

Polybenzimidazole-Graft-Polyvinylphosphonic Acid—Proton Conducting Fuel Cell Membranes

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ABSTRACT: A new method for the preparation of polybenzimidazole (PBI)-based membranes, containing high concentrations of immobilized phosphonic acid groups, has been developed. The procedure used is carried out in two steps: (1) Synthesis of modified PBIs, containing 1,2-dihydroxypropyl groups and preparation of films there from; (2) Introduction of vinylphosphonic acid (VPA) and initiator (cerium ammonium nitrate) in the film, subsequent grafting of VPA from the active sites of the PBI backbone. Membranes with different length of the grafted polyvinylphosphonic acid chains were prepared. The molar ratio grafted VPA units per PBI repeating unit reaches 7.8. Proton conductivity was measured at 120°C and relative humidity (RH) 20–100%. For the membrane with highest concentration of phosphonic acid groups the proton conductivity was 35 mS cm⁻¹ at 100% RH and 8 mS cm⁻¹ at 20% RH. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1223–1231, 2013

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INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFC) are considered as promising candidates for mobile and stationary power generation devices. The development of solid polymer electrolytes for such electrochemical devices has involved considerable efforts both from academia and industry.¹ The proton exchange membrane is the most important component of the PEMFC. It has to fulfill harsh requirements such as high proton conductivity, low gas permeability, chemical and mechanical stability, long term operation under severe conditions. Depending on the application (mobile and backup devices, automotive, and stationary power plants) the PEMFC is operated at very different conditions – temperature from subzero to 200°C and humidity in the range 0–100% RH. At low humidity (up to 20% RH) and temperatures up to 100°C proton conductivities up to 5 mS cm⁻¹ are acceptable.² The same membranes, if operated at 100% RH, can reach 100 mS cm⁻¹. Membranes, comprising polybenzimidazole (PBI), doped with phosphoric acid (PA) exhibit proton conductivities up to 200 mS cm⁻¹, but can be operated only over 100°C and are mainly used for stationary applications. For automotive applications the membrane has to retain its performance for more than 5000 h and for stationary power plants—over 20,000 h.^{3,4}

At present, the most widely used proton conductive membranes are based on perfluorinated polyelectrolytes with attached sulfo groups (Nafion, Flemion, HyflonIon, Dow membrane). These materials have high proton conductivity, excellent chemical stability and mechanical strength, and potentially long term durability. The main drawbacks of these materials are high cost and strong dependence of the proton conductivity on water contents in the membrane. Such membranes can function properly only in the highly hydrated state. In order to maintain high water content complex water management is needed and the operation temperature is usually limited to the boiling point of water.⁵ Various polymers, containing sulfonic acid groups have been developed during the last years – sulphonated polyetheretherketones, polyethersulfones, polyimides, etc. Despite of being relatively cheaper than the perfluorinated types, these membranes suffer the same restrictions – low operating temperatures and complex water management.

In Polymer Electrolyte Membrane (PEM) acids can replace water as proton conductors. Polymers, bearing basic groups that can interact ionically with strong or medium strong acids are widely used for practice application. High proton conductivity could be achieved using amphoteric acids like phosphoric and phosphonic acids. Having in mind the proton conductivity

mechanism, phosphoric or phosphonic acids are interesting because they are more amphoteric, having both proton donor (POH) and proton acceptor (PO-) groups. They can form dynamic hydrogen bond networks, in which protons can be readily transferred by hydrogen bond breaking and forming processes, as shown by Kreuer et al.^{6–8} Other important features of phosphoric or phosphonic acids are their excellent thermal stability and low vapor pressure at elevated temperatures.

PBI has been synthesized for the first time by Marvel in the early sixties of the last century as thermostable polymer. All PBIs (m- and p- PBI, ABPBI as well as different modified PBIs, containing alkyl and OH groups) exhibit no proton conductivity, unless groups supplying protons as charge carriers (like SO₃H, PO₃H₂, or strong acids – HCl, H₂SO₄, H₃PO₄) are introduced in the polymer. In this way solid polymer electrolyte is formed.

The most successful material for high temperature PEMFC is based on PBI doped with phosphoric acid (PBI/PA membranes). After being proposed for the first time in 1995, wide range of PA doped PBI membranes have been developed and systematically studied.^{9,10} The basic character of PBI allows doping levels (PA molecules per PBI repeating unit) up to 40, resulting in very high proton conductivity – over 20 mS cm⁻¹ at 190°C.^{11,12} PBI/PA membranes have to be operated at temperatures above 100°C. Under this temperature the water, formed as product of the reaction dilutes the electrolyte. With the drained water PA is slowly removed. The result is a drop in cell performance due to lowered PA contents in the membrane. This problem could be solved by the immobilization of acid groups in the PBI – either by covalent or ionic bonding. Bozkurt et al.¹³ have studied membranes based on poly(2,5-polybenzimidazole) (ABPBI) and polyvinylphosphonic acid (PVPA) blends. In the anhydrous state the proton conductivity of the membranes (mole ratio ABPBI:PVPA from 1: 0.5 to 1: 4) is in the range 10⁻³ mS cm⁻¹ while at 50% relative humidity the membrane with ratio 1: 4 reaches 4 mS cm⁻¹ at 20°C. These results show that even such high concentration of –PO₃H₂ groups (up to 4 per ABPBI unit) is not sufficient for achieving high proton conductivity neither in the hydrated nor in the anhydrous state.

“Grafting trough” approach has been used for the preparation of PBI membranes with very high concentrations of immobilized –PO₃H₂ groups. Polymerization/cross linking was performed in the matrix of a modified PBI, bearing vinylbenzyl substituents.¹⁴ The membranes prepared contain up to 12 vinylphosphonic acid (VPA) units per PBI unit. The proton conductivity (measured at anhydrous conditions, 160°C) depends strongly on the concentration of –PO₃H₂ groups. For the membrane with molar ratio PBI:VPA = 1: 3, proton conductivity is 2 mS cm⁻¹, while for the material with ratio 1: 12 it reaches 28 mS cm⁻¹.

Another example for PBI membrane, containing immobilized VPA groups is the Celtec V® membrane developed by PEMEAS GmbH.¹⁵ VPA was cross-linked in the PBI matrix. The preparation procedure has not been described but having in mind the proton conductivity achieved (100 mS cm⁻¹ at 80°C, measured in water) the –PO₃H₂ contents has to be rather high.

Mechanically strong and flexible polymer electrolyte membranes with very high local concentrations of immobilized proton conduc-

tive –PO₃H₂ were prepared by grafting PVPA side chains onto polysulfones.¹⁶ They showed high proton conductivity up to 5 mS cm⁻¹ under nominally dry conditions at 120°C and up to 9.2 mS m⁻¹ and 100% relative humidity (RH) at the same temperature. The efforts, involved in the preparation of membranes, containing high concentrations of immobilized VPA groups^{14–16} show that the higher contents of such groups leads to higher proton conductivities both in the anhydrous and fully hydrated state of the membrane.

In this study, we report a new synthetic route for the preparation of PBI membranes with grafted polyvinylphosphonic acid (PVPA) chains. Meta-polybenzimidazole (m-PBI) was modified by introducing 1,2-dihydroxypropyl groups by N-alkylation with glycidol. VPA was grafted from the hydroxyalkyl sites using cerium ammonium nitrate (CAN) as initiator. Using this procedure, membranes with high concentrations of immobilized VPA units (up to 7.8 VPA per PBI) were prepared. Characterization has been carried out by gravimetric measurements, ¹H NMR spectroscopy, DSC and thermo gravimetric analysis (TGA). Proton conductivity measurements were performed at 120°C and RH 20–100%.

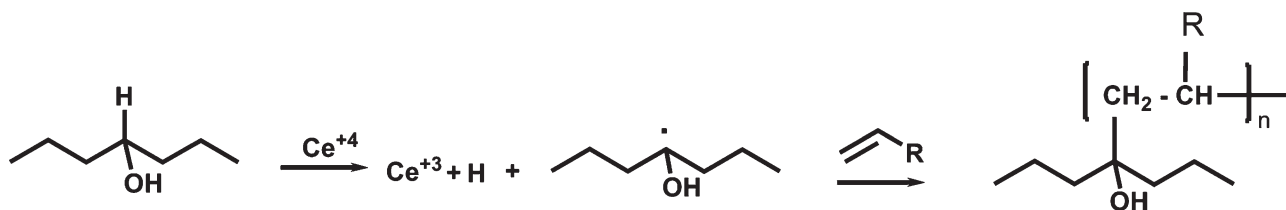
EXPERIMENTAL

Materials

Poly[*m*-phenylene-bis(5,5'-benzimidazole)] (PBI), was supplied by BASF Fuel Cell GmbH as 15 wt % solution in *N,N*-dimethylacetamide (DMAc) (inherent viscosity = 1.26 dL g⁻¹). Glycidol, CAN, and potassium carbonate were purchased from Aldrich. VPA (Clariant, 95%) was supplied by BASF Fuel Cell GmbH.

Methods

The ¹H NMR spectra were recorded in dimethyl sulfoxide (DMSO)-*d*₆ or H₂SO₄-*d*₂ on a Bruker Advance DRX 250 spectrometer using the solvent protons as internal standard. DSC analysis was performed using Perkin Elmer 8500 apparatus. The samples were heated from –40°C to 450°C at a heating rate of 10°C/min in nitrogen (flow rate of 20 mL/min). TGA was performed on Perkin Elmer 4000 apparatus - heating rate of 20°C/min in nitrogen, temperature range 30–420°C. The proton conductivity measurements were carried out with 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*.^{17–19} The design of the four electrode cell is similar to the already applied by Mikhailenko et al. for Nafion at room temperature, RH of 100 and 65%.²⁰ It consists of two pairs stainless steel electrodes. Each pair consists of two short-circuited opposing electrodes with a PEM clamped in between. The membrane is in a concurrent contact with the two electrode pairs. The distance between the two pairs was fixed before the measurements. The thin electrodes (1 mm) ensure that almost the entire surface of the PEM is in contact with the conditioned air required for fast and reliable humidity exchange. Thus, notwithstanding the four electrodes used, the proton conductivity is measured by two probe method in longitudinal direction. The *EasyTest Cell* gas chamber, filled with environmental air, was used for conditioning and controlling the temperature and the RH. The spectra were taken at zero DC



