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ELECTRICAL CONDUCTIVITY AND MORPHOLOGY STUDY OF POLYANILINE POWDER SYNTHESISED WITH VARIOUS DOPING IONS

Powdered polyaniline (PANI) was synthesised chemically with different doping anions namely hydrochloric acid, sulphuric acid and para-toluenesulfonic acid (pTSA). Two-step synthetic procedure was utilised at low temperature. The highest reaction efficiency was found for chlorine-doped PANI. Structural characterization with FTIR revealed the vibration bands characteristic to formation of the emeraldine salt. The surface morphology of doped PANIs was studied by SEM images which showed near globular shape and porous structures with different size of the aggregated particles. They were smaller for Cl⁻ or pTS⁻-doped PANI while for SO₄²⁻ the size was markedly larger. The XRD patterns revealed that there are ordered regions especially for pTS⁻ doped PANI, while the highest conductivity value was recorded for Cl⁻ doped one followed by organic pTS⁻ doped and SO₄²⁻ doped one.

Keywords: polyaniline, conductive polymers, conductivity, morphology

1. Introduction

From the group of conducting polymers polyaniline (PANI) is a promising candidate as material for microelectronics, battery electrodes or sensors owing to its facile chemical synthesis at moderate cost, easy doping process and good environmental stability [1]. PANI has several chemical forms with emeraldine salt being conductive one. The exact value of electrical conductivity depends on several factors like polymer conjugation length [2], doping level [3] and the type of utilised dopant [4]. The studies of the PANI nanostructure has revealed that their electrical properties can be tuned by changing the dimensionality [5]. PANI can be synthesised by oxidation of monomer (aniline – ANI) in aqueous acidic solutions electrochemically or chemically [6]. It is known that a better quality polyaniline, with fewer defect sites (i.e., chain ends and/or polymer branching) and of a higher molecular weight may lead to improvements in its mechanical and electrical properties [7].

In the present study three PANI polymers were synthesised chemically with different doping anions to detect the influence of various ions on materials conductivity. The synthesis was performed with various acids to show their impact on the final polymerization product. The novelty of this work is the combined comparison of the results of morphology studies and conductivity values measured for powdered samples. The various acid solutions were used for polymerization namely hydrochloric acid (HCl, 1.0 M), sulphuric acid (H₂SO₄, 1.0 M) and p-toluenesulfonic acid (pTSA, 1.0 M).

2. Experimental (materials and methods)

2.1. Synthesis of PANIs

The synthesis was based on two-step procedure. In step 1 acidic aqueous solutions of ANI (0.186 g, 2.0 mmol, 0.2 M) in chosen acid solution was placed in cooling bath and stored at –5°C. The oxidation of aniline is exothermic process hence the temperature of the reaction mixture was controlled steadily. The ammonium peroxydisulfate (APS, 0.570 g, 2.5 mmol, 0.25 M) solution was added drop wise to the chilled beaker containing acidified aniline solution. The stoichiometric APS vs. aniline ratio was 1.25. After completion of reaction (24 h) in step 2 the final dark green PANI precipitate was collected on a filter paper and washed. In the first step of purification the sample was washed with acid solution used to prepare the samples (0.2 M, 50 mL) and in the second step it was extracted with acetone (50 mL). Afterwards polyaniline salt (emeraldine) powder was dried in air for 1 hour and then placed in heating device at 60°C to remove the excessive solvent and humidity. The synthesis was performed with 3 various acids of the same concentration (1.0 M).

