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PAPER

Synthesis and characterization of poly(*para*-phenylene disulfonic acid), its copolymers and their *n*-alkylbenzene grafts as proton exchange membranes: high conductivity at low relative humidity

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Water insoluble poly(*para*-phenylene disulfonic acid) and its copolymers were synthesized by direct polymerization of 1,4-dibromobenzene-2,5-disulfonic acid and 4,4′-dibromobiphenyl-3,3′-disulfonic acid lithium salts using Ullmann coupling and subsequent grafting of long-tail alkylbenzene groups onto the polymer backbones. Copolymers with ion exchange capacities of 4.3 to 7.7 meq. g^{-1} were obtained. Polymers and copolymers prepared under optimized polymerization conditions were characterized by NMR, TGA, DSC and viscometry. The physicochemical characteristics of the copolymers were tailored by adjusting monomer compositions and by varying the grafting reaction temperature and time. These polymers could hold eight or more strongly bound water molecules per acid group, which facilitated their high conductivity. In the dry state, the polymers were very brittle. Membranes prepared from these polymers exhibited proton conductivity as much as ten times higher than that of Nafion® 212, at elevated temperature and low relative humidity.

Introduction

Proton exchange membrane fuel cells (PEMFCs) have attracted the attention of many researchers as one of the next-generation power technologies for automotive, stationary and portable applications. The proton exchange membrane (PEM) is one of the key challenges in the PEMFC development in terms of performance and production cost. Perfluorosulfonic acid (PFSA) polymers, such as Nafion®, Aciplex®, and Flemion®, stand as the state-of-art PEM materials due to their efficient proton conduction, permselectivity, and long term thermal and chemical stability.[1–3] Nafion conductivity reaches 100 mS cm^{-1} in the fully hydrated protonic form, but decreases at elevated temperature (above 80 °C) because of water loss and structural and morphological changes. Thermally stable polymers with good water affinity and reliability at higher temperatures are desired for solid polymer electrolyte fuel cells. Acid-functionalized aromatic hydrocarbon polymers such as poly(phenylene sulfone)s,[4,5] poly(arylene ether ketone)s,[6–8] polyimides,[9–11] poly(phenylene)s,[12–14] and polybenzimidazoles[15–20] have been extensively investigated as alternative membrane materials for PEMFCs. These polymers have rigid aromatic backbones that confer high thermal stability, mechanical strength and reasonably good resistance to oxidation.

During the past decade our group studied a number of rigid rod, nematic liquid crystalline poly(aromatic sulfonic acid) polymers and copolymers.[11,14,21–31] Since their backbones are packed in parallel, incorporation of bulky grafts forces the chains apart and generates long nanopores lined with sulfonic groups that hold water very tightly. Conductivity remains relatively high at low relative humidity, in contrast with Nafion® and poly(phenylene ether sulfonic acid) systems. We call this induced inter-chain porosity a “frozen-in free volume”.[21] Initial work used poly(naphthalene bis-imide)s[11,25,29–31] but those polymers hydrolyzed slowly in the acid form. Recent efforts have focused on poly(phenylene sulfonic acid)s, which do not hydrolyze and show exceptional stability.

A new synthetic method was developed to prepare the rigid rod polymers, poly(biphenylene disulfonic acid), PBPDSA, and poly(*para*-phenylene disulfonic acid), PPDSA, using the Ullmann reaction.[14,21–24,26] Their conductivity at low relative humidity was remarkable compared to other PEMs. It met or exceeded US Department of Energy objectives for 2010 and later. However, these homopolymers were soluble in water and brittle when dry. In the present study, we describe a new approach to obtain water-insoluble materials by grafting long-tail alkylbenzenes on PPDSA and its biphenyl disulfonic acid copolymer to generate hydrophobic alkyl phenyl sulfone substituent groups. The reaction conditions were optimized and the resulting polymer and copolymer structures were characterized using NMR, TGA, DSC and viscometry. The structural characteristics of the polymers and

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copolymers could be readily tailored by adjusting monomer compositions and by varying the grafting reaction temperature and time. The water uptake, dimensional swelling and proton conductivity were studied. The membranes were relatively brittle when dry. They exhibited proton conductivity much higher than that of Nafion® at elevated temperature and low relative humidity.

Experimental

Materials

All chemicals were purchased from Sigma-Aldrich Corporation. Copper powder (99%, 400 mesh) was activated according to a previously reported procedure,[32] vacuum dried and used immediately. *N*-Methyl-2-pyrrolidone (NMP) was dried by stirring with calcium hydride at 60 °C and distilled under vacuum before use. 1,4-Dibromobenzene (98%), 4,4′-dibromobiphenyl (98%), fuming sulfuric acid (12–17% SO_3), *n*-octylbenzene (OcB, 98%), *n*-dodecylbenzene (DDB, 97%) and other reagents and solvents were used as received.

4,4′-Dibromobiphenyl 3,3′-disulfonic acid (DBBPDSA) was synthesized from 4,4′-dibromobiphenyl using fuming sulfuric acid according to a previously reported procedure.[26] δ_H(600 MHz; D_2O; $\delta_{dioxane} = 3.75$): 8.05 (2H, d), 7.62 (2H, d), 7.35 (2H, q); δ_C(150 MHz, D_2O, $\delta_{dioxane} = 67.19$): 142.5 (C–SO_3H), 138.4 (C–C), 136.2 (C–H), 131.0 (C–H), 127.5 (C–H), 119.4 (C–Br). 1,4-Dibromobenzene 2,5-disulfonic acid (DBBDSA) was synthesized from 1,4-dibromobenzene using fuming sulfuric acid.[23] δ_H(600 MHz; D_2O; $\delta_{dioxane} = 3.75$): 8.34 (s, 2H); δ_C(150 MHz, D_2O, $\delta_{dioxane} = 67.19$): 145.4 (C–SO_3H), 135.6 (C–H), 118.7 (C–Br).

Polymerization

DBBDSA–Li salt (16.1 g, 0.04 mole) and freshly activated and predried copper powder (25.4 g, 0.4 mole) were placed in a 1000 mL three-neck heavy-duty flask with a magnetic stirring bar, and dried at 135 °C under high vacuum (0.03 Torr) for 48 hours. Freshly distilled NMP (750 mL) was added to the system using a double-tipped needle under argon pressure. The mixture was degassed by bubbling argon for 30 minutes and then polymerized at 140 °C for 36 hours under vigorous stirring. After polymerization, the mixture was filtered. The solid was stirred at room temperature with 800 mL DI water for 24 hours and the mixture was filtered to remove insoluble copper powder and CuBr. The water solution was concentrated to ~50 mL and purified by ultrafiltration using 0.01 M HCl solution (2000 mL). The purified polymer solution was passed through an H^+ ion exchange column to remove any strongly bound cations. After water was evaporated, the polymer was dried under vacuum (10 Torr) at 90 °C for 48 hours to give poly(*para*-phenylene, 2,5-disulfonic acid) (PPDSA) (7.8 g, yield = 84%). Poly(biphenylene 3,3′-disulfonic acid) (PBPDSA) and poly(biphenyl disulfonic acid-*co*-phenylene disulfonic acid) copolymers were made following a similar procedure. The copolymers are denoted as B*x*P100-*x* (*e.g.*, B20P80, B40P60), where ‘*x*’ is the mol % of biphenyl segments in the copolymer.