Scheme 1. Grafting of vinyl monomers on polymers containing $-CHOH$ groups, initiated by Ce^{+4} .

current and AC amplitude of 100 mV. The method applied is an AC alternative to the already presented for dc proton conductivity measurements in the *EasyTest Cell*.¹⁹

Synthesis of Poly(benzimidazoles) Containing $-CH_2CH(OH)CH_2OH$ Groups (modified PBIs)

In a three neck flask, equipped with a reflux condenser and inert gas inlet 100.0 g 15 wt % solution of PBI in DMAc (containing 15.0 g PBI, 0.0487 mol) was heated at 90°C and stirred for 2 h (magnetic stirrer). According to the desired degree of modification (DM) potassium carbonate K_2CO_3 (0.7–1.4 g, 0.007–0.014 mol) and 15 mL DMAc were added. The reaction mixture was stirred at 90°C for at least 12 h until the carbonate is fully dissolved. Glycidol (0.78–3.12 g, 0.01–0.042 mol), dissolved in 15 mL DMAc was added drop wise for 1 h and the reaction mixture was stirred at 90°C for another 12 h. After cooling down and precipitation in a mixture $H_2O:CH_3OH/2:1$, the product was filtered of, washed abundantly with hot water and dried at 100°C to constant weight.

The DM was calculated from 1H NMR data (ratio of the relative intensities of the aliphatic protons from the 1,2-dihydroxypropyl group and aromatic protons from PBI).

Preparation of Thin Films from Modified PBIs

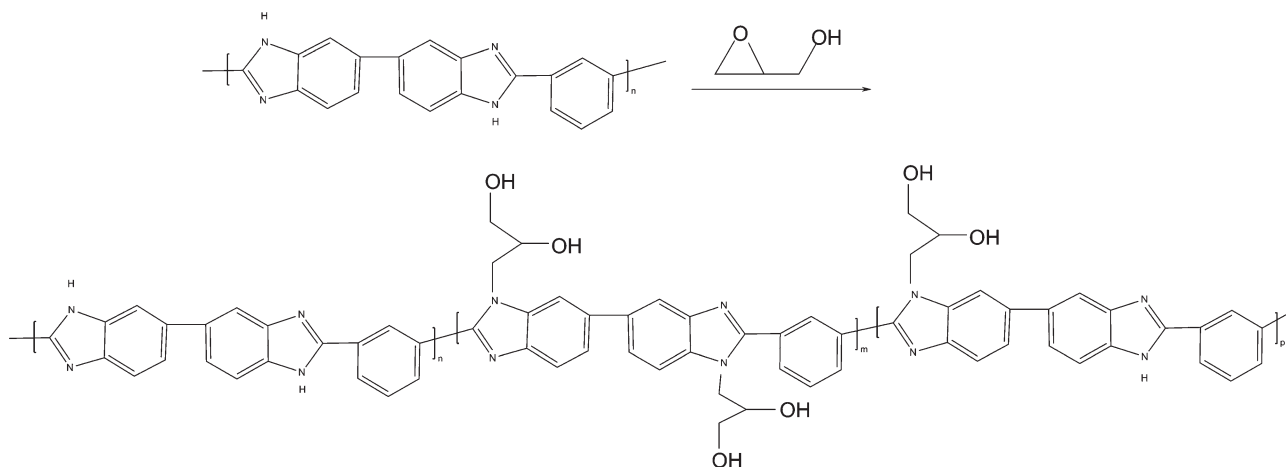
For casting films, 10 wt % solutions of the modified PBIs were prepared. Films were cast on a glass plate, using a doctor blade (gap 0.6 mm). The solvent DMAc was partially removed from the wet, non-self-supporting film by gentle heating (40–50°C) in air. Before being fully dry, the film was removed from the substrate and washed abundantly with hot water for removing the

rest of the solvent. After drying at 100°C for 24 h, smooth, homogeneous, flexible film (thickness 50–80 μm) were obtained.

Preparation of Membranes, Comprising Modified PBIs with Grafted PVPA Chains
Introduction of VPhA and Initiator CAN in Modified PBIs Films. The procedure is carried out in two steps:

Preparation of swollen membranes, containing VPA. Before starting, the membranes from modified PBIs were kept in water for at least 24 h. In this way they absorb about 20 to 32% water (PBIs with higher DM retain more water). This is very favorable for the further swelling in VPA. In a closed vessel a wet film of modified PBI, was immersed in a bath, containing 85 wt % VPA and 15 wt % water. The vessel was transferred into a furnace preheated at 60°C and kept at this temperature for 4 h. In order to achieve even swelling of the film, the vessel was taken out several times and gently shaken. After cooling down to room temperature (RT), the film was taken out and measured. Usually the dimensions increased up to 100% and weight uptake (according to the weight of the PBI in the starting film) was in the range 500–700%. PBIs with higher DM showed higher degree of swelling.

