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Polysulfones Grafted with Poly(vinylphosphonic acid) for Highly Proton Conducting Fuel Cell Membranes in the Hydrated and Nominally Dry State

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ABSTRACT: Mechanically strong and flexible membranes with very high local concentrations of immobilized proton-conducting phosphonic acid have been achieved by grafting poly(vinylphosphonic acid) side chains onto polysulfones. The graft copolymers were prepared by anionic polymerization of diethyl vinylphosphonate initiated from lithiated polysulfones, followed by quantitative cleavage of the ester functions. The resulting phosphonic acid units acted like monoprotic acids to indicate a high level of intramolecular interactions, and the phase-separated nature of the copolymers was shown by dual glass transitions. Fully polymeric membranes were conveniently cast from solution and showed high proton conductivities, e.g., 5 mS/cm under nominally dry conditions at 120 °C and up to 93 mS/cm under 100% relative humidity at the same temperature. The corresponding conductivities measured for Nafion 115 under the same conditions were 0.04 and 105 mS/cm, respectively. The former membranes furthermore showed high thermal stability with decomposition temperatures exceeding 300 °C under air. Additions of 2−5 wt % of a perfluorosulfonic acid polymer to the phosphonated membranes were found to reduce the water uptake significantly, thus improving the mechanical properties. The conductivity of these fully polymeric doped membranes was generally observed to be enhanced, or at least to remain at the same level, under both humidified and nominally dry conditions. The findings of this study demonstrate that phosphonated membranes with a proper macromolecular design may potentially show some important advantages in relation to the more commonly studied sulfonated membranes in fuel cell applications.

Introduction

A wide range of different polymer electrolyte membrane fuel cells (PEMFCs) are currently developed as future power sources for automotive, stationary, and portable applications. One of the key challenges in advancing the PEMFC technology lies presently in the development of new durable membranes that allow operation in a broad temperature window, typically from subzero degrees up to ∼120 °C, at low humidification with water vapor partial pressures below 0.5 bar or with no humidification at all.[1] The background is the pressing need to reduce the complexity and the cost and to increase the efficiency of systems for especially automotive applications.[1,2]

The basic functions of a PEMFC membrane are to separate the electrodes and the reactant gases and to efficiently conduct protons from the anode to the cathode within a wide range of operation conditions and without loss of performance over time. The proton conducting membranes employed in PEMFCs are today typically based on polymers with hydrated sulfonic acid units. For example, the current state-of-the-art membranes, e.g. Nafion, are based on perfluorosulfonic acid polymers. When hydrated, these membranes characteristically form a percolating network of water-containing nanopores embedded in a hydrophobic polymer-rich phase domain.[3,4] The acid units of the polymer function as the proton source and are dissociated by the water which acts as the proton solvent and thus facilitates the proton transport in the nanopores. Hence, membranes based on sulfonated polymers rely critically on water for the proton conduction. The conductivity of these membranes consequently suffers quite dramatically at temperatures above 90 °C due to the loss of water. Various efforts to substitute the water with less volatile proton conducting compounds have been made, and membranes based on polybenzimidazole (PBI) doped with phosphoric acid have perhaps been most extensively studied in this respect.[5,6] In these membranes the phosphoric acid acts as both proton source and solvent. At low humidity the membranes typically show high conductivities at temperatures approaching 200 °C as long as they are highly swollen (above ∼90%) with phosphoric acid. However, as the temperature is decreased, the water uptake of the membranes increases and the acid is leached out from the membranes, causing problems.

Loss of proton conducting species from the membranes may be prevented if intrinsically proton conducting compounds, acting both as the proton source and solvent, are immobilized by covalent bonds to the membrane polymers.[7] These compounds must be amphoteric to function as both proton donor and acceptor in order to enable self-dissociation to form a high concentration of intrinsic charge carriers. Furthermore, the compounds must form dynamic hydrogen-bonded networks to enable efficient intrinsic structure diffusion.[7] Amphoteric compounds that have been tethered to polymeric structures and studied as proton conductors currently include phosphonic acid[8,9] and heterocycles such as imidazole,[10–13] benzimidazole,[11,13–17] and triazole.[13,18] Work by Kreuer et al.[10–12] and others[13–18] has shown that the local mobility of the heterocycles have to be retained after the immobilization in order to facilitate structure diffusion to attain high conductivities. This is typically achieved by keeping the glass transition temperatures (T_gs) low and by attaching the heterocycles to the polymers via flexible side chains or "spacer" units. Recent work has shown that this strategy fails when it comes to polymers tethered with phosphonic acid.[19] The results have instead indicated that very high local concentrations of phosphonic acid, forming large hydrogen-bonded aggregates, are needed in order to reach high proton conductivities.[19] Consequently, different synthetic immobilization strategies have to be developed and evaluated to minimize local dilution effects and aggregation constraints of the acid units.[9,20]

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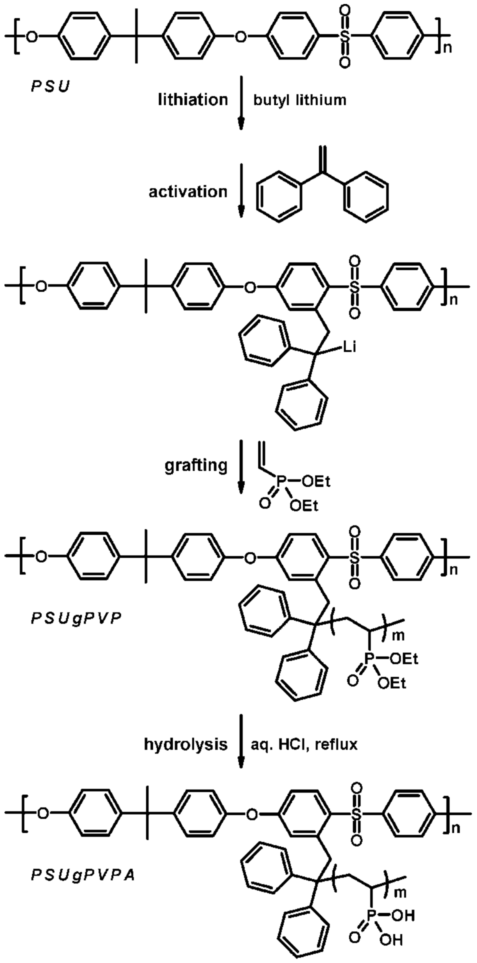
The present work is aimed at achieving multifunctional membranes with phase-separated morphologies to combine high proton conductivity under both wet and dry conditions, high thermal stability, restricted water uptake, and good mechanical properties. Poly(vinylphosphonic acid) (PVPA) was chosen as the phosphonated component in these membranes because of its extremely high concentration of phosphonic acid directly attached to a flexible polymer main chain. Neat linear PVPA has poor film forming properties and the high acid concentration also makes it water-soluble. The water uptake characteristics and proton conductivity of this polymer have recently been reported.[21] Moreover, PBI membranes containing interpenetrating cross-linked PVPA networks are currently developed by BASF fuel cells and have very recently been evaluated as membranes for direct methanol fuel cells.[22]

Synthetic pathways to phosphonated polymers have recently been extensively reviewed[20] and can be divided into phosphonations of premade polymers[23–29] and polymerizations using phosphonated monomers.[30–34] However, only very few phosphonated polymers have been specifically designed for membranes with proton conduction under nominally dry conditions.[8,9] PVPA has most commonly been prepared by radical polymerizations of vinylphosphonates in the acid or ester form.[35–43] Only in a few cases has PVPA been prepared by anionic polymerizations of vinylphosphonates in the ester form.[44–47] For example, PVPA may be prepared by anionic polymerization of diethyl vinylphosphonate under classical conditions in tetrahydrofuran initiated by butyllithium at −78 °C,[47] followed by hydrolysis of the ester groups. In the present case, well-defined graft copolymers were prepared by anionic polymerizations of diethyl vinylphosphonate initiated from lithiated polysulfones (PSUs). Hydrolysis of the ester groups produced soluble graft copolymers with different contents of PVPA. Thus, graft copolymers with well-separated PVPA side chains along stiff and hydrophobic PSU main chains were prepared. After structural characterization of the copolymers, membranes were cast from solution and evaluated with respect to, e.g., thermal stability, water uptake, and proton conductivity under both humidified and nominally dry conditions. In addition, phosphonated membranes were doped with small amounts of a perfluorosulfonic acid polymer in order to reduce the water uptake under immersed conditions and to further improve membrane properties.

