Coupling of Hyperbranched and Linear Poly(Ether Sulfone)s in the Solid State

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Keywords: hyperbranched, fuel cell, poly(ether sulfone), ultraviolet, Michler's ketone

1. Introduction

Development of fuel cells as an alternative source of renewable energy has received an increased attention in the face of growing technological and environmental pressures.[1,2] Fuel cells can be powered by both hydrogen gas and methanol as a fuel source, which can be derived from non-petroleum and agricultural sources. Hydrogen gas can serve as a power storage material from electrolysis of power from solar cells or excess power production and methanol is an attractive fuel source to replace batteries in handheld electronics.[1] However, fuel cells have yet to realize broad application due to a number of developmental issues.

One developmental issue is that of the proton exchange membrane. In a fuel cell assembly, the proton exchange membrane separates the oxidation and reduction half-reactions to allow harnessing of the generated electrons.[2] The proton exchange membrane transfers protons generated from the fuel at the anode to the cathode to reduce oxygen to water. The majority of reported proton exchange fuel cell membranes are designed around the continuous polyelectrolyte architecture, such as Nafion.[2,3] The mechanism associated with these types of structures is the formation of water pores within the membrane and motion of the protons through the film by proton-‘hopping’ from one acid site to another.[2,4] The stability of the pore within the film is derived from the rearrangement of the polymer chains bearing the acid groups to stabilize the water-polymer interface. While this architecture is able to conduct protons efficiently, the excess water within the pore serves as pathway for fuel crossover. The power output of a fuel cell is mitigated by reactions occurring without the need to pass electrons to the anode.[5]

Water management at operating temperatures near or above 100°C is also a factor that needs to be considered.[6,7] The stabilization of the water pore architecture comes at the cost of a reduction of polymer chain entropy. As the temperature of the system is increased, the polymer chain entropy re-exerts itself and causes the pores to destabilize. The loss of the water pores causes a drop in the proton conductivity of the membrane and significantly reduces the power output.

Hyperbranched polymers offer the possibility of overcoming these issues. Hyperbranched polymers are derived from a one-pot reaction from ABX-type monomers.[8] The basic structure of a hyperbranched polymer can be described as containing terminal units, linear units, and branching units which generates an average of one end-group per a repeat unit and has a physical behavior similar to that of dendrimers. Compared to linear analogues of similar molecular weight, hyperbranched polymers generally have a lower viscosity and higher solubility, which is consistent with a molecule having fewer chain entanglements, i.e., less entropy. However, low entropy molecules, such as hyperbranched polymers, also do not make mechanically robust films.

Blending a hyperbranched polymer bearing sulfonic acid groups with a linear polymer should provide a film that has both the proton conductivity and mechanical robustness necessary for a proton exchange membrane. Formation of co-
continuous phases via spinodal decomposition should give two advantages over continuous polyelectrolyte architectures. First, the framework created by the linear polymer would act as a restraining force against swelling and subsequent pore formation. Second, the low entropy of the hyperbranched molecule should be unable to allow reorganization of the sulfonic acid groups to stabilize the water-polymer interface of the pore. This should create a proton channel in the hyperbranched phase, which should lead to more efficient proton conduction.

Linear poly(ether sulfone) polymers (Scheme 1a) have been well-studied for use as fuel cell membranes and are generated via nucleophilic aromatic substitution.[9] The hyperbranched poly(ether sulfone) (Scheme 1b) based on an AB₂ type monomer is easily accessible through electrophilic addition to an aromatic ring. [8,10]

Hyperbranched poly(ether sulfone)s bearing sulfonic acid end-groups are water soluble, which can complicate film processing and possibly long-term stability. Preparation of the hyperbranched poly(ether sulfone) (Scheme 1b) based on an AB₂ type monomer is easily accessible through electrophilic addition to an aromatic ring. [8,10]

2. Methods

2.1 Synthesis of Poly(Ether Sulfone) with Methylhydroquinone

The linear polymer was synthesized using established procedures for nucleophilic aromatic substitution.[9] 4,4´-Hydroxyphenylether (99 mol%), methylhydroquinone (1 mol%), and K₂CO₃ were heated at 160°C in N,N-dimethylacetamide (DMAc) and toluene to azetopete water. After the toluene was removed under vacuum, 4,4´-dichlorophenylsulfone was added and heated overnight (> 16h) at 172°C which yielded a viscous solution. The polymer was purified by precipitation in methanol, redissolved in THF, followed by a second precipitation, and vacuum drying. Molecular weight (M_w) and polydispersity were measured to be 227,000 g/mol and 1.86 by gel permeation chromatography in dimethylformamide (DMF GPC).

2.2 Synthesis of Hyperbranched Poly(Ether Sulfone) Sulfonyl Chloride

The hyperbranched polymer was synthesized according to established procedures for Friedel-Craft aromatic substitution with minor modifications [10]. 4,4´-(m-Phenylene-dioxy)-bis-(benzenesulfonyl chloride) was dissolved in chloroform with 10w% FeCl₃ and heated at 70°C for 10h. Afterwards, the chloroform was evaporated and the remaining material was dissolved in DMAc, precipitated in methanol, and then dried in vacuo. Molecular weight (M_w) and polydispersity were measured to be 27,900 g/mol and 1.54 by DMF GPC.

2.3 Preparation of Blend Films

Solutions for casting were prepared by dissolving the hyperbranched polymer (20 w%) with the linear polymer (80 w%) in DMAc, so that the total polymer content was 20 w%. A second solution was prepared in an identical fashion, but with 5 eq. 4,4´-bis(dimethylamino)benzophenone, Michler’s Ketone (MK), per hyperbranched polymer chain. The solution was then cast on a glass plate at 125 μm thickness using a doctor blade set. The film was then dried in vacuo at 150°C for two hours. Water was then used to assist the removal of the films from the glass plate.

2.4 UV Irradiation of Films

Films with and without MK were divided into four pieces and irradiated with a Hg lamp (Hamamatsu Lightning Cure LC6) for 0, 1, 10, and 30 min at a distance of ~30cm under ambient atmosphere.

2.5 Sulfonyl Chloride Conversion to Sulfonic Acid

Films were heated in 16M H₂SO₄ at 50°C for 3h. After removal from the acid, the films were placed flat on a glass Petri dish and quenched with water. They were then immersed in 0.1N HCl at room temperature for 2h and finally vacuum dried at 30°C for 2h between glass plates held together with clips.

2.6 Proton Conductivity Testing
The dried films were cut to 5mm x 40mm and thickness was measured with a micrometer. The films were then placed in a custom built four-probe cell, placed in an Espec model# SH-221 oven, and equilibrated to 80°C and 90% relative humidity (RH). Measurements were then taken every 10 min for 1h using a Solartron SI 1280B using an AC amplitude of 0.01mA and a frequency sweep from 20000Hz to 0.1Hz. Measurements are the average of all measurements from two samples.

3. Results and Discussion
3.1 Film Casting and Preparation
The blending drying conditions were chosen to generate phase separation via spinodal decomposition. The use of the sulfonyl chloride hyperbranched polymer instead of the sulfonic acid form, in addition to being a chemical handle, allows a higher loading into the solution without precipitation of the linear polymer, which is sensitive to protic material. The films were dried at elevated temperatures under vacuum to remove DMAC. Phase formation generated a spinodal-like structure with domains less than 5 μm in size (Fig.1). The MK-containing film appears to have a slightly smaller domain size than that of the film without. It is important to note here that the film lack any spherically shaped domains.

![Fig.1: Optical images of dried blend film without (a) and with (b) Michler's ketone. The scale bar represents 5 μm.](image1)

3.2 UV Treatment
Films were irradiated with UV light from a HG lamp. The sulfonyl chloride group is known to produce radicals via homolytic cleavage of the sulfur-chlorine bond.[11] Additionally, the benzylc position of aromatic rings are known to stabilize radicals. The intention in this system is to generate radical coupling of a sulfone radical and a benzyl radical to tether the hyperbranched polymer to the linear polymer phase.

