

# Study of the incorporation of protic ionic liquids into hydrophilic and hydrophobic rigid-rod elastomeric polymers

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## Abstract

A series of polymers was synthesized that contain a rigid aromatic backbone connected through triazine linkages that are cross-linked by flexible diamine-terminated poly(ethylene oxide) oligomers. Polymers were made that contained both hydrophilic sulfonated aromatic and hydrophobic pyridinium triflate backbones. Thermal and mechanical properties of the resulting polymer films were studied, as well as uptake of water and protic ionic liquids. Ionic liquid uptake varied from 41 to 440%, depending upon the nature of the polymer. The ionic liquid-doped films were analyzed for proton conductivity at high temperatures ( $> 150\text{ }^{\circ}\text{C}$ ) under non-humidified conditions. Conductivities as high as  $5 \times 10^{-2}\text{ S/cm}$  were observed at  $150\text{ }^{\circ}\text{C}$ .

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**Keywords:** Proton exchange membrane; Poly(pyridinium triflate)s; Melamine

## 1. Introduction

Proton exchange membrane (PEM) fuel cells have been the focus of considerable research to find efficient low emission power generation devices for stationary uninterruptible power sources, residential power, portable devices, and alternatives to internal combustion engines [1–5]. Furthermore, NASA has interest in fuel cells for space exploration, space suits, and unmanned air vehicles. The current state of the art membranes used in fuel cells are perfluorinated sulfonic acid membranes, such as Nafion<sup>®</sup>, made by Dupont [6]. Nafion shows excellent thermal and mechanical stability, as well as high proton conductivity when hydrated. The good low temperature proton conductivity of Nafion is believed to be due to phase separation between the hydrophobic perfluorinated backbone and the hydrophilic sulfonic acid groups, with protons being carried by water between the hydrophilic regions. The hydrated sulfonic acid aggregates form channels through which water carries protons [7]. However, perfluorinated sulfonic acid membranes have several disadvantages, such as cost and high methanol

permeability. Nafion membranes also become much less conductive above  $80\text{ }^{\circ}\text{C}$  due to dehydration of the membrane.

Many sulfonated organic polymers have been made as low cost alternatives to perfluorinated sulfonic acids [2,8]. Examples include polyether ether ketones [9,10], poly(arylene ether sulfone)s [11,12], and polyimides [13,14]. Most of these sulfonated organic polymers that have been reported are similar in structural features. The polymers have a linear aromatic backbone with the sulfonic acid groups attached directly to the aromatic rings.

It would be advantageous to operate PEM fuel cells at temperatures above  $100\text{ }^{\circ}\text{C}$  for several reasons, such as enhancement of electrode reactions, higher tolerance toward CO poisoning of the catalyst, reduced electrode flooding, and greater system efficiency [15]. However, at these higher temperatures, the fuel cell would have to be operated under high pressure, or water would have to be replaced with a less volatile proton carrier. In Nafion, water has been replaced by such media as phosphoric acid [16], phosphotungstic acid [17], and zirconium phosphates [18]. Organic polymer–inorganic composites include sulfonated polyether ether ketones with zirconium phosphates [19] and heteropolyacids [20], polybenzimidazoles doped with phosphoric acid [21–23] and polytungstic acid [24], and poly(ethylene oxide) doped with acidic tungsten oxide clusters [25,26].

Another proton carrying medium that is receiving interest is protic ionic liquids (ILs). Ionic liquids are interesting because of their high thermal stability, negligible vapor pressure, and

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high conductivity. One would expect ILs to provide good proton conductivity compared to inorganic media because of their higher mobility. In fact, some protic ILs have been shown to be more conductive than aqueous electrolytes at room temperature [27]. Susan et al. recently observed that the ionic liquid made from a 1:1 ratio imidazole and bis(trifluoromethanesulfonyl)imide (imid-TFSI) exhibits a conductivity of 0.0271 S/cm at 130 °C, with a decomposition temperature > 370 °C [28].

