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## TNT-BASED SULFONATED POLYNAPHTHYLIMIDES USEFUL AS PROTON EXCHANGE MEMBRANES FOR FUEL CELLS (PEMFCs)

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**Abstract.** PEMFC Fuel Cell uses a polymer membrane as an electrolyte. It is used in all applications with dynamic loads, especially in mobile applications but also as combined heat and power units in households. The development of the membranes ion-conductivity has much increased over the last 30 years. Today “Nafion”-based membranes achieve a power density up to 1 W/cm<sup>2</sup> active area. In the last 10 years the successful adoption of the PEMFC in different prototypes could be demonstrated. For a market-introduction a few “teething problem” like life-time and costs have to be solved.

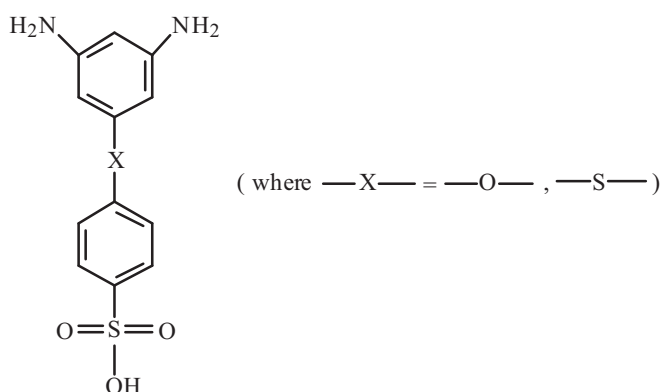
In this context scientists have high expectations in the development of high-temperature membranes. Cells with these temperatures can be operated over 373 K.

Regarding our investigations on the synthesis of aromatic condensation monomers and polymers based on 2,4,6-trinitrotoluene (TNT) we have developed new side-chain-sulfonated aromatic diamines (SCSADAs) and polymers there from. Generally these diamines are prepared using multistep synthetic procedures; as a result they are expensive and unavailable. Our approach shows that the acidic groups on the pendant phenyl groups are more stable to hydrolysis than those with acidic groups directly attached to the main chains. Acidified polymers are stable up to 423 K.

**Keywords:** PEMFCs fuel cells, TNT-based polymer, membrane, sulfonated polynaphthylimide.

## 1. Introduction

In the past decades great interest has been focused on the development of polymer electrolyte fuel cells (PEFCs) and direct methanol fuel cells (DMFC) as a clean power source of energy for transportation, stationary and portable power applications [1-10]. Polymer electrolyte membrane (PEM) is one of the key components in PEFC and DMFC systems. Sulfonated polynaphthylimides (SPNIs) with six-membered imide rings have been developed as promising candidates for PEM [11, 12]. Among SPNIs of especially great interest are side-chain-type SPNIs, where the sulfonic acid groups are bonded to the pendant groups [11-17]. Such polymers with acidic groups on the pendant phenyl groups are more stable to hydrolysis than those with acidic groups directly attached to the main chains [18, 19]. Side-chain-type SPNIs are usually prepared by the interaction of bis (naphthalic anhydrides) – mainly naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (DANTCA) – with side-chain-sulfonated aromatic diamines (SCSADAs) [11-17]. Generally these diamines are prepared using multistep synthetic procedures; as a result they are expensive and unavailable. In the line of our investigations on the synthesis of aromatic condensation monomers and polymers based on 2,4,6-trinitrotoluene (TNT) [20-22] we have developed new SCSADAs of general formula showed in Fig. 1 and SPNIs there from.



**Fig. 1.** Sulfonated diamines based on 2,4,6-trinitrotoluene (TNT)

## 2. Experimental

### 2.1. Synthesis of Diamines

3,5-Dinitrodiphenyl ether was prepared using the following procedure. Solution of trinitrobenzene (5.33 g, 0.025 mol) in 5 ml of DMSO, heated to 353 K, was added to the mixture of 2.35 g (0.025 mol) of phenol, 20 ml of DMSO and 1.6 g (0.0125 mol) of  $K_2CO_3$ . The mixture was maintained at this temperature for 3 h and poured in 125 ml of water. The precipitate formed was filtered off and dried. Yield of 3,5-dinitrodiphenyl ether is 6.2 g (95 %); m.p. 392.5–393.5 K. NMP<sup>1</sup>H spectrum (DMSO- $d_6$ ): 7.13 (d, 2H); 7.33 (t, 1H); 7.49 (t, 2H); 8.09 (d, 2H); 8.71 (t, 1H). Mass-spectrum: 260 ( $M^+$ ).

3,5-Dinitrodiphenyl ether-4'-sulfonic acid was prepared in accordance with the following procedure: 7 ml (0.105 mol) of chlorosulfonic acid were added dropwise to the stirred suspension of 26 g (0.1 mol) of 3,5-dinitrodiphenyl ether in 135 ml of dichloroethane there. The solution obtained was refluxed for 6.5 h. Then the reaction mixture was cooled and diluted with 600 ml of  $CCl_4$ . The precipitate formed was filtered off, washed with pure  $CCl_4$  and dried over KOH. Yield is 30.3 g (89 %); m.p. 341–343 K. NMP<sup>1</sup>H spectrum (DMSO- $d_6$ ): 7.18 (d, 2H,  $^3J = 9.2$ ); 7.72 (d, 2H,  $^3J = 9.2$ ); 8.17 (d, 2H,  $^4J = 1.8$ ); 8.57 (t, 1H,  $^4J = 1.8$ ).

3,5-Dinitrodiphenyl ether-4'-sulfonic acid monohydrochloride was prepared in accordance with the following procedure: mixture of 6.80 g (0.02 mol) of 3,5-dinitrodiphenyl ether-4'-sulfonic acid, 70 ml of methanol, 0.8 g (0.02 mol) of NaOH, 7.8 ml of  $H_2N-NH_2 \cdot H_2O$ , 0.09 g of  $FeCl_3 \cdot 6H_2O$ , 4 g of activated charcoal and 30 ml of water was boiled with reflux condenser for 7.5 h and filtered. The filtrate was evaporated in vacuum; residue was dried, placed in the mixture of conc. HCl (10 ml) and  $H_2O$  (10 ml) and heated to reflux. The precipitate formed

was filtered off, dried in vacuum over  $P_2O_5$ . Yield of 3,5-diaminodiphenyl ether-4'-sulfonic acid thus obtained is 4.13 g (65 %); m.p. > 623 K. NMP<sup>1</sup>H spectrum (DMSO- $d_6$ ): 6.31 (d, 2H,  $^4J = 1.8$ ); 6.49 (t, 1H,  $^4J = 1.8$ ); 7.02 (d, 2H,  $^3J = 8.5$ ); 7.66 (d, 2H,  $^3J = 8.5$ ).

3,5-Diaminodiphenyl ether-4'-sulfonic acid was prepared analogously.

### 2.2. Synthesis of Polynaphthylimides

1.58 g (0.005 mol) of 3,5-diaminodiphenyl ether-4'-sulfonic acid monohydrochloride, 1.25 ml of phenol and 1.4 mol of triethylamine were placed in the three-necked 100 ml reaction flask, equipped with stirrer, argon inlet and reflux condenser. The reaction mixture was heated at 323 K until complete dissolution of the diamine. Then 0.005 mol of the corresponding dianhydride, 0.005 mol of benzoic acid and 0.005 mol of benzimidazole were added to the reaction solution. The mixture was heated at 353 K for 4 h; then the temperature was raised up to 453 K and the mixture was stirred at this temperature for 20 h. After cooling to room temperature the polymer was precipitated in acetone, extracted with acetone in Soxhlet apparatus and dried in vacuum at 373 K for 10 h.

