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Synthesis and characterization of controlled molecular weight disulfonated poly(arylene ether sulfone) copolymers and their applications to proton exchange membranes☆

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Abstract

tert-Butylphenyl terminated disulfonated poly(arylene ether sulfone) copolymers with controlled molecular weights (M_n), 20–50 kg mol^{-1}, were successfully prepared by direct copolymerization of the two activated halides, biphenol and the endcapper, 4-*tert*-butylphenol. The high molecular weight copolymer (molecular weight over 80 kg mol^{-1}) was also synthesized with 1:1 stoichiometry without an endcapping reagent. The chemical compositions and the molecular weights of the endcapped copolymers were characterized by their ^{1}H NMR spectra utilizing the 18 unique protons at the chain ends. Modified intrinsic viscosity measurements in 0.05 M LiBr/NMP solution further correlated well with NMR results. Combining the endcapping chemistry with proton NMR end group analysis and intrinsic viscosity measurements, one can demonstrate a powerful tool for characterizing molecular weight of sulfonated poly(arylene ether sulfone) random copolymers. This enables one to further investigate the influence of molecular weight on several critical parameters important for proton exchange membranes, including water uptake, in-plane protonic conductivity and selected mechanical properties. These are briefly discussed herein and will be more fully described in subsequent publications.

Keywords: Disulfonated poly(arylene ether sulfone) copolymer; Controlled molecular weight; Proton exchange membrane fuel cells

1. Introduction

Proton exchange membrane (PEM) fuel cells attracted much attention in recent years as promising green energy device. One of the key components for PEM fuel cell is the polymeric electrolyte membrane, which serves as the barrier for fuels and the electrolyte for transporting protons from the anode to cathode. According to the type of the fuel used, there are two kinds of PEM fuel cells: hydrogen/air fuel cells and direct methanol fuel cells (DMFCs). The perfluorinated sulfonic acid copolymers such as DuPont's Nafion®, are promising PEM materials due to their good mechanical, thermal and chemical stability as well as good protonic conductivity at lower temperatures (<80 °C). However, the high methanol crossover, the reduction in conductivity at higher temperature and the cost are the major drawbacks that limit their commercial application [1–3]. Therefore, to develop the alternative membrane materials that will overcome these drawbacks is important.

Many families of polymers with differing chemical structures and various strategies for incorporation of sulfonic acid groups have been explored as PEM materials [3]. Sulfonated poly(arylene ether sulfone)s are good candidates due to their good acid and thermal oxidative stabilities, high-glass transition temperatures and excellent mechanical strengths [4]. Sulfonated poly(arylene ether sulfone)s have been earlier prepared via polymer modification route, where sulfonate groups were achieved on polymer chain by sulfonating agents, such as concentrated sulfuric acid or sulfur trioxide [5,6]. Our group have reported synthesis of poly (arylene ether sulfone) copolymers by directly copolymerizing sulfonated monomers. This procedure is more preferable relative to post modification method because of its easy control

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☆ For the special issue of Polymer in celebrating Dr James E. McGrath's 70th birthday.

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of the degree of sulfonation, high acidity, and the ease of side reactions related to the post polymer modification technique [7–9]. Other copolymers synthesized in our group by direct copolymerization for PEMs have included: sulfonated poly (arylene ether phosphine oxide) [10], poly(arylene ether ketone)s [11,12], poly(phenyl sulfide sulfone)s [13], substituted polyphenylenes [14], poly(arylene ether) copolymers containing aromatic nitriles [15], and naphthalene based polyimides [16].

Molecular weight is a fundamental parameter affecting all mechanical behavior of polymers as is well known. Most reports of new proton exchange membrane materials have included information on ion content expressed either by the equivalent weight (EW, $g\,mol^{-1}$) or by the ion exchange capacity (IEC, mequiv. g^{-1}), protonic conductivity, and water uptake. Despite the large body of research on this topic, there is almost nothing in the PEM literature describing molecular weights of candidate materials, even including Nafion [3]! Wang et al. [17] previously synthesized controlled molecular weight (M_n) poly(arylene ether sulfone) (M_n from 20 to 40 $kg\,mol^{-1}$) by offsetting stoichiometry with a *t*-butylphenyl endcapping reagent. The *t*-butylphenyl concentrations relative to the polymer backbone were characterized by proton NMR to calculate the molecular weight of the copolymers. They provided intrinsic viscosity (IV) data for these copolymers, and they found that the intrinsic viscosities were not comparable to those of non-sulfonated polymers, since the polymer electrolyte chains interact via sulfonate groups. In our group, we have begun to utilize NMP with 0.05 M LiBr to measure the intrinsic viscosity. The small amount of salt effectively suppressed the polyelectrolyte effect allowing improved characterization of the ion containing materials.

The overall aim of our research is to establish molecular weight vs. mechanical and electrical property correlations for sulfonated poly(arylene ether sulfone) copolymers that could be used as proton exchange membranes in fuel cells. In this paper, poly(arylene ether sulfone) copolymers with 35 mol% disulfonated monomer repeat unit were successfully synthesized via direct copolymerization method [8,9]. The number average molecular weights of the copolymers were controlled from 20 to 50 $kg\,mol^{-1}$ by *tert*-butylphenol endcapping reagent and was characterized by the combination of proton NMR and intrinsic viscosity. The intrinsic viscosities were measured using NMP as solvent with 0.05 M lithium bromide to break up the ion group aggregation. The linear correlation of Log M_n with Log intrinsic viscosity showed that this method can provide more accurate molecular weight information. On the basis of this, the effects of the molecular weight on the properties of proton exchange membranes, such as water swelling, protonic conductivity, and mechanical properties were investigated.

2. Experimental

2.1. Materials

Highly purified 4,4′-dichlorodiphenyl sulfone (DCDPS) and biphenol (BP) were kindly provided by Solvay Advanced Polymers and Eastman Chemical, respectively. They were well dried in vacuo before polymerization but otherwise used as received. The 4-*tert*-butylphenol (TB) endcapper was purchased from Aldrich and was purified by sublimation. The 3,3′-disulfonated 4,4′-dichlorodiphenyl sulfone (SDCDPS) was synthesized as reported earlier [8]. The solvent *N*,*N*-dimethylacetamide (DMAc, Fisher) was vacuum-distilled from calcium hydride onto molecular sieves and stored under nitrogen before use. Potassium carbonate was dried in vacuo before copolymerization. Toluene and methanol were obtained from Aldrich and used as received.

2.2. Synthesis of disulfonated poly(arylene ether sulfone) copolymers with controlled molecular weight

The aromatic nucleophilic step growth copolymerization was conducted in a three-neck flask equipped with a mechanical stirrer, nitrogen inlet and a Dean Stark trap. One typical polymerization for a controlled molecular weight of 40 $kg\,mol^{-1}$ (BPS35-40) copolymer was as follows: the 4,4′-biphenol (5.000 g, 26.866 mmol), 4,4′-dichlorodiphenyl sulfone (5.075 g, 17.671 mmol), 3,3′-disulfonated 4,4′-dichlorodiphenyl sulfone (4.674 g, 9.515 mmol) and 4-*tert*-butylphenol (0.096 g, 0.641 mmol) were added to the flask, followed by 1.15 equiv. of potassium carbonate. Dry DMAc was introduced to afford about a 20% solids concentration and toluene was used as an azeotropic agent. The reaction mixture was heated under reflux at 160 °C for 4 h, which stripped off most of the toluene to dehydrate the system. Finally, the bath temperature was raised slowly to 175 °C for 24 h, which caused the DMAc to reflux. The viscous solution was cooled to room temperature, and then diluted with DMAc to form about a 20% copolymer solution. The copolymer was isolated by precipitation in deionized water, filtered and dried in a vacuum oven at 120 °C for 24 h. Dried polymer was ground into powders and then washed extensively with methanol and deionized water several times to completely remove salt and any potential residual endcapping reagent, and finally vacuum dried at 120 °C for 24 h. The molecular weights of the copolymers were controlled by varying the ratio of monofunctional monomer TB to difunctional monomer 4,4′-biphenol. The copolymers synthesized were designated as BPS35-*xx* (salt form) or BPSH35-*xx* (acid form), where 35 means that all copolymers were containing 35% (mol%) of disulfonated repeat units, and *xx* represents the target molecular weight as *xx* $kg\,mol^{-1}$.

2.3. Membrane preparation

The salt form copolymers were dissolved in DMAc (5–10% w/v) at room temperature. The solutions were first filtered with 0.45 μm syringe filters, and then cast onto clean glass substrates. The films were carefully dried with infrared heat at gradually increasing temperatures (up to ∼60 °C). The membranes were removed from the glass plates by submersion in water and then were dried in vacuo at 150 °C for at least 24 h.