2.2. Analytical methods

Obtained materials were characterized with spectrophotometric technique – Fourier-transform infrared spectroscopy (FTIR). The spectra were recorded for powdered PANI at room

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temperature using Shimadzu IR Prestige-21 instrument equipped with ATR head. UV-visible spectra of aniline oligomers solutions in acetone were taken using Biowave II UV-visible spectrophotometer with appropriate dilution procedure. Surface morphology and chemical composition were investigated using a scanning electron microscope (JEOL JSM-6480) equipped with an energy dispersive spectroscopy (EDS) detector. Electrical conductivity measurements were performed using an AGILENT 34401A Multimeter. The powdered dried polymers were placed in the home made measuring system. During measurements constant axial pressure was applied for probe of about 0.95 mm thickness. Sample proper resistance and conductivity were determined by relation shown as Eq. (1) and Eq. (2).

$$R = \frac{\rho \cdot l}{S} \quad (1)$$

$$\sigma = \frac{l}{R \cdot S} \quad (2)$$

where: R – resistance [Ω]; ρ – proper resistance [$\Omega \cdot \text{m}$], l – layer thickness ($9.5 \cdot 10^{-4}$) [m], S – surface of PANI pill ($S = 7.85 \cdot 10^{-5}$ for $r = 5 \cdot 10^{-3}$ m) [m^2], σ – electrical conductivity [$\text{S} \cdot \text{m}$].

Structural investigation of obtained materials were conducted by powder X-ray diffraction (XRD) method using a Empyrean Panalytical diffractometer and CuK_α ($\lambda = 0.1542$ nm) radiation equipped with PIXcel^{3D} detector. The data collection was over the 2-theta range of 5° to 100° in steps of 0.02° .

3. Results and discussion

3.1. Polymerisation

In the course of reaction one could notice changes of the colour when the reaction mixture evolved from homogenous, clear transparent one into dark green suspension (Fig. 1).

All synthesis were performed in highly acidic medium (pH in range 0-1 as $\text{pK}_a^{\text{H}_2\text{SO}_4(1)} = -3.0$, $\text{pK}_a^{\text{HCl}} = -8.0$ and

$\text{pK}_a^{\text{pTSA}} = -2.8$) to produce highly conductive PANI, since only under these conditions highly conducting dark-green emeraldine can be obtained.

Oxidation of monomer occurs by the action of oxidizing agent (APS). Oxidative polymerization may be considered as a type of polycondensation when radical-cation oxidation sites undergoes recombination and fragments of any length may recombine. In each case different amount of the final product was obtained, which reflects various efficiency (E) of the polymerization reaction. This parameter can be calculated based on the stoichiometry of the reaction presented in Fig. 2 [8].

The reaction efficiency (E) was calculated according to Eq. (3).

$$E = \frac{m_{\text{polymer}}}{m_{\text{monomer}}} \cdot 100\% \quad (3)$$

The efficiency was equal to 62.5 % (for Cl^-), 57.9 % (for SO_4^{2-}), and 34.5 % (for pTSA^-), which indicates significant difference between organic and inorganic dopants ions. The decreasing sequence of E illustrate the proneness of the aniline to form long chains in the presence of Cl^- as precipitated product contained insoluble, longer fraction. As presented in the reaction shown in the Fig. 2 it is important to remember that only the SO_4^{2-} doped PANI is one with single counter-ion system. Hence in the other two cases (Cl^- -doped and pTSA^- -doped PANIs) multi doping process may occur with mutual competition between ions able to balance charge of protonated nitrogen [9].

3.2. Chemical structure

Chemical characterization of PANIs performed by FTIR technique (Fig. 3) showed the vibration bands characteristic of the formation of the emeraldine salt form of polyaniline as the bands at $1570\text{-}1590$ and $1480\text{-}1500$ cm^{-1} can be assigned to quinoid (Q) and benzenoid (B) ring stretching, respectively. The band which appears as a shoulder at $1200\text{-}1220$ cm^{-1} can be attributed to the C-NH^+ stretching band being characteristic of

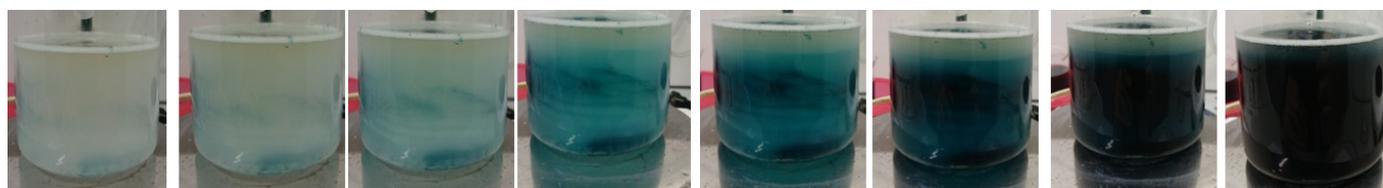


Fig. 1. Changes in the colour of the reaction mixture with the increased time of reaction (H_2SO_4 assisted reaction)

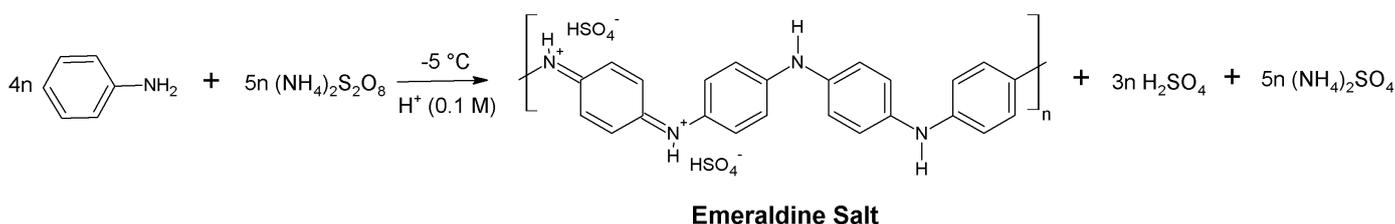


Fig. 2. Oxidative polymerization of aniline with ammonium persulfate

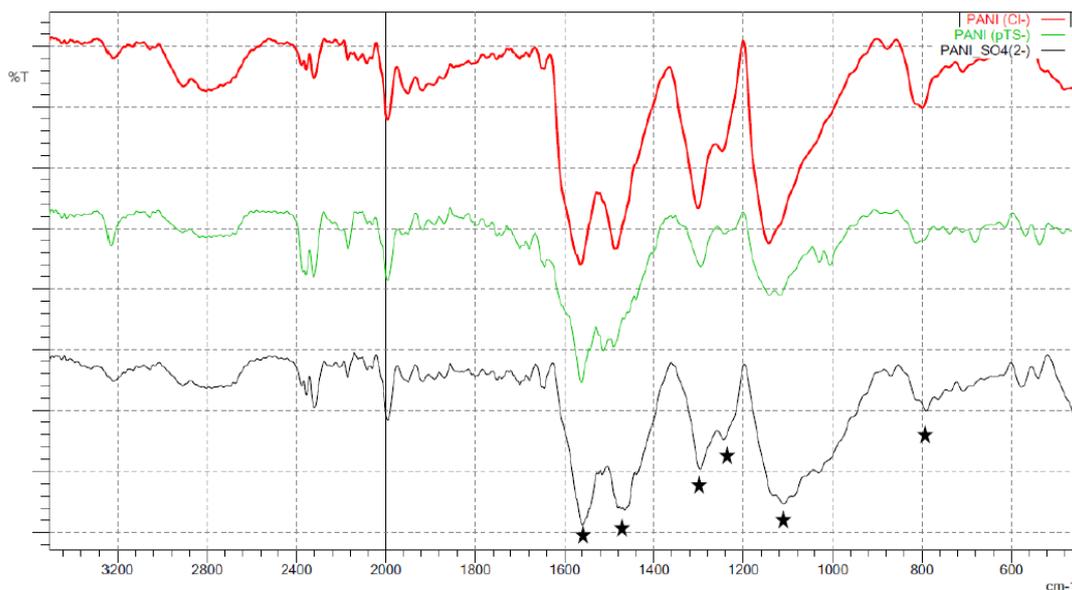


Fig. 3. FTIR spectra of PANI powder: PANI (Cl^-) – red line, PANI (pTS^-) – green line, PANI (SO_4^{2-}) – black line (stars denote main characteristic peaks corresponding to the vibrations of the polyaniline described in details in text)