#### *Preparation of SPNIs in acidic form.*

Films on glass substrate were cast from 5–7 % solutions of the SPNIs (in triethylammonium salts forms) in DMSO; the films were dried at 353 K for 1 h, then at 373 K for 1 h and at 393 K for 10 h. Films thus obtained were soaked in methanol for 48 h at 313 K to remove the traces of solvent and then in 1M  $H_2SO_4$  at 313 K for 72 h. The acidified films were washed with water (48 h at 313 K) and dried in vacuum for 3 h at 333 and 353 K.

## 3. Results and Discussion

New SCSADAs were prepared in accordance with Fig. 2 starting with 1,3,5-trinitrobenzene (TNB) – TNT oxidative demethylation product [23].

TNB transformations included:

- substitution of one nitro group under the action of phenol [24, 25] or thiophenol [26, 27];
- sulfonation of 3,5-dinitrodiphenylether and 3,5-dinitrodiphenyl sulfide thus obtained;
- reduction of the 3,5-diaminoarylene-4'-sulfonic acids thus obtained with hydrazine-hydrate and  $FeCl_3 \cdot 6H_2O$ .

Structures of the target 3,5-diaminoarylene-4'-sulfonic acids and intermediate compounds were confirmed using elemental analysis (Table 1), NMR<sup>1</sup>H-spectroscopy, mass-spectral analysis and FTIR analysis.

It is necessary to note that purification of 3,5-diaminoarylene-4'-sulfonic acids is rather problematic. Up to date only 3,5-diaminodiphenyl ether was isolated and purified in the form of monohydrochloride. Purification of 3,5-diaminodiphenyl sulfide-4'-sulfonic acid is in progress.