Grafting

A typical grafting reaction was performed as follows: PPDSA (2.0 g, 8 mmol) and H_3PO_4 (16.8 g, 150 mmol) were placed in a 100 mL 3-neck round bottom flask, heated to 80 °C and stirred at 100 rpm. After 60 minutes, a homogeneous solution formed. *n*-Octylbenzene, OcB (1.9 mL, 8 mmol), was added to the solution. P_2O_5 (22.5 g, 160 mmol) was then added in batches of 0.5 g in order to keep the temperature below 80 °C. After the P_2O_5 addition was complete, an argon inlet and a condenser were fitted to the flask, the temperature was raised to 125 °C and the reaction mixture was stirred for 20 hours under argon. After cooling to room temperature, ice water (50 mL) was added to the mixture with vigorous stirring; concentrated hydrochloric acid (15 mL) was added to precipitate the polymer. The precipitate was centrifuged, washed twice with 6 M hydrochloric acid and dried under vacuum at 90 °C for 24 hours. The product was further purified by dissolving it in methanol (10 mL) and pouring the solution into hexanes (600 mL) to precipitate the polymer and remove unreacted OcB. The precipitate was filtered and dried under vacuum at 90 °C for 48 hours. 1.70 g of purified grafted polymer was obtained. The grafting degree was determined by NMR as 11%. The grafted polymer was labelled PPDSA-*g*-OcB11%. PPDSA-*g*-OcB17%, B20P80-*g*-OcB07%, B20P80-*g*-OcB18% and *n*-dodecylbenzene (DDB) grafted polymers were also obtained using similar procedures by varying the reaction temperature and time.

The grafted polymers and copolymers were dissolved in isopropanol to prepare ~20 wt% solutions and cast in 7 cm diameter Teflon dishes. The dishes were covered with a filter paper and stored in a closed cabinet for 24 hours at room temperature to let the isopropanol evaporate. The dishes were then heated for 48 hours at 90 °C under vacuum. The dried membranes could easily be removed from the dishes. 1 × 4 cm strips were then cut from the membranes.

Characterizations

^1H and ^{13}C spectra were recorded on a Varian Inova NMR spectrometer operating at a proton frequency of 600 MHz and a carbon frequency of 150 MHz. Deuterium oxide or deuterated methanol was used to dissolve polymer samples, with added dioxane or solvent residual peak as chemical shift reference. Differential Scanning Calorimetry (DSC) was carried out on a Modulated TA Q2000 Differential Scanning Calorimeter at a heating rate of 10 °C min^{-1} at a nitrogen flow rate of 40 mL min^{-1}. The samples were equilibrated in a relative humidity chamber before being hermetically sealed in an aluminium pan. Thermal analysis was performed on a TA Instrument Q500 Thermogravimetric Analyzer (TGA) at a nitrogen flow rate of 50 mL min^{-1} and a heating rate of 20 °C min^{-1} using a sample weight of 2–4 mg. The samples were dried at 110 °C under vacuum (10 Torr) for 48 hours before TGA analysis.

The viscosities of the polymers and copolymers were measured as follows: a 50 mg polymer sample was dissolved in 10 mL of dimethylformamide (DMF) and the solution was filtered using a 0.45 μm syringe filter. The polymer solution was diluted six times and the solution flow time (t) at 35.0 °C was measured at each concentration using a Cannon-Ubbelohde viscometer. The DMF solvent flow time (t_0) was also measured under the same conditions. The relative viscosity (η_{rel}) is defined as $\eta_{rel} = t/t_0$ and the specific viscosity (η_{sp}) is defined as $\eta_{sp} = \eta_{rel} - 1$. The reduced viscosity is defined as $\eta_{sp}/c = (\eta_{rel} - 1)/c$, where c is the concentration of polymer in grams per deciliter (g dL^{-1}).

The equivalent weights (EWs) and ion-exchange capacities (IECs) of the polymer membranes were determined by titration of the acid forms. The membranes were dried in a vacuum (10 Torr) at 90 °C for 24 hours, weighed, and placed in an aqueous 2 M NaCl solution for at least 24 hours. The solutions were then titrated with a 0.01 M NaOH solution using bromothymol blue as an indicator. The NaOH solution was calibrated using potassium hydrogen phthalate immediately before use. Our NMR and TGA studies showed that the membranes still contained one water molecule per sulfonic acid group under these drying conditions.[21,22] When determining EW, this one water molecule must be subtracted. So, the EW [g mol^{-1}] and IEC [meq. g^{-1}] of the membranes were calculated using the following equations:

$$\mathrm{EW} = \frac{Wt_{\mathrm{dry}}}{V_{\mathrm{NaOH}} \times M_{\mathrm{NaOH}}} - M_{\mathrm{H_2O}} \tag{1}$$

$$\mathrm{IEC} = \frac{1000}{\mathrm{EW}} \tag{2}$$

where Wt_{dry} is the weight of the "dry" membrane in grams and M_{NaOH} is the molarity of the NaOH solution. $M_{\mathrm{H_2O}}$ is the molecular weight of water, 18 g mol^{-1}, and V_{NaOH} is the volume of NaOH required to reach the end point in liters.

The membrane water uptake was determined by equilibrating the samples in a series of relative humidity chambers at room temperature. The membranes were first dried at 90 °C for 48 hours and quickly weighed on a digital electronic balance. The dry membranes in open weighing bottles were then put into each of nine saturated salt solution chambers employed for humidity control at room temperature:[33,34] LiCl (11.3%), KAc (23.1%), $MgCl_2$ (33.1%), K_2CO_3 (43.2%), $Mg(NO_3)_2$ (54.4%), $NaNO_2$ (66.0%), NaCl (75.9%), KCl (85.1%), and K_2SO_4 (97.6%). The membranes were weighed after reaching equilibrium (~48 hours) at that humidity. Wt_{wet} and Wt_{dry} are the weights of the wet and dry membranes and the water uptake (WU) was calculated by

$$\mathrm{WU} = \frac{Wt_{\mathrm{wet}} - Wt_{\mathrm{dry}}}{Wt_{\mathrm{dry}}} \tag{3}$$

Our earlier studies showed that the dry membranes still contained one water molecule per sulfonic acid group under the current drying conditions.[21,22] The number of water molecules per sulfonic acid, λ, at a given relative humidity can be calculated by the following equation:

$$\lambda = \frac{\left(Wt_{\mathrm{wet}} - Wt_{\mathrm{dry}}\right) \times \left(\mathrm{EW} + M_{\mathrm{H_2O}}\right)}{Wt_{\mathrm{dry}} \times M_{\mathrm{H_2O}}} + 1 \tag{4}$$

where EW is the equivalent weight of the polymer and $M_{\mathrm{H_2O}}$ the molecular weight of water, 18 g mol^{-1}. The water contents of the equilibrated and the dry samples were also analyzed by ^{1}H NMR. The samples were dissolved in deuterated methanol and the water to polymer peak was correlated. In order to correct the OH content of the deuterated methanol, its NMR spectrum was measured. The solution CD_2HOD area was multiplied by the OH/CD_2HOD area ratio in the reference and subtracted from the OH area.

The lengths (L_{wet}), widths (W_{wet}) and thicknesses (T_{wet}) were also measured for membranes equilibrated using saturated KCl solution (85.1% RH) at room temperature. Then these membranes were dried under vacuum (10 Torr) at 90 °C for 24 hours and their length (L_{dry}), width (W_{dry}) and thickness (T_{dry}) were measured again. The dimensional changes, ΔL, ΔW, ΔT, and ΔV are defined as

$$\Delta L = \frac{L_{\mathrm{wet}} - L_{\mathrm{dry}}}{L_{\mathrm{dry}}},$$

$$\Delta W = \frac{W_{\mathrm{wet}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}},$$

$$\Delta T = \frac{T_{\mathrm{wet}} - T_{\mathrm{dry}}}{T_{\mathrm{dry}}},$$

and

$$\Delta V = (1 + \Delta L)(1 + \Delta W)(1 + \Delta T) - 1$$

The membrane proton conductivity was measured by electrochemical impedance spectroscopy (EIS) using a four-electrode cell connected to a Solartron 1260 frequency response analyzer (FRA) and a Solartron 1287 potentiostat. The custom made PTFE cell with four graphite electrodes was enclosed in a stainless steel humidity chamber placed in a heating oven with a built-in temperature controller. The cell temperature was set to 80 °C and the relative humidity was controlled by placing a small container with a saturated salt solution inside the humidity chamber. The following saturated salt solutions were employed for humidity control[34] at 80 °C: LiCl (10.5%), KAc (15.1%), $MgCl_2$ (26.1%), K_2CO_3 (41.1%), NaBr (51.4%), $NaNO_2$ (57.4%), $NaNO_3$ (65.4%), KCl (78.9%), and K_2SO_4 (94.1%). After the sample was equilibrated at a given humidity (~12 hours), AC impedance scans were performed over a frequency range of 1 Hz to 20 kHz. The real (Z') and imaginary (Z'') impedance components were plotted and the resistance (R) was taken as the value of Z' when the curve was extrapolated to $Z'' = 0$. The humidity was increased by changing the saturated salt solution, starting with the lowest relative humidity container. The in-plane proton conductivity of the membrane was calculated using eqn (5):

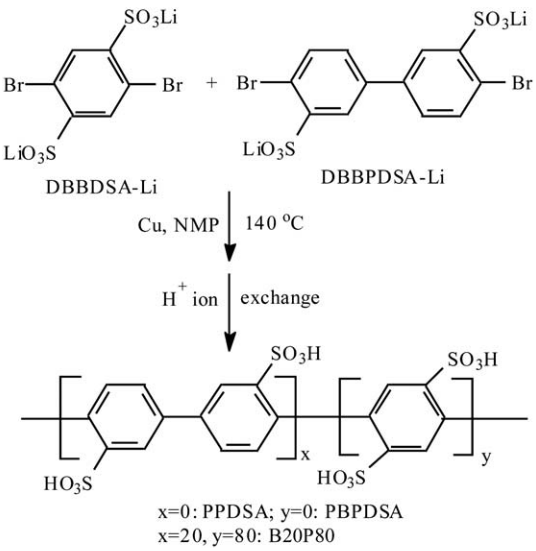
$$\sigma = \frac{L}{R \times W \times T} \tag{5}$$

where σ is the proton conductivity (S cm^{-1}), L the distance between the reference electrodes (cm), R the membrane resistance (Ω), W the membrane width (cm) and T the membrane thickness (cm).

Results and discussion

Polymerization

1,4-Dibromobenzene and 4,4′-dibromobiphenyl were sulfonated using fuming sulfuric acid to obtain 1,4-dibromobenzene-2,5-disulfonic acid (DBBDSA) and 4,4′-dibromobiphenyl-3,3′-disulfonic acid (DBBPDSA) monomers. Homopolymerization of DBBDSA and DBBPDSA, and their copolymerization at a 4 : 1 mole ratio were carried out at 140 °C in *N*-methyl



Scheme 1 Synthesis of PPDSA, PBPDSA and B20P80.

pyrrolidinone (NMP) using copper as the coupling reagent (Ullmann reaction), as outlined in Scheme 1.

The reaction is heterogeneous and the polymer precipitates during polymerization, which limits the molecular weight. The mechanism of Ullmann coupling has been extensively studied.[35–38] It was proposed that coordination of the electron-withdrawing group *ortho* to the carbon–halogen bond with the copper surface facilitates the transfer of electron density from the copper to the carbon attached to the halogen.[35,36] This complex then acts as a nucleophile to attack another molecule of aryl halide, resulting in the desired carbon–carbon bond formation.

The ^{1}H NMR spectrum of PBPDSA in CD_3OD is shown in Fig. 1(A). The three main peaks are assigned to three chemically distinguishable protons in the PBPDSA backbone: $\delta(a) = 8.45$, $\delta(b) = 7.85$, and $\delta(c) = 7.64$ ppm. The small peaks at 8.22 and 8.37 ppm are from the end group 2 and 2′ protons. The ratio of the peak areas at 8.45 to that at 8.22 ppm gives a measure of the degree of polymerization of PBPDSA, 42 for this polymer, a molecular weight of 13 000 g mol^{-1}.

A typical ^{1}H NMR spectrum of PPDSA is shown in Fig. 1(B). From the PPDSA structure, one would expect a single peak; however, there are two main peaks about 0.1 ppm apart in the region of 8.00–8.20 ppm. The peak area at 8.12 ppm is usually about 1/3 that at 8.20 ppm. This smaller peak is probably due to conformational isomerism of the rigid rod backbone. Other small peaks at 7.86, 7.88, 7.94, 8.05, and 8.15 ppm (referred to as the solvent CD_2HOD peak at 3.31 ppm) are attributed to end group protons. If there are no side reactions, we would expect one or at most, two peaks from the end residues. Since there are many more small peaks, it is possible that some of the copper activated C–Br end groups reacted with trace amounts of water during or after polymerization to form C–H end groups. Using the 7.94 ppm peak area as reference (one terminal hydrogen), the degree of polymerization of PPDSA is estimated to be 120, a molecular weight of 28 000 g mol^{-1}.

Fig. 1(C) shows the ^{1}H NMR spectrum of copolymer B20P80. The two main peaks in the PPDSA homopolymer, assigned as *a*′, become narrower in copolymer B20P80, with one extra peak in the middle. As shown in Fig. 1, the *a* proton in the copolymer has the same chemical shift as in PBPDSA homopolymer, but *b* and *c* protons shift to a higher ppm compared to the homopolymer due to the changed chemical environment in the copolymer. Since the end group peaks in the copolymer spectrum overlap with the main peaks, the degree of polymerization of B20P80 could not be estimated by ^{1}H NMR.

Some chemical shift differences between the copolymer and homopolymers can also be seen in their ^{13}C NMR spectra, Fig. 2. Since the biphenyl moieties and phenyl moieties have very similar structures and any interactions between these structures are

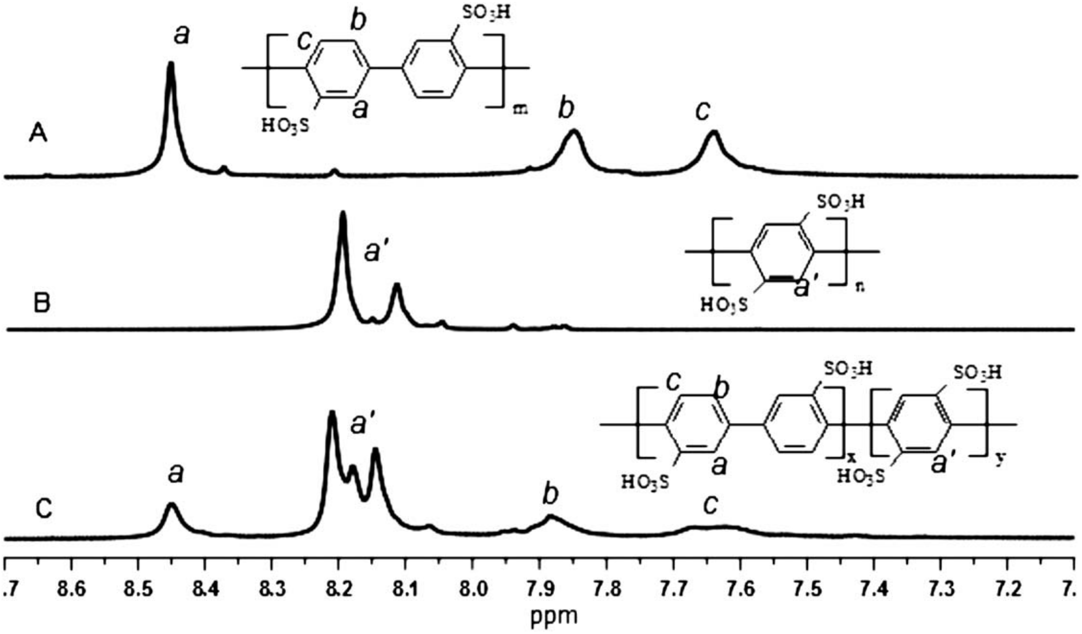


Fig. 1 600 MHz ^{1}H NMR spectra of PBPDSA (A), PPDSA (B) and B20P80 (C) in CD_3OD.

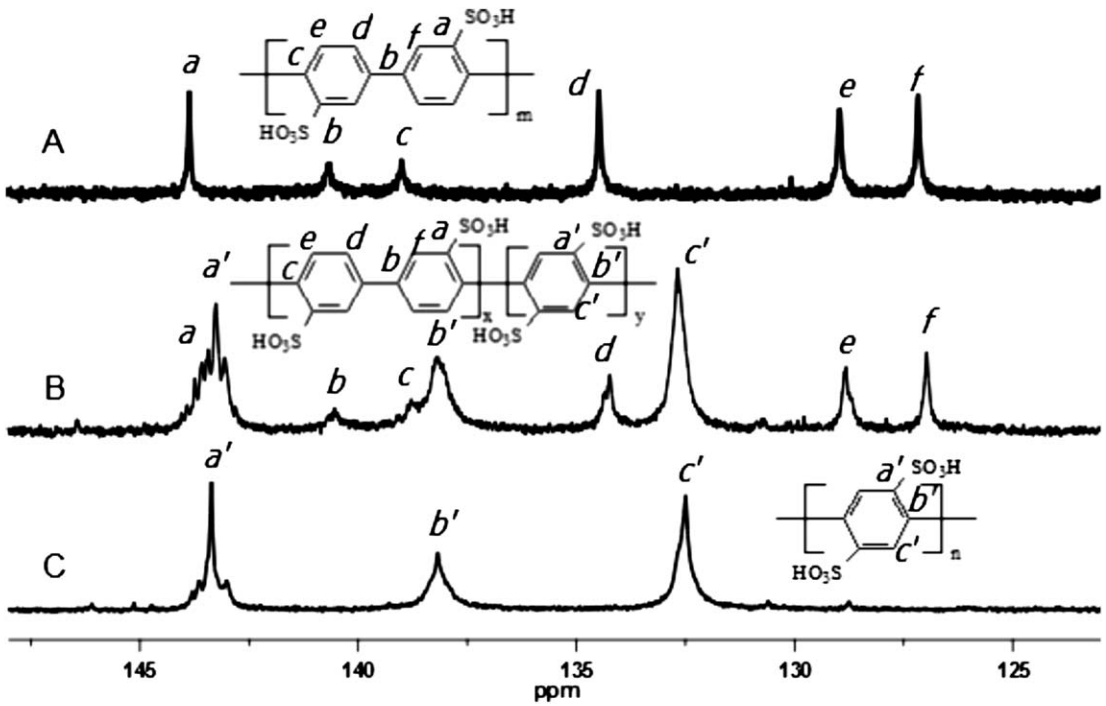
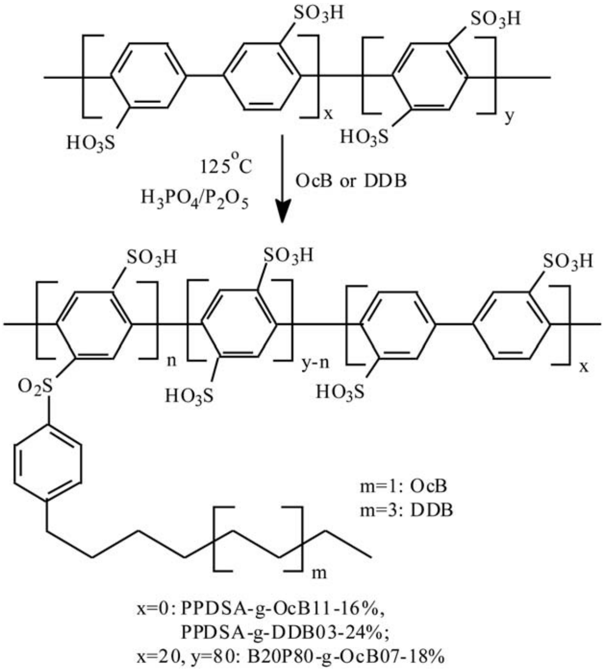


Fig. 2 150 MHz ^{13}C NMR spectra of PBPDSA (A), B20P80 (B) and PPDSA (C) in CD$_3$OD.

4–5 bonds away, the changes between homo- and co-polymers are very tiny in ^{13}C spectra.

Grafting reaction

n-Octylbenzene (OcB) and *n*-dodecylbenzne (DDB) were grafted onto PPDSA and B20P80 in polyphosphoric acid, as illustrated in Scheme 2. The grafting degree, defined as the mol% of sulfonic acid in the polymer or copolymer reacted with alkylbenzene to form sulfone groups, was controlled by varying the reaction time and temperature. It was measured by ^{1}H NMR.



Scheme 2 Synthesis of *n*-octylbenzene (OcB) and *n*-dodecylbenzene (DDB) grafted polymers.

A typical ^{1}H NMR spectrum of the purified PPDSA-*g*-OcB11% is shown in Fig. 3. The peaks at 0.89, 1.29, 1.67 and 2.66 ppm are from the *n*-octyl group protons of the grafted OcB. The peaks from 7 to 9 ppm are from the PPDSA backbone protons plus the aromatic protons of the grafted OcB. For an OcB grafted PPDSA, the grafting degree was calculated as follows. The aliphatic proton area between 0.5 and 3.0 ppm was set to 17. An area of 4 (remaining protons on the grafted alkylphenyl sulfone) was subtracted from the total aromatic proton area between 7.0 and 9.0 ppm. The numerical inverse of the remaining aromatic proton area is the grafted mole fraction. For Fig. 3, the grafting degree is calculated as $1/(13.2 - 4) \times 100\% = 11\%$. The grafted polymer is denoted as PPDSA-*g*-OcB11%. It was soluble in DMF, DMSO, DMAc, methanol, ethanol, 2-propanol, 1-butanol, 1-hexanol, *etc.*, but insoluble in hexane, methylene chloride and water. The other OcB and DDB grafted polymers were obtained using the same procedure, but varying the reaction temperature and time.

