Hyperbranched-linear poly(ether sulfone) blend films for proton exchange membranes

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Abstract

Hyperbranched poly(ether sulfone) polymers having sulfonyl chloride end-groups is blended at up to 30 w% with linear poly(ether ether ether sulfone)s and a two-phase system is generated via spinodal decomposition upon drying from a DMAc solution. Conversion of the end-groups from sulfonyl chloride to sulfonic acid is accomplished using $16 M H_2SO_4$ that is also believed to introduce additional sulfonic acid groups at the interface of the linear polymer. The blend films before and after conversion to sulfonic acid have similar tensile strengths as films composed of solely linear polymer (yield stress >40 MPa and Young's modulus >3 GPa m). These films are designed to test the viability of hyperbranched polymers as fuel cell membranes. Proton conductivities of up to $0.03 S cm^{-1}$ are observed at 80 °C and 90% R.H indicating a good potential for use of hyperbranched polymers as a proton conduction material.
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Keywords: Hyperbranched polymer; Fuel cell; Poly(ether sulfone); Spinodal decomposition

1. Introduction

Development of fuel cells for commercial applications has been hindered by development of suitable materials, including those for the proton exchange membrane [1–3]. The current membrane used for many fuel cell assemblies is Nafion®, a sulfonated fluoropolymer, and many materials being developed mimic its basic architecture of a continuous polymer electrolyte [1,4]. Many materials have been synthesized with high proton conductivities though they also have high water uptake and fuel crossover due to the mechanism of proton conduction for continuous polyelectrolytes [4,5]. A high water uptake makes water management at operating temperatures difficult while fuel crossover diminishes power output.

The mechanism used to describe the proton conduction in Nafion and other proton exchange membranes involves the formation of water-filled pores and channels within the film.[6,7] Proton conduction occurs by a 'hopping' mechanism through the film. The pores are generated by rearrangement of the polymer chain to bring hydrophilic sulfonic acid groups in contact with the water and migrate hydrophobic segments away [6]. The mobility of the polymer chains, however, is problematic at elevated temperatures. Not only is management of the liquid water critical for proton hopping more difficult as one approaches the boiling point, but the coiling of the linear chains due to increased temperature begins to also destabilize the pores [8,9].

Hyperbranched polymers have a large number of end-groups and a dendritic-like structure [10]. Unlike dendrimers, hyperbranched polymers can be synthesized in one step from AB_X-type monomers, where X is two or more. The resulting polymer has an assortment of branch points, linear units, and terminal groups that, for the case of AB_2-type monomers, have on average one end-group per repeat unit. The resulting products do not crosslink and have lower viscosity than linear analogous. The lower viscosity is a result of fewer chain entanglements by the polymer chain. This can lead to difficulties in using hyperbranched polymers in situations where mechanical robustness is necessary.

To overcome the mechanical deficiencies of hyperbranched polymers yet access the multitude of functional groups that

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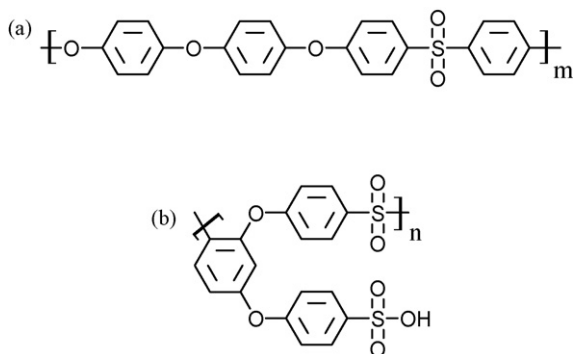
Scheme 1. (a) Linear poly(ether sulfone) and (b) Hyperbranched poly(ether sulfone) linear unit.

they contain, we proposed to prepare blends with a linear analogue to serve as a structural polymer. Hyperbranched poly(ether sulfone) bearing sulfonic acid end-groups blended with linear poly(ether sulfone) (Scheme 1) was targeted as sulfonated PES-type polymers have shown potential as fuel cell membranes [11]. The blend film is expected to undergo spinodal decomposition into bi-continuous phases with a high concentration of acid groups from the hyperbranched polymer for proton conduction in one phase and retain the mechanical robustness of the linear polymer in the other. Herein, we report the preparation of hyperbranched and linear polymer blends and preliminary investigations for use as a fuel cell membrane.