Introduction of initiator (CAN) into the swollen film. The swollen film, obtained in step (a) was transferred to a closed vessel containing 80 wt % VPA, 10 wt % CAN and 10 wt % water. The vessel was kept in the dark for 6 h at RT in order to exchange VPA from the membrane with VPA containing CAN. The weight of the resulting membranes was about 10% lower than that of starting ones.



Scheme 2. Modification of m-PBI with glycidol.

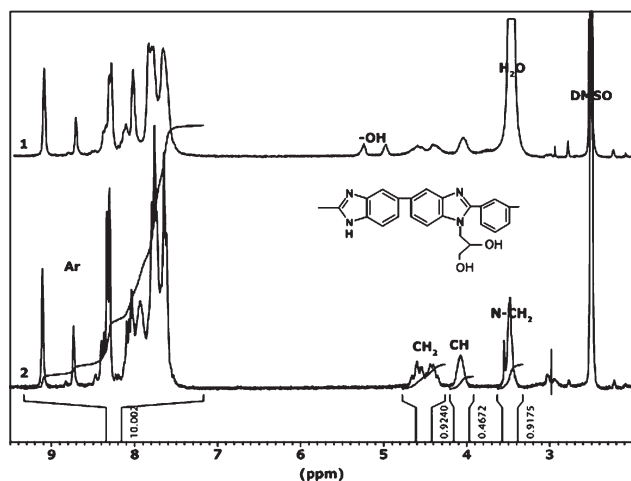


Figure 1. ^1H NMR spectra (DMSO- d_6) of modified PBI M4 (DM = 23%): 1–RT, 2–after D_2O exchange.

Grafting of VPA from Modified PBIs

Grafting of VPA from the modified PBI was carried out thermally. The swollen membrane, prepared in step (b) (containing VPA, CAN, and water) was placed on a silicon foil in a closed Petri dish. It was transferred into a preheated furnace (70°C) and kept there for 12 h. The membranes obtained were rather stiff, but after absorbing about 10% atmosphere moisture they become flexible. Prior to characterization the membranes were thoroughly washed with hot water and dried to constant weight. The amount of polyvinylphosphonic acid (PVPA) grafted onto the PBI backbone was determined gravimetrically (weight ratio PBI/grafted PVPA was calculated from the weight uptake) and from ^1H NMR data.

RESULTS AND DISCUSSION

The grafting of vinyl monomers from polymers, containing hydroxyalkyl groups, is a well known procedure for polymer preparation. Radicals can be selectively generated on polymers like cellulose, starch, polyvinyl alcohol etc., by oxidation with transition metal ions - Co^{3+} , Ce^{4+} , Mn^{3+} , V^{5+} , and Fe^{3+} .^{21–23} In this study we used CAN ($(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, CAN) as initiator (Scheme 1).

Radical polymerization (grafting from) can be started from these active sites. In this way a polymer with side chains,

Table I. Preparation of Macroinitiators (PBIs containing 1,2-dihydroxypropyl groups)

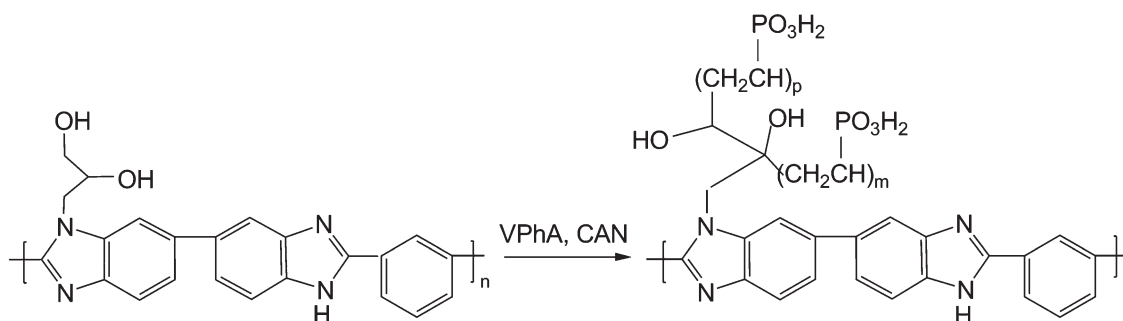
Sample	Mole GI/PBI	Theoretical DM	Determined DM	1,2-Dihydroxypropyl groups/PBI
M1	0.1	10	9.2	0.18
M2	0.12	10	9.7	0.19
M3	0.20	20	18.7	0.34
M4	0.24	24	23.0	0.46
M5	0.40	40	34.5	0.69
M6	0.44	44	39.3	0.79

attached to the polymer backbone can be obtained. The main advantage of this method is that the reaction proceeds smoothly at acidic condition in the presence of water and the amount of non grafted homopolymer formed is relatively low. As already mentioned, PBI, containing high concentrations of immobilized phosphonic acid groups^{14,15} and polysulfones with grafted polyvinylphosphonic acid chains¹⁶ can be regarded as promising materials for membranes in PEMFCs.

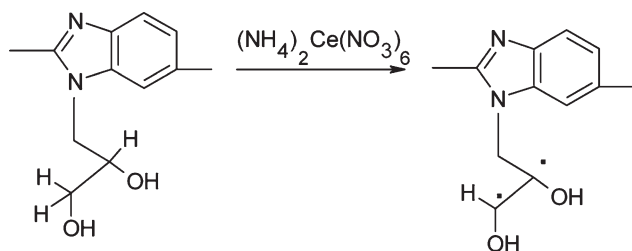
The objective of this study was to prepare modified PBIs, containing 1,2-dihydroxypropyl groups (macroinitiators) and in a second step to perform polymerization of VPA, starting from the macroinitiator active sites. The expected result was a hairy rod polymer, containing high concentrations of immobilized $-\text{PO}_3\text{H}_2$ groups. This approach offers vast synthetic possibilities. Macroinitiators, containing different amounts of attached 1,2-dihydroxypropyl groups can be prepared. Polymerization of VPA from these active sites should result in PBI-graft PVPA polymers with different distribution and length of the grafted PVPA chains.

Synthesis of Macroinitiators—Modified PBIs, Containing 1,2-dihydroxypropyl Groups

Celasole® (15 wt % solution of m-PBI in dimethyl acetamide (DMAc)) was used as starting material. Glycidol (GI) was chosen as modifying agent and K_2CO_3 as catalyst. *N*-alkylation of PBI was performed by stirring a DMAc solution of the reagents for 12 h at 90°C (Scheme 2). Using this procedure PBIs with different DM were prepared. The DM represents the number of substituents (1,2-dihydroxypropyl groups) per PBI unit. For example: two substituents on each PBI unit correspond to DM = 100%, one substituent on each PBI unit correspond to DM



Scheme 3. Grafting VPA from PBIs, containing 1,2-dihydroxypropyl groups.



Scheme 4. Formation of active sites on PBI containing 1,2-dihydroxypropyl group.

= 50%. DM was determined from ^1H NMR data. The ^1H NMR spectrum of such material.

In the ^1H NMR spectrum of the starting m-PBI, the aromatic protons appear as a multiplet at 7.5–9.5 ppm. In the modified PBI, the new picks in range 3.3–5.5 ppm show the presence of 1,2-dihydroxypropyl groups. The signals of the two $-\text{OH}$ protons (4.9–5.5 ppm at RT) disappear after deuterium exchange and all aliphatic protons become clearly visible (as shown in Figure 1). DM can be easily calculated from the ratio of the integral intensities (aromatic/aliphatic protons). Varying the concentration of glycidol in the reaction mixture, modified PBIs with different DM were prepared (Table I).

From Table I it can be seen that the achieved DMs are rather close to the theoretical ones. After precipitation of the reaction mixture in water and filtering off the modified PBI, the precipitate was washed abundantly with hot water and dried. Smooth, flexible, homogeneous films were prepared from 10 wt % solutions in DMAc.

Grafting of Polyvinylphosphonic Acid on Modified PBIs — Preparation of Membranes

Several years ago, we confirmed the feasibility of our approach—we successfully prepared PBIs with grafted polyvinylphosphonic acid chains, starting from modified PBIs, containing 1,2-dihydroxypropyl groups²⁴ (Scheme 3).

In our initial experiments, the reaction was carried out in solution. Modified PBI and initiator CAN were dissolved in VPA

and the reaction mixture was heated and stirred for several hours. After isolation, the products obtained were characterized by ^1H NMR spectroscopy. The desired chemical structure was confirmed but the products were almost totally insoluble (the only solvent found was deuterated sulfuric acid). No membranes could be prepared from these materials.

Later on considerable advance was achieved, when the grafting was performed in a film. Modified PBI and CAN were dissolved in VPA and a thin film was cast on a glass plate, using a doctor blade with defined gap (0.2–0.8 mm). The film was heated in an oven at temperatures above 50°C. In this way membranes of relatively good quality were prepared. The main difficulty of this method was the preparation of the reaction solution, especially the introduction of the initiator CAN. Another drawback was the considerable waste of VPA. Although materials with weight ratios PBI/Graft PVPA up to 1: 1.8 were prepared, only a small part of the VPA from the solution (less than 20%) had polymerized from the PBI active sites. In this study, we report an improved procedure for the preparation of membranes, comprising modified PBI with high concentration of immobilized VPA groups (up to 16) in the grafted PVPA chains (PBI-graft-PVPA membranes).