Unfortunately, an IL cannot form a membrane in a PEM fuel cell. The IL must be imbibed into a material that has the mechanical strength, chemical stability and thermal stability to function within a PEM fuel cell. Ionic liquids have been imbibed into Nafion [29,30] and Teflon [31]. However, these perfluorinated membranes typically have low IL uptakes (typically < 30%). Our laboratory has synthesized a series of polymers that contain rigid sulfonated aromatic backbones that are cross-linked with diamine-terminated PEO oligomers. The purpose of the aromatic backbone is to provide mechanical strength to the polymer film, which is further reinforced by cross-linking. The PEO oligomers enable the film to swell in the presence of solvent to help aid the imbibing process. The volatile solvent can then be removed so the film can shrink and trap the ionic liquid. In addition, to better suit humidified conditions we designed a hydrophobic aromatic polymer backbone with a high affinity for the ionic liquids used in this study. Poly(pyridinium triflate)s were chosen for this purpose [31] since, like imidazolium-based ionic liquids, the polymer contains charged heterocyclic rings with perfluorinated sulfonate counterions.

## 2. Experimental

### 2.1. Starting materials

Cyanuric chloride and 4,4'-oxydianiline (4,4-oda) were purchased from Aldrich Chemical Company and used as received. Diisopropylethylamine (Hünig's base) was purchased from Aldrich in biotech grade and used as received. 4,4'-Diamino-2,2'-biphenyldisulfonic acid (DAS) containing 30% water was purchased from TCI Chemical Company and dried in a vacuum oven at 100 °C for 24 h. 4-(2-(4-Aminophenyl)-1,1,1,3,3,3-hexafluoropropan-2-yl)benzenamine was purchased from Chriskev and used as received. Monoamine and diamine-terminated polyalkylene oxide oligomers (Jeffamine<sup>®</sup> XTJ-500 (600 MW diamine), XTJ-502 (2000 MW diamine), and XTJ-506 (1000 MW monoamine)) were kindly provided by Huntsman Corporation and used as received. Nafion films were cast onto microscope slides from 20 wt% dispersions in alcohols, air-dried until tack-free, dried at 70 °C under vacuum for 2 h, soaked in water for 2 h, and air-dried. Diaminopyridinium triflates (pyr-oda and pyr-CF<sub>3</sub>) were synthesized according to a literature procedure [32].

### 2.2. Characterization

Differential scanning calorimetry (DSC) was measured on a Series Q1000 modulated DSC with an auto-sampler at

a heating rate of 5 °C/min. A TA thermogravimetric analysis (TGA) was used. Measurements were conducted under air with samples loaded onto a platinum pan. The TGA heats at a rate of 10 °C/min from room temperature to 750 °C. The analysis was completed using Universal Analysis software. Tensile testing was performed on an Instron with ASTM D-638 Type V dog bone shaped samples. The samples were cut from polymer films using an in-house made punch. On the day of testing, the temperature was 73 °F (23 °C) and humidity was 50%. For conductivity measurements, films were cut into 5/8 in. diameter circles and sandwiched between stainless steel electrodes. Conductivity measurements were performed using a Solartron 1287 potentiostat and a Solartron 1260 frequency response analyzer. These instruments measured AC impedance at frequencies between 0.1 Hz and 100 kHz. The real component of the impedance was plotted with respect to the imaginary component and the resistance of the film was taken at the frequency that produced the lowest imaginary response. All measurements were performed without added humidity in an oven that was equilibrated at each temperature for 20 min.

### 2.3. Synthesis of polymer containing 100% DAS + cyanuric chloride

DAS, 7.83 g (22.7 mmol) and sodium carbonate 4.83 g (45.6 mmol) were dissolved in 60 mL H<sub>2</sub>O. The solution was cooled in an ice bath and 4.20 g (22.7 mmol) cyanuric chloride in 20 mL THF was added. The ice bath was removed and the reaction was stirred overnight to give a highly viscous purple solution. The solution was then poured into 1000 mL methanol to form a purple precipitate. The powder was dried under vacuum at 60 °C for 12 h to give 11.51 g of product. We assume that the final precipitate still contains 100% of the NaCl that was generated during the reaction and the powder is 76.9% of the polymer by weight.