2. Experimental

2.1. General procedures

Used as received: K_2CO_3, toluene, $POCl_3$, 4,4'-dichlorodiphenylsulfone, acetone, methanol, and $FeCl_3$. DMAc was distilled from CaH_2 and stored over molecular sieves. ODH was recrystallized from a methanol-water solution. 16 M H_2SO_4 was prepared by dilution of conc. H_2SO_4.

2.2. Linear poly(ether ether ether sulfone) synthesis (PEEES)

A typical synthesis is as follows: [11] A 250 mL round-bottom flask equipped with a Dean–Stark trap, condenser, and magnetic stirrer was charged with 8.34 g (41.2 mmol) ODH, 7.52 g (54.5 mmol) K_2CO_3, 36 mL DMAc, and 20 mL toluene. The system was blanketed with N_2 and heated to 160 °C for 1.5 h to azeotrope water. The system was then heated to 175 °C for 2 h to remove the majority of toluene. The remaining toluene was removed at 50 °C for 1.5 h using a diaphragm vacuum pump. To the flask was then added 11.80 g (41.1 mmol) 4,4'-dichlorodiphenylsulfone and 20 mL DMAc. A reflux condenser was equipped and the system was heated under N_2 at 172.5 °C for 16 h. The viscous solution was precipitated in acetone, washed with methanol, dried in vacuo, dissolved in DMAc, precipitated in methanol, and vacuum dried yielding 13.3 g (78% yield) of polymer.

The viscosity of the product was 0.40 for a 0.5 g dL^{-1} solution in DMAc at 30 °C and the molecular weight was determined to be 42,600 g mol^{-1} by GPC. The onset of thermal decomposition was determined by TGA to be 394 °C and the glass transition temperature was determined to be 182 °C by DSC.

2.3. HB-SO₂Cl synthesis

Preparation of the AB_2 monomer, 4,4'-(m-phenylene-dioxy)-bis-(benzenesulfonyl chloride), has been previously reported and the procedure was used without modification.[12] The prepared AB_2 monomer (1.02 g, 2.22 mmol) was dissolved in $CHCl_3$ (2.74 mL) with $FeCl_3$ (0.106 g, 0.65 mmol) and heated under N_2 at 70 °C for 10 h. The $CHCl_3$ was then removed via rotary evaporation and the remaining solid was re-dissolved in DMAc then precipitated in methanol. The precipitate was filtered off, washed with methanol, and then dried in vacuo at 80 °C (0.771 g, 82% yield).

2.4. Film preparation

Polymer films were cast from a solution of 20 w% solids in DMAc. The desired weight percentages of the linear and hyperbranched-sulfonyl chloride polymers were co-dissolved with $FeCl_3$ (eq. $FeCl_3$ per hyperbranched chain) then cast onto a glass plate using a doctor blade set to a 125 μm gap. The cast films were then dried in vacuo at 150 °C for 3 h. Some films (as noted) received an additional heating time of 2 h at 220 °C.

2.5. Hyperbranched end-group conversion

Films were immersed in 16 M H_2SO_4 for 3 h at 50 °C. They were then removed, diluted with H_2O, and then immersed in 0.1 M HCl for 2 h. Films were then placed between two glass plates and dried in vacuo at 30 °C for 2 h.

2.6. Measurements

Viscosity was measured using a #2 Ostwald dropping pipette in a Kinematic viscosity bath TV-5S water bath at 30 °C. Polymer solutions were prepared in a volumetric flask to a concentration of 0.5 g dL^{-1} in DMAc.

Differential scanning calorimetry (DSC) was performed on a Seiko Exstar 6000 from 20 °C to 300 °C at 10 °C min^{-1} under N_2 atmosphere in an Al pan. All sample were run for two cycles and calculation were based off the second cycle.

Thermogravimetric analysis (TGA) was performed with a Seiko TMA/SS 6000 at 10 °C min^{-1} under a N_2 flow using Pt pans.

Gel permeation chromatography (GPC) was performed with a Viscotek TDA 302 using DMF with 0.01 M LiCl. Molecular weights and polydispersity were determined by comparison against referenced polystyrene standards.

Tensile measurements were performed with a Toyo Baldwin Tensilon/UTM-II-20 and recorded on a Toyo Baldwin AR-6000 chart recorder. Test samples were prepared as 5 mm × 40 mm

strips and thickness was measured via micrometer. Gap between grips was set to 2 cm. Draw speed was 4 mm s^{-1}. All calculations are based on a minimum of five samples.

Nuclear magnetic resonance (NMR) was performed on a JEOL JNM-AL-300 NMR using DMSO as the deuterated solvent.