Characterizations

The viscosities of the protonated polymers and grafted polymers in DMF solution were measured at 35.0 °C. The reduced viscosity as a function of concentration for some representative polymers is shown in Fig. 4. The reduced viscosities at ~0.5 g dL^{-1} are 0.6 and 0.7 dL g^{-1} for PPDSA and B20P80 respectively. The reduced viscosities of both PPDSA and B20P80 increase when the polymer concentration is below 0.2 g dL^{-1}. The viscosities of B20P80-*g*-OcB18% and PPDSA-*g*-DDB24% are higher than those of the

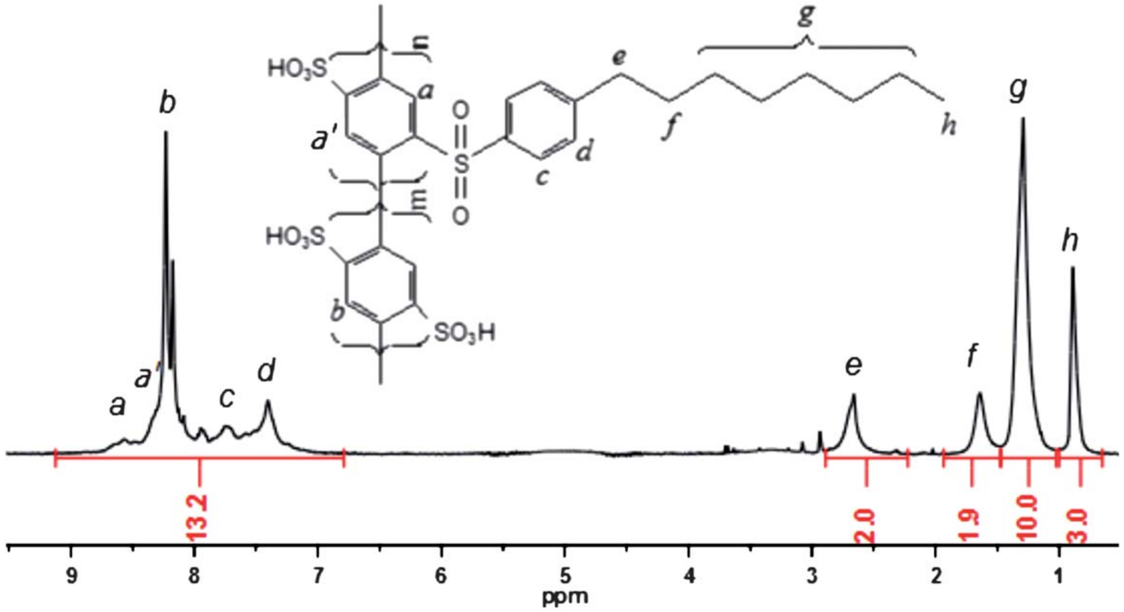


Fig. 3 600 MHz ^{1}H NMR spectrum of PPDSA-*g*-OcB11% in CD$_3$OD (water and solvent peaks were suppressed for illustration purpose).

base polymers, 1.2 and 1.9 dL g^{-1} at ~0.5 g dL^{-1}, rising when the polymer concentration is below 0.3 g dL^{-1}. All the grafted polymers behave similarly. When viscosities were measured in dilute LiCl solutions (not shown here), they were slightly lower but followed the same trend as in salt-free solution, rising when polymer concentration dropped below 0.2–0.3 g dL^{-1}. This is not a typical polyelectrolyte effect. A similar phenomenon was also found in nitrated,[39] sulfonated[40] and carboxylated[41] poly(*p*-phenylene) polymers. These polymer backbones are linear and rigid, very different from flexible polyelectrolytes in dilute solution. Several theories have been proposed to describe these unusual characteristics.[42–44] Ballauff *et al.*[43] suggested that this 'very pronounced polyelectrolyte effect' was caused by a long-range intermolecular electrostatic repulsion of the dissolved macroions rather than due to conformational changes. A self-consistent mode-coupling theory was proposed by Miyazaki *et al.*[44] The reduced viscosities at ~0.5 g dL^{-1} concentration, plus other characterization, for some polymers and grafted polymers are listed in Table 1. The reduced viscosities of all grafted polymers are higher than those of base polymers; the higher the OcB or DDB content, the higher the reduced viscosity.

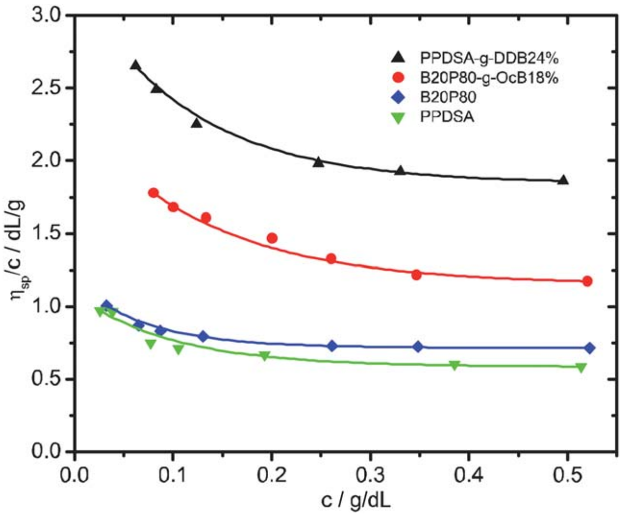


Fig. 4 The reduced viscosity as a function of concentration for protonated PPDSA, B20P80, B20P80-*g*-OcB18% and PPDSA-*g*-DDB24% in DMF at 35.0 °C. (Cannon-Ubbelohde viscometer, type: 0C C453).

The equivalent weights (EWs) and ion exchange capacities (IECs) of PPDSA, B20P80 and their grafted polymers were determined by titration; the results are given in Table 1. Our earlier studies showed that vacuum dried (10 Torr, 90 °C) PPDSA membranes still contained about one water molecule per sulfonic acid group.[21,22] The EW values listed in Table 1 have already been corrected for that water content and are in good agreement with the theoretical ones within experimental error. As a comparison, data for Nafion NR-212 are also listed.

The thermal stability of the polymer and grafted polymer membranes was investigated by thermogravimetric analysis (TGA). Fig. 5 shows representative TGA curves for some polymers. Most of them show a 3-stage degradation behaviour. Although the polymers were dried under vacuum at 110 °C for 48 hours immediately prior to the analysis, they still showed an initial weight loss due to the evaporation of tightly bound water, and plateaued at or above 210 °C. All tightly bound water was lost below 210 °C. PPDSA remains stable to about 310 °C; the other polymers start losing weight at a somewhat lower temperature. The weight fraction lost in the second weight loss stage for the base polymer corresponds to a loss of about one acid plus one water molecule for every two acid groups. A third stage of weight loss starts at about 510 °C; this might be associated with the degradation of polymer aromatic backbones or further acid loss. The TGA curve of B20P80 is similar to that of PPDSA. The initial weight loss is due to the evaporation of tightly bound water. B20P80 has two further stages of weight loss, like PPDSA. However, B20P80 starts to lose sulfonic acid groups at 280 °C, 30 °C lower than PPDSA; because it has 33% *p*-phenylene mono-sulfonic acid moieties, it is

Table 1 Reduced viscosity (η_{sp}/c), equivalent weight (EW), ion exchange capacity (IEC), proton conductivity (σ) and solubility of PPDSA, B20P80 and their grafted polymers, together with Nafion NR-212 as comparison