### 2.4. Film casting

The above powder, 1.81 g (1.39 g polymer, 2.79 mmol) was dissolved in 10 mL H<sub>2</sub>O. 2.80 g (1.40 mmol) 2000 MW diamine was then added. Once the diamine dissolved, the solution was doctored onto a glass plate. The film was air-dried overnight in a fume hood, followed by curing at 160 °C overnight in a vacuum oven. The film was then acidified in boiling 0.5 M H<sub>2</sub>SO<sub>4</sub> for 2 h, followed by boiling in H<sub>2</sub>O for 1 h [12]. During the acidification process, the film changed from cloudy purple to clear purple.

### 2.5. Synthesis of the polymer containing 100% pyr-oda + cyanuric chloride

Pyr-oda 1.52 g (1.27 mmol), 0.20 g (1.4 mmol) K<sub>2</sub>CO<sub>3</sub> and 5 mL DMAc were charged into a three-neck flask equipped with an overhead stirrer, nitrogen inlet, and drying tube. Once pyr-oda dissolved, 0.234 g (1.27 mmol) cyanuric chloride in 2 mL DMAc was added. The reaction immediately became lighter in color. 0.1 mL diisopropylethylamine was then added

to catalyze the reaction. The reaction was stirred overnight under a constant nitrogen purge. More diisopropylethylamine was added occasionally. 1.27 g (0.635 mmol) 2000 MW diamine was then added to the highly viscous solution. The contents of the reaction were then transferred into glass vials, centrifuged, and doctored onto a glass plate. The film was air-dried overnight in a fume hood, followed by curing at 160 °C overnight in a vacuum oven. The film was then peeled from the glass substrate and washed with boiling H<sub>2</sub>O for 1 h. Precipitation of the polymer by pouring into water to remove inorganic salts produced a material that was insoluble in organic solvents. Therefore, the polymer was cast directly from the reaction.

### 2.6. Synthesis of the polymer containing 50% pyr-oda + 50% DAS + cyanuric chloride

Pyr-oda, 0.998 g (.830 mmol), 0.292 g (0.848 mmol) DAS, 0.39 g (2.8 mmol) K<sub>2</sub>CO<sub>3</sub>, and 6 mL DMAc were charged into a three-neck flask equipped with an overhead stirrer, nitrogen inlet, and drying tube. 0.310 g (1.68 mmol) cyanuric chloride in 3 mL DMAc was then added, followed by 0.1 mL diisopropylethylamine. The reaction was stirred overnight under a constant nitrogen purge with more diisopropylethylamine being added occasionally. 1.68 g (0.840 mmol) 2000 MW diamine was then added. The contents of the reaction were then transferred into glass vials, centrifuged, and doctored onto a glass plate. The film was then cast, cured, and acidified in the same manner as the polymer with 100% DAS.

### 2.7. Water uptake

To measure the water uptake, a piece of polymer film was weighed and then soaked in water for 1 h. The film was then removed from the water, quickly blotted with a paper towel, and weighed immediately. Films would typically return to their

presoaking weight within 15 min of removing the sample from water, regardless of composition.

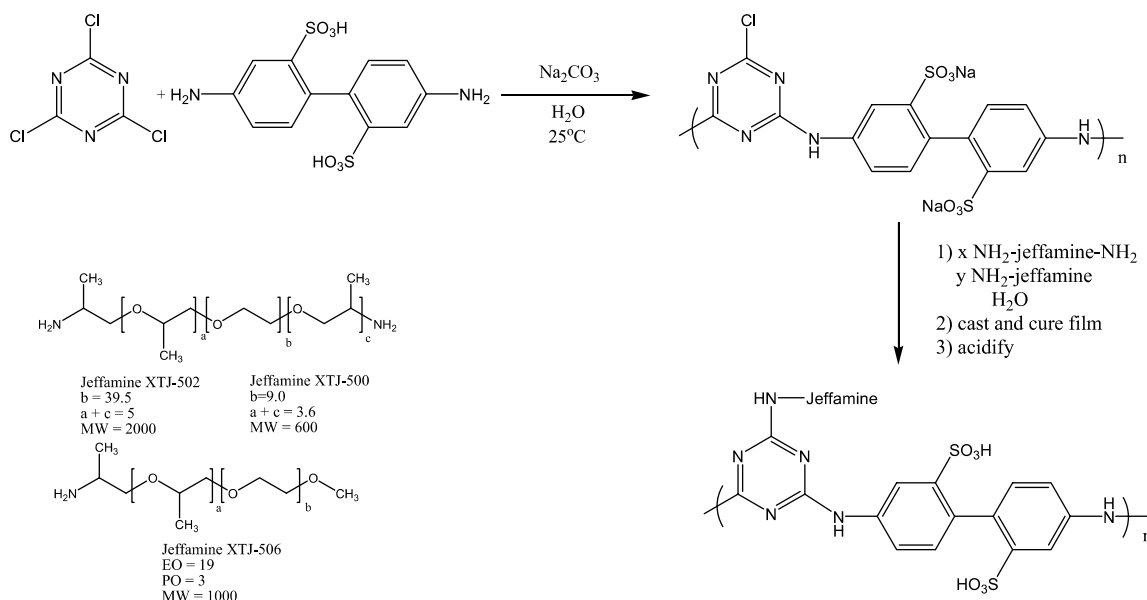
### 2.8. Imbibing of ionic liquids

Ionic liquids were prepared by mixing imidazole in a 1:1 molar ratio with either sulfuric acid, triflic acid, or bis(trifluoromethane sulfonyl)imide in an ice bath. Water was then added to make a solution that was 50 wt% ionic liquid. Polymer films were then soaked in these solutions in a covered Petri dish for 3 days. The films were then removed from the solution, blotted with a paper towel, and allowed to dry in a fume hood for several hours.

## 3. Results

### 3.1. Polymer synthesis and film casting

The reaction of cyanuric chloride with primary amines is well known [33,34]. The reaction is chemoselective. The first two reactive sites on cyanuric chloride typically react at, or below, room temperature [35,36]. The third reactive site requires temperatures of at least 70 °C. Scheme 1 shows the synthesis of the polymer made from the reaction of DAS with cyanuric chloride. The reaction is run in water and Na<sub>2</sub>CO<sub>3</sub> is added to both deprotonate the sulfonic acid groups and remove HCl that is generated during the course of the reaction. The contents turn into a highly viscous solution within a few hours at room temperature. The polymer is then isolated by precipitation in methanol. Unfortunately, the polymer could not be separated from NaCl that is generated during the course of the reaction since they are both soluble in water, but not in organic solvents. Therefore, we assume that 100% of the NaCl generated is in the isolated precipitate. At this point, the linear polymer is water soluble and still has a highly reactive group on the triazine ring. These issues are remedied by mixing the



Scheme 1. Synthesis of rigid-rod elastomer with sulfonated diamine.

polymer with diamine-terminated PEOs (Jeffamines) that can react with the triazine functional group as a cross-linking agent. It has been shown previously that polymers made from cyanuric chloride can be cross-linked by curing with Jeffamines above 140 °C [37]. The polymer and Jeffamines are dissolved in water and cast into a film. After curing overnight at 160 °C, the polymer is no longer soluble in water or organic solvents. The film is then acidified and washed by a procedure used previously with sulfonated poly(ether sulfone)s [12] to produce a film that is both strong and flexible. Two different sets of Jeffamines were used to observe their effects on IL imbibing and mechanical properties. A 2000 MW diamine was used, as well as a 1:1 ratio of 600 MW diamine and 1000 MW monoamine. In all cases, the films containing 2000 MW diamine were both more flexible and held more ionic liquid than films containing 600 MW diamine and 1000 MW monoamine. The films initially had a cloudy appearance, which becomes clear after the acidification process.

Polymer films that are made from DAS and cyanuric chloride swell strongly in water, which can cause mechanical problems if humidified conditions are desired. To address this issue, a set of polymer films were also made that were designed to be less hygroscopic, but still be attractive from the viewpoint of imbibing the ionic liquids used in this study. In order to do this, we opted to replace the sulfonated diamine with two different diamino-pyridinium triflates (Scheme 2). The design was to attract the ionic liquids to the polymer by a like-dissolves-like approach. For one pyridinium salt (pyr-oda), an ether bridge was added to provide good flexibility. For the other pyridinium salt (pyr-CF<sub>3</sub>), a hexafluoropropane linking group was used to improve miscibility with imidazolium salts having fluorinated anions. Neither monomer was water soluble, so the reaction was run in DMAc. It was initially observed that the reaction would not build up viscosity at room temperature, indicating little increase in molecular weight. The reaction would start to build up viscosity when run at 40 °C, but would quickly turn into an insoluble gel. By adding catalytic amounts of diisopropylethylamine, the reaction mixture would become highly viscous at room temperature. The tertiary aliphatic amine is a strong base that can act as an acid scavenger of HCl in the reaction. The polymers were initially precipitated by pouring into water. However, the resulting powders would not redissolve in organic solvents. Therefore, films were cast

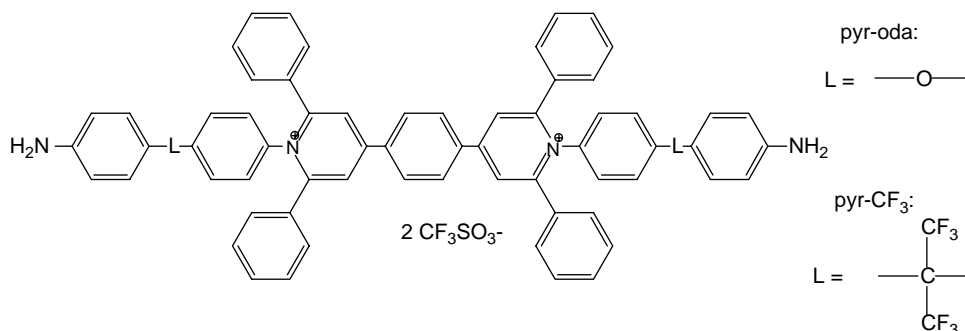
directly from the reaction mixture after Jeffamines were added. Polymer films that contained a 1:1 ratio of sulfonated diamine and diamino-pyridinium triflate were made in this same manner.

### 3.2. Water and ionic liquid uptake

Water uptake was measured by soaking the film in water for an hour and measuring the weight before and after. Table 1 shows a high uptake (> 100% uptake by weight) for films that contain 100% DAS in the main polymer chain. This was expected since both DAS and PEO are hydrophilic. When DAS is replaced by a hydrophobic pyridinium triflate, the water uptake decreases dramatically (< 10% uptake). When a 1:1 ratio of DAS to pyridinium triflate is in the film, water uptake increases slightly to 20–50%. The films that were more rigid (containing 600 MW diamine and 1000 MW monoamine) also had a lower uptake of water. It was also observed, that with all of the films studied, the adsorbed water would evaporate very quickly (5–15 min). This is most likely due to the elastomeric nature of the polymers contracting and ‘squeezing’ water out.

Three protic ionic liquids were chosen for this study: imidazolium–trifluoromethanesulfonimide (imid-TFSI), imidazolium–trifluoromethanesulfonic acid (imid-CF<sub>3</sub>SO<sub>3</sub>H), and imidazolium–sulfuric acid (imid-H<sub>2</sub>SO<sub>4</sub>) (shown in Scheme 3). The ILs were diluted to a 50 wt% solution in water and imbibed into each polymer film by immersing the film in the solution at room temperature. Water was used to swell the films to aid the imbibing process. Several trends were observed (Table 1). First, imid-H<sub>2</sub>SO<sub>4</sub> was imbibed least into all films, regardless of composition. This is the only IL used with an inorganic anion, and may be less interactive with the polymer than the ILs with organic anions. Secondly, as observed with water uptake, the more rigid films uptake less IL. The difference between pyr-oda and pyr-CF<sub>3</sub> is that an ether linkage is replaced by hexafluoropropane. It was hoped that the addition of a fluorinated group would increase the uptake of ILs with perfluorinated anions. However, there does not seem to be a clear trend as to whether the fluorinated group helps this process.

The most interesting observation is that the uptake of imid-TFSI versus imid-CF<sub>3</sub>SO<sub>3</sub>H depends on the nature of the polymer. Films that contain 100% DAS have a higher uptake of imid-CF<sub>3</sub>SO<sub>3</sub>H. Films that contain any pyridinium triflates



Scheme 2. Pyridinium-containing diamines.