Infrared spectroscopy (FT-IR) was performed on a Jasco FT/IR 460 Plus. Samples were prepared by preparation of thin films (<10 μm thick) or by solvent deposition onto a KBr plate and dried.

Polarized optical microscopy (POM) was performed on an Olympus BX51 using a 50× magnification lens with 10× magnification eyepiece for 500× magnification total. Images were captured using an Olympus PDMCII/OL digital camera. Scale bars are estimated from measurement of items with a known thickness.

Ion exchange capacity (IEC) was measured via titration using Eq. (1):

$$IEC = (eq_1 - eq_2)/m_{film} \qquad (1)$$

where IEC is the ion exchange capacity, eq_1 is the equivalents of NaOH in the stock solution, eq_2 is the equivalents of NaOH after sample incubation, and m_{film} is the dry mass of the polymer film. Samples were vacuum dried, weighed, and then placed in 15 mL 0.01 M NaOH for 4 h. A 10 mL aliquot of either the NaOH stock or film-incubated NaOH was removed and titrated with 0.01 M HCl while monitoring with a TOA-DK HM-20P pH meter. To avoid affects of dissolved CO$_2$, the data below pH 3.5 was fitted to ideal strong acid-strong base equilibrium and the initial NaOH concentration (eq_1 or eq_2) was extrapolated from the fitted equation. Concentration of the stock solution was always measured the same day as the sample NaOH solution to minimize differences in CO$_2$ concentration and pH drift.

Proton conductivity was measured using a Solatron SI 1280B and a four-probe PTFE cell using bare Pt plates for the source and drain electrodes and Pt wires as the voltage electrodes. Proton conductivity was calculated by Eq. (2):

$$PC = D_V (Z \, W_{film} \, T_{film})^{-1}, \qquad (2)$$

where PC is proton conductivity in S cm^{-1}. Measurements used an AC amplitude of 0.01 mA and a sweep frequency of 20,000–0.1 Hz to determine the complex impedance and phase angle. The complex impedance at the minimum phase angle (ideally zero) was used for Z. The voltage electrodes were set 1.5 cm (D_V) apart. Samples were cut to 5 mm (W_{film}) × 40 mm dimensions via cutting die. Thickness (T_{film}) was measured by micrometer after cutting. Temperature and humidity were controlled by an Espec model #SH-221 oven. All samples were initially measured from the dry state.

3. Results and discussion

3.1. Preparation of poly(ether ether ether sulfone)

Linear poly(ether ether ether sulfone) (PEEES) was prepared via nucleophilic aromatic substitution of 4,4′-
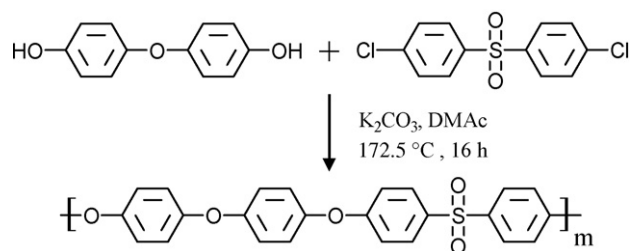
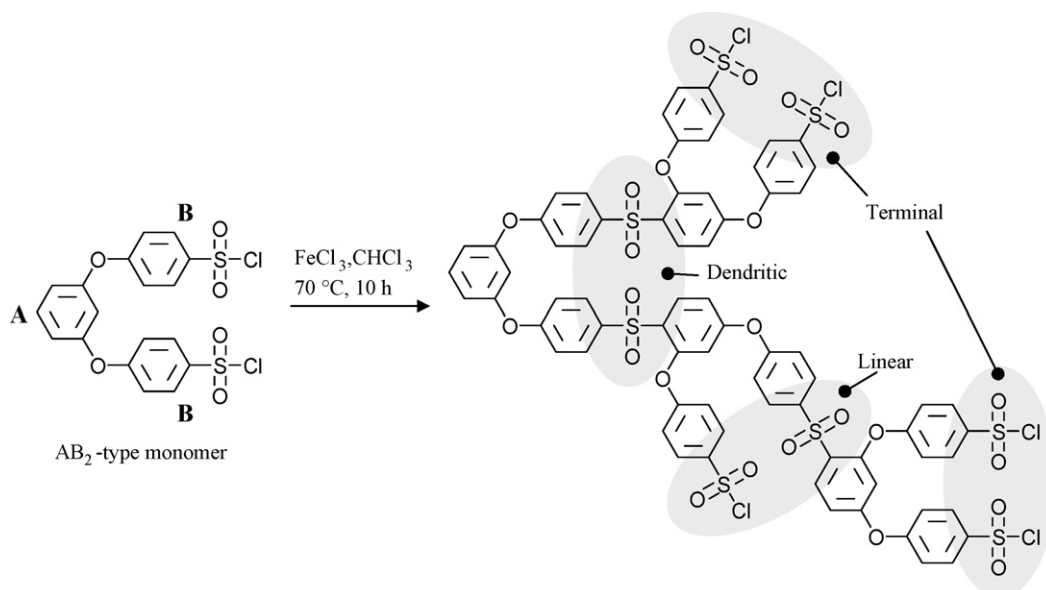Scheme 2. Synthesis of poly(ether ether ether sulfone) (PEEES).

