$  19.73 (100) and 25.19° (110) were observed. Compared to PANI-EB, the intensities of the two last peaks ( $2\theta$  19.73 and 25.19°) were strongly reduced.<sup>40</sup> This was proved by the decrease in the degree of crystallinity ( $X_c$ ) from 9.64 % for PANI-EB to 8.70 % for PANI-IAs.

#### Thermogravimetry (TG)

The thermal stability of the PANI-IAs was evaluated using TG. Polyaniline salt powder (PANI-IAs) showed poor thermal stability. As seen in Fig. 7, the degradation occurred in three stages; the first mass loss was assigned to the evaporation of water and residual solvents,<sup>41,42</sup> in the second temperature region (200–270 °C), the degradation was due to the start of loss of the sulphonic and carboxylic groups of itaconic acid.<sup>43</sup> This was followed by a broad loss of mass starting from 270 °C. This mass loss was probably due to the dehydration and the decomposition of the chemical structure of the short PANI chains.<sup>44</sup>

It is important to notice that more than 50% of the initial mass was conserved for temperatures up to 500 °C. This residual mass was related to the existence of reticule polymer, which is formed at high temperatures.<sup>45</sup>

*DSC thermal analysis*

The DSC curve for PANI-IAs (Fig. 8) showed two endothermic peaks around 35–184 °C and 200–350 °C. The first endothermic transition is related to the excess water existing in the PANI lattice that influences the conductivity and crystal structure of PANI.<sup>46</sup> The second thermal transition, which was centred at 290 °C, involved the beginning of PANI-IAs degradation (decarboxylation) and the detachment of doping agent. In Fig. 9, there was an absence of dopant carboxylic groups after DSC analysis, which confirmed that complete decarboxylation had occurred.

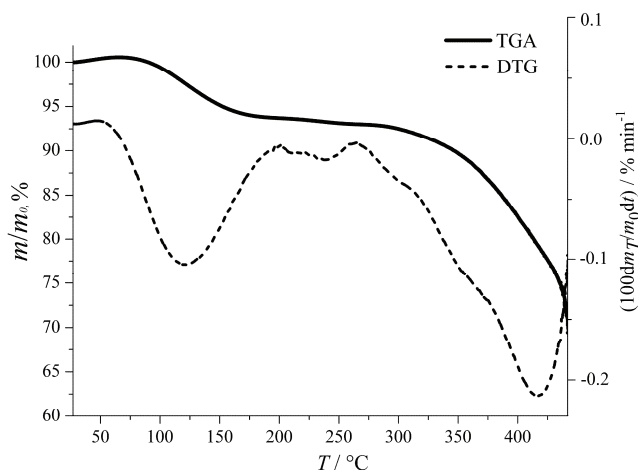


Fig. 7. Thermogravimetric analysis of PANI-IAs.

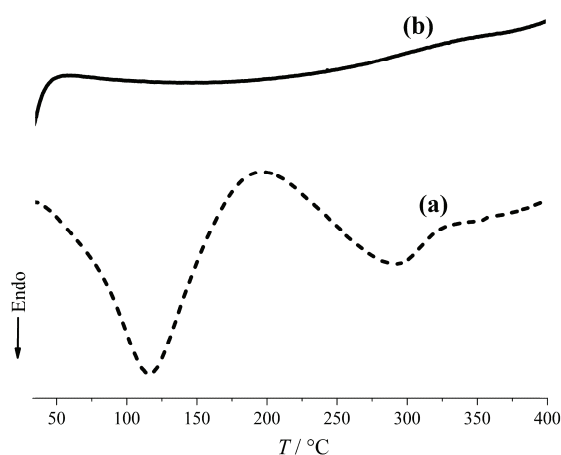


Fig. 8. DSC thermal analysis curves of the PANI-IAs powder under a nitrogen atmosphere: a) first run and b) second run (heating rate: 10 °C min<sup>-1</sup>).

The curve b shown in Fig. 8 represents the second scan DSC thermogram of the same PANI-IAs sample. There are no significant endothermic or exothermic

peaks on this curve. This is because almost all the moisture had evaporated from the PANI-IAs sample during the first thermal treatment run. Moreover, a cross-linking reaction may have occurred during the first thermal analysis run and may have resulted in a 3D chemical structure. This crosslinking reaction, illustrated in Scheme 3,<sup>47</sup> was the result of the coupling of two neighbouring  $-N=Q=N-$  groups.