Table 1  
Water and ionic liquid uptake

	Ar	Cross-linker	H <sub>2</sub> O uptake (wt%)	Imid/H <sub>2</sub> SO <sub>4</sub> uptake (wt%)	Imid/CF <sub>3</sub> SO <sub>3</sub> H uptake (wt%)	Imid/TFSI uptake (wt%)
A	DAS	2000	187	91	258	175
B	DAS	1:1 600:1000	128	95	159	125
C	Pyr-oda	2000	10	44	71	136
D	Pyr-oda	1:1 600:1000	0	13	<sup>a</sup>	112
E	Pyr-CF <sub>3</sub>	2000	7	<sup>a</sup>	41	137
F	50% DAS 50% pyr-oda	2000	52	52	114	278
G	50% DAS 50% pyr-oda	1:1 600:1000	25	42	<sup>a</sup>	224
H	50% DAS 50% pyr-CF <sub>3</sub>	2000	31	<sup>a</sup>	127	440
I	Nafion	None	25	<sup>a</sup>	12	26

<sup>a</sup> Not measured.

have a higher uptake of imid-TFSI. A possible reason why imid-CF<sub>3</sub>SO<sub>3</sub>H imbibes more strongly into films A and B is because the IL is smaller and can fit between polymer chains more easily. In any films that contain pyridinium salts, there is likely to be a counterion exchange in the polymer from CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> to TFSI<sup>-</sup>. The TFSI anion is known to have a plasticizing effect on polymers that contain PEO [38]. The increasing film flexibility could increase the amount of IL that can be incorporated.

Another interesting observation is that, while the water uptake of Nafion is higher than films containing pyridinium triflates (films D and E), the IL uptake is much lower. The uptake of imid-CF<sub>3</sub>SO<sub>3</sub>H is 41% in film E versus 12% in Nafion. The difference in uptake of imid-TFSI is even more dramatic, being 137% in film E versus 26% in Nafion.

### 3.3. Thermal and mechanical properties

Table 2 shows the onset of decomposition for three polymers that are cross-linked with 2000 MW diamine. Films that contain pyridinium triflate monomers appear to be more stable than those made from the sulfonated diamine. Also, films that contain only DAS as the monomer are more stable as the sodium salt than in the acidic state. However, films that contained both DAS and pyridinium triflate monomers did not show any difference in stability between the salt and acid forms. When ionic liquid is added, the high temperature stability is lowered, which appears to be independent of which IL is used. The decomposition is occurring within the polymer structure, since these temperatures are well below the  $T_d$  of the IL [28].

Tensile testing was performed on a number of polymers to further understand the mechanical properties of these films, as well as to help explain the trends that were observed in levels of IL doping. To make this testing a viable option for our film

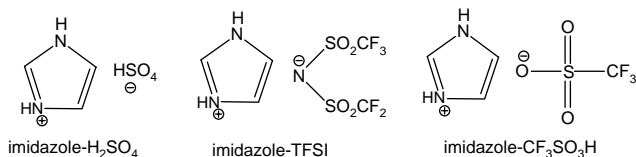
size, a 2.5 in. long dog bone shape was used with a maximum width of 3/8 in. and minimum width of 1/8 in. (ATSM D-638). Table 3 shows the results for five different polymers. For a point of reference, Kapton was also tested by this method and compared with data reported by Dupont. Their data for Nafion is reported as well. There is a slight difference in the results obtained for Kapton between the two methods, but close enough to allow for general comparisons between the polymers reported.

Films were much lower in strength than Kapton but similar in strength to Nafion. The polymer with the shorter cross-linking unit (film B) was both the strongest and least flexible of the samples. All films that were cross-linked with 2000 MW diamine were similar in strength, but films that contained DAS showed better elongation than those with pyridinium triflates. Of these films, A, E, and F had their ultimate strength at the yield point. As expected, films with pyr-oda were more flexible than films with pyr-CF<sub>3</sub> due to the flexibility of the ether linkage compared to hexafluoropropane. Films that contained DAS had a lower modulus than films that contained pyridinium salt, even though DAS is a more rigid molecule. There are two possible reasons for this. First, DAS is a smaller monomer, which requires more diamine coil to be added. Films A, C, and F contain 33, 57, and 46% rigid-rod portion, respectively. Also, films that contain DAS are more hygroscopic, leading to a higher uptake of water as a plasticizer. When films A, C, and F were dried under vacuum at 120 °C for 5 h, they had weight losses of 18, 4.6, and 6.1%, respectively. This weight loss is most likely attributed to water.

All of the films had both a higher modulus than Nafion and a much lower elongation at break. Based on the mechanical properties, one would expect Nafion to be better at

Table 2  
Onset of decomposition temperatures, in °C, of polymers cross-linked with 2000 MW Jeffamine

Ar	Salt form	Acid form	Imid/H <sub>2</sub> SO <sub>4</sub> imbibed	Imid/CF <sub>3</sub> SO <sub>3</sub> H imbibed	Imid/TFSI imbibed
DAS	321	298	262	262	250
Pyr-oda	355	–	262	259	271
50% DAS	342	342	250	281	282
50% Pyr-oda					



Scheme 3. Protic ionic liquids.

Table 3  
Room temperature tensile properties of various films

	Ar	Diamine	Strength at peak (MPa)	% Elongation at break	Modulus (GPa)
–	Kapton	–	189	40	2.91
–	Kapton <sup>a</sup>	–	148	60	3.7
–	Nafion <sup>b</sup>	–	43	225	0.249
A	DAS	2000	18.2	93	0.41
B	DAS	600	41.2	8.9	1.19
C	Pyr-oda	2000	24.0	46	0.82
E	Pyr-CF <sub>3</sub>	2000	34.4	22	1.30
F	50% DAS 50% Pyr-oda	2000	22.0	68	0.72

<sup>a</sup> Values reported by Dupont according to ASTM D-882.

<sup>b</sup> Values reported by Dupont according to ASTM D-882 at 23 °C and 50% RH.

incorporating ionic liquid. However, the results from Table 1 show that the rigid-rod polymers are much better at incorporating ILs under the conditions used in this study. For films that contain DAS, this most likely comes from the ability of these polymers to swell in water while the IL is added. Nafion contains mostly hydrophobic perfluoroalkyl groups and does not swell nearly as much. Also, the rigid-rod backbone is cross-linked by hydrophilic PEO units that allow the rod portion to separate in water so the IL can intercalate into the film, which may explain why the non-sulfonated polymers (D and E) swell less in water than Nafion but have a higher IL uptake.

### 3.4. Conductivity

Figs. 1 and 2 show the conductivities of various polymers imbibed with imid-TFSI and imid-CF<sub>3</sub>SO<sub>3</sub>H, respectively. Film H imbibed with 440% imid-TFSI was not tested because the film was too brittle. Conductivities of a few films imbibed with imid-H<sub>2</sub>SO<sub>4</sub> were measured as well. However, the stainless steel electrodes became corroded after each of these measurements and conductivity work with this ionic liquid was discontinued. Figs. 1 and 2 both show that, within the high temperature region, conductivity tends to increase with increasing amounts of IL imbibed in the sample. The film in Fig. 1 that contains the most IL (1:1 DAS:pyr-oda doped with

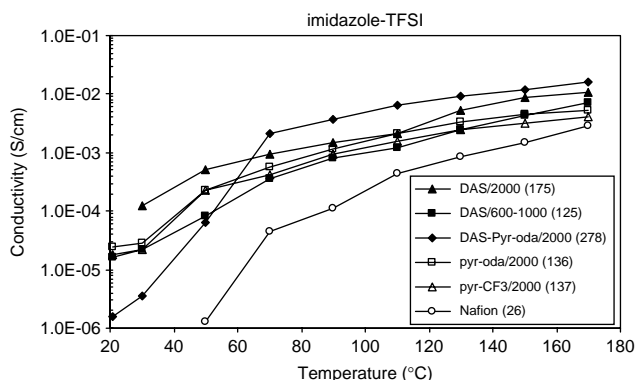


Fig. 1. Conductivities of films doped with imidazole-TFSI. Percentage of IL uptake is in parentheses.