di(chlorophenyl)sulfone with 4,4′-di(hydroxyphenyl)ether (Scheme 2) [11]. Trace amounts of water remaining in the 4,4′-di(hydroxyphenyl)ether that can adversely affect generation of high molecular weight polymer were accounted for by comparing the ^{1}H NMR spectra of the starting material to that of a deuterated solvent blank. The deuterated solvent's residual proton peak was used as an internal standard to differentiate between water from the solvent and water from the starting material so an equimolar amount of 4,4′-di(chlorophenyl)sulfone could be calculated and added. Typically, the purified reaction product had a viscosity of 0.40 in DMAc. GPC analysis in DMF indicates a molecular weight (M_w) of 42,600 g mol^{-1} and a polydispersity index (PDI) of 1.98. ^{1}H NMR indicates a doublet at 7.88 ppm (*ortho*-sulfone protons) and an unresolved multiplet at 6.78–7.16 ppm. The doublet and unresolved multiplet integrate to a 1:3 ratio, consistent with what would be expect for the linear PEEES.

3.2. Preparation of hyperbranched poly(ether sulfone)-sulfonyl chloride

Hyperbranched poly(ether sulfone) was prepared by Freidel–Craft acylation using FeCl$_3$ as the catalyst (Scheme 3) [12]. The hyperbranched polymer was prepared from an AB$_2$-type monomer where the 'A' species is the electron-rich core phenyl ring and the 'B' species are the electron-deficient sulfonyl chloride substituted phenyl rings. Sulfone formation occurs ortho to either of the A-ring's ether groups, which subsequently deactivates the ring to further sulfone formation. The B-ring with the sulfonyl chloride is already deactivated, so will not react with sulfonyl chlorides from another B-ring. Hyperbranched polymers from AB$_2$-type monomer will have on average one end-group per repeat unit, though any particular repeat unit within the polymer can have zero, one or two end-groups. Reaction of both of a monomer 'B' groups generates a dendritic unit, a single 'B' group reaction yields a linear unit, and both 'B' groups remaining unreacted yield a terminal unit. GPC analysis indicated a molecular weight (M_w) of 27,900 g mol^{-1} and a PDI of 1.54. ^{1}H NMR indicated several, very broad, unresolved peaks between 6.6 and 8.3 ppm. The FT-IR spectrum contains a peak at 1376 cm^{-1}, consistent with the S=O stretching of sulfonyl chloride.

3.3. Blend, film forming and curing observations

Films were prepared by casting from a DMAc solution containing the hyperbranched-sulfonyl chloride and linear polymers

Scheme 3. Synthesis of hyperbranched poly(ether sulfone)-sulfonyl chloride from AB_2-type monomer. Dendritic, linear, and terminal repeat units are noted on the polymer structure.

at 20 w% total solids. The solutions also had a small amount of $FeCl_3$ added to act as a catalyst to promote reaction of some hyperbranched end-groups with electron rich aromatic rings of the linear polymer (*vide infra*). Additionally, the linear polymer is very sensitive toward protic moieties in solution so using the hyperbranched polymer in the sulfonyl chloride form allowed for a greater weight percent of hyperbranched polymer in the coating solution than using the sulfonic acid form.

3.3.1. Film preparation

Coating thickness was controlled using a doctor blade with a 125 μm gap. The cast films were then dried *in vacuo* at elevated temperature (150 °C) to quickly remove the DMAc. After drying, films had a thickness that was typically ~12% that of the coating thickness (Table 1). The films are optically transparent after drying, though the film prepared at 30 w% was haziness due to a larger amount or size of the phase-separation.