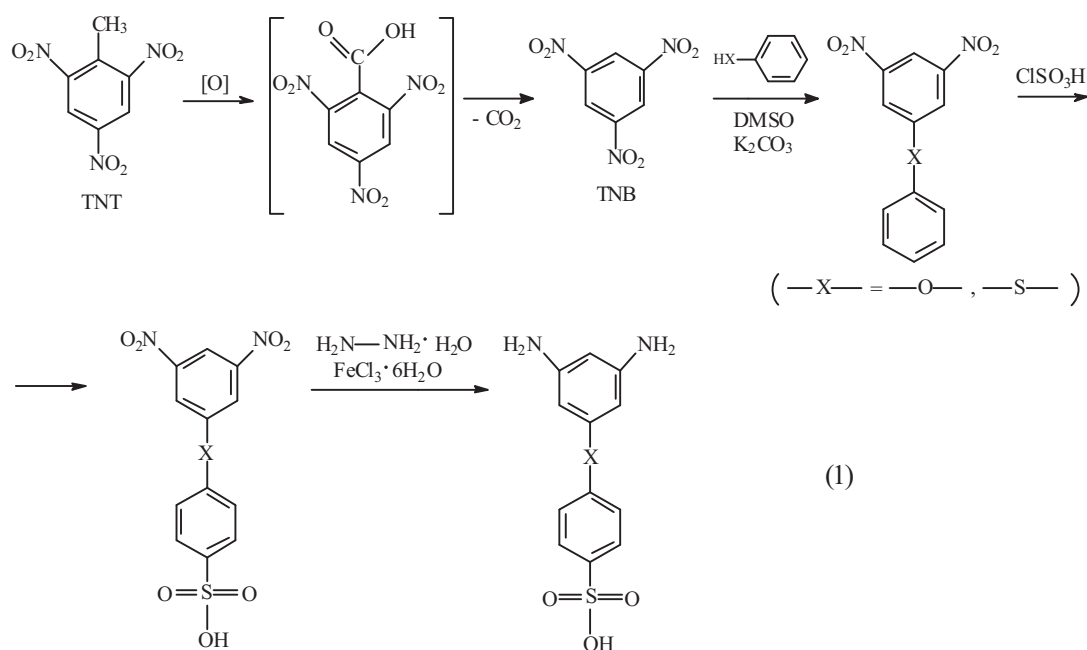


Fig. 2. Oxidative demethylation of TNT to TNB and following transformations

Some properties of the compounds of general formula

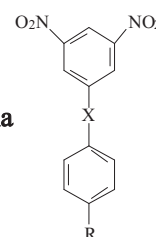


Table 1

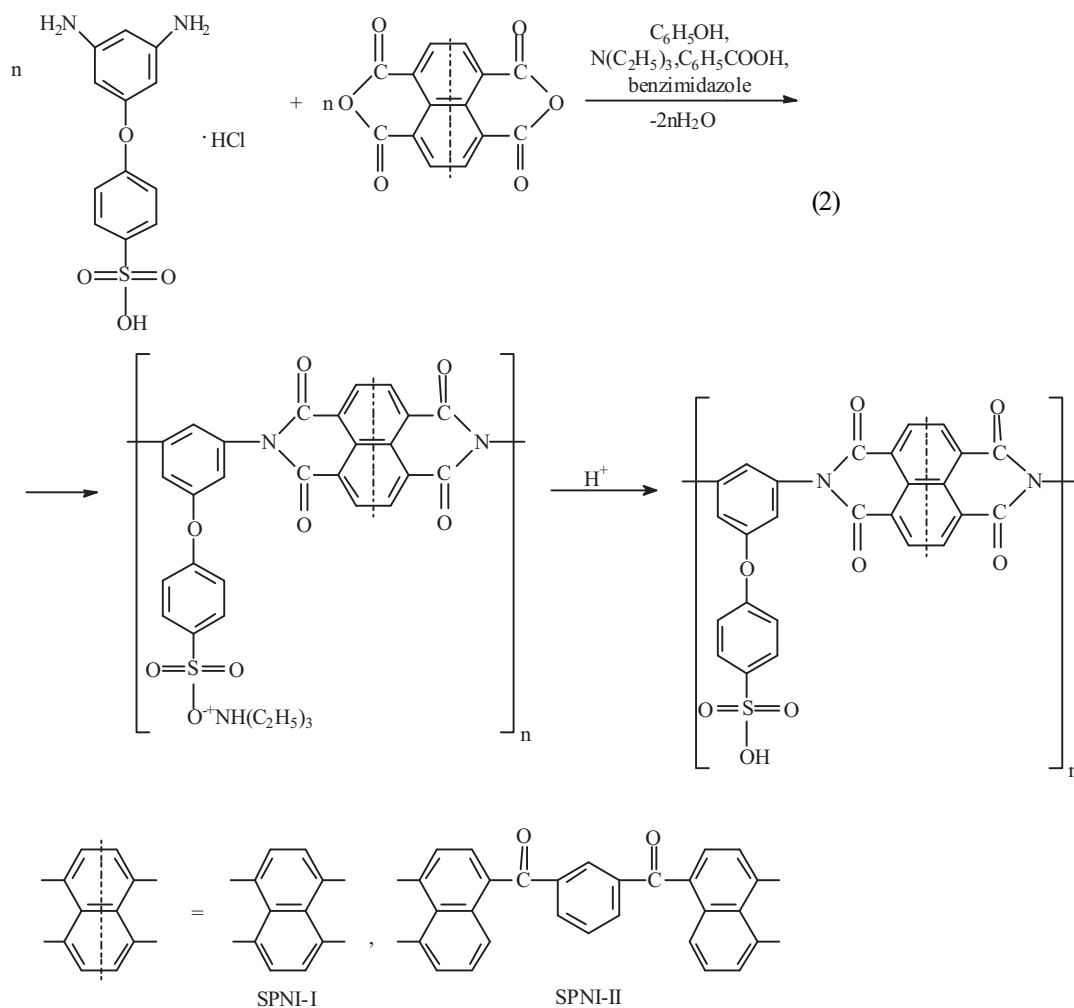
-X-	-R	m.p., K	Elemental analysis				Yield, %
			Found / Calculated, %				
			C	H	N	S	
-O-	-H	119.5-120.5	<u>55.80</u>	<u>3.20</u>	<u>10.90</u>	—	95
			55.39	3.10	10.77		
-S-	-H	97-98	<u>52.17</u>	<u>2.92</u>	<u>10.14</u>	<u>11.60</u>	89
			52.28	3.02	10.55	11.47	
-O-	-SO <sub>3</sub> H	68-70	<u>42.16</u>	<u>2.50</u>	<u>8.01</u>	<u>9.24</u>	89
			42.36	2.37	8.23	9.42	
-S*	-SO <sub>3</sub> H	116	<u>37.56</u>	<u>2.77</u>	—	<u>16.88</u>	97
			37.60	2.89		16.78	