polaron form of emeraldine salt (Fig. 4) [10]. Moreover, a shoulder at 1150 cm^{-1} can be attributed to the stretching vibration of $-\text{NH}^+$ (in the $\text{B}-\text{NH}^+ = \text{Q}$ segment) in bipolaron form of emeraldine salt [11]. The shift in the peak positions for $\text{C} = \text{C}$ bond of quinonoid structure and $\text{N} = \text{Q} = \text{N}$ vibration were observed. This is due to the difference in the efficiency of undergoing oxidation of aniline and doping on polyaniline system. The comparison of

the intensities of the IR bands specific to vibrations of quinoid ($1570\text{--}1590\text{ cm}^{-1}$) and benzenoid ($1480\text{--}1500\text{ cm}^{-1}$) units (Fig. 4) indicates that quinoid structures are dominant, which can be explained by the presence of trapped oligomer species in samples [12–14]. The vibration of $\text{C}-\text{N}$ structure in quinonoid ring can also be found at 1304 cm^{-1} , while $\text{C}-\text{N}$ structure of benzenoid ring was present at 1240 cm^{-1} with $\text{C}-\text{H}$ out-of-plane bending for

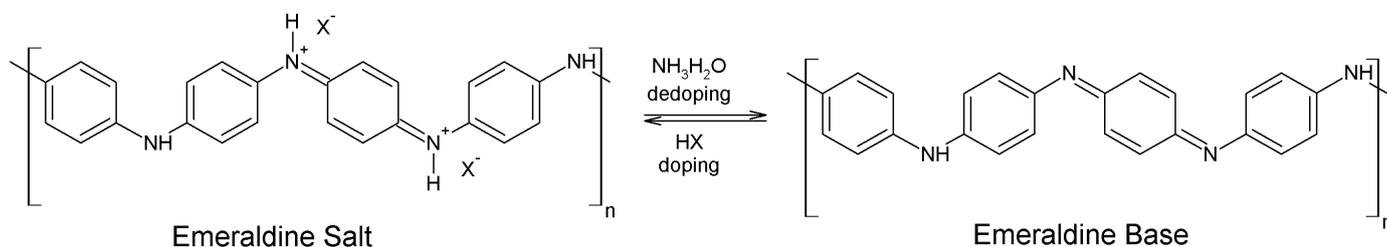


Fig. 4. Doping/dedoping of PANI chains

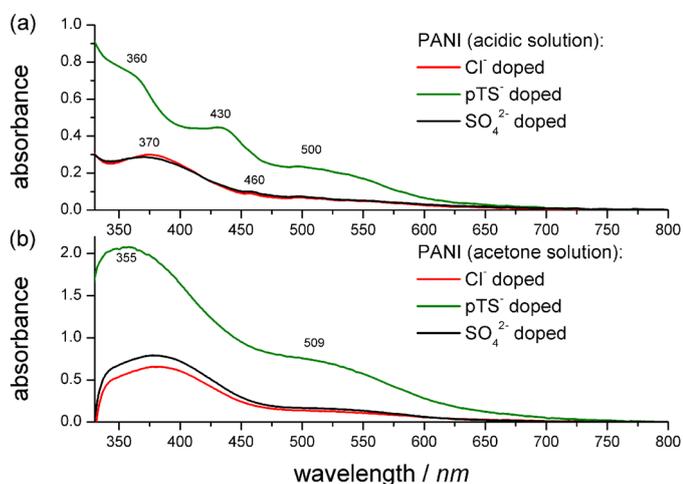


Fig. 5. Electronic spectra of oligomeric solution of PANI: (a) acidic solutions, (b) acetone solutions

a 1,4-substituted benzene visible at 880 cm^{-1} . The FTIR spectra show also presence of *p*-toluenesulfonic doping ion pTS^- (1030 , 1000 , 610 cm^{-1}).