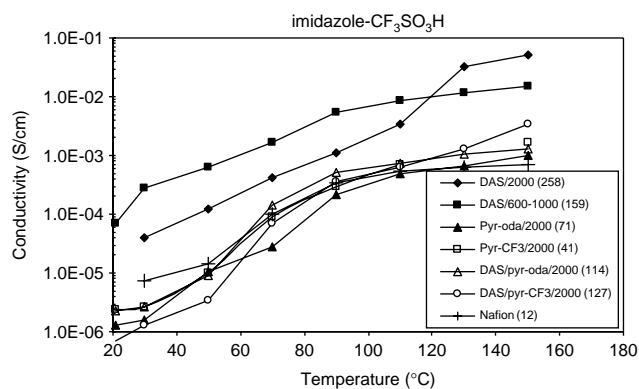


Fig. 2. Conductivity of films doped with imidazole-CF<sub>3</sub>SO<sub>3</sub>H. Percentage of IL uptake is in parentheses.

278% imid-TFSI) is the least conductive at lower temperatures. The conductivity then increases by over three orders of magnitude between 20 and 70 °C, followed by a less rapid increase above the IL melting point at 73 °C [28]. The most conductive sample in Fig. 2 also contains the most IL. This film shows a sharp increase in conductivity between 110 and 130 °C, which is not easily explained. We measured the melting point of this salt to be 174–180 °C.

In both Figs. 1 and 2, the conductivities at high temperatures appear to be proportional to the relative amounts of IL imbibed in the film. Film F has the highest uptake of imid-TFSI (278%), and has a conductivity of  $1.2 \times 10^{-2}$  S/cm at 150 °C. Film A has the highest uptake of imid-CF<sub>3</sub>SO<sub>3</sub>H (258%), with a conductivity of  $5.0 \times 10^{-2}$  S/cm at 150 °C. It is a bit surprising that the conductivity of Film A imbibed with imid-CF<sub>3</sub>SO<sub>3</sub>H is over four times more conductive than Film F imbibed with imid-TFSI since imid-TFSI is in the liquid state at this temperature and imid-CF<sub>3</sub>SO<sub>3</sub>H is not. However, imid-CF<sub>3</sub>SO<sub>3</sub>H is smaller and probably more mobile within the polymer matrix. Also, imid-CF<sub>3</sub>SO<sub>3</sub>H also has a higher density of protons because of its lower molecular weight. One gram of imid-CF<sub>3</sub>SO<sub>3</sub>H has 1.6 times the number of protons as one gram of imid-TFSI. Film A also has a higher concentration of aromatic sulfonic acid groups along the polymer backbone than Film F.

In both Figs. 1 and 2, the least conductive sample is Nafion doped with ionic liquid. Nafion also has the lowest IL uptake in each case. This provides evidence that even with Nafion, the non-humidified high temperature conductivity appears to be dictated more by the amount of IL present than by the acidity of the sulfonic acid groups on the polymer backbone.

## 4. Summary

Several proton-conducting polymers were made that contained rigid aromatic backbones and flexible cross-linking groups. The polymer backbone was connected through a triazine unit that was cross-linked during the curing cycle with diamine-terminated PEO's. The hydrophilicity of the backbone, as well as the flexibility of the film were varied to study the uptake of water and protic ionic liquids. In general, the

films had a higher modulus and less elongation than Nafion, but were much better at imbibing ionic liquids. For films with a hydrophilic backbone (sulfonated aromatic), the ability to imbibe IL's is most likely due to good swelling in water to aid the imbibing process. However, films with a hydrophobic backbone (pyridinium triflate) had a lower water uptake than Nafion, and yet had a much higher IL uptake. Tensile properties show that this is probably not due to film flexibility. It is most likely that the ILs have a stronger affinity for the pyridinium triflate backbone because of these similarities in chemical structure.

Conductivities of various films were measured under non-humidified conditions up to  $> 150$  °C. Conductivity within the high temperature regime appears to depend mostly on the amount of IL present. The highest conductivity reached in this study was  $5 \times 10^{-2}$  S/cm at 150 °C for a sample imbibed with 258% imid-CF<sub>3</sub>SO<sub>3</sub>H. In general, films that were imbibed with large amounts of imid-CF<sub>3</sub>SO<sub>3</sub>H were more conductive than those imbibed with large amounts of imid-TFSI, even though imid-TFSI is a liquid at the measurement temperatures. It is postulated that the films containing imid-CF<sub>3</sub>SO<sub>3</sub>H are more conductive due to a higher density of charge carriers.

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