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Chemical synthesis and characterization of highly soluble conducting polyaniline in mixtures of common solvents

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Abstract: This work presents the synthesis and characterization of soluble and conducting polyaniline–poly(itaconic acid) PANI–PIA according to a chemical polymerization route. This polymerization pathway leads to the formation of doped polyaniline salts, which are highly soluble in a number of mixtures between organic common polar solvents and water, the solubility reaches 4 mg mL⁻¹. The effect of synthesis parameters, such as doping level, on the conductivity was investigated and a study of the solubility and other properties of the resulting PANI salts were also undertaken. The maximum of conductivity was found equal to 2.48×10⁻⁴ S cm⁻¹ for fully protonated PANI-EB. In addition, the synthesized materials were characterized by various methods, *i.e.*, viscosity measurements, XRD analysis and FTIR and UV–Vis spectroscopy. Finally, TGA was performed to obtain some information concerning the thermal behaviour of the materials.

Keywords: conducting polymer; PANI; itaconic acid; polymerization; solubility properties.

INTRODUCTION

The synthesis and improvement of new materials with special properties have attracted much attention in the last decade. Polyaniline (PANI) is one of the most promising polymers due to its good flexibility, low cost, oxidative stability and unique conduction mechanism.^{1–3} However, there are some major drawbacks, which limit its application, such as low thermal stability and poor solubility in common solvents due to the stiffness of backbone and H-bonding interactions between adjacent chains.^{4,5}

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Recently a number of studies have been devoted to the search for different synthetic methods that allow PANI to be obtained with good solubility in the presence of different polymeric acids with different structures,^{6–9} which improve processibility, special electrical conductivity and optical and spectroscopic properties.

Barrios *et al.*¹⁰ reported the electro-synthesis of PANI in the presence of poly(itaconic acid) and they evaluated the effect of the presence of dicarboxylic acids on the electrochemical behaviour of the obtained films. Nevertheless, the electrochemical methods generated polyaniline with very low solubility that was difficult to process and had restricted application.

Travas-Sejdic *et al.*¹¹ studied the electrochemical properties of self-assembled multilayer films based on polyaniline and two polyanions: poly(styrene sulphonate) (PSSA) and an oligonucleotide (ON), and found by cyclic voltammetry experiments that PANI/PSSA and PANI/ON films had different electrochemical behaviours, with PANI/ON films showing lower electroactivity.

Gizdavic-Nikolaidis *et al.*¹² recently demonstrated that a conductive polymer nanofibrillar network of poly(lactic acid) can be electrospun with PANI, and its copolymers with *m*-aminobenzoic acid (*m*-ABA) from DMSO/THF solutions. Abdul Rahman *et al.*¹³ found that the number average molecular weights of the copolymers decreased significantly with increasing *m*-ABA fraction in the copolymers, and the solubility increased with increasing proportion of *m*-ABA. This increase was due not only to the functional COOH groups, but also to the decrease in the average length of the polymer chains.

Gribkova *et al.*¹⁴ reported the chemical polymerization of aniline in the presence of aromatic polyamides containing sulphonic groups. They observed that the presence of the flexible-chain of polyamides with a regular distribution of sulphonic groups along the polymer chain allowed the polyaniline to exhibit a random coil conformation in the presence of strong electrolytes and the formation of water-soluble interpolymer complexes of PANI with polyacids.

Wang *et al.*¹⁵ prepared polyaniline nanorods by chemical oxidative polymerization using itaconic acid as dopant. The polyaniline salt obtained, compared to the undoped form, possessed high productivity, conductivity and excellent solubility in organic solvents such as NMP, THF and DMF, which reached 19 mg mL⁻¹.

The main goal of the present work was the chemical doping of PANI in the presence of poly(itaconic acid) (PIA). PIA is a very exciting material due to its biocompatibility with natural systems. In addition, PIA is very attractive because it has two negatively charged carboxylic groups in each monomer unit. The essential advantage of the resultant PANI was the possibility of producing conductive PANI blends with good solubility. The spectral, thermal and electrical properties of the obtained PANI molecular composites were studied.

EXPERIMENTAL

Materials

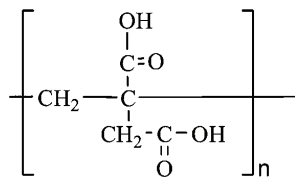
Aniline (ANI, 99 % pure) was purchased from Fluka. Other provided materials were hydrochloric acid (35.37 %) from Organics Stinnes Chemicals, methanol (99.5 %) and ammonium peroxodisulphate (APS, 99 %) from Prolabo. Potassium peroxodisulphate (PPS, 99 %) was from Riedel-de Haën, acetone (99 %) from Acros Organics, while ammonia (25 % solution), *N*-methylpyrrolidone (NMP, 99.5 %) and tetrahydrofuran (THF, 99 %) were from Merck. Itaconic acid (99 %) was purchased from Aldrich, dimethyl sulphoxide (DMSO, 100 %) from Analytical Reagent. Deionised water was used throughout the experiments and all chemicals were used without previous purification.

