

ORIGINAL PAPER

Oxidative polymerization of anilinium 5-sulfosalicylate
with peroxydisulfate in water^aBudimir Marjanović*, ^bIvan Juranić, ^cSlavko Mentus,
^cGordana Ćirić-Marjanović, ^dPetr Holler^aCentrohem, Vuka Karadžića bb, 22300 Stara Pazova, Serbia^bFaculty of Chemistry, ^cFaculty of Physical Chemistry, University of Belgrade,
Studentski trg 12–16, 11158 Belgrade, Serbia^dInstitute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic

Received 8 May 2010; Revised 18 June 2010; Accepted 19 June 2010

Anilinium 5-sulfosalicylate was prepared and characterized by elemental analysis, and FTIR and NMR spectroscopies. It was polymerized in an aqueous solution using ammonium peroxydisulfate as an oxidant. The precipitated polyaniline 5-sulfosalicylate exhibited high thermal stability and conductivity of 0.13 S cm^{-1} . Its mass-average molar mass and polydispersity index were determined by gel-permeation chromatography as $22,900 \text{ g mol}^{-1}$ and 2.7, respectively. Elemental analysis and FTIR spectroscopy study of polyaniline 5-sulfosalicylate revealed the doping level and the oxidation state between emeraldine and protoemeraldine salt while corresponding studies of the polyaniline base indicate a small extent of the covalent bonding of 5-sulfosalicylate anions to polyaniline chains. © 2010 Institute of Chemistry, Slovak Academy of Sciences

Keywords: anilinium 5-sulfosalicylate, peroxydisulfate, oxidative polymerization, conducting polymer, polyaniline

Introduction

Polyaniline (PANI) has been one of the most extensively studied conducting polymers for the past two decades because of its unique set of electronic properties, good environmental stability, ease of preparation by chemical and electrochemical oxidative polymerization of aniline and its salts, and versatile applicability in various areas such as batteries, non-linear optics, sensors, catalysts, anti-corrosive coatings, and shielding of electromagnetic interference (Gospodinova & Terlemezyan, 1998). PANI has a variety of redox and acid-base forms (Stejskal et al., 1996), with quite different optical, magnetic, and electrical properties. The most important form of PANI is green emeraldine salt which reaches the conductivity of about $1\text{--}10 \text{ S cm}^{-1}$ for granular PANI powders (Stejskal &

Gilbert, 2002), $\sim 10^2 \text{ S cm}^{-1}$ for PANI powders with nanospherical morphology (Ha & Jang, 2005), and $\sim 10^3 \text{ S cm}^{-1}$ for PANI films (Lee et al., 2006). It contains, depending on the synthesis route and isolation procedure, various proportions of diamagnetic $[(-\text{B}-\text{NH}^+=\text{Q}=\text{NH}^+-)]_n(-\text{B}-\text{NH}-)_{2n}(\text{A}^-)_{2n}$ and paramagnetic $[(-\text{B}-\text{NH}^+-\text{B}-\text{NH}-)]_n(\text{A}^-)_n$ units; in preceding formulae B, Q, and A^- denote a benzenoid ring, quinonoid ring, and a dopant anion, respectively. Oxidative polymerization of aniline in aqueous solutions of strong acids ($\text{pH} < 2.0$) at room temperature is a typical method for the preparation of the conducting PANI emeraldine salt (Stejskal et al., 2008; Stejskal & Gilbert, 2002). The most frequently used oxidant is ammonium peroxydisulfate (APS) because of its high oxidation power and excellent solubility.

*Corresponding author, e-mail: cenhem@verat.net

In numerous oxidative polymerization experiments with “equimolar” quantities of commercially available aniline and the corresponding acid, without the knowledge of their exact purity, there is up to a few surplus percent of aniline or acid. This leads to significant differences in the initial pH of the oxidative polymerization process, known to have a crucial impact on the polymerization mechanism, and molecular and supramolecular structure of PANI (Ćirić-Marjanović et al., 2006a, 2007, 2008a, 2008b, 2008c, 2009a, 2009b; Konyushenko et al., 2006, 2010; Trchová et al., 2006; Stejskal et al., 2006, 2009; Janošević et al., 2008). Since the initial pH of the reaction mixture was usually not recorded, this variation of the initial pH could be the major reason for pronounced irreproducibility of the most of already published results in the field of PANI research noticed by MacDiarmid et al. (2001) in the well known statement “–there are as many different types of polyaniline as there are people who make it!” Therefore, it can be expected that polymerization of purified aniline salts would provide more reproducible results. It should also be stressed that the handling of solid aniline salts is much less hazardous than the handling of liquid aniline. Finally, because the anilinium cation is much less oxidizable than nonprotonated aniline molecule (Ćirić-Marjanović et al., 2006a), crystalline aniline salts are much more resistant against oxidative degradation by atmospheric oxygen during the storage compared to liquid aniline. However, oxidative chemical polymerization of commercially available aniline salts such as hydrochloride and sulfate gives PANI salts which are almost insoluble in common solvents. The lack of solubility limits the processability of ordinary PANI emeraldine salts, and these unprocessable products usually must be transformed by a dedoping-redoping procedure to more processable PANI doped with functionalized acids. Many attempts to synthesize processable PANI salts by the oxidation of aniline with peroxydisulfate in the presence of various functionalized acids have failed because hydrogen sulfate, formed as a by-product during the polymerization [$n \text{ C}_6\text{H}_5\text{NH}_2 + n \text{ S}_2\text{O}_8^{2-} \rightarrow (-\text{C}_6\text{H}_4\text{NH}-)_n + 2n \text{ HSO}_4^-$], was incorporated into the PANI structure instead of a functionalized dopant anion, especially in the case of aniline and weak acids salts (Stejskal et al., 2004). That is why the quest for an aniline salt with functionalized acid which could be directly oxidized with APS to the processable conducting PANI emeraldine salt presents a challenge.