It is important to determine the presence and amount of the short chain fractions in the reaction system. The presence of oligomers not only lowers the efficiency of the synthesis but also influences on possibility and course of nanostructures formation [15]. Electronic spectra of oligomeric solution of PANI recorded in both the acidic (Fig. 5a) and acetone (Fig. 5b) solutions revealed broad absorption bands. The acidic solutions (a) revealed dominant broad band with maximum at app. 370 nm with minor band at 460 nm for inorganic dopants (SO_4^{2-} and Cl^-) and three bands for organic pTS^- one (at 360 , 430 and 500 nm). For all 3 solutions onset wavelength of absorption is located at about 625 nm . It suggests that during synthesis chain of similar conjugation length were formed, however there is much more

diversity in chain length in case of organic dopant. Moreover pTS⁻ ion-based solution is the one with the highest absorption value, significantly higher than for inorganic dopants, which support the conclusion that it changes markedly the condition in reaction medium. By changing the solvent into acetone one can spot that the character and position of the bands are similar in each case, but again the absorbance of organic dopant solution is the highest, followed by SO₄²⁻ one and finally Cl⁻. The observation of intensity of absorbance is directly related to concentration of oligomers after PANI synthesis. Formation of oligomers can be treated as side reaction leading to decrease in reaction efficiency. Hence this result is congruent with calculated reaction efficiency as content of oligomers obtained in the synthesis was the highest in pTS⁻ system, followed by SO₄²⁻ and Cl⁻ ones.

3.3. Morphology

SEM images show the surface morphology of doped PANIs (Fig. 6), which reveals near globular shape and porous structures with different size of the aggregated particles. For Cl⁻-doped and pTS⁻-doped PANI the particles are smaller (Fig. 6a and b) but for SO₄²⁻ (Fig. 6c) markedly larger particles are observed. pTS⁻ has similar impact onto PANI morphology as Cl⁻ does, which is known for its specific adsorption.

Both of the used inorganic acid are strong ones and dissociate completely, with two stages of dissociation for H₂SO₄. The monoprotic acid behave similarly in terms of influence on morphology of powdered PANIs. For Cl⁻ doped PANI specific adsorption of ion takes place favored by its smaller dimension in comparison to HSO₄⁻ one. In case of large, organic pTS⁻ dopant additional intermolecular attraction may occur as a result of the planar structure of the phenyl ring. Hence the dopant ion tends to localise in the vicinity of the aniline ring leading to mutual p-electronic interaction enforced by electrostatic attraction of imine nitrogen cation and anionic part of the dopant. Such tendency may be a driving force of local ordering within the macromolecules.

The chemical composition of materials studied by Energy Dispersive X-ray analysis confirmed presence of respective doping ions (Table 1).

TABLE 1

Chemical composition of the PANI samples with various doping ions

PANI	At. % C	At. % N	At. % O	At. % S	At. % Cl
SO ₄ ²⁻ doped	66.3	20.0	7.2	6.4	—
Cl ⁻ doped	70.2	27.9	—	0.4	1.3
pTS ⁻ doped	66.5	26.7	4.2	2.7	—

Since basic elements of the sample are elements with low atomic numbers (C,N,O) its measured content is given in approximate values. The result shows the presence of 6.4 wt.% of sulphur element for SO₄²⁻ doped PANI, 1.3 wt.% of chloride

