ANHYDROUS STATE PROTON AND LITHIUM ION CONDUCTING SOLID POLYMER ELECTROLYTES BASED ON SULFONATED BISPHENOL-A-POLY(ARYLENE ETHERS)

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ABSTRACT

Sulfonated polymer based solid polymer electrolytes (SPEs) have received considerable interest in recent years because of their wide variety of applications particularly in fuel cells, batteries, supercapacitors, and electrochromic devices. The present research was focused on three interrelated subtopics. First, two different bisphenol-A-poly(arylene ethers), polyetherimide (PEI) and polysulfone (PSU) were sulfonated by a post sulfonation method to various degrees of sulfonation, and their thermal and mechanical properties were examined. The effects of poly(arylene ether) chemical structure, reaction time, concentration, and types of sulfonating agents on sulfonation reaction were investigated. It was found that deactivation of bisphenol A unit caused by the electron withdrawing imide, retarded the sulfonation of PEI compared to PSU. Sulfonation conducted with a high concentration of sulfonating agent and/or prolonged reaction time exhibited evidence of degradation at the isopropylidene unit. The degradation occurred through the same mechanistic pathway with the two different sulfonating agents, chlorosulfonic acid (CSA) and trimethylsilyl chlorosulfonate (TMSCS). The degradation was faster with CSA than its silyl ester, TMSCS, and was evident even at low acid concentration.
Second, novel anhydrous proton conducting solid polymer electrolytes (SPEs) were prepared by the incorporation of 1H-1,2,4-triazole (Taz) as a proton solvent in sulfonated polyetherimide (SPEI) matrix. The size, shape, and state of dispersion (crystal morphology) of triazole crystals in SPEI were examined as a function of degree of sulfonation and triazole concentration. Increasing sulfonic acid content caused reduction of triazole crystallite size, hence the depression of melting temperature and their uniform distribution throughout the sulfonated polymer matrix. The increased rate of structure diffusion within the smaller size crystals due to the improved molecular mobility contributed significantly to the anhydrous state proton conductivity.

Third, a new category of single lithium ion conducting SPEs was developed by crosslinking a polyether epoxy, poly(ethylene glycol)diglicidyl ether (PEGDGE) (lithium ion solvent), in sulfonated polysulfone (SPSU) matrix. The effects of degree of sulfonation and electrolyte composition on ionic conductivity, thermal, and tensile properties of SPEs were investigated. It was found that ion-dipole interactions between lithium sulfonate (SO$_3$Li) and PEGDGE were responsible for the reduction in size of the dispersed epoxy phase and increased thermal stability. Lithium sulfonate promoted compatibilization and also caused improvement in elongation at break. A low molecular weight electrolyte salt, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was further dissolved in PEGDGE phase prior to its crosslinking in SPSU matrix, and the ionic conductivity and thermal properties were evaluated as a function of doping level. The ionic conductivity showed remarkable improvement compared to the undoped system.
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CHAPTER I
INTRODUCTION

Solid polymer electrolyte (SPE) is a key component in portable electrochemical devices including fuel cells, rechargeable batteries, electrochromic displays, and supercapacitors. The past decade has produced spectacular advances in exploring the science and engineering of electrochemical cells to keep pace with today’s information rich mobile society. The heat-resistant electrolyte is required for high temperature operation of a proton exchange membrane fuel cell (PEMFC) to improve heat utilization of fuel cell stack, thermal, and water management, increase the rate of electrode reactions, and tolerance to CO poisoning. The conventional lithium ion cell contains an electrolyte solution consisting of lithium salt in flammable organic solvents. The heat generated due to electrical short circuit (dendritic growth) or release of oxygen from cathode in lithium ion cells causes combustion of flammable electrolytes and hazardous failure of the light weight power system. Thus the development of solid polymer electrolytes is being driven by increasing demand for durable and heat-resistant electrolyte separators for portable electronic devices. In addition to thermal stability, use of polymer in electrolyte material offers advantages of ease of processability, light weight, high energy density, shape versatility, safety, and lack of toxicity.
SPE consists of mainly two phases – ion donor and solvent. The sulfonated polymers with the sulfonate ion anchored to the polymer backbone (polyelectrolytes), are potential ion donors due to their attractive feature of single cation conductivity. Ion conduction in SPE takes place in the solvent phase, and ionic conductivity is proportional to the concentration and mobility of the charge carriers in the conducting phase. The solvent for proton conduction, required to have self-dissociation characteristics, amphoteric nature (i.e., with proton donor - acceptor sites), and capable of forming intermolecular hydrogen bonds. In Li⁺ conducting SPE, the solvent molecule possesses heteroatoms with unshared electron pairs (Lewis base) such as ether oxygen or amine nitrogen, and cation solvation is accomplished through Lewis acid-base interaction. The most well known proton and lithium ion solvents in SPEs are water and polyethylene oxide, respectively.

In the past decade, substantial research activities on proton conducting polymer electrolyte for fuel cell applications were focused on hydrated Nafion because this commercially available perfluorosulfonic acid copolymer meets most of the requirements in terms of high proton conductivity, high thermal stability, chemical resistance, and good mechanical strength. However, high price, limited operation temperature up to ~100°C, and high methanol permeability have motivated the development of sulfonated poly(arylene) main chain polyelectrolytes due to their excellent chemical, thermal and mechanical stability next to Nafion. Examples include sulfonated polystyrene, poly(ethersulfone)s, polyimides and poly(etherimides), poly(etherketones), poly(phenylenesulfides), poly(phenylquinoxaline), poly(benzimidazole), etc.
The proton conductivity in water arises from the contribution of two mechanistic pathways\textsuperscript{4-10} (i) structure diffusion (Grotthuss-type mechanism) involving intermolecular proton transfer within hydrogen bonded network or structure, followed by hydrogen bond breaking and formation, and (ii) vehicular diffusion involving hydrodynamic diffusion of the protonated water molecules. The temperature-dependent proton conductivity in hydrated Nafion followed the Arrhenius relation, implying conduction occurred in water, independent of polymer backbone. Kreuer described the microstructural features of Nafion compared to sulfonated poly(ether ketones) (SPEK). The morphological differences were attributed to the rigidity of main chain backbone of SPEK, less hydrophobicity of the aromatic polymer, and lower acidity of sulfonic acid groups\textsuperscript{11-13}. Gebel discussed the microstructure evolution of Nafion from dry state to aqueous solution\textsuperscript{7}. Several studies have reported the significant role of different states of water in sulfonated polymer in determining proton transport\textsuperscript{14-22}. Laporta et al. proposed that above $\lambda = 5$ ($\lambda$ is moles of water/-SO$_3$H), formation of continuous aqueous phase through cluster coalescence was responsible for drastic improvement in proton conductivity\textsuperscript{15}.

Proton conductivity in conventional sulfonated polyelectrolytes depends on water content; hence, it decreases significantly above 80\textdegree C due to the evaporation of water from the matrix. This practical difficulty has motivated the seeking of anhydrous proton conducting SPEs with high conductivity at high temperature. Research works on phosphoric acid doped in polybenzimidazole matrix at high acid to polymer ratio, substitution of water by aromatic heterocycles, such as imidazole, pyrazole, triazole, benzimidazole in sulfonated polymers showed encouraging results\textsuperscript{10,23-26}. 

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IH-1,2,4-triazole is a promising aromatic heterocycle that can act as a proton solvent like water\(^\text{10}\). It is a crystalline solid and has a melting point of \(\sim120^\circ\text{C}\) and a boiling point of \(\sim256^\circ\text{C}\). It has high proton conductivity only above the melting point. It is electrochemically more stable than imidazole due to low electron density. Both triazole and triazolium ions (\(pK_{a1} = 2.39, pK_{a2} = 9.97\)) with lower \(pK_a\) compared to imidazole (\(pK_{a1} = 7.18, pK_{a2} = 14.52\)) have better proton donating tendency. These favorable criteria justify its selection as an efficient proton solvent in this study.

Conventional ionically conducting SPEs are solid solutions of low molecular weight electrolyte salt in polymer, first developed by Wright and co-workers in 1973, by dissolving alkali metal salt in poly(ethylene oxide)\(^\text{1,27-36}\). The pioneering work was followed by several researchers; Armand and coworkers reported the most promising SPE using a weakly coordinating anion, bis(trifluoromethylsulfonyl)imide (TFSI)\(^\text{29}\). The ion transport in polymer electrolytes results from a solvation-desolvation process i.e., occurs through the formation and breaking of the co-ordinate bonds between the cations and host polymer (Lewis acid-base interaction), mainly located in the amorphous phase. Thus, the high degree of crystallinity (\(\sim85\%\)) in PEO causes a significant decrease in ionic conductivity (\(\sigma < 10^{-8}\text{ S/cm}\)) below the crystalline melting point, \(\sim65^\circ\text{C}\). The ionic conductivity is directly related to the segmental motion of the polymer chains; thus the variation of conductivity with temperature follows the Vogel-Tamman-Fulcher (VTF) equation.

Conventional SPEs have certain problems: low lithium ion transference number (0.3-0.5) and polarization of batteries caused by the concentration gradient of the electrolyte salt. These practical difficulties arise due to the significant contribution of anion transport.
to ionic conductivity owing to its weak interactions with the host polymer. Few studies have addressed the issue through the approach of attaching the sulfonate group to the polymer backbone to reduce the mobility of anion. However, these materials exhibited high conductivity only in the presence of a solvent \(^1,^2,^7\). Polyether epoxy, poly(ethylene glycol)diglycidyl ether (PEGDGE) is liquid with ether oxygen in the repeat unit. The hydroxyl groups generated upon crosslinking of epoxy are expected to solvate the sulfonate anions. This is why PEGDGE was used as lithium ion solvent in developing lithium ion conducting SPEs.

Inspite of extensive studies on proton and lithium ion conducting SPEs, many questions remain unanswered, particularly with the solid-state solvent in sulfonated polymer matrix. A fundamental understanding of two-component single ion conducting SPE design and the interrelationship between solvent morphology and ion conduction phenomena have not yet been explored. For example, what factors dictate the size, shape, and state of dispersion (morphology) of a solid state solvent dispersed in sulfonated polymer matrix? What is the effect of solvent morphology on ion conductivity?

The sulfonation of polyetherimide with chlorosulfonic acid has been reported by few researchers. In present study, for the first time, sulfonated bisphenol A polyetherimide (SPEI) was synthesized using trimethylsilylchlorosulfonate. Another bisphenol-A-poly(arylene ether), polysulfone (PSU) was also post sulfonated under identical conditions to evaluate the influence of the electron withdrawing group in the poly(arylene ether) backbone on sulfonation. The effect of reaction time, concentration, and type of sulfonating agents on sulfonation were investigated to provide a better understanding of the necessary conditions required to achieve maximum degree of sulfonation through
minimizing degradation and the probable degradation mechanism. The thermal and mechanical properties of sulfonated poly(arylene ethers) were characterized as a function of sulfonation level. In addition, two novel proton and lithium ion conducting SPEs based on sulfonated bisphenol-A-poly(arylene ethers) were developed. SPEI was utilized in the preparation of anhydrous proton conducting polymer electrolytes through the incorporation of 1H-1,2,4-triazole (Taz) in the sulfonated polymer matrix. The interactions between SPEI and triazole and its influence on crystal morphology (size, shape, and state of dispersion) were investigated as a function of degree of sulfonation and SPE composition and correlated with proton conduction mechanism. The preparation of single lithium ion conducting SPE based on lithium salt of sulfonated polysulfone (SPSU(X)Li) and poly(ethylene glycol)diglycidyl ether (PEGDGE) crosslinked by 4,4' diaminodiphenyl sulfone (DDS) is also described. The sulfonate ion induced compatibilization and its effect on solvent phase morphology, ionic conductivity, thermal, and tensile properties were studied as a function of sulfonation level and PEGDGE concentration. The epoxy phase was further doped with a low molecular weight electrolyte salt, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) to provide a fundamental understanding of the impact of TFSI anion contribution to the ionic conductivity.
CHAPTER II
LITERATURE REVIEW

The development of sulfonated aromatic polymer based solid polymer electrolytes (SPEs) have received considerable interest in the past decade due to their wide variety of applications. With electrolyte salt in polymer, both the cations and anions contribute to the ionic conductivity while in polyelectrolytes, with the anions anchored to the polymer backbone, only the cations are mobile. These materials are promising candidates to obtain high cation transference number (i.e., high ratio of the charge carried by the cation compared to the total transported charge). In addition, they are not susceptible to the build-up of a resistive salt layer at the electrode-electrolyte interface like polymer electrolytes. Polyelectrolytes require the presence of a plasticizer to achieve high ionic conductivity through the solvation of the ion exchange sites. The influence of ion-plasticizer interactions on ion transport has been the focus of several studies in recent years with particular emphasis on the hydrated Nafion system as proton exchange membranes in fuel cell technology. Aromatic heterocycles have been recognized as a potential proton solvent in developing anhydrous proton conducting electrolytes due to their amphoteric (proton donor-acceptor sites) nature, intermolecular hydrogen bond formation, and self-dissociation characteristics like water.
In this chapter, a brief review on sulfonated polymer based polyelectrolytes is presented regarding the synthetic routes, applications, sulfonate ion induced interactions, morphological features, and related proton conduction mechanism mainly in hydrated systems. Since lithium ion conducting polyelectrolytes were also investigated in our research in addition to anhydrous state proton conduction, the literature survey also includes lithium ion conducting solid polymer electrolytes with more focus on polymer chemical structure and salt solvation in controlling ionic conductivity.

2.1 Sulfonated polymer based polyelectrolytes

Several research has been focused on synthesis of both aliphatic and aromatic sulfonated polymer based polyelectrolytes due to their unique feature of single ion conductivity.

2.1.1 Structure

Polyelectrolytes are polymers that contain bonded ionic groups. In a sulfonated polymer, the sulfonate anion is covalently bonded to the polymer backbone, while the counter cation is free to move. The mobility of the counterion depends on the strength of the ionic bond, the temperature, and the presence of ionic liquids which promotes dissociation, such as water. The most widely studied perfluorosulfonate copolymer, Nafion, a product of the Dupont Chemical Co., contains polytetrafluoroethylene (Teflon-
like) backbone and generally less than 15mol% perfluorovinyl ether side chain terminated with a sulfonic acid group at its end \(^1,2,27,28\), shown in Figure 2.1(a).

In recent years, a lot of scientific interests have motivated the development of numerous types of arylene main chain polyelectrolytes due to their thermal, chemical, and mechanical stabilities comparable to Nafion \(^3\). Examples include poly(styrene sulfonic acid), sulfonated poly(ethersulfone)s, different polyimides, and poly(etherimide)s, poly(etherketone)s, poly(phenylenesulfide)s, poly(phenylquinoxaline), poly(benzimidazole), etc. The chemical structures of a few sulfonated polyarylene main chain polymers are shown as representatives in the Figure 2.1(a).

2.1.2 Morphology

In some sulfonated polyelectrolytes including Nafion, a typical morphological feature is evident; owing to the hydrophobicity of the backbone with high hydrophilicity of the sulfonic acid functional groups in one macromolecule, hydrophobic/hydrophilic nanophase separation takes place especially in the presence of water (Figure 2.1(b)) \(^1,3\). The sulfonic acid groups aggregate to form hydrophilic domains. These ionic domains constitute electrostatic network-physical crosslinks that restrict the mobility of the chains locally and enhance the glass transition temperature and mechanical properties of the polymers. When hydrophilic domains are hydrated, protonic charge carriers form by dissociation of acidic functional groups. Thus, the well-connected hydrophilic domains are responsible for proton and water transport. The hydrophobic domains provide morphological stability and prevent the polymer from dissolving in water \(^1,4\). The
morphology of Nafion membrane has been characterized by various researchers utilizing small angle x-ray and neutron scattering techniques \(^5,6,7\).

In sulfonated polystyrene (SPS) based polyelectrolytes, the ionic groups are randomly distributed along the polymer chain. It has been extensively studied due to its completely amorphous nature as opposed to perfluorosulfonate and sulfonated polyurethane, in which properties are complicated by the crystallinity. In a widely accepted model on the morphology of SPS, Eisenberg et al. proposed that each ion pair attached to the polymer backbone resides within a rigid multiplet which anchors the chain, thus giving rise to a region of restricted mobility surrounding each multiplet \(^8,9\). The thickness of the region, which mainly consists of hydrocarbon chains, was postulated to be the order of the persistence length of the polymer. The individual multiplets act as crosslink and raise the \(T_g\) of the polymer. As the ion content increases, the regions of restricted mobility surrounding each multiplet overlap and form a large contiguous phase of restricted mobility. This separate phase is known as cluster (The concept differs slightly from the definition of ionic cluster in perfluorosulfonate polymer matrix, where clusters refer to nanophase separated, hydrated ionic aggregates \(^10\) rather than regions of closely spaced multiplets). The cluster phase exhibits its own \(T_g\), higher than the \(T_g\) of the unclustered phase.

The evidence of cluster formation in random ionomers is the existence of two peaks in the loss tangent (\(\tan \delta\)) vs temperature curves and the “ionic” peak observed in small-angle-X-ray scattering (SAXS) study, which is attributed to the intermultiplet spacing in the cluster region. The two glass transitions correspond to the nonpolar matrix and the cluster regions \(^8\).
Figure 2.1 Sulfonated polymers (a) chemical structure, (b) hydrophobic/hydrophilic nanophase separation in presence of water.\textsuperscript{14}
Several studies have addressed the large number of factors influencing the multiplet formation and ion clustering in sulfonated polymers, such as the functionality level, $T_g$ of the parent polymer, molecular weight, nature of counter cation, position of the ion pairs relative to the polymer backbone, steric constraints in ion pair aggregation, dielectric constant of the host polymer, amount and nature of added low molecular weight compound (plasticizer), thermal history of the samples, etc. In sulfonated polymers with relatively rigid chains (e.g., sulfonated polyarylenes), two distinct morphological regions do not exist. It was observed that the $T_g$ of sulfonated poly(ether ether ketone) ($T_g$ of the host polymer was 150°C) increased at a rate of $9.4 \times 10^4 \, ^\circ\text{C} \, \text{gmol}^{-1}$ with respect to equivalent weight, while for sulfonated polystyrene ($T_g$ of the host polymer was 100°C), the rate was $3.4 \times 10^4 \, ^\circ\text{C} \, \text{gmol}^{-1}$. This behavior has been described by a key feature of the Eisenberg model, i.e., the intermultiplet distance should be approximately twice the persistence length for the two-phase morphology to be observed. In sulfonated polyarylenes, restricted chain mobility gives rise to long persistence length; the intermultiplet distance being shorter than twice the persistence length causes the entire polymer to be clustered and thus exhibits single-phase behavior. The observed increase in $T_g$ at higher rate in these rigid polyelectrolytes at low ion content is due to the onset of clustering as opposed to the crosslinking effects of the multiplets in relatively flexible sulfonated polystyrene at similar ion content.
2.1.2.1 Hydration effect

Kreuer $^{10,12,13}$ discussed nanoscale morphology of Nafion and compared it with sulfonated poly(ether ketones) (SPEK). Hydrophobic/hydrophilic phase separation was observed in SPEK in the hydrated state. The separation length obtained from the position of the peaks in small angle x-ray scattering was found to be smaller with a wider distribution of domain size and larger internal interface between the two domains in SPEK in comparison to Nafion.

Based on these findings, the following microstructural features of Nafion compared to sulfonated poly(ether ketone) (SPEK) in the hydrated state were summarized (Figure 2.2) $^{13}$ the water-filled channels in Nafion are wide, the hydration pockets are more separated, and the percolated hydration structure is less branched and well-connected. There is less hydrophobic/hydrophilic interface and intersulfonate separation, with no dead end channels. These morphological differences between the two membranes arise due to rigidity of the main chain backbone, less hydrophobicity of the aromatic polymer and lower acidity of sulfonic acid groups.

The effect of different counterions and degree of hydration on the sulfonate sites of a perfluorosulfonate copolymer was examined by FTIR spectroscopy and a four-state model of ionic-hydrate association was proposed $^{14}$. Laporta et al. investigated the state of water in Nafion $^{15}$. The first water molecule absorbed by Nafion membrane appeared to cause dissociation of $\text{–SO}_3\text{H}$ groups with the formation of $\text{–SO}_3^-$ and hydronium $\text{H}_3\text{O}^+$ ions. The size of cluster was found to increase (from $\lambda = 3$ to 5, $\lambda$ is moles of water/-$\text{SO}_3\text{H}$) with increasing water content (from 47% to 79% RH) until a threshold value ($\lambda = 5\text{–}6$) was reached. The model can explain the conductivity threshold value corresponding
to a water content of $\lambda = 5$ above which conductivity rises roughly linearly until reaching the value of 0.06 S/cm for $\lambda = 14$. For $\lambda = 5$, the proton has high mobility within the clusters but there is no continuity between the clusters, and hence no continuous proton transfer. For $\lambda > 5$ (from 90% RH), the clusters coalesce, conductivity increases and the behavior is in accord with the formation of continuous phase similar to that of bulk water.

Figure 2.2 Schematic representation of the nanoscopic hydration structures of Nafion and a sulfonated polyetherketone$^{13}$. 
Kim et al.\textsuperscript{16} proposed that the state of water plays a significant role in determining the transport properties of the membranes. The state of water in disulfonated poly(arylene ether sulfone) copolymers and Nafion was quantified by pressure differential scanning calorimetry (DSC) and $^1$H pulse NMR techniques. In ionic polymers, different states have been illustrated as follows: 1) nonfreezing water – strongly bound to the polymer chain and causes reduction in glass transition temperature (plasticization), 2) freezable water – weakly bound to the polymer chain or nonfreezing water which exhibits a broad melting endotherm, and 3) free water – not intimately bound to the polymer chain and behaves like bulk water, displaying a sharp melting point at 0\degree C.

The microstructure evolution of Nafion from the dry to solution through the water swollen state was investigated by Gebel using small–angle scattering techniques\textsuperscript{7}. A qualitative model, schematically shown in Figure 2.3, was proposed. In the dry state, Nafion matrix contains isolated spherical ionic clusters with diameters of 1.5 nm and a inter-cluster distance of 2.7 nm. The clusters swell upon absorption of water with the ionic groups at the polymer-water interface to minimize the interfacial energy. The cluster diameter at this stage is close to 2 nm while the inter–cluster distance is about 3 nm indicating that the clusters are still isolated as also evident from the extremely low value of ionic conductivity. With further increase in water content, 0.3 <\(\phi_w<0.5\) (\(\phi_w\) is the volume fraction of water), structural reorganization takes place with the formation of connecting cylinders of water between the swollen spherical clusters which was referred to onset of percolation. An inversion of the structure occurs at \(\phi_w>0.5\) and the structure
Figure 2.3 Schematic representation of the structural evolution of PFSI from dry state to solution.
resembles a connected network of rods. Finally, the rodlike structures separate to form a colloidal dispersion of isolated rods as the membrane “dissolves” in water.

2.1.2.2 Plasticization effect

The effect of polar and nonpolar plasticizers on the properties of polyelectrolytes has been reported in the literature \(^{17,18}\). Nonpolar plasticizers (e.g., dioctyl phthalate) were found to plasticize both the matrix and the cluster regions leading to a remarkable and in some cases parallel decrease in the cluster and matrix \(T_g\). Internally plasticized sulfonated polystyrene with covalently-attached alkyl chains showed analogous decrease in the cluster and matrix \(T_g\). Polar plasticizers (e.g., glycerol) caused reduction in cluster \(T_g\) of the polyelectrolyte. Kim et al. \(^{17}\) studied the plasticization of sulfonated polystyrene with surfactant molecules having ionic head groups identical to the ionic group in the polymer chain. Sodium dodecylbenzenesulfonate used as surfactant in sulfonated polystyrene caused a large decrease in cluster \(T_g\) with increase in weight percent of the surfactant, while the matrix \(T_g\) was found to be relatively less dependent on the surfactant concentration.

Numerous studies were attempted to subdue the ionic interactions by utilizing various metal counterions, but the effect was not significant. In an investigation of the effect of counterions on the melt viscosity, Weiss and Agarwal \(^{18}\) observed that the counter metal ions increase the melt viscosity of propylene-acrylic acid graft copolymer markedly, while the acidic group neutralized with tributylamine exhibited a lower viscosity compared to the unneutralized copolymer. These researchers also studied the influence of
a number of alkyl groups and alkyl chain length in various aliphatic amine based counterions on the thermal, mechanical and rheological behavior of sulfonated polystyrene (SPS). The glass transition temperature, modulus, and melt viscosity increased with metal or ammonium counterion compared to the unsulfonated polymer but decreased with increasing the number of substituents on nitrogen. Longer chain amines behaved as internal plasticizers; sulfonated polystyrene containing 21 mol% tristearylammonium substituent was essentially a rubber at room temperature. Page and co-workers \(^6\) utilized a series of alkyl ammonium ions to systematically alter the strength of electrostatic interactions in Nafion. They found within the nanophase–seperated morphology of Nafion, weak interaction between ion pairs in the system containing the large counterions reduces the efficiency of the physical cross-links to locally restrict the mobility of chains, yielding a relatively larger population of chains with higher mobility. Johnson and coworkers \(^19\) studied the influence of different counterions on physical properties of SPSU at a low level of sulfonation. They observed significant variation in thermomechanical behavior between the divalent and monovalent counterions; extensive enhancement in the rubbery plateau and modulus was reported with magnesium counterion compared to the sodium salt form above the glass transition temperature.

Robertson et al. \(^20\) investigated the interaction between sulfonated poly(ether ether ketone) with the casting solvents dimethylformamide (DMF) and dimethylacetamide (DMAc) by NMR techniques and the influence of the interaction on proton conductivity. They found that the amide group in DMF readily forms hydrogen bond with the sulfonic acid group of SPEEK even at temperature as low as 60\(^\circ\)C. DMAc is less susceptible to form hydrogen-bonded complex which occurs only at above 100\(^\circ\)C. Both of these
solvents undergo sulfonic acid catalyzed thermal degradation. The solvent interaction reduces the proton conductivity. Guan et al. 21 studied the effect of casting solvents on the morphology and performance of sulfonated polyethersulfone (SPES) membranes. Residual solvents caused reduction in $T_g$.

2.2 Applications of sulfonated polymers

The ion conducting polymer electrolyte membranes are key components in three major applications; fuel cells, batteries, and electrochromic devices 22. The prime requirement for the conversion of chemical energy into electrical energy in an electrochemical cell is high ion conductivity across the polymer electrolyte membrane and the electrode compatible electrolyte material. The basic elements of an electrochemical cell are illustrated in Figure 2.4. Polymer electrolyte membrane is capable of functioning both as separator and electrolyte. In addition, it combines the advantages of easy processability, light weight, safety, and lack of toxicity.

2.2.1 Fuel cells

Fuel cells are classified into five major types depending on the nature of electrolyte: alkaline fuel cell (AFC), polymer electrolyte membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC). Figure 2.5 summarizes the electrochemical reactions that take place in various fuel cell systems. The attractive features of a fuel cell, which act as motivation of current research interest include clean exhaust emission (free of environmentally undesirable
Figure 2.4 Basic structure of an electrochemical cell\textsuperscript{22}. 

Electrolyte or Pure Ionic Conductor (May contain a porous insulating material to maintain physical separation of the anode and cathode)
Figure 2.5 Summary of reactions in various fuel cells\textsuperscript{22}. 

\textbf{Figure 2.5 Summary of reactions in various fuel cells}
gases such as nitrogen oxides, carbon monoxide, and residual hydrocarbons), high energy efficiency and their possibility as an effective solution to the coming petroleum shortage.

The polymer electrolyte fuel cell (PEMFC) was first developed by GE for the Gemini space craft employing poly(styrene sulfonic acid) membrane $^{22}$. The second GE PEMFC which powered the Biosatellite space craft, utilized Nafion as electrolyte membrane. PEMFCs are promising power sources for both vehicular transportation and portable stationary applications $^{2}$. A PEMFC consists of two porous platinum electrodes with a solid polymer electrolyte membrane sandwiched between them. The single cell assemblies can be mechanically compressed across electrically conductive separators, known as bipolar plates, to fabricate electrochemical stacks. PEM fuel cells require humidified gases, hydrogen and oxygen (or air), as fuel for the operation. The electrochemical reactions that occur at both electrodes are as follows:

Anode: \( \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \)

Cathode: \( \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \)

Overall: \( \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Electrical Energy} + \text{Heat energy} \)

The proton exchange membrane is one of the most important components of a fuel cell. It performs two basic functions: 1) acting as a separator to prevent mixing of the oxidant (i.e., pure oxygen or air) with hydrogen gas or methanol; and 2) acting as an electrolyte to transport protons from the anode to cathode. The following properties of the membranes are desired: a) high conductivity at high temperature (> 100°C) without any electronic conductivity, b) high thermal stability c) high chemical and electrochemical
stability under the fuel cell operating conditions, d) good mechanical stability and strength, e) low permeability to reactants, f) surface properties compatible for (interfacial) bonding catalytic electrodes to the membranes, and g) low cost.

The harsh chemical and physical environment in a fuel cell includes active noble metal catalysts at the electrodes, chemically aggressive fuels like methanol and its partial oxidation products, oxidants like oxygen, and formation of reactive radicals at the electrodes, especially at the cathode and high operation temperature (>100°C). The commercially available perfluorosulfonic acid copolymer, Dupont’s Nafion has been recognized as the potential matrix material due to their high conductivity, high thermal and chemical stability, and good mechanical strength. However, the high price, complicated synthetic procedure, limited operation temperature of about 100°C and high methanol permeability have motivated in seeking of suitable alternatives. In the last decades, a lot of research has been directed to the development of poly(arylene) main chain polyelectrolytes due to their excellent chemical, thermal and mechanical stability next to Nafion \(^2,3\). A large number of polymers have been sulfonated to obtain proton conductivity. Examples include poly styrene, poly(ethersulfone)s, polyimides and poly(etherimide)s, poly(etherketone)s, poly(phenylenesulfide)s, poly(phenylquinoxaline), poly(benzimidazole), etc. The disadvantages associated with these classes of polymers are lower conductivity compared to Nafion, reversible desulfonation at a temperature lower than the degradation temperature of the backbone, and loss of mechanical strength due to the high degree of swelling at the higher sulfonation level.

Proton conduction in sulfonated polyelectrolytes takes place in the presence of water. Conductivity decreases drastically above 80°C due to the evaporation of water from the
matrix. This practical difficulty has stimulated the growing interest in developing novel anhydrous polymer electrolyte membranes with high proton conductivity at high temperatures. Among several approaches, oxo-acid doped in basic polymer matrix at high acid-to-polymer ratio, such as phosphoric acid complexed with polybenzimidazole\textsuperscript{23, 24}, substitution of water by heterocycles, such as imidazole, pyrazole in sulfonated polymers\textsuperscript{25,26}, have shown encouraging results.

2.2.2 Flexible batteries

Electrochemical charge storage devices play a very significant role in technical applications including computers, communication devices, electric vehicles, spaceships, industrial and laboratory equipments\textsuperscript{1,27,28}. The past decade has produced spectacular advances in battery technology based on Li metal, nickel-cadmium, nickel–metal hydride, Li ion etc.\textsuperscript{29,30} A battery consists of several electrochemical cells connected in a series and/or parallel to provide the required voltage and capacity. Each cell contains a positive electrode (cathode) and a negative electrode (anode) separated by an electrolyte. When these electrodes are connected externally, chemical reactions occur at the electrodes, liberating electrons which flow through the external circuit, while the electrolyte enables ion transfer within the cell. The amount of electrical energy, expressed as either per unit weight (known as specific energy in Wh kg\textsuperscript{-1}) or per unit volume (known as energy density in Wh l\textsuperscript{-1}), that a battery can provide is a function of cell potential and specific charge (also known as capacity in Ah kg\textsuperscript{-1}), and both of the parameters are directly related to the chemistry of the system. The conventional cell
configurations are illustrated in the Figure 2.6(a). Among the various existing technologies, Li-based batteries have received most attention due to the fact that Li is the most electropositive (-3.04 V versus standard hydrogen electrode) and the lightest metal (equivalent weight 6.94 g mol\(^{-1}\) and specific gravity 0.53 g cm\(^{-1}\)) and forms thin passivating films which are ionically conducting thus providing the storage system with high energy density, light weight, and longer lifespan compared to the other technologies.

Various inorganic compounds were found to react reversibly with alkali metals. These compounds are known as intercalation compounds. TiS\(_2\) was one of the best intercalation compounds, utilized by Exxon\(^{31,32}\). Li metal was used as a negative electrode and dioxalane solution of lithium perchlorate as the electrolyte. The cell encountered the problem of uneven Li growth (dendritic) as the metal was replated during each discharge-recharge cycle (Figure 2.6(b)), which led to explosion hazards. The use of Li in the ionic state rather than metallic state solve the dendritic problem\(^{33}\).

The discovery of a reversible, low-voltage Li intercalation-deintercalation process in carbonaceous material provides Li–ion cells with potential exceeding 3.6V (three times that of the alkaline system) and specific energy of 120-150 W h kg\(^{-1}\); therefore they are used in most high performance portable electronic devices\(^{34,35}\).

In addition to the electrodes, the electrolyte is also the key component of a battery. The most recent development of electrolytes for lithium ion batteries is focused on the replacement of the liquid electrolyte by a polymer electrolyte since it provides the unique combination of high energy density, long life, and ease of processability inherent of
Figure 2.6 Lithium battery (a) schematic illustration of the electrode reactions\(^{67}\), (b) dendritic growth at the Li surface of a rechargeable Li-metal battery\(^{29}\).
polymeric materials. Conventional solid polymer electrolytes (SPE) are obtained by dissolving alkali metal salts in polyether matrix (immobile solvent), first reported by Wright \(36\) in 1973 followed by many researchers \(^{1,27,28}\). The solvent donor number (number of ether oxygen atoms), dielectric constant, lattice energy of the salt and delocalization of anion negative charge strongly influence the salt solvation and its state of dissociation in the polymer. The polymer electrolyte plays three major roles in a battery. It acts as an ion carrier and interelectrode separator which further eliminates the requirement of an inert porous separator used in liquid electrolyte batteries and ensures good contact with the electrodes. Replacement of liquid electrolyte by polymer offers several advantages such as design flexibility and shape versatility of the device, light weight, electrochemical stability, safety and lack of toxicity as it eliminates the use of reactive corrosive solvents. The large surface-to-thickness ratio compensates for the low ionic mobility and also results in low current density, which makes the electrochemical processes more reversible and energy efficient. The high viscosity of the polymer electrolyte prevents electrolyte penetration inside the electrode material and preserve the integrity of the boundary at the electrode-electrolyte interface.

Although solid polymer electrolyte (SPE) replaced the liquid electrolytes, it cannot be applied to portable devices as high ionic conductivity is obtained at a temperature of about 80\(^\circ\)C. Several studies reported in the literature focused on developing Li hybrid polymer electrolyte (Li-HPE) batteries \(^{37,38}\). Hybrid electrolyte consists of three components: polymer matrix swollen with liquid solvent and salt. The problems associated with dendritic growth of Li were still a safety issue. Bellcore researchers \(^{37}\) developed the reliable and rechargeable thin film battery consisting of copolymer of
vinylidene fluoride and hexafluoro propylene of P(VDF-HFP) membranes swollen by liquid electrolyte, with Li-based 3d-metal oxide dispersed at one surface and carbon at the other surface.

Killian et al.\(^{39}\) fabricated an all-polymer battery with pyrrole electopolymerized on the graphite fiber substrate as cathode and polypyrrole/polystyrenesulfonate on graphite fiber substrate as anode sandwiched with a layer of solution cast polyacrylonitrile gel electrolyte. The cell provided a specific charge capacity of 22 mAh g\(^{-1}\) at a cell potential of 0.4V and showed no loss of capacity upto 100 cycles.

The principal limitations associated with the solid polymer electrolytes currently available are low ionic conductivity at low temperature (<0\(^\circ\)C), anion contribution to the total conductivity, and decrease in the stability window with increasing temperature. For PEO-LiCF\(_3\)SO\(_3\), the redox stability domain varies from 3.77V at 100\(^\circ\)C, 3.3 V at 140\(^\circ\)C to 1.91V at 170\(^\circ\)C\(^{40}\).

The Li\(^+\) transference number plays a significant role in the performance of lithium batteries. The cationic transference number of unity, characteristic of single (lithium) ion conductor, is more relevant for the application. Single ion conductors can be obtained by anchoring the anions to the polymer backbone. Few studies have addressed the use of polyelectrolyes based on sulfonated polymers such as poly(4-styrene sulfonate)\(^ {41,42}\), poly(lithium 2 acrylamido-2-methyl propane sulfonate)\(^ {43}\), perfluoroalkyl sulfonate\(^ {44}\), crosslinked poly[oligo(oxyethylene)methacrylate-co-lithiummethacryloyl hexylsulfonate\(^ {45}\) in single ion conducting SPE. However, conductivity is low in these materials (ca.<10\(^{-5}\) S/cm at room temperature) and improves significantly in presence of a plasticizer\(^ {46,47}\), by means of blending\(^ {48}\), copolymerizing\(^ {49,50,51}\).
2.2.3 Electrochromic devices

The development of solid state electrochromic materials has gained attention in recent years due to their potential applications in electrooptical devices: electrochromic displays, optical modulators, adjustable reflectance mirrors of vehicles, sunglasses, and smart window glasses designed to save energy in buildings through the control of sunlight transmission. Electrochromism is defined as reversible color change due to electrochemical insertion/extraction of electrons and ions (such as H$^+$ or Li$^+$) into mostly inorganic materials (electrochromics). Electrochromism was first discovered in tungsten oxide (WO$_3$) and later found in oxides of nickel, molybdenum, cobalt, chromium, manganese etc $^1$. The favorable characteristics of this material include ease of thin film deposition, reversibility and stability during cycle operation. Many organic electrochromic materials have also been developed including dye, pigments, and conducting polymers $^{52,53}$. Electrochromic devices consist of multilayer thin film electrochemical cells that have at least one electrochromic material. The components of the device (Figure 2.7) are: (1) an electrically conducting transparent film on a glass substrate (e.g. indium tin oxide (ITO) coated glass substrate), (2) a film of electrochromic material (which possesses both ionic and electronic conductivity), (3) ionically conducting electrolyte, and (4) an electrically conducting counter electrode (complimentary electrochromic material).

The growing interest in solid polymer electrolytes for electrochromic devices is motivated by their flexible film forming ability, good optical contrast, memory effect, image stability, ability to operate over a wide range of temperature and good adherence to the neighbouring electrochromic layers leading to compact large area device fabrication.
p(TMC) - poly(trimethylene carbonate)

Figure 2.7 Schematic representation of an electrochromic display\(^1\).
As in a flexible battery, the ionically conducting phase is formed by dissolving salts in host polymer matrices. Different polymer electrolytes have been proposed based on polyethylene oxide, poly(amide 6-b-ethylene oxide), and natural polymers such as hydroxyethylcellulose or modified starch. There also exist proton conducting polymer electrolytes; examples include phosphoric acid doped polyvinylpyrrolidone, Nafion-H, and poly-2-acrylamido-2-methyl propanesulfonic acid. For all forms of electrochromic devices, high ionic conductivity is required for quick response in electrochromic reaction. The high molecular weight PEO-based polymer electrolytes showed very slow reaction kinetics at room temperature, which improved significantly above the melting temperature of PEO. The response time was improved with amorphous polymer electrolytes and plasticizing salts.

Although high ionic conductivity is essential for quick response, it leads to spreading of the electrochromic image at ambient temperature, resulting in low resolution. The problem can be overcome by using thermally responsive polymer electrolytes. These polymer electrolytes possess high conductivity at high temperature but very low conductivity at ambient temperature thus enabling the electrochromic reaction leading to image formation only at higher temperature. The crystal to amorphous transition and the glass transition temperatures have been exploited to fabricate thermoelectrochromic displays. In high molecular weight PEO-based polymer electrolytes, below the crystalline melting temperature there is no electrochromic effect, while above the melting point there is remarkable improvement in response time to the applied voltage.
2.3 Proton conduction mechanism

In most of the polyelectrolytes, proton conduction takes place in a second, low molecular weight solvent phase (e.g., H$_2$O, H$_3$PO$_4$, imidazole, pyrazole). Specific interactions between the sulfonate groups and the protonic charge carriers significantly influence the transport behavior of the proton conducting phase. Examples include sulfonated polymers in the hydrated state $^{12,13}$, basic polymer (e.g PBI) and oxo-acid complexes $^{23,24}$, and heterocycle intercalated into sulfonated polymer matrices $^{25,26}$.

2.3.1 Hydrated systems

The mechanistic features of mobility of protonic charge carriers in systems containing water as the proton solvent have been investigated by many researchers $^{10,59,60}$. The unusually high mobility of protons in water and aqueous solutions is explained in terms of contribution of structure diffusion (Grotthus mechanism or relay mechanism) as the dominant conduction process $^{10,12,61}$, with some contribution of vehicular diffusion. Structure diffusion involves intermolecular proton transfer within the hydrogen bonded pattern, known as structure, followed by structural reorganization through hydrogen bond breaking and formation while the hydrodynamic diffusion of the protonated water molecules is referred to as vehicular diffusion.

Diffusion of the protonated water molecules contribute $\approx 22\%$ to the total proton conductivity, assuming diffusion coefficients of H$_2$O and H$_3$O$^+$ (or H$_5$O$_2^+$) are the same, due to the high self-diffusion coefficient of water ($D_{H_2O} = 2.25 \times 10^{-5} \text{cm}^2/\text{s}$ at room temperature). The relative contributions of structure diffusion and vehicular diffusion
depend on temperature, pressure, acid concentration, and types of ions\textsuperscript{10}. Increasing acid concentration causes biasing of the hydrogen-bond pattern (i.e., gradual increase in proton donors than the proton acceptor “sites”), as a consequence, structure diffusion is markedly suppressed.

The excess proton within hydrogen-bonded network (protonic defect) in aqueous acidic solution exists either as a part of a dimer (H\textsubscript{3}O\textsubscript{2}\textsuperscript{+}, Zundel ion) or as a part of hydrated hydronium ion (H\textsubscript{9}O\textsubscript{4}\textsuperscript{+}, Eigen ion). In the Eigen ion, the excess protonic charge is distributed over three hydronium protons – oxygen of the hydronium ion coincides with the centre of symmetry of the coordination pattern. In the Zundel ion, each of the two water molecules, sharing the excess proton acts as proton donor through two hydrogen bonds. The center of symmetry of the coordination pattern coincides with the centre of excess charge. As depicted in Figure 2.8, in the transition of a Zundel ion into another Zundel ion through an Eigen ion, the center of excess charge is displaced by about one molecular separation. This displacement of protons within contracted strong hydrogen bonds (primary hydration shell, shaded region in Figure 2.8) is accompanied by reorientation of water dipoles, which require breaking and formation of weaker hydrogen bonds in the outer region of the complex (secondary hydration shell).

Proton conduction in heterogeneous systems such as hydrated sulfonated polymers is more complex than in water\textsuperscript{10,12}. Hydrophobic/hydrophilic nano-separation takes place in the presence of water. The acidic functional groups aggregate to form hydrophilic domains which are responsible for the transport of protons and water. The factors influencing the distribution of protons within the hydrophilic domains are the
Figure 2.8 Proton conduction mechanism in water\textsuperscript{10}. 
acidity (pKₐ) of the functional group, spatial separation distance between the acidic
anions (~0.6-0.9 nm) and the local dielectric constant of the water of hydration. Several
studies have also revealed two different water environments in perfluorosulfonate
ionomers ⁶⁰,⁶². “Bulk water” at the central region of the hydrophilic domains, where the
proton mobility is very fast and “surface water” at the hydrophobic/hydrophilic interface
along the array of sulfonate groups. The mobility of the protons in this region is
significantly low due to the strong electrostatic attraction between the SO₃⁻ groups and
protonic charge carriers.

The proton conductivity is strongly influenced by its nanostructure and water content.
At a low degree of hydration, the number of water/water contacts is less compared to
bulk water. Relatively strong hydrogen bond formation causes a reduction in the
dielectric constant and also the rate of hydrogen bond formation and breaking.
Furthermore, the concentration of the excess protons in the aqueous phase is increased,
and the hydrogen bonds become biased in this environment, suppressing the structure
diffusion, also evident in aqueous solution of acid. Thus, the overall rate of proton
transport at low water content is also low. At a higher degree of hydration, the dominant
conduction mechanism is structure diffusion (proton mobility diffusion coefficient higher
than water self-diffusion coefficient, Dₐ > D₇₀), while at intermediate and low degrees
of hydration it is mainly vehicular in nature. At high water content, the channels form a
continuous water pathway from cluster to cluster as shown in Figure 2.9. The electro-
osmotic flow described by vehicular diffusion occurs, and in presence of a continuous
aqueous network, Zundel and Eigen ions are formed. The protonic charge carriers hop
from acid site to acid site through the clusters and across the collapsed channels.
Figure 2.9 Transport mechanism in membrane, a complete network allows hydrated proton move from cluster to cluster through sulfonic acid site\textsuperscript{59}.
A similar explanation regarding the effect of hydration on the proton conduction was reported by Kreuer and co-workers from the measurement of diffusion coefficient. With an increasing degree of hydration, the water self-diffusion coefficient, $D_{H2O}$, and conductivity diffusion coefficient, $D_\sigma$ (obtained from conductivity data via the Nernst–Einstein relationship assuming complete dissociation of sulfonic acid groups) approach the values of bulk water for both polymers, and at high water content, $D_\sigma$ is greater than $D_{H2O}$, an effect similar to that observed in dilute solution. This clearly indicates the major contribution of structure diffusion to proton mobility with very little role of vehicular diffusion. Furthermore, the water/polymer interaction is small in the hydrophilic domains at a higher volume fraction of water, percolation is similar in both microstructures, and as a consequence both $D_{H2O}$ and $D_\sigma$ are comparable in these two different polyelectrolytes. The decrease of both transport coefficients with decreasing water content is due to the percolation effect. $D_\sigma$ approaches $D_{H2O}$ in Nafion and drops drastically below $D_{H2O}$ for SPEK at a low degree of hydration owing to the association of the protonic charge carriers with the immobile counter anions and also gradual suppression of structure diffusion. Thus at a low level of hydration, proton transport occurs mainly by vehicle mechanism as in a concentrated aqueous acid solution. In SPEKK, the mobility of protonic charge carriers ($D_\sigma$) reduces abruptly compared to water self-diffusion coefficient ($D_{H2O}$) (Figure 2.10), and this has been explained by the fact that the excess protons in these sulfonated polymers are localized in the vicinity of the acidic functional groups owing to their lower acidity and lower dielectric constant of the water of hydration.
Figure 2.10 Proton mobility, $D_\sigma$ and water self-diffusion coefficient, $D_{H_2O}$ as a function of water volume fraction in Nafion and sulfonated polyetherketone.$^{12}$
The morphology and transport properties in sulfonated polyarylene-based proton exchange membranes is distinctly different compared to Nafion. The factors influencing the conductivity are acidity, microstructure and water content. Nafion has higher conductivity than these polyelectrolytes, and this is mainly due to its greater effective ion density due to the greater acidity, as perfluoroalkyl sulfonic acids are superacid, with \( pK_a \) between methane sulfonic acid \( (pK_a = -1.0) \) and triflic acid \( (pK_a = -5.1) \). On the contrary, the electron donating ether substituent in S-PEEK lowers the acidity; the reported \( pK_a \) value of 2.8 causes dissociation of only 3.9% of acid groups. The activation energy of proton transport obtained from the slope of Arrhenius plot is more reliable for Nafion compared to the sulfonated polyarylene, in which the measured activation energy is described to be greater than the actual value. The two variables contributing to conductivity are water content and dissociation constant of weak acid. The ion content increases with temperature in addition to the mobility of protonic charge carriers. On the other hand, increase in temperature does not change the ion density in Nafion as it is fully ionized at room temperature.

2.3.2 Anhydrous systems

The limited operation temperature of fuel cells with hydrated Nafion has motivated in finding a suitable anhydrous system. In the following, a survey of existing literature on phosphoric acid doped in basic polymer matrix and substitution of water by aromatic heterocycles such as imidazole, pyrazole, benzimidazole is presented.
2.3.2.1 Phosphoric acid adducts

Pure phosphoric acid is a highly viscous liquid above its melting point ($T_m = 42^\circ$C). It has been considered as an almost-ideal proton conductor. In contrast to water, there are more donors than acceptor sites. Water exhibits high mobility but low concentration of intrinsic charge carriers. On the other hand, the high conductivity observed in phosphoric acid originates from high intrinsic charge carrier concentration owing to the high degree of self-dissociation of phosphoric acid $H_2PO_4^-$, $H_4PO_4^+$, $H_3O^+$, and $H_2P_2O_4^{2-}$ are the main dissociation products. $^1H$ and $^{31}P$ PFG NMR study revealed 98% of the conductivity arises from structure diffusion of protons, and there is no evidence of suppression of structure diffusion by external doping, despite the high concentration of protons.

Wainright et al. $^{23,64}$ introduced polybenzimidazole and phosphoric acid complexes, the most relevant material to the present date. The conductivity was found to increase with increasing oxo-acid concentration, with the value approaching that of pure acid at high acid content. There was no evidence of the participation of the polymer chains in the conduction process. The strong acid/base interaction between the nonprotonated nitrogen of the PBI repeat unit and the phosphoric acid does not significantly influence the intrinsic charge carrier density.

2.3.2.2 Heterocycle based systems

The substitution of water by heterocycles such as imidazole, pyrazole or benzimidazole was also reported to give high proton conductivity in acidic polymers $^{10,25}$. The heterocycles can act as a proton solvent similar to water, owing to their amphoteric
nature (proton donor and acceptor sites), intermolecular hydrogen bond formation and ability to undergo self dissociation. The pK_a value is a measure of proton donor ability and thus is an important parameter in determining the rate of proton transport. The physical properties of the aromatic heterocycles are summarized in Table 2.1. The self-dissociation constant of heterocycles, especially imidazole, is greater than water but ~ two order of magnitude lower than phosphoric acid. The mobility of protonic

Table 2.1 Fundamental physical properties of proton solvents\textsuperscript{10,25}

<table>
<thead>
<tr>
<th>Proton Solvent</th>
<th>Melting point(°C)</th>
<th>Boiling point(°C)</th>
<th>pK\textsubscript{a1}\textsuperscript{a}</th>
<th>pK\textsubscript{a2}\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100</td>
<td>0</td>
<td>-1.74</td>
<td>15.74</td>
</tr>
<tr>
<td>Imidazole</td>
<td>89</td>
<td>257</td>
<td>7.18</td>
<td>14.52</td>
</tr>
<tr>
<td>Pyrazole</td>
<td>67-70</td>
<td>186-188</td>
<td>2.57</td>
<td>14.21</td>
</tr>
<tr>
<td>1,2,4 triazole</td>
<td>120</td>
<td>256</td>
<td>2.39</td>
<td>9.97</td>
</tr>
<tr>
<td>1,2,3 triazole</td>
<td>23</td>
<td>203/752mm</td>
<td>1.17</td>
<td>9.26</td>
</tr>
<tr>
<td>Benzimidazole</td>
<td>172-174</td>
<td>360</td>
<td>5.56</td>
<td>13.2</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>98-99</td>
<td>350</td>
<td>1.6</td>
<td>8.57</td>
</tr>
</tbody>
</table>

\textsuperscript{a} pK\textsubscript{a1} represents the pKa of hydronium/azolium ions

\textsuperscript{b} pK\textsubscript{a2} refers to pKa of water/azoles
charge carriers is ~ 4.5 times higher than the molecular diffusion coefficient at the melting point of imidazole, a direct indication of fast intermolecular proton transfer by structure diffusion similar to that in water. At a given temperature, the transport coefficients (i.e., mobility of protonic defects and molecular diffusion coefficients) are similar to those of water relative to the respective melting points. The temperature and concentration dependence of proton transfer and molecular diffusion rates are also similar to that observed in hydrated ionomers. A very similar proton conduction mechanism in liquid imidazole to that of water has been described: the excess proton resides in an imidazole moiety in which both nitrogen atoms are protonated and hence act as proton donors toward the two next nearest imidazoles (Figure 2.11). This leads to the formation of Imi…ImiH⁺…Imi complex in which the hydrogen bonds are slightly contracted compared to the average bond length of the system. The hydrogen–bonded structure in imidazole is chainlike (i.e., low dimensional) with the two protonated nitrogen atoms directed out of the chain. This pattern rapidly changes by hydrogen bond breaking and formation processes which lead to complete proton transfer. At higher temperature, the mobility of the protonic charge carriers is greater in imidazole than in pyrazole while at lower temperature the behavior is just opposite, indicating that intermolecular proton transfer is the rate-limiting step at high temperature but at low temperature the hydrogen bond breaking and formation is rate determining because the degree of association in imidazole is to some extent higher than in pyrazole.

Schuster et al. introduced polymeric systems in which the proton solvating heterocycles were immobilized by tethering to a polymer backbone via flexible spacers. The proton transport in the immobilized heterocycle-based systems takes place mainly by
Figure 2.11 Proton conduction mechanism in liquid imidazole\textsuperscript{10}.
structure diffusion (Grotthus mechanism) comprising proton transfer between heterocycles and their reorganization because long range diffusion of protonated heterocycles (vehicle mechanism) is highly suppressed. However, the proton conductivity of these materials was too low to meet the demands of practical applications; hence, the immobilized heterocycles were further doped with acid. The conductivity reached 2.6 ms/cm at 120°C in a model compound (imidazole terminated ethylene oxide oligomer) doped with 16 mol% triflic acid.

2.4 Lithium ion conducting solid polymer electrolytes

The most recent development of electrolytes for Li-batteries is geared towards replacement of flammable liquid electrolytes by polymer electrolytes. Two classes of lithium ion conducting solid polymer electrolytes are discussed below:

2.4.1 Electrolyte salt in polymer

Solid polymer electrolytes are made by dissolving a low molecular weight lithium salt in appropriate host polymer matrix. The pioneering work of Wright and co-workers \(^{36}\) in 1973 with poly(ethylene oxide) and alkali metal salt complex was continued by several researchers due to the wide variety of applications of these materials in high energy density batteries, electrochromic displays, smart windows, and sensors \(^{1,27,67,68}\). In such polymer electrolytes, both cations and anions contribute to ionic conductivity (bi-ionic conductors). Solvent-free polymer electrolytes obtained through direct interaction of salt and a polymer are discussed below:
2.4.1.1 Salt solvation in polymer matrix

Salt dissolution in polymer matrix is accomplished through the solvation of cations or anions or both. Anion solvation generally occurs through hydrogen bonding or interaction with Lewis acids. Cation solvation takes place through the unshared electron pairs on heteroatoms such as ether -O-, sulfide -S-, amine -N-, phosphorous -P-, carbonyl C=O and cyano C≡N. Three factors play significant roles in controlling the salt/polymer interactions: (1) Electron pair donor/donor number (measures the ability of the solvent to donate the electrons to solvate the cations, (2) Acceptor number (quantifies the anion solvation ability of the solvent), and (3) Entropy. In polymer electrolytes the entropy of dissolution is generally negative because the loss of entropy of the polymer chains, due to their co-ordination with the cations, outweighs the entropy gain resulting from the breakup of the crystal lattice of the salt and subsequent ionic disorder.

The polymer-salt complex formation corresponds to the competition between the following enthalpy changes: lattice energy of the salt (positive) + cohesive energy of the polymer (positive) \(\rightarrow\) solvation energy (negative) + cohesive energy of the complex (negative). The lattice energy of the salt and the solvation enthalpy are the two major enthalpy terms associated with the dissolution of salt in polymer. The salts with smaller ionic radii and higher ionic charges have higher lattice energies. The solvation enthalpy depends on the strength of the co-ordinate bond formed between the cations and the groups on the polymer chains since anion solvation rarely occurs in polymer matrix. The solubility is most commonly explained in terms of Lewis acid-base interactions. The strongest interactions take place between hard acid (small cations without valence electrons) and hard base (non-polarizable ligands of high electronegativity) or soft acid
(large cations with valence electrons that can be easily polarized or removed) and soft base (more polarizable groups). Thus the best electron donors for hard Lewis acids (e.g., Li\(^+\), Na\(^+\), Mg\(^{2+}\), Ca\(^{2+}\)) are in the following order (order of electronegativity): -O-> -NH->-S-. This also explains the strong complexation abilities of polyethers with Li\(^+\). However, the bond involving transition metal cations is not dictated entirely by electrostatic forces and poly(ethyleneimine), PEI exhibits strong solvation ability, and its higher donor number (~30) compared to ether oxygen (~20) compensates for the lower concentration of electron pairs on nitrogen and lesser electronegativity.

The larger anions, either monoatomic (e.g., I\(^-\)) or polyatomic with delocalized negative charge (e.g., CF\(_3\)SO\(_3\)^-) require little solvation. The appropriate anions for polyether-based polymer electrolytes are expected to be in the order: F\(^-\)<< Cl\(^-\) < I\(^-\)~ SCN\(^-\) < ClO\(_4\)\(^-\) < CF\(_3\)SO\(_3\)\(^-\) < BF\(_4\)\(^-\) ~ AsF\(_6\)\(^-\). Thus the anions can be soft (e.g., I\(^-\)) or hard (e.g., CF\(_3\)SO\(_3\)\(^-\)) bases, and the order also corresponds to the lattice energy of the salt. Salts with both soft cations and anions (e.g., AgI) have no solubility in PEO, while in the case of soft-hard interactions as in AgCF\(_3\)SO\(_3\), the low lattice energy can compensate for the low solvation energy of the cation in polyether. The most promising SPE was developed by Armand and co-workers\(^{69}\) using a weakly coordinating anion, bis(trifluoromethylsulfonyl)imide (TFSI). LiTFSI has a high degree of dissociation due to the low lattice energy of the salt and extensive negative charge delocalization\(^{29}\).

2.4.1.2 Role of polymer chemical structure

A polymer that has a strong co-ordinating group dissolves salts easily. Some representatives are listed below\(^{68}\):
1. Poly(ethylene oxide) (PEO) (CH$_2$-CH$_2$-O)$_n$

2. Poly(ethylene oxide) (PEO) (CH$_2$-CH$_2$-O)$_n$ (chemical (trifunctional urethane) and radiation crosslinked)

3. Poly(ethylene glycol, siloxane), (chemical (trifunctional urethane) linked)

   $$((\text{CH}_3-(\text{OC}_2\text{H}_4)_m-\text{O-C}_3\text{H}_6\text{SiCH}_3\text{O})_n(\text{Si}(\text{CH}_3)_2\text{O})_2$$

4. Poly(propylene oxide) (PPO) (CH$_2$-CH(CH$_3$)-O)$_n$

5. Poly(ethylene succinate) (PES) (-C$_2$H$_4$-O-CO-C$_2$H$_4$-CO-O)$_n$

6. Poly(aziridine) and Poly(N-methyl aziridine) (CH$_2$-CH$_2$-NH)$_n$, CH$_2$-CH$_2$-NCH$_3$-$_n$

7. Poly(methylene sulfide) ((CH$_2$)$_p$-S)$_n$ (p=2.5)

8. Poly(bis-methoxy-ethoxy-ethoxy) phosphazene ((CH$_3$O-C$_2$H$_4$-OC$_2$H$_4$O)$_2$PN)$_n$

9. Poly(ethylene adipate) (C$_2$H$_4$-O-CO-C$_2$H$_4$)$_n$

10. Poly(oligo oxyethylene )methacrylate ((CH$_2$-(CH)-CO-(OC$_2$H$_4$))$_p$OCH$_3$)$_n$

11. Poly(propiolactone) (O-CH$_2$CH$_2$-CO-)$_n$

12. Poly(dioxolane-co-trioxymethylene) (CH$_2$O)$_n$(CH$_2$CH$_2$-O)$_p$

The ethylene oxide unit shows better complexing ability than propylene oxide, as the steric hindrance introduced by the methyl groups in propylene oxide reduces the stability of the complex. Figure 2.12 compares the complexing ability of polyethylene oxide (PEO) and polypropylene oxide (PPO) with various alkali metal salts.

Solid polymer electrolytes based on high molecular weight PEO contain crystalline PEO and/or high melting polymer-salt complex. The conductivity data for these SPEs vary considerably due to the complex phase behavior of PEO-salt mixture. The high
Figure 2.12 Complex formation ability of poly(ethylene oxide) and poly(propylene oxide) with various alkali metal salts.\textsuperscript{68}
degree of crystallinity (~ 85%) in PEO has a detrimental effect on ionic conductivity (\(\sigma < 10^{-8} \text{ S/cm}\)) below the crystalline melting point (~65°C). The conductivity can reach \(10^{-5} \text{ S/cm}\) at around 100°C but the mechanical properties are poor due to the melting of crystalline phase. Thus, several studies have focused on synthesizing polymers which are amorphous at lower temperature. Atactic PPO appears to an amorphous host polymer, and the random arrangement of the methyl groups along the chain prevent the crystallization. However, above 60-65°C, the conductivity of PPO-salt systems is lower than analogous PEO-salt complexes, and the steric hindrance of the methyl groups limits the segmental motion required to promote conductivity in addition to the decrease in stability of the polymer-salt complex. In contrast, PEO chains are capable of adopting a helical conformation with an oxygen-lined cavity that has ideal distances for oxygen-cation interactions.

Recognizing the fact that segmental motion of the polymer chains is related to the efficiency of ion transport, considerable research has focused on developing “low –T_g” polymer matrix. One approach was the addition of plasticizer in the polymer leading to “hybrid polymer electrolytes” \(^{27,29,67}\). The plasticizers used were polar organic solvent (e.g., ethylene carbonate, propylene carbonate, \(\gamma\)-butyrolactone) or low molecular weight polyether (e.g., polyethylene glycol ethers) introduced in a small amount (10-25%) in polymer matrix to lower the glass transition temperature. Another hybrid network structure, gel electrolyte, defined as a system consists of polymer network swollen with a large fraction of liquid plasticizer (60-95%) is characterized by high ambient ionic conductivity but a lack of chemical stability under working condition of battery. It has poor mechanical properties compared to the solid polymer electrolytes \(^{70}\).
Polymer electrolytes of low Tg and optimum ionic conductivity were synthesized by copolymerizing a flexible unit such as dimethylsiloxane (DMS) or polyphosphazene and short PEO segments. The linear chain copolymer of PEO and DMS showed a T_g of -80°C and a good level of room temperature conductivity (~10^{-4} S/cm) with a LiClO_4 concentration of Li/O=0.04 71. In addition to linear chain polymers, a wide variety of comb branched copolymers were investigated, in which low molecular weight PEO chains were grafted to the polymer backbone 72. These systems were liquid at room temperature with similar conductivity at the same salt concentration (~10^{-4} S/cm with LiClO_4 (Li/O=0.04)). However, the chemical stabilities were poor due to the susceptibility of Si-O-C bonds to hydrolysis. Smid and co-workers improved the chemical stability by attaching the polyether units via a stable Si-C bond 73. The comb branched systems based on polyphosphazene (MEEP) backbones with PEO side chains were investigated by Shriver et al 74. The room temperature conductivity achieved was below 10^{-5} S/cm with CF_3SO_3Li salt (Li/O=0.04) although the host polymer was completely amorphous with glass transition temperature around -80°C. Inoue et al. studied polystyrene derivatives in which PEO side chains were mechanically decoupled from the rigid polymer backbone via phosphazene spacer. The conductivity of the system approached 10^{-5} S/cm at room temperature, complexing with LiClO_4 salt (Li/O=0.035) 75.

Crosslinked solid polymer electrolytes that do not crystallize and offer the advantage of good dimensional stability are attractive candidates for use in thin film Li–ion batteries. The crosslink density needs to be optimized in these materials since it has an adverse effect on ionic mobility. Chemical crosslinking has been used extensively to prepare amorphous mechanically stable SPE such as in networks based on polyether
crosslinked polyphosphazene (MEEP)\(^1\), polyethertriols crosslinked by diisocyanates or glycidyl ethers \(^76\), and polyethers with different terminal functional groups crosslinked by an appropriate crosslinker \(^27\). In addition to chemical crosslinking, radiation crosslinking has also been utilized to produce SPE networks since it has the advantage in that the polymer electrolyte films can be designed to the desired shape and thickness and can be introduced in the device prior to crosslinking. It also allows the maintenance of excellent contact between the electrolyte and electrode surface and the film thickness even after crosslinking.

SPEs with supramolecular architectures (“hairy rod molecules”), in which flexible side chains are attached to the stiff polymer chain backbone, have been attractive candidates in the development of solid polymer electrolytes in recent years. This type of material offers the advantage of minimizing the separator film thickness and hence the electrical resistance of the solid state electrochemical cell. Lauter and coworkers reported that poly(p-phenylene) (PPP) as rigid backbone with flexible oligo(ethylene oxide) (EO) side chains is a striking example of molecularly reinforced SPE \(^77,78\). The highest value of conductivity was achieved with the longest EO side chains (the longest possible chain length at which the crystallization of PEO can be avoided). However, the reinforcing effect was reduced with increasing side chain length since the formation of the layered structure of PPP was responsible for the reinforcement. The optimization between conductivity and reinforcing effect was found in PPP(EO)\(_{5/6}\). The room temperature ionic conductivity of PPP-reinforced SPEs was further improved to \(10^{-4}\) S/cm by plasticizing with TEGDME (tetraethylene glycol dimethyl ether). However, these reinforced SPEs are
expected to be electrochemically unstable due to their susceptibility to undergo redox reactions because of the \( \pi \)-conjugated electronic structure.

2.4.1.3 Ion conduction mechanism

The ionic conductivity in solid polymer electrolytes can be expressed by the following equation:

\[
\sigma = n(ze)\mu
\]

where \( \sigma \) is the ionic conductivity in S/cm, \( n \) is the number of charge carriers, \( ze \) is the charge expressed as the multiple of the electron charge, here \( z = 1 \) and \( \mu \) is the mobility of the ions. The ion transport in polymer electrolytes results from a solvation-desolvation process along the polymer chains mainly located in the amorphous phase, and ionic conductivity is directly related to the segmental motion of the polymer chains, thus conductivity increases with increasing chain mobility \(^1\). The variation of conductivity with temperature of polymer electrolytes follows the Vogel Tamman-Fulcher (VTF) equation as described below, which further indicates ion transport assisted by the segmental motion of the host polymer.

\[
\sigma = A T^{-1/2} \exp \left( -\frac{B}{R(T - T_0)} \right)
\]

where the constant \( A \) is proportional to the concentration of charge carriers, \( B \) is the pseudoactivation energy which depends on segmental mobility of the polymer chains, \( R \) is the universal gas constant and \( T_0 \) is a reference temperature close to the glass transition temperature.
In conventional polymer electrolytes, which are solid solutions of electrolyte salts in polymer, the maximum conductivity is usually achieved at optimum salt concentration \(^{79,80}\). This behavior was explained by the contribution of two opposing factors: concentration of charge carriers and ionic mobility controlled by ionic cross-linking formed due to polymer-salt interaction. At lower salt concentrations, the increase in the number of charge carriers with increasing salt concentration offsets the decrease in ionic mobility caused by increased crosslinking density. Above a limiting salt concentration, the reduction in segmental mobility dominates and is no longer compensated by the increase in number of charge carriers. The ion conduction (cation transport) mechanism in such polymer electrolytes is described in Figure 2.13. The segmental motions promote ion mobility through the formation and breaking of the co-ordinate bonds between the cations and host polymer, thus providing free volume in which the ions can diffuse under the influence of an electric field. Figure 2.13(a) depicts a cation motion through the co-ordinating sites of a single polymer chain and between sites of neighbouring chains. Figure 2.13(b) shows movement of ions between ion clusters. Interchain, rather than intrachain, hopping is more likely to occur. Molecular dynamics simulations reveal that a Li\(^+\) is complexed to approximately five ether oxygen atoms of a PEO chain (as shown in Figure 2.13(b)), and the mobility of the cation is decreased due to the complexation.
2.4.2 Single lithium ion conducting polyelectrolytes

Conventional salt-in-polymer electrolytes have certain limitations: the counter anions in the polymer electrolytes have weak interactions with the polyethers; hence, transport more easily compared to cations resulting low lithium ion transference number.

Figure 2.13 Schematic of lithium ion conduction mechanism (a) segmental motion assisted diffusion of ion in a host polymer matrix, the circles represent electron donor (Lewis base) sites, (b) complexation of Li$^+$ during interchain hopping. 

---

[Image of the schematic diagram as described in the text]
(0.3-0.5). The migration of anions causes concentration gradient of the electrolyte salt and polarization of batteries in practical application, which further reduces the Li⁺ transference number. In addition, the mobile anions take part in undesirable side reactions at the electrodes. These practical difficulties have motivated in seeking of suitable alternatives. To date, two approaches have been reported to reduce the mobility of anions. The first one deals with the introduction of interacting sites that will preferentially interact with the anions and in the other, anions are covalently bonded to the polymer backbone (“single ion conducting polyelectrolytes”). The higher molecular weight of polyanions compared to Li⁺ improves the cation transference number of the system. Doyle et al. reported an improvement in the cell performance of a lithium polymer electrolyte battery using a single ion conductor, inspite of the lower ionic conductivity of the single ion conducting polymer electrolyte compared to a bi-ion conducting polymer electrolyte.

A variety of polyelectrolytes have been investigated in which the anions were anchored to polyether or siloxane main chains. However, strong ion pairing resulted in too low conductivity to meet the demands of battery applications. Watanabe and co-workers proposed a novel strategy to control the cation transference number by alloying lithium salt of polymeric imide anions that have structural similarity with the low molecular weight imide salt, lithium bis(trifluoromethylsulfonyl)imide (LiTFSI), in a polyether matrix. The highest conductivity was achieved in polyether electrolytes alloyed with poly(5-oxo-3-oxy-4-trifluoromethyl-1,2,4-pentafluoropentylene sulfonylimide lithium) (LiPPI). Few studies have addressed the use of polyelectrolytes based on sulfonated polymers such as poly(4-styrene sulfonate), poly(lithium 2 acrylamido-2-
methyl propane sulfonate$^{43}$, perfluoroalkyl sulfonate$^{44}$, crosslinked poly[oligo(oxyethylene)methacrylate-co-lithiummethacryloyl hexylsulfonate $^{45}$ in single ion conducting SPE. However, conductivity is low in these materials and improves significantly in presence of a plasticizer $^{46,47}$. Higashi et al $^{90}$ reported a new class of polyelectrolytes having polyphosphazene backbone and both sulfonate and oligoethers in side chains. The ionic conductivity in these materials reached $4.5 \times 10^{-4}$ S/cm at $80^\circ$C.

2.5 Sulfonated bisphenol -A- based poly(arylene ether) synthesis

Poly(arylene ethers) are a class of well-known high performance engineering thermoplastics that possess high glass transition temperature, high thermal stability, excellent mechanical properties, and high resistance to hydrolysis and oxidation. There are many varieties of poly(arylene ethers) such as poly(ether sulfones), poly(ether ketones), and poly (ether imides).

The sulfonated polymers have received considerable interest in the last decade because of their wide variety of applications in the electronics, medical and automotive industries. Sulfonated poly(phenylene oxide) and polysulfone are widely used as desalination membranes for reverse osmosis and water purification $^{91,92}$. Sulfonated poly(ether sulfones) $^{93,94}$, and poly(etherimide)$^{95}$ membranes have been reported to be useful in ultrafiltration. A major drawback of the application is membrane fouling, which has been minimized by increasing the hydrophilicity of the polymer through sulfonation. The water-soluble sulfonated polystyrene, with a high degree of sulfonation, is useful as a thickener and flocculant. The dyeability of propylene-styrene copolymer can be improved
by sulfonation \textsuperscript{96}. Sulfonated polyphenylsulfone has been claimed for applications as dental plaque barriers and in hemodialysis membranes; the hemocompatibility is directly related to the degree of sulfonation \textsuperscript{97,98}. The synthetic routes of these materials are discussed below:

2.5.1 Post sulfonation

To date, different post sulfonation methods to introduce sulfonic acid groups in the poly(ether sulfone) repeat units are available; various routes shown in Figure 2.14.

In most commonly known post sulfonation routes, the sulfonic acid groups are introduced at the activated sites of the repeat unit by electrophilic substitution, predominantly ortho to the aromatic ether link. Sulfonation at the deactivated sites of the repeat unit promotes higher acidity and enhanced stability due to the strong electron-withdrawing sulfone group. In the case of the bisphenol-A-based system, only one sulfonic acid group per repeat unit can be introduced by the post sulfonation reactions.

Quentin \textsuperscript{99} first reported the sulfonation of bisphenol-A-polysulfone by chlorosulfonic acid. The pioneering work followed by many researchers showed several detrimental side reactions such as branching and crosslinking \textsuperscript{100,101}. Noshay and Robeson \textsuperscript{102} utilized sulfur trioxide – triethyl phosphate complex (SO\textsubscript{3}-TEP) to sulfonate polysulfone at room temperature. The level of sulfonation was controlled by the ratio of SO\textsubscript{3} to TEP. This mild sulfonating agent minimizes the undesirable side reactions to a greater extent, and the modification method is cheap; however, the reaction is difficult to control and is exothermic and inconvenient owing to the high reactivity and toxicity of sulfur tri
The effect of sulfonation on mechanical properties of sulfonated polysulfone (SPSU) synthesized by this method was also investigated. SPSU in the sodium salt form

Figure 2.14 Post sulfonation of bisphenol-A- poly(ether sulfones) by various post sulfonation routes.
with a 50% degree of sulfonation was found to be melt processable. Sulfonation resulted in the reduction in gas permeability, and the increase in hydrophilicity as reflected by the drop in contact angle.

Recently, silyl-protected sulfonating agent, a mixture of trimethylsilyl chloride and chlorosulfonic acid or trimethylsilyl chlorosulfonate, was used to sulfonate polysulfone. A quantitative and regiospecific method of introducing a sulfonic acid group at the ortho sulfone site of bisphenol-A polysulfone was introduced by Kerres et al. In this method, the polymer was reacted with n-butyllithium and then with sulfur dioxide (SO$_2$) followed by oxidation/hydrolysis. The sulfonated polysulfone obtained via the metalation route exhibited increased hydrolytic stability, high ionic conductivity and ion-exchange capacity. However, the process, which is based on the three successive steps of metalation – sulfination – oxidation, is relatively complicated to be scaled up and difficult to control.

Shen et al. reported synthesis of sulfonated poly(etherimide) (PEI) by chlorosulfonic acid (CSA) in 1,2 dichloroethane. The degree of sulfonation was varied by the ratio of CSA/PEI repeat unit and reaction time. It was observed for SPEI with higher IEC, $M_w$ reduces significantly, indicating degradation of polymer backbone in presence of the strong sulfonating agent.

2.5.2 Direct step-growth polymerization

Modification of monomers followed by polymerization has been studied by several research groups. The sulfonation of 4,4'- dichlorodiphenylsulfone (DCDPS) with two
sulfonic acid groups per repeat unit was described by Udea et al.\textsuperscript{109}. Mecham et al.\textsuperscript{110} modified the procedure of direct polymerization to prepare highly sulfonated poly(arylene ether sulfone). The molecular weight and the end groups of the polymers were controlled by the addition of the monofunctional endcapper. McGrath and co-workers\textsuperscript{111} developed novel wholly aromatic sulfonated poly(arylene ether sulfone) copolymers employing a high molar concentration of SDCDPS and exploiting a potassium carbonate mediated aromatic nucleophilic substitution; the scheme of the polycondensation is shown in Figure 2.15. High molecular weight copolymers were obtained at 190°C in N-methyl-2-pyrrolidinone (NMP) using the DCDPS/SDCDPS system.

The synthesis of sulfonated polyimides by direct copolymerization is described in the literature\textsuperscript{112,113}. In this approach, the sulfonic acid group is introduced in the polyimide backbone by using sulfonated monomers. Faure and his coworkers\textsuperscript{114} synthesize a series of five and six membered ring polyimides from oxydiphthalic dianhydride (ODPA) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA). The sulfonic acid group was introduced in the polymer backbone by using a commercially available sulfonated diamine monomer, 2,2’-benzidinedisulfonic acid (BDSA). The level of sulfonation was controlled by varying the molar ratio of BDSA and nonsulfonated diamines, 4,4’-diaminodiphenyl ether (ODA) during copolymerization. 4,4’-diaminodiphenyl ether-2,2’-disulfonic acid based polyimides were found to possess a flexible structure, good water stability and high proton conductivity compared to that of Nafion 117 \textsuperscript{113}. The introduction of aliphatic segments in the main and side chains of polyimide was found to improve the hydrolytic stability without sacrificing proton conductivity or oxidative and
mechanical stability \(^{112}\). The aggregation of ionic groups in these polyimides was suppressed by branching and small (<5 nm) hydrophilic domains are distributed.

![Reaction scheme of synthesis](image)

Figure 2.15 Reaction scheme of synthesis (a) 4,4'-dichlorodiphenylsulfone (S-DCDPS)monomer\(^{104}\), (b) sulfonated poly(arylene ether sulfone)s by direct copolymerization\(^{111}\).
throughout the matrix as revealed by scanning transmission electron microscopy (STEM).

2.6 Sulfonated polymer based blends

Polymer blending is a common and simple way to develop new materials with desirable properties. However, incompatibility of the components causes micro and macroscopic phase separation and limits the usefulness of the blends. This arises due to positive enthalpy and hence positive $\Delta G$ of mixing. As described in Table 2.2, the introduction of sulfonate groups at the macromolecular main chain backbone can induce specific intermolecular interactions, including acid-base interaction, hydrogen bonding, ion-dipole or dipole-dipole interaction, charge transfer and transition metal complexation. The strength of specific interactions and the phase behavior of the resulting blend can be manipulated by varying the structure of the polyelectrolyte, the functionality level, and the type of counterion.

The specific interactions and their influence on ionic conductivity have been reported in few previous studies. Kerres et al. introduced novel acid-base polymer blends which contain a network of ionic crosslinks (polysalt) formed by proton transfer from polymer acid to polymeric base $^{115,116}$. Examples include sulfonated polysulfone (SPSU), sulfonated polyether sulfone (SPES), sulfonated poly(etheretherketone) as the acidic compound and PSU diaminated at the ortho position to the sulfone bridge, poly(4-vinylpyridine), poly(benzimidazole) (PBI), poly(ethyleneimine) (PEI) as the basic compounds. The acid-base blend membranes showed excellent thermal stability, and the
polysalt groups were found to exist in the dry state. It was suggested that the size and the
density of the repeat units of the acidic and basic blend components should be
comparable in size to ensure complete ionic crosslinking \(^{86}\). It was observed that
calculated ion exchange capacity (IEC) was same as that obtained experimentally for
sPSU/PBI blend while for sPSU/PEI blends experimental IEC was higher than the
calculated value. This was attributed to the difference in functional group densities of
sPSU and PEI, and hence, it was not possible for many amino groups to find the acidic
counterpart, whereas the difference was minimized in the case of sPSU/PBI blends. In
PEI based blends, incomplete polysalt formation resulted in a high degree of swelling.
For effective suppression of swelling by ionic crosslinking, the polybase should be strong
enough to ensure complete polysalt formation, so PBI is a good candidate in this respect.
Increased ionic crosslinking density caused reduction in swelling and hindered proton
transport across the conducting channels in sPEKEKK/PBI blends \(^{117,118}\).

The preparative techniques influence the morphology of the blends. The method in
which the ionic crosslinks were formed during film formation led to homogeneous
morphology and a lesser degree of swelling, while weak van-der Waals and dipole-dipole
interactions between the acidic and basic blend components caused partial phase
separation. The degree of swelling was also very high in the later case \(^{118}\).

Diemede et al.\(^{119}\) studied the phase separation behavior of polybenzimidazole
(PBI)/sulfonated polysulfone (SPSF) blends as a function of degree of sulfonation and
blend composition. Specific interactions between the N-H groups of PBI and sulfonic
acid group of polysulfone induce miscibility. Sodium sulfonated polysulfone formed
miscible blends with polyamide 11 at a temperature close to the amide melting
temperature. Specific interactions between Na$^+$ and the carbonyl oxygen atom and hydrogen bonding involving sulfonate and NH groups of amide were found to induce miscibility. Significant miscibility improvement was achieved in the blends of polyamide-6 and sulfonated polystyrene ionomers with lithium, zinc and manganese counterions as a consequence of specific interactions between amide and sulfonate groups.

Table 2.2 Different types of sulfonated polymer based blends

<table>
<thead>
<tr>
<th>Interaction type</th>
<th>Systems</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Van der Waals/dipole-dipole interaction</td>
<td>Blends from sulfonated PSU and unmodified PSU</td>
<td>Inhomogeneous morphology, Unacceptably high swelling, Leaching out of s-PSf due to insufficient entanglement</td>
</tr>
<tr>
<td>H-bridges</td>
<td>Blends from sulfonated PEEK and poly(ether imide)(PEI) or polyamide (PA)</td>
<td>Partially inhomogeneous morphology, unacceptably high swelling, insufficient hydrolytic stability of amide/imide bonds in acidic environment</td>
</tr>
<tr>
<td>Electrostatic interaction (ionic cross-linking)/hydrogen bridges</td>
<td>Blends of s-PEEK/s-PSf and basic polymers (commercial and self developed)</td>
<td>In most cases homogeneous morphology, partial high swelling at elevated temperature</td>
</tr>
</tbody>
</table>
CHAPTER III
EXPERIMENTAL

3.1 Materials

Two bisphenol-A-poly(arylene ethers), polysulfone (UDEL \textsuperscript{RM} P-1700) and polyetherimide (ULTEM 1000) were used for the study. Bisphenol A polysulfone (PSU), with $M_w = 35,000$, $M_n = 20,000-24,000$, density = 1.24 g/cm$^3$ and $T_g = 185-190^\circ$C, was obtained from Solvay Advanced Polymers, L.L.C. Bisphenol A polyetherimide (PEI) with $M_w = 30,000$, $M_n = 12,000$, density = 1.27 g/cm$^3$ and $T_g = 215-219^\circ$C, was supplied by GE Plastics. Polysulfone and polyetherimide pellets were dried at 130$^\circ$C for 8-9h under vacuum prior to use. Figure 3.1 shows the chemical structures of poly(arylene ethers), PSU and PEI.

UDEL polysulfone and ULTEM polyetherimide are high performance, amorphous, engineering thermoplastics. The repeat units of these two polymers are comprised of phenylene units linked by three different chemical groups - isopropylidene, ether and sulfone (polysulfone)/ imide (polyetherimide)-each contributing specific properties to the polymers. The phenylene ether segment contributes flexibility to the polymer backbone augmented by the isopropylidene link manifested in higher toughness and ease of processability. The sulfone group imparts hydrolytic stability, thermo-oxidative, and melt
stability and high use temperature. In the electronegative sulfone group, the sulfur is in highest oxidation state which is responsible for excellent thermo-oxidative stability and

![Chemical structure](image)

Figure 3.1 Chemical structure (a) bisphenol A polysulfone (UDEL \textsuperscript{\textregistered} P-1700), (b) polyetherimide (ULTEM 1000).
high long-term use of the polymer. In contrast, the imide group is hydrolyzable depending on the chemical structure of polyimide. The ether linkage provides thermal and hydrolytic stability. The cyclic imide group of polyimides makes them insoluble and infusible but ULTEM polyetherimide dissolves in several solvents and is also melt processable.

Two sulfonating agents, trimethylsilyl chlorosulfonate (TMSCS) and chlorosulfonic acid (CSA) were used. The chemical structures are shown in Figure 3.2. TMSCS (molecular weight: 188.71, density: 1.225 g/cm$^3$, boiling point: 168-169$^\circ$C) and CSA (molecular weight: 116.52, density: 1.753 g/cm$^3$, boiling point: 151-152$^\circ$C/755 mmHg) were purchased from Aldrich Chemical Co. and used as received. TMSCS was taken out using a syringe under positive nitrogen pressure. The containers were stored in a desiccators.

Methylene chloride was dried over molecular sieves prior to its use as a sulfonation reaction medium. Dimethylacetamide (DMAc) was used for casting films without further purification. Methanol, isopropanol, and acetone were used to precipitate sulfonated polysulfone and polyetherimide.

1H-1,2,4 triazole (Taz), with molecular weight 69.07, density 1.274 g/cm$^3$, melting point 119-121$^\circ$C and boiling point 256-260$^\circ$C, was purchased from Aldrich Chemical Co. The chemical structure is provided in Figure 3.3.

The aliphatic polyether epoxy, poly(ethylene glycol)diglycidyl ether (PEGDGE), was obtained from Aldrich Chemical Co., had molecular weight 526 and specific gravity 1.14 g/cm$^3$. The aromatic diamine (tetrafunctional), 4,4’ dianinodiphenyl sulfone (DDS), used as a curing agent, was supplied by Aldrich Chemical Co. It is solid at room temperature.
Figure 3.2 Chemical structure of sulfonating agents (a) trimethylsilyl chlorosulfonate (TMSCS), (b) chlorosulfonic acid (CSA).

Figure 3.3 Chemical structure of 1H-1,2,4 triazole.
with molecular weight 248.3 and melting point 175-177°C. The chemical structures of PEGDGE and the curing agent, DDS are shown in Figure 3.4.

The low molecular weight electrolyte salt, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), with molecular weight 287.08 and melting point 234-238°C was purchased from Aldrich Chemical Co. Figure 3.5 shows the chemical structure of LiTFSI.

3.2 Procedure

The sulfonation and the preparation of proton and lithium ion conducting solid polymer electrolytes are described below:

3.2.1 Sulfonation of bisphenol –A- poly(arylene ethers)

Two bisphenol A poly(arylene ethers), polyetherimide (PEI) and polysulfone (PSU) were sulfonated by the following procedure:

To a 250 mL, three-necked round bottom flask fitted with a condenser, addition funnel, and nitrogen sparge tube, 5 grams of dried polymer were dissolved in 25 mL methylene chloride (~20 % w/v solution). The solution was purged with nitrogen for one hour and trimethylsilyl chlorosulfonate (TMSCS) diluted in DCM was added slowly from a dropping funnel. The solution was stirred vigorously at ~30°C. The reaction mixture after the desired time was precipitated in acetone for polyetherimide and methanol/isopropanol for polysulfone. The fibrous precipitate was filtered, washed with the nonsolvent. The sulfonated polyetherimide (SPEI) and sulfonated polysulfone (SPSU) were dried under a vacuum for 24h at room temperature and 90°C, respectively. Different
degrees of sulfonation were achieved by varying the mole ratio of the sulfonating agent to
the PAE repeat unit and/or the reaction time described in Table 3.1. Sulfonated poly(arylene ethers) were designated as SPAE(X)H, where X refers to degree of sulfonation.

\[
\text{CH}_2\text{-CH-CH}_2\text{-O-(CH}_2\text{CH}_2\text{O)}_9\text{-CH}_2\text{-CH-CH}_2
\]

Poly(ethylene glycol)diglycidyl ether (PEGDGE)

\[
\text{H}_2\text{N-}
\]
\[
\text{S}
\]
\[
\text{O}
\]
\[
\text{O}
\]
\[
\text{NH}_2
\]

4,4’ diaminodiphenyl sulfone (DDS)

Figure 3.4 Chemical structure of polyether epoxy, PEGDGE and diamine curing agent, DDS.

\[
\left[\text{F}_3\text{C-S}^\ominus\text{N-SO}_2\text{CF}_3\right]^{\oplus}\text{Li}^{\ominus}
\]

Figure 3.5 Chemical structure of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI).
Table 3.1 Sample designations and sulfonation conditions of SPAE systems

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Concentration of sulfonating agent $x^*$</th>
<th>Reaction time (h)</th>
<th>Degree of sulfonation (DS;%)</th>
<th>Ion exchange capacity (IEC) (meq/g)</th>
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</thead>
<tbody>
<tr>
<td>With TMSCS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPEI(16)H</td>
<td>0.7</td>
<td>24</td>
<td>16</td>
<td>0.35</td>
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<tr>
<td>SPEI(18)H</td>
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<td>48</td>
<td>18</td>
<td>0.39</td>
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<tr>
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<td>72</td>
<td>22</td>
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<td>SPEI(34)H</td>
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<td>SPSU(30)H</td>
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<td>48</td>
<td>30</td>
<td>0.64</td>
</tr>
<tr>
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<td>72</td>
<td>32</td>
<td>0.69</td>
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<tr>
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<td>1.1</td>
<td>24</td>
<td>40</td>
<td>0.84</td>
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<tr>
<td>SPSU(40)H</td>
<td>1.5</td>
<td>6</td>
<td>40</td>
<td>0.85</td>
</tr>
<tr>
<td>SPSU(65)H</td>
<td>1.5</td>
<td>24</td>
<td>65</td>
<td>1.31</td>
</tr>
<tr>
<td>SPSU(70)H</td>
<td>1.5</td>
<td>48</td>
<td>70</td>
<td>1.4</td>
</tr>
<tr>
<td>SPSU(76)H</td>
<td>1.5</td>
<td>72</td>
<td>76</td>
<td>1.52</td>
</tr>
<tr>
<td>SPSU(57)H</td>
<td>2</td>
<td>24</td>
<td>57</td>
<td>1.17</td>
</tr>
</tbody>
</table>

*x* is defined as number of moles of sulfonating agent per mole of polyarylene ether repeat unit.
Scanning Electron micrograph (SEM) of SPEI hollow fiber obtained after precipitation in acetone is shown in Figure 3.6.

PEI was also sulfonated using chlorosulfonic acid by the aforementioned method for comparative study. 5 grams of dried polymer was dissolved in 25 mL methylene chloride taken in a three-necked round bottom. The solution was purged with nitrogen and the desired amount of chlorosulfonic acid diluted in methylene chloride was added slowly using a dropping funnel. The solution was stirred vigorously at ~30°C. The reaction mixture after the desired time was precipitated in acetone. The sulfonated polyetherimide (SPEI) was dried under a vacuum for 24h at room temperature.

3.2.2 Lithium ion exchange of bisphenol–A- poly(arylene ethers)

Sulfonated polyetherimide and polysulfone in acid form were dissolved in dimethylacetamide (DMAc), and films were prepared by casting the solutions in glass petri dishes. The solvent was evaporated at 70°C in a hood. The films were then dried under high vacuum initially at ~60°C for 4-5h followed by 120°C for 24h. Lithium salt of sulfonated polyetherimide and polysulfone were prepared by soaking in lithium hydroxide solution, and the samples were designated as SPSU(X)Li, where X refers to degree of sulfonation. The ion-exchange capacity (IEC) was determined by the following method:

A dry film of the sulfonated polymer in acid form was soaked in a 0.1N lithium hydroxide solution for 24h at ambient temperature. Then 10 mL of the solution was back
Figure 3.6 SEM micrograph of the cross-section of SPEI hollow fiber.
titrated with 0.1N hydrochloric acid using phenolphthalein as indicator. The IEC was calculated using the following equation:

$$ IEC = \frac{(B - P) \times 0.1 \times f}{w} $$

3.1

where B is the volume of hydrochloric acid used to neutralize the blank sample (unsulfonated), P is the volume of acid required to neutralize the sulfonated polymer, 0.1, normality of the acid, the factor f corresponds to the ratio of the volume of the LiOH used to neutralize the sulfonated polymer to the volume taken for titration, and w is the weight of the sample (g). The weight used in this calculation was the weight of the dried film in Li⁺ form after IEC determination.

DS and IEC are related by the following equation:

$$ DS = \frac{M_0 \times IEC}{1 - 80 \times IEC} $$

3.2

where IEC is the ion exchange capacity (eq/g), M₀ is the mass of the repeat unit of the unsulfonated polymer (M₀ of PSU is 442), and 80 is the formula weight of the sulfonate group.

3.2.3 Polymer electrolyte preparation

Sulfonated polyetherimide and lithium ion exchanged sulfonated polysulfone were used in preparation of proton and lithium ion conducting solid polymer electrolytes. The methodologies are described as follow:
3.2.3.1 Sulfonated polyetherimide/1H-1,2,4 triazole polymer electrolytes

Anhydrous proton conducting polyelectrolytes were prepared by solution blending of the desired amount of SPEI and 1H-1,2,4-triazole (Taz) (5% w/v) in dimethyl acetamide (DMAc). The solutions were stirred for 2h and the films were cast on a glass substrate followed by drying at 70°C until the solvent evaporated in the fume hood. The films were dried under vacuum for 48h at room temperature. Homogeneous films were obtained. The sulfonated polyetherimides in the acidic form, with three different sulfonation levels 22, 48 and 62% were used to prepare the blends. The polymer electrolyte compositions are described in Table 3.2.

3.2.3.2 Lithium salt of sulfonated polysulfone (SPSU-Li)/poly(ethylene glycol) diglycidyl ether (PEGDGE) polymer electrolytes

SPSU(X)Li and PEGDGE in desired amounts were dissolved in dimethylacetamide (DMAc), and the stoichiometric amount of the curing agent, DDS, was added to the mixture. The solutions were stirred at room temperature for 2h, and the films were casted on a teflon-coated aluminium boats followed by drying at 70°C in the fume hood. The films were further dried at 60°C under vacuum (~28 in Hg) for 48h to remove the trace amount of solvent. The film thickness was controlled by maintaining the same solution concentration and using boats of the same size. The samples were cured at 120-150°C for ~6h. The sulfonated polysulfones in the lithium salt form with three different sulfonation levels of 23, 40 and 76% were used. The polymer electrolyte compositions are described
in Table 3.3. The concentration of SPSU(X)Li in SPE s was expressed as the molar ratio of ether oxygen of PEGDGE to lithium sulfonate of sulfonated polysulfone, \([\text{O}]/[\text{Li}^+]\).

3.2.3.3 LiTFSI salt doped SPSU-Li/PEGDGE

LiTFSI in PEGDGE and lithium salt of sulfonated polysulfone with 76% sulfonation level, SPSU(76)Li in DMAc was dissolved separately. The solutions were mixed, and the

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Degree of sulfonation (DS;%)</th>
<th>Triazole content (wt%)</th>
<th>(\lambda^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPEI(22)H/Taz 100/0</td>
<td>22</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SPEI(22)H/Taz 90/10</td>
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<td>SPEI(22)H/Taz 70/30</td>
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<td>30</td>
<td>13</td>
</tr>
<tr>
<td>SPEI(22)H/Taz 50/50</td>
<td>22</td>
<td>50</td>
<td>31</td>
</tr>
<tr>
<td>SPEI(48)H/Taz 100/0</td>
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<td>2</td>
</tr>
<tr>
<td>SPEI(48)H/Taz 70/30</td>
<td>48</td>
<td>30</td>
<td>6</td>
</tr>
<tr>
<td>SPEI(48)H/Taz 50/50</td>
<td>48</td>
<td>50</td>
<td>15</td>
</tr>
<tr>
<td>SPEI(62)H/Taz 100/0</td>
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<td>5</td>
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<td>8</td>
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<td>62</td>
<td>50</td>
<td>12</td>
</tr>
</tbody>
</table>

\(\lambda\) is defined as number of moles of triazole per mole of sulfonic acid group.
Table 3.3 Sample designations and compositions of SPSU(X)Li/PEGDGE polymer electrolytes

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Degree of sulfonation (DS)(%)$^a$</th>
<th>Li$^+$ ion exchange Capacity (meq/g)$^b$</th>
<th>Wt(%) of SPSU(X) Li</th>
<th>Wt(%) of PEGDGE</th>
<th>[O]/[Li$^+$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPSU(23)Li/PEGDGE 100/0</td>
<td>23</td>
<td>0.49</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SPSU(23)Li/PEGDGE 71/29</td>
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<td>0.49</td>
<td>71</td>
<td>29</td>
<td>19</td>
</tr>
<tr>
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<td>23</td>
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<td>56</td>
<td>44</td>
<td>36</td>
</tr>
<tr>
<td>SPSU(40)Li/PEGDGE 100/0</td>
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<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SPSU(40)Li/PEGDGE 71/29</td>
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<td>0.85</td>
<td>71</td>
<td>29</td>
<td>11</td>
</tr>
<tr>
<td>SPSU(40)Li/PEGDGE 56/44</td>
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<td>0.85</td>
<td>56</td>
<td>44</td>
<td>21</td>
</tr>
<tr>
<td>SPSU(76)Li/PEGDGE 100/0</td>
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<td>1.51</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SPSU(76)Li/PEGDGE 71/29</td>
<td>76</td>
<td>1.51</td>
<td>71</td>
<td>29</td>
<td>6</td>
</tr>
<tr>
<td>SPSU(76)Li/PEGDGE 56/44</td>
<td>76</td>
<td>1.51</td>
<td>56</td>
<td>44</td>
<td>12</td>
</tr>
<tr>
<td>SPSU(76)Li/PEGDGE 45/55</td>
<td>76</td>
<td>1.51</td>
<td>45</td>
<td>55</td>
<td>18</td>
</tr>
<tr>
<td>SPSU(76)Li/PEGDGE 33/67</td>
<td>76</td>
<td>1.51</td>
<td>33</td>
<td>67</td>
<td>30</td>
</tr>
<tr>
<td>SPSU(76)Li/PEGDGE 0/100</td>
<td>76</td>
<td>1.51</td>
<td>0</td>
<td>100</td>
<td>$\infty$</td>
</tr>
</tbody>
</table>

$^a$ DS was determined by $^1$H NMR in DMSO-d$_6$.

$^b$ Lithium ion exchange capacities were obtained from titration.
stoichiometric amount of DDS was added to it followed by stirring at room temperature for 2h. The films were casted, dried, and cured following the same procedure mentioned above. The samples were designated as SPSU(76)Li/PEGDGE/LiTFSI.

PEGDGE/LiTFSI samples were prepared for comparative study. LiTFSI was dissolved in PEGDGE. After complete dissolution, the stoichiometric amount of DDS was added to it followed by dimethylacetamide. The solution was stirred at room temperature for 2h. The films were casted, dried and cured using the same procedure mentioned above. SPSU(76)Li/PEGDGE/LiTFSI and PEGDGE/LiTFSI compositions are shown in Table 3.4. The lithium ion concentration in SPEs was expressed as the molar ratio of ether oxygen of PEGDGE to summation of lithium ion sulfonate of sulfonated polysulfone and LiTFSI, [O]/[Li$^+$].

3.3 Characterization

In this section, the techniques utilized to investigate the properties of solid polymer electrolytes and the detailed characterization procedures are discussed.

3.3.1 Spectroscopic studies

Proton Nuclear Magnetic Resonance ($^1$H NMR) and Fourier Transform Infrared (FTIR) spectroscopy were utilized to obtain the chemical composition of the polymers used in this research.
3.3.1.1 $^1$H NMR spectroscopy

The sulfonated poly(arylene ethers) were characterized and the degree of sulfonation of SPAE was quantified by $^1$H Nuclear magnetic Resonance ($^1$H NMR) spectroscopy, recorded by Varian 300 MHz. All spectra were obtained from ~3% (w/v) DMSO-d$_6$ solution at room temperature. The acid-base complex formation in SPEI(X)H/Taz polymer electrolytes was also analyzed by $^1$H NMR. For this purpose, the desired amounts of SPEI(62)H and triazole were dissolved in DMSO-d$_6$ taken in an NMR tube.

Table 3.4 Sample designations and compositions of SPSU(X)Li/PEGDGE/LiTFSI and PEGDGE/LiTFSI polymer electrolytes

<table>
<thead>
<tr>
<th></th>
<th>Degree of sulfonation (DS) (%)</th>
<th>Wt(%) of SPSU(X)Li</th>
<th>Wt(%) of PEGDGE</th>
<th>Wt of LiTFSI per 100 PEGDGE</th>
<th>[O]/[Li$^+$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPSU(76)Li/PEGDGE/</td>
<td>76</td>
<td>33</td>
<td>67</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>LiTFSI</td>
<td>76</td>
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<td>67</td>
<td>13</td>
<td>18</td>
</tr>
<tr>
<td></td>
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<td>76</td>
<td>33</td>
<td>67</td>
<td>47</td>
<td>6</td>
</tr>
<tr>
<td>PEGDGE/LiTFSI</td>
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<td>-</td>
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<td>0</td>
<td>$\infty$</td>
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<td>-</td>
<td>-</td>
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<td>12</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>109</td>
<td>6</td>
</tr>
</tbody>
</table>
The spectrum of each sample was obtained at room temperature using solution concentration (~3% (w/v)).

3.3.1.2 FTIR spectroscopy

The characterization of sulfonated poly(arylene ethers) (SPAE) and the intermolecular interactions in proton conducting SPEI(X)H/Taz, lithium ion conducting SPSU(X)Li/PEGDGE, and PEGDGE/LiTFSI were examined by Fourier Transform Infrared spectroscopy (FTIR) recorded in attenuated total reflection (ATR) mode using the Nicolet 380 FTIR model. FTIR spectra of the samples were scanned in the absorbance mode from 4000 to 400 cm\(^{-1}\) with 32 scans and a resolution of 4 cm\(^{-1}\).

The sample specimens of proton conducting SPEI(X)H/Taz, lithium ion conducting SPSU(X)Li/PEGDGE for FT-IR analysis were prepared by casting thin films from 5% (w/v) DMAc solution followed by drying at 70\(^\circ\)C until the solvent evaporated and at room temperature under vacuum for 24h for SPEI(X)H/Taz, at 60\(^\circ\)C under vacuum for 48h for SPSU(X)Li/PEGDGE. Lithium ion conducting samples were further cured at 120-150\(^\circ\)C for ~ 6h.

3.3.2 Solution viscosity measurements

Viscosity measurements of SPAEs were performed in DMAc solution using an Ubbelohde capillary viscometer. The temperature was maintained at 35\pm2 \(^\circ\)C during the measurement. SPAEs in acid form dissolved in DMAc and hence was used for the
viscosity measurement. Inherent viscosity was determined by varying SPAE solution concentration and the values are provided for 0.4 g/dL.

3.3.3 X-ray

In this study, wide angle x-ray diffraction was used to interpret the morphology of proton conducting solid polymer electrolytes. Small angle x-ray scattering was utilized to characterize the ion clustering in sulfonated bisphenol-A-poly(arylene ethers).

3.3.3.1 Wide angle x-ray diffraction

The crystal morphology of triazole in the SPEI(X)H was characterized by wide-angle x-ray diffraction (WAXD). WAXD film patterns were obtained by using Bruker AXS D8. X-ray was monochromatized with a nickel foil filter (\(\lambda_{CuK\alpha} = 1.54\ \text{Å}\)). The generator was operated at 40 kV and 40 mA. The sample to film distance was kept constant at 15 cm for all samples.

3.3.3.2 Small angle x-ray scattering

In small angle x-ray scattering, the coherently scattered intensity is given by the following equation:

\[
I(q) = \sum_i \sum_j d_i d_j \exp[-i q (r_i - r_j)]
\]  

3.3
Where \( q \) is the scattering vector, which is related to scattering angle through the following relationship:

\[
q = \frac{4\pi}{\lambda} \sin \theta
\]

\( \theta \) is half of the scattering angle (2\( \theta \)) and \( \lambda \) is the wavelength of radiation, \( d_i \) is the scattering factor, and \( r_i \) is the vector drawn from an arbitrary origin to a point \( i \). The equation can be simplified for a system with two scattering components

\[
I(q) = C(d_1 - d_2)^2 S(q)
\]

where

\[
S(q) = \left\langle \sum_i \sum_j \exp[-iq \cdot (r_i - r_j)] \right\rangle^2
\]

\( \langle \ \rangle \) denotes average, \( d_1 \) and \( d_2 \) are the scattering factors of region 1 and 2, \( C \) is a constant. \( d_1 - d_2 \) is determined by the difference in electron density, \( \rho_1 \) and \( \rho_2 \).

\[
(d_1 - d_2)^2 = (\rho_1^e - \rho_2^e)^2
\]

SAXS measurements were performed by a Rigaku X-ray diffractometer (Cu-K\( \alpha \) radiation). The exposure time was 30 min and the data was calibrated with silver behenate for low 2\( \theta \) region. The SAXS pattern is provided after subtracting background scattering from the sample scan.
3.3.4 Morphology

The morphology of the solid polymer electrolytes was characterized by optical and atomic force microscopic techniques. The procedures are discussed below:

3.3.4.1 Optical microscope

The crystal morphology of triazole in the SPEI(X)H was characterized by a Lietz Laborlux polarized optical microscope. The sample specimens for optical micrographs were prepared by casting thin films from 5% (w/v) DMAc solution on glass slides followed by drying at 70°C until the solvent evaporated and at room temperature under vacuum for 24h.