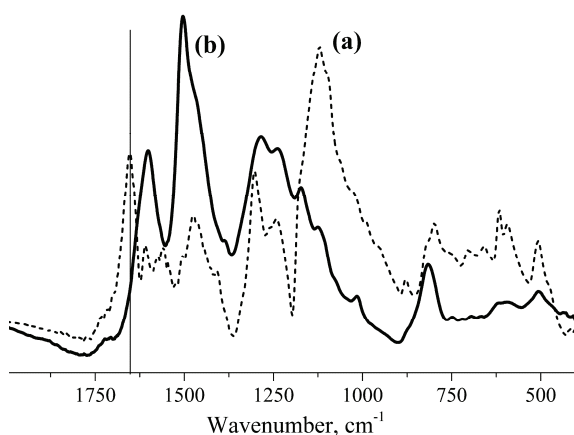
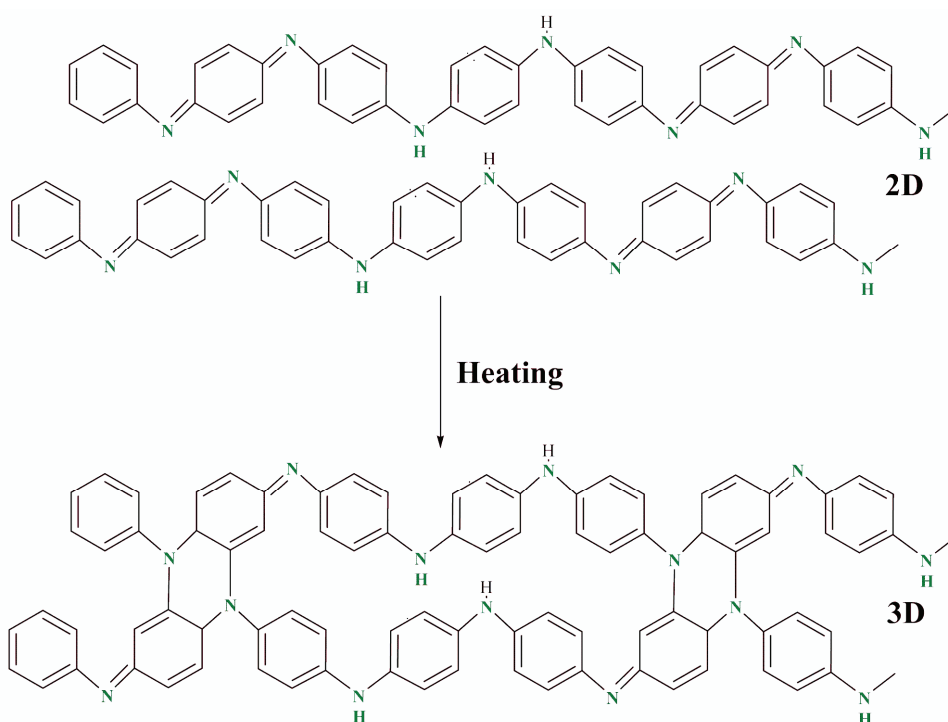


Fig. 9. FTIR spectra of PANI-IAs: a) before and b) after DSC analysis.



Scheme 3. Thermal crosslinking reaction between the PANI molecular chains.

## CONCLUSIONS

The sulphonation of itaconic acid was successfully performed in a simple chemical reaction. The doping of PANI–EB by the synthesised dopant (IAs) was effectively realised. The results of this study provide further that the use of IAs as a novel sulphonic dopant for polyaniline delivers a significant improvement in the solubility of the polyaniline salt compared to those reported previously. The maximum solubility reached  $44 \text{ mg mL}^{-1}$  in pure DMSO as polar organic solvent at room temperature. It was shown that a conducting form of PANI that is thermally stable up to  $200 \text{ }^\circ\text{C}$  could be prepared. The characterization of the PANI–IAs confirmed the success in obtaining good conductivity that reaches  $0.13 \text{ S cm}^{-1}$  for fully doped PANI–EB. A low degree of crystallinity was found for the conducting form of PANI compared to the non-doped one.

## ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА НОВЕ ПРОВОДНЕ И У ДИМЕТИЛСУЛФОКСИДУ  
ВЕОМА РАСТВОРНЕ СОЛИ ПОЛИАНИЛИНА

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У раду је приказана синтеза нове растворне и проводне соли полианилина оксидативном полимеризацијом у присуству новог агенса за допирање. Агенс за допирање (IAs) је синтетисан сулфонованем итаконске киселине (IA) концентрованом сумпорном киселином у тетрахидрофурану (THF). Со допираног полианилина (PANI–IAs) је веома растворна у диметилсулфоксиду (DMSO) на собној температури, при чему се достиже растворљивост од  $44 \text{ mg mL}^{-1}$ . Мерења проводљивости допираног полианилина, добијеног таложењем у THF, показала су да се максимална проводљивост од  $0,13 \text{ S cm}^{-1}$  достиже у при потпуном протоновању полианилина у облику емералдинске базе. Поред тога, узорци соли полианилина су карактерисани термогравиметријском анализом (TGA), диференцијалном сканирајућом спектроскопијом (DSC), дифракцијом X-зрака (XRD), као и UV–Vis и FTIR спектроскопијом.

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