Table 1
Thickness, water uptake, and re-solubility in DMAc

HB w%	Process conditions	Thickness (μm)	Water uptake	DMAc solubility
0	Dried	17	1.005	Y
0	Cured	17	1.021	Y
10	Dried	12	1.020	Y
10	Cured	11	1.070	N
20	Dried	14	1.066	Y
20	Cured	10	1.032	N
30	Dried	9	1.025	Y
30	Cured	10	1.034	N
Nafion 117	–	205	1.180	–

All films were 'Dried' at 150 °C while 'Cured' films were also heated at 220 °C. Thickness measurements are the average of four measurements over three samples (12 total). Water uptake was calculated after 16 h of water immersion and is relative to the vacuum dried mass. DMAc re-solubility was investigated on films prior to H_2SO_4 treatment.

3.3.2. Phase Imaging

Optical microscope images of the dried films indicate a phase separation that is spinodal-like in appearance (Fig. 1a–d). The films cast with 10 and 20 w% hyperbranched polymer exhibit a uniform spinodal phase structure. For the film cast at 30 w% hyperbranched polymer, while there are still spinodal-like features, there are a number of features that appear more spherical. The appearance of spherical phases would also explain the increased haziness observed for the 30 w% film. This would indicate that compositions prepared at or above 30 w% hyperbranched polymer have access to a non-spinodal phase separation pathway.

3.3.3. Tethering Chemistry

In order to reduce or prevent leeching of the water-soluble, sulfonic acid-terminated hyperbranched polymer from the membrane, it was desired to covalently attach it to the linear polymer. We believe this could be accomplished by the same chemistry that generated the sulfonyl chloride-terminated hyperbranched polymer (Scheme 4). PEEES possesses electron-rich aromatic rings similar to the A-ring of the AB_2 monomer. $FeCl_3$ as a catalyst for a Freidel–Craft-type aromatic sulfonation in DMAc or in the solid state are not typical conditions for this type of reaction. Attempts to polymerize AB_2 monomer in DMAc with $FeCl_3$ yielded no product, however, the conditions within the film after phase formation should contain little if any DMAc. Thus, the only question is if a reaction along the hyperbranched-linear phase boundary can occur to form a covalent bond. Confirming that such a reaction occurred was complicated since the sulfone bond generated is not a unique bond to the system and generated in such small amount that identification by FT-IR and NMR analyses were inconclusive. To indirectly verify that tethering does occur a portion of each of the dried films was further heated *in vacuo* well above the T_g at 220 °C. For the 10 w% film, the POM images phase features have less definition than
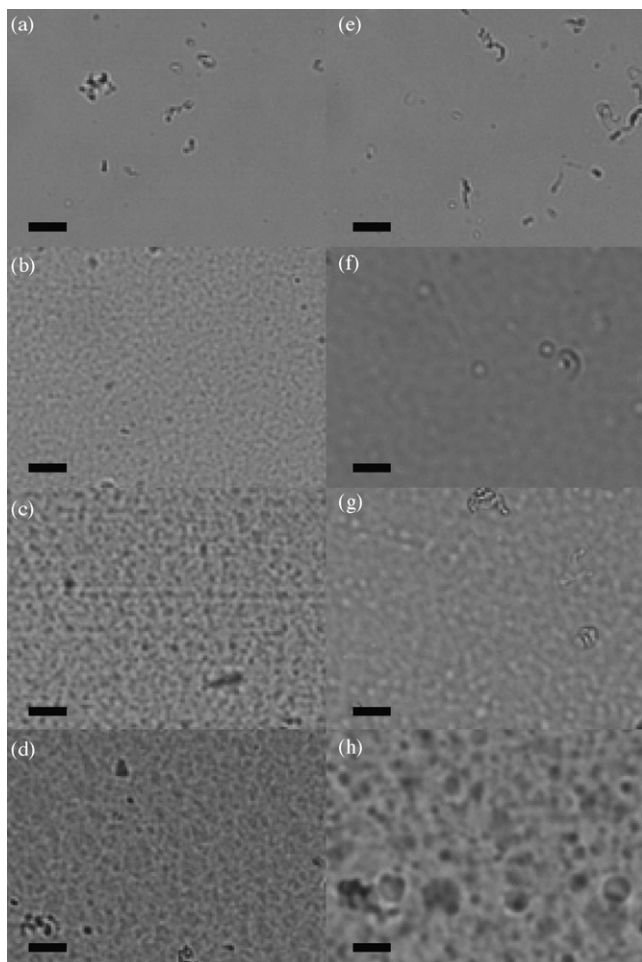
Fig. 1. Optical micrographs of blend films of 0 (a, e—top), 10 (b, f), 20 (c, g), and 30 (d, h—bottom) wt% hyperbranched polymer after drying (a–d) and curing (e–h). Scale bar indicates 10 μm.