\* includes 1.5 mole of H<sub>2</sub>O

Synthesis of SPNIs on the basis of 3,5-diaminodiphenyl ether-4'-sulfonic acid monohydrochloride was carried out by the interaction of this monomer with DANTCA and 1,3-bis-(1,8-dicarboxynaphthoyl-4)-benzene dianhydride [28] in accordance with Fig. 3.

The general method [11, 12] was used for the preparation of SPNIs modified procedure – polymers were

synthesized in phenol using triethylamine (for deprotonation of amino groups and formation of SPNIs in the form of their triethylammonium salts), benzoic acid and benzimidazole catalyzing polycyclocondensation process [29]. Formation of SPNIs in the forms of their triethylammonium salts results in homogeneous polycondensation processes and prevents desulfonation



**Fig. 3.** Synthesis of the sulfonated polynaphthylimides

reactions. Reactions were carried out at 453 K for 10 h. Homogeneous polycyclocondensation processes led to the formation of SPNIs triethylammonium salts completely soluble in *m*-cresol and dipolar aprotic solvents – DMSO, DMA, DMF, N-MP.

Structure of SPNIs triethylammonium salts was confirmed using FTIR-spectroscopy and NMR<sup>1</sup>H-spectroscopy data. The FTIR spectra show characteristic naphthylimide absorptions at 1714–1716 cm<sup>-1</sup> ( $\nu_{\text{C=O}}$ ), 1674–1679 cm<sup>-1</sup> ( $\nu_{\text{C=O}}$ ), 1331–1333 cm<sup>-1</sup> ( $\nu_{\text{CN}}^{\text{sym}}$  imide) [30–34] and 758–768 cm<sup>-1</sup> ( $\nu_{\text{CN}}^{\text{asym}}$  deformation vibrations of naphthylimide cycle) [34–38].

Sulfonic group absorption was observed at 1168 cm<sup>-1</sup> ( $\nu_{\text{S=O}}^{\text{asym}}$ ) [30, 31, 33] and 1027–1029 cm<sup>-1</sup> ( $\nu_{\text{S=O}}^{\text{sym}}$ ) [31, 33]. Absorption maxima at 1232–1249 cm<sup>-1</sup> are attributed to asym. C–O vibrations [39].

Analysis of SPNI-II triethylammonium salt FTIR-spectrum has demonstrated that absorption maximum at 1674 cm<sup>-1</sup> is broadened; probably, it is the result of overlapping of absorption bands typical for asymmetric naphthylimide carbonyl vibration and diarylketone carbonyl

vibration (which is usually observed at 1660 cm<sup>-1</sup> [39]). Absorption maximum at 780 cm<sup>-1</sup> may be attributed to the deformative vibration of C–CH in disubstituted aromatic rings [39]. Very weak absorption maximum at 1773 cm<sup>-1</sup> may be attributed to carbonyls of the anhydride terminal groups [39].

Absorption maxima at 2691–2701 cm<sup>-1</sup> and 2498 cm<sup>-1</sup> are attributed to SPNIs triethylammonium salts.

Polymers obtained demonstrate relatively high solution viscosities (Table 2).

Their weight average molecular weights ( $M_w$ ) determined using GPC method were equal to 416 700 (SPNI-I) and 589 800 (SPNI-II); their number average molecular weights were equal to 277 500 (SPNI-I) and 124 800 (SPNI-II). It seems to be quite possible that very high values of the molecular weights are due to polymer chain associations in solutions [30]; anyway only brittle films were cast from SPNIs triethylammonium salts solutions in DMSO.