PANI properties depend not only on the oxidation state and the degree of protonation, but also on the nature of the dopant anions. It was reported that PANI solubility, crystallinity, thermal stability, electrochemical stability at higher potentials, and anticorrosive properties improve using 5-sulfosalicylic acid (SSA) as a dopant (Trivedi & Dhawan, 1993; Raghunathan et al., 1996; Tawde et

al., 2002; Ćirić-Marjanović et al., 2006b). Conducting PANI 5-sulfosalicylate (PANI.SSA) has been successfully prepared by chemical and electrochemical oxidation of aniline in the presence of SSA (Janošević et al., 2008; Trivedi & Dhawan, 1993; Raghunathan et al., 1996; Ćirić-Marjanović et al., 2006b, 2007) using the mole ratio $[\text{SSA}]/[\text{aniline}]$ in the broad range from 0.25 to 10.0. PANI.SSA nanotubes and nanorods were synthesized using the ratio $[\text{SSA}]/[\text{aniline}] = 0.25$, while granular PANI.SSA was obtained at $[\text{SSA}]/[\text{aniline}] \geq 0.5$ (Janošević et al., 2008). Anilinium 5-sulfosalicylate (ANI.SSA) looks as a promising monomer for efficient one-pot synthesis of a processable PANI salt with functionalized acid mainly because SSA, like all similar sulfonic acids (camphorsulfonic acid, etc.), is an excellent proton donor ($\text{p}K_{\text{a}1} < 1$) which can form a stable salt with PANI. Because the SSA anion is more oxidizable than the anilinium cation (Ćirić-Marjanović et al., 2007), some SSA covalent bonding to PANI chains, besides the ordinary ionic interactions, is expected. This covalent bonding could improve the solubility of PANI.SSA in polar solvents. In addition, the well known undesirable hydrolysis of the PANI emeraldine salt can be suppressed by the carboxylic acid group of SSA. This means that the SSA anion has inherent buffer properties and, consequently, that PANI.SSA is more stable toward basic environment than ordinary PANI emeraldine salts. It is known that various substituted phenols act as excellent “secondary dopants” (MacDiarmid & Epstein, 1995). It follows that SSA, as a phenolic compound substituted with sulfonic and carboxylic acid groups, also shows a useful secondary doping effect.

In the present work, ANI.SSA was prepared, characterized by elemental analysis, FTIR and NMR spectroscopies (^1H and ^{13}C), and used as a monomer for oxidative polymerization with APS. Obtained polymer, PANI.SSA, was characterized by elemental analysis, gel-permeation chromatography (GPC), conductivity measurements, thermogravimetric analysis (TGA), and FTIR spectroscopy.

Experimental

Aniline was distilled under reduced pressure and stored under argon prior to use. APS, SSA dihydrate, propan-2-ol, ethanol, diethyl ether, and acetone were of analytical grade and were used as received from Centrohem (Serbia).

Monomer ANI.SSA was synthesized by slow addition of aniline (9.0 g) to the solution of SSA dihydrate (25.0 g) in propan-2-ol (50.0 g) under stirring. The obtained precipitate of ANI.SSA was filtered, washed with diethyl ether and air-dried. Crude ANI.SSA was purified by recrystallization from ethanol. White crystalline powder was obtained.

Chemical oxidative polymerization of ANI.SSA was carried out by the addition of an oxidant solu-

Table 1. Elemental analysis data, yield and melting point (M.p.) of ANI.SSA

Compound	Formula	M_r	w_i (calc.)/%					Yield (%)
			w_i (found)/%					
			C	H	N	S	O	M.p. (°C)
ANI.SSA	$C_{13}H_{13}NO_6S$	311.31	50.16	4.21	4.50	10.30	30.83	76.6
			49.92	4.24	4.54	10.53	30.77	

tion (2.5 mmol of APS in 5 mL of distilled water) to the monomer solution containing 2 mmol of ANI.SSA dissolved in 15 mL of distilled water (pH 1.90). The reaction mixture was stirred at room temperature for 36 h. The precipitated dark green product was filtered and washed with 10 mL of aqueous 1 M SSA, and then with 25 mL of acetone and 25 mL of diethyl ether. Obtained PANI.SSA was dried in vacuum at room temperature for 3 h. Protonated polymer was deprotonated with an excess of 0.5 M NaOH for 1 h and the resulting PANI base was separated on a filter, washed with distilled water, and dried in vacuum at room temperature for 3 h. The yield of PANI was 82.2 %.

1H and ^{13}C nuclear magnetic resonance (NMR) spectra of ANI.SSA were recorded at 200/50 MHz with tetramethylsilane (TMS) as an internal standard on a Varian “Gemini 200” spectrometer (USA) in D_2O . Chemical shifts are expressed downfield from TMS. Infrared spectra of ANI.SSA and PANI.SSA powdered samples dispersed in KBr pellets were recorded in the range of 400–4000 cm^{-1} using a Perkin–Elmer FT-IR 1725X Spectrometer (USA). Molecular masses of PANI.SSA were assessed by gel permeation chromatography using a 500×8 mm Labio GM 1000 column (Czech Republic) operating with *N*-methyl-2-pyrrolidone and calibrated with polystyrene standards using toluene as an internal standard and spectrophotometric detection at the wavelength of 290 nm. Samples for GPC measurements were prepared by dissolving 10 mg of polymeric sample in 5 mL of *N*-methyl-2-pyrrolidone containing 100 mg of triethanolamine to deprotonate the sample and to improve its solubility. Mobile phase, *N*-methyl-2-pyrrolidone, contained 0.5 % LiBr to prevent aggregation. Flow rate was 1 mL min^{-1} . For conductivity measurements, PANI.SSA samples were pressed into pellets, 10 mm in diameter and 1 mm thick, under the pressure of 124 MPa using a hydraulic pellet press. The conductivity was measured between stainless pistons at room temperature by means of an ac bridge (Wayne Kerr Universal Bridge B 224, United Kingdom) at the fixed frequency of 1.5 kHz. During the measurement, pressure was maintained at the mentioned value. Thermal analysis was carried out in air using a TA Instruments Model SDT 2960 thermoanalytical device

(USA), with the flow rate of 90 mL min^{-1} and the heating rate of 15 °C min^{-1} from room temperature to 800 °C.

Results and discussion

ANI.SSA characterization

The determined elemental composition (w_i (found)/%, Table 1) of the synthesized ANI.SSA (Fig. 1) is in excellent agreement with that calculated (w_i (calc.)/%, Table 1) from the expected compound formula ($C_{13}H_{13}NO_6S$, Table 1) thus indicating high purity of the synthesized ANI.SSA. Molecular structure of ANI.SSA (Fig. 1) was confirmed by spectral data (Table 2).

Sulfonic acid salt form of ANI.SSA (Fig. 1) is in accordance with the well-known acidic properties of SSA ($pK_{a(SO_3H)} < 1$, $pK_{a(COOH)} \sim 2.85$, $pK_{a(OH)} \sim 13.4$) (Butler & Bates, 1976), and the fact that SSA can release its sulfonic acid hydrogen to Lewis base nitrogen atoms forming 1 : 1 molecular adducts in general (Smith et al., 2004, 2005). ANI.SSA behaves as a weak acid ($pK_{a(COOH)} \sim 2.85$, $pK_{a(C_6H_5NH_3^+)} \sim 4.6$, $pK_{a(OH)} \sim 13.4$) and partially dissociates in aqueous solutions (Fig. 1). Acidity of an ANI.SSA aqueous solution depends on the ANI.SSA concentration ($[ANI.SSA]$). Since $[H^+] = [ANI.SSA^-]$ (Fig. 1), acidity can be predicted by solving the equation $[H^+]^2 + K_{a(COOH)}[H^+] - K_{a(COOH)}[ANI.SSA] = 0$. Experimentally determined pH of the ANI.SSA solution (1.90) is in excellent agreement with the theoretically predicted value (1.89) for the applied ANI.SSA concentration (0.133 M).

PANI.SSA characterization

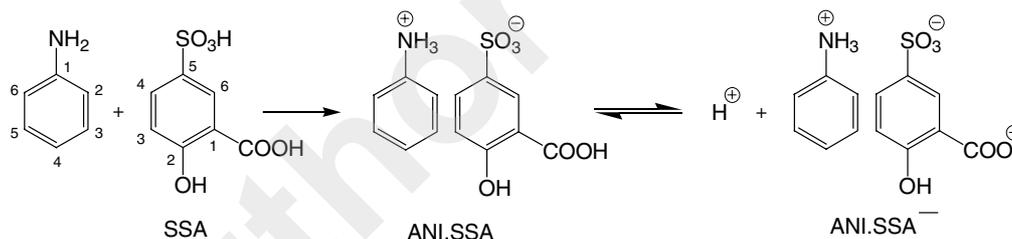
Based on the elemental analysis data of PANI.SSA, empirical formula of PANI.SSA was determined: $[C_6H_5N]^{0.39+}(SSA^-)_{0.324}(HSO_4^-)_{0.066}(H_2O)_{0.35}$ (Table 3), where $[C_6H_5N]^{0.39+}$ denotes the partially positively charged unit of the PANI chain and SSA^- denotes the 5-sulfosalicylate anion. This indicates a significantly higher extent of SSA^- incorporation, compared with hydrogen sulfate, in PANI.SSA. The average charge of C_6H_5N unit (0.39) in PANI.SSA indi-

Table 2. Spectral data of ANI.SSA

Compound	Spectral data
ANI.SSA	IR: $\tilde{\nu}/\text{cm}^{-1}$: 3404 ($\nu(\text{O—H})$), 2998 ($\nu(\text{N—H}^+$ in $-\text{NH}_3^+$)/ $\nu(\text{O—H})$), 2593 ($-\text{NH}_3^+$ overtone), 1669 ($\nu(\text{C=O})$), 1608 (ring $\nu(\text{C=C})$ /asym. $-\text{NH}_3^+$ def. vib.), 1589 (ring $\nu(\text{C=C})$), 1519 (ring $\nu(\text{C=C})$ /sym. $-\text{NH}_3^+$ def. vib.), 1493, 1477, and 1434 (ring $\nu(\text{C=C})$), 1353 and 1198 (O—H def. vib. and C—O stretch. combination in phenol), 1173 (asym. $\nu(-\text{SO}_3^-)$ sulfonic acid salt), 1125 ($\delta(\text{C—H})$), 1082 ($\nu(\text{C—COOH})$), 1030 (sym. $\nu(-\text{SO}_3^-)$ sulfonic acid salt), 885, 835, and 804 ($\gamma(\text{C—H})$ in SSA), 743 and 688 ($\gamma(\text{C—H})$ in $\text{C}_6\text{H}_5\text{NH}_3^+$), 664 (γ/δ (SSA benzene ring)), 595 (γ (SSA benzene ring), $\gamma(\text{OH})$, $\delta(\text{SO}_2)$) ^1H NMR (D_2O), δ : 7.07 (d, 1H, HC(3) in SSA), 7.37–7.59 (m, 5H, in $\text{C}_6\text{H}_5\text{NH}_3^+$), 7.88 (d, 1H, HC(4) in SSA), 8.26 (s, 1H, HC(6) in SSA) ^{13}C NMR (D_2O), δ : 116.9 (C(3) in SSA), 122.0 (C(1) in SSA), 127.5–128.3 (6C in $\text{C}_6\text{H}_5\text{NH}_3^+$), 129.2 (C(6) in SSA), 131.6 (C(5) in SSA), 133.0 (C(4) in SSA), 161.4 (C(2) in SSA)

Table 3. Elemental analysis data and empirical formulae of PANI.SSA salt and the corresponding PANI base

Polymer product	Formula	$w_i(\text{found})/\%$				
		C	H	N	S	O
PANI.SSA	$[\text{C}_6\text{H}_5\text{N}]^{0.39+}(\text{SSA}^-)_{0.324}(\text{HSO}_4^-)_{0.066}(\text{H}_2\text{O})_{0.35}$	54.94	4.30	7.75	6.92	26.09
PANI base	$[\text{C}_6\text{H}_{4.5}\text{N}](\text{SSA})_{0.026}(\text{H}_2\text{O})_{0.274}$	74.12	5.22	13.97	0.83	5.86

**Fig. 1.** Formation of ANI.SSA and its partial dissociation in an aqueous solution.

cates an oxidation state lower than that of the emeraldine polycation $[(-\text{C}_6\text{H}_4\text{NH}-\text{C}_6\text{H}_4\text{NH}^+-)]_n$ which has the average charge of 0.5 for the $\text{C}_6\text{H}_5\text{N}$ unit, and higher than that of the protoemeraldine polycation $[(-\text{C}_6\text{H}_4\text{NH}-)]_n(-\text{C}_6\text{H}_4\text{NH}^+-)]_n$ which has the average charge of 0.25 for the $\text{C}_6\text{H}_5\text{N}$ unit. Sulfur content in the PANI base indicates a small extent of sulfosalicylate covalent bonding to PANI (~ 1 SSA per 40 aniline units, Table 3).

Gel permeation chromatography revealed one large peak corresponding to higher molar mass and one small peak belonging to shorter oligomeric chains (Fig. 2). The mass-average and number-average molar masses, M_w and M_n , were calculated to amount to 22,900 g mol^{-1} and 8,490 g mol^{-1} , respectively, while molar mass approaches the maximum value of about 100,000 g mol^{-1} . Polydispersity index is 2.7.

PANI.SSA shows low solubility in ethanol, acetone, acetonitrile and tetrahydrofuran. However, PANI.SSA was found to be soluble in dimethyl sulfoxide, *N,N*-dimethylformamide and *N*-methyl-2-pyrrolidone. The maximum solubility of 9.8 g L^{-1} was observed in dimethyl sulfoxide.

Conductivity of green PANI.SSA powder was found to be 0.13 S cm^{-1} . This value is by one order of magnitude higher than that reported for the PANI base doped with SSA (Palaniappan et al., 2004), and of the same magnitude as that found for PANI synthesized by the oxidative polymerization of aniline with APS in an aqueous medium in the presence of a large surplus of SSA ($[\text{SSA}]/[\text{aniline}] = 10$, $\sigma = 0.2 \text{ S cm}^{-1}$, Trivedi & Dhawan, 1993).

Thermal stability of PANI.SSA in air was studied by thermogravimetric analysis (TGA, Fig. 3a) and differential thermal analysis (DTA, Fig. 3b). The first mass loss from 30 °C to about 240 °C observed on the TGA curve, and an endothermic peak at around 50 °C present on the DTA curve correspond to the release of residual water. Mass loss in the temperature range from about 240 °C to 650 °C was attributed to the release of SSA and sulfuric acid from the PANI matrix, followed by progressive degradation and decomposition of the PANI backbone. It should be noted that the onset of decomposition in a nitrogen stream at around 200–225 °C was first observed by Neoh et al. (1995) for PANI.SSA prepared by doping of the PANI

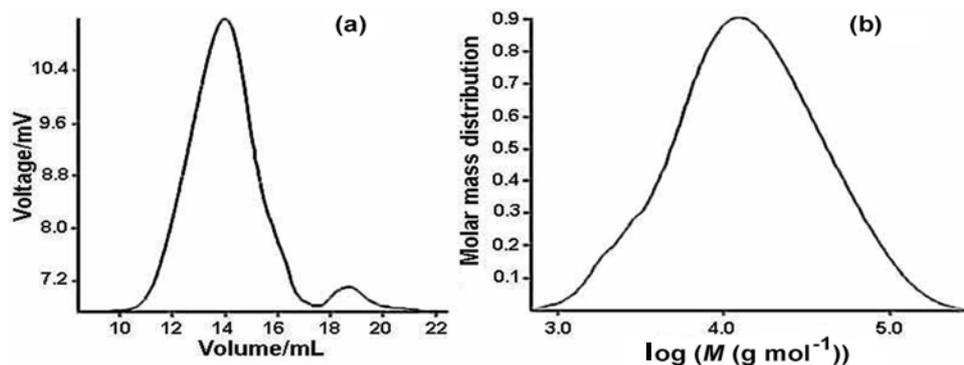


Fig. 2. Gel permeation chromatogram of PANI.SSA (a) and corresponding molar mass distribution (b).