before (Fig. 1e–h). For the 20 and 30 w% films, there are only minor changes to the film morphology, as they seem to shift to a slightly more spherical phase structure. Films prepared at both 150 °C and 220 °C were then reintroduced into DMAc. The films that were only dried at 150 °C re-dissolved within sec-

onds, whereas the films heated at 220 °C swelled and persisted in solution for several weeks. This would indicate that the several end-groups from the hyperbranched polymer reacted with several linear polymer chains to form a crosslinked network. This observation and other indirect measurements (*vide infra*) support that tethering of the hyperbranched polymer chains to the structural phase of the linear polymer does occur.

3.4. Film conversion and observations

The sulfonyl chloride version of the hyperbranched polymer is not suitable to conduct protons. Reported methods for converting sulfonyl chloride groups to sulfonic acid groups, such as heating in hot water, did not produce the desired functional group conversion. It was believed that during the drying process, a thin film of linear polymer formed at the polymer-air interface and was preventing conversion to the sulfonic acid groups by published means. To remedy this, the surface polymer was sulfonated using 16 M H_2SO_4. Sulfuric acid of this concentration proved strong enough to sulfonate the linear polymer to allow access to the hyperbranched phase, yet not so strong that it swelled and dissolved the structural polymer. Conversion of the hyperbranched phase from the sulfonyl chloride to the sulfonic acid is readily apparent by an increased turbidity of the film, which we attribute to a larger difference in refractive index between the two phases. FT-IR spectra indicate an increase in OH-stretching region, consistent with acid formation (Fig. 2). POM images of the films before and after sulfuric acid treatment show little difference in the phase structure (Fig. 3).

3.4.1. Ion exchange capacity

The ion exchange capacity values for the treated films correlate to the amount of hyperbranched polymer in the blended film (Fig. 4). Maximum values observed were around 0.4 meq g^{-1} for the 30 w% dried films. Comparison of the dried and heated films reveals the heated films have lower IEC values than the films that were only dried. This reinforces the previous observation that sulfonyl chloride groups are consumed during the additional heating step causing insolubility in DMAc. Additionally, all samples lie slightly below the theoretical value that
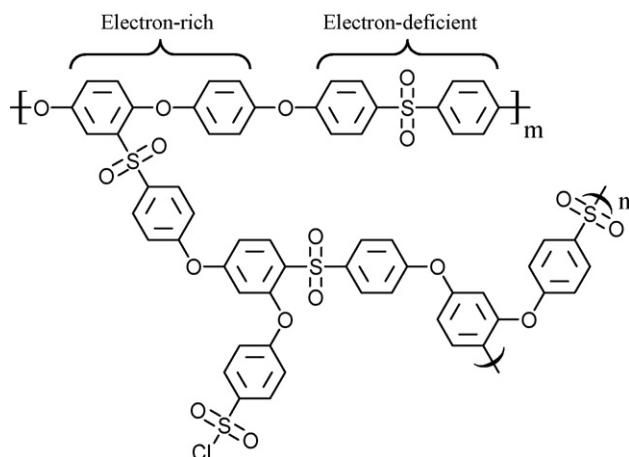
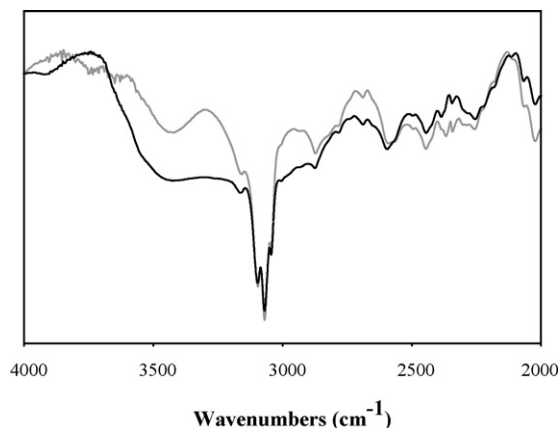Scheme 4. Desired location for covalently linking the hyperbranched polymer at the phase-phase interface.