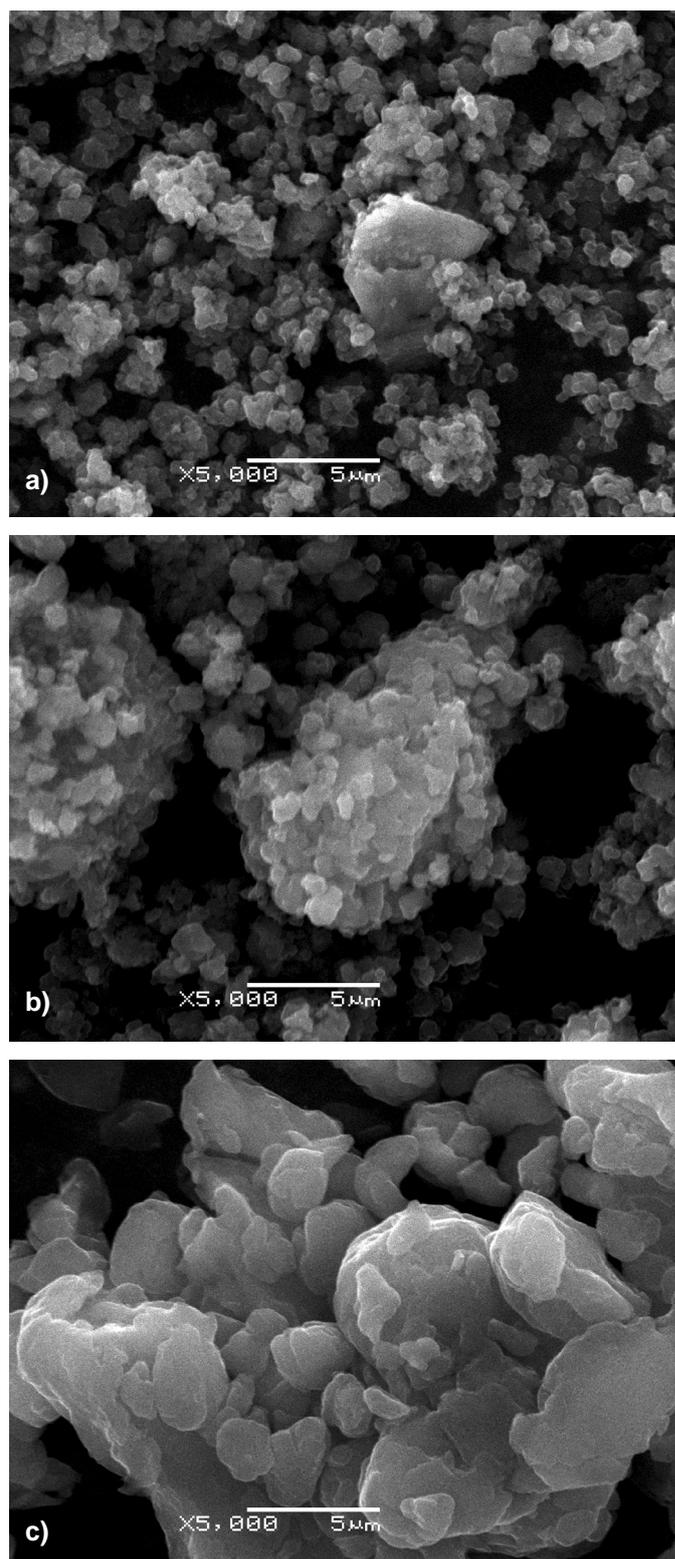


Fig. 6. SEM images of the PANI synthesised with various doping ions: (a) Cl⁻, (b) pTS⁻, (c) SO₄²⁻

element for Cl⁻ doped PANI and 4.2 wt.% of sulphur element for pTS⁻ doped PANI. The amount of the N in PANI samples is high and departs from its theoretical content calculated upon the chemical structure of the mer unit as the atomic C : N ratio is 6 : 1. It is caused by the leftovers of APS not washed at the preparation stage.

3.4. Electrical conductivity

Upon the measured resistance of powdered samples the proper resistance (ρ) was calculated (Fig. 7a). It is apparent that the conductivity of the polyaniline is the highest for Cl^- doped one (as the proper resistance is the lowest) followed by organic pTS^- doped one and finally the lowest among researched group for SO_4^{2-} doped one. The obtained values are moderate (probably due to washing with acetone) in comparison to the literature values of conductivity for PANI doped material which is $10 \text{ S} \cdot \text{cm}^{-1}$ [16]. The electrical conductivity depends mainly on the number and mobility of the charge carriers. For polyaniline it is also connected with ability to protonate the nitrogen group. Hence in the mentioned order this reaction is favoured for Cl^- doped material and handicapped for SO_4^{2-} doped one. The results suggest that monoprotic acid leads to more conductive sample. The explanation for the observed behavior may be double charge of sulphate ion. It seems plausible that in this case there is an interaction between neighbouring ammonium nitrogens (either intermolecular or intramolecular) which provokes the macromolecules to bend or fold. Such conformational changes can lead to less planar structure with reduced mobility