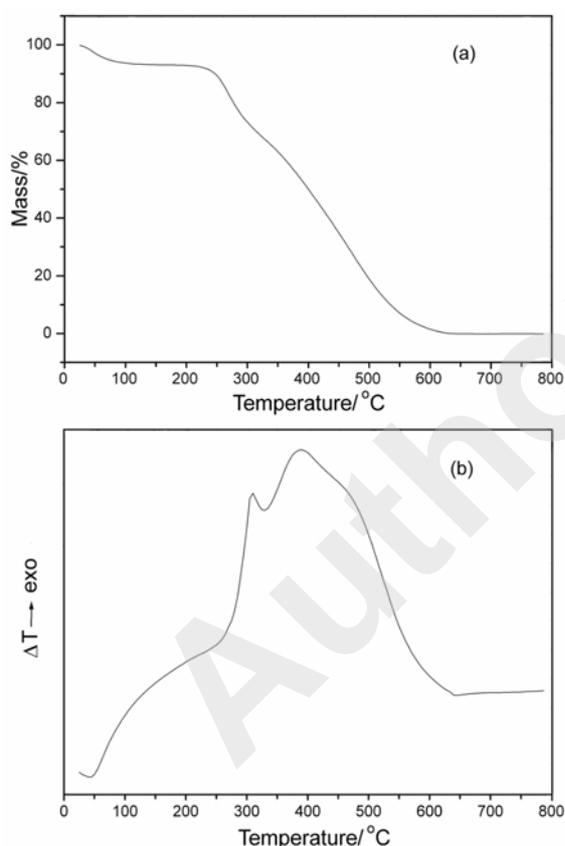


Fig. 3. TGA (a) and DTA (b) curve for PANI.SSA recorded in air stream.

base with SSA. This indicates higher thermal stability of PANI.SSA synthesized by oxidative polymerization of ANI.SSA with peroxydisulfate in comparison with PANI.SSA prepared by the standard dedoping-redoping procedure. DTA curve of PANI.SSA exhibits an exothermic peak with the maximum at 300°C attributable to the thermal oxidative degradation and combustion of the oligoaniline fraction in PANI.SSA. Exothermic DTA peak with the maximum at 400°C and a shoulder at 460°C are both attributable to high molecular masses PANI chains showing a combustion process splitted into two phases.

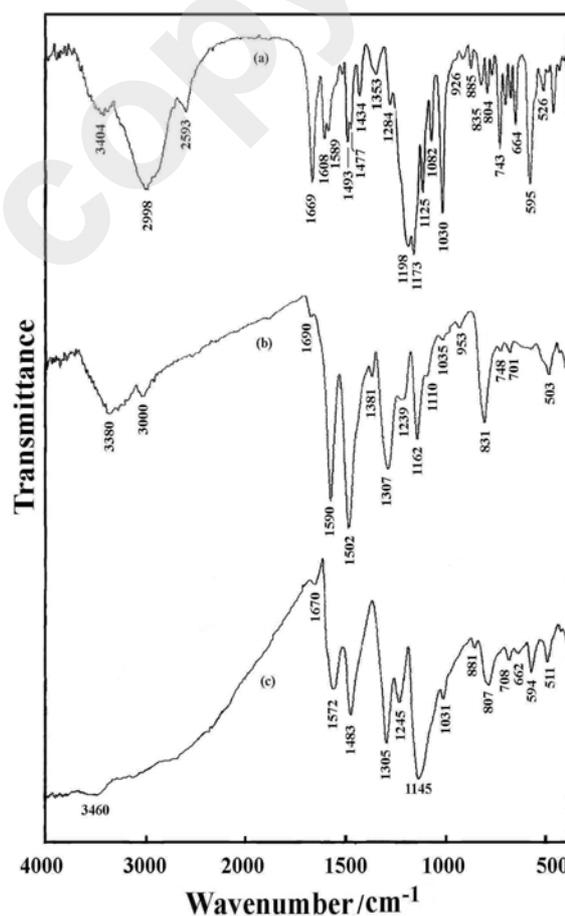


Fig. 4. FTIR spectra of (a) ANI.SSA, (b) PANI base, and (c) PANI.SSA.