Fig. 2. FT-IR of a 20 w% HB dried film before (gray line) and after (black line) treatment with 16 M H_2SO_4 at 50 °C for 3 h.
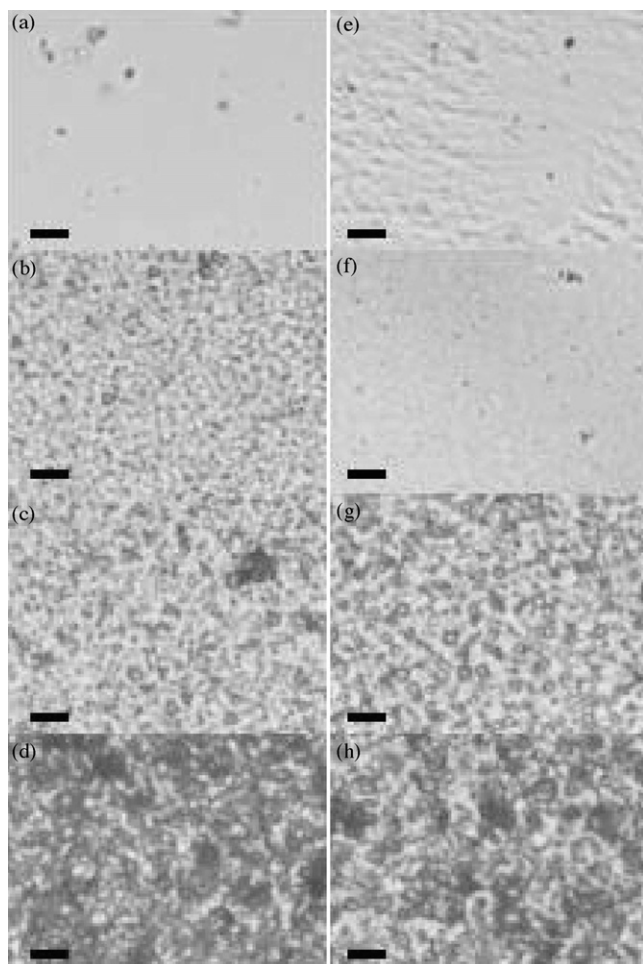
Fig. 3. Optical micrographs of 16M H_2SO_4 treated blend films of 0 (a, e—top), 10 (b, f), 20 (c, g), and 30 (d, h—bottom) wt% hyperbranched polymer after drying (a–d) and curing (e–h). Scale bar indicates 10 μm.
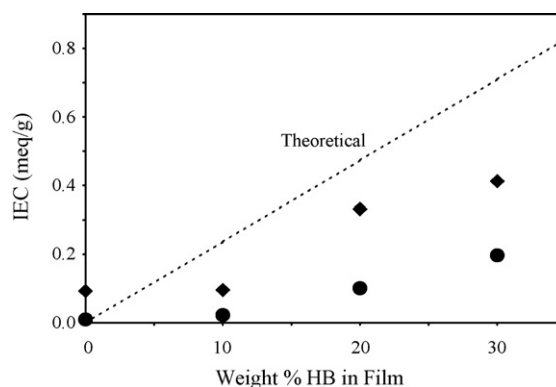

Fig. 4. Ion exchange capacity (IEC) of dried blend films (♦) and cured blend films (●) as measured by back titration of NaOH. Dashed line indicated the theoretical IEC based on the amount of HB polymer. Reported values are the average of three samples. Error values are ± 0.12 or less.

would be expected if all the end-groups of the added hyperbranched polymer were converted to sulfonic acids. Leeching of non-tethered hyperbranched polymer, excessive consumption of end-groups during tethering, and phase isolation are some possibilities could explain the lower than theoretical IEC value, however, no specific reasons have been identified at this time.

3.5. Film properties

The mechanical strength of the blend films were compared to that of the pure linear polymer (Table 2). Young's modulus is

only slightly decreased (same order of magnitude) for all samples from the pure polymer film and the yield stress at break is nominally the same. This would indicate that the structural polymer forms a continuous phase and is not compromised by the presence of the hyperbranched polymer or by the effects of sulfonation. The affect of blending and sulfonation both increase the elongation of the samples, likely due to additional strain release modes along phase boundaries and, in the case of the converted film, hydrogen-bonding/water uptake can add even more strain release modes.