Synthesis of PANI

The synthesis of the PANI-EB was 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. Then, an aqueous solution of APS (11.8 g + 50 mL deionised water) was added to the above mixture in one portion (the mole ratio ANI:APS = 1). The resulting solution was stirred for 30 min to ensure complete mixing, and then the reaction was followed by continuous stirring at 2 °C for 4 h. The precipitate that formed was filtered off, washed with deionised water and methanol until the filtrate was colourless to remove excess acid and possible oligomers. Finally, the powder was dried under vacuum for 48 h. Then, the obtained PANI as the emeraldine salt (PANI-ES) was stirred in 1 M solution of ammonium hydroxide at room temperature for 72 h to completely convert it to emeraldine base (PANI-EB) form. Upon filtering and drying under a dynamic vacuum in an oven at 60 °C for 24 h, the base form of PANI was obtained as a blue powder. The yield of the polymerization was 80 %.

Poly(itaconic acid) synthesis

The synthesis was carried out similarly to that described in work of Larez *et al.*¹⁶ Thus deionised water (10 mL) was heated until boiling and left to reach ambient temperature with continuous stirring and under nitrogen bubbling. Itaconic acid (IA, 0.023 mol) and PPS (2.22×10^{-4} mol) were added and the system was sealed and placed in a thermostatic bath at 60 °C with continuous stirring during 48 h. A heterogeneous mixture was initially obtained due to an incomplete dissolving of IA that went transparent after 5 min. After the polymerization reaction time was over, the reactor was left to cool down to room temperature under continuous stirring (about 30 min). Polymer was separated by precipitation in cool acetone. The repeat unit of the resulting polymer (PIA) is shown in Scheme 1.

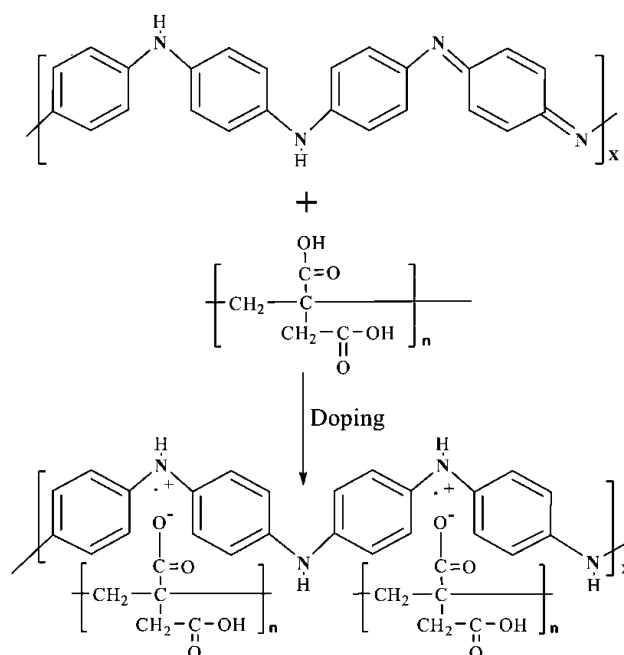


Scheme 1. Chemical structure of the repeat unit of poly(itaconic acid) PIA.

Doping

The polymeric acid-doped PANI was prepared by mixing 0.9 g of PANI-EB (0.0025 mol, based on the approximate tetrameric repeat unit) in a THF dispersion with the appropriate quantity

of poly(itaconic acid) solution of different mole ratios (based on its acidic repeat unit). The suspension was sonicated in a bath-type sonicator for 2 h followed by electromagnetic stirring (12 h) to make the dispersion homogeneous. The dispersion of PANI-PIA was filtered using polytetrafluoroethylene membrane filters of pore size 0.45 μm . The resultant powder was washed with large quantities of distilled water until the filtrate became colourless and the powder was dried in an oven at 60 $^{\circ}\text{C}$ for 24 h. The reaction mechanism is shown in Scheme 2.



Scheme 2. Mechanism of PANI-EB doping with PIA.

Characterization

The Fourier transform infrared (FTIR) spectra were recorded between 400 and 4000 cm^{-1} from KBr pellets on an infrared Fourier transform spectrometer (Shimadzu type 8400 S). The UV-Vis spectra of all samples dissolved in different solvents were recorded using a UV-Vis spectrometer Shimadzu UV-2401PC, in the wavelength range of 250–900 nm. The intrinsic viscosity measurements of solutions were made using a Micro-Ubbelohde Schott-Gerate viscosimeter. The X-ray powder diffraction patterns were recorded on a PANalytical X'Pert PRO diffractometer fitted with $\text{CuK}\alpha$ radiation ($\lambda = 1.5404 \text{ nm}$) at 40 kV and 40 mA in the 2θ range 5– 60° region. Thermogravimetric (TG) analysis was performed using a Setaram MTB instrument with “ 10^{-8} ” sensitivity, operating at a heating rate of 10 $^{\circ}\text{C min}^{-1}$, from room temperature up to 450 $^{\circ}\text{C}$ under an air atmosphere. The sample mass ranged between 3 and 6 mg.

RESULTS AND DISCUSSION

Conductivity measurements

The electrical conductivity measurements of compressed pellets of PIA-doped PANI were made by the conventional four-point probe technique at room

temperature; the data are plotted in Fig. 1. The curve showing the evolution of the electric conductivity (σ) according to the doping level follows an exponential form. Indeed, the values of the electrical conductivity order of 10^{-4} were found for PANI-PIA, whereby a high conductivity value of $2.48 \times 10^{-4} \text{ S cm}^{-1}$ for the PANI-PIA was reached when the PANI-EB (conductivity value of $8.14 \times 10^{-10} \text{ S cm}^{-1}$) was fully protonated, showing that the resultant PANI-PIA was less conductive than the PANI-HCl, which has a conductivity of 4.6 S cm^{-1} . This was confirmed by the narrower band gap for PANI-HCl around 3.2 eV compared with the PANI-PIA (Table I). Note that each measured value of conductivity is an average of four measurements for each face of the pellet.