3.3.4.2 Atomic force microscope

The surface morphologies of the solid polymer electrolyte films were investigated by atomic force microscopy (AFM) using a Multi Mode Scanning Probe Microscope model with a Nanoscope IIIa Controller. The samples of SPEI(X)H/Taz polymer electrolytes were prepared by mixing the desired weight fractions of SPEI and triazole in dimethylacetamide solutions. Thin films were obtained by casting the solutions on pucks. The solvent was slowly evaporated at 60°C and then at room temperature in a vacuum oven for 24h. The samples of SPSU(X)Li/PEGDGE for AFM were prepared by mixing the desired amounts of SPSU, PEGDGE and DDS in dimethylacetamide solutions. Thin films were casted on AFM puck. The solvent was evaporated at 70°C and then at ~60°C in a vacuum oven for 48h followed by curing at 120-150°C for ~6h. The atomic force
microscope was operated in tapping mode using silicon cantilever probes with the spring constant ranging between 20-80 Nm$^{-1}$. The resonance frequency of the oscillating probe was in the range of 250-300 kHz. The topography and phase images were recorded simultaneously under ambient conditions with a scan rate of ~1 Hz for 5µm scan size, and ~2 Hz for 0.5-1 µm scan size with constant integral and proportional gain for all samples. Scanning was performed at different locations of each sample to ensure the reproducibility of the images.

3.3.5 Ionic conductivity measurements

The proton and ionic conductivity were determined by impedance measurement using an alternating current method (Figure 3.7). The polymer film was sandwiched between two stainless steel electrodes in a two terminal method. In the frequency range 100 Hz to 100 kHz, a Hewlett Packard 4274A impedance analyzer was used to obtain the magnitude of impedance, $|Z|$, and the phase angle, $\theta$. The bulk resistance of the film was taken as the value of $Z'$ (real axis) which produced the minimum imaginary response ($Z''$). The resistance was converted to specific conductivity, $\sigma$ (unit Siemens/cm) by the following equation:

$$\sigma = \frac{l}{R_b} \, A$$

3.8

where $l$ is the distance between the electrodes and $A$ is the film surface area perpendicular to the flow direction. The temperature dependent of proton conductivity was studied by attaching the whole assembly with a heating device and using a heating rate of 10ºC/min.
3.3.6 Thermal properties

The characterization of thermal properties such as degradation and transition temperatures of SPAEs and solid polymer electrolytes are discussed below:

3.3.6.1 Thermogravimetric analysis

Thermal degradation of SPAEs and proton and lithium ion conducting solid polymer electrolytes were investigated using a Thermal Advantage Q500 modulated thermogravimetric analyzer (TGA). The samples were heated from room temperature to 800ºC at a heating rate of 10ºC/min in nitrogen atmosphere.

Figure 3.7 Schematic diagram for the measurement of ionic conductivity by two terminal method.
3.3.6.2 Differential scanning calorimetry

The thermal transitions in SPAEs and solid polymer electrolytes were determined by a TA 2920 Differential Scanning Calorimeter (DSC). The samples were heated at a heating rate of 10°C/min. All experiments were performed with 10-12 mg sample, sealed in aluminium hermetic pans under nitrogen atmosphere.

3.3.7 Tensile properties

Tensile tests were carried out at room temperature using an Instron 5567 tensile testing machine with a crosshead speed of 50 mm/min and load cell of 1kN. The tensile properties were determined according to ASTM D 882 – 02 with a slight modification: the gage length was maintained at 25 mm in all cases and a paper holder was used to prevent grip slippage. The paper holder was prepared in rectangular form, 60 mm long and 15 mm wide with an inner rectangular hole of 25 mm length and 8 mm width. The specimen film was attached to the holder using tape on both sides. The length of the specimen was greater than 25 mm and the width ~5 mm. After mounting the specimen film supported by the paper holder onto the tensile testing machine, the two straps of the holder were cut prior to the testing so that the tensile load applied to the film.
CHAPTER IV

SULFONATION OF BISPHEONOL-A-POLY(ARYLENE ETHERS)

4.1 Introduction

The most important issues of a sulfonation route are the toxicity level of the sulfonating agent, homogeneity of the reaction medium, control of the degree of sulfonation, and expense of the process. The optimum sulfonation level is desired for maximizing the performance of these materials in terms of mechanical and thermal properties. To date, sulfonation of polyetherimide with chlorosulfonic acid has been reported in previous studies \(^{108,124}\). In this section, for the first time, a controlled post sulfonation route for bisphenol-A-polyetherimide by using trimethylsilyl chlorosulfonate is described. The effect of the electron withdrawing group in the deactivated unit of poly(arylene ether) backbone on sulfonation is discussed. The reaction conditions were optimized with respect to the reaction time, concentration and type of sulfonating agent. The thermal and mechanical properties of sulfonated poly(arylene ethers) were also characterized.
4.2 Characterization of sulfonation by trimethylsilyl chlorosulfonate

The sulfonation of two bisphenol-A-poly(arylene ethers), polyetherimide (PEI) and polysulfone (PSU) by trimethylsilyl chlorosulfonate was characterized by 1H NMR and FTIR spectroscopy.

4.2.1 $^1$H NMR spectroscopy

Post sulfonated poly(arylene ethers) (SPAEs) are most commonly synthesized via aromatic electrophilic substitution. The need for an electron donating activating group has been well established, and when the activating group is ortho- or preferably para- to the sulfonic acid group, milder sulfonating conditions (0-30°C) give a high yield of the sulfonated polymer. The sulfonation of bisphenol-A-poly(arylene ethers) (PAE) with trimethylsilyl chlorosulfonate (TMSCS) occurred in the following steps: an electrophilic substitution followed by acid catalyzed cleavage of silyl ester of sulfonated bisphenol-A-poly(arylene ether); the reaction scheme is shown in Figure 4.1(a) and the detail mechanism is described in Figure 4.1(b). The slow rate determining step of the electrophilic substitution was the attack of trimethylsilyl sulfonate electrophile at the site ortho to the ether linkage of bisphenol A unit and the expulsion of chloride (Figure 4.1(b)). The electron donating activating group stabilized the intermediate complex. The second step was the decomposition of the intermediate through the release of proton. The cleavage of silyl ester occurred in the subsequent step in presence of water or alcohol and was catalyzed by HCl liberated in the reaction. It was reported that in the post-sulfonation reaction, only one sulfonic acid group per repeat unit of bisphenol A based polymers
Figure 4.1 Sulfonation of bisphenol A poly(arylene ethers) by trimethylsilyl chlorosulfonate (a) reaction scheme, (b) sulfonation reaction mechanism
Figure 4.1 Sulfonation of bisphenol A poly(arylene ethers) by trimethylsilyl chlorosulfonate (a) reaction scheme, (b) sulfonation reaction mechanism (continued).
could be introduced and the acid group location of the electrophilic substitution was restricted at the activated ring ortho to the ether linkage \(^{102,125}\). The di-substitution was hindered due to the deactivation caused by the sulfonic acid group in the monosulfonated repeat unit.

The introduction of a sulfonic acid group in the activated bisphenol A moiety of polyetherimide (PEI) and polysulfone (PSU) is evident from \(^1\)H NMR spectra, shown in Figure 4.2 and 4.3. The spectra shows appearance of singlet at 7.79 ppm (e) assigned to the protons adjacent to the sulfonic acid group and two doublets at 6.98 (i,j) and 7.88 ppm (f,g) associated with the sulfonated bisphenol A unit as depicted in Figures. It is apparent that the peak intensity increases with increasing degree of sulfonation.

The chemical shift positions of SPAE-s are shown in Table 4.1. The cleavage of silyl ester of sulfonated polysulfone (SPSU) was accomplished during precipitation in methanol/isopropanol and occurred due to the absorbed moisture while precipitation in acetone, for sulfonated polyether imide (SPEI). The ease of hydrolysis was probably due to the electron withdrawing effect of imide and catalyzed by HCl generated in the sulfonation.

The degree of sulfonation (DS) was quantified by \(^1\)H NMR in DMSO-\(d_6^{126}\). The analysis is based on the chemical structure of SPEI. There are 18 aromatic protons in the non-sulfonated repeat unit and 16 aromatic protons in the sulfonated repeat unit with one proton adjacent to sulfonic acid group at 7.79 ppm. The peak at 7.79 ppm was used for quantification since it is well resolved from all other peaks. The degree of sulfonation was determined by the following equation:
Figure 4.2 $^1$H NMR spectra of SPEI(X)H sulfonated by trimethylsilyl chlorosulfonate (X refers to degree of sulfonation).
Figure 4.3 $^1$H NMR spectra of SPSU(X)H sulfonated by trimethylsilyl chlorosulfonate (X refers to degree of sulfonation).
Table 4.1 Peak annotations and chemical shifts of protons in SPAEs

<table>
<thead>
<tr>
<th>Positions</th>
<th>( \partial ) (ppm)</th>
<th>SPEI</th>
<th>SPSU</th>
</tr>
</thead>
<tbody>
<tr>
<td>a,b</td>
<td>7.1</td>
<td>7.08</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>7.35</td>
<td>7.31</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>7.93</td>
<td>7.91</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>7.79</td>
<td>7.71</td>
<td></td>
</tr>
<tr>
<td>f,g</td>
<td>7.88</td>
<td>7.84</td>
<td></td>
</tr>
<tr>
<td>i,j</td>
<td>6.98</td>
<td>6.94</td>
<td></td>
</tr>
<tr>
<td>k</td>
<td>7.64</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>p,q</td>
<td>7.51</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

\[ DS = \frac{18R}{1 + 2R}, \quad R = \frac{A_e}{A} \tag{4.1} \]

\( R \) is defined as the ratio of the area under the peak at 7.79 ppm, \( A_e \), to the sum of the area under the peaks corresponding to all other aromatic protons, \( A \). The sulfonation level of SPSU with 16 aromatic protons in the non-sulfonated repeat unit and 14 aromatic protons in the sulfonated repeat unit, was obtained by a similar method using the formula:

\[ DS = \frac{16R}{1 + 2R}, \quad R = \frac{A_e}{A} \tag{4.2} \]

The degree of sulfonation and the corresponding ion exchange capacities are given in Table 3.1.

4.2.2 FTIR spectroscopy

FTIR spectra of SPEI(X)H and SPSU(X)H are shown in Figure 4.4 and 4.5 respectively. In SPAE, the absorption band at 1010 cm\(^{-1}\) was assigned to the symmetric stretching of the diphenylether unit along the polyarylene ether main chain and in plane
ring vibration of para-substituted aryl ether. The absorption peak at 1360/1370 cm\(^{-1}\) assigned to symmetric bending deformation of methyl groups in isopropylidene units is insensitive to sulfonation. The bands at 1028, 1090 and 1160 cm\(^{-1}\) were attributed to the symmetric and asymmetric stretching of the sulfonate group. The peak at 1160 cm\(^{-1}\) was

![Figure 4.4 FTIR spectra of SPEI(X)H at various sulfonation levels (X refers to degree of sulfonation).](image-url)
Figure 4.5 FTIR spectra of SPSU(X)H at different sulfonation levels (X refers to degree of sulfonation).

- 1370, symmetric bending deformation of methyl groups
- 1090, free sulfonate group stretching
- 1020, hydrogen bonded sulfonate group stretching
- 1010, stretching of p-substituted diphenyl ether

Wave number (cm$^{-1}$)

SPSU(76)H
SPSU(40)H
SPSU(23)H
PSU
overlapped with sulfone asymmetric stretching. The effect of counterion on the sulfonate characteristic peaks has been documented in the literature - symmetric stretching peak of sodium sulfonate at 1063 cm\(^{-1}\) in Nafion shifted to 1053 cm\(^{-1}\) in the acid form\(^{119,127}\). In present study, for the acid form of sulfonated polyarylene ethers, extensive hydrogen bond formation resulted in broad absorption bands at 1020 and 1160 cm\(^{-1}\) due to symmetric and asymmetric stretching of the sulfonic acid group with a relatively sharp peak at 1090 cm\(^{-1}\), associated with free sulfonic acid groups shown in Figures 4.4 and 4.5. The symmetric stretching band of sulfonate group overlapped with aryl ether peak. The spectral changes observed with increased degree of sulfonation are as follows: (i) progressive increase in intensity of the peak at 1090 cm\(^{-1}\), (ii) broadening of the absorption bands at 1010 and 1160 cm\(^{-1}\).

4.3 Effect of poly(arylene ether) chemical structure

Figure 4.6 illustrates the effect of poly(arylene ether) (PAE) chemical structure on the degree of sulfonation. Two bisphenol A based PAE, PEI and PSU, were studied and comparison was made with similar trimethylsilyl chlorosulfonate concentration, x, defined as the ratio of the number of moles of sulfonating agent to the number of moles of PAE repeat unit, and all reactions were carried out at 30\(^{\circ}\)C for 24 h. The degree of sulfonation exhibits identical trends, and the level is higher in SPSU than in SPEI. The location of the sulfonic acid group in the activated aromatic ring was governed by the electron donating tendency of the ether oxygen. The variation in reaction rates with PEI
and PSU and as a consequence different degree of sulfonation obtained under identical conditions indicate that different electron withdrawing groups in the deactivated units,

Figure 4.6 Plots of degree of sulfonation as a function of trimethylsilyl chlorosulfonate concentration, $x$ for SPEI and SPSU. The data points are connected by straight line segments to guide the eye.
shown in Figure 4.7, also had influence on sulfonation although it occurred at the same bisphenol A unit of both PAEs. The stronger electron withdrawing imide offered a higher activation energy barrier to the attacking electrophile (trimethylsilyl sulfonate) through the increased delocalization of ether electrons than the less electron withdrawing sulfone group and hence reduced the reaction rate. The higher $\partial$ values corresponding to the protons in SPEI (shown in Table 4.1) compared to that in SPSU further support this explanation.

4.4 Effect of reaction time and trimethylsilyl chlorosulfonate concentration

The influence of reaction time on post sulfonation of PAE-s was investigated by terminating the reactions after 6, 24, 48, and 72h using trimethylsilyl chlorosulfonate (TMSCS), shown in Figure 4.8. The solutions were homogeneous throughout the reaction and even after 72 h. Two different mole fractions of TMSCS, 0.7 and 1.5 were used. In all cases, the reaction was faster initially and slowed down after 24 h. The variation in sulfonation levels with TMSCS concentration in mole fraction, $x$ is described in Figure 4.6. All of the reactions were conducted at $30^\circ$C for 24h. Similar trends are observed with PEI and PSU. The degree of sulfonation increases with increasing sulfonating agent concentration up to $x= 1.5$, beyond this point it declines. The observed retardation beyond a certain period or sulfonating agent concentration was possibly due to the onset of degradation of PAE backbone. The initial high sulfonation rate caused generation of a large amount of HCl, and in the presence of an acid, sulfonation and degradation occurred simultaneously, thus reducing the efficiency of the sulfonating agent.
Figure 4.7 Chemical structures of two different poly(arylene ethers), sulfonation site shown by arrow.
Figure 4.8 Plots of degree of sulfonation as a function of reaction time for two different concentrations of trimethylsilyl chlorosulfonate, $x=0.7$, and $x=1.5$. The open and solid symbols are for SPSU and SPEI respectively. The data points are connected by straight line segments to guide the eye.
4.5 Comparison of two different sulfonating agents – trimethylsilyl chlorosulfonate (TMSCS) vs chlorosulfonic acid (CSA)

The effect of two different sulfonating agents – chlorosulfonic acid (CSA) and its trimethylsilyl ester, TMSCS, on sulfonation was systematically studied by analyzing sulfonated polyetherimides synthesized under various reaction conditions. The reaction medium was perfectly homogeneous with TMSCS while the reaction product was precipitated immediately after the addition of CSA. Several evidences of structural modification are observed in $^1$H NMR and FTIR spectra (Figure 4.9 – 4.11). In $^1$H NMR spectra (Figure 4.9) a new peak appears at 5.76 ppm for PEI sulfonated by CSA, and the intensity increases with the sulfonating agent concentration and reaction time. The chemical shift at 1.69 ppm corresponding to methyl protons of isopropylidene unit gradually shifted to higher value upon increasing concentration of CSA (Figure 4.10). In FTIR spectra, shown in Figure 4.11, a series of new absorption bands are seen at 1770, 1610 and 1470 cm$^{-1}$ in SPEI sulfonated using CSA.

Spectroscopic analysis suggests acid catalyzed degradation of PEI during sulfonation, the probable mechanism is depicted in Figure 4.12. Degradation initiated through the attack of Cl$^-$, released in the first step of sulfonation, at the methyl proton of isopropylidene unit. The peak at 5.76 ppm observed in $^1$H NMR (Figure 4.9) corresponds to the vinyl protons generated due to the cleavage. FTIR analysis also indicates generation of vinyl group in the degradation products while sulfonation is conducted with CSA (Figure 4.11), as evident from the following observations: (i) appearance of peak at 1610 cm$^{-1}$ assigned to the conjugated C=C stretching, (ii) new peaks seen at 1770 and 1470 cm$^{-1}$ corresponding to C-H deformation of C= CH$_2$.
Figure 4.9 $^1$H NMR spectra of SPEI sulfonated by trimethylsilyl chlorosulfonate (TMSCS) and chlorosulfonic acid (CSA) in $\delta$ = 5.5-6 ppm region.

Figure 4.10 Effect of two different sulfonating agents on the chemical shift position of isopropylidene unit at $\delta$ = 1.69 ppm in $^1$H NMR.
Figure 4.11 FTIR spectra of SPEI sulfonated by trimethylsilyl chlorosulfonate (TMSCS) and chlorosulfonic acid (CSA).

$$\begin{align*}
\text{CSA (X=0.7, t=24h)} \\
\text{CSA (X=0.7, t=6h)} \\
\text{CSA (X=1.5, t=24h)} \\
\text{CSA (X=1.5, t=6h)} \\
\text{TMSCS (X=1.5, t=24h)}
\end{align*}$$

1770, overtone band of C-H deformation
1610, C=C stretching
1470, C-H deformation in alkene

Figure 4.12 Mechanism of acid catalyzed degradation of SPEI during sulfonation.
In $^1$H NMR spectra (Figure 4.13), it is seen that the peak at 5.76 ppm also appears during sulfonation of PEI with TMSCS after 72 h but is not observed with SPSU under identical conditions. Evidence of degradation in SPEI(62)H is also reflected by the lower viscosity value compared to SPSU. The drastic loss of mechanical strength of SPEI(62)H than other SPAEs, described in the following section, is also an indication of degradation. Thus, it can be concluded that the sulfonation and degradation were fairly competitive with CSA and evident even at low acid concentration ($x=0.7$). HCl liberated during sulfonation of PEI with TMSCS caused degradation at high sulfonating agent concentration ($x \geq 1.5$) or after a long time ($x=1.5$, $t=72$ h). However, degradation occurred through the same mechanistic path, illustrated in Figure 4.12, with the two different sulfonating agents.

4.6 Effect of sulfonation on thermal properties of SPAEs

TGA curves of SPAE exhibited a three-step degradation pattern compared to one in unsulfonated PAE in nitrogen atmosphere; the profiles for SPEI and SPSU are shown in Figure 4.14 and 4.15 respectively. In SPAE, the first step at $\sim$100°C was due to the loss of water bonded to sulfonic acid. The second step in the temperature range between 200 and 400°C was attributed to partial desulfonation; as reported by TGA-FTIR and TGA-mass spectrometry (MS) study$^{128}$. The third step was related to the decomposition of the main chain. The temperature corresponding to the peak on derivative-weight (%) vs temperature plots, $T_{\text{max}}$ and the corresponding weight loss of sulfonated poly(arylene ethers) for the second and third step are compiled in Table 4.2. The thermal stability was
affected by the type of the electron withdrawing groups (imide vs sulfone) in the deactivated unit of SPAE. All SPAEs were thermally stable up to 500°C. $T_{\text{max}}$ of both

Figure 4.13 $^1$H NMR spectra of SPEI and SPSU sulfonated by trimethylsilyl chlorosulfonate in $\delta=5.5\text{-}6$ ppm region after 72h.
Figure 4.14 TGA thermograms for SPEI(X)H at various degrees of sulfonation, X.
Figure 4.15 TGA thermograms for SPSU(X)H at various sulfonation levels, X.
second and third step were higher for SPEI than SPSU indicating better thermal stability of the sulfonated polyetherimides.

DSC thermograms of SPEI and SPSU in the acid form are displayed in Figure 4.16 and 4.17 respectively. The determination of $T_g$ with accuracy was difficult at higher sulfonation levels due to the onset of desulfonation in the same temperature range. DSC curves of SPAEs exhibit a wide glass transition region; $T_g$ decreases with increasing sulfonation level. Recently Bai et al. also reported a similar behavior in sulfonated poly(arylenethioethersulfone) $^{126}$. According to the previous studies, the sulfonic acid groups in random sulfonated copolymers associate to form ionic domains or clusters $^8,9,129$. The evidence of cluster formation is the existence of two glass transition temperatures associated with the nonpolar matrix and the ionic cluster region and the ionic peak observed in small angle X-ray scattering (SAXS), attributed to the
Figure 4.16 DSC thermograms of SPEI(X)H at different sulfonation levels.
Figure 4.17 DSC thermograms of SPSU(X)H at different degrees of sulfonation.
intermultiplet spacing in the cluster region. The factors influencing ion clustering are \( T_g \) of the parent polymer, ionic group content, nature of the ionic group, position of the ionic group relative to the polymer backbone, type of counter ion, steric constraints in the ion pair aggregation, amount and nature of the added low molecular weight compound (plasticizer). Figure 4.18 depicts SAXS analysis of SPAE systems. The ion clustering is not evident even at higher sulfonation level. Furthermore, single \( T_g \) was observed for all SPAEs. This may be attributed to the restricted chain mobility of PAEs due to the rigid polymer backbone (\( T_g \) of PEI is 221ºC and \( T_g \) of PSU is 191ºC) which offered hindrance to the phase separation. The results obtained in the study are in good agreement with that reported in the literature. \(^8,11\) Two distinct morphological regions were found to exist in sulfonated polystyrene (\( T_g \) of the host polymer is 100ºC) while sulfonated poly(ether ether ketone) (\( T_g \) of the host polymer is 150ºC) exhibited single phase behavior.

4.7 Effect of sulfonation on viscosity and mechanical properties of SPAEs

Table 4.3 describes variation in inherent viscosity of SPAEs with degree of sulfonation. The viscosity increases with sulfonation level and the values of SPSUs are to some extent larger than those of SPEI. This was due to the acid catalyzed degradation of polymer chains during sulfonation of PEI resulting in an appreciable decrease in inherent viscosity. The polyelectrolyte behavior upon diluting SPAE solutions in DMAc was observed at higher degree of sulfonation, 62% for SPEI and 40 and 76% for SPSU. No polyelectrolyte effect was observed at a lower sulfonation level of SPAE and the
Figure 4.18 Small angle x-ray for SPEI(62)H and SPSU(76)H (a) SAXS patterns, (b) I vs q plots.
Table 4.3 Viscosity and tensile properties of SPAEs

<table>
<thead>
<tr>
<th>Sample id.</th>
<th>Tensile Strength (MPa)</th>
<th>Strain at Break (%)</th>
<th>Tensile Modulus (MPa)</th>
<th>$\eta_i$ (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI</td>
<td>75.2</td>
<td>4</td>
<td>2161.9</td>
<td>0.14</td>
</tr>
<tr>
<td>SPEI(22)H</td>
<td>64.6</td>
<td>4</td>
<td>1912.1</td>
<td>0.16</td>
</tr>
<tr>
<td>SPEI(48)H</td>
<td>30.5</td>
<td>2</td>
<td>1532.1</td>
<td>0.2</td>
</tr>
<tr>
<td>SPEI(62)H</td>
<td>13.4</td>
<td>2</td>
<td>709.1</td>
<td>0.47</td>
</tr>
<tr>
<td>PSU</td>
<td>77.6</td>
<td>14</td>
<td>2071.5</td>
<td>0.11</td>
</tr>
<tr>
<td>SPSU(23)H</td>
<td>59.4</td>
<td>11</td>
<td>1970.3</td>
<td>0.59</td>
</tr>
<tr>
<td>SPSU(40)H</td>
<td>53.3</td>
<td>8</td>
<td>1585.9</td>
<td>0.63</td>
</tr>
<tr>
<td>SPSU(76)H</td>
<td>37.9</td>
<td>6</td>
<td>1385.1</td>
<td>0.83</td>
</tr>
</tbody>
</table>

behavior was similar to that of unsulfonated polymers. This can be attributed to the lesser ionic character of SPAEs at low degrees of sulfonation, which did not favor the polymer aggregation. Due to this variation in behavior with sulfonation level, inherent viscosity values of SPAE solutions with 0.4 g/dL concentration are provided for the ease of comparison.