3.5.1. Proton conductivity

Proton conductivity of the films was measured using the four-probe impedance method (Fig. 5). Films were initially in a dry state and measured at 80 °C and 90% relative humidity. The proton conductivity of the films increases with increasing hyperbranched polymer content. The conductivities of the dried films are slightly higher than the corresponding films that received additional heating, with the exception of the 10 w% films. The slightly higher proton conductivity of the cured 10 w% film may be related to slightly different morphology seen in Fig. 3f versus its dried counterpart (3b). However, the relative error in the measurement precludes any deeper speculation at this point. All films are slightly lower than the accepted range for Nafion 117 (0.08–0.10 S cm^{-1}) though they are of the same order of magnitude. One possible reason for the lower values might be due to the reduced amount of free water within the film as these films have an upper limit of water uptake of ∼7% compared to ∼18% for that of Nafion 117. Other possible reasons include fewer sulfonic

Table 2
Mechanical properties measured by tensile testing

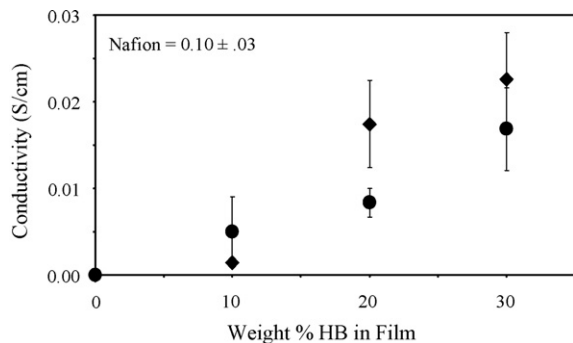|	Yield elongation	Yield stress (MPa)	Young's modulus (GPa m)
0 w% HB	1.03 ± 0.01	50.0 ± 9.0	4.95 ± 0.62
10 w% Cured HB	1.07 ± 0.02	55.0 ± 5.2	2.49 ± 0.24
10 w% Cured HB after H_2SO_4	1.29 ± 0.17	29.9 ± 6.7	1.83 ± 0.19
20 w% Cured HB	1.07 ± 0.01	67.5 ± 5.0	3.95 ± 0.12
20 w% Cured HB after H_2SO_4	1.20 ± 0.08	41.6 ± 7.4	3.19 ± 0.51
30 w% Cured HB	1.08 ± 0.07	39.5 ± 4.1	2.72 ± 0.33
30 w% Cured HB after H_2SO_4	1.30 ± 0.15	19.9 ± 4.1	0.98 ± 0.17

Fig. 5. Proton conductivities of dried (♦) and cured (●) blend films as measured by the 4-probe method at 80 °C and 90% R.H. Reported values are the average of three samples. The reported value for Nafion 117 was obtained under identical conditions.

acid groups and possible isolation of hyperbranched phase into spherical domains, i.e., collapse of the spinodal phase, during the drying and heating steps.

3.6. Blend film vs. polyelectrolyte discussion

The bi-continuous phase structure of these blend membranes makes direct comparisons to more common polyelectrolyte membranes difficult. The acid groups in polyelectrolyte membranes are homogeneously distributed and require water to drive the formation of conduits for proton travel. The membranes presented here have heterogeneously distributed acid groups with the proton conduits formed by the phase separation. These hyperbanched-linear blend membranes contain a small volume that has a high acid concentration and a large volume that is devoid of acid groups. Thus, even though the IEC and proton conductivity are low compared to Nafion, these values are a bulk average of both the conducting and non-conducting phases. Clearly the values for the pure hyperbranched phase are higher. However, calculating that value accurately requires knowledge of the fraction of hyperbranched polymer that may have leeched out, non-continuous (spherical) phase, and end-groups reacted to form tethering bonds to the linear polymer. The chemical similarities between the hyperbranched, linear, and tethering chemistry make this sort of analysis difficult. Ongoing studies, instead, are focusing on measuring the current density output from a fuel cell assembly as a more direct means to assess membrane performance for this novel architecture.

4. Conclusions

These results indicate great potential for the use of hyperbranched polymers as the proton conduction phase for fuel cell membranes. The inherent limitation of hyperbranched polymers to generate robust films is overcome by blending with a linear polymer. The phase structure generated during the film forming process is spinodal and the hyperbranched polymer could be tethered to the linear polymer by $FeCl_3$-catalyzed sulfonation in the solid state to prevent leeching of the hyperbranched phase. The proton conductivities generated from these initial results is of the same order of magnitude as that of Nafion. Ongoing studies include reducing the domain size of the spinodal phase, improving water management capabilities, investigating alternate chemistries to tether the hyperbranched phase to the linear phase, and analysis of performance in a fuel cell assembly.

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