

Proton conductive PBI membranes, containing cross-linked polyvinylsulfonic acid, for PEM fuel cells

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Here we present an easy and efficient procedure for the immobilization of proton-donating sulfo-groups in a polymer matrix. Sodium vinyl sulfonate was polymerized/cross-linked in a para-polybenzimidazole (p-PBI) matrix. After acidification semi-interpenetrating networks, comprising p-PBI, containing cross-linked polyvinylsulfonic acid (cr-PVSA), have been obtained. Polymerization/crosslinking has been initiated either thermally or by UV irradiation. Two series of membranes, containing high concentrations of water insoluble acid groups, have been prepared. Proton conductivity was measured at 60, 80 and 95 °C and 100% relative humidity. The highest proton conductivity achieved was 63.2 mS.cm⁻¹.

Keywords: p-Polybenzimidazole-membranes, polyvinylsulfonic acid, cross-linking, semi-interpenetrating network, fuel cells, proton conductivity.

INTRODUCTION

The polymer electrolyte membrane fuel cell (PEM FC) generates electricity from an electrochemical reaction in which oxygen (air) and a fuel (e.g. hydrogen) combine to form water and heat. The polymer electrolyte membrane (PEM) is the heart of the fuel cell. PEM FC with membrane, containing sulfonic groups (-SO₃H) are usually operated at temperatures up to 80 °C and high RH (up to 100%).

At present the most widely used proton conductive membranes are based on perfluorinated poly-electrolytes with attached super-acidic sulfo groups (Nafion[®], Flemion[®], HyflonIon[®], Dow membrane). These materials have high proton conductivity, excellent chemical stability, mechanical strength and potentially long term durability. The main drawbacks of these commercial membranes are their high cost and strong dependence of the proton conductivity on water contents in the membrane (difficulties with the so called water-management, due to increased hydrophobicity of the polymer backbone). Such membranes can function properly only in the highly hydrated state. In order to maintain high wa-

ter content, complex water management is needed and the operation temperature is usually limited to the boiling point of water. Various polymers, containing sulfonic acid groups have been developed during the last years – sulfonated polyetheretherketones and polyether-sulfones, polyimides, sulfonated polybenzimidazoles etc. Despite of being relatively cheaper than the perfluorinated Nafion[®]-types, these membranes suffer the same restrictions – low operating temperatures and complex water management as well as lower proton-conductivity, inferior to the Nafion membrane.

Different types of PBI membranes with immobilized acidic groups have been described –PBIs with -SO₃H groups in the main chain, PBI, containing cross-linked/grafted polyvinylphosphonic acid (PVPA) [1] and PBI with grafted PVPA chains [2].

The three most widely studied PBIs are meta-, para- and AB-PBI. Ion conductive membranes, based on these materials exhibit excellent physico-mechanical properties and chemical stability.

The efforts, involved in the preparation of membranes, containing high concentrations of immobilized vinyl phosphonic or vinylsulfonic acid groups, show that the higher contents of such groups results in higher proton conductivity both in the anhydrous and at fully hydrated state of the membrane [2, 3]. Several years ago we have reported membranes, comprising m-PBI, containing cross-linked

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polyvinylphosphonic acid. We also showed that this method can be applied for the preparation of semi-interpenetrating networks PBI/cross-linked polyvinylsulfonic acid.

Here we report a further development of this cheap, extremely easy and efficient method for preparation of p-PBI membranes, containing cross-linked PVSA as well as characterization of the membranes prepared.

EXPERIMENTAL

Materials

2.0 wt.% solution of p-PBI in polyphosphoric acid (PPA) was kindly supplied by BASF Fuel Cell GmbH. Vinylsulfonic acid sodium salt solution 25 wt.% in H₂O (technical grade), EtOH (96%), initiator V50: 2, 2'-Azobis(2-methylpropionamide) dihydrochloride and crosslinker: triallyl-s-triazine-2, 4, 6 (1H, 3H, 5H)-trion (98%, stabilized) were purchased from Merck and used as received.