FTIR spectrum of PANI.SSA (Fig. 4) shows characteristic peaks of the PANI emeraldine salt at 1572 cm⁻¹ (quinonoid (Q) ring stretching), 1483 cm⁻¹ (benzenoid (B) ring stretching), 1305 cm⁻¹ (the C—N stretching of secondary aromatic amine), 1245 cm⁻¹ (the C—N⁺ stretching), 1145 cm⁻¹ (the B—NH⁺=Q a stretching), and a band at 807 cm⁻¹ (aromatic C—H out-of-plane deformation vibration of 1,4-disubstituted benzene ring, $\gamma(\text{C—H})$, in linear

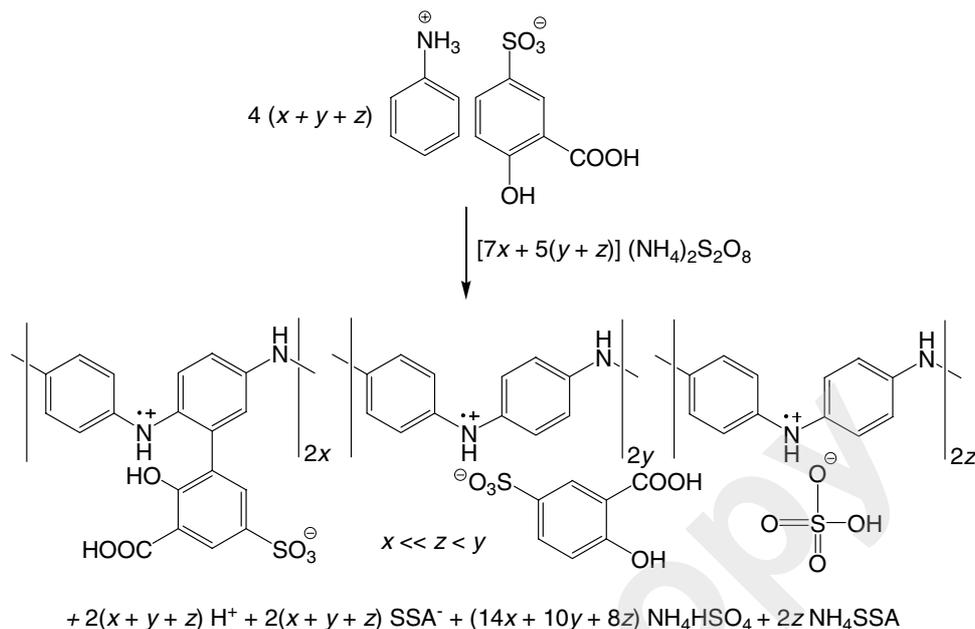


Fig. 5. Formation of functionalized emeraldine salt of PANI.SSA by oxidation of ANI.SSA with APS.

PANI backbone) (Janošević et al., 2008). The broad band observed at about 3460 cm^{-1} corresponds to the N—H stretching vibration of a secondary amine in the PANI backbone. The presence of SSA anions in PANI.SSA samples is confirmed by the characteristic bands observed at 1670 cm^{-1} (C=O stretching in COOH), 881 cm^{-1} ($\gamma(\text{C—H})$ vibrations of 1,2,4-trisubstituted SSA ring), and 662 cm^{-1} (in-plane bending and/or out-of-plane bending of SSA ring). The bands at 1031 cm^{-1} (symmetric stretching of SO_3^- group in SSA and HSO_4^- anions) and 594 cm^{-1} (out-of-plane bending of SSA ring/ $\delta(\text{SO}_2)$ in SSA and HSO_4^- anions) are attributable to both SSA and HSO_4^- anions. Asymmetric stretching of the SO_3^- group in SSA and HSO_4^- anions contribute to the strong band at 1145 cm^{-1} . The coexistence of both SSA monovalent anions and hydrogen sulfate anions in PANI.SSA is a consequence of complete one-proton dissociation of the corresponding strong acids, SSA and sulfuric acid (formed as a by-product during polymerization), and suppressed second-proton dissociation of both acids, $\text{p}K_{\text{a}2}(\text{SSA}) = 2.85$ and $\text{p}K_{\text{a}2}(\text{H}_2\text{SO}_4) = 2.0$, at the end of the polymerization process when the reaction mixture became highly acidic, pH of about 1.5.

FTIR spectrum of the PANI base (Fig. 4) shows characteristic peaks of the PANI emeraldine base at 1590 cm^{-1} (quinonoid (Q) ring stretching), 1502 cm^{-1} (benzenoid (B) ring stretching), 1381 cm^{-1} (the C—N stretching in QB_tQ unit, B_t denotes a *trans*-benzenoid unit), 1307 cm^{-1} (the C—N stretching in QB_cQ , QBB , and BBQ units, B_c denotes a *cis*-benzenoid unit), 1162 cm^{-1} (the N=Q=N stretching), and a band at 831 cm^{-1} (aromatic C—H out-of-plane deformation vibration of 1,4-disubstituted benzene ring, $\gamma(\text{C—H})$, in linear PANI backbone) (Trchová et al.,

2006; Janošević et al., 2008). Bands of SSA anions are still present in the FTIR spectrum of the PANI base, although weakened and slightly shifted (1690 cm^{-1} , 1035 cm^{-1} , 660 cm^{-1} , and 591 cm^{-1}) in comparison with the corresponding bands in PANI.SSA. The existence of SSA in the PANI base can be explained by a certain extent of covalent bonding between SSA and the PANI backbone. The observed shifting of the SSA bands is due to the fact that the SSA covalently bonded to the PANI base chain exists in a dianion form because of the deprotonation of both the sulfonic and the carboxylic acid groups of SSA upon the dedoping of PANI.SSA.

Taking into account PANI.SSA characterization data, as well as previously reported finding (Ćirić-Marjanović et al., 2007) that couplings between the growing PANI chain and SSA mainly comprise reactions between C2, C3, C5, and C6 positions of the aniline unit in the PANI backbone and C3 position of SSA, the structure of PANI.SSA has been proposed (Fig. 5).