	η_{sp}/c^a	EW^b	EW$_{cal}{}^c$	IEC^b	σ^d	
Sample	dL g^{-1}	g mol^{-1}	g mol^{-1}	meq. g^{-1}	S cm^{-1}	Solubility (H-form)
PPDSA	0.6	120	118	8.3	0.39	H_2O, alcohol, DMF, DMAc, DMSO
B20P80	0.7	125	126	8.0	0.44	H_2O, alcohol, DMF, DMAc, DMSO
PPDSA-*g*-DDB03%	1.0	130	128	7.7	0.28	H_2O, alcohol, DMF, DMAc, DMSO
B20P80-*g*-OcB07%	1.1	157	148	6.4	0.26	alcohol, DMF, DMAc, DMSO
PPDSA-*g*-OcB11%	0.9	159	154	6.3	0.15	alcohol, DMF, DMAc, DMSO
PPDSA-*g*-DDB10%	1.4	160	157	6.3	0.18	alcohol, DMF, DMAc, DMSO
PPDSA-*g*-OcB16%	1.2	175	173	5.7	0.13	alcohol, DMF, DMAc, DMSO
B20P80-*g*-OcB18%	1.2	193	191	5.2	0.09	alcohol, DMF, DMAc, DMSO
PPDSA-*g*-DDB24%	1.9	230	227	4.3	0.05	alcohol, DMF, DMAc, DMSO
Nafion NR-212	n/a	1050	1100	0.95	0.03	n/a

[a] Measured at 0.5 g dL^{-1} in DMF, 35.0 °C. [b] Determined by titration. [c] Calculated EW, based on structure. [d] Measured at 80 °C, 51% RH.

less stable than PPDSA with 100% *p*-phenylene di-sulfonic acid repeat groups (two strong electron-withdrawing groups). After the initial water loss, grafted polymers PPDSA-*g*-DDB24% and B20P80-*g*-OcB18% start to lose sulfonic acid groups at about 255 °C. The large fractional weight loss between 255 and 500 °C implies that grafted long-tail alkylbenzene groups probably are being lost, as well as acid groups.

The water content of the dried polymer samples can be estimated from the TGA curves. For PPDSA, the drop due to water loss up to 210 °C is 13.1 weight percent; the remaining polymer weight percent is 86.9. λ, the mole ratio of water (molecular weight, 18 g mol^{-1}) to polymer PPDSA (EW = 118 g mol^{-1}), is $13.1 \times 118/(18 \times 86.9) \approx 1.0$. For B20P80 (EW = 126 g mol^{-1}), the weight loss up to 210 °C is 11.4 percent; the remaining polymer is 88.6 weight percent; λ is $11.4 \times 126/(18 \times 88.6) \approx 0.9$. For PPDSA-*g*-DDB24% (EW = 227 g mol^{-1}), λ is $8.3 \times 227/(18 \times 91.7) \approx 1.1$; while for B20P80-*g*-OcB18% (EW = 191 g mol^{-1}), λ is $9.7 \times 191/(18 \times 90.3) \approx 1.1$. The dry polymer water content determined by TGA is in good agreement with the titration results, Table 1, and consistent with our previous findings for PPDSA.[21,22]

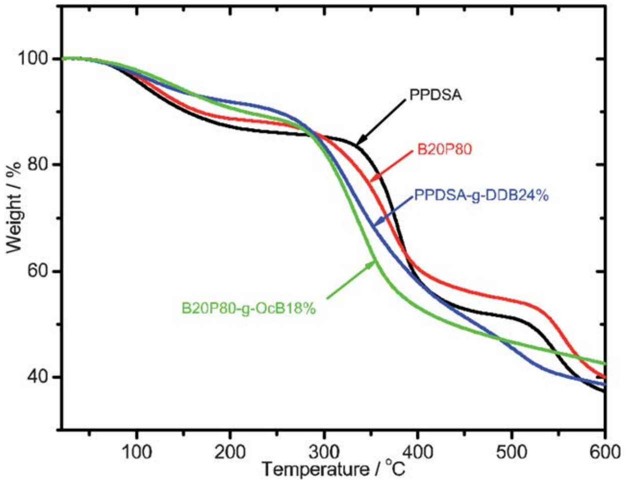


Fig. 5 TGA curves for PPDSA, B20P80, PPDSA-*g*-DDB24% and B20P80-*g*-OcB18% at a nitrogen flow rate of 40 mL min^{-1} and at a heating rate of 20 °C min^{-1}.

Water uptake and dimensional changes

The water uptake of a PEM plays an important role in its proton conductivity and mechanical properties. Generally, the absorbed water facilitates proton transport, but excessive water uptake decreases polymer modulus and strength as well as proton conductivity. Therefore, water uptake needs to be controlled in the appropriate range. The water uptake and λ at room

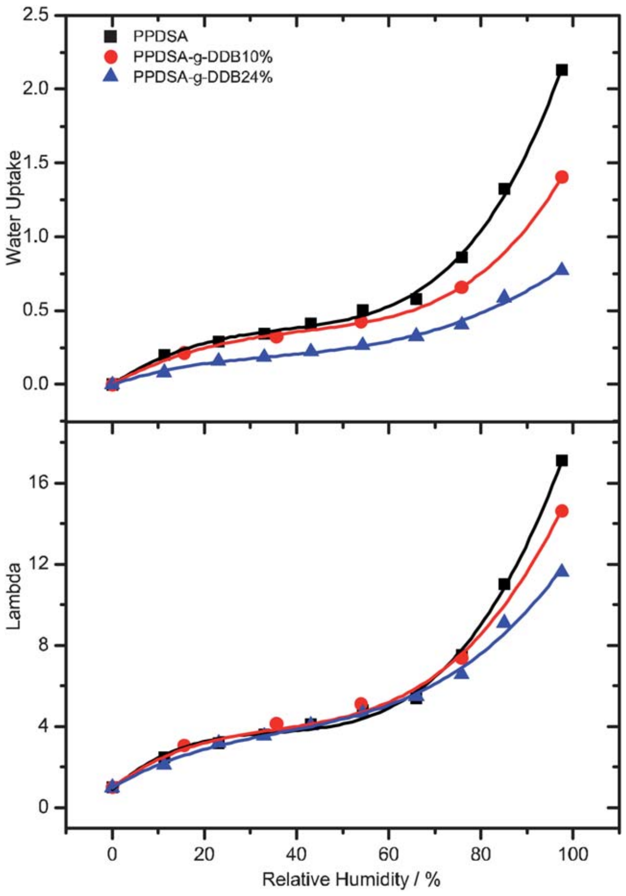


Fig. 6 Water uptake (top) and lambda (bottom) as a function of relative humidity at room temperature for PPDSA, PPDSA-*g*-DDB10% and PPDSA-*g*-DDB24% membranes.