Methods

The ¹H NMR spectra were recorded in H₂SO₄-d₂ on a Bruker Advance DRX 250 spectrometer using the solvent protons as internal standard. TGA was performed on Perkin Elmer 4000 apparatus – heating rate of 10 °C / min in nitrogen, temperature range 30–300 °C. FT-IR spectra were recorded on FT-IR Bruker-Vector 22 spectrometer (KBr pellets), UV irradiation was performed with Hoenle UV technology 400 W lamp, 20 cm from the filter.

All proton conductivity measurements were performed at Zentrum für Brennstoffzellen Technik ZBT GmbH, Duisburg, Germany. The EasyCell Test method [4], developed at Institute of Electrochemistry and Electrical Sources, Bulgarian Academy of Sciences, has been used.

Proton conductivity measurements were performed at 60, 80 and 95 °C and relative humid-

ity (RH) 100% (Tabl. 1). The proton conductivity measurements were carried out on Solartron Analytical 1287 Electrochemical Interface and 1255 Impedance Phase Analyzer (Farnborough, UK), connected to a computer equipped with CoreWare™, CoreView™, ZPlot™, and ZView™ (Scribner Associates, Inc.). The membranes studied were adjusted in four electrode cell placed in the conditioning chamber of the EasyTest Cell [4–6].

Membrane preparation

In order to incorporate high concentrations of immobilized sulfonic acid groups (–SO₃H) in the p-PBI matrix, a method involving simultaneous polymerization/cross-linking of sodium vinyl sulfonate (VSA-Na) in the p-PBI matrix was applied. After acidification, semi-interpenetrating networks p-PBI, containing cross-linked polyvinyl sulfonic acid (further denoted as **PBI-sipn-PVSA**) are obtained as shown in Figure 1.

The procedure for preparation of p-PBI membranes, containing cross-linked PVSA includes the following simple steps (Fig. 2):

Step 1. Preparation of “starting membrane”:

2.0 wt.% solution of p-PBI in polyphosphoric acid (PPA) was used for casting of the starting membranes. The inherent viscosity of p-PBI used is 3.6 dL/g. It was determined at polymer concentration of 0.2 g/dL in concentrated sulfuric acid (96%) at 30 °C, using an Ubbelohde viscometer.

Using a casting knife (gap 0.6 mm) a membrane was cast on a glass substrate and kept in air for several hours (start of the sol-gel process - hydrolysis of PPA to H₃PO₄).

Step 2. Preparation of porous p-PBI films, filled with water.

The membrane was then immersed in a water bath – further hydrolysis of PPA to H₃PO₄ and removal of the acid from the membrane takes place. After abundant washing with water, rests of H₃PO₄

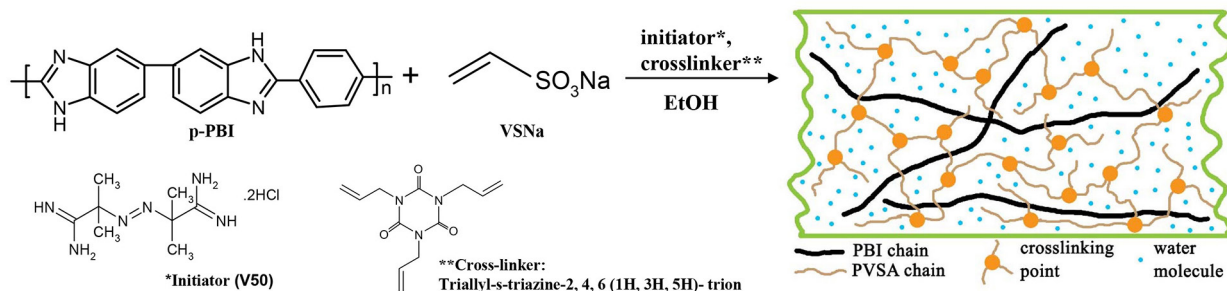


Fig. 1. Preparation of semi-interpenetrating network p-PBI-sipn-PVSA.

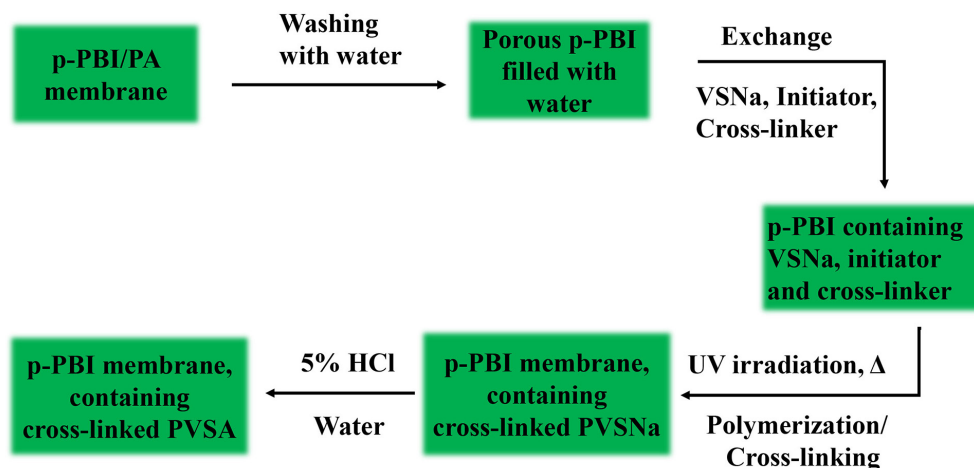


Fig. 2. Procedure for preparation of p-PBI-sipn-PVSA membranes.

were removed with 5 wt.% aqueous NH_3 , followed by washing in deionized water. In this way porous p-PBI film, filled with water, is obtained. It contains only 14 wt. % PBI, the rest is water.

Step 3. *Exchanging water with VSA-sodium salt (VSA-Na).*

The membrane obtained in step 2 was transferred into a bath, containing EtOH, 25% aqueous solution of VSA-Na, cross-linker (triallyl-s-triazine-2,4,6 (1H, 3H, 5H)-trion, 2-5 wt.%) and initiator (V 50 – 2, 2'-azobis(2-methylpropionamide) dihydrochloride, 1–2 wt.%). Exchange of water was completed in about 3 hours at room temperature (RT) in the dark.

Step 4. *Polymerization/ cross-linking of VSA-Na in the PBI matrix, induced thermally or by UV irradiation.*

Simultaneous polymerization/cross-linking of VSA-Na in the p-PBI matrix: The film prepared in Step 3 was irradiated with UV light (up to 4 h) or heated in a furnace (80 °C) for up to 96 h.

Step 5. *Acidification – transformation of PVSA-Na to PVSA.*

The film from step 4 was washed with water (removal of non-crosslinked PVSA), then in with 5% HCl and deionized water. The result is transformation of the $-\text{SO}_3\text{Na}$ group to $-\text{SO}_3\text{H}$. Using this procedure membranes of very good quality (smooth, flexible, no defects) were obtained.

For the determination of the amount cross-linked PVSA in the membrane (sulfonic acid groups per PBI repeat unit), two methods have been used:

Method 1: Gravimetric method: a piece of the porous membrane filled with water was weighted

and dried to constant weight. The difference gives the weight of PBI in the wet membrane (14 wt.%). The same procedure is performed with the final membrane, containing water insoluble $-\text{SO}_3\text{H}$ groups. From the difference of the weights (dry PBI containing cross linked PVSA and dry PBI in the wet membrane) the amount of $-\text{SO}_3\text{H}$ groups in the membrane can be calculated.

Method 2: From ^1H NMR: the amount of $-\text{SO}_3\text{H}$ groups in the membrane can be calculated from the ratio $-\text{CH}_2-\text{CH}$ protons/aromatic PBI protons.

The values, obtained by both methods are very close. For the membrane M_{UV4} the ratio VSA groups per PBI repeating unit, determined gravimetrically is 4.6, while the value obtained from ^1H NMR analysis was 4.4.

The method used offers vast opportunities for varying different parameters during membrane preparation – in the third step: composition of bath (concentration of VSA-Na, initiator, cross-linker and co-solvent in the bath), temperature and duration of treatment; in the fourth step: intensity and duration of the UV irradiation, temperature and duration of the thermal treatment.

RESULTS AND DISCUSSION

Using the procedure, schematically shown in Figure 2, two series of p-PBI-sipn-PVSA membranes were we prepared:

Series 1: 4 samples (M_{T1} , M_{T2} , M_{T3} , M_{T4}) p-PBI-sipn-PVSA membranes, obtained after thermal treatment – duration 24, 48, 72 and 96 h.

Series 2: 4 samples (M_{UV1} , M_{UV2} , M_{UV3} , M_{UV4}) p-PB-sipn-PVSA membranes, obtained after UV irradiation – duration 1, 2, 3 and 4 h.

The best results (highest proton conductivity) were obtained for the last two samples of each series (i.e. M_{T3} , M_{T4} , M_{UV3} , M_{UV4}), presented in Table 1. The other four samples showed much lower proton conductivity, obviously due to lower contents of immobilized $-SO_3H$ groups.

The 1H NMR spectrum of M_{uv4} (the membrane with highest proton conductivity) is presented in Fig. 3. The peaks for the aromatic protons from the benzimidazole rings (10 protons) appear in the

region 7.00–8.00 ppm. The peaks of the aliphatic protons ($-CH_2-CH-$) from VSA (13.2 protons) are observed between 1 ppm and 3.5 ppm. As one VSA group has 3 protons, 13.2 protons correspond to 4.4 VSA groups. In this way the membrane contains to 4.4 VSA groups per PBI unit (10 H). This result is very close to the gravimetrically determined value (4.6 VSA groups per PBI unit, Table 1).

The FT-IR spectrum (Fig. 4) of pristine p-PBI showed sharp band around 3435 cm^{-1} , which is

Table 1. Proton conductivity measurements of the best PBI-sipn-PVSA membranes

Membrane p-PBI/cr-PVSA	Method of polymerization/ cross-linking	VSA units per PBI unit	Proton conductivity σ , $\text{mS}\cdot\text{cm}^{-1}$		
			60 °C	80 °C	95 °C
M_{T3}	Thermal treatment, 80 °C, 72 h	3.0	25.0	29.2	31.5
M_{T4}	Thermal treatment, 80 °C, 96 h	3.6	28.0	38.2	45.2
M_{UV3}	UV irradiation, 3 h	3.7	29.1	37.3	42.2
M_{UV4}	UV irradiation, 4 h	4.6	51.3	55.3	63.2

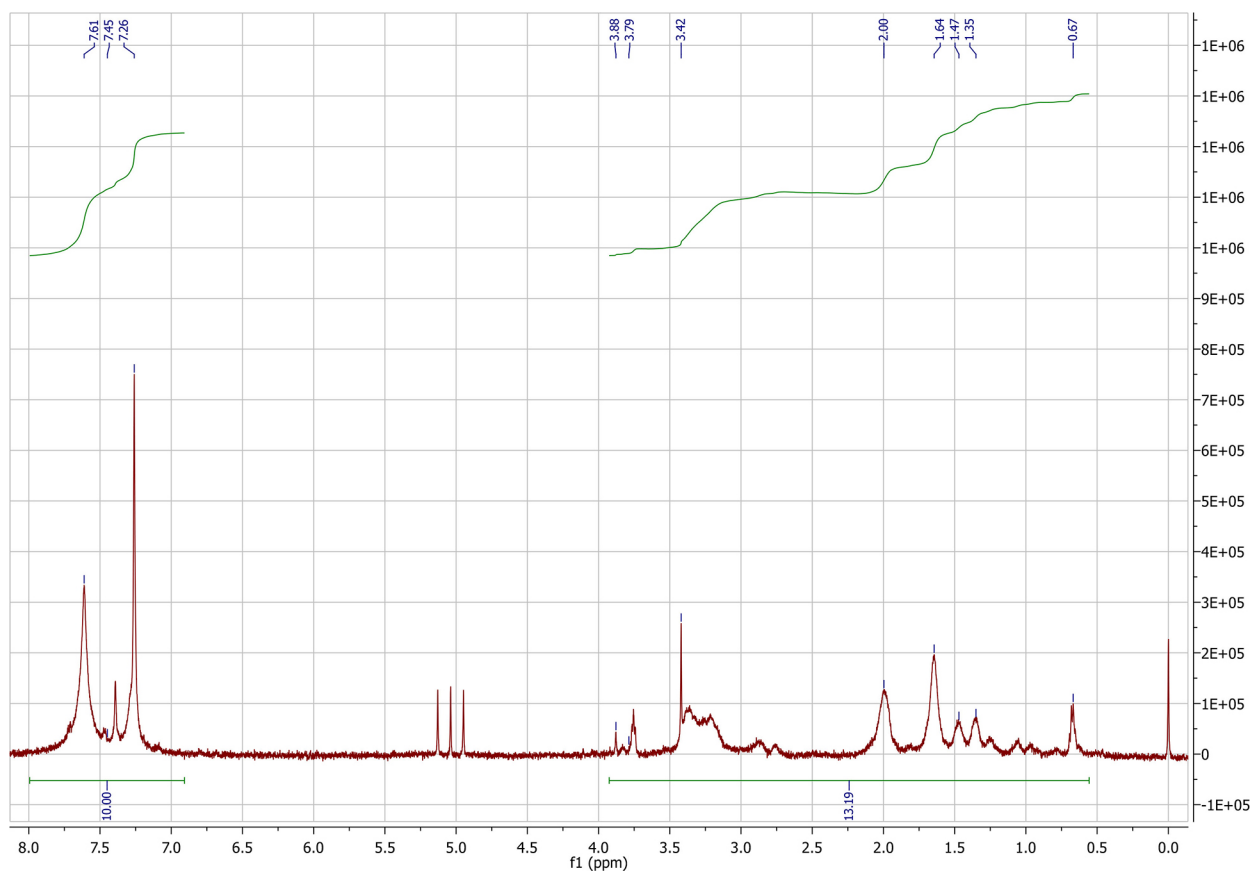


Fig. 3. 1H NMR spectrum of p-PBI-sipn-PVSA membrane (M_{uv4}).

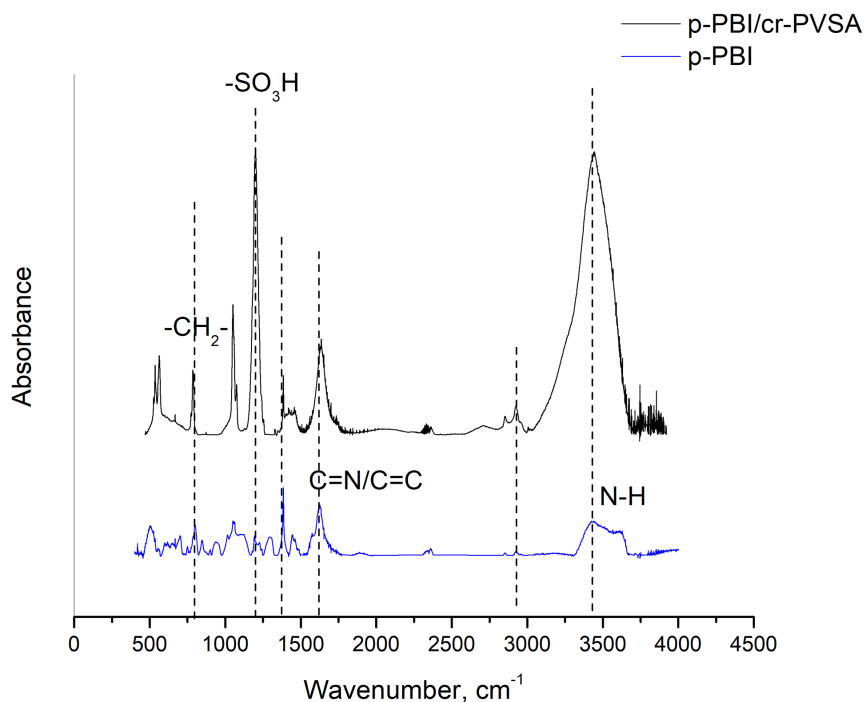


Fig. 4. FT-IR spectra of pristine p-PBI and p-PBI containing PVSA.

attributed to the stretching vibrations of isolated N—H bonds in the imidazole ring. The absorptions in a region of $1630\text{--}1500\text{ cm}^{-1}$ are attributed to the vibration of C=C and C=N. The strong band at 1388 cm^{-1} has to be attributed to the in plane deformation of the benzimidazole rings [7–10].