Experimental Section

Materials. PSU (Udel P-1700, Solvay Advanced Polymers, 28 kg/mol) was dried overnight in a vacuum oven at 60 °C prior to use. Tetrahydrofuran (THF; Merck, p.a.; >99.8%) was dried over 5 wt % molecular sieves (Acros; 4 Å, 8−12 mesh). The latter were activated at 250 °C for 48 h in a circulating air oven and subsequently cooled to room temperature under vacuum. The residual water content after this procedure has been reported to be less than 28 ppm.[48] Dimethyl sulfoxide (DMSO; Merck; 99%), *n*-hexane (Prolabo; 96%), 2-propanol (Prolabo; >98%), 1,1-diphenylethylene (DPE; Aldrich; 99%), *n*-hexylphosphonic acid (Alfa Aeser), and diethyl vinylphosphonate (DEVP; Fluka; ≥97%) were used as received. A solution of *n*-butyllithium (*n*-BuLi; Acros; 2.5 M) in hexanes was titrated before use by employing the method of Burchat et al.[49] The concentration of *n*-BuLi was thus determined to be 2.2 mol/L. Potentiometric acid−base titrations were carried out using a standard sodium hydroxide solution (Merck Titrisol; [NaOH] = 0.1 mol/L). Doped membranes were prepared using a solution of Nafion 117 (N11; Fluka; ∼5% in a mixture of lower aliphatic alcohols and water). A Nafion 115 (N115) membrane was pretreated to improve the high-temperature stability[50] and was then used as a reference material in the conductivity measurements.

Scheme 1. Synthetic Pathway for Grafting PVPA Side Chains from Polyfunctional PSU Macroinitiators by Anionic Polymerization of DEVP Followed by Cleavage of the Ester Functions



Grafting PVPA from PSU. The grafting reactions were carried out according to Scheme 1 by first allowing DPE to react with lithiated PSU. The nucleophilic 1,1-diphenylalkyl anion formed in the addition reaction was then utilized for the initiation of anionic polymerization of DEVP. The concentrations of the reactants used in the syntheses are given in Table 1.

Here, the preparation of graft copolymer PSUgPVPA8 will serve as a typical example. This sample was prepared by first dissolving 1.0 g (2.26 mmol) of PSU in 200 mL of anhydrous THF in a round-bottom glass reactor fitted with a gas inlet and outlet, a thermometer, and a septum. The solution was cooled to −70 °C and degassed several times. Next, 0.9 mL (2.26 mmol) of *n*-BuLi was added dropwise to form a yellow-orange solution of lithiated PSU. After 1 h, a volume of 40 μL (0.22 mmol) of DPE was added. After leaving the reaction for 30 min, 1.75 mL (11 mmol) of DEVP was added all at once by syringe, and the polymerization was left to proceed for 5 h at −70 °C. At the addition of the monomer the solution turned opaque and violet, and the viscosity increased markedly. The reaction was stopped by the addition of ∼1 mL of 2-propanol to the mixture, where after the solution gradually became clear and orange. The grafted copolymer was then precipitated in 800 mL of hexane. Next, the white precipitate was filtered off, dried, and washed several times with distilled water. Finally, the copolymer was dried under vacuum for 24 h at 60 °C. The copolymer in the ester form, denoted PSUgPVP8, was readily converted into the acid form (PSUgPVPA8) in aqueous hydrochloric acid. In a typical reaction, 2 g of PSU-PVP8 was placed in 50 mL of fuming hydrochloric acid. After 8 h of reflux, the copolymer was filtered off and carefully washed with water. The copolymer was finally dried under vacuum for 48 h at 60 °C.

Copolymer Characterization. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker 400 MHz spectrometer using deuterated

Table 1. Preparation and Characterization Data of the Graft Copolymers

copolymer	ratios of the reactants [DPE]:[DEVP]:[PSU][a] (mmol/L:mmol/L:mmol/L)	*DS*	DEVP monomer yield (%)	theoretical IEC (mequiv/g)	PVPA content (wt %)	$\bar{M}_n$ graft copolymer (g/mol)	$\bar{M}_n$ side chain (g/mol)
PSUgPVPA5	9.00:58.0:22.6	0.4	82	3.0	33	40 000	500
PSUgPVPA6	4.52:115:22.6	0.2	71	4.3	47	52 000	2000
PSUgPVPA7	2.26:58.0:22.6	0.1	74	2.9	32	40 000	2000
PSUgPVPA8	1.13:58.0:11.3	0.1	77	4.4	47	52 000	4000
PSUgPVPA9	0.753:58.0:7.53	0.1	70	5.3	57	62 000	5800

[a] [PSU] expressed as the concentration of repeating units.

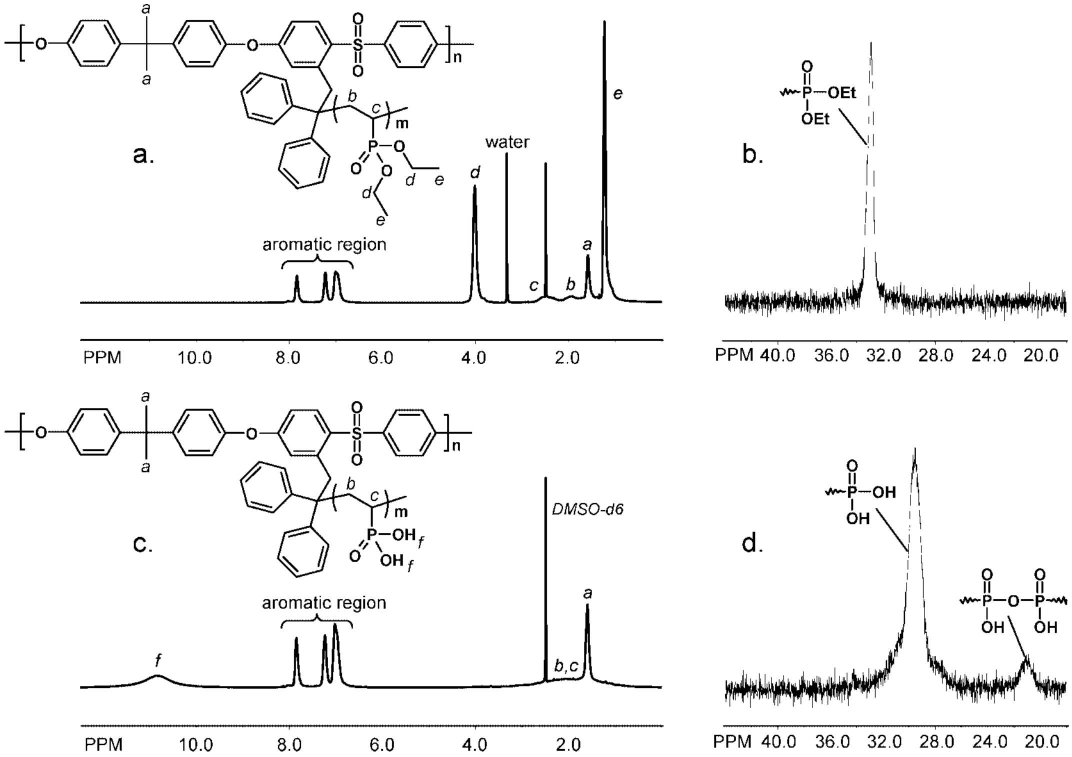


Figure 1. ^{1}H NMR (left) and ^{31}P NMR (right) spectra of a PSU carrying phosphonated side chains in the ester form (a, b) and in the acid form (c, d), respectively. Data were collected using DMSO-d_6 solutions of PSUgPVP8 and PSUgPVPA8, respectively.

dimethyl sulfoxide (DMSO-d_6) solutions of all the graft copolymers. Representative spectra are shown in Figure 1. The ratio between the integrated peak of the CH_2 protons of the phosphonic ester at $\delta = 4.1$ ppm and the integrated peaks of the aromatic protons of the main chain between $\delta = 6.8-8.1$ ppm was used in the calculations of the PVPA content and the theoretical ion exchange capacity (*IEC*) of the hydrolyzed copolymers (Table 1). The present copolymers showed a pronounced polyelectrolyte effect, and the phosphonic acid units acted as monoprotic acids in the potentiometric titrations described below. Thus, in the calculation of the theoretical *IEC*, defined as the number of mequiv per g protonated membrane, only one of the two protons of the phosphonic acid group was considered.