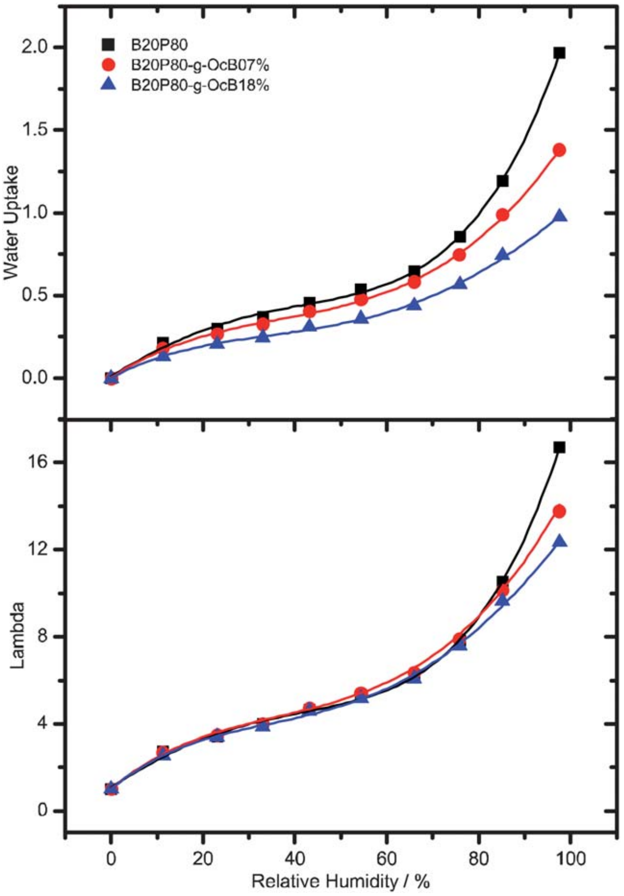


Fig. 7 Water uptake (top) and lambda (bottom) as a function of relative humidity at room temperature for B20P80, B20P80-*g*-OcB07% and B20P80-*g*-OcB18% membranes.

temperature of some selected polymer membranes as a function of relative humidity are shown in Figs. 6 and 7.

PPDSA fractional water uptake increases with increasing relative humidity, reaching 2.13 at 98% RH which corresponds to absorption of 17.1 water molecules per sulfonic acid group. At this high humidity the PPDSA membrane loses its mechanical stability, deforms and sticks to the glass weighing vial. The water uptake at high relative humidity decreases dramatically with increasing grafted long-tail alkylbenzene content. At 98% RH, a dried 10% DDB graft's weight increased by a factor of 1.40 while that of a 24% DDB graft increased only 0.77, corresponding to λs of 14.6 and 11.6, respectively. The decreasing water uptake and λ is probably due to the hydrophobic bonding of the grafted alkylbenzene groups that act as physical crosslinks preventing the polymer gel from expanding indefinitely at high relative humidity. Below 75% RH, λ at a given relative humidity is independent of the graft content; the curves overlap that of PPDSA. DDB grafted PPDSA membranes are brittle at low relative humidity. At high relative humidity, the materials become very soft and lose their strength very quickly.

The fractional water uptake of B20P80 reached 1.97 at 98% RH, corresponding to 16.7 water molecules per sulfonic acid group. Grafting with *n*-octylbenzene, OcB, reduced the fractional water uptake to 1.38 for B20P80-*g*-OcB07%, and 0.98 for B20P80-*g*-OcB18%, corresponding to λs of 13.8 and 12.3, respectively. B20P80-*g*-OcB07% and B20P80-*g*-OcB18% membranes have a Young's modulus of ~6 GPa and an elongation at break of ~1% at 20% RH (stress–strain curves not shown), which was indicative of inherent brittleness of this material. At high relative humidity, the membranes became very soft and lost their mechanical strength. In boiling water, the membranes broke into small pieces but did not dissolve.

The water uptake and dimensional changes of some membranes from 0 to 85% RH were also investigated and the results are summarized in Table 2. At 85% RH, both PPDSA and B20P80 absorbed more water than their own weights and became very soft, making it impossible to measure their dimensional changes. Within experimental error, all the grafted polymer films swelled equally in lateral dimensions (in-plane direction) but much more in thickness, indicating that these membranes are anisotropic. It may be speculated that almost all polymer molecules are in domains with their backbone parallel to the membrane surface. As the membrane absorbs water, chain separation increases. Swelling in the plane is hindered by other domains with chains oriented perpendicular to the swelling direction, but the through-plane swelling has no such hindrance. It can be seen from Table 2 that through-plane swelling decreased as long-tail alkyl benzene grafting increased. This can be rationalized by postulating that the long-tails act as physical crosslinks due to hydrophobic bonding and limit the swelling in this direction.

State of water

Since the polymers and their grafts absorbed a large amount of water when equilibrated at high RH, the question arises – what fraction was strongly bound? Therefore, low-temperature DSC was performed on samples equilibrated at different RHs; typical examples are shown in Fig. 8.

B20P80-*g*-OcB18% equilibrated at 98% RH shows an exothermic freezing peak at about −25 °C in the cooling cycle and an endothermic melting peak at about −5 °C in the heating cycle, which indicates the presence of loosely bound, freezable water in the polymer membrane. The areas of these two peaks are very close; the average is about 68 J g^{-1}. Since the heat of fusion of water is about 333.6 J g^{-1},[45] the freezable water in this grafted copolymer was calculated as 0.20 g per gram of sample. The water uptake was about 0.98 for B20P80-*g*-OcB18% equilibrated

Table 2 Water uptakes and dimensional changes of some membranes from 0 to 85% RH at room temperature

		Dimensional change			
Sample	WU^a	ΔL^a	ΔW^a	ΔT^a	ΔV^a
PPDSA	1.32	—	—	—	—
B20P80	1.19	—	—	—	—
B20P80-*g*-OcB07%	0.95	0.14	0.14	0.49	0.94
PPDSA-*g*-OcB11%	0.94	0.13	0.13	0.48	0.89
B20P80-*g*-OcB18%	0.74	0.13	0.14	0.42	0.83
PPDSA-*g*-DDB24%	0.59	0.12	0.13	0.29	0.63

[a] WU, ΔL, ΔW, ΔT and ΔV are the water uptake, length, width, thickness and fractional volume changes of the membranes from 0 to 85% RH.

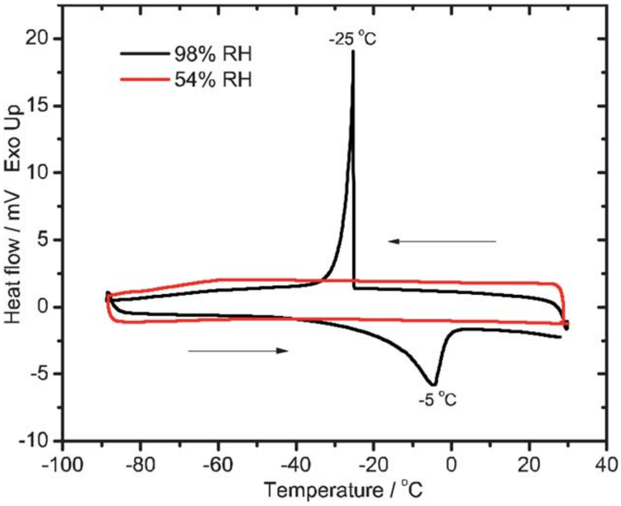


Fig. 8 DSC thermograms of the B20P80-*g*-OcB18% membrane (heating rate: 10 °C min^{-1}). Samples were equilibrated at 98% or 54% RH prior to measurements.

at 98% RH, corresponding to ~0.54 g water per gram of sample, including one water molecule per SO_3H in the dried sample. The freezable water fraction, determined by DSC, is $0.20/0.54 = 0.37$ of the total water uptake. The rest, 0.63, is non-freezable water, strongly bound to the sulfonic acid groups. When the water content is calculated as lambda, out of the total 12.3 water molecules per sulfonic acid group, there were 4.6 freezable water molecules and 7.7 non-freezable water molecules. When the polymer was equilibrated at 54% RH, $\lambda = 5.5$, there were no exotherms or endotherms within the scanned temperature range (Fig. 8, bottom), suggesting that all the absorbed water was strongly bound. The total λ and its freezable and non-freezable components for all samples equilibrated at 98% RH, determined by DSC, are listed in Table 3. Within the experimental error, the non-freezable water content for all membranes is ~8 water molecules per sulfonic acid. As a comparison, at room temperature and 100% RH, the numbers of non-freezable bound water molecules per sulfonic group in Nafion 117 were reported as 9 and 10 by Lue and Shieh,[46] and Corti *et al.*,[47] respectively at 100% RH using FTIR, but about 5–7 using DSC by Pineri *et al.*[48] At 0 °C and 100% RH, Pineri *et al.*[48] found a λ of 6.0. Table 3 shows that the effect of grafting OcB or DDB is to decrease the loosely bound, freezable water in the polymers.