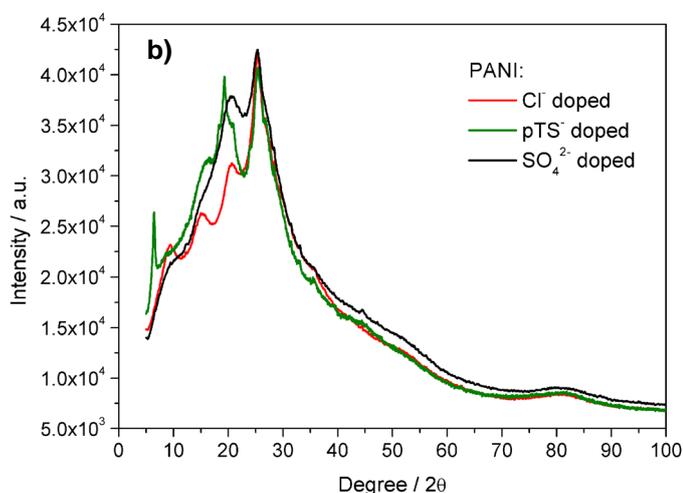
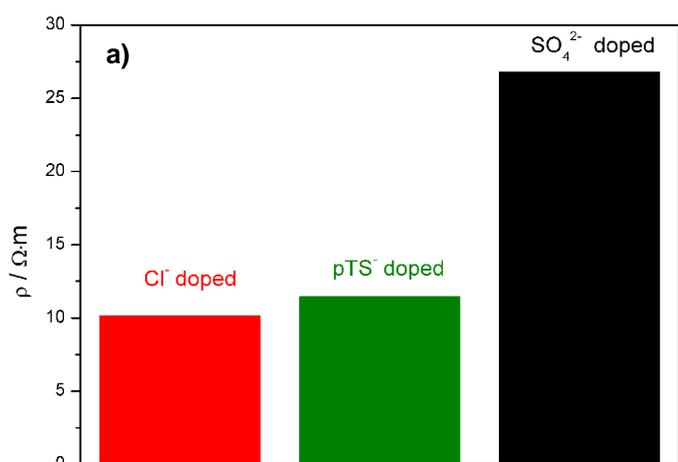


Fig. 7. Powder doped PANI (a) room temperature proper resistance, (b) X-ray diffraction pattern

of the charge carriers. The proposed structural changes can also be responsible for more aggregated form of SO_4^{2-} doped PANI visible on SEM images. Also the efficiency of the synthesis is slightly higher with formation of more conjugated carbon skeleton.

In case of organic pTS^- ion although it is large its utilisation leads to moderate conductivity with successful formation of percolation path for propagating charge. This could be connected with mentioned planar structure of the aromatic ring while such interaction induce local arrangement accompanied by chains ordering.

3.5. Crystallinity

To investigate the possibility of formation of arranged regions we performed XRD studies. The XRD patterns (Fig. 7b) reveal that the doped PANI is nearly amorphous polymer as for all samples the central broad bands were recorded, which are characteristic of an amorphous structure. However there are discrepancies among the synthesised samples. The acute diffraction peaks, observed at $2\theta = 25.30^\circ$, 20.57° (for SO_4^{2-}), 25.35 , 20.65 (for Cl^-) and 19.31 , 25.33 (for pTS^-) represent material with partially crystalline structure. The literature data of $2\theta = 28.72^\circ$ and 22.74° are ascribed to the periodicity parallel and perpendicular to the polymer chains of PANI, respectively [17,18]. Moreover small and acute peak at 6.49° [13], assigned to the crystal structure can be noted for pTS^- doped PANI. The organization of the polymer chains is connected with the action of respective doping ions. Close proximity of similar charges leads to the electrostatic repulsion between the polymer chains, which results in the straightening up of the polymer chains. It produces their mutual alignment with respect to one another providing increased crystallinity of the material.