The degree of substitution (*DS*), i.e. the average number of side chains per repeating unit of PSU, was calculated from the molar ratio between the DPE and the PSU units used in the reactions (Table 1). These calculations were based on the assumptions that the reaction of DPE with the lithiated PSUs was quantitative and that all the 1,1-diphenylalkyl anions formed in the process, and only these, initiated the polymerization of DEVP. In strong support of these assumptions it can mentioned that for the copolymers with $DS = 0.2-0.4$ it was possible to more precisely calculate the *DS* by integration and comparison of the ^{1}H NMR signals arising from the protons *ortho* to the sulfone bridge for substituted PSUs at $\delta = 8.0$ ppm and the signals originating from protons in the *ortho* position to the sulfone bridge for nonsubstituted PSUs at $\delta = 7.85$ ppm. The latter calculations produced results that were very similar, or identical within the error of the method, to those obtained using the molar ratios of DPE and the PSU units in the reactions. As expected, spectra from the copolymers in both acid and ester form gave the same results, and for example, the *DS* of PSUgPVPA5 was more precisely evaluated by NMR spectroscopy to be 0.37, which was in excellent accordance with the value given in Table 1 for this copolymer. The overall number-average molecular weights (M_ns) of the graft copolymers were calculated from their respective content of PVPA and the M_n of the neat PSU, and the M_n of the side chains were calculated on the basis of *DS* and the content of PVPA. Finally, the monomer yield was calculated by comparing the amount of DEVP charged in the reactions with the respective amount that was accounted for in the copolymers.

In order to obtain additional structural information on the copolymers, Fourier transform infrared (FTIR) analysis was performed on the copolymers in both their ester and acid form. The polymers were first carefully dried, then ground with KBr, and pressed into tablets. The measurements were carried out in transmission mode using a Bruker IFS66 spectrometer.

Potentiometric titrations of the PSUgPVPA copolymers and *n*-hexylphosphonic acid were conducted with a Mettler Toledo MP220 pH meter at 25 °C. Dispersions of PSUgPVPA copolymers and a solution of *n*-hexylphosphonic acid (1 g/L) were prepared in water and subsequently titrated using a 0.1 N standard solution of NaOH.

Membrane Preparation. Transparent, flexible, and mechanically strong membranes were conveniently cast in Petri dishes from 5 wt % solutions of the graft copolymers in their acid form in DMSO at 90 °C under a continuous nitrogen flow during 24 h. The 80−120 μm thick membranes were then dried in a vacuum oven at 50 °C for 24 h. To ensure that no residual impurities or solvent were present in the membranes, they were first leached with Millipore water for at least 12 h and then again dried in the vacuum oven at 50 °C for 48 h. Doped membranes containing 2.0−18.4 wt % N11 and either the PSUgPVPA8 or the PSUgPVPA9 copolymer were prepared by first dissolving the latter copolymers in DMSO at 80 °C. Volumes of the N11 solution were then added under stirring to obtain solutions containing the desired concentrations. Solutions with a combined concentration of 5 wt % of polymer were then stirred for another 2 h before the membranes were cast as described above.

Evaluation of the Water Uptake and Swelling. In order to measure the water uptake (W_{water}) under immersed conditions, the membranes were first dried under vacuum at 50 °C for 48 h to obtain their dry weights (W_{dry}). The membranes were then immersed in deionized water for 24 h, at temperatures between 20 and 120 °C, to achieve the equilibrium water uptake. Excess water on the surface was quickly removed with tissue paper before the weights of the swollen membranes (W_{wet}) were obtained. The water uptake was also evaluated after placing the membranes in desiccators with controlled relative humidities (RHs) until a constant weight was noted. Control of the RH was achieved by keeping saturated salt solutions in the respective desiccator: $CuSO_4$ for 98% RH, NaBr for 60% RH, K_2CO_3 for 43% RH, and LiCl for 12% RH. The water uptake was then calculated as

$$W_{\mathrm{water}} = [(W_{\mathrm{wet}} - W_{\mathrm{dry}})/W_{\mathrm{dry}}] \times 100\% \qquad (1)$$

The relative area increase of the membranes was evaluated by measuring the areas of circular membranes (diameter of 2 cm in the dry state) after reaching the equilibrium water uptake under immersed conditions.

Thermal Analysis. Thermogravimetric analysis (TGA) was carried out using a TA Instruments Q500 TGA. Measurements were carried out under air at a heating rate of 1 °C/min, as well as under nitrogen at 10 °C/min. In all cases the samples were kept at 150 °C for 10 min before the respective heating runs. The temperatures at 5 wt % loss ($T_{\mathrm{d,5\%}}$) were noted in the TGA traces.

Differential scanning calorimetry (DSC) was performed on both nominally dry and humidified membranes with the samples in hermetically sealed aluminum pans using a TA Instruments Q1000 DSC. In the analysis of the nominally dry membranes, the samples were first heated to 240 °C and then cooled to 50 °C before heating to 300 °C. The heating and cooling rate was set to 10 °C/min, and the reported values of the T_gs were taken from the second heating scan. Analyses on fully hydrated membranes were run on samples equilibrated at 20 °C under immersed conditions in order to detect freezable water. In this case, the samples were analyzed during cooling from 25 to −60 °C, and then during heating to 25 °C, at a scan rate of 5 °C/min. Calculation of the amount of freezable water in the samples was performed by integrating the peak area of the melt endotherms. The degree of crystallinity of the water in the membranes was subsequently obtained from the heat of fusion of pure ice, 334 J/g.[51]

Proton Conductivity Measurements. The proton conductivity was evaluated by electrochemical impedance spectroscopy (EIS) using a Novocontrol high-resolution dielectric analyzer V 1.01S equipped with a Novocontrol temperature system. The measurements were carried out in the plane of the membranes (8 × 8 mm) using two polished stainless steel electrodes. The proton conductivity was measured between −20 and 120 °C under fully immersed conditions, at 100% RH and under nominally dry conditions. In the latter case, slightly hydrated membranes were first mounted in an open cell and then dried at 40 °C for 1 h under vacuum in order to ensure good electrical contact. The cell was then closed before the measurements. Notably, there was no change in the measured conductivity for membranes dried for longer times. Impedance data were gathered over the frequency range of 10^{-1}−10^{7} Hz at a voltage amplitude of 50 mV and were subsequently analyzed using the software WinDeta from Novocontrol.

Results and Discussion

Copolymer Synthesis and Characterization. PSU was successfully grafted with PVPA side chains by anionic polymerization of DEVP from PSU macroinitiators, followed by hydrolysis of the ester groups of the DEVP units. As seen in Scheme 1, the initiating sites were achieved in two steps by first introducing lithiated sites on PSU dissolved in THF using *n*-BuLi at −70 °C. The lithiation of the PSU is exclusively directed to the positions *ortho* to the sulfone links.[52,53] In the next step, DPE was added to the lithiated sites to form the initiating 1,1-diphenylalkyl anions. Preliminary attempts to initiate polymerization directly from lithiated sites on PSU gave very low monomer yields after long reaction times, showing the inefficient nucleophilic power and initiating capacity of the arylsulfone anion. In contrast, DPE is known to normally react quantitatively with aryl- and alkyllithium compounds to form 1,1-diphenylalkyl anions that are capable of initiating polymerization of many different vinyl monomers.[54] Furthermore, the steric arrangement prevents self-polymerization of DPE. In the present case, the use of DPE proved quite efficient. The monomer yield reached 70−82% after polymerizing for 5 h at −70 °C. No attempts to further improve the yield, e.g, by increasing the polymerization time, were made in this work.

As seen in Table 1, the series of graft copolymers prepared in this study contained between 30 and 60 wt % of PVPA side chains with M_n = 500−5800 g/mol. The value of *DS* was kept at 0.1, 0.2, and 0.4 in the series of samples. These values imply that the average molecular weight of the hydrophobic PSU segments in between each PVPA graft was approximately 4400, 2200, and 1100 g/mol, respectively. The rigid hydrophobic PSU main chains and the strongly hydrogen-bonding PVPA side chains can be expected to be strongly immiscible. Indeed, two glass transitions were identified by DSC analysis for all the copolymers. The concentration of acid units in phosphonated polymers is normally influenced by the occurrence of equilibrium condensation reactions, leading to the formation of water and anhydride products at high temperatures.[19] Consequently, the T_g of the PVPA phase was found to increase with increasing annealing temperature because of the increasing degree of cross-linking caused by an increasing concentration of anhydride bridges (P−O−P bonds). Thus, the condensation reactions continued as long as the segmental mobility was sufficient. Figure 2 shows the DSC heating traces recorded after annealing at high temperature (240 °C). As seen, the first glass transition was registered between T_g = 184 and 191 °C, virtually overlapping with the value of the neat PSU at T_g = 188 °C. The second glass transition was found at approximately T_g = 250 °C and was ascribed to the PVPA phase. Notably, the magnitudes of the ΔC_p value in connection with the glass transitions were proportional to the concentration of the respective phase in the copolymers. The DSC results thus confirmed that the copolymers had the appropriate macromolecular design to achieve membranes with phase-separated morphologies containing a phosphonated polymer phase to facilitate proton conduction and an amorphous high-T_g polymer phase to retain the morphology and the mechanical properties at high temperatures and RHs.

Typical ^{1}H and ^{31}P NMR spectra of a copolymer in the ester form are given in parts a and b of Figure 1, respectively. As seen in Figure 1a, the CH_2 and CH_3 protons of the diethylphosphonic ester were found by ^{1}H NMR at δ = 4.1 and 1.2 ppm, respectively. ^{13}C NMR spectra (not shown) confirmed the presence of these units by the occurrence of peaks at δ = 61.4 ppm for P−O−CH_2− and at δ = 16.7 ppm for P−O−CH_2−CH_3. The presence of the phosphonated side chains was further confirmed by the two broad peaks in the ^{1}H NMR spectrum between δ = 1.7−2.8 ppm originating from the C*H*

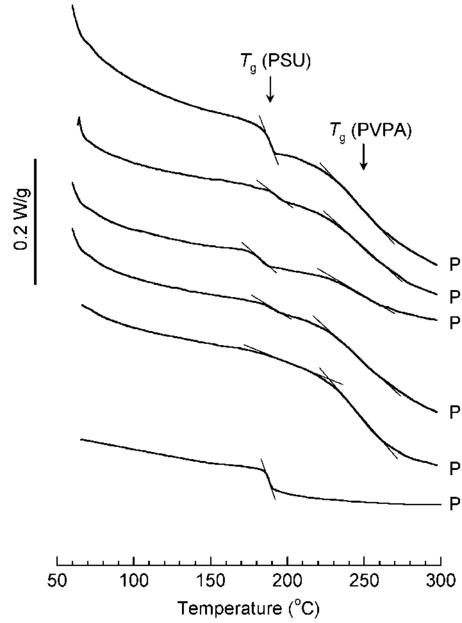


Figure 2. DSC heating traces of the graft copolymers in the acid form after annealing at 240 °C. The thin lines indicate the glass transitions of the PSU and PVPA phases.

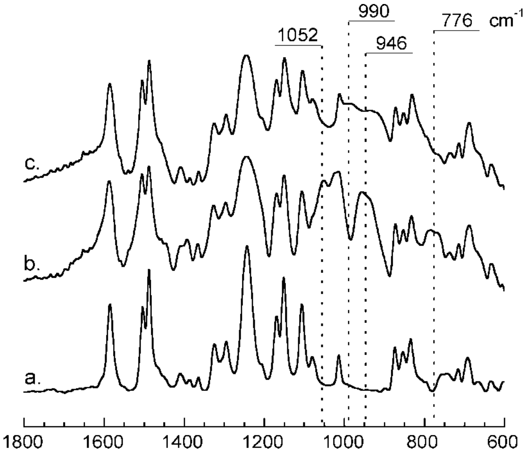


Figure 3. FTIR spectra of neat PSU (a), PSUgPVP8 (b), and PSUgPVPA8 (c).

and CH_2 protons of the PVPA backbone. The ^{31}P spectra showed a single peak at 32.8 ppm from the diethyl ester derivative (Figure 1b). The hydrolysis in refluxing aqueous HCl proved to be quantitative for all the copolymers. As seen in the ^{1}H spectrum of a hydrolyzed copolymer in Figure 1c, this was confirmed by the complete disappearance of the characteristic peaks of the diethyl ester. ^{13}C NMR spectra (not shown) verified the same. The ^{1}H spectra now showed a broad peak between $\delta = 10-12$ ppm, confirming the presence of the phosphonic acid groups. The complete hydrolysis was further verified by the ^{31}P NMR analysis (Figure 1d), where the shift of the diethyl ester derivative disappeared and the shift of the diacid form of phosphonic acid appeared at $\delta = 29.2$ ppm. In the spectra of the current hydrolyzed samples a small signal found at $\delta = 21$ ppm confirmed the presence of anhydrides produced through condensation of the phosphonic acid groups by P−O−P bond formation.

The FTIR spectra shown in Figure 3 further confirmed the presence of phosphonic groups. The phosphoryl (P=O) stretching is usually found to absorb at 1320−1200 cm^{-1}. However, the considerable overlap between absorptions bands originating from the asymmetric stretches of the sulfone and phenyl ether linkages at 1292−1326 and 1238 cm^{-1}, respectively, did not allow for a definite identification. Nevertheless, in comparison with the FTIR spectrum of the neat PSU (curve a in Figure 3), four new bands were clearly identified for the copolymers in the ester form (curve b in Figure 3). The bands at 1052 and 1023 cm^{-1}, as well as the band at 776 cm^{-1}, were assigned to (P)−O−C absorptions of the ester group, and the band at 946 cm^{-1} was ascribed to P−O−(C) vibrations.[28] These bands disappeared after hydrolysis, and the (P)−O−H bending vibration at 990 cm^{-1} and a broad (P)−O−H stretching band at 2300 cm^{-1} appeared for the acidic copolymers (not shown).

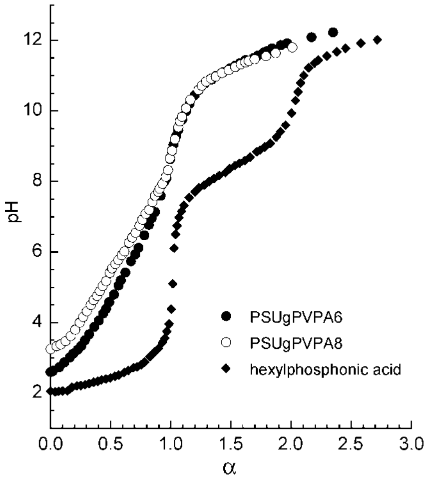


Figure 4. Titration data of PSUgPVPA6, PSUgPVPA8, and *n*-hexylphosphonic acid at 1 g/L in water. The factor α indicates the degree of neutralization, i.e., moles of NaOH added per mole of phosphonic acid.

Potentiometric pH titrations were carried out on the present graft copolymers to study possible polyelectrolyte effects and to verify the theoretical *IEC*s calculated from NMR data. These titrations are relevant for understanding the proton conductivity in the nominally dry state and for assessing charge carrier concentrations in the hydrated state. In Figure 4, the titration curves of the PSUgPVPA6 and -8 copolymers are presented along with the curve of *n*-hexylphosphonic acid. As seen, the curve of *n*-hexylphosphonic acid showed the anticipated behavior of a diprotic acid with two distinct steps for the addition of 1 and 2 equiv of base, respectively. The curve indicated a pK_{a1} value of 2.45 and a pK_{a2} value of 8.45, which is in good agreement with data on alkylphosphonic acids reported by Crofts et al.[55] In contrast, the titration curves of the copolymers showed only one step for the addition of 1 equiv of base. This demonstrated that the phosphonic acid units along the PVPA side chains behaved like monoprotic acids, most probably because the close proximity of the acid units only allowed the dissociation of one proton for electrostatic reasons. As seen in Figure 4, the pH increases of the copolymers during the titrations were much more continuous than for *n*-hexylphosphonic acid. This is expected from the wide spectrum of pK_a values that results from a high degree of intramolecular interactions of the acid units of a polyelectrolyte. The titration curves of the copolymers thus indicated that the PVPA side chains of the copolymers are likely to form phases with very high local concentrations of interacting phosphonic acid units that are critical for efficient proton conduction in the nominally dry state. The data recorded for the copolymers agree very well with the results reported by Bingöl et al. on the behavior of a PVPA homopolymer.[42] On the other hand, the phosphonic acid units of poly(*m*-phenylenephosphonic acid) show a distinct diprotic behavior, presumably because of the larger interacid distance

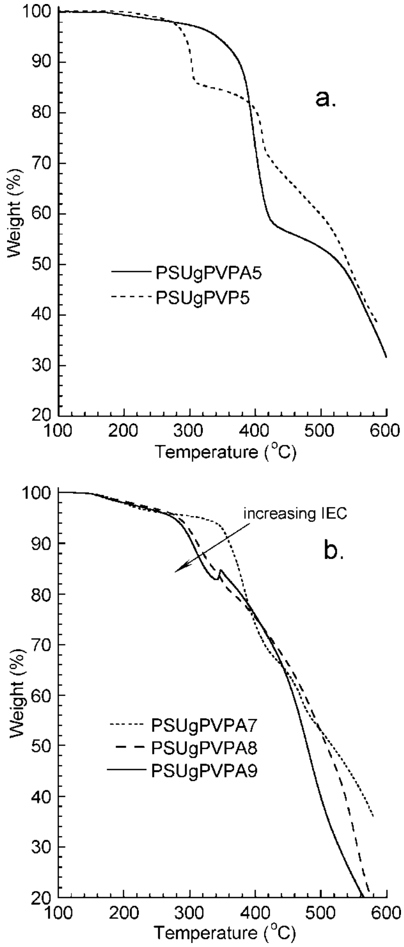


Figure 5. TGA traces of PSUgPVP5 (ester) and PSUgPVPA5 (acid) as recorded under nitrogen at 10 °C/min (a) and TGA traces of PSUs carrying PVPA side chains in the acid form ($DS = 0.1$) as recorded under air at 1 °C/min (b).

and the higher chain stiffness of this polymer.[56] The experimental *IEC* data derived from the present titrations were in excellent agreement with the theoretical *IEC* data in Table 1; e.g., for PSUgPVPA8 the experimental and theoretical *IEC* values were 4.35 and 4.4 mequiv/g, respectively.

All the grafted copolymers in the acid form were readily soluble in DMSO and 1-methyl-2 pyrrolidinone (NMP). The two samples with the highest *IEC* values, PSUgPVPA8 and -9, were also soluble in *N,N*-dimethylacetamide (DMAc). Furthermore, the acidic copolymers gave flexible, transparent, and mechanically strong membranes when cast from DMSO solutions at 90 °C under a nitrogen atmosphere.

Thermal Stability. The copolymers were characterized by TGA both under nitrogen at a heating rate of 10 °C/min and under air at 1 °C/min. Figure 5a shows typical TGA traces recorded under nitrogen for the copolymers in the ester and in the acid form. As seen, the copolymer in the ester form showed a first degradation step between 250 and 350 °C. The magnitude of the step was directly correlated with the phosphonate ester content. This degradation was ascribed to the decomposition of the ester units to form ethylene and phosphonic acid units,[57] possibly followed by a subsequent formation and loss of water by self-condensation at these high temperatures. A second degradation step was noted between 350 and 400 °C, most probably connected with the cleavage of the C−P bond. The copolymers in the acid form showed a small initial weight loss already from 150 °C, ascribed to reversible self-condensation and desorption of water. A large degradation step at ~340 °C was connected with the cleavage of C−P bonds, and then polymer backbone degradation occurred at higher temperatures.

A high thermo-oxidative stability of PEMFC membranes is a key property required for sustained fuel cell operation at high temperatures. Figure 5b shows the TGA traces recorded under air at 1 °C/min for the hydrolyzed copolymers having $DS = 0.1$. All the copolymers showed an initial weight loss linked to reversible self-condensation between 150 and 180 °C. The first irreversible weight loss, ascribed to C−P bond cleavage, occurred at 260−340 °C depending on the content of PVPA. As expected, an increased content of PVPA in the copolymers led to a decreased onset of degradation at a given value of *DS*. The temperatures at which 5% weight losses were noted for the different samples are given in Table 2.

For comparison, the degradation of neat PVPA under inert atmosphere and air has been reported to be 380 and 330 °C, respectively.[21] A temporary weight increase was noted above 350 °C for copolymer samples with a high PVPA content, as seen for sample PSUgPVPA9 in Figure 5b. This increase most probably originated from oxygen uptake in connection with the oxidation of the phosphorus. From the data collected during slow heating under dry air, the phosphonated copolymers can be expected to have the thermal stability necessary for fuel cell operation. Moreover, the samples were treated in refluxing concentrated hydrochloric acid solutions during the hydrolysis step without any signs of degradation, demonstrating a high hydrolytic stability of the copolymers in the acid form. Nevertheless, ultimately in-situ fuel cell evaluations are required in order to evaluate the true durability of the present phosphonated membranes.

Water Uptake Characteristics. The water uptake determines to a large degree the proton conductivity and the mechanical properties of PEMFC membranes. The water uptake of a membrane based on a sulfonated polymer typically depends on the *IEC*, and these membranes characteristically take up an excessive amount of water and lose their mechanical integrity when a certain critical temperature is exceeded at a given degree of sulfonation. In comparison with sulfonated polymers, the lower acidity and the higher degree of hydrogen bonding of the phosphonic acid groups lead to reductions in the number of absorbed water molecules per acid group (λ) in a phosphonated membrane. An appropriate molecular design of phosphonated copolymers may thus provide membrane morphologies that allow for the high acid concentrations necessary to achieve conductivity under nominally dry conditions without excessive water uptake under highly humidified conditions. It can be mentioned that the acidity and λ value can be significantly enhanced by attachment of the phosphonic acid groups to polymers via electron withdrawing $-CF_2-$ links.[29] However, this weakens considerably the strength of the C−P bond, leading to low thermal stability.

Figure 6a presents the gravimetrically determined equilibrium water uptake under immersed conditions between 20 and 120 °C expressed as $\lambda = [H_2O]/[-PO_3H_2]$. As expected, the water uptake was found to increase with the temperature and the *IEC*. All the copolymers, except PSUgPVPA9, showed a steady and quite moderate increase of the water uptake with the temperature. Membrane PSUgPVPA9, with the largest PVPA content (57 wt %) in the series, most likely went through a phase-inversion process between 20 and 60 °C where the morphology changed to accommodate dramatically increasing amounts of water. Above 60 °C, the increase of the water uptake with the temperature was stabilized. It should be mentioned that this membrane did not lose its mechanical integrity even though it contained 274 wt % of water at 120 °C. The value of *DS* also showed an influence on the water uptake as seen in Figure 6a and Table 2. A low value of *DS* of the graft copolymers

Table 2. Data on the Thermal Stability and the Water Uptake of the Neat Graft Copolymer Membranes

copolymer	*DS*	theor *IEC* (mequiv/g)	$T_{d,5\%}$[a] (°C)	W_{water}[b] (wt %)	area increase[b] (%)	λ[b] [H_2O]:[$-PO_3H_2$]	$\lambda_{freezable}$[b] [H_2O]:[$-PO_3H_2$]
PSUgPVPA5	0.4	3.0	320	20	7	3.7	0
PSUgPVPA6	0.2	4.3	297	67	16	8.6	0
PSUgPVPA7	0.1	2.9	320	31	9	6.0	0
PSUgPVPA8	0.1	4.4	286	71	24	9.0	0.9
PSUgPVPA9	0.1	5.3	279	125	35	13.5	7.6

[a] Temperature for the detection of 5% weight loss when heated under air at 1 °C/min. [b] Data for membranes equilibrated at 20 °C under immersed conditions.