The salt form membranes were completely converted into their acid forms by boiling the membranes in 0.5 M sulfuric acid for 2 h, followed by boiling in deionized water for another 2 h. The acid form membranes were washed with deionized water completely and then stored in fresh deionized water at room temperature.

2.4. Characterization

^{1}H NMR spectra were conducted with a Varian Unity 400 NMR spectrometer in DMSO-d_6. Intrinsic viscosities (IV) were determined in NMP with or without 0.05 M LiBr at 25 °C using an Ubbelohde viscometer.

The water uptake was obtained by measuring the difference in the weight between dry and fully hydrated membranes. The sample films were equilibrated in deionized water at room temperature for at least 48 h. Then the membranes were dried in the vacuum oven at 110 °C for 24 h. Weights of wet and dry membranes were measured. The ratio of weight gain to the original membrane weight was taken as the water uptake (WU) according to Eq. (1)

$$\mathrm{WU} = \frac{W_{\mathrm{wet}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}} \times 100\% \tag{1}$$

where W_{wet} and W_{dry} are the masses of wet and dried samples, respectively.

Proton conductivity at 30 °C at full hydration (in liquid water) was determined in a window cell geometry [18] using a Solartron (1252 + 1287) Impedance/Gain-Phase Analyzer over the frequency range of 10 Hz–1 MHz. The cell geometry was chosen to ensure that the membrane resistance dominated the response of the system. The resistance of the film was taken at the frequency which produced the minimum imaginary response [19]. The conductivity of the membrane can be calculated from the measured resistance and the geometry of the cell according to Eq. (2)

$$\sigma = \frac{l}{Z'A} \tag{2}$$

where σ is the proton conductivity, l is the length between the electrodes, A is the cross sectional area available for proton transport, and Z' is the real impedance response.

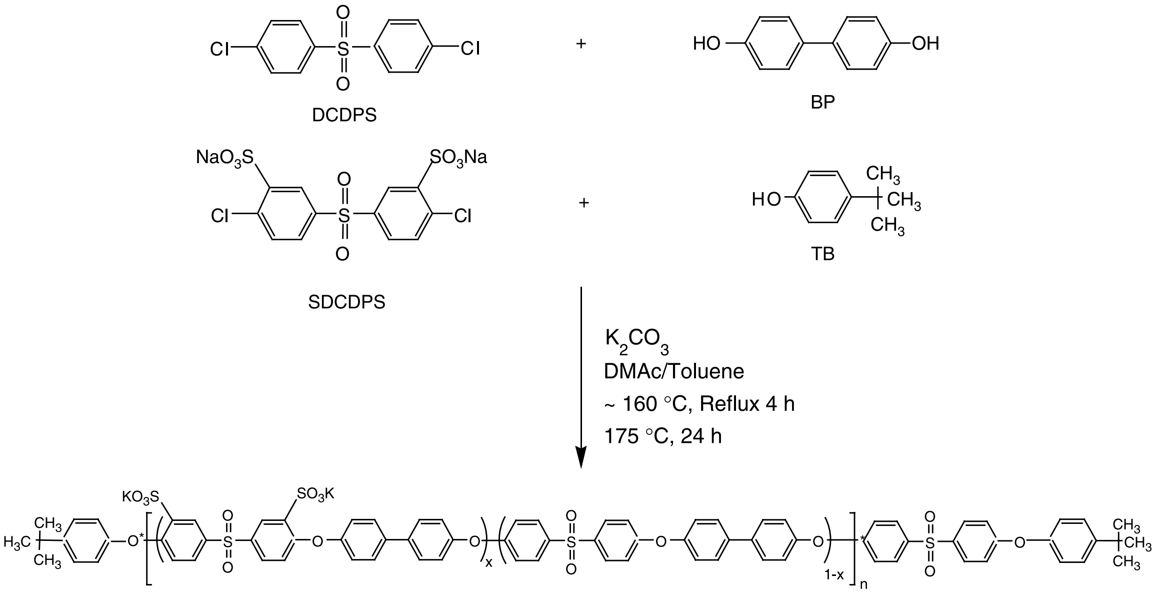
In determining proton conductivity in liquid water, membranes were equilibrated at 30 °C in DI water for 24 h prior to the testing.

Mechanical tensile tests were performed using an Instron 4468 Universal Testing Machine at room temperature and 40% relative humidity, with a crosshead displacement speed of 5 mm min^{-1}. The gauge lengths were all set to 40 mm. Pneumatic grips were employed with a pressure of 207 kPa. The specimens with thickness around 50 μm and size of 60 mm × 12 mm were used for testing. For each film, four replicates were tested. Since the stress–strain curves of the specimens that lasted the longest under stretching represent the real mechanical behavior of the films better (i.e. the specimen did not fail by macroscopic defects), the curve with the largest elongation at break was chosen to plot in Fig. 5. Thermogravimetric analysis was performed in air with a heating rate of 5 °C min^{-1} to determine the water contents of the test specimens, which were shown to be about 10%.

3. Results and discussion

3.1. Synthesis and characterization of copolymers

The *tert*-butylphenyl terminated BPS35 series copolymers were successfully synthesized by the aromatic nucleophilic substitution reaction of 3,3′-disulfonated 4,4′-dichlorodiphenyl sulfone, 4,4′-dichlorodiphenyl sulfone, 4,4′-biphenol and 4-*tert*-butylphenol in DMAc, which contained toluene as an azeotropic agent to dehydrate the system (Scheme 1). The monofunctional



Scheme 1. Synthesis of *tert*-butylphenyl terminated poly(arylene ether sulfone) copolymers containing 35 mol% disulfonate repeat unit.

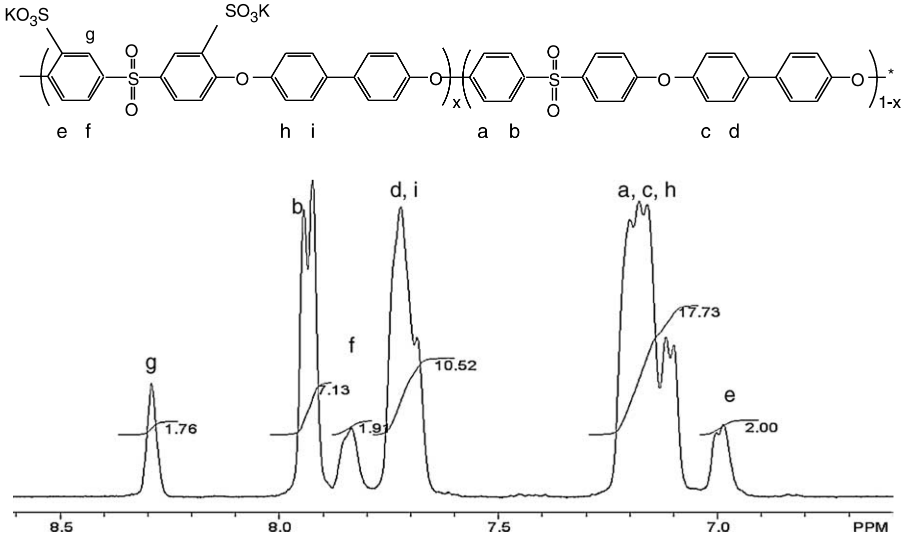


Fig. 1. The copolymer structures and degree of sulfonation were determined by ^{1}H NMR spectra in aromatic region (BPS35-50 copolymer).

monomer, 4-*tert*-butylphenol, was used as the endcapping reagent, in which the phenol functional group has similar reactivity as biphenol. The mole ratio of the *tert*-butylphenol monomer to the difunctional comonomers was varied to control the stoichiometry in accordance with the modified Carother's equation [20]. The molecular weights were controlled from 20 to 50 kg mol^{-1}. For all copolymers, the mole ratio of SDCDPS to DCDPS was fixed to 3.5/6.5. The copolymers were first isolated by precipitation of the reaction solutions in stirred deionized water and dried in oven. Then the dried crude copolymers were ground into powders and washed extensively with methanol and deionized water to remove any possible residual endcapping agent and salt. It is very important that all the inorganic salts involved in the condensation process, and any possible residue starting monomers need to be removed as complete as possible, since any of these impurities in the final products would interfere the characterization of viscosity and molecular weight by NMR as discussed in the following paragraphs.

For comparison, a BPS35-control copolymer with high-molecular weight was synthesized with 1:1 stoichiometry and no endcapping reagent.

The ^{1}H NMR spectra were used to identify the molecular structure of the copolymers and to confirm the degree of sulfonation. The peak assignments of the aromatic region of BPS35-50 (Fig. 1) confirm the anticipated chemical structure. The degree of sulfonation was determined from the integral ratios of proton peaks e, f, g, and b. The chemical shifts for the three protons (e, f and g) attached to the sulfonated unit are 7.0, 7.7 and 8.3 ppm, respectively, while the peak at 7.8 ppm corresponds to the proton b attached on the non-sulfonated unit. The mole content of sulfonated unit in BPS35-50 copolymer chain is 34.6% based on the integrals of b proton to the average of e, f and g protons. The calculation could be described by the Eq. (3):

$$\text{Degree of sulfonation (\%)} = \frac{\lfloor (H_e + H_f + H_g)/3 \rfloor /2}{\lfloor (H_e + H_f + H_g)/3 \rfloor /2 + H_b/4} = 34.6\% \tag{3}$$

Table 1 lists the contents of sulfonated units in the series of copolymers. All the values are in good agreement with the ratio of feed monomers (SDCDPS/DCDPS—35/65), which suggests that all the starting monomers were successfully incorporated into the copolymer chains.

The molecular weights of the copolymers were calculated from the relative ^{1}H NMR integrals of the *tert*-butyl endgroups and the aromatic resonances. For example, Fig. 2 shows the proton NMR spectrum of a copolymer with target molecular weight 50 kg mol^{-1} (BPS35-50), in which methyl protons were observed at 1.2 ppm. The presence of the *tert*-butyl peak in BPS35-50 proton NMR confirms that *tert*-butylphenol was chemically attached at the ends of copolymer, and only the chemical bonded TB groups are useful in quantitatively calculating the molecular weight of one polymer chain based on its ^{1}H NMR spectrum. While there are 18 methyl protons on the two *tert*-butyl endgroups of one polymer chain, two sources contribute to the aromatic protons: the sulfonated or non-sulfonated aromatic repeat units in the interior of the polymer chain, and the terminal phenyl rings. There are 16 and 14 phenyl protons for non-sulfonated and sulfonated units,

Table 1
Characterization of BPS35 copolymers

Target M_n (kg mol^{-1})	M_n by NMR (kg mol^{-1})	IV[a] (dL g^{-1})	SDCDPS (%)	
			Target	Experimental (by NMR)
20	19.9	0.43	35	33.9
30	28.8	0.48	35	34.1
40	38.1	0.63	35	34.7
50	48.0	0.74	35	34.6
Control[b]	83.1[c]	1.04[d]	35	34.2

[a] Intrinsic viscosities were determined in 0.05 M LiBr/NMP solution at 25 °C.

[b] Control copolymer was prepared with 1:1 stoichiometry without *tert*-butylphenol.

[c] M_n of the control copolymer was derived from the log(IV)–log(M_n) plot.

[d] Intrinsic viscosity of the control copolymer without LiBr was 2.79 dL g^{-1}.

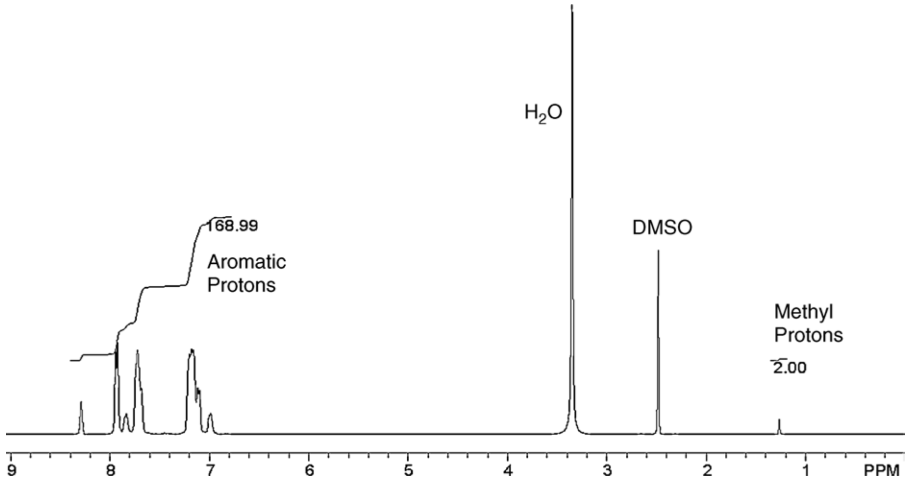


Fig. 2. Molecular weights can be calculated from the relative ^{1}H NMR integrals of the *tert*-butyl endgroups and the aromatic resonances (BPS35-50 copolymer in DMSO-d_6).

respectively. Since the experimental degree of sulfonation for BPS35-50 was calculated to be 34.6% by proton NMR, the average protons per repeat unit is $16\times0.654+14\times0.346=15.3$, and the total number of phenyl protons from the interior repeat units are 15.3n, where n is the number of the average polymer chain repeat units. Assuming 100% conversion of all monomers in the condensation polymerization, two types terminal groups existed in these copolymers, as shown in Scheme 1. One terminal group (left side) is a simple 4-*tert*-butylphenol residue, which contains four phenyl protons Another terminal group (right side) is a residue of 4-*tert*-butylphenol, which contains four phenyl protons, and is attached with either a disulfonated monomer (34.6% possibility) or non-sulfonated dihalide monomer (65.4% possibility), so the total phenyl protons at this end is $4+(8\times0.654+6\times0.346)=11.3$. Therefore, the total average phenyl protons from two terminal groups are $11.3+4=15.3$, and the total phenyl protons in one polymer chain is $15.3n+15.3$. The number ratio of aromatic to methyl protons equals to the integration ratio of the two types protons in ^{1}H NMR spectrum, so the molecular weight of copolymer was calculated from the Eq. (4)

$$\frac{15.3\times n+15.3}{18}=\frac{168.99\leftarrow \text{Aromatic protons}}{2\leftarrow \text{Methyl protons}} \tag{4}$$

where n is the number of repeat unit, which was calculated to be 98.41. Accordingly the average molecular weight (M_n) of the BPS35-50 copolymer was calculated to be: $M_n=98.41\times 481.7\ (\text{g mol}^{-1})+585.4\ (\text{g mol}^{-1})=47{,}989\ \text{g mol}^{-1}$, where 481.7 g mol^{-1} is the average molecular weight per repeat unit, and 585.4 g mol^{-1} is the molar mass of the two endgroups. Molecular weights of 20–40 kg mol^{-1} copolymers were prepared and characterized using the similar technique (Table 1). It is obvious that the experimental molecular weights are in close agreement with the targeted values, which on the other hand confirmed the close 100% conversion of all the monomers.

Viscosity is one of the most important parameters in charactering polymer property. Simple dilute solution viscosity measurements are widely used in polymer science, but have not been well developed for ion-containing PEMs. One possible reason is that by comparing neutral and charged

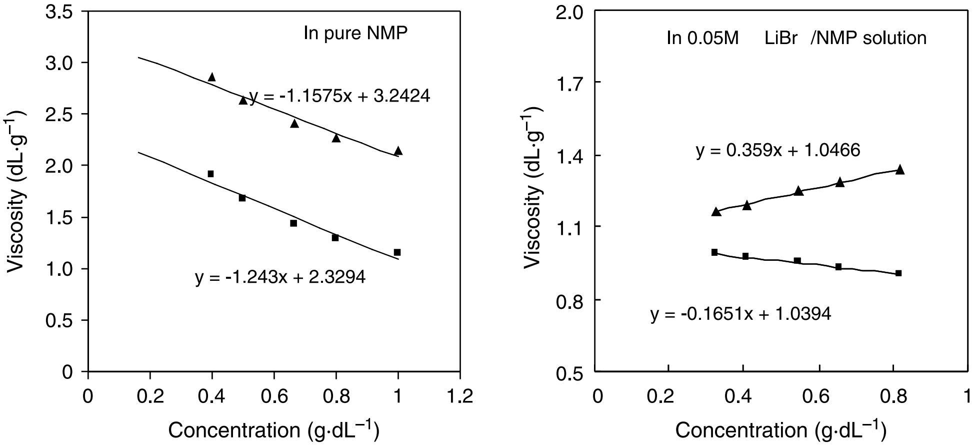


Fig. 3. Correlations of reduced (▲) and inherent (■) viscosities with copolymer concentration of BPS35-control in pure NMP (a), and NMP containing 0.05 M LiBr (b).