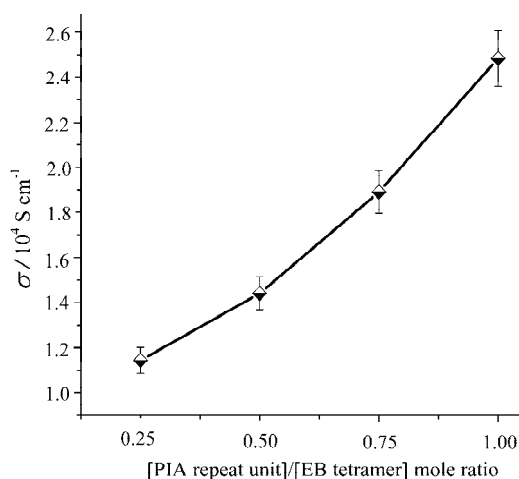


Fig. 1. The conductivity of PANI-PIA at different [PIA repeat unit]/[EB tetramer] mole ratio.

TABLE I. Conductivity and the energy band gap of different forms of PANI

Sample	UV-Vis band, nm		Conductivity, S cm^{-1}	Energy band gap, eV
	1	2		
PANI-HCl	387	467	4.60	3.20
PANI-EB	331	626	8.14×10^{-10}	–
PANI-PIA	304	347	2.48×10^{-4}	4.08

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of IA and its polymer (PIA) are shown in Fig. 2. The assignments of the FTIR bands of IA, PIA, PANI-EB and PANI-PIA are given in Table II. The spectra of IA and PIA showed a broad band between 2775 and 3480 cm^{-1} ,¹⁷ which was attributed to O-H stretching vibrations. The spectrum of IA showed peaks at around 1700,¹⁸ 1430¹⁸ and 1220 cm^{-1} ,¹⁹ indicating the stretching vibrations of C=O (carboxylic acid), C-O-H in plane and C-O, respectively.

The spectrum of the PIA showed the peaks at around 1730,²⁰ 1400¹⁹ and 1193 cm^{-1} ,²¹ indicating the stretching vibrations of C=O, C-O-H and C-O,

respectively. The peak at 1629 cm^{-1} in the curve ($t = 0\text{ h}$) in Fig. 2,¹⁸ characterizes the presence of C=C bond coming from itaconic acid. However, this peak was absent in PIA spectrum, which confirmed the polymerization of IA.

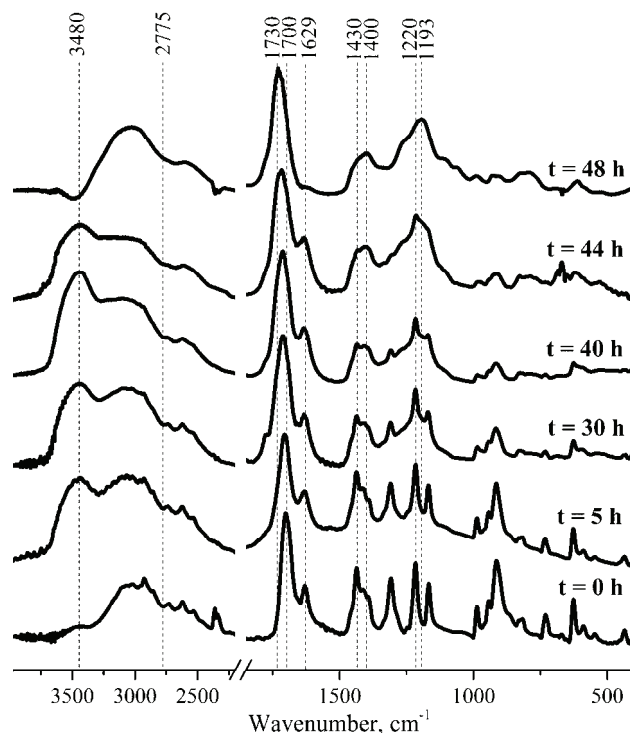


Fig. 2. Kinetics of the polymerization reaction of itaconic acid from IA ($t = 0\text{ h}$) to PIA ($t = 48\text{ h}$) determined by FTIR spectroscopy.

TABLE II. Assignment of FTIR bands (wavenumber, cm^{-1}) of IA, PIA, PANI-EB and PANI-PIA

Sample		Assignment
IA	PIA	
2775–3480 ¹⁷	2775–3480 ¹⁷	O–H stretching vibration
1700 ¹⁸	1730 ²⁰	C=O stretching vibration
1629 ¹⁸	–	C=C stretching vibration
1430 ¹⁸	1400 ¹⁹	C–O–H stretching vibration
1220 ¹⁹	1193 ²¹	C–O in of plane bending vibration
PANI-EB		Assignment
PANI-PIA		
3435 ²²	3435 ²²	N–H stretching vibration
–	1719 ²⁷	C=O stretching vibration
1583 ²³	1568 ²⁸	N=Q=N Stretching rings
1494 ²⁴	1485 ²⁹	N–B–N stretching ring
1292 ²⁵	1292 ²⁵	C–N ⁺ stretching in secondary amines
511 ²⁶	511 ²⁶	C–H out-of-plane bending 1,4 ring

The position of wavenumber of C=O stretching depends on hydrogen bonding and conjugation within the molecule. With polymerisation of IA, the C=O stretching band was shifted to higher wavenumbers, because the possibility of conjugation with a C=C band resulting in delocalization of the C=O group was eliminated on polymerisation.¹⁸ In addition, shifting of the typical bands for the C–O and C–O–H groups were detected. This effect is related to hydrogen bonding between the COOH groups of PIA.