In the FT-IR spectrum of p-PBI-sipn-PVSA (Fig. 4), despite of the bands, characteristic for the p-PBI rings, a medium band at 796 cm^{-1} due to the polymeric methylene group ($-\text{CH}_2-$) is clearly visible. The intense peak at 1200 cm^{-1} originates from the sulfonic acid group. The band at 1373 cm^{-1} is assigned to CH_2 bond deformation. The band at 2926 cm^{-1} is due to CH_2 stretching vibration. Stretching vibration of -OH group of water molecule is a broad band and observed at about 3442 cm^{-1} [10].

As already mentioned, two types of p-PBI-sipn-PVSA membranes were prepared: thermally treated and UV-irradiated. In the PEM FC sulfonated membranes are usually operated at temperatures up to $80\text{ }^\circ\text{C}$ and high relative humidity (up to 100%). The thermal stability of the membranes was studied by TGA in the range $30\text{--}300\text{ }^\circ\text{C}$ (Fig. 5). It can be seen that up to $100\text{ }^\circ\text{C}$ the weight loss is only 1–2.5% (Fig. 5). Further loss of water is observed up to $150\text{ }^\circ\text{C}$. Up to $300\text{ }^\circ\text{C}$ the weight loss could be attributed to anhydride formation from the sulfonic acid groups. The curves for both materials are almost identical, the difference being only 1–2% in the whole range.

In our opinion for polymerization/cross-linking of VPA-Na in the p-PBI matrix better results were achieved by UV irradiation. Depending on irradiation time up to 75% of the VSA-Na in the film can be cross-linked for 4h. Similar result could be obtained heating at $80\text{ }^\circ\text{C}$ for 3–4 days. In both cases films of very good quality (smooth, flexible, no defects) were prepared.

For the best samples very good proton conductivity was obtained. The contents of VSA groups is in the range 3 to 4.6 $-\text{SO}_3\text{H}$ groups per PBI unit. The membrane with highest $-\text{SO}_3\text{H}$ contents showed the best conductivity – $63.2\text{ mS}\cdot\text{cm}^{-1}$ at $95\text{ }^\circ\text{C}$ and 100% RH (Table 1). Sulfonated Nafion[®]-type membranes exhibit proton conductivity in the range $85\text{--}100\text{ mS}\cdot\text{cm}^{-1}$ [11]. The conductivity of phosphoric acid-doped sulfonated polysulfones and their blends with polybenzimidazole is $10\text{ mS}\cdot\text{cm}^{-1}$ at a very low acid-doping level [12].

CONCLUSION

Using an original method for polymerization/crosslinking of VSA in a p-PBI matrix two series of membranes with high contents of immobilized sulfonic acid groups have been prepared by thermal treatment and UV-irradiation of a p-PBI film, containing VSA-Na salt, cross-linker and initiator. For the best samples the concentration of $-\text{SO}_3\text{H}$ groups