Table 3 The nature of absorbed water determined by DSC for PPDSA, B20P80 and their grafted polymers equilibrated at 98% RH at room temperature compared with that of Nafion 117 (at 100% RH)

		λ		
Sample	WU[a]	Total	frz[b]	nfrz[c]
PPDSA	2.13	17.1	8.1	9.0
B20P80	1.97	16.7	7.9	8.8
PPDSA-*g*-DDB03%	1.89	16.3	7.0	9.3
B20P80-*g*-OcB07%	1.38	13.8	6.7	7.1
PPDSA-*g*-OcB11%	1.44	14.8	7.0	7.8
PPDSA-*g*-DDB10%	1.40	14.6	6.1	8.5
PPDSA-*g*-OcB16%	1.20	13.7	6.1	7.6
B20P80-*g*-OcB18%	0.98	12.3	4.6	7.7
PPDSA-*g*-DDB24%	0.77	11.6	3.5	8.1
Nafion 117[d]	0.24	14.7	5.6	9.1
Nafion 117[e]	0.22	13.4	3.1	10.3
Nafion 117[f]	0.18	11.0	4.2	6.8

[a] Water uptakes. [b] Freezable water. [c] Non-freezable water. [d] Data calculated from ref. 46. [e] Data calculated from ref. 47. [f] Data calculated from ref. 48.

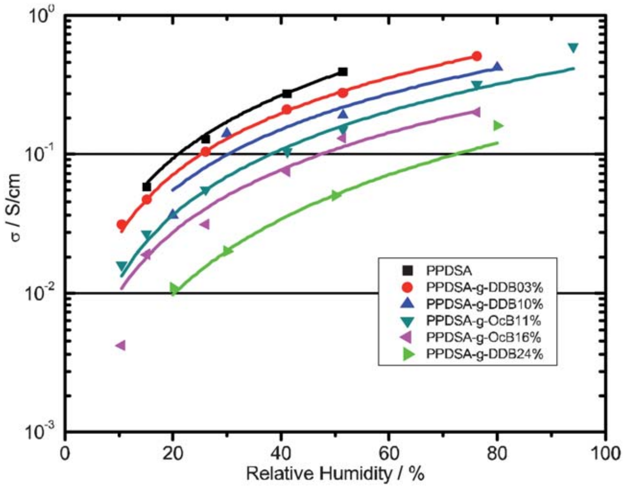


Fig. 9 Proton conductivity of PPDSA and its grafted polymer membranes as a function of relative humidity at 80 °C.

Proton conductivity

Proton conductivity is very important for fuel cell performance. High proton conductivity is needed to achieve high power densities in PEMFCs. The proton conductivity of PPDSA, B20P80 and their grafted polymers, as well as Nafion NR-212 for comparison, as a function of relative humidity was measured at 80 °C, Fig. 9 and 10.

As can be seen, all the new polyelectrolytes have higher proton conductivity than Nafion® NR-212. At 80 °C, PPDSA and B20P80 conductivities are about 11-14 times higher than that of

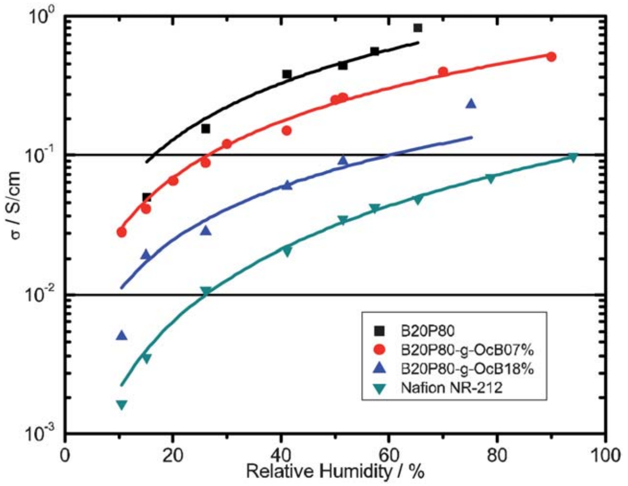


Fig. 10 Proton conductivity of B20P80, B20P80-*g*-OcB07%, B20P80-*g*-OcB18% and Nafion NR-212 as a function of relative humidity at 80 °C.

Nafion® NR-212 over the measured relative humidity range. It should be noted that the conductivity of B20P80 exceeds that of PPDSA. We believe that the presence of the biphenyl segments might contribute to an increase in the frozen-in free volume with a resultant increase of proton conductivity. No structural characterization was performed, however, to quantify the conformational or configurational differences. Since PPDSA and B20P80 have a very high IEC ($\geq$8.0 meq. g^{-1}) and are water soluble, at high relative humidity the membranes absorb large amounts of water, swell significantly and eventually deform; their conductivity could not be measured above 65% RH. Among all the grafted polymer membranes, the conductivity of PPDSA-*g*-DDB03% is very close to that of PPDSA, but the resultant membrane is still water-soluble, losing its mechanical strength and dimensional stability at higher relative humidity. The proton conductivity of the polymer membranes decreases with the increase of alkylbenzene graft fraction. However, PPDSA-*g*-DDB10%, PPDSA-*g*-OcB11% and B20P80-*g*-OcB07% membranes are water insoluble with proton conductivity about three times that of Nafion® NR-212. Their conductivity of 0.10-0.14 S cm^{-1} at 30% RH and 80 °C reaches or exceeds the US Department of Energy 2015 target of 0.10 S cm^{-1}. The observed high conductivity, especially at low relative humidity, is attributed to the high IEC and high λ due to the "frozen-in free volume"[21] in these membranes.

Conclusions

Poly(*para*-phenylene disulfonic acid), PPDSA, and poly(biphenyl disulfonic acid-*co*-phenylene disulfonic acid), B20P80, were synthesized through Ullmann coupling in *N*-methyl pyrrolidinone using copper as the coupling reagent. Water insoluble poly(*para*-phenylene sulfonic acid)s were obtained by grafting long-tail alkylbenzene on the polymer backbones *via* sulfone bridges. NMR, TGA, DSC and viscometry were used for structural characterization of the polymers. The grafting degree was tailored by varying the grafting reaction temperature and time. Water absorption and conductivity for all the materials were measured. These polymers had a very high IEC and absorbed water strongly at low humidity, which facilitated fast proton transport. Membranes cast from these polymers exhibited excellent proton conductivity at elevated temperature and low relative humidity, tenfold higher than that of Nafion® 212. This exceptional conductivity could make these materials great candidates for membranes in proton exchange fuel cells operating at elevated temperature, if the mechanical properties could be improved.

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