Figure 4.19 and 4.20 compare tensile stress-strain plots of unmodified PEI and PSU with the corresponding sulfonated polymers; the results are also summarized in Table 4.3 for the ease of comparison. The tensile strength, modulus, and elongation at break of SPAEs are lower compared to the virgin polymers, and the values gradually decrease with increasing degree of sulfonation. A significant reduction in the tensile parameters of SPEI(62)H was due to the polyetherimide chain scission at the isopropylidene unit as evident from the spectroscopic analysis described in the previous section.
Figure 4.19 Stress-strain plots for SPEI(X)H at different degrees of sulfonation, X, sulfonated by trimethylsilyl chlorosulfonate.
Figure 4.20 Stress-strain plots for SPSU(X)H at different degrees of sulfonation, X, sulfonated by trimethylsilyl chlorosulfonate.
4.8 Conclusions

Two different bisphenol A poly (arylene ethers), polyetherimide (PEI) and polysulfone (PSU), were sulfonated to various degrees by a controlled post sulfonation route using trimethylsilyl chlorosulfonate (TMSCS). The introduction of sulfonic acid group at the activated bisphenol A unit was confirmed by $^1$H NMR and FTIR spectroscopy. The highest sulfonation level was obtained with 1.5 mole fraction of the sulfonating agent at 30°C for both PEI and PSU. The sulfonation was faster initially, but the rate decreased markedly beyond 24h. The stronger electron withdrawing imide caused a reduction in the degree of sulfonation of PEI compared to PSU under identical conditions. The influence of degree of sulfonation on thermal and tensile properties of SPAEs were also investigated. Sulfonation with chlorosulfonic acid exhibited evidence of degradation at lower sulfonating agent concentration. Degradation was also evident while sulfonating PEI with TMSCS in the later stage of sulfonation and at higher sulfonating agent concentration and followed the same mechanistic pathway with both sulfonating agents.
CHAPTER V
ANHYDROUS STATE PROTON CONDUCTION IN SULFONATED POLYETHERIMIDE WITH 1H-1,2,4 TRIAZOLE AS PROTON SOLVENT

5.1 Introduction

1H-1,2,4 triazole is a promising aromatic heterocycle that possesses the necessary structural features of a proton solvent – it has proton donor-acceptor sites, intermolecular hydrogen bond formation, and self-dissociation characteristics. It was used in replacement of water in different polymer matrices such as sulfonated polysulfone and hybrid inorganic-organic polymer network\textsuperscript{130}, Nafion\textsuperscript{131}, poly(vinyl phosphonic acid) and poly(2-acrylamido-2-methyl-1-propane sulfonic acid)\textsuperscript{132}. It is a crystalline solid with higher melting and boiling points of \~120\degree C and 256\degree C respectively, compared to water. It has high proton conductivity above its melting point. It is electrochemically more stable than imidazole attributed to the lower electron density. Both triazole and triazolium ions (pK\textsubscript{a1} = 2.39, pK\textsubscript{a2} = 9.97) have lower pK\textsubscript{a} compared to imidazole (pK\textsubscript{a1} = 7.18, pK\textsubscript{a2} = 14.52), and hence have better proton donating tendency. These favorable criteria justify its selection as a potential solid state proton solvent. To date, no literature has addressed the crystal morphology of a heterocycles in sulfonated polymer...
matrix. In this section, the preparation of novel anhydrous proton conducting solid polymer electrolytes (SPEs) is described by the incorporation of 1H-1,2,4-triazole (Taz) in sulfonated polyetherimide (SPEI). The influence of crystal morphology of 1,2,4 triazole in sulfonated bisphenol-A-polyetherimide (SPEI) matrix on anhydrous state proton conductivity is discussed. The crystal morphology is defined as size, shape, and state of dispersion of crystallites. The miscibility of SPEI with triazole was examined as a function of degree of sulfonation and electrolyte composition. The specific interactions were characterized by Fourier transform infrared (FTIR), $^1$H Nuclear magnetic resonance (NMR) spectroscopy and differential scanning calorimetry (DSC). The crystal morphology was investigated by optical microscope and wide angle X-ray diffraction (WAXD) techniques. Atomic force microscopy (AFM) was utilized to explore the direct spatial mapping of surface topography and heterogeneity in the polyelectrolyte films. WAXD and AFM were used complementarily to interpret the results.

5.2 Analysis of specific interactions between immobilized sulfonic acid groups and 1H-1,2,4 triazole

The noncovalent interactions in SPEI(X)H/Taz proton conducting solid polymer electrolytes are discussed below:

5.2.1 FTIR spectroscopic analysis

In FTIR spectra of triazole (curve 1 in Figure 5.1 and 5.2), two doublets at 1270, 1260 cm$^{-1}$ and 1180, 1144 cm$^{-1}$ were assigned to C-N asymmetric and symmetric stretching
and the absorption bands at 1060 and 1020 cm$^{-1}$ were due to N-N asymmetric and symmetric stretching respectively. The bands at 978, 955, 881 and 669 cm$^{-1}$ were attributed to the ring deformation and ring torsion$^{133,134,135}$. The characteristic absorption bands of sulfonated polyetherimide in acid form, SPEI(X)H are described in Chapter IV.

Figure 5.1 Effect of degree of sulfonation on ring torsion of triazole in 650-1000 cm$^{-1}$ region for 70/30 compositions.
Based on the FTIR spectra of the individual components, the spectral regions at 650-1000 and 800-1300 cm\(^{-1}\) are focused to characterize the specific interactions between immobilized sulfonic acid groups of SPEI(X)H and triazole as a function of degree of sulfonation and triazole concentration (weight percent). The characteristic bands involved in the interactions are depicted in Table 5.1.

![FTIR spectra](image)

**Figure 5.2** Effect of degree of sulfonation on triazole characteristics bands in 800-1300 cm\(^{-1}\) region for 50/50 compositions.
Table 5.1 FT-IR absorption bands of SPEI and 1H-1,2,4 triazole involved in intermolecular interactions

<table>
<thead>
<tr>
<th>Components</th>
<th>Wavenumber(cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triazole</td>
<td>669</td>
<td>ring torsion</td>
</tr>
<tr>
<td>Triazole</td>
<td>978,954,881</td>
<td>ring deformation</td>
</tr>
<tr>
<td>Triazole</td>
<td>1060</td>
<td>N-N asymmetric stretching</td>
</tr>
<tr>
<td>Triazole</td>
<td>1144</td>
<td>C-H deformation/C-N symmetric stretching</td>
</tr>
<tr>
<td>Triazole</td>
<td>1260</td>
<td>C-N asymmetric stretching</td>
</tr>
<tr>
<td>SPEI</td>
<td>1090</td>
<td>symmetric stretching of sulfonic acid group</td>
</tr>
</tbody>
</table>

The effect of sulfonation level and triazole content on the absorption bands of triazole in SPEI(X)H/Taz can be summarized as follows (Figure 5.1 – 5.3): (i) the absorption bands located at 669, 881, 954 and 978 cm⁻¹ in SPEI(X)H/Taz 70/30 compositions broaden and exhibit red shift with increasing sulfonation level compared to DMAc cast triazole (Figure 5.1). The shift is prominent in SPEI(22)H/Taz 70/30; beyond 22% sulfonation level it becomes insignificant while the peak area increases with degree of sulfonation, particularly at 881 and 978 cm⁻¹. The peaks are relatively sharp in SPEI(X)H/Taz 50/50 composition and exhibit slight blue shift (Figure 5.2), (ii) a new peak appears at 972 cm⁻¹ in SPEI(62)H/Taz 50/50, (iii) The C-H deformation, C-N and N-N stretching peaks at 1144, 1260 and 1060 cm⁻¹ also show slight blue shift with increasing sulfonic acid content, the effect is more prominent in 50/50 composition as displayed in Figure 5.2.

It has been well documented in literature that in pure triazole, molecules are in self-association through N-H---N and C-H---N intermolecular hydrogen bonding.\cite{136}
Figure 5.3 FTIR spectra of sulfonate symmetric stretching at various triazole concentrations in SPEI(62)H/Taz.
In SPEI matrix, triazole molecules were hydrogen bonded to sulfonic acid groups in addition to their self association. With increasing sulfonation level, the extent of the intermolecular interactions between triazole molecules and SPEI enhanced. The interactions caused red shift of the bands characterizing triazole ring deformation and ring torsion. At a given triazole concentration, e.g. 30 wt%, a certain amount of triazole molecules were involved in strong interactions with sulfonic acid groups, and the remaining were weakly bound and self-associated triazole. The strength of specific interactions in decreasing order is: triazolium ion – sulfonate anion > triazole- sulfonate > triazole – sulfonic acid ≈ triazole-triazole > triazole-hydrophobic polyetherimide backbone. The bands corresponding to strongly and weakly bound triazole overlap in most cases, exhibiting peak broadening except in SPEI(62)H/Taz 50/50 composition, where the strongly bound triazole molecules appear as a new peak at 972 cm⁻¹, shown in Figure 5.2. At a constant triazole concentration (30 wt%), with increasing degree of sulfonation, the amount of triazole involved in specific interactions with sulfonic acid groups increased, thus increasing peak area rather than peak maxima. In SPEI(X)H/Taz 50/50 composition, weakly bound/self-associated triazole molecules predominated and the slight blue shifts observed for the triazole characteristic bands were attributed to the weakening of N----H-N and C-H---N hydrogen bonds in bulk triazole; thus the effect is seen at higher triazole concentration. A similar behavior was observed in PBI/SPSU and PBI/poly(vinyl-acetate-stat-vinyl alcohol) blends where the blue shift of N-H stretch was illustrated as weakening of self-association in PBI. In sulfonated polymers, the symmetric stretching of sulfonic acid group is very sensitive to local environments and has been used to examine the specific interactions in
polymer blends\textsuperscript{15,119}. In the present study on SPEI(X)/Taz proton conducting polymer electrolytes, the absorption band at 1090 cm\textsuperscript{-1} due to symmetric stretching of free sulfonic acid groups was used to monitor the specific interactions as there is no absorption band of triazole at this location. As illustrated in Figure 5.3, the peak exhibits a shift to higher wave number with increasing triazole concentration, more pronounced in SPEI(62)H/Taz 50/50. The addition of triazole in SPEI caused protonation of nitrogen atoms in heterocyclic ring (acid-base interaction). The sulfonic acid groups of SPEI were involved in hydrogen bonding with triazole molecules, and the strength of the hydrogen bonds differ from hydrogen bonding interactions in bulk triazole or SPEI. As the number of triazole molecules interacting with sulfonic acid site of SPEI increased, the peak shifted to higher wavenumber implying strengthening of S=O bond of sulfonic acid group. The same trend was reported for Nafion/polypyrrole composites; the symmetric stretching of sulfonate shifted to higher frequency with increasing polypyrrole content\textsuperscript{127}.

5.2.2 \textsuperscript{1}H NMR spectroscopic analysis

NMR titration has been widely used to evaluate the extent of proton transfer from a dopant acid to the model heterocyclic compound\textsuperscript{66,138,139}. Schuster et al.\textsuperscript{66} quantified the protonation constants of imidazole in the presence of trifluoroacetic and acetic acid. The estimated equilibrium constant value using trifluoroacetic acid as dopant was in the range of 60 and 160 depending on temperature during measurement. The protonation of triazole by sulfonic acid groups of SPEI (62)H was examined by \textsuperscript{1}H NMR spectroscopy. The variation in chemical shift ($\delta_{\text{obs}}$) value corresponding to C(5)H of triazole ring at 8.28
ppm was analyzed at different SPEI(62)H/Taz compositions since SPEI has no peak in the region (Figure 5.4). $\partial_{\text{obs}}$ gradually shifted to higher value with increasing SPEI concentration ($\geq 56$ wt%). No significant change of chemical shift was observed at lower acid concentration as shown in Figure 5.5. Our attempt to determine the protonation constant of triazole in SPEI was not successful probably due to the weaker acidity of sulfonic acid since it is located at the activated bisphenol A unit of PEI. The change in chemical shift with SPEI concentration provided proof for the formation of SPEI-Taz acid-base complex.

5.2.3 Differential scanning calorimetry

Figures 5.6 and 5.7 illustrate the influence of degree of sulfonation on the melting endotherm of triazole for two compositions, SPEI(X)H/Taz 70/30 and 50/50. It is apparent that increased specific interactions between triazole molecules and SPEI with increasing sulfonation level cause melting temperature depression of triazole. The effect of triazole concentration on melting temperature and enthalpy of fusion at different sulfonation levels in SPEI(X)/Taz is demonstrated in Figures 5.8 and 5.9. The melting peak and enthalpy shift to higher value with increasing triazole concentration. The results are also compiled in Table 5.2.

Triazole molecules crystallized in SPEI matrix were in different states of association: (i) triazole strongly bound to the sulfonic acid sites; (ii) weakly bound triazole, i.e. molecules weakly bound to the specific binding sites of the polymer or to the strongly bound triazole and/or self-associated free triazole. At a given degree of sulfonation,
Figure 5.4 $^1$H NMR spectra of chemical shift of triazole (C(5)H) in SPEI(62)H matrix at different concentrations.
Figure 5.5 Plot of proton chemical shift (C(5)H of triazole) as a function of triazole concentration in weight percent.
Figure 5.6 Effect of degree of sulfonation on melting temperature of triazole in SPEI(X)H/Taz 70/30 compositions.
Figure 5.7 Effect of degree of sulfonation on melting temperature of triazole in SPEI(X)H/Taz 50/50 compositions.
Table 5.2 Variation of melting temperature of triazole, and proton conductivity in SPEI(X)H/Taz polymer electrolytes

<table>
<thead>
<tr>
<th>Degree of sulfonation (DS)(%)</th>
<th>Triazole content (wt%)</th>
<th>$\lambda$</th>
<th>$T_m$(°C)</th>
<th>Conductivity (S/cm)</th>
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* Samples failed during measurement.
Figure 5.8 DSC traces of proton conducting polymer electrolytes, SPEI(22)H/Taz at different triazole concentrations.
Figure 5.9 Melting temperature and enthalpy of fusion as a function of triazole concentration at different sulfonation levels.
a certain fraction of triazole molecules were strongly bonded to the sulfonic acid groups and the remaining, were weakly bound or free triazole. With increasing triazole concentration, the weakly bound triazole concentration increased causing the melting endotherm shift to higher temperature and approach to that of bulk triazole. Figure 5.7 (curve 3 and 4) also shows two endotherms in SPEI(48)H/Taz and SPEI(62)H/Taz 50/50, a broad melting peak within 60-70°C is assigned to the strongly associated triazole and a relatively sharp peak at 100-105°C due to the weakly associated triazole. The splitting of the absorption bands due to the strongly and weakly bound triazole molecules was also evident in the FTIR spectra for SPEI(62)H/Taz 50/50 (Figure 5.2). It was difficult to quantify strongly and weakly bound triazole by DSC due to numerous contributing factors: (1) overlapping of melting endotherms, (2) enthalpy of fusion, a function of the strength of interaction in addition to concentration, and (3) the change in heat capacity associated with the highly dispersed triazole in SPEI matrix at higher sulfonation level or the concentration of triazole (e.g., in SPEI(X)H/Taz 90/10 composition) was too small and beyond the detection limit of the technique.

5.3 Crystal morphology of triazole in sulfonated polyetherimide

The specific interactions between sulfonic acids and triazole molecules had influence on triazole crystal morphology. In this section, the size, shape, and state of dispersion of triazole crystals in sulfonated polyetherimide is discussed.
Figure 5.10 Optical micrographs of 5 %w/v DMAc cast solution (a) pure triazole crystals, (b) SPEI(22)H/Taz 50/50, (c) SPEI(62)H/Taz 50/50.
5.3.1 Optical microscopy

The effect of degree of sulfonation on the crystal morphology of triazole in SPEI was investigated by an optical microscope. Figure 5.10 depicts the optical micrographs under cross polarization for neat triazole and SPEI(X)H/Taz 50/50 casted from 5% w/v DMAc solution. In SPEI(22)H/Taz 50/50, continuous crystal domains are observed (Figure 5.10b), while noncontinuous bead-like crystal domains form in SPEI(62)H/Taz 50/50 (Figure 5.10c). With decreasing triazole concentration below 50 wt%, the crystal size decreased and became too small to be visible by polarized microscope.

5.3.2 Wide angle x-ray diffraction

The room temperature crystal structure of 1,2,4 triazole was first studied by Deuschl. 1H-1,2,4 triazole is orthorhombic with Pbcn space group symmetry and unit cell parameters calculated as a = 9.69 ± 0.04 Å, b = 9.38 ± 0.04 Å and c = 7.14 ± 0.03 Å, possesses eight molecules in the unit cell. Triazole exists in two tautomeric forms. The nitrogen-bonded hydrogen atom was not found at room temperature. The crystal structure was further investigated by Goldstein et al. at a low temperature of about -160°C. The tautomeric hydrogen was detected in 1 position. The triazole ring is planar; the molecules are in self-association through N-H---N and C-H---N hydrogen bonds and form corrugated sheet structure. WAXD patterns of SPEI(X)H/Taz are shown in Figures 5.11-5.13. Comparison of x-ray diffraction patterns of DMAc cast pure triazole with triazole crystallized in SPEI(X)H at different sulfonation levels shows a sequence of spots for pure triazole; these spots gradually lie on Debye-Scherrer rings and produce smooth,
continuous rings. The rings are relatively uniform and continuous in SPEI(62)H/Taz 60/40 but completely disappear for SPEI(62)H/Taz 70/30.

Figure 5.14 compares WAXD diffractograms of triazole in SPEI(X)H at different degrees of sulfonation with that of pure solution cast triazole, for $\theta \sim 17.7^\circ$ corresponding to (111) lattice planes. The apparent lateral crystal size defined as the size
Figure 5.13 WAXD patterns (a) SPEI(22)H/Taz 50/50, (b) SPEI(48)H/Taz 50/50, (c) SPEI(62)H/Taz 50/50.

Figure 5.14 WAXD diffractograms of SPEI(X)H/Taz 50/50 at different degrees of sulfonation, X for (111) lattice plane. The pattern for DMAc cast triazole is presented as a reference.
in the direction perpendicular to the reflection plane, hkl, L\text{hkl}, was determined from the peak position and peak width using the Scherrer equation\textsuperscript{141}:

\[ L\text{hkl} = \frac{0.9\lambda}{\beta\text{hkl} \cos\theta} \tag{5.1} \]

where \( \lambda \) is the wave length of x-ray, \( \beta\text{hkl} \) is the crystal reflection width (in radian) at half the maximum intensity, \( \theta \) is the Bragg angle of hkl reflection and 0.9 is the value set to the crystal shape factor. The results are summarized in Table 5.3. It is observed in Figure 5.14 that the peak associated with (111) diffraction of triazole gradually broadens with an increasing degree of sulfonation and the peak maxima appears at wider angle compared to that in pure triazole, indicating that the lattice planes in triazole crystallites within SPEI were more closely spaced than in pure triazole. There is little variation in peak maxima value with sulfonation level. The peak broadening was due to the reduction in crystal size due to increased interaction with sulfonic acid groups (Table 5.3). The effect of triazole concentration on (111) diffraction in SPEI(22)H/Taz is shown in Figure 5.15. The peak intensity increases with triazole weight percent and the maxima shifts towards that of solution cast pure triazole. This trend also indicates the existence of two different degrees of interactions between triazole and sulfonic acid, as evident from DSC thermograms and FTIR spectroscopy. In the strongly associated triazole molecules the lattice planes were more closely spaced than in pure and weakly bound triazole. The behavior of loosely bound triazole molecules closely resembled to that of bulk triazole.
In SPEI(X)H/Taz, the sulfonic acid groups provided strong binding sites and induced nucleation of triazole. The crystals grown from triazole in DMAc solution showed a spotty pattern because of their larger size. At constant triazole weight percent, the increased degree of sulfonation caused enhanced nucleation density and thus reduction

Figure 5.15 WAXD profiles of SPEI(22)H/Taz at different triazole concentrations.
of crystal size and increased number of crystal domains. Furthermore, the uniform
distribution of the acidic groups in SPEI also resulted in homogeneous dispersion of
triazole crystals throughout the sulfonated polymer matrix. A larger number of smaller
size crystallites covered a broader spectrum of angles in the azimuthal direction and thus
eventually formed Debye-Scherrer rings. Cullity reported a similar spot to ring pattern
formation in metallurgical crystals attributed to the decrease in grain size. The
detection of crystal reflection peaks by WAXD was affected by the triazole concentration
and the crystal size. At low triazole concentration (i.e., in SPEI(X)H/Taz 90/10) and for
small crystal size as in SPEI(62)H/Taz 70/30 (Figure 5.12 (c)), the signals are too weak
to be detected by x-ray diffraction. This assertion was further confirmed by atomic force
microscopy.

Table 5.3 Comparison of d –spacing and crystal size measured by WAXD technique

<table>
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<th>Degree of sulfonation (DS) (%)</th>
<th>Triazole content (wt%)</th>
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<th>d spacing (Å)</th>
<th>$L_{(111)}$ (nm)</th>
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5.3.3 Atomic force microscopy

In Figure 5.16, three dimensional topographic (left) and the corresponding phase
images (right) of SPEI(X)H/Taz 70/30 compositions with different sulfonation levels, 22,
48 and 62 are depicted. The operational parameters were kept constant for all samples to minimize the effect of operating conditions on contrast variation particularly in phase images, described in the experimental section. In SPEI(X)H/Taz film surface, some distinct features are apparent, which are not observed in neat SPEI, hence assigned to the triazole crystal domains. The variation in size, shape, and dispersity of triazole crystal domains is evident with increasing sulfonation level. The domains are elevated (brighter in color) at a lower degree of sulfonation (22%), while they are depressed (darker in color) with respect to the surrounding matrix at sulfonation level. In SPEI(62)H/Taz height image, a majority of the domains have relatively circular cross-sections with a reduction in size compared to that in SPEI(48)H/Taz, also seen at higher magnification, scan size 500 nm (Figures 5.17(a) and (b)). Moreover, the triazole crystallites are uniformly distributed all over the surface at higher sulfonation level.

The phase images of SPEI(62)H/Taz polymer electrolytes with varying triazole concentration (weight percent) are displayed in Figure 5.18. The phase images have crystal domains brighter in color within relatively darker color matrix; the size of the domains increases with increasing triazole content. In SPEI(62)H/Taz 70/30 and 60/40 compositions, the domains have circular cross-section while in SPEI(62)H/Taz 50/50 composition, two distinct domains are visible – smaller (darker in color) domains are separated from larger (brighter in color) domains. In SPEI(62)H/Taz 90/10 composition, the crystallites have relatively loose structures due to the insufficient amount of triazole. At a higher triazole weight percent, dense domain structures are evident. In SPEI(62)H/Taz 50/50 (Figure 5.18 (d)), it is also seen that the crystal domains are interconnected.
Figure 5.16 Tapping mode height (left) and three dimensional topographic images (right) of SPEI(X)H/Taz 70/30 (scan size = 5 µm) (a) X=22%, (b) X=48%, (c) X=62%, X refers to degree of sulfonation.
Figure 5.17 Height images of SPEI(X)H/Taz at higher magnification (a) X=48% 70/30 (scan size = 500 nm), (b) X=62% 70/30 (scan size = 500 nm), (c) X=62% 60/40, (scan size = 1 µm), X refers to degree of sulfonation.
Figure 5.18 Phase images of SPEI(62)H/Taz at various triazole concentrations in weight percent (scan size = 5 µm) (a) 10%, (b) 30%, (c) 40%, (d) 50%.
The sulfonic acid groups were the nucleation sites for triazole crystallization in SPEI matrix. The driving force was the specific interactions between triazole and sulfonic acid and the uniform distribution of acidic groups resulted in homogeneous dispersion of the crystallites. The circular cross-section of the crystal domain due to the uniform radial growth was a function of number of sulfonic acid groups participating in each domain (i.e., degree of sulfonation) and triazole concentration, since the circular domains were not observed at lower sulfonation level or higher triazole concentration such as in SPEI(48)H/Taz 70/30 or SPEI(62)H/Taz 50/50 and evident only in SPEI(62)H/Taz 70/30 and 60/40 compositions. With increasing sulfonation level, the increased number of nucleation sites caused crystal size reduction at a given triazole concentration. The triazole molecules at a lower degree of sulfonation were not intimately bound to polymer chains thus produced roughness on the surface. The solvation of triazole by SPEI and hence size reduction caused the melting point depression of triazole. The onset of melting of these smaller size crystals was close to room temperature. The softening of crystal domains was probably responsible for the contrast reversal in three-dimensional topographic images, as the hills collapsed into valleys (Figure 5.16). In most cases, the strongly bound triazoles were surrounded by the weakly bound molecules, resulting in contrast variation within each domain. In SPEI(62)H/Taz 50/50 composition, these states of triazole were distinguished as evident from two distinct crystal domains in phase image (Figure 5.18(d)), two melting transitions and splitting of absorption bands in FTIR spectra. A similar concept of controlled crystallization of a small inorganic molecule in host polymer matrix has been exploited in previous studies on biomineralization process. Lin et al. reported strong binding of cadmium sulfide to ether oxygen atoms of
polyethylene oxide (PEO) induced nucleation and resulted crystals of uniform size and morphology. The sulfonic acid induced crystal morphology of triazole played a significant role in regulating proton transport in SPEI/Taz solid polymer electrolytes.

5.4 Thermal properties

The thermal stability of SPEI(X)H/Taz 70/30 was studied by thermogravimetric analysis, varying degree of sulfonation, X and depicted in Figure 5.19. DMAC cast pure triazole shows evidence of evaporation above 150°C. The evaporation of triazole from SPEI(X)H matrix appears to be slower, the difference is clearly seen between 22 and 62% sulfonation level. Thus the noncovalent bonding of triazole to the sulfonic acid sites probably prevented evaporation of the heterocycle from SPEI matrix to a certain temperature.