The new procedure includes three steps:

Preparation of Swollen Films. The first experiment was performed with 95% VPA. The film of modified PBI was kept immersed in the acid (closed vessel) for a defined time at temperatures up to 90°C. The swelling was too fast and uneven, the films became too soft and difficult to handle. The most suitable conditions found were a bath of VPA, containing 15% water, swelling times 3–4 h at 70–90°C (depending on DM). Upon swelling the starting film increases its dimensions up to 100% and its weight goes up to 600–700 wt %. At swelling times higher than 4 h, the weight uptake can exceed 1000% but the films are too soft to be handled.

Introduction of Initiator CAN. In the second step, the VPA from the swollen membranes was exchanged with VPA, containing CAN. It is important to mention that the water (10%) in the second bath is essential for the following grafting reaction.

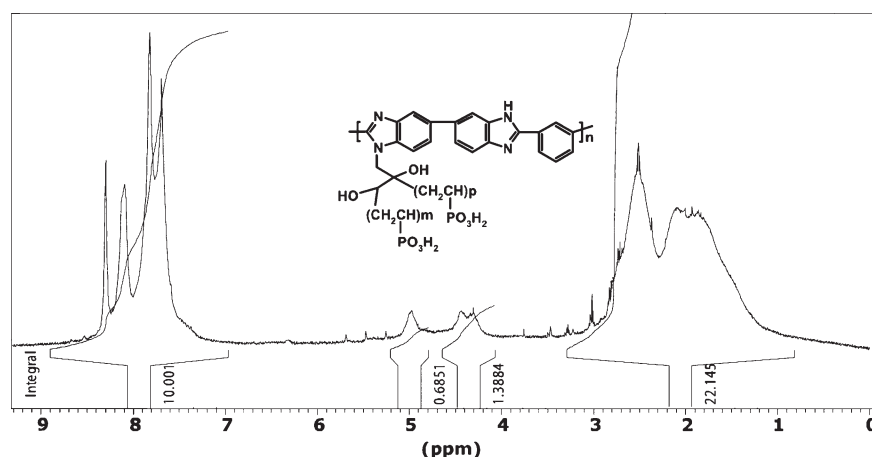


Figure 2. ^1H NMR spectrum ($\text{H}_2\text{SO}_4\text{-d}_2$, RT) of M5Gr (DM = 34.5%).

Table II. Characterization of PBI-Graft-PVPA Membranes (MGr)

Sample	Starting membrane	1,2-Propandioyl groups per PBI in the starting membrane	Weight ratio PBI/graftPVPA	Number of VPA units per PBI	Number of VPA units per substituent	Average length of the grafted chain
M1Gr	M1	0.18	1.92	5.7	29.4	14.7
M2Gr	M2	0.19	2.10	6.2	32.2	16.1
M3Gr	M3	0.34	1.82	5.7	15.2	7.6
M5Gr	M5	0.69	2.17	7.1	10.4	5.2
M6Gr	M6	0.79	2.31	7.8	9.4	4.7

The exchange was performed at RT. The bath can be used many times if kept in the dark.

Grafting PVPA from the Modified PBI. In the presence of Ce^{4+} ions and water radicals are formed on the 1,2-dihydroxypropyl sites of the modified PBI (Scheme 4)

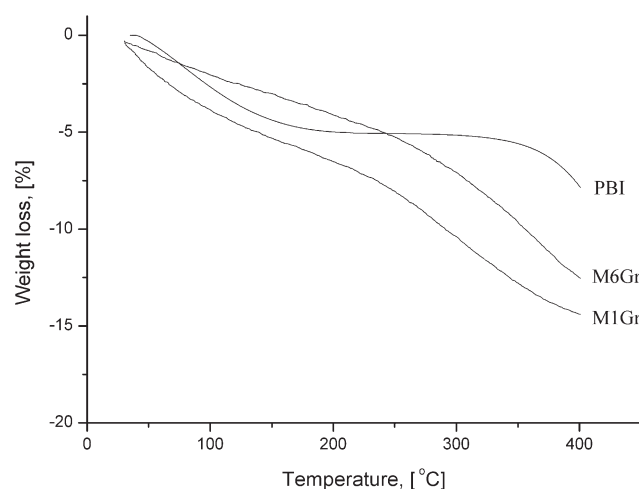
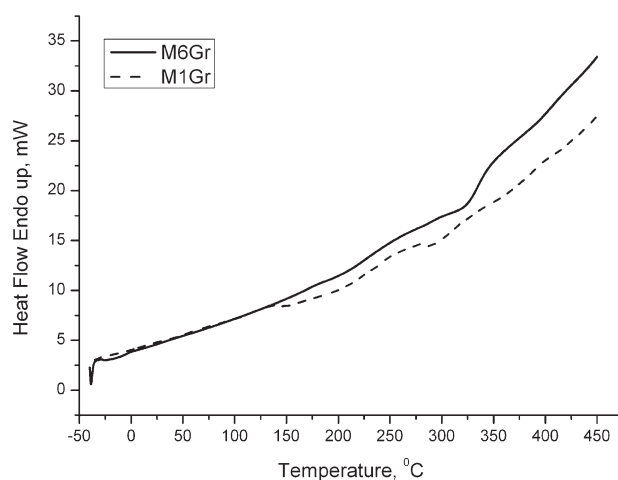
Polymerization can be started there from these active sites. In our case, the reaction was carried out in the PBI membrane, already containing VPA, CAN, and water. Grafting proceeds thermally at temperatures above 50°C. The resulting membranes, containing modified PBI with grafted PVPA onto it and some PVPA, were smooth and homogeneous but rather stiff. After absorbing about 10% atmosphere moisture they became flexible. Thickness of the final membranes was in the range 150–250 μm . Applying this procedure, a series of grafted membranes (denoted MGr) were prepared