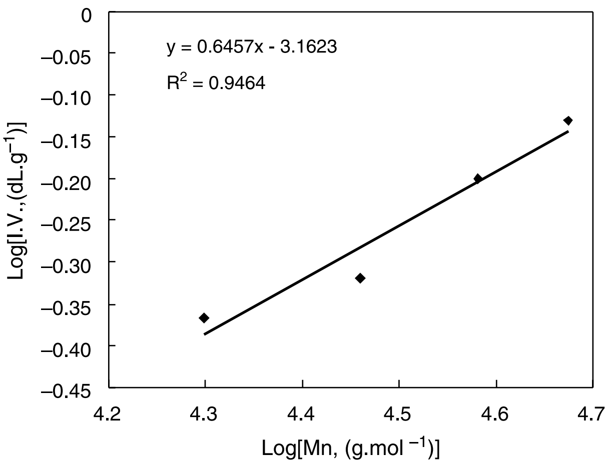


Fig. 4. Relationship between Log(intrinsic viscosity) and Log(M_n) for BPS-35 copolymers.

macromolecules, neutral systems retain their random coil conformation down to very low concentrations. In contrast, it is well known that as one dilutes a charged macromolecule the so called ‘polyelectrolyte effect’ appears. This effect produces a more extended chain showing higher dilute solution viscosities as the concentration is reduced, largely due to charge repulsion [21].

It is also well known within the biomembrane community that dilute solution viscosities of polyelectrolytes should be measured in the presence of a low-molar mass salt, which is able to screen the charges. It is recognized that the optimum salt concentration might depend upon the chemical structures, molar mass range, charged densities, etc. We have established that as little as 0.05 M LiBr allows one to obtain the correct intrinsic viscosity values (Fig. 3).

Both reduced and inherent viscosities of BPS35-control were measured in NMP with or without LiBr in the polymer concentration range of 0.15–1.0 g dL^{-1}. Correlations of viscosities and concentration are plotted in Fig. 3(a) (without LiBr) and (b) (with 0.05 M LiBr). In the case of polymer solution without LiBr, both reduced and inherent viscosities increase as polymer concentration decreases, consistent with the idea of the polyelectrolyte effect. However, the introduction of lithium bromide into polymer solution made the viscosities (reduced and inherent)–concentration relationships of BPS35-control very similar to a non-charged polymer solution, as shown in Fig. 3(b). The conventional extrapolation of reduced and inherent viscosities to the infinite dilute solution gives us the relatively accurate intrinsic viscosity of BPS35-control (1.04 dL g^{-1}), which is much lower than the value measured in pure NMP (2.79 dL g^{-1}). As summarized in Table 1, intrinsic viscosities of all copolymers agree quite well with their designed and measured molecular weights. The intrinsic viscosity measurements of the copolymers could be compared to one another since the only difference in polymer structure is the endgroups, which is less than 1% by weight.

A fairly good linear relationship of Log(M_n) and Log(IV) for 4-*tert*-butylphenol endcapped copolymers is plotted in Fig. 4. This relationship provides us an alternative but powerful tool in characterizing molecular weights of polymers with similar chemical composition. For example, the molecular weight of BPS35-control copolymer was estimated from the above linear relationship to be 83.1 kg mol^{-1}. Moreover, this technique can be used to other PEM as well, such as sulfonated poly(arylene ether ketone)s, polyimides and more.

3.2. Membrane characterization

These controlled molecular weight copolymers enabled us to examine the influence of molecular weight on several different critical parameters important for proton exchange membranes. Sulfonated copolymers tend to phase separate in hydrophilic and hydrophobic domain morphology. Water resides in these hydrophilic domains and plays a critical role in proton transport [22]. Kim et al. [23] reported increasing water uptake and proton conductivity with increasing degree of disulfonation for BPSH copolymers. High-proton conductivity is desirable but high water uptake results in excessive swelling and poor dimensional stability. Understanding the influence of molecular weight on water uptake and conductivity for the copolymer at a particular degree of disulfonation will lead in optimizing the overall fuel cell performance. In Table 2, the water uptake and conductivity of BPSH35-*xx* copolymers in liquid water at room temperature is provided. The water uptake was found to decrease modestly as the molecular weight of

Table 2
The results of water swelling and conductivity test for BPSH35 copolymers with controlled molecular weights in liquid water at 30 °C

Target M_n (kg mol^{-1})	IEC[a] (mequiv. g^{-1})	Water uptake (%)	Conductivity (S cm^{-1})
20	1.49	40	0.070
30	1.50	43	0.080
40	1.52	42	0.081
50	1.52	38	0.080
Control	1.50	36	0.077

[a] IEC = (1000/$MW_{repeatunit}$) × degree of sulfonation × 2(–SO_3H), where degree of sulfonation was determined by ^1H NMR.