The FTIR spectrum of pure polyaniline (PANI-EB) is shown in Fig. 3. The formation of polyaniline was confirmed from the predominant peaks at the wavenumber of 1583 cm^{-1} , corresponding to C=C stretching of the quinoid ring,²³ 1494 cm^{-1} for C=C stretching of the benzenoid ring,²⁴ 1292 cm^{-1} for C–N⁺ stretching,²⁵ and 511 cm^{-1} for C–H out-of-plane bending.²⁶ After PIA doping, the quinoid and benzenoid ring bands were shifted to lower wavenumbers by 15 and 9 cm^{-1} , respectively. This red shift phenomenon, corresponding to the transformation of quinoid rings into benzenoid rings, may result from conjugation effects after doping with the polymeric acid.²⁸

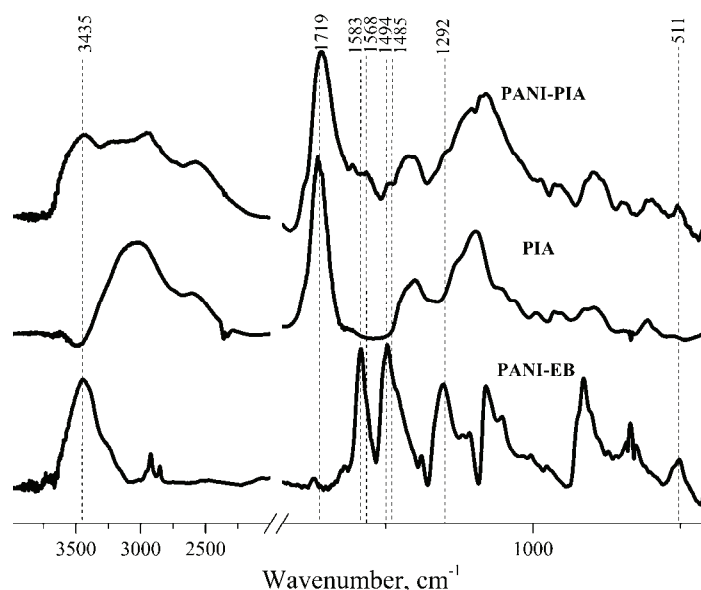


Fig. 3. FTIR spectra of PANI-EB, PIA and PANI-PIA.

UV-Vis spectroscopy

Absorption spectroscopy is a valuable tool for detecting the presence of PANI base and its salts. All the absorption spectra of the PANI-PIA samples and the PIA spectrum, Fig. 4, showed a peak in the range of 249–285 nm, corresponding

to $\pi-\pi^*$ or $n-\pi^*$ transitions in the carbonyl groups of the poly(itaconic acid),³⁰ (Table III).

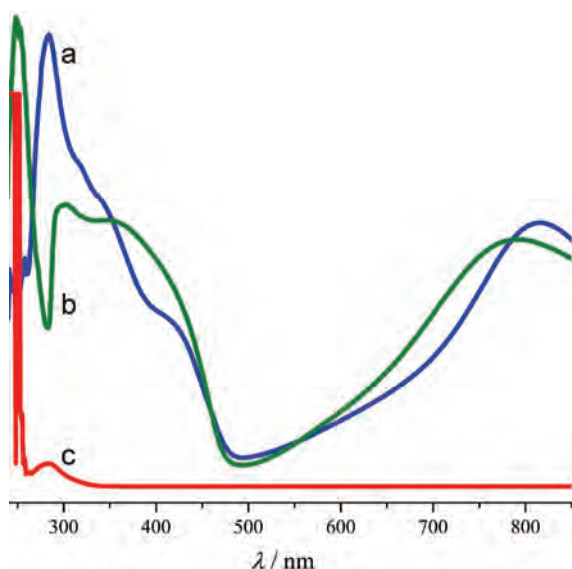


Fig. 4. UV-Vis spectra of: a) water/NMP, b) water/THF and c) PIA and PANI-PIA salts recorded in different solvents.

TABLE III. Absorption bands (λ / nm) of PIA and PANI-PIA samples in different solvents

Sample (solvent)	Attribution of absorption bands			
	$\pi-\pi^*$ and/or $n-\pi^*$	$\pi-\pi^*$	Polaron- π^*	π -Polaron
PIA (water)	282	—	—	—
PANI-PIA (THF/water)	249	304	347	790
PANI-PIA (NMP/water)	285	347	410	816

The electronic absorption spectra of the PANI-PIA samples in different solvents showed bands corresponding to the following transitions: $\pi-\pi^*$ (304–347 nm), polaron- π^* (347–410 nm), and π -polaron (in the region from 790 to 816 nm) of the alternating benzenoid-quinoid structures, respectively.^{31,32} The finding of the latter two absorption bands in the electronic spectra of all the PANI-PIA samples indicates that these polymers were well doped.

When the solvent molecules interact with a PANI-PIA, its chain configuration may be changed depending on the structure and polarity of the solvents, which is reflected by peak shifts.³³

Solubility determination

PANI-PIA dispersion in THF/water mixture (20 mL) was oscillated in a bath-type sonicator for 2 h at room temperature. The suspension was filtrated to remove undissolved polyaniline. The obtained solution was analyzed by UV-Vis spectroscopy to confirm the protonated state of PANI, then it was dried in an oven

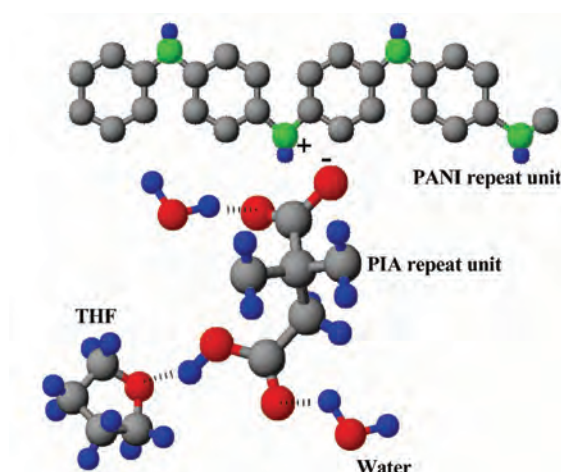
at 60 °C for 12 h. The maximum solubility was the quantity of resulting polyaniline powder after drying 20 mL of solvents mixture with an optimal volume ratio, which is measured in mg mL^{-1} . Note that the optimal ratio was determined by the intrinsic viscosity method.

The solutions of PANI-PIA in different solvents are shown in Fig. 5. The picture proves that the PANI synthesized in the present work was highly soluble in tetrahydrofuran/water and NMP/water mixtures with a dark green colour (Fig. 5a and b, respectively).



Fig. 5. Photographs of solutions of PANI-PIA in mixtures, a) water/THF = 0.428 and b) water/NMP = 0.428.

The carbonyl groups of extended polyacid chain of the PIA facilitate the solubility of PANI in some polar solvents.³⁴ PANI-PIA is not soluble in pure THF and NMP. The presence of water with each organic solvent improves the solubility of the PANI-PIA significantly, which could be explained by the number of carboxylic groups that is higher than the number of hydroxyl groups in the dopant which require a solvent with more groups containing hydrogen to create hydrogen bond. These groups (C=O), more negatively charged can create a stronger hydrogen bond with the water hydrogen. This idea is presented schematically in Scheme 3.



Scheme 3. Effect of the presence of water as co-solvent on PANI-PIA solution in THF.

Intrinsic viscosity

The viscosity of macromolecular substances in solution is one of the most commonly used methods for characterizations. Intrinsic viscosity is defined as the limiting value of the ratio of specific viscosity to concentration of the solute (η_{sp}/c), extrapolated to zero concentration.

Different solutions of PANI–PIA were prepared with different volume ratios of solvents (THF or NMP)/water at room temperature. This method is based on the calculation of the difference between the efflux time of the mixture of solvents (t_0) and polymeric solution (t) between two points in a capillary tube.

Basing on the most recent work performed by Yilmaz *et al.*³⁵ using the values of constant K and α at room temperature (26 °C) obtained for the leuco-emeraldine form in NMP solution in the presence of LiCl:

$$K = 2.34 \times 10^{-2} \text{ mL g}^{-1} \text{ and } \alpha = 0.73$$

$$[\eta] = K\bar{M}_v^\alpha \quad (1)$$

If two values are introduced into the Mark–Houwink equation (Eq. (1)),³⁶ the obtained value of the intrinsic viscosity $[\eta] = 13.26 \text{ mL g}^{-1}$ of the emeraldine salt form results in an apparent viscosity average molar mass of $\bar{M}_v = 5915 \text{ g mol}^{-1}$.

The evolutions of the intrinsic viscosity of solutions having various (THF or NMP)/water volume ratios of polyaniline doped with poly(itaconic acid) are shown in Fig. 6. The increase in viscosity with increasing water content indicates an increase in the hydrodynamic volume of the doped polymer chains, consistent with a progressive change in molecular conformation from “compact coil” to “expanded coil”.³⁷ This type of behaviour indicates that water interacts more strongly with the polymer chains and/or with poly(itaconic acid) (PIA) dopant

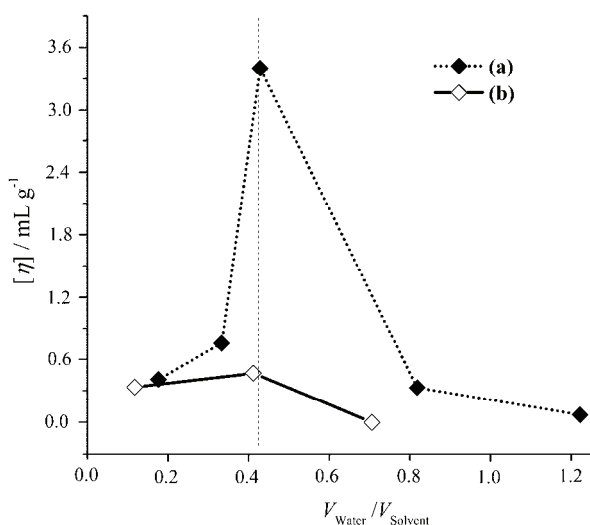


Fig. 6. Relationship between the intrinsic viscosities of polyaniline doped with poly(itaconic acid) and volume ratio of the mixtures of: a) water/THF and b) water/NMP.