5.5 Anhydrous state proton conductivity

Complex impedance analysis for pure triazole and SPEI(X)H/Taz polymer electrolytes at various sulfonation levels was performed and illustrated in Figures 5.20 – 5.23. The Cole-Cole plots highlight a portion of the impedance spectrum in the frequency range from 100 Hz to 100 kHz, where the frequency increases from right to left. $R_b$, the bulk resistance, and $C_b$, the bulk capacitance, represent the polarization of the immobile
Figure 5.19 TGA thermograms of SPEI(X)H/Taz 70/30 at various sulfonation levels.
Figure 5.20 Complex impedance plots of triazole at different temperatures.
Figure 5.21 Complex impedance plots of SPEI(22)H/Taz at different temperatures. The open, grey filled, and solid symbols represent 90/10, 70/30, and 50/50 compositions respectively. The symbols representing different temperatures are shown only in the first plot.
Figure 5.22 Complex impedance plots of SPEI(48)H/Taz at different temperatures. The open, grey filled, and solid symbols represent 90/10, 70/30, and 50/50 compositions respectively. The symbols representing different temperatures are shown only in the first plot.
Figure 5.23 Complex impedance plots of SPEI(62)H/Taz at different temperatures. The open, grey filled, cross hair, and solid symbols represent 90/10, 70/30, 60/40, and 50/50 compositions respectively. The symbols representing different temperatures are shown only in the first plot.
polymer chains and migration of ions respectively. At high frequency, the semicircular arc is mostly associated with the bulk properties of the polymer electrolytes, $R_b$ and $C_b$ while at low frequencies, $C_b$ becomes negligible, the vertical spike displaced at a distance $R_b$ along the real axis is obtained and is due to the contribution of $R_b$. In this case the bulk resistance, $R_b$ of polymer electrolyte was taken as the value of $Z'$ at the intersection of the semicircle and spike or the starting point of the spike where only vertical spikes were observed. The frequency range over which either the semicircle or the slanted line segment (vertical spike) is seen depends on the conductivity of the material. For example semicircle and arc to spike transition region are mostly observed with pure triazole or SPEI(22)H/Taz (Figures 5.20 and 5.21); however, at a higher degree of sulfonation such as in SPEI(62)H/Taz, the transition regions and mainly the spikes are visible over the entire temperature range (Figure 5.23). The semicircle to spike transition point shifts to lower resistance and higher frequency for each sample with increasing temperature.

Figure 5.24 describes the plots of proton conductivity against triazole concentration in weight percent (Figure 5.24(a)), and $\lambda$, defined as number of moles of triazole per mole of sulfonic acid group ($n_{Taz}/n_{SO3H}$) (Figure 5.24(b)) at various degrees of sulfonation. The conductivity values are also summarized in Table 5.2. At a given sulfonation level, upon increasing weight percent, conductivity increases up to 30-40 wt% triazole, beyond which it falls. This can be attributed to the fact that above a certain weight percent of triazole content, the behavior of polymer electrolyte approached the properties of bulk triazole for which significant conductivity is obtained only above its melting point (~$120^\circ$C). It is also apparent that the conductivity increases with the degree of sulfonation at a constant triazole weight percent and $\lambda$. This behavior can be explained in terms of
Figure 5.24 Proton conductivity at 30°C in SPEI(X)H/Taz polymer electrolytes at various degrees of sulfonation (a) conductivity against triazole weight percent, (b) conductivity against $\lambda$. 
relative ratio of sulfonic acid bound triazole to free triazole; the increase in the ratio resulted significant rise in conductivity at 30°C.

The proton conductivity of SPEI(X)H/Taz shows Arrhenius-type temperature dependence. A linear least square fit to the data is presented in Figure 5.25. As the glass transition temperature of SPEI was higher than the temperature employed in the measurement, large-scale segmental mobility was hindered, proton transport occurred in the triazole phase, and the polymer chains did not participate in conduction. The conductivity vs triazole concentration (weight percent) at different temperatures, shown in Figure 5.26, exhibits a remarkable conductivity increase at ~60°C in SPEI(62)H/Taz while the conductivity increase takes place at ~80°C in SPEI(22)H/Taz. This can be correlated to the melting temperature depression of triazole crystals in SPEI at these sulfonation levels.

The proton conductivity in proton solvents such as water or heterocycles arises from the contribution of two mechanistic pathways, as reported by a few researchers 10,12,59; (i) structure diffusion (Grotthuss-type mechanism) involving intermolecular proton transfer within the ‘structure’ (i.e., hydrogen bonded network formed by solvent molecules) through hydrogen bond breaking and formation, (ii) vehicular diffusion involving long-range diffusion of the protonated solvent molecules. Figure 5.27(a) shows the random distribution of sulfonic acid groups in SPEI matrix. The crystallization of triazole at these acidic sites and the interconnected crystal domains at higher triazole concentration are depicted in Figure 5.27(b) and (c) respectively. The spectroscopic study, described in the previous section demonstrated acid-base interaction between sulfonic acid and triazole molecule. WAXD and AFM analysis revealed gradual reduction of triazole crystal size.
Figure 5.25 Temperature dependent proton conductivity of SPEI(X)H/Taz polymer electrolytes.
Figure 5.26 Proton conductivity as a function of triazole concentration in SPEI(X)H/Taz polymer electrolytes at different temperatures. The open and solid symbols represent 22 and 62% sulfonation level respectively.
and their uniform distribution throughout the polymer matrix with increasing sulfonation level. The reduction in size caused the melting point depression of triazole crystals. Within each crystal domain, a certain fraction of triazole molecules was strongly bound to the sulfonic acid binding sites. Those remaining were weakly bound or self associated free triazole, shown by an arrow from Figure 5.27(b). The anticipated mechanistic pathway of anhydrous state proton conduction in SPEI(X)H/Taz polymer electrolytes can be explained as follows: proton conduction occurred in the triazole phase (proton solvent) and the immobile sulfonic acid played the role of proton donor. The excess proton originating from immobile sulfonic acid groups of SPEI caused protonation of the triazole ring (triazolium ion formation). The neutral and protonated triazole molecules formed hydrogen bonded network or ‘structure’, and intermolecular proton transfer within the structure occurred through hydrogen bond breaking and formation similar to that in water\textsuperscript{10}; structure diffusion is shown at the bottom of Figure 5.27. As the onset of melting of the smaller size triazole crystals in SPEI matrix was close to room temperature at a higher degree of sulfonation (62%), the improved molecular mobility further increased the rate of structure diffusion far below the melting temperature of pure triazole. The concentration of triazolium ions increased with increasing sulfonation level. Comparing the 70/30 composition of SPEI(62)H/Taz and SPEI(22)H/Taz, conductivity in the former is higher by a factor of about 10 at 30\degree C, reflecting the role of triazolium ions as a source of charge carriers. The proton self-diffusion coefficient in 1H-1,2,4 triazole/C\textsubscript{12}PhSO\textsubscript{3}H with 9 mol% acid concentration was 2.0x10\textsuperscript{-10} m\textsuperscript{2}/s, one-fourth of the conductivity diffusion coefficient (7.2x 10\textsuperscript{-10} m\textsuperscript{2}/s), implying the major contribution of structure diffusion to proton transport in presence of an acid\textsuperscript{130}. The results obtained in
Figure 5.27 Schematic illustration of the morphology evolution of triazole crystals in sulfonated polyetherimide matrix (a) random distribution of sulfonic acid groups in SPEI, (b) crystallization of triazole at sulfonic acid sites, (c) interconnected triazole crystal domains. Intermolecular proton transfer between protonated and unprotonated triazole molecules through hydrogen bonded network in SPEI(X)H/1,2,4-triazole matrix (structure diffusion) shown by an arrow at the bottom.
the present study are in close analogy to that reported by Goward et al. on the basis of solid state NMR \(^{143}\). The mobile NH protons involved in weak hydrogen bonds contributed significantly to structure diffusion. Schuster et al. proposed structure diffusion as the dominant conduction mechanism in proton conducting immobilized heterocycles \(^{66}\). Proton transport was found to occur within the crystal aggregates formed by the imidazole units through hydrogen bonding. Thus it can be concluded that below the melting temperature of pure triazole, the proton conductivity was mainly due to the contribution of structure diffusion and occurred effectively within the smaller crystal domains of triazole in SPEI matrix due to the improved molecular mobility. However, as triazole crystals were melted, high mobility of the triazolium ions (\(\mu\)), in addition to structure diffusion, contributed to proton conductivity (vehicle diffusion). This explains the significant rise in conductivity of SPEI(X)H/Taz across the melting temperature range- for SPEI(62)H/Taz the improvement was at \(~60^\circ\)C compared to \(~80^\circ\)C in SPEI(22)H/Taz. 1H-1,2,4 triazole exists in two tautomeric forms at room temperature, and the tautomerization occurs through intra- and intermolecular hydrogen bonding \(^{136}\). The proton transfer within the tautomers of triazole and triazolium ion might also have contributed to the proton conductivity of the solid polymer electrolytes.

5.6 Conclusions

In this study, novel anhydrous proton conducting solid polymer electrolytes (SPEs) were prepared by incorporation of 1H-1,2,4-triazole (Taz) in SPEI matrix. The influence of crystal morphology of 1,2,4 triazole (Taz) as a solid proton solvent dispersed in
sulfonated polyetherimide (SPEI) matrix on anhydrous state proton conductivity was investigated. FTIR spectroscopy and DSC analysis revealed specific interactions between immobilized sulfonic acid groups and triazole molecules. The effect of interactions on size, shape and state of dispersion of triazole crystals were analyzed as a function of degree of sulfonation and triazole concentration (weight percent). The sulfonic acid groups offered strong binding sites and induced nucleation of triazole crystals. WAXD and AFM study showed gradual reduction in crystal size and their uniform distribution throughout SPEI with increasing sulfonation level. The decrease in size caused melting point depression of triazole. Thus the molecular mobility in some of these smaller size crystals improved below the melting temperature of pure triazole. Within each crystal domain, two different states of triazole molecules were evident; strongly bound and weakly bound/self associated free triazole and intermolecular proton transfer occurred through the hydrogen bonded structure formed by these triazole molecules (structure diffusion).
6.1 Lithium salt of sulfonated polysulfone (SPSU-Li)/polyether epoxy (PEGDGE) – single lithium ion conducting polymer electrolytes

Few studies have addressed the use of sulfonated polymers such as poly(lithium-4-styrene sulfonate)\textsuperscript{41}, poly(lithium 2 acrylamido-2-methyl propane sulfonate)\textsuperscript{43} in developing single ion conducting SPE. The conductivity of these materials is low and improves significantly in the presence of a plasticizer\textsuperscript{46}.

6.1.1 Introduction

In this section, methodology to synthesize a novel category of single ion conducting solid polymer electrolytes (SPEs) based on lithium salt of sulfonated polysulfone (SPSU(X)Li) and polyether epoxy, poly(ethylene glycol)diglycidyl ether (PEGDGE) crosslinked by 4,4’ diaminodiphenyl sulfone (DDS) is described. The sulfonate ion promoted compatibility of SPSU(X)Li and PEGDGE was examined as a function of sulfonation level and SPE composition. The morphology, ionic conductivity, thermal, and tensile properties were investigated and correlated with the compatibilization process.
6.1.2 Characterization of lithium salts of sulfonated poly(arylene ethers)

Lithium ion exchange of SPEI and SPSU was conducted following the method described in section 3.2.2. The method was not successful with SPEI due to the hydrolysis of imide ring. $^1$H NMR and FTIR spectra of SPEI(62)H, before and after lithium hydroxide treatment are compared in Figure 6.1(a) and 6.1(b). Significant modification of the peaks in the aromatic region is observed in $^1$H NMR spectrum (Figure 6.1(a)). The appearance of two broad peaks at 13.54 and 14.14 ppm for LiOH soaked SPEI, can be attributed to NH protons of amide. In the FTIR spectrum of SPEI(62)H after LiOH treatment (Figure 6.1(b)), the broad bands at 1560 and 1660 cm$^{-1}$ correspond to stretching of amide carbonyl groups appear and the carbonyl stretching peaks of imide also show marked decrease in intensity. Thus, the spectroscopic analysis provides proof of hydrolysis of imide ring initiated through the nucleophilic attack at two asymmetric carbonyls leading to the formation of two different amides.

Figure 6.2 displays FTIR spectra of polysulfone (PSU) and lithium salts of sulfonated polysulfone, SPSU(X)Li with three different degrees of sulfonation, 23, 40 and 76%. The prominent absorption peaks at 1028 and 1093 cm$^{-1}$ corresponding to sulfonate symmetric stretching can be seen, the band intensity increases with increasing sulfonation level.

Comparing SPSU(76)Li and SPSU(76)H (shown in Figure 6.2), extensive hydrogen bond formation in SPSU(76)H shows a broad absorption band at 1028 cm$^{-1}$, overlaps with the diphenyl ether stretching vibration at 1014 cm$^{-1}$, while in SPSU(76)Li,
Figure 6.1 Spectra of SPEI(62)H before and after LiOH treatment (a) $^1$H NMR, (b) FTIR.
Figure 6.1 Spectra of SPEI(62)H before and after LiOH treatment (a) $^1$H NMR, (b) FTIR (continued)
Figure 6.2 FTIR spectra of lithium salt of sulfonated polysulfone, SPSU(X)Li, at various sulfonation levels (X refers to degree of sulfonation).
a prominent well resolved absorption peak at 1028 cm\(^{-1}\) is observed. A slight red shift of sulfone stretching bands at 1325 and 1152 cm\(^{-1}\) takes place in sulfonated polysulfones, indicative of specific interactions between sulfonate and main chain sulfone groups.

6.1.3 Analysis of specific interactions in SPSU(X)Li/PEGDGE polymer electrolytes

In sulfonated polymers, the symmetric stretching of sulfonate group at 1028 cm\(^{-1}\) is very sensitive to the local environment\(^{119}\) and was used to monitor the specific intermolecular interactions between SPSU(X)Li and PEGDGE in this study. The effect of degree of sulfonation on the peak position is depicted in Figure 6.3. The peak maxima exhibits slight blue shift and the width of the band increases with increasing sulfonate group content reflecting a broad distribution of vibration frequencies of sulfonate groups in the presence of PEGDGE. Figure 6.4 depicts FTIR spectra of SPSU(76)Li/PEGDGE system in 900-1200 cm\(^{-1}\) region as a function of epoxy concentration. In all compositions, disappearance of epoxide characteristic band at 912 cm\(^{-1}\) suggests complete curing of PEGDGE network. The following spectral changes can be seen: (a) the peak at 1014 cm\(^{-1}\) attributed to the symmetric stretching of diphenyl ether units, shows a decrease in intensity with decreasing SPSU(76)Li weight percent; and (b) the sulfonate symmetric stretching band located at 1028 cm\(^{-1}\) in all compositions shows a slight red shift.

Thus, the secondary hydroxyl groups generated through DDS crosslinking of PEGDGE were involved in hydrogen bonding with sulfonate groups of SPSU(X)Li. The sulfonate ions hydrogen bonded to hydroxyl groups appear at higher frequency than the non-associated ions, and the hydroxyl associated and non-associated sulfonate bands
Figure 6.3 FTIR spectra showing effect of degree of sulfonation on symmetric stretching of sulfonate in SPSU(X)Li/PEGDGE 71/29 compositions.
Figure 6.4 FTIR spectra of SPSU(X)Li/PEGDGE polymer electrolytes in 900-1200 cm$^{-1}$ stretching region at various PEGDGE concentrations.
overlap, causing peak broadening. The blue shift of sulfonate stretching band with increasing sulfonation level was due to the strengthening of S=O bond of the sulfonate group due to its interaction with hydroxyl groups of PEGDGE. We further analyze the hydroxyl stretching region.

The high frequency deconvoluted FTIR spectra of SPSU(76)Li/PEGDGE systems at various PEGDGE concentration is displayed in Figure 6.5 and 6.6. The bands located at 3490 and 3370 cm\(^{-1}\) were attributed to free and hydrogen bonded hydroxyl groups respectively in crosslinked epoxy network. The intensity of hydroxyl stretching bands increases with increasing PEGDGE concentration. It is also apparent from Figure 6.5 that the peak corresponding to free hydroxyl stretching remains unchanged in SPSU(76)Li/PEGDGE while the hydrogen bonded hydroxyl stretch shifts to a higher wave number, clearly seen in 45/55 and 33/67 compositions with peak broadening. The increase in the width of the band suggests that a certain fraction of hydroxyl groups were involved in hydrogen bonding with sulfonate anions and the blue shift of hydroxyl bands implies stronger sulfonate-hydroxyl ion-dipole interaction in SPSU(76)Li/PEGDGE than the hydroxyl-hydroxyl and/or hydroxyl-ether dipole-dipole interactions in bulk PEGDGE network.

Several studies have investigated the influence of cation complexation on COC and CH\(_2\) absorption bands in polyethylene oxide-salt electrolytes\(^{144,145}\). In this study, analysis of COC asymmetric stretching region (1050-1125 cm\(^{-1}\)) (Figure 6.4) was difficult due to the presence of characteristic bands of SPSU(76)Li in this region. The composition dependency of C-H stretching at 2870 and 2950 cm\(^{-1}\) in SPSU(76)Li/PEGDGE is
illustrated in Figure 6.6. The peak at 2870 and 2950 cm\(^{-1}\) exhibit an increase in intensity with gradual blue shift of the peak at 2870 cm\(^{-1}\) upon increasing PEGDGE content.

Figure 6.5 FTIR spectra of C-H stretching region at various PEGDGE concentrations in SPSU(X)Li/PEGDGE polymer electrolytes.
Figure 6.6 FTIR spectra of O-H stretching region at different PEGDGE concentrations in SPSU(X)Li/PEGDGE polymer electrolytes.
A new peak is visible at ~2925 cm\(^{-1}\) in SPSU(76)Li/PEGDGE 56/44, while at higher epoxy concentration (>44 wt%), it overlaps with the band at 2950 cm\(^{-1}\). It is expected that upon increasing PEGDGE concentration, the ether oxygen atoms (Lewis base) of polyether epoxy were co-ordinated to Li\(^+\) ions of lithium sulfonate groups (Lewis acid-base interaction). This interaction caused strengthening of C-H bond in SPSU(76)Li/PEGDGE than in bulk PEGDGE network.

6.1.4 Morphology

Figure 6.7 displays tapping mode AFM images (topographic (left) and phase image (right)) of SPSU(76)Li/PEGDGE 71/29 compositions at various degrees of sulfonation. The heterogeneous two-phase morphology is observed in all samples. It is noteworthy that the scan size for the samples with 76% sulfonation level is smaller (1.00 µm) than those with 23 and 40% (2.5 µm). The size of the dispersed epoxy phase gradually reduces and the size distribution becomes narrower with increasing degree of sulfonation. The influence of PEGDGE concentration on phase morphology of SPSU(76)Li/PEGDGE are shown in Figures 6.7 and 6.8. The images demonstrate increase in size of the dispersed phase and in SPSU(76)Li/PEGDGE 33/67 composition more "co-continuous" phase morphology is observed as the larger amount of epoxy phase masks the SPSU domains, shown in Figure 6.8(b). It is also apparent that the variation in height was responsible for the phase contrast in the samples. In SPSU(76)Li/PEGDGE 71/29 composition domains have relatively circular cross-sections with average diameter ranging from 40 to 350 nm.
Figure 6.7 Tapping mode height (left) and phase images (right) of SPSU(X)Li/PEGDGE 71/29 (scan size = 5 µm) (a) X=23%, (b) X=40%, (c) X=76%.
Figure 6.8 Tapping mode height (left) and phase images (right) of SPSU(76)Li/PEGDGE (scan size = 5 µm) for two different compositions (a) 56/44, (b) 33/67.
As mentioned earlier, the polar hydroxyl and ether groups present in crosslinked epoxy phase were involved in interaction with sulfonate and Li\(^+\) ions of SPSU(X)Li. The extent of interactions enhanced with increasing sulfonate ion concentration and caused reduction in size of the dispersed epoxy phase. The wide distribution of domain size in SPSU(23)Li/PEGDGE 71/29 and increase in size with PEGDGE concentration also indicate that a certain fraction of polyether epoxy involved in specific interactions with SO\(_3\)Li formed relatively smaller size domains while the remaining free polyether chains that did not participate in interactions with SO\(_3\)Li due to insufficient sulfonate groups formed larger domains in SPSU(X)Li matrix.

The optical clarity also provides an indication of miscibility in polymer blends\(^{146,147}\). Figure 6.9 presents optical clarity of SPSU(X)Li/PEGDGE samples. All SPSU(X)Li/PEGDGE films were transparent except the samples with 23% sulfonation level. This can be attributed to the domain size of epoxy phase in SPSU(X)Li matrix smaller than the wavelength of visible light at higher sulfonation level (40 and 76%). The formation of larger size domains caused loss of clarity in SPSU(23)Li based samples.

6.1.5 Thermal analysis

Thermogravimetric analysis (TGA) was used to study the thermal stability of SPSU(X)Li/PEGDGE systems. The temperatures corresponding to the peak on derivative-weight (\%) vs temperature curve, T\(_d\), are provided in Table 6.1. DDS curing improves the degradation temperature of PEGDGE due to the insertion of diphenyl
sulfone crosslinks in the epoxy network (Figure 6.10). SPSU(X)Li exhibits better thermal stability than the corresponding acid forms, as significant degradation takes place above

Figure 6.9 Optical clarity of SPSU(X)Li/PEGDGE polymer electrolytes (a) X=23% 71/29, (b) X=23% 56/55, (c) X=40% 71/29, (d) X=40% 56/44, (e) X=76% 71/29, (f) X=76% 56/44, (g) X=76% 45/55, (h) X=76% 33/67. In each case the film was kept on a white paper with PE written on it.
460°C compared to 320°C in the respective acid; thermograms for SPSU(76)Li and SPSU(76)H are shown in Figure 6.11. SPEs of SPSU(X)Li/PEGDGE show a two-step degradation. $T_{dI}$ corresponds to the decomposition of crosslinked epoxy network, and $T_{dII}$ is associated with the decomposition of SPSU(X)Li phase, depicted in Figures 6.12-6.14. The degradation temperature of PEGDGE phase improves with increasing degree of sulfonation presented for SPSU(X)Li/PEGDGE 71/29 and 56/44 in Figures 6.12 and 6.13 respectively. The composition dependence of TGA thermograms is described in Figure 6.14. $T_{dI}$ increases with increasing PEGDGE weight percent, while $T_{dII}$ reduces with increasing epoxy concentration. This behavior can be explained in terms of stronger ion-dipole interactions between PEGDGE and SO$_3$Li groups compared to the dipole-

### Table 6.1 Thermal degradation of SPSU(X)Li/PEGDGE polymer electrolytes

<table>
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<th>Sample Designation</th>
<th>Thermal degradation(°C)</th>
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<td>$T_{dI}$</td>
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<td></td>
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<tr>
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<tr>
<td>SPSU(76)Li/PEGDGE 33/67</td>
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<td>PEGDGE (DDS crosslinked)</td>
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Figure 6.10 TGA thermograms showing effect of DDS crosslinking on thermal degradation of polyether epoxy, PEGDGE.
Figure 6.11 TGA thermograms of lithium salt of sulfonated polysulfones, SPSU(X)Li, at various sulfonation levels, X.
Figure 6.12 Effect of degree of sulfonation on thermal degradation in SPSU(X)Li/PEGDGE 71/29 polymer electrolytes.
Figure 6.13 Effect of degree of sulfonation on thermal degradation in SPSU(X)Li/PEGDGE 56/44 polymer electrolytes.
dipole interactions in the pure epoxy network. The physical crosslinks formed through ion-dipole interactions in PEGDGE improved the thermal stability of the epoxy phase.

Figure 6.15 displays the DSC thermograms of SPSU(X)Li at various degrees of sulfonation. $T_g$ of lithium salt of sulfonated polysulfone gradually increases and broadens with increasing sulfonation level. The specific interactions between lithium sulfonate groups caused immobilization of polymer chains, resulting in an increase in $T_g$. SO$_3$Li groups are randomly located along the polymer chains, and each individual chain does not have the same number of sulfonate groups. Thus, sulfonated polysulfone chains at higher sulfonation levels undergo relaxation at different temperatures. The wide distribution of relaxation temperatures was responsible for the broadening of glass transition.

The thermal transitions of SPSU(X)Li/PEGDGE systems are illustrated in Figure 6.16. A transition in the temperature range 0-100°C is evident in all samples; the inflection point shifts to a lower temperature with increasing PEGDGE concentration. The transition is broad in SPSU(X)Li/PEGDGE compared to the bulk epoxy network and the width, $\Delta T_g$ decreases upon increasing PEGDGE content. Thus, the observed transition is attributed to the $T_g$ of PEGDGE network. The width of a transition is defined as the difference between onset and end point of the transition and corresponds to the relaxation temperature distribution of the polymer chains. The complexed polyether chains in SPSU(X)Li matrix formed through ion-dipole interactions between SO$_3$Li and PEGDGE underwent relaxation at a higher temperature than free polyether segments and the wide distribution of relaxation temperatures caused broad thermal transition. With
increasing PEGDGE concentration, the larger number of free polyether chains caused \( T_g \) of the epoxy phase shift towards that of bulk network simultaneously reduced the relaxation temperature distribution.

Figure 6.14 TGA thermograms of SPSU(76)Li/PEGDGE at different PEGDGE concentrations in weight percent.

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Figure 6.14 TGA thermograms of SPSU(76)Li/PEGDGE at different PEGDGE concentrations in weight percent.
Figure 6.15 DSC traces of lithium salt of sulfonated polysulfones, SPSU(X)Li at various sulfonation levels, X.
Figure 6.16 DSC traces of SPSU(X)Li/PEGDGE polymer electrolytes.
Two thermal transitions are observed in SPSU(X)Li/PEGDGE 71/29. The unaffected inflection in the same temperature range as in SPSU(23)Li (T_g ~ 202.6 °C) was due to the SPSU phase that did not participate in specific interactions with PEGDGE because of the low sulfonate ion concentration. The larger size domains of the dispersed epoxy phase observed in AFM images (Figure 6.7a) were probably formed by the free polyether chains in SPSU(X)Li matrix. ∆T_g can be correlated to distribution of the domain size since the broad transition is observed for SPSU(23)Li/PEGDGE 71/29, the sample with wide domain size distribution. The thermal transition associated with the T_g of SPSU(76)Li phase was not detected in SPSU(76)Li/PEGDGE at higher PEGDGE concentration probably due to the broad transition in sulfonated polysulfones at higher sulfonation levels (Figure 6-15) and dilution effect.