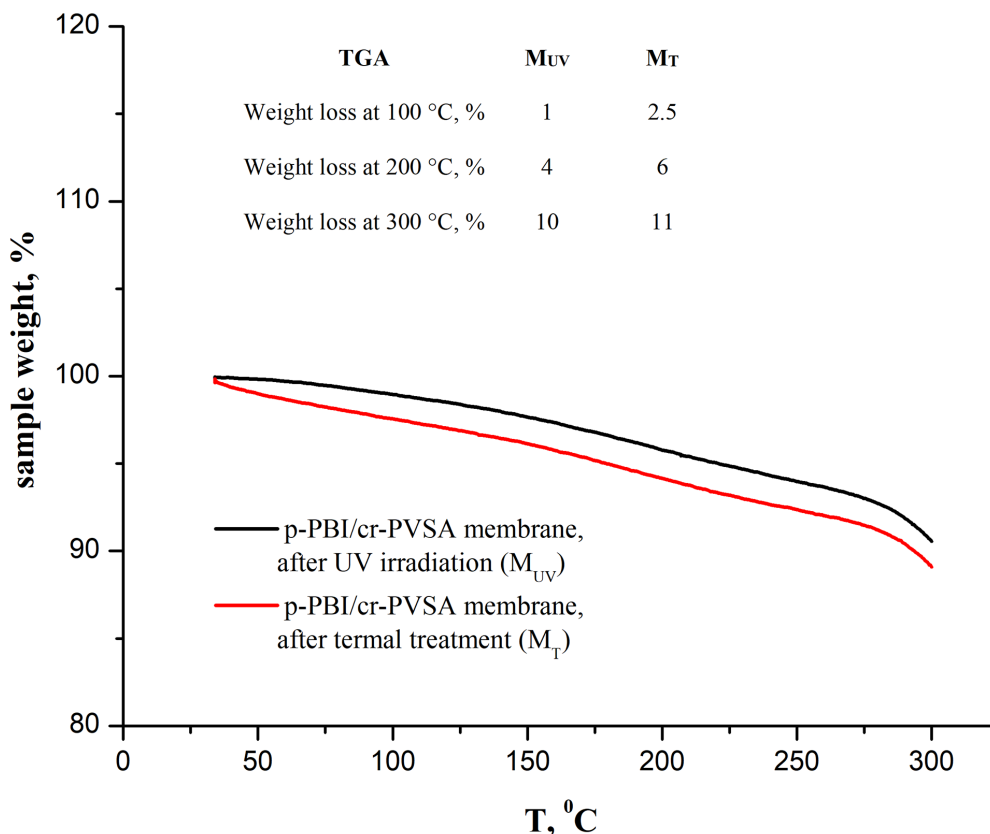


Fig. 5. TGA of PBI-sipn-PVSA membranes, obtained by UV irradiation and thermal treatment.

is 3–4.6 per PBI unit. At 60–95 °C and 100% RH the PBI-sipn-PVSA membranes show proton conductivity close to that of Nafion®-type membranes. Sulfonated Nafion®-type membranes usually exhibit $\sigma = 85\text{--}100 \text{ mS}\cdot\text{cm}^{-1}$, while our best membrane showed proton conductivity $63.2 \text{ mS}\cdot\text{cm}^{-1}$. The results showed that UV irradiation is superior to the thermal treatment as a method for obtaining semi-interpenetrating networks p-PBI-sipn-PVSA. These membranes can be regarded as cheap alternative to the very expensive Nafion type membranes.

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ПРОТОН-ПРОВОДЯЩИ МЕМБРАНИ, СЪДЪРЖАЩИ
ОМРЕЖЕНА ПОЛИВИНИЛСУЛФОНОВА КИСЕЛИНА,
ИЗПОЛЗВАНИ КАТО ПОЛИМЕРЕЛЕКТРОЛИТНИ
МЕМБРАНИ ЗА ГОРИВНИ КЛЕТКИ

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(Резюме)

Тук представяме нов подход за имобилизиране на протондонорни сулфо-групи в полимерната матрица. Разработена е лесна и ефикасна процедура за изготвяне на полу-проникващи мрежи от пара-полибензимидазол (п-ПБИ), съдържащ омрежена поливинилсулфонова киселина (омр-ПВСК). Тя е описана в 5 лесни стъпки. Прилагайки описаната по-горе процедура, изготвихме две серии мембрани, съдържащи водонерастворими групи на винилсулфоновата киселина във високи концентрации. Най-високата стойност на протонната проводимост, измерена за така получените мембрани е $63.2 \text{ mS}\cdot\text{cm}^{-1}$ ($T = 95 \text{ }^\circ\text{C}$, относителна влажност 100%).