anions than does THF. Conversely, when the value 0.428 for the volume ratio was exceeded, the intrinsic viscosity began to decrease with further water addition, which could be explained as follows: the PANI-PIA chains take an extended coil conformation also because there are H-bonding interactions of the hydrogen of the amine groups with the oxygen present in the molecular structure of THF. When the value of the volume ratio was more than 0.428, the water excess was used to decrease the interaction chain-organic solvent that led thereafter to decreases in the hydrodynamic volume of the chains of the doped polyaniline (compact coil). The change in intrinsic viscosity values is so large that also the quality of solvent/water mixture for PANI-EB and PANI-PIA should be considered. Namely, water in this case can act as a non-solvent. After reaching an optimal proportion between solvent and water (good solvation, intermolecular interaction), its increased share might worsen the solvent quality, which could lead to more compact random coils due to stronger intramolecular chain interaction.³⁸

Thermogravimetry (TGA)

The results of the thermogravimetric analysis of the pure PIA and PANI-PIA samples are presented in Fig. 7. Four degradation steps could be observed for PIA (Fig. 7, curve b) in the temperature range from 26–450 °C, with a residue of 30 wt. %. In the temperature region from 50–280 °C, two processes were detected; the first one is assigned to the elimination of free water adsorbed to the hydrophilic polymer and presence of residual solvent in the polymer,³⁹ and the second to anhydride ring formation in the PIA chain.⁴⁰ In the second temperature region, from 280 to 450 °C, two degradation stages were observed, probably related to some decarboxylation and carbonization processes.^{16,41}

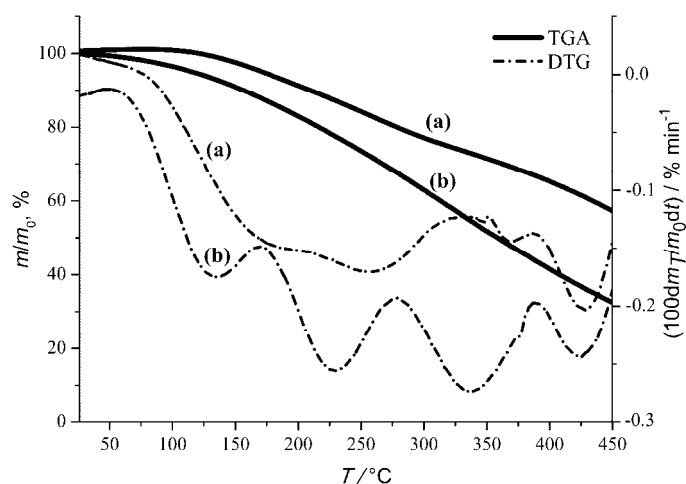


Fig. 7. Thermogravimetric (TG) and differential TG (DTG) curves for: a) PANI-PIA and b) PIA.

In the TGA thermograms of the PANI-PIA shown in Fig. 7, curve a, there are three major stages of weight losses of PANI-PIA powder sample. The first weight loss occurred around 67–198 °C (10 %) resulting from the elimination of water and other volatiles.⁴² The second stage in the temperature range 198–337 °C was assigned to the decomposition of excess dopant PIA.⁴³ The third weight loss at the higher temperature could be attributed to the detachment of doping agent and the chemical decomposition of the short chains of PANI with maximum decomposition rates at 367 and 427 °C, respectively.⁴⁴

It is notable that as much of 50 % of the initial mass was preserved for temperatures up to 500 °C. This residual mass relates to the existence of reticulate polymer, which is formed at high temperatures,⁴⁵ and the influence of the doping agent on a real thermal stability is not clear in this temperature region.

X-Ray diffraction pattern (XRD)

The X-ray diffraction pattern of PANI-EB, PIA and PANI-PIA are given in Fig. 8. The crystalline (I_c) and amorphous (I_a) peaks were both integrated in 2θ space. From these integrated peaks areas (I_c , I_a), the ratio X_c/X_a can be calculated by $X_c/X_a = 1.8 \times (I_c/I_a)$. A Ryland factor of 1.8 is commonly used for semi-crystalline polymers.⁴⁵ The percentage of crystallinity X_c (%) was obtained as:⁴⁶

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

The XRD pattern of PANI-EB (Fig. 8, curve a) contains some sharp peaks at 2θ 9.57, 15.22, 20.75 and 24.29°, representing the crystal planes of (001), (011), (100) and (110) of dedoped PANI, respectively.⁴⁷ The peak intensities are listed in Table IV, indicating the pseudo orthorhombic space.²⁶ The peak centred at 2θ 24.29° could be ascribed to periodicity perpendicular to the polymer chain

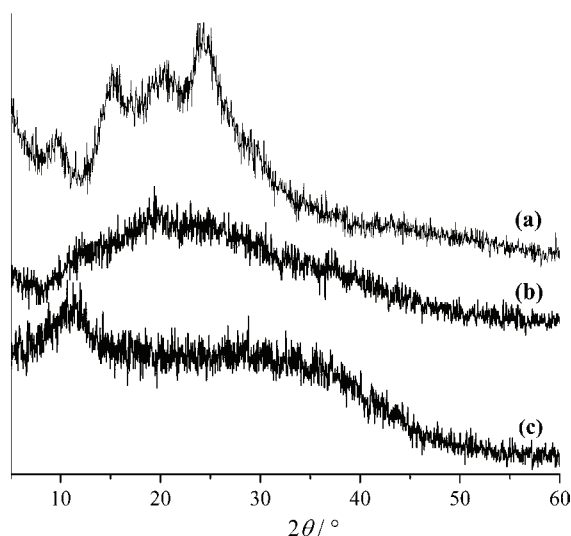


Fig. 8. XRD patterns of: a) PANI-EB, b) PANI-PIA and c) PIA.