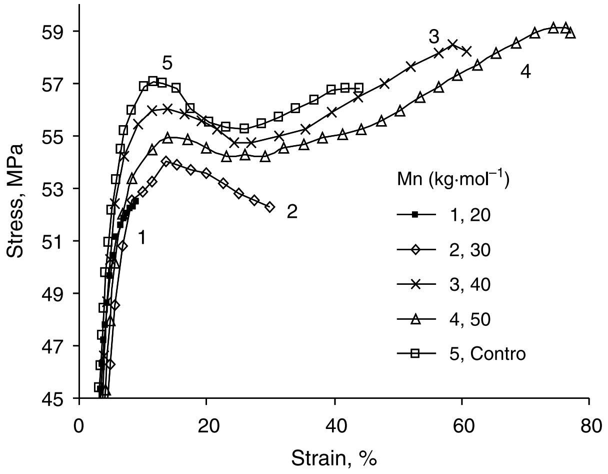


Fig. 5. Stress–strain curves of BPSH35 copolymers (thin films) as function of molecular weight.

Table 3
The tensile properties of BPSH35 copolymers (thin films) as function of molecular weight

M_n (kg mol^{-1})	Modulus (GPa)	Yield strain (%)	Yield stress (MPa)	Strength[a] (MPa)	Elongation at break[a] (%)
20	1.46±0.28	3.04±0.38	39.6±7.7	52.0	15.7
30	1.08±0.23	4.34±0.21	38.0±8.4	52.1	32.3
40	1.36±0.24	4.83±0.28	47.9±7.7	57.7	63.4
50	1.53±0.27	4.23±0.69	44.1±10.2	59.0	78.7
Control	1.92±0.30	3.68±0.79	58.1±7.1	66.3	48.8

[a] For strength and elongation at break data, the values are from the highest stress–strain curves.

BPSH35-*xx* increased from 20 to 80 kg mol^{-1}. But, at this point it is difficult to correlate the influence of molecular weight for the copolymers on proton transport under fully hydrated conditions. The small deviations in the conductivity values are well within the experimental error range of 10%. However, determination of proton conductivity under partially hydrated conditions for these copolymers with varying molecular weight is ongoing. This will give a better understanding about the influence of molecular weight on proton transport.

The mechanical properties of PEMs, such as fatigue resistance, are very important for the development of non-fluorinated PEMs operated at both room and elevated temperatures. It is believed that mechanical properties of PEMs should be enhanced by high molecular weight. We have generated stress–strain curves that show the modulus, strength, and elongation to break of PEM films were significantly influenced by the molecular weight. These materials were measured under ambient conditions with 40% relative humidity to investigate the effect of molecular weight (Fig. 5 and Table 3). It can be seen that Young's modulus, yield stress/strain and elongation at break were all affected by the sample molecular weight. Among these parameters, the elongation at break varied the most with molecular weight, increasing from approximately 15% for BPSH35-20 to 78% for BPSH35-50. This behavior was attributed to more chain entanglements at higher molecular weights. It is reasonable to expect that high-molecular weight could be important for preventing pinhole formation, even at elevated temperatures, and the molecular weight may also improve fatigue resistance and long term stability, which will be investigated in the future.

4. Conclusions

A series of controlled molecular weight, poly(arylene ether sulfone) copolymers containing 35 mol% disulfonated monomer per repeat unit were synthesized and characterized by ^{1}H NMR, intrinsic viscosity, water uptake, proton conductivity, and mechanical property. Small amount of lithium bromide (0.05 M) in NMP can effectively suppress the 'polyelectrolyte effect' appearing in measuring the intrinsic viscosity of a charged macromolecule, which allowed obtaining more accurate data than previously used simple dilute solution viscosity measurements. Combing ^{1}H NMR analysis of end groups and intrinsic viscosity measurements, we can conclude that the molecular weights of the synthesized copolymers were from 20 to 50 kg mol^{-1}, which are much closed to our designed values. The effects of molecular weights on the properties of proton exchange membranes were also studied. It was found that with increasing the molecular weights, the water uptake decreased modestly. And the molecular weight was found to have no obvious influence on proton conductivity under fully hydrated conditions. Furthermore, the mechanical properties of the membrane, such as the modulus strength and elongation at break were improved by increasing the molecular weight as well. The characterizations of conductivity, water uptake, and mechanical properties provide us some very useful guidelines in designing sulfonated polymers as PEM.

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