Characterization of the Membranes

Characterization of PBI-graft-PVPA membranes was carried out after abundant washing with hot water (removing impurities and homopolymer PVPA). The chemical composition of the membranes was determined from 1H NMR data and gravimetric measurements. Figure 2 shows the 1H NMR spectrum of a PBI-graft-PVPA material.

The signals of the 1,2- dihydroxypropyl groups from the modified PBI do not overlap with the signals, originating from the

grafted PVPA chains (0.8–3.2 ppm). This makes the calculation of VPA units per PBI unit and the average length of the grafted PVPA chains possible. As result of the grafting reaction, the vicinity of the $-OH$ groups has been changed (two protons removed). The signal of the single proton from the $>CHOH$ group (1H) appears at 5.0 ppm. The other signal (doublet at 4.2–4.6 ppm, 2H) could be attributed to the protons of the $-NCH_2-$ group. This result proves that polymerization has started from all active sites (1,2- propandioyl groups). The number of VPA groups in the grafted PVPA chains can be calculated from the integral intensity of the $-CHCH_2-$ groups in the region 0.8–3.2 ppm—21.14 protons correspond to 7.36 VPA units per PBI. The starting M5 membrane bears 0.69 1,2- dihydroxypropyl group per repeating PBI unit. The grafted membrane M5Gr contains 7.3 VPA per PBI. Thus the number of VPA groups per substituent is 10.7 and the average length of the grafted chain – 5.3. Similar data have been obtained from gravimetric measurements. From the weight uptake, due to the grafted PVPA chains, the weight ratio PBI/grafted PVPA was determined. From this value, the number of VPA groups per PBI unit and per substituent were calculated, as well as the average length of the grafted chain. For all samples, the parameters calculated from gravimetric measurements, were just a bit lower than the values obtained by 1H NMR data. The parameters of the grafted membranes prepared (calculated from gravimetric data) are presented in Table II. The data from Table II show that the grafting from the active sites in the modified membranes has

**Figure 3.** TGA curves of M1Gr and M6Gr membranes.**Figure 4.** DSC curves of M1Gr and M6Gr membranes.

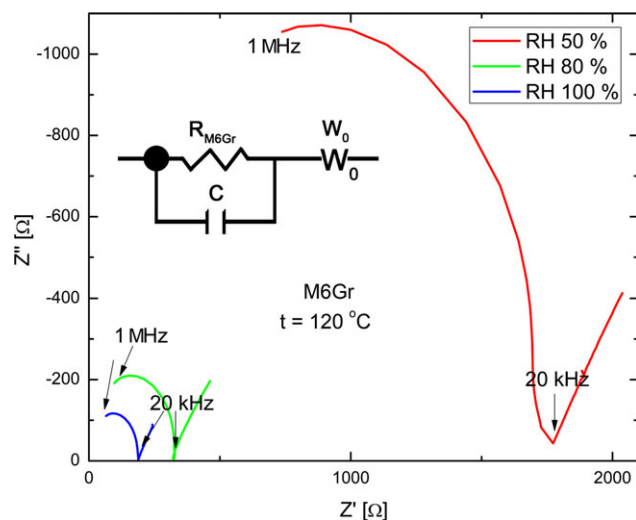


Figure 5. Impedance spectra of M6Gr. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resulted in materials, containing 5.72 to 7.8 VPA units per PBI repeating unit. The concentration of 1,2-dihydroxypropyl groups per PBI in the starting membrane determines the length of the grafted chains. For MGr2 (prepared from M1, one substituent for 5 PBI units) the grafted chains have 16 VPA units, while for M6Gr (prepared from M6, 0.8 substituent on each PBI unit) the chains are much shorter – less than 5 VPA units.

Thermal Stability

The thermal gravimetric analysis of two PBI-graft-PVPA membranes (M1Gr with 5.7 VPA groups per PBI and M6Gr with 7.8 VPA groups per PBI) is presented in Figure 3. Up to 200°C the weight loss is less than 5%, and about 13% at 400°C. The TGA

Table III. Proton Conductivities of PBI-Graft-PVPA Membranes, Measured at 120°C and Different RH

Sample	VPA units per PBI	Proton conductivity, mS cm ⁻¹			
		RH 100%	RH 80%	RH 50%	RH 20%
M1Gr	5.7	9.7	2.1	1.5	0.5
M3Gr	5.7	8.3	5.1	1.1	0.5
M2Gr	6.2	15.1	6.8	2.6	0.6
M6Gr	7.8	35.0	20.1	4.2	0.8

curve for M1Gr (Figure 3) shows two regions of weight loss. The first one starts at 75°C and at 150°C the weight loss reaches about of 6% (most probably loss of water). Above 150°C, the polymer remains stable up to 250°C with total weight loss of 8%. In the range 250–400°C the weight loss is faster and reaches 13%. TGA curve of M6Gr shows only one regions of weight loss starting at 250°C with about 6% weight loss. The total weight loss at 400°C is 12%.

Differential scanning calorimetry (DSC) measurements were carried out in order to determine the glass transition temperature of the two selected samples (M1Gr and M6Gr). The thermograms are presented in Figure 4. With decreasing the average length of the grafted chains from 14.7 (M1Gr) to 4.7 (M6Gr) lowered T_g has been observed at -4.5°C. This membrane exhibits a T_g below room temperature and in this case increase of the conductivity can be attributed to the higher mobility of the propyl spacer with attached shorter PVPA chains on PBI backbone. The decrease in T_g for M6Gr could also be correlated to elimination of the hydrogen bonds. A similar effect was observed by Sukumar et al.¹⁴

Table IV. Proton Conductivities of Different Solid Polymer Electrolytes, Containing Vinyl Phosphonic Acid Groups

No	Polymer	Proton conductivity (mS/cm ⁻¹)	Temperature (°C)	Relative humidity (%)	Reference
1	Polystyrene-Poly(vinylphosphonic acid) block Copolymers	30	25	98	[25]
2	Poly[(CTFE- <i>alt</i> -IEVE)- <i>co</i> -(CTFE-EVE)] ^a	20	25	95	[26]
3	Poly(N-phenylacrylamide), phosphonated	19	80	50	[27]
4	Poly(vinylpyrrolidone- <i>co</i> -vinylphosphonic acid) copolymers	0.1	100	100	[28]
5	Chitosan/poly(vinyl phosphonic acid) complex	30	120	100	[29]
6	PEEK/PVBPA BAB block copolymer ^b	7.5	160	50	[30]
7	Poly(arylene ether sulfone), phosphonated	12	100	100	[31]

^awhere CTFE, IEVE, and EVE stand for chlorotrifluoroethylene, 2-iodoethyl vinyl ether, and ethyl vinyl ether. ^bwhere PEEK and PVBPA stand for poly(ether ether ketone), poly(vinylbenzylphosphonic acid).

Proton Conductivity Measurements

The *EasyTest Cell* technique^{17–19} was used for measuring the proton conductivity. The impedance spectrum for M6Gr obtained at 120°C and different RH (Figure 5) consists of semicircle in the high frequency range (due to the bulk resistance of the membrane in parallel with the capacitance of the cell) represented by the capacitor in the model and a straight line with angle close to 45° (due to diffusion of the protons) represented by the open Warburg element.

For proton conductivity estimation, there is even no need to analyze the whole spectrum but simply to register the low frequency end of the semicircle. The resistance obtained can be converted to specific conductivity (σ) of the membrane by the following equation:

$$\sigma = \frac{D}{RTL},$$

where D , distance between the electrode pairs; R , resistance; T , membrane thickness; and L , length of the contact electrode/membrane. The calculated specific proton conductivities of PBI-graft-PVPA membranes are presented in Table III. As it could be expected, in the whole testing range of humidity the number of VPA units per PBI is a determining factor for the proton conductivities of the prepared membranes. The data from the proton conductivity measurements shows two trends. The proton conductivity strongly depends on the concentration of $-\text{PO}_3\text{H}_2$ groups and on RH. Higher amount of immobilized VPA group results in higher conductivity. Lowering the RH from 100% to 20% leads to drastic decrease of proton conductivity. From the data obtained, no dependence between length of the grafted PVPA chain and proton conductivity can be derived.

The proton conductivities of the described new PBIs with grafted polyvinyl phosphonic chains are close or better than the conductivities of other solid polymer electrolytes containing of considerable amount of $-\text{PO}_3\text{H}_2$ groups (Table IV).

The new method developed gives vast opportunities for preparation of grafted membranes with different chemical composition. A lot of parameters can be easily varied – type and denseness of the active sites on the modified PBI backbone, amount of the introduced VPA groups, length of the grafted chains. A more detailed study of such materials is under way.

CONCLUSIONS

An original procedure for the preparation of PBI membranes, containing grafted PVPA chains has been developed. The process involves several steps: preparation of modified PBIs containing 1,2-dihydroxypropyl groups (macroinitiators), preparation of thin films there from, introducing VPA and initiator (CAN) in the films, grafting of VPA from the active sites of the PBI backbone. Membranes of very good quality with high concentrations of immobilized VPA groups (up to 7.8 VPA groups per PBI) have been prepared. The proton conductivity of such membranes reaches 35 mS cm^{-1} in the fully hydrated state.

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