(π stacking),⁴⁷ and the peak centred at 2θ 20.75° may be ascribed to periodicity parallel to the conjugated chain of PANI (emeraldine base).⁴⁸ The sharpness of the peaks represents the degree of orientation of the polymer chains in that particular crystal plane, and the intensity represents the population of crystallites in that plane.⁴⁹ This result suggests a low degree of crystallinity of 9.64 %.

TABLE IV. The 2θ values, intensity and indexation (hkl) of PANI-EB, PIA and PANI-PIA

Sample	$2\theta / ^\circ$	Intensity, a.u.	$d / \text{Å}$	(hkl)	Crystallinity, $X_c / \%$
PANI-EB	09.57	167.46	09.23	001	9.64
	15.22	176.44	05.82	011	
	20.75	202.06	04.28	100	
	24.29	203.40	03.66	110	
PIA	11.80	016.88	07.50	–	9.50
PANI-PIA	19.99	008.60	04.44	100	2.03
	37.27	005.71	02.41	110	

As shown in Fig. 8, curve c, the poly(itaconic acid) showed a moderate degree of crystallinity ($X_c = 9.5$ %, broad peaks in the spectrum) and a single sharp peak at 11.8°. On the other hand, the diffractogram of PANI-PIA powder, presented in Fig. 8, curve b showed two peaks; the first at 19.99° and the other at 37.27° with a characteristics distances of 4.44 and 2.41 Å, respectively. It should be noted that the chains of the PANI-PIA were less ordered than those of the PANI-EB, which was confirmed by the value of $X_c = 2.03$ % for PANI-PIA.

CONCLUSIONS

Soluble conducting polyaniline salts were successfully synthesized *via* chemical polymerization. Undoped and poly(itaconic acid)-doped polyaniline were characterized by a number of methods. The doped polyaniline had good solubility in mixtures of NMP/water and THF/water with a maximum solubility of 4 mg mL⁻¹ in the latter mixture at room temperature; on the other hand, this polyaniline salt was not soluble in the pure polar organic solvents (THF and NMP) except when the temperature is above 60 °C. The optimum volume ratio of 0.42 between water and THF was determined by intrinsic viscosity measurements. The electrical conductivity of the doped form of polyaniline presents a proportional relationship with the concentration of the doping agent (PIA). A decrease in crystallinity was detected in the new PANI salt due to the presence of poly(itaconic acid) in the composite.

ИЗВОД
СИНТЕЗА И КАРАКТЕРИЗАЦИЈА ПРОВОДНОГ И У СМЕШИ РАСТВОРАЧА ВЕОМА
РАСТВОРНОГ ПОЛИАНИЛИНА

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У раду је приказана синтеза и карактеризација растворног и проводног полианилина PANI–PIA добијеног хемијским поступком тј. полимеризацијом. На овај начин је добијена со полианилина допираног поли(итаконском киселином), која је веома растворна у бројним смешама поларних органских растварача и воде, при чему је достигнута растворљивост од 4 mg mL⁻¹. Анализиран је утицај параметара синтезе, као што је степен допирања, на проводљивост, растворљивост и друга својства синтетисаних PANI–PIA соли. Максимална проводљивост у износу од 2,48×10⁻⁴ S cm⁻¹ је остварена при потпуном протоновању полианилина у облику емералдинске базе (PANI-EB). Поред тога, синтетисани материјали су додатно карактерисани вискозиметријом разблажених раствора, UV–Vis спектроскопијом, дифракцијом X-зрака (XRD), инфрацрвеном спектроскопијом и термогравиметријском анализом (TGA) за анализу њихових термичких својстава.

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REFERENCES

1. Y. G. Han, T. Kusunose, T. Sekino, *J. Polym. Sci.*, **B 47** (2009) 1024
2. A. Rahy, D. J. Yang, *Mater. Lett.* **62** (2008) 4311
3. F. G. Souza Jr., B. G. Soares, J. C. Pinto, *Eur. Polym. J.* **44** (2008) 3908
4. M. G. Mikhael, A. B. Padias, H. K. Hall Jr., *J. Polym. Sci.*, **A 35** (1997) 1673
5. J. Q. Dong, Q. Shen, *J. Polym. Sci.*, **B 47** (2009) 2036
6. K. Shannon, J. Fernandez, *J. Chem. Soc. Chem. Commun.* **5** (1994) 643
7. L. Sun, H. Liu, R. Clark, S. C. Yang, *Synth. Met.* **84** (1997) 67
8. G. L. Yuan, N. Kuramoto, S. J. Su, *Synth. Met.* **129** (2002) 173
9. J. Tarver, J. E. Yoo, T. J. Dennes, J. Schwartz, Y. L. Loo, *Chem. Mater.* **21** (2009) 280
10. E. M. Barrios, G. A. Mujica, C. L. Velasquez, Y. Martinez, *J. Electroanal. Chem.* **586** (2006) 128
11. J. Travas-Sejdic, R. Soman, H. Peng, *Thin Solid Films* **497** (2006) 96
12. M. Gizdavic-Nikolaidis, S. Ray, A. J. Easteal, in *Proceedings of Int. Conf. Adv. Mater. Nanotechnol. (AMN-4)*, Dunedin, New Zealand, 2009
13. N. Abdul Rahman, M. Gizdavic-Nikolaidis, S. Ray, A. J. Easteal, J. Travas-Sejdic, *Synth. Met.* **160** (2010) 2015
14. O. L. Gribkova, A. A. Nekrasov, M. Trchova, V. F. Ivanov, V. I. Sazikov, A. B. Razova, V. A. Tverskoy, A. V. Vannikov, *Polymer* **52** (2011) 2474
15. Y. Wang, H. Zheng, L. Jia, H. Li, T. Li, K. Chen, Y. Gu, J. Ding, *J. Macromol. Sci.*, **A 51** (2014) 577
16. C. Larez, F. Canelon, E. Millan, G. Perdomo, I. Katime, *Polym. Bull.* **49** (2002) 119
17. X. Li, M. Wan, X. Li, G. Zhao, *Polymer* **50** (2009) 4529
18. B. Stuart, *Infrared spectroscopy: fundamentals and applications*, Wiley, Chichester, 2004, p. 71
19. G. Taskin, O. Sanli, G. Asman, *Appl. Surf. Sci.* **257** (2011) 9444