4. Conclusion

Powdered polyaniline (PANI) was synthesised chemically with 3 various doping anions. Commonly used two-step synthetic procedure allowed to produce powdered material, insoluble in reaction environment. The nature of doping ion has an influence on both efficiency of reaction and ability to conduct current. Spectral analysis showed that the conductive form of the polymer was synthesised, which was accompanied by formation of soluble short oligomeric chains fractions. The morphology of the PANI powders is diverse depending on the doping ion type i.e., for SO_4^{2-} dopant the particles are larger, whereas in case of Cl^- and p-TS^- , the particles are smaller. This order found reflection in conduction ability of the respective materials as the highest conductivity was recorded for inorganic Cl^- doped PANI, followed by pTS^- doped and SO_4^{2-} doped one. The XRD patterns revealed partial arrangement of the chains especially for organic pTS^- doped PANI.

REFERENCES

- [1] H. Zhang, X. Wang, J. Li, F. Wang, *Synth. Met.* **159**, 1508-1511 (2009).
- [2] Y. Yang, S. Chen, L. Xu, *Macromol. Rapid Commun.* **32** (7), 593-597 (2011).
- [3] J. Jin, Q. Wang, M.A. Haque, *J. Phys. D* **43** (205302), 1-5 (2010).
- [4] J. Stejskal, D. Hlavata, P. Holler, M. Trchova, J. Proles, I. Sapurina, *Polym. Int.* **53**, 294-300 (2004).
- [5] Y. Wang, H.D. Tran, L. Liao, X. Duan, R.B. Kaner, *J. Am. Chem. Soc.* **132**, 10365-10373 (2010).
- [6] N.S. Sariciftci, H. Kuzmany, H. Neugebauer, A. Neckel, *The Journal of Chemical Physics* **92**, 4530-4539 (1990).
- [7] P.N. Adams, P.J. Laughlin, A.P. Monkman, *Synth. Met.* **76**, 157-160 (1996).
- [8] I.Y. Sapurina, M.A. Shishov, *Oxidative Polymerization of Aniline: Molecular Synthesis of Polyaniline and the Formation of Supramolecular Structures*, in: *New Polymers for Special Applications* (Chapter 9) (2012).
- [9] Y. Gawli, A. Banerjee, D. Dhakras, M. Deo, D. Bulani, P. Wadgaonkar, M. Shelke, S. Ogale, *Sci. Rep.* **6**, 21002: 1-10 (2016), doi: 10.1038/srep21002.
- [10] G. Ciric-Marjanovic, L. Dragicevic, M. Milojevic, M. Mojovic, S. Mentus, B. Dojcinovic, B. Marjanovic, J. Stejskal, *J. Phys. Chem. B* **113** (20), 7116-7127 (2009).
- [11] G. Ciric-Marjanovic, V. Dondur, M. Milojevic, M. Mojovic, S. Mentus, A. Radulovic, Z. Vukovic, J. Stejskal, *Langmuir* **25** (5), 3122-3131 (2009).
- [12] A. Mostafaei, F. Nasirpour, *Prog. Org. Coat.* **77**, 146-159 (2014).
- [13] X. Du, Y. Xu, L. Xiong, Y. Bai, J. Zhu, S. Mao, *J. Appl. Polym. Sci.* **131**, 40827-40837 (2014).
- [14] M. Trchová, J. Stejskal, *Pure Appl. Chem.* **83** (10), 1803-1817 (2011).
- [15] J. Stejskal, I. Sapurina, M. Trchová, *Prog. Polym. Sci.* **35**, 1420-1481 (2010).
- [16] J. Stejskal, I. Sapurina, J. Prokes, J. Zemek, *Synth. Met.* **105**, 195-202 (1999).
- [17] J. Bhadra, N.K. Madi, N.J. Al-Thani, M.A. Al-Maadeed, *Synth. Met.* **191**, 126-134 (2014).
- [18] J. Vivekanandan, V. Ponnusamy, A. Mahudswaran, P.S. Vijayanand, *Arch. Appl. Sci. Res.* **3** (6), 147-153 (2011).