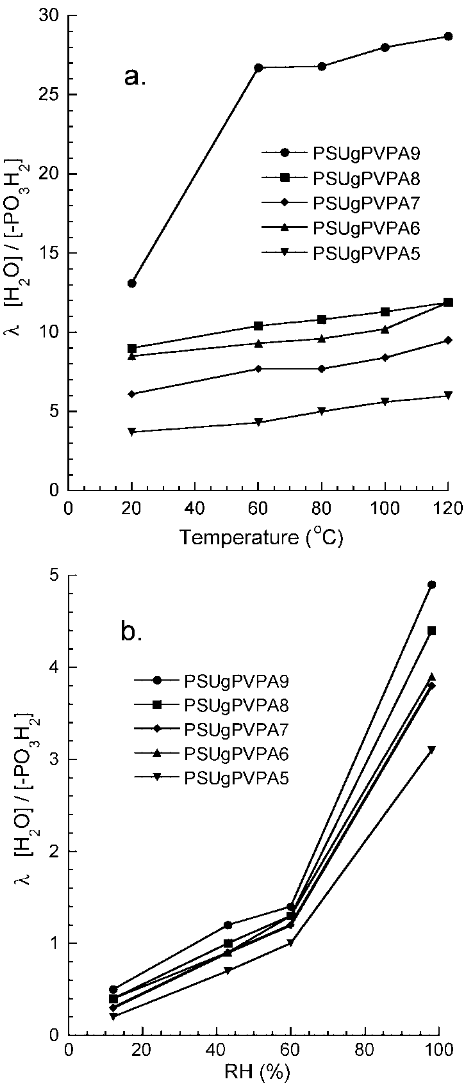


Figure 6. Water uptake of the phosphonated copolymer membranes under immersed conditions as a function of temperature (a) and under different relative humidities in air at 20 °C (b).

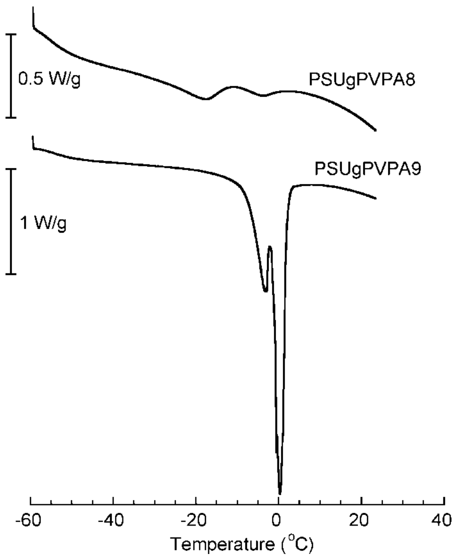


Figure 7. DSC traces of phosphonated copolymer membranes equilibrated under immersed conditions at 20 °C. The data were collected during heating at 10 °C/min.

indicated long PSU segments between the grafted PVPA side chains, most likely giving rise to larger phase domains in the membrane. Copolymer PSUgPVPA7 (*IEC* = 2.9, *DS* = 0.1) showed a markedly (~50%) higher water uptake in comparison to PSUgPVPA5 (*IEC* = 3.0, *DS* = 0.4), indicating that the morphology with the presumably larger phosphonated phase domains of the former copolymer had a greater ability to take up and accommodate more water. Although the values of λ measured under immersed conditions for the copolymers were fairly modest at 20 °C in comparison to sulfonated polymer membranes, they still represented an overall water uptake of 20, 32, 66, 71, and 125 wt % for the membranes PSUgPVPA5, -7, -6, -8, and -9, respectively. It is clear that the water uptake of the last copolymer membranes in the series needs to be restricted before practical use in PEMFCs.

The water uptake was also investigated for all the membranes after equilibration under air with different values of RH (12−98%) at room temperature. As expected, the results showed that the water uptake, expressed as λ in Figure 6b, increased with increasing RH and *IEC*. The value of λ at 98% RH was between 4 and 5, which was markedly lower than that reported for Nafion, $\lambda \sim 14$ (*IEC* = 0.9, at 100% RH).[58] Yet, the overall water uptake at 98% RH was between 17 and 46 wt % for the copolymers and has been reported to be ~23 wt % for Nafion 117 at 20 °C. Kaltbeitzel et al. have very recently measured the water uptake for neat linear PVPA with a molecular weight of 62 000 g/mol.[21] They reported a water uptake of ~20 wt % at 60% RH and ~85 wt % at 98% RH at 24 °C.

The amount of freezable water was evaluated by DSC by integrating water melting peaks recorded after equilibration of the membranes under immersed conditions. This constitutes a method to study the local environment of the water in the membranes.[59,60] According to this method, water can be classified into freezable or nonfreezable water. Nonfreezable water shows no crystallization or melting peaks in DSC analyses and arises from water that is strongly bound to the polymer. Freezable water, on the other hand, is liquidlike or only weakly polarized and exhibits similar thermal transitions as bulk water. It should be mentioned that the outcome of this method depends on the exact conditions under which the measurements are performed. During the DSC measurements of the copolymers, freezable water was only detected in the two membranes with the highest PVPA content, PSUgPVPA8 and -9. As seen in Figure 7, the DSC heating traces of the hydrated PSUgPVPA8 showed quite broad and small melting peaks at −18 and −4 °C, while the trace of PSUgPVPA9 showed a small peak at −4 °C and a large peak at 0 °C. Thus, only the latter membrane contained something resembling "true" bulk water. The numbers of freezable water molecules per phosphonic acid unit, $\lambda_{freezable}$,

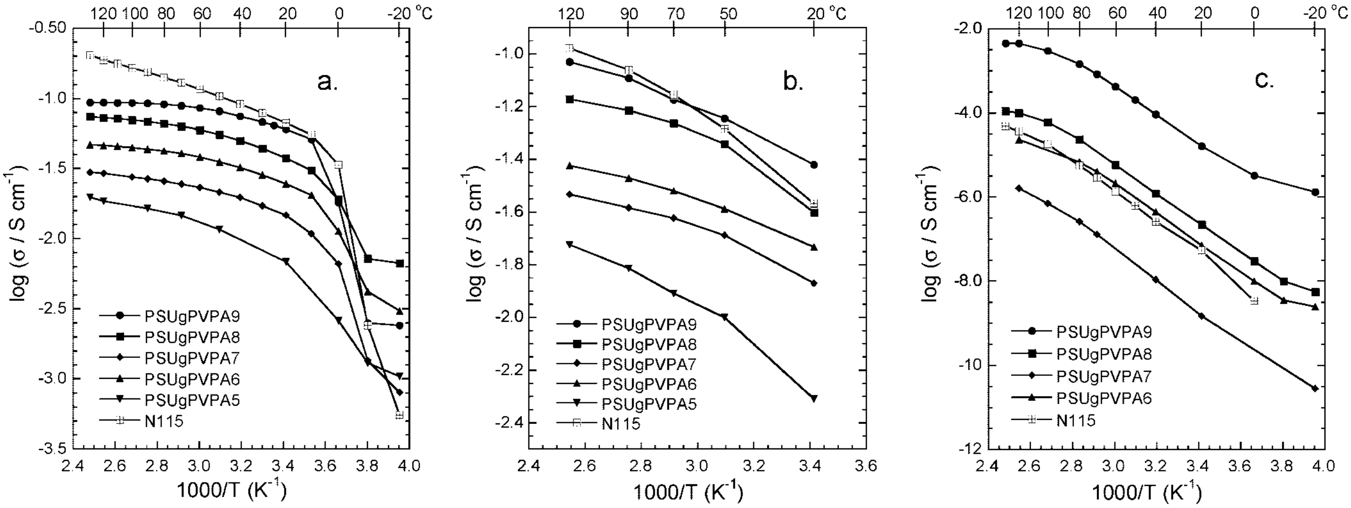
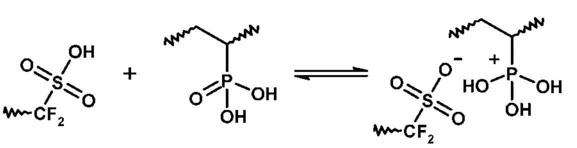


Figure 8. Proton conductivity of the neat phosphonated copolymer membranes and N115. Arrhenius plots of data measured under immersed conditions (a), at 100% relative humidity (b), and under nominally dry conditions (c). Please note the different scales on the axes.

Scheme 2. Complex Formation by Proton Transfer from the Superacidic Perfluorosulfonic Acid to the Amphoteric Phosphonic Acid



were 0.9 and 7.6 for PSUgPVPA8 and PSUgPVPA9, respectively. The observed results may be explained by a decreased local acid concentration, and thus a increased ability for the water to freeze, as the *IEC* and the λ value increase in a given series of membranes. Holdcroft and co-workers have recently investigated the uptake of freezable water by different sulfonated polymer systems.[60] For example, fully hydrated Nafion 117 at 25 °C was found to have $\lambda = 20$ and $\lambda_{\text{freezable}} = 9$. More detailed investigations are needed to clarify the distribution and interactions of the water in the domains of the phosphonated copolymer membranes.

Proton Conductivity under Hydrated Conditions. The proton conductivity of the membrane is of particular importance and plays a significant role for the performance of the PEMFC, where the conductivity is linked to the power density. Figure 8a presents the proton conductivity of the phosphonated membranes measured by EIS under fully immersed conditions in the cell. The corresponding conductivity of N115 was included as a reference. As seen, the conductivity below 0 °C increased sharply during heating for all the samples because of melting of the absorbed water. This effect was the most pronounced for the N115 membrane. Above subzero temperatures, the conductivity of the phosphonated membranes seemingly followed a non-Arrhenius behavior with convexly shaped curves. This is in contrast to the N115 membrane which clearly followed an Arrhenius behavior. Thus, the conductivity of the phosphonated membranes varied less with the temperature than the N115 membrane under these conditions. At high temperatures, the conductivity of membrane PSUgPVPA9, with the highest value of *IEC*, was seemingly constant with the temperature. This observation was ascribed to the large water uptake of this membrane under immersed conditions (Figure 6a), causing a clearly noticeable diluting effect on the phosphonic acid concentration. The level of conductivity of the phosphonated membranes was found to be between 19 and 95 mS/cm at 120 °C, depending on *IEC*, which may be compared to 188 mS/cm for the perfluorosulfonate membrane.

Figure 8b shows the proton conductivity as measured under air at 100% RH. Notably, the conductivity of the phosphonated membranes suffered far less than that of membrane N115 from the transition from fully immersed conditions to air at 100% RH. As seen, the conductivity of membrane PSUgPVPA9 now compared more favorably to that of N115, showing higher values below 50 °C and just slightly lower values at 70−120 °C. Thus, the conductivity of the former membranes reached between 19 and 93 mS/cm at 120 °C, depending on the *IEC*, which may be compared with 105 mS/cm for N115. It should be noted, however, that the phosphonated membranes had higher *IEC* values and larger degrees of water uptake over the whole temperature range studied. Li et al. have prepared and investigated cross-linked hybrid networks functionalized with phosphonic acid and reported conductivities of around 50 mS/cm at 100 °C and 100% RH.[8]

Proton Conductivity under Nominally Dry Conditions. Water is always present in systems containing phosphonic acid because of the self-condensation equilibrium. Membranes kept under vacuum at elevated temperatures for long periods of time are best described as "nominally" dry.[19] Thus, phosphonic acid systems may be viewed as a "source of water" under dry conditions, and it has recently been suggested that the conductivity of nominally dry phosphonated membranes may primarily be due to this small amount of water present.[19] Figure 7c shows the conductivity of the phosphonated membranes under nominally dry conditions. As expected, the conductivity was drastically reduced in relation to that of the humidified membranes. Above subzero temperatures, the conductivity followed Arrhenius relationships up to temperatures of ~80 °C. In this temperature region, the apparent activation energy was calculated to be 67, 68, 66, and 65 kJ/mol for the membranes PSUgPVPA6, -7, -8, and -9, respectively. These values agreed very well with the activation energy of 65 kJ/mol reported for the proton conductivity of neat PVPA measured under nominally dry conditions.[33] Above 80 °C, the conductivity increase with the temperature started to level off. This effect was ascribed to progressively increasing concentrations of condensation products, leading to loss of phosphonic acid units and increasing constraints in the proton conducting phase. As seen in Figure 8c, the effect was most pronounced for the membranes with the highest *IEC* values. Still, the condensation reactions had no dramatically negative effect on the conductivity, at least not up to 130 °C, and the conductivity reached 4.6 mS/cm for membrane PSUgPVPA9 at 120 °C. As anticipated, the conductivity of N115 suffered greatly from the dry condition of

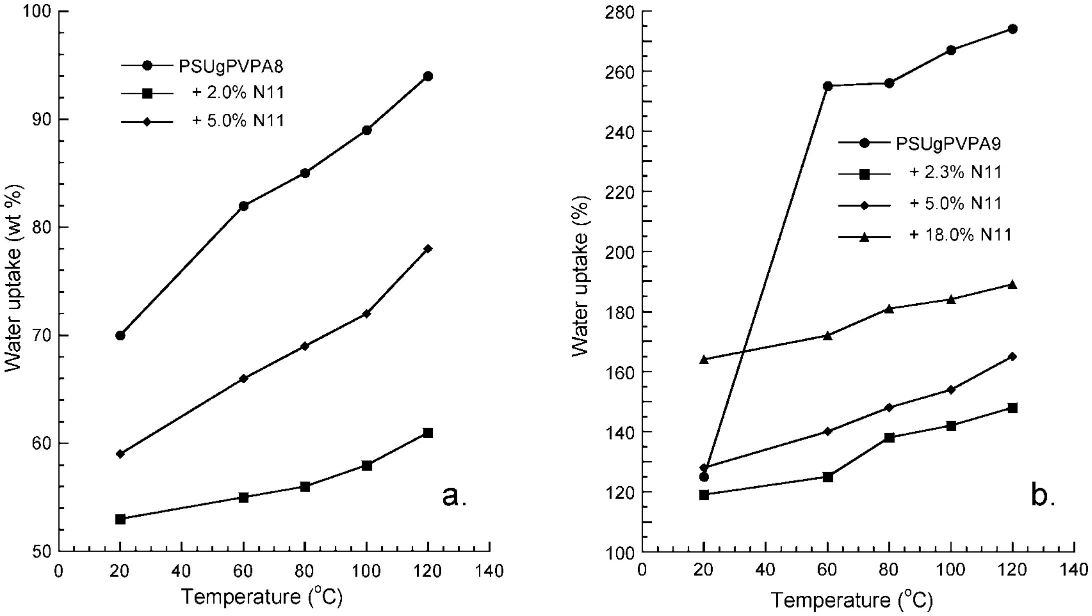


Figure 9. Water uptake of the neat phosphonated membranes PSUgPVPA8 (a) and PSUgPVPA9 (b) and of the respective membranes doped with N11, as measured under immersed conditions.

the measurement and only reached 0.036 mS/cm at the same temperature. In comparison, the conductivity of neat linear PVPA (M_n = 62 000 g/mol) has been reported to be ~0.1 mS/cm under nominally dry conditions.[21] One possible explanation for the higher conductivity of the present graft copolymer membranes may be a higher mobility of the relatively short side chains in relation to the high-molecular-weight PVPA. The conductivity of the phosphonated hybrid networks studied by Li et al. reached ~0.1 mS/cm under dry argon.[8] Moreover, Steininger and co-workers have reported that oligosiloxanes densely tethered with phosphonic acid via short spacers reach ~2 mS/cm at 130 °C under nominally dry conditions.[9]

Water Uptake and Conductivity of Membranes Doped with a Perfluorosulfonic Acid Polymer. As already mentioned above, high concentrations of phosphonic acid are necessary for high conductivity under nominally dry conditions. However, these membranes are likely to take up excessively large amounts of water under high RH and, especially, under immersed conditions leading to dilution effects and poor mechanical properties. A proven strategy to restrict the water uptake of PEMFC membranes is to introduce cross-links, either by covalent bonds or by strong physical interactions, e.g., by the formation of suitable polymeric complexes. Kerres and co-workers have developed membranes in which strong acid—base complexes are formed through the blending of sulfonated polymers and polymers functionalized with basic amine or pyridine groups.[61] Moreover, the doping of intrinsically proton conducting imidazole functional oligomers with 5—10% of superacidic CF_3SO_3H has been reported to enhance the conductivity by as much as a factor 50 at 120 °C under dry conditions.[12] In the present case, given the amphoteric character of phosphonic acid, we decided to investigate the doping of selected phosphonated copolymers with a perfluorosulfonic acid polymer (N11). The purpose was here to identify approaches to restrict the water uptake without negative effects on the conductivity, under both high-humidity and dry conditions. Because of the superacidic nature of N11 ($pK_a \sim -6$), proton transfer to the amphoteric phosphonic acid units is likely to occur during the membrane casting procedure. This leads to interpolymeric cross-linking through the formation of sulfonate—phosphonium complexes, as shown in Scheme 2.

Membranes based on the two phosphonated copolymers with the highest values of *IEC*, PSUgPVPA8 and -9, were doped with N11 and studied with respect to water uptake and proton conductivity. The doped membranes contained between 2 and 18 wt % of N11, corresponding to a [$-SO_3$]:[$-PO_3$] ratio of between 1:250 and 1:25. Parts a and b of Figure 9 present the water uptake of the doped membranes based on PSUgPVPA8 and -9, respectively, as a function of temperature under immersed conditions. The corresponding water uptake of the neat copolymer membranes is also shown.

Doping the membranes with ~2 wt % of N11 resulted in sharply decreased water uptakes in both cases. Consequently, the water uptake at 120 °C decreased from 94 to 61 wt % for the doped PSUgPVPA8 membranes and from 273 to 147 wt % for the doped PSUgPVPA9 membranes. The phase inversion process leading to excessive water uptake of the neat PSUgPVPA9 membrane was not observed after the doping (Figure 9b). Thus, the presence of N11 efficiently reduced the water uptake to more acceptable levels and also resulted in the formation of more elastic membranes with better mechanical properties in relation to the undoped copolymers membranes. Further increases of the concentration of N11 in the blends gave membranes with gradually increasing levels of water uptake. It may be envisaged that the presence of small concentrations of N11 were able to efficiently cross-link the membranes by the formation of interpolymeric sulfonate—phosphonium complexes. However, the presence of additional N11 led to increasing degrees of nonefficient cross-linking and increasing concentrations of hydrophilic complexes in the membranes, resulting in increased water uptake. Moreover, membranes containing 18 wt % N11 were opaque, an indication of phase separation.

The proton conductivity at 100% RH is given in parts a and b of Figure 10 for the membranes based on PSUgPVPA8 and -9, respectively. The presence of N11 improved the conductivity at 20 °C quite significantly, especially for the PSUgPVPA9 membranes. With ~2 wt % N11 added, the conductivity at 120 °C first decreased but then increased significantly at 5 wt %. The decrease in conductivity at 2 wt % N11 added may be explained by the considerable decrease in the water uptake for these doped membranes in relation to the undoped ones. Figure 10c shows the conductivity under nominally dry conditions for the two phosphonated copolymer membranes before and after

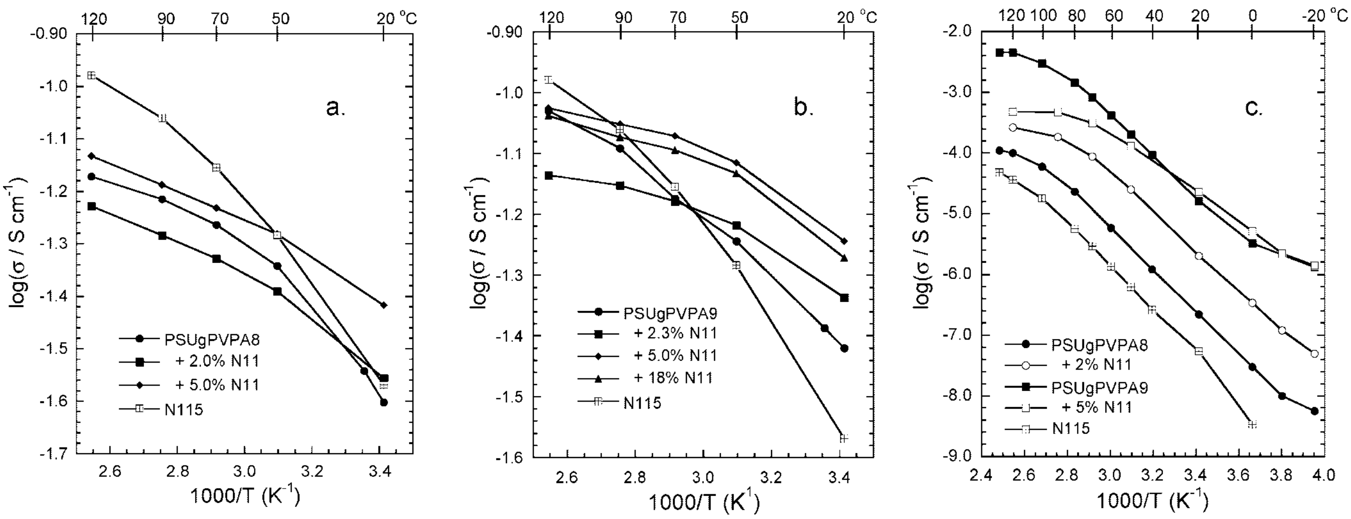


Figure 10. Proton conductivity of phosphonated copolymer membranes doped with N11. Arrhenius plots of data measured at 100% RH for membranes containing PSUgPVPA8 (a) and PSUgPVPA9 (b) and of data measured under nominally dry conditions (c). The corresponding data of N115 has been included for reference. Please note the different scales on the axes.

doping with N11. As seen in the case of PSUgPVPA8, the addition of 2 wt % N11 enhanced the conductivity in the range of almost an order of magnitude in the studied temperature region. Notably, the activation energy for the conductivity of the doped membrane was virtually the same as for the neat copolymer membrane (66 kJ/mol) in the linear region between 0 and 80 °C. An addition of 5 wt % N11 to PSUgPVPA9 gave a membrane with a conductivity in the same range as the neat copolymer membrane at low temperatures (<50 °C). However, at higher temperatures the conductivity was lower than that of the neat copolymer membrane. The conductivity of all the membranes suffered at temperatures above 80 °C because of self-condensation.

Conclusions

PSU was successfully grafted with PVPA using an anionic grafting strategy. Graft copolymers with different values of *DS* and PVPA contents were thus synthesized and carefully characterized. The graft copolymers displayed a number of features important for use as fuel cell membranes. They were prepared from inexpensive starting materials and were all soluble and nicely film-forming from solution. The resulting membranes were phase-separated because of the inherent immiscibility of the stiff and hydrophobic backbone polymer and the strongly hydrogen-bonding side chains. The PVPA side chains thus formed separate phases in the membranes with very high local concentrations of interacting phosphonic acid units, giving rise to large hydrogen-bonded aggregates. These aggregates are essential for efficient proton conduction in the nominally dry state. The thermal stability of the membranes was sufficiently high under air with $T_{d,5\%}$ at 260−340 °C, depending on *IEC* and *DS*. At 120 °C the membrane with the highest PVPA content in the study (57 wt %) reached a conductivity of 4.6 mS/cm under nominally dry conditions and 93 mS/cm under 100% RH. However, at high temperatures the performance of this membrane was limited by condensation reactions under dry conditions and, especially, by high levels of water uptake under immersed conditions. Yet, by adding small concentrations of N11 to the phosphonated membranes with the highest PVPA contents, the water uptake was efficiently reduced under immersed conditions. At the same time the conductivity was enhanced, especially at low temperatures. Increasing the doping levels beyond 5 wt % caused increasing water uptake and decreasing conductivities. The results further showed that it was possible to enhance the conductivity under nominally dry conditions by additions of small amounts of N11. The presence of the perfluorosulfonate polymer in these membranes may further increase the compatibility with Nafion-impregnated electrode layers which will facilitate the preparation of membrane-electrode assemblies. The findings of this study have demonstrated that phosphonated membranes with a proper macromolecular design may potentially show some important advantages in relation to the commonly studied sulfonated membranes in PEMFC applications.

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