20. S. N. Dobic, J. M. Filipovic, S. L. Tomic, *Chem. Eng. J.* **179** (2012) 372
21. B. D. Mistry, *A Handbook of Spectroscopic Data Chemistry (UV, IR, PMR, ¹³CNMR and Mass Spectroscopy)*, Oxford Book Co., Jaipur, 2009, p. 26
22. D. S. Patil, J. S. Shaikh, D. S. Dalavi, S. S. Kalagi, P. S. Patil, *Mater. Chem. Phys.* **128** (2011) 449
23. P. Xu, Q. Tang, H. Chen, B. He, *Electrochim. Acta* **125** (2014) 163
24. J. H. Sung, S. J. Kim, K. H. Lee, *J. Power Sources* **126** (2004) 258
25. E. Ozkazanc, S. Zor, H. Ozkazanc, H. Y. Guney, U. Abaci, *Mater. Chem. Phys.* **133** (2012) 356
26. A. Mirmohseni, M. S. Seyed Dorraji, M. G. Hosseini, *Electrochim. Acta* **70** (2012) 182
27. J. M. Filipovic, L. Katsikas, I. G. Popovic, S. J. Velickovic, T. A. Djakov, D. M. Petrovic-Djakov, *J. Therm. Anal.* **49** (1997) 335
28. L. Chen, Y. Zhai, H. Ding, G. Zhou, Y. Zhu, D. Hui, *Composites, B* **45** (2013) 111
29. J. Gong, X. J. Cui, Z. W. Xie, S. G. Wang, L. Y. Qu, *Synth. Met.* **129** (2002) 187
30. Y. Cao, *Synth. Met.* **35** (1990) 319
31. I. Sasaki, J. Janata, M. Josowicz, *Polym. Degrad. Stab.* **92** (2007) 1408
32. J. Chen, B. J. Winther, Y. Pornputtkul, K. West, L. M. Kane, G. G. Wallace, *Electrochem. Solid State Lett.* **9** (2006) 11
33. D. Yang, B. R. Mattes, *J. Polym. Sci., B* **40** (2002) 2702
34. Y. Cao, P. Smith, A. J. Heeger, *Synth. Met.* **48** (1992) 91
35. F. Yilmaz, Z. Kucukyavuz, *Polym. Int.* **59** (2010) 552
36. J. Velickovic, J. Filipovic, D. P. Djakov, *Polym. Bull.* **32** (1994) 169
37. A. G. MacDiarmid, A. J. Epstein, *Synth. Met.* **65** (1994) 103
38. E. Zagar, M. Zigon, *Polymer* **41** (2000) 3513
39. S. L. Tomić, J. M. Filipović, *Polym Bull.* **52** (2004) 355
40. S. M. Mokhtar, E. M. Youssef, M. A. Abd El-Ghaffar, *J. Macromol. Sci. – Pure Appl. Chem., A* **38** (2001) 19
41. K. M. Krušić, E. Džunuzović, S. Trifunović, J. Filipović, *Eur. Polym. J.* **40** (2004) 793
42. B. Salma, G. Salma, A. Khurshid, A. S. Anwar-ul-Haq, *Synth. Met.* **162** (2012) 2259
43. H. Farrokhzad, T. V. Gerven, B. V. der Bruggen, *Eur. Polym. J.* **49** (2013) 3234
44. N. Naar, S. Lamouri, B. Belaabed, T. Kouroughli, N. Gabouze, *Polym. J.* **41** (2009) 432
45. D. Tsocheva, T. Zlatkov, L. Terlemezyan, *J. Therm. Anal.* **53** (1998) 895
46. P. J. Rae, D. M. Dattelbaum, *Polymer* **45** (2004) 7615T. Abdiryim, X.-G. Zhang, R. Jamal, *Mater. Chem. Phys.* **90** (2005) 367
47. M. Hasik, A. Drelinkiewicz, E. Wenda, C. Paluszkiwicz, S. Quillard, *J. Mol. Struct.* **596** (2001) 89
48. B. Belaabed, J. L. Wojkiewicz, S. Lamouri, N. El Kamchi, T. Lasri, *J. Alloys Compd.* **527** (2012) 137.