Conclusions

Anilinium 5-sulfosalicylate was synthesized for the first time by simple and scalable neutralization of 5-sulfosalicylic acid with aniline in a propan-2-ol medium, and polymerized in an aqueous solution using ammonium peroxydisulfate as an oxidant. Precipitated polyaniline 5-sulfosalicylate shows the doping level of 0.39 monovalent dopant anions (SSA and hydrogen sulfate) per an aniline unit indicating thus an oxidation state between the emeraldine and protoemeraldine salts. Polyaniline 5-sulfosalicylate is conducting (0.13 S cm^{-1}) and thermally stable up to

about 240 °C. Its mass-average and number-average molar masses and polydispersity index were determined by gel-permeation chromatography to amount to 22,900 g mol⁻¹, 8,490 g mol⁻¹, and 2.7, respectively. Elemental analysis and the FTIR spectroscopy study of polyaniline 5-sulfosalicylate indicate prevalent incorporation of 5-sulfosalicylate anions into polyaniline 5-sulfosalicylate chains compared with hydrogen sulfate anions which are formed by peroxydisulfate reduction. A small extent of 5-sulfosalicylate anions covalent bonding to polyaniline chains was found by elemental analysis and FTIR spectroscopy of the corresponding polyaniline base. The present study has proved the advantageous use of anilinium 5-sulfosalicylate, which can be easily prepared on industrial scale in high yields and stored without decomposition in the air at room temperature, in an efficient one-pot synthesis of functionalized, thermally stable, conducting polyaniline 5-sulfosalicylate.

Acknowledgements. The authors acknowledge the Ministry of Science and Technological Development of Serbia (Contracts Nos 142047 and 142010) for financial support.

References

- Butler, R. A., & Bates, R. G. (1976). Double potassium salt of sulfosalicylic acid in acidimetry and pH control. *Analytical Chemistry*, 48, 1669–1671. DOI: 10.1021/ac50006a011.
- Čirić-Marjanović, G., Dondur, V., Milojević, M., Mojović, M., Mentus, S., Radulović, A., Vuković, Z., & Stejskal, J. (2009a). Synthesis and characterization of conducting self-assembled polyaniline nanotubes/zeolite nanocomposite. *Langmuir*, 25, 3122–3131. DOI: 10.1021/la8030396.
- Čirić-Marjanović, G., Dragičević, Lj., Milojević, M., Mojović, M., Mentus, S., Dojčinić, B., Marjanović, B., & Stejskal, J. (2009b). Synthesis and characterization of self-assembled polyaniline nanotubes/silica nanocomposites. *The Journal of Physical Chemistry B*, 113, 7116–7127. DOI: 10.1021/jp900096b.
- Čirić-Marjanović, G., Janošević, A., Marjanović, B., Trchová, M., Stejskal, J., & Holler, P. (2007). Chemical oxidative polymerization of dianilinium 5-sulfosalicylate. *Russian Journal of Physical Chemistry A, Focus on Chemistry*, 81, 1418–1424. DOI: 10.1134/S0036024407090130.
- Čirić-Marjanović, G., Konyushenko, E. N., Trchová, M., & Stejskal, J. (2008a). Chemical oxidative polymerization of anilinium sulfate versus aniline: Theory and experiment. *Synthetic Metals*, 158, 200–211. DOI: 10.1016/j.synthmet.2008.01.005.
- Čirić-Marjanović, G., Trchová, M., & Stejskal, J. (2008b). Theoretical study of the oxidative polymerization of aniline with peroxydisulfate: Tetramer formation. *International Journal of Quantum Chemistry*, 108, 318–333. DOI: 10.1002/qua.21506.
- Čirić-Marjanović, G., Trchová, M., & Stejskal, J. (2008c). The chemical oxidative polymerization of aniline in water: Raman spectroscopy. *Journal of Raman Spectroscopy*, 39, 1375–1387. DOI: 10.1002/jrs.2007.
- Čirić-Marjanović, G., Trchová, M., & Stejskal, J. (2006a). MNDO-PM3 Study of the early stages of the chemical oxidative polymerization of aniline. *Collection of Czechoslovak Chemical Communications*, 71, 1407–1426. DOI: 10.1135/cccc20061407.
- Čirić-Marjanović, G. N., Marjanović, B. N., Popović, M. M., Panić, V. V., & Mišković-Stanković, V. B. (2006b). Anilinium 5-sulfosalicylate electropolymerization on mild steel from an aqueous solution of sodium 5-sulfosalicylate/disodium 5-sulfosalicylate. *Russian Journal of Electrochemistry*, 42, 1358–1364. DOI: 10.1134/S1023193506120147.
- Gospodinova, N., & Terlemezyan, L. (1998). Conducting polymers prepared by oxidative polymerization: polyaniline. *Progress in Polymer Science*, 23, 1443–1484. DOI: 10.1016/S0079-6700(98)00008-2.
- Ha, J., & Jang, J. (2005). Chemical synthesis of highly conductive polyaniline nanoparticles and applications for magnetic carbon nanomaterials. *Applied Chemistry*, 9, 73–76.
- Janošević, A., Čirić-Marjanović, G., Marjanović, B., Holler, P., Trchová, M., & Stejskal, J. (2008). Synthesis and characterization of conducting polyaniline 5-sulfosalicylate nanotubes. *Nanotechnology*, 19, 135606. DOI: 10.1088/0957-4484/19/13/135606.
- Konyushenko, E. N., Stejskal, J., Šeděnková, I., Trchová, M., Sapurina, I., Cieslar, M., & Prokeš, J. (2006). Polyaniline nanotubes: conditions of formation. *Polymer International*, 55, 31–39. DOI: 10.1002/pi.1899.
- Konyushenko, E. N., Trchová, M., Stejskal, J., & Sapurina, I. (2010). The role of acidity profile in the nanotubular growth of polyaniline. *Chemical Papers*, 64, 56–64. DOI: 10.2478/s11696-009-0101-z.
- Lee, K., Cho, S., Park, S. H., Heeger, A. J., Lee, C.-W., & Lee, S.-H. (2006). Metallic transport in polyaniline. *Nature*, 441, 65–68. DOI: 10.1038/nature04705.
- MacDiarmid, A. G., & Epstein, A. J. (1995). Secondary doping in polyaniline. *Synthetic Metals*, 69, 85–92. DOI: 10.1016/0379-6779(94)02374-8.
- MacDiarmid, A. G., Jones, W. E., Jr., Norris, I. D., Gao, J., Johnson, A. T., Jr., Pinto, N. J., Hone, J., Han, B., Ko, F. K., Okuzaki, H., & Llaguno, M. (2001). Electrostatically-generated nanofibers of electronic polymers. *Synthetic Metals*, 119, 27–30. DOI: 10.1016/S0379-6779(00)00597-X.
- Neoh, K. G., Pun, M. Y., Kang, E. T., & Tan, K. L. (1995). Polyaniline treated with organic acids: doping characteristics and stability. *Synthetic Metals*, 73, 209–215. DOI: 10.1016/0379-6779(95)80018-2.
- Palaniappan, S., John, A., Amarnath, C. A., & Rao, V. J. (2004). Mannich-type reaction in solvent free condition using reusable polyaniline catalyst. *Journal of Molecular Catalysis A: Chemical*, 218, 47–53. DOI: 10.1016/j.molcata.2004.04.010.
- Raghunathan, A., Rangarajan, G., & Trivedi, D. C. (1996). ¹³C CPMAS NMR, XRD, d.c. and a.c. electrical conductivity of aromatic acids doped polyaniline. *Synthetic Metals*, 81, 39–47. DOI: 10.1016/0379-6779(96)80227-X.
- Smith, G., Wermuth, U. D., & Healy, P. C. (2005). Layered structures in proton-transfer compounds of 5-sulfosalicylic acid with the aromatic polyamines 2,6-diaminopyridine and 1,4-phenylenediamine. *Acta Crystallographica Section C*, 61, o555–o558. DOI: 10.1107/S010827010502439X.
- Smith, G., Wermuth, U. D., & White, J. M. (2004). Hydrogen bonding in proton-transfer compounds of 5-sulfosalicylic acid with bicyclic heteroaromatic Lewis bases. *Acta Crystallographica Section C*, 60, o575–o581. DOI: 10.1107/S010827010401457X.
- Stejskal, J., & Gilbert, R. G. (2002). Polyaniline. Preparation of a conducting polymer (IUPAC Technical Report). *Pure and Applied Chemistry*, 74, 857–867. DOI: 10.1351/pac200274050857.
- Stejskal, J., Hlavatá, D., Holler, P., Trchová, M., Prokeš, J., & Sapurina, I. (2004). Polyaniline prepared in the presence of various acids: a conductivity study. *Polymer International*, 53, 294–300. DOI: 10.1002/pi.1406.