6.1.6 Ionic conductivity

The complex impedance plots for SPSU(X)Li/PEGDGE polymer electrolytes are shown in Figures 6.17 and 6.18. In the 100 Hz to 100 KHz frequency range, whether a semicircle or vertical spike will be visible depends on the conductivity of the SPE. Cole-cole plots depict a semicircle at lower degrees of sulfonation (i.e., X=23 and 40%) for SPSU(X)Li/PEGDGE 71/29 and 56/44 compositions and the pattern shifts to lower Z’ value with increasing temperature. For SPSU(76)Li/PEGDGE, semicircle and mostly arc to spike transition regions are observed with similar shift upon increasing temperature. The lithium ion conductivity values are compiled in Table 6.2. The variation in ionic
Figure 6.17 Complex impedance plots of SPSU(23)Li/PEGDGE and SPSU(40)Li/PEGDGE 71/29 and 56/44 compositions at different temperatures. The open, grey filled, cross hair, and solid symbols represent SPSU(23)Li/PEGDGE 71/29, SPSU(23)Li/PEGDGE 56/44, SPSU(40)Li/PEGDGE 71/29, and SPSU(40)Li/PEGDGE 56/44 respectively. The symbols representing different temperatures are shown only in the first plot.
Figure 6.18  Complex impedance plots of SPSU(76)Li/PEGDGE at different temperatures. The open, grey filled, cross hair, and solid symbols represent 71/29, 56/44, 45/55, and 33/67 respectively. The symbols representing different temperatures are shown only in the first plot.
Table 6.2 Ionic conductivity of Li⁺ conducting solid polymer electrolytes

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conductivity ($\sigma$) with temperature was studied as a function of degree of sulfonation and PEGDGE content (Figure 6.19). At a given PEGDGE concentration (44 wt%),

![Figure 6.19 Temperature dependent ionic conductivity of SPSU(X)Li/PEGDGE polymer electrolytes.](image)

Figure 6.19 Temperature dependent ionic conductivity of SPSU(X)Li/PEGDGE polymer electrolytes.
conductivity improves significantly with increasing sulfonation level. Figure 6.19 also displays the influence of PEGDGE concentration on temperature dependent conductivity of SPSU(76)Li/PEGDGE. At a lower temperature (~30°C), there is little variation in conductivity with composition except in SPSU(76)Li/PEGDGE 33/67. At a high temperature the difference is prominent, and σ increases with SPSU(76)Li weight percent. Figures 6.20(a) and (b) show random distribution of lithium sulfonate (SO$_3$Li) groups in SPSU(X)Li matrix and phase separation in SPSU(X)Li/PEGDGE polymer electrolyte at intermediate PEGDGE concentration respectively. Li$^+$ ion conduction mechanism within each domain is shown by an arrow. The transport of Li$^+$ ions occurred in PEGDGE phase and SPSU(X)Li acted as Li$^+$ ion donor. The concentration of charge carriers and segmental mobility of polyether chains are the two major factors influencing ionic conductivity. SO$_3$Li groups were mainly located at the interface due to the ion-dipole interactions with polyether epoxy which also caused dissociation of the polymeric lithium salt. The solvated free Li$^+$ ions were the major contributors to conductivity. At a lower temperature (~30°C), the conductivity was high in SPSU(76)Li/PEGDGE 33/67 composition since its glass transition temperature was below room temperature. The lower charge carrier concentration in the system due to low salt content was compensated by the larger free volume available for segmental motion (low T$_g$). At a higher temperature (>120°C), conductivity improved with increasing Li$^+$ ion concentration as the difference between segmental mobility was less pronounced beyond the glass transition temperature of the matrix. At 160°C, σ reached the value of $10^{-4}$ S/cm in SPSU(76)Li/PEGDGE 71/29. It is also seen in Figure 6.19 that the Arrhenius plots
Figure 6.20 Schematic representation of phase separation in SPSU(X)Li/PEGDGE polymer electrolytes (a) random distribution of lithium sulfonate in SPSU(X)Li matrix, (b) morphology of SPSU(X)Li/PEGDGE at intermediate PEGDGE concentration. Lithium ion conduction mechanism within the dispersed epoxy phase is shown by an arrow.
deviate from linearity at high temperature implying ionic conductivity coupled with the segmental motion of polyether chains occurred above $T_g$ of SPEs. Less deviation from linearity for SPSU(76)Li/PEGDGE 33/67 at higher temperature indicates that segmental mobility varied slightly with temperature in the sample.

6.1.7 Tensile properties

Figure 6.21 shows the stress-strain plots for SPSU(X)Li/PEGDGE. The tensile properties are summarized in Table 6.3. Neat SPSU(X)Li used in this study exhibited less than 40% elongation at break, with Young’s modulus ranging 1350-1725 MPa and tensile strength about 37-56 MPa with the gradual reduction of strength and modulus with increasing sulfonation level. We attempted to measure the tensile properties of DDS cured PEGDGE, but these materials failed at the grip. It is seen in Figure 6.21 that the presence of crosslinked epoxy phase in SPSU(X)Li matrix shows a significant improvement in elongation at break while deteriorating the tensile strength and modulus. Thus, the crosslinking of PEGDGE in SPSU(76)Li/PEGDGE caused brittle to ductile transformation of the system. The behavior can be correlated with the increase in size of PEGDGE phase in SPSU(76)Li/PEGDGE with increasing epoxy concentration (Figures 6.7 and 6.8); beyond 55 wt% epoxy content, the behavior approaches the properties of bulk epoxy network and the elongation at break declined.

The effect of sulfonation level on tensile properties for SPSU(X)Li/PEGDGE 71/29 and 56/44 compositions indicates that elongation at break improves with increasing
sulfonate concentration. With increasing degree of sulfonation, the specific interactions between SPSU(X)Li and polyether epoxy became predominant. Lithium sulfonate

![Stress-strain plots of SPSU(X)Li/PEGDGE polymer electrolytes.](image)

Figure 6.21 Stress-strain plots of SPSU(X)Li/PEGDGE polymer electrolytes.
Table 6.3 Tensile properties of SPSU(X)Li/PEGDGE polymer electrolytes

<table>
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promoted compatibility of the two components in SPSU(X)Li/PEGDGE resulted in reduction of dispersed phase size and better interfacial adhesion which in turn caused improvement in elongation at break. The composition with 55 wt% epoxy in SPSU(76)Li/PEGDGE 45/55 shows a better result than 67 wt%. It may be due to the fact that 55 wt% epoxy saturated almost all the sulfonate ion exchange sites located at the interface between SPSU(76)Li and PEGDGE phases causing maximum property enhancement; beyond this point the tensile property deteriorated. Su et al.\textsuperscript{148,149} described the role of hydroxyl functional groups in promoting in-situ compatibilization between hydroxyl functionalized polystyrene (PS) and polybutylene terephthalate (PBT). In the reactive PA/PSU blends, Weber et al. reported that in situ formation of polysulfone (PSU)- polyamide (PA) copolymer upon addition of phthalic anhydride terminated PSU was responsible for particle size reduction of PA dispersed phase and caused significant improvement in toughness\textsuperscript{150}. 

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6.1.8 Conclusions

Lithium salts of sulfonated polysulfone (SPSU(X)Li) at three different sulfonation levels were synthesized by post sulfonation route using trimethylsilyl chlorosulfonate followed by ion exchange process. The sulfonation reaction at the activated bisphenol A moiety was confirmed from $^1$H NMR spectra. Solvent free single ion conducting solid polymer electrolytes (SPEs) were prepared by crosslinking a polyether epoxy, poly(ethylene glycol)diglycidyl ether (PEGDGE) by 4,4’ diaminodiphenyl sulfone (DDS) in SPSU(X)Li matrix. DSC analysis revealed compatibilization of SPSU(X)Li and PEGDGE attributed to the specific interactions between SO$_3$Li of SPSU(X)Li and ether and hydroxyl groups of epoxy. These interactions improved the thermal stability of the PEGDGE phase in the sulfonated polymer matrix compared to the bulk epoxy network. The enhanced compatibilization with increasing degree of sulfonation of SPSU(X)Li caused size reduction of the dispersed epoxy phase and resulted in improvement of elongation at break. The Arrhenius plots for the temperature dependent ionic conductivity of SPEs showed deviation from linearity at high temperatures, indicative of ionic conductivity assisted by segmental mobility of the polymer chains above the glass transition temperature. The ionic conductivity reached the value of $\sim 10^{-4}$ S/cm for SPSU(76)Li/PEGDGE 71/29 at 160$^\circ$C, which is effective for applications in electrochemical devices operating at high temperature.
6.2 Lithium bis(trifluoromethanesulfonyle)imide (LiTFSI) salt doped SPSU(76)Li/PEGDGE system – dual ion conducting polymer electrolytes

The characterization of polymeric lithium salt (SPSU(X)Li) and polyether epoxy, PEGDGE system, provides fundamental understanding of the impact of lithium ion concentration versus flexible host polymer matrix in regulating ion transport behavior. However, these solid polymer electrolytes have not achieved high enough ionic conductivity desired for practical applications. Lithium bis(trifluoromethanesulfonyle)imide (LiTFSI) was recognized as a potential electrolyte salt due to its high degree of dissociation and excellent electrochemical properties. In our laboratory, SPEs based on polyurethane/polyether modified polysiloxane blends were developed and investigated. The polymer electrolytes with LiTFSI showed promising results.

6.2.1 Introduction

In this section, SPSU(76)Li/PEGDGE 33/67 was further doped with LiTFSI. The morphology, thermal behavior, and ionic conductivity were investigated as a function of doping level. FTIR spectroscopy was utilized to explore the intermolecular interactions responsible for the solvation of LiTFSI salt in PEGDGE matrix.

6.2.2 Characterization of intermolecular interactions in PEGDGE (uncrosslinked)/LiTFSI

Figures 6.22 - 6.25 show FTIR spectra of PEGDGE(uncrosslinked)/LiTFSI at various salt concentrations. The characteristic absorption bands of PEGDGE at 1090 and 2890
cm\(^{-1}\) assigned to C-O and CH\(_2\) stretching, respectively, were analyzed to understand the state of polymer-salt complex formation. As shown in Figure 6.22, the C-O absorption
Figure 6.23 FTIR spectra showing effect of salt concentration on C-H stretching in liquid PEGDGE/LiTFSI polymer electrolytes.
Figure 6.24 FTIR spectra of sulfone stretching at 1350 cm$^{-1}$ in PEGDGE/LiTFSI polymer electrolyte at various salt concentrations.
Figure 6.25 FTIR spectra showing effect of salt concentration on sulfone stretching (700-810 cm$^{-1}$) in PEGDGE (uncrosslinked)/LiTFSI polymer electrolytes.
peak progressively broadens and shifts to a lower wavenumber with increasing salt concentration. As expected, the intensity of the peak decreases with increasing salt content due to dilution effect. It is also apparent in Figure 6.23 that the CH$_2$ absorption band exhibits a blue shift with increasing [O]/[Li$^+$] ratio and a new peak gradually appears at 2930 cm$^{-1}$ prominent at [O]/[Li$^+$] = 6. A similar shift of COC and CH$_2$ stretching in polyethylene oxide-salt electrolytes has been reported in a few previous studies.$^{144,145}$

Numerous studies have utilized FTIR spectroscopy to identify the ‘free’ ions (fully dissociated/solvated ion pairs) and contact ion pair in solid polymer electrolytes. Figures 6.24 and 6.25 highlight the characteristics bands of TFSI anion, asymmetric stretching of sulfone at 1330 cm$^{-1}$, and symmetric and asymmetric stretching of SNS at 746 and 798 cm$^{-1}$, respectively. The peak maxima in all cases shift to a higher wave number with increasing salt concentration indicating formation of larger amount of contact ion pair at high salt concentration while in dilute solution; at LiTFSI concentration [O]/[Li$^+$] = 18, high concentration of free ions caused red shift of SNS stretching bands. Thus the observed spectral changes of PEGDGE and LiTFSI characteristic bands suggest intermolecular interactions between the salt and ether oxygen of polyether chains (Lewis acid base interaction).

6.2.3 AFM image analysis

Tapping mode AFM images (height (left) and phase (right)) of SPSU(76)Li/PEGDGE/LiTFSI at three different salt concentrations are demonstrated in
Figure 6.26 Tapping mode height (left) and phase images (right) of SPSU(76)Li/PEGDGE/LiTFSI (scan size = 2.5 µm) for different [O]/[Li\(^+\)] (a) 18, (b) 12, (c) 6.
Figure 6.26. After dissolution of salt in PEGDGE phase, there is little variation in contrast within SPSU(76)Li/PEGDGE 33/67 matrix; LiTFSI phase has brighter contrast with respect to the matrix. The contrast variation in phase imaging can be due to topographic changes, deformation at tip-sample contact, experimental conditions and is sensitive to stiffness, viscoelasticity, and chemical composition of the sample surface. In present case, although experimental conditions were kept identical for all samples, it was difficult to distinguish between the factors governing phase image contrast since there were chemical and mechanical heterogeneities in addition to topographic changes. As seen in Figure 6.26, there is significant difference in LiTFSI domain structure with doping level. The polymer electrolytes, at a lower LiTFSI salt concentration, have smaller size domains while at a higher salt concentration ([O]/[Li$^+$] = 6), larger size aggregates are formed. The uniform dispersion of salt in the matrix is seen at intermediate LiTFSI concentration, [O]/[Li$^+$] = 12. Thus, the dissolution of LiTFSI in PEGDGE followed by crosslinking in SPSU(76)Li, exhibited heterogeneous phase morphology in which the domain size increased with increasing salt concentration.

The optical clarity of the samples are shown in Figure 6.27. At a lower salt concentration (i.e., [O]/[Li$^+$] = 12, 18), the films are transparent inspite of the heterogeneous phase morphology and become non uniform and opaque at higher salt content. This behavior was due to the difference between the LiTFSI domain size and wavelength of the visible light. The domains with size smaller than the wave length of visible light formed at low salt concentration caused transparency while the loss of optical clarity was a consequence of the formation of larger size aggregates at higher salt concentration.
Figure 6.27 Optical clarity of SPSU(76)Li/PEGDGE/LiTFSI for different [O]/[Li⁺] (a) 18, (b) 12, (c) 6. In each case the film was kept on a white paper with PE written on it.
6.2.4 Thermal behavior

Figures 6.28 and 6.29 show the thermal degradation behavior of PEGDGE/LiTFSI and LiTFSI salt doped in SPSU(76)Li/PEGDGE 33/67, investigated by thermogravimetric analysis. The degradation temperatures are compiled in Table 6.4. The TG curves of DDS cured PEGDGE with dissolved LiTFSI (Figure 6.28) exhibit a two-step weight loss: the initial step corresponding to the decomposition of PEGDGE network and the final step was due to the weight loss corresponding to LiTFSI. The degradation temperature of PEGDGE phase improves with increasing salt concentration. It is also seen from Table 6.4 that the degradation temperature of epoxy phase increases with the doping level in SPSU(76)Li/PEGDGE/LiTFSI indicative of higher thermal stability of physically crosslinked epoxy phase due to the specific interactions between the host polymer and Li\(^+\) ions, consistent with the result obtained for SPSU(X)Li/PEGDGE system. It should be noted that the degradation temperature of epoxy network formed in presence of polymeric lithium salt, SPSU(X)Li or low molecular weight salt, LiTFSI is lower than that of crosslinked PEGDGE.

The thermal transitions in DDS crosslinked polyether epoxy, PEGDGE doped with various concentration of LiTFSI salt and SPSU(76)Li/PEGDGE/LiTFSI polymer electrolytes are shown in Figure 6.30 and 6.31. An endotherm was observed at \(~14.8^\circ C\) in PEGDGE/LiTFSI and \(15.7^\circ C\) in SPSU(76)/Li/PEGDGE/LiTFSI for \([O]/[Li^+] = 6\) due to the melting or phase transition of LiTFSI as mentioned in the literature \(^{152}\). The enthalpy progressively decreases with decreasing salt concentration. The determination of glass transition temperature of crosslinked PEGDGE in presence of LiTFSI was not possible due to its overlapping with the melting endotherm.
Figure 6.28 TGA thermograms of PEGDGE (DDS crosslinked)/LiTFSI polymer electrolytes at different salt concentrations.
Figure 6.29 TGA thermograms of SPSU(76)Li/PEGDGE 33/67 doped with different concentration of LiTFSI salt.
Figure 6.30 DSC traces of PEGDGE (DDS crosslinking)/LiTFSI polymer electrolytes.
Figure 6.31 DSC traces of SPSU(76)Li/PEGDGE 33/67 doped with different concentration of LiTFSI salt.
Table 6.4 Thermal degradation of SPSU(76)Li/PEGDGE/LiTFSI and PEGDGE/LiTFSI polymer electrolytes

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6.2.5 Ionic conductivity

The complex impedance plots for PEGDGE/LiTFSI and SPSU(76)/PEGDGE/LiTFSI at different temperatures are shown in Figures 6.32 and 6.33. The semicircles are mainly observed at low lithium ion concentration, [O]/[Li$^+$] = 18 and at 60°C in both SPSU(76)Li/PEGDGE/LiTFSI and PEGDGE/LiTFSI systems. The arc to spike transition region is visible with increasing salt concentration and temperature, and at [O]/[Li$^+$] = 6, and at high temperatures mostly vertical spikes are seen. The conductivity data is compiled in Table 6.2. Figure 6.34 compares temperature dependent ionic conductivity of PEGDGE/LiTFSI and SPSU(76)Li/PEGDGE/LiTFSI systems with different salt concentrations. The temperature dependent ionic conductivity of polymer electrolytes
exhibits the Vogel-Tamman-Fulcher (VTF) relationship implying that ion transport was assisted by the segmental motion of polyether chains. It is apparent that the conductivity

Figure 6.32 Complex impedance plots of PEGDGE/LiTFSI polymer electrolytes at different temperatures. The open, grey filled, and symbols with cross-hair represent \([\text{O}]/[\text{Li}^+]\) 6, 12, and 18 respectively. The symbols representing different temperatures are shown only in the first plot.
Figure 6.33 Complex impedance plots of SPSU(76)Li/PEGDGE/LiTFSI at different temperatures. The open, grey filled, and symbols with cross-hair represent [O]/[Li\(^+\)] 6, 12, and 18 respectively. The symbols representing different temperatures are shown only in the first plot.
Figure 6.34 Temperature dependent ionic conductivity of PEGDGE/LiTFSI (filled symbols) and SPSU(76)Li/PEGDGE/LiTFSI (open symbols) polymer electrolytes.
increases monotonically with increasing LiTFSI concentration. Upon doping with ~47 parts of LiTFSI, the conductivity increases 10-230 times depending on the temperature of measurement compared to SPSU(76)Li/PEGDGE 33/67, reaching a value of ~5x10^{-4} S/cm at 140ºC. Figure 6.35 shows ion conduction mechanism in undoped and LiTFSI doped SPSU(76)Li/PEGDGE 33/67. The salt solvation in epoxy matrix was a consequence of the polymer-salt interactions, Li^{+} ions coordinated to the ether oxygen atoms of PEGDGE (Lewis acid-base interaction). The ionic association increased with increasing LiTFSI concentration. The progression from free ions, ion pair to aggregate formation occurred with increasing LiTFSI concentration. Due to the larger size of TFSI anion, LiTFSI ion pair is of same size as the anion and being uncharged has higher mobility in PEGDGE. Moreover, the formation of the ion pair reduced the polyether epoxy-LiTFSI interaction. Thus, the increase in conductivity with salt concentration at 30ºC was due to the increase in concentration of free ions contact ion pairs. Comparison of conductivity data in Table 6.2 shows that at an identical [O]/[Li^{+}] ratio, conductivity is higher in LiTFSI doped SPSU(76)Li/PEGDGE than in undoped samples at almost all temperatures. In the temperature range of 30-80ºC, this was probably due to the contribution of ion pairs and better segmental mobility in the doped SPE compared to the undoped system. At higher temperatures, the difference between segmental mobility in LiTFSI doped and undoped polymer electrolytes was less, thus, the increase was attributed solely to the transport of free ions with major contribution of anions. The low lithium ion transference number of about 0.25 reported for LiTFSI containing polymer electrolyte also reflected higher mobility of TFSI anion in the matrix. 153.
Figure 6.35 Schematic illustration of lithium ion conduction mechanism in LiTFSI doped SPSU(76)Li/PEGDGE 33/67 polymer electrolytes.
6.2.6 Conclusions

In this section, the polyether epoxy phase of SPSU(76)Li/PEGDGE 33/67 was doped with three different concentrations of LiTFSI salt. FTIR analysis revealed specific interactions between polyether epoxy and LiTFSI. The doped samples exhibited heterogeneous phase morphology. The physically crosslinked epoxy phase formed due to PEGDGE-LiTFSI interactions showed higher thermal stability compared to the bulk epoxy network. The conductivity increased 10-230 times depending on the temperature of measurement and LiTFSI concentration compared to SPSU(76)Li/PEGDGE 33/67. The ionic conductivity – temperature plots followed the Vogel-Tamman-Fulcher (VTF) relationship indicating that ionic conductivity assisted by the segmental motion of polyether chains occurred in LiTFSI doped polymer electrolytes.

6.3 Application in electrochemical cell

Of particular interest to us is the fabrication of all polymer electrochemical cell into thin film structure. The present study on the development of proton and lithium ion conducting solid polymer electrolytes (SPEs) is the first step of electrochemical cell construction. We are conducting a joint project in collaboration with Lockheed to study the cyclic properties and electrochemical stabilities of SPEs prior to their application in electrochemical cells. The characterization of electrochemical performance of LiTFSI doped SPSU(76)Li/PEGDGE and PEGDGE/LiTFSI polymer electrolyte-electrode assembly is in progress. The SPEs are expected to exhibit promising results at high temperatures.
CHAPTER VII
SUMMARY

Two different bisphenol A based poly (arylene ethers) (PAEs)- polyetherimide (PEI) and polysulfone (PSU) were sulfonated by post sulfonation route using a silyl ester of chlorosulfonic acid, trimethylsilyl chlorosulfonate (TMSCS). The degree of sulfonation was controlled by varying the mole ratio of the sulfonating agent to the PAE repeat unit and/or the reaction time. The introduction of sulfonic acid group at the activated bisphenol A unit was confirmed by $^1$H NMR spectroscopy. The stronger electron withdrawing imide group caused deactivation of bisphenol A moiety and reduced the sulfonation reaction rate of PEI compared to PSU. The maximum sulfonation level was achieved with 1.5 mole fraction of the sulfonating agent at 30°C with both PEI and PSU. The sulfonated polyarylene ethers (SPAEs) exhibited characteristic three-step degradation. The tensile properties deteriorated with increasing degree of sulfonation. Sulfonation was also conducted with chlorosulfonic acid (CSA). It was found that sulfonation and degradation were competitive with and occurred through the same mechanistic pathway i.e., at the isopropylidene unit with the two different sulfonating agents, CSA and TMSCS. The degradation rate was faster with CSA and also observed at a low acid concentration. Degradation was evident with high sulfonating agent
concentration and/or prolonged reaction time using TMSCS and responsible for obtaining lower degree of sulfonation under these conditions.

Novel anhydrous proton conducting solid polymer electrolytes (SPE s) were prepared based on sulfonated bisphenol-A-polyetherimide (SPEI) and 1H-1,2,4 triazole (Taz) as a solid state proton solvent. The conductivity reached about $5 \times 10^{-5}$ S/cm at $30^\circ$C and $10^{-2}$ S/cm at $140^\circ$C in SPEI(62)H/Taz 60/40, the conductivity value at higher temperature is comparable to that in hydrated Nafion. The temperature dependent proton conductivity of SPEs exhibited Arrhenius behavior implying proton conduction was independent of the polymer chain mobility. The effect of degree of sulfonation and triazole concentration on size, shape, and dispersibility (crystal morphology) of triazole crystals in SPEI matrix were investigated and correlated with proton conduction. FTIR spectroscopy and DSC analysis revealed specific interactions between immobilized sulfonic acid groups of SPEI and triazole molecules. At a constant triazole weight percent, increased sulfonation level caused enhanced nucleation density, reduction in crystallite size, and uniform crystal distribution throughout the sulfonated polymer matrix. The decrease in size caused depression of triazole melting temperature and thus the molecular mobility in smaller size crystals improved below the melting temperature of pure triazole. Within each crystal domain, two different degrees of association between triazole and sulfonic acid were evident: strongly bound and weakly bound /self-associated free triazole. It was proposed that intermolecular proton transfer within the smaller size crystals was assisted by the improved molecular mobility and occurred through the hydrogen bonded structure formed by these triazole molecules (structure diffusion).
Another new class of single lithium ion conducting solid polymer electrolytes (SPEs) was prepared by crosslinking poly(ethylene glycol)diglicidyl ether (PEGDGE) with 4,4’ diaminodiphenylsulfone (DDS) in sulfonated polysulfone, SPSU(X)Li matrix. The ionic conductivity, thermal stability, and tensile properties were investigated as a function of sulfonation level and PEGDGE concentration. The size of the dispersed epoxy phase decreased with increasing degree of sulfonation in SPSU(X)Li/PEGDGE 71/29. The ion-dipole interactions between lithium sulfonate (SO\textsubscript{3}Li) of SPSU and hydroxyl group generated during crosslinking and ether oxygen of PEGDGE exhibited improved thermal stability compared to the bulk epoxy network. Lithium sulfonate promoted compatibilization also caused improvement in elongation at break of SPEs as compared to SPSU(X)Li. The ionic conductivity reached $\sim 10^{-4}$ S/cm for SPSU(76)Li/PEGDGE 71/29 at 160ºC. The temperature dependent ionic conductivity exhibited deviation from Arrhenius behavior at high temperature. The epoxy phase in SPSU(76)Li/PEGDGE 33/67 was further doped with a low molecular weight electrolyte salt, LiTFSI. The ionic conductivity was 230 times higher in the doped SPE with $[O]/[\text{Li}^+] = 6$ compared to the undoped system, attributed to the contribution of TFSI anions particularly at higher temperature. The ionic conductivity followed VTF type temperature dependence indicative of ion transport assisted by the segmental motion of polyether chains. The characterization of cyclic properties and electrochemical performance of SPEs are in progress.
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