The films were exposed from 1, 10, or 30 minutes under ambient conditions. The MK-containing films, which have a slight blue-isch tint from the MK, exhibit a photo bleaching indicating that the MK is able to absorb the UV energy even while in the bulk polymer.

3.3 Conversion to Sulfonic Acid
After UV irradiation, the films were immersed in 16M sulfuric acid. This is designed to both convert the sulfonyl chloride to sulfonic acid and to functionalize the surface of the linear phase. After treatment, the films had varying degrees of turbidity. The turbidity of the non-MK films was varied more than those prepared with MK, and the films receiving less UV irradiation showed less turbid (Fig.2). Additionally, the film with MK that was treated for 30 min had become very brittle after the sulfonation unlike any of the other films.

![Fig.2: Optical images of sulfuric acid treated films without (a) and with (b) Michler's ketone with UV exposure times of 0, 1, 10, and 30 min. The scale bar represents 25 μm.](image2)

3.4 Measurement of Proton Conductivity
The proton conductivity of the prepared films was measured by four-probe impedance at 80°C and 90% RH (Table 1). On the whole,
Table 1: Conductivity are the average of fourteen four-probe impedance measurements taken every ten minutes at 80°C and 90%RH over two samples. Thickness is the average of eight measurements over two samples.

<table>
<thead>
<tr>
<th>UV Irradiation (min)</th>
<th>MK (yes/no)</th>
<th>Conductivity (mS/cm)</th>
<th>Film Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>no</td>
<td>4.1 ± 3.3</td>
<td>5.8 ± 1.7</td>
</tr>
<tr>
<td>0</td>
<td>yes</td>
<td>13.2 ± 10.2</td>
<td>10.0 ± 3.9</td>
</tr>
<tr>
<td>1</td>
<td>no</td>
<td>9.6 ± 7.8</td>
<td>6.5 ± 1.9</td>
</tr>
<tr>
<td>1</td>
<td>yes</td>
<td>13.1 ± 6.0</td>
<td>8.8 ± 1.2</td>
</tr>
<tr>
<td>10</td>
<td>no</td>
<td>5.3 ± 2.5</td>
<td>13.4 ± 2.8</td>
</tr>
<tr>
<td>10</td>
<td>yes</td>
<td>17.1 ± 2.9</td>
<td>10.1 ± 1.2</td>
</tr>
<tr>
<td>30</td>
<td>no</td>
<td>14.1 ± 7.1</td>
<td>6.4 ± 1.4</td>
</tr>
<tr>
<td>30</td>
<td>yes</td>
<td>16.2 ± 7.6</td>
<td>7.8 ± 4.5</td>
</tr>
</tbody>
</table>

exposure to UV tends to increase the conductivity of the films. The films with MK added have a consistently higher conductivity than those films without MK. The conductivity results coupled with the optical images suggest that MK does help stabilize the hyperbranched phase within the film.

3.5 Discussion on Tethering Mechanism
While more research needs to be done to elucidate the reaction pathway to help optimize the system, the most likely pathway is that MK abstracts a benzylic hydrogen from the methyl group from the methyldihydroquinone units incorporated into the linear chain.[12,13] Simultaneously, sulfone radicals are generated either by chlorine abstraction by MK or direct cleavage by UV light. These two radicals then combine to form a covalent methylene sulfone bond to tether the hyperbranched polymer to the interface of the linear polymer phase. For the case of the non-MK containing film irradiated for 30 min with UV light, direct homolytic cleavage of the sulfur-chlorine bond is the most probable pathway. Therefore, It is concluded that the chlorine radical abstracts a hydrogen likely to evolve hydrogen chloride. Then, radical combination could be occurred (vide infra).

4. Conclusion

Tethering hyperbranched polymers to the linear structural polymer in a blend film improves the proton conductivity for use as fuel cell membranes. The use of UV irradiation and a radical initiator can be used to facilitate tethering the hyperbranched polymer to the linear polymer while in the solid state, i.e., dry film.

Acknowledgements
This work was supported by the New Energy and Industrial Technology Development Organization (NEDO).

References