- Stejskal, J., Kratochvíl, P., & Jenkins, A. D. (1996). The formation of polyaniline and the nature of its structures. *Polymer*, 37, 367–369. DOI: 10.1016/0032-3861(96)81113-X.
- Stejskal, J., Sapurina, I., Trchová, M., Konyushenko, E. N., & Holler, P. (2006). The genesis of polyaniline nanotubes. *Polymer*, 47, 8253–8262. DOI: 10.1016/j.polymer.2006.10.007.
- Stejskal, J., Trchová, M., Brožová, L., & Prokeš, J. (2009). Reduction of silver nitrate by polyaniline nanotubes to produce silver–polyaniline composites. *Chemical Papers*, 63, 77–83. DOI: 10.2478/s11696-008-0086-z.
- Stejskal, J., Trchová, M., Kovářová, J., Prokeš, J., & Omastová, M. (2008). Polyaniline-coated cellulose fibers decorated with silver nanoparticles. *Chemical Papers*, 62, 181–186. DOI: 10.2478/s11696-008-0009-z.
- Tawde, S., Mukesh, D., & Yakhmi, J. V. (2002). Redox behavior of polyaniline as influenced by aromatic sulphonate anions: cyclic voltammetry and molecular modeling. *Synthetic Metals*, 125, 401–413. DOI: 10.1016/S0379-6779(01)00483-0.
- Trchová, M., Šeděnková, I., Konyushenko, E. N., Stejskal, J., Holler, P., & Čirić-Marjanović, G. (2006). Evolution of polyaniline nanotubes: The oxidation of aniline in water. *The Journal of Physical Chemistry B*, 110, 9461–9468. DOI: 10.1021/jp057528g.
- Trivedi, D. C., & Dhawan, S. K. (1993). Investigations on the effect of 5-sulfosalicylic acid on the properties of polyaniline. *Synthetic Metals*, 58, 309–324. DOI: 10.1016/0379-6779(93)91140-W.