The cast films were dried at 353–393 K for 10 h, soaked in methanol to remove the residual solvent and then

**Some properties of sulfonated polynaphthylimides triethylammonium salts of general formula**

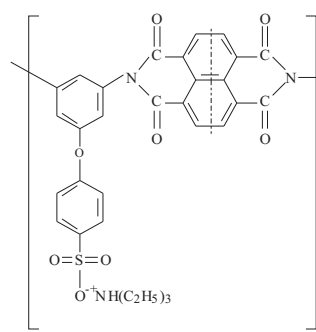
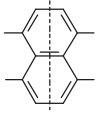
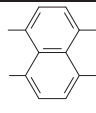
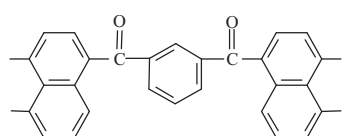


Table 2

	$\eta_{red}$ , (DMSO, 0.5%), dl/g	$\frac{M_w}{M_n}$
	1.14	$\frac{416700}{277500}$
	1.07	$\frac{589800}{124800}$

proton exchange treatment was performed by immersing the membranes into 1 M H<sub>2</sub>SO<sub>4</sub> solution at 313 K for 72 h [17].

Transformation of SPNIs triethylammonium salts into SPNIs acidic forms was confirmed using FTIR analysis data; this transformation was accompanied by disappearance of absorption maxima at 2691–2701 cm<sup>-1</sup> and 2498 cm<sup>-1</sup>.

SPNIs containing sulfonic acid groups did not dissolve completely in polar aprotic solvents – DMSO, DMA and N-MP; this observation is in good agreement with [17].

Thermal stability of SPNIs in their triethylammonium salts and acidic forms was investigated by DTGA (air,  $\Delta T=4.5$  K/min). It was found that for all the polymers investigated the weight loss below 423 K was observed; it is attributed to the loss of sorbed water. Above 423 K, a two-step degradation profile was observed for all the polymers. The weight loss below 673–723 K was attributed to desulfonation, whereas the weight loss above 773 K was attributed to the decomposition of polymer backbones. Such profiles are typical for all SPNIs described previously [11, 12].

The acidified polymers displayed higher degradation temperatures than their corresponding triethylammonium sulfonate salt forms; this observation is in good agreement with [40].

## 4. Conclusions

Sulfonated polynaphthylimides (SPNIs) with six-membered imide rings have been developed as promising candidates for PEM. Among SPNIs of especially great interest are side-chain-type SPNIs, where the sulfonic acid groups are bonded to the pendant groups. Such polymers with acidic groups on the pendant phenyl groups are more stable to hydrolysis than those with acidic groups directly attached to the main chains. Side-chain-type SPNIs have been successfully prepared by the interaction of bis(naphthalic anhydrides) with side-chain-sulfonated aromatic diamines (SCSADAs).

## Acknowledgments

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**ВИКОРИСТАННЯ СУЛЬФОВАНИХ  
ПОЛІНАФТИЛІМІДІВ НА ОСНОВІ ТНТ  
ДЛЯ ПРОТОННИХ ОБМІННИХ МЕМБРАН  
ПАЛИВНИХ ЕЛЕМЕНТІВ**

*Анотація.* З використанням синтезованих ароматично конденсованих мономерів і полімерів на основі 2,4,6-тринітродоуолу (ТНТ) розроблені методи одержання нових ароматичних діамінів, що містять сульфонатні бічні ланцюги та полімерів на їх основі. Незважаючи на те, що такі діаміни описані в літературі, в запропонованій роботі розглянуто новий підхід до створення таких сполук, який є дешевшим і доступнішим. Враховуючи те, що сульфонатні групи знаходяться в бічних ланцюгах до фенольних груп, такі сполуки, порівняно із речовинами, які містять кислотні групи безпосередньо в головному ланцюгу, є більш термостійкими і витримують температуру до 423 К.

*Ключові слова:* протонні обмінні мембрани паливних елементів, полімери на основі ТНТ, сульфований полінафтилімід.