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POLYAMINE BASED POLYMER ELECTROLYTE
MODIFICATION AND PERFORMANCE

A Dissertation

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degree of

Doctor of Philosophy

By

LIEYU HU
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POLYAMINE BASED POLYMER ELECTROLYTES
MODIFICATION AND PERFORMANCE

A Dissertation APPROVED FOR THE
DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY

BY

Daniel T. Glatzhofer

Roger Frech

Kenneth Nicholas

Ralph Wheeler

John Furneaux

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ABSTRACT

Relatively unexplored polyamine-based polymer electrolytes are being studied as key components in next generation power sources: high energy density and light weight solid state polymer batteries. Understanding the relationship between backbone modification and the resulting property changes of the polyamine-based polymer electrolytes is the focus of the first part of this dissertation. Linear poly(propyleneimine) (LPPI) was synthesized. LPPI were spectroscopically compared with linear poly(ethyleneimine) (LPEI) as a polymer electrolyte host for lithium trifluoromethanesulfonate (LiTf). Infrared spectroscopy (IR) reveals that the ionic association state of LPPI/LiTf is independent of salt concentration, while that of LPEI/LiTf shifts with salt concentration. Differential Scanning Calorimetry (DSC) shows a decrease of crystalline melting endotherms with increasing LiTf concentration in both systems. However, LPPI/LiTf has a relatively constant T_g with changing LiTf concentration, while that of LPEI/LiTf is LiTf concentration dependent. These observations show that both LPPI and LPEI are disrupted into crystalline and amorphous phases upon the addition of salt. However, the amorphous phase of LPPI/LiTf has a relatively constant composition while that of LPEI/LiTf is constantly changing. Consistent with these observations, LPPI/LiTf and LPEI/LiTf have different temperature-dependent ionic conductivity behaviors although they are of similar magnitude, up to 10^{-7} S/cm at room temperature and $10^{-3.5}$ S/cm at 70 °C. Linear poly(N-methylpropylenimine) (LPMPI) was synthesized from LPPI and was compared to linear poly(N-methylethylenimine) (LPMEI). Research on LPMPI polymer electrolytes is ongoing.

A viable method for forming neutrally cross-linked solid polymer electrolytes (SPE) by synthetically combining both conductivity enhancing functionality and crosslink-enabling

functionality on a polyamine backbone was established. In order to find an appropriate crosslinking functionality, inexpensive branched poly(N-allylethylenimine) (BPAEI) was synthesized from commercially available branched PEI. BPAEI was cross-linked using 2,2-azobis(2-amidinopropane) dihydrochloride (V-50) as radical initiator in the presence of LiTf to form a rubber-like SPE. Although IR shows most Tf⁻ ions stay as ‘free’ ions, the overall conductivity is poor due to a loss of polymer flexibility upon crosslinking as indicated by DSC. The highest conductivity achieved in this system is about 10⁻⁵ S/cm at 80 °C. The optimum conditions (20:1 N:Li⁺ ratio, 60:1 N:initiator) for best conductivity were determined.

Linear poly(N-allylethylenimine-co-N-(2-(2-methoxyethoxy)ethylenimine) (LPAG2EI), in which the ratio between the allylic side-chain and G2 side-chain is roughly 1:1, was synthesized. Neutral SPEs with various amounts of LiTf were prepared using the optimum V-50 composition. IR indicates that Tf⁻ appears to exist mainly as ‘free’ ion while DSC shows a relatively low T_g (-15 °C) and no crystalline phase even at a high salt composition (5:1, N:Li⁺). Cross-linked LPAG2EI/LiTf SPEs have good physical properties and outstanding ionic conductivity, above 10⁻⁵ S/cm at 35 °C.

Finally, lithium secondary batteries that function at room temperature were built using LPAG2EI based SPE and recycled at different temperatures and drain rates for preliminary evaluation. Although the recycling results were not consistently reproducible, we were able to obtain specific capacities about 90 mAh/g at 100 °C with the charge/discharge current densities at 10/20 $\mu\text{A}/\text{cm}^2$. With the increase of cycle number, the recycling efficiency gradually approached 100%.

CHAPTER I

1. Introduction:

The use of batteries has grown tremendously all over the world. Since Alessandro Volta introduced the practical electrochemical cell battery in 1800, battery manufacturing has grown into a 40 billion dollar industry. In addition, the global demand for primary and secondary batteries is projected to grow over 6.6% annually through 2008 to \$65 billion.¹ In the developing regions of Africa, Eastern Europe, Latin America and Asia, the above-average market growth is stimulated by the acceleration in economic growth, ongoing industrialization efforts, and rising personal income levels. In the battery field, the market growth for lithium ion batteries is outpacing all the other kinds of batteries. Many battery companies are investing large amounts of money towards developing batteries that are safer, better, and environmentally more friendly.

The electrolyte, which separates the cathode from the anode in a battery, is one of the most important areas of study. There are many different categories of electrolytes. In general, current commercialized batteries use non-solid electrolytes, which present many disadvantages such as leakage, low energy density, and the need for the battery to be oriented properly for use. True solid state polymer electrolytes, which may be able to overcome these disadvantages, have been studied for more than twenty years.² The research discussed in this thesis is to contribute to the understanding of the effect of backbone modification, side-chain modification, and crosslinking on the ionic conductivity and other properties of poly(ethylenimine) base polymer electrolyte hosts. Development of a true solid state polymer electrolyte will be the long term target of this research. In Chapter One, a brief history of batteries will be discussed, followed by a discussion

of future battery developments. Subsequently, background materials on batteries, solid state batteries, and polymer electrolytes will be reviewed. Finally, a brief review of polyamine based polymer electrolyte hosts is followed by a detailed discussion of the project goals. In the chapters that follow, background materials on specific polymer electrolyte host materials, the syntheses of these materials, and their evaluation will be discussed.

2. The History of Batteries:

Ever since lightning was witnessed by our ancestors, human beings have been fascinated by electricity and have wanted to be able to manipulate this wonderful power of nature. An ancient Greek, Thales, observed that an electric charge could be generated by rubbing amber. However, it was not until three thousand years later that electricity was unveiled by humankind. In 1729, the English physicist Stephen Gray first described electrical conductivity. Later on, in 1748, the American statesman and inventor Benjamin Franklin conducted his famous experiment of flying a kite with a key attached during electrical storms and studied the properties of electricity for the first time. With a dream of utilizing electricity in his mind, he coined the term “battery” to describe an array of charged glass plates, which could be used to store electricity and release it later. During the 1790s, Italian physician Luigi Galvani made frog muscles twitch by jolting them with a spark from an electrostatic machine. His discoveries provided the research cornerstone for later inventors.³

The voltaic pile, the first practical device for generating a consistent flow of electricity, was invented at the turn of 19th century by an Italian named Alessandro Volta. As shown in **Figure I-1**, a voltaic pile was constructed of alternating discs of zinc and copper with pieces of cardboard soaked in acidic solution between the metals. The device produced a reliable and

steady current of electricity. The voltaic pile was the first "wet cell battery" and Volta's discovery of a method for converting chemical energy into electrical energy has been the basis for nearly all batteries ever since. Due to his extraordinary contribution to humankind, the unit of the electrical potential difference, the Volt, which causes a current of one ampere to flow through a resistance of one ohm, is named after him.^{3,4}

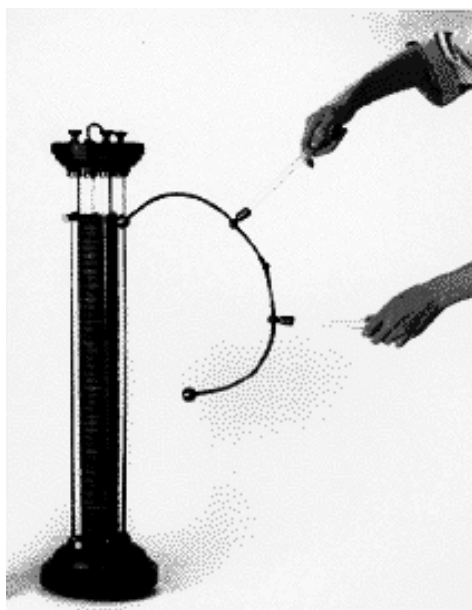


Figure I-1: Voltaic Pile³

In the years after, many scientists created improvements to the liquid electrolyte battery. In 1836, John F. Daniel improved the voltaic pile and invented the somewhat safer and less corrosive Daniel Cell that used two electrolytes: copper sulfate and zinc sulfate. In 1839, Sir William Grove invented the Grove Cell, which consisted of zinc in dilute sulfuric acid and platinum in concentrated nitric acid, separated by a porous pot. The Grove cell offered strong current output and almost doubled the voltage of the original Daniel Cell. In 1841, Robert Wilhelm Bunsen invented the Bunsen Cell, which used carbon electrodes instead of the

expensive platinum electrodes used in the Grove Cell.^{3,4} This invention made the large scale use of batteries possible. One thing worth mentioning is that Grove was also the inventor of the fuel cell. Almost 150 years ago, he invented a “gas voltaic battery” that combines hydrogen and oxygen to produce electricity. This prototype was the forerunner of all modern fuel cells.

The next revolution in electrical energy storage was the invention of the rechargeable lead-acid battery in 1859 by the French inventor Gaston Plante.^{3,4} This chemical battery is composed of one thin lead plate and one lead oxide plate separated by rubber sheets immersed in a dilute sulfuric acid solution. However, unlike the other previous batteries, the flow of electrons could be reversed after it was discharged and the battery could be recharged. The lead-acid battery was very reliable and is still primarily used in automobiles. However, the chemistry, which will be discussed later, hasn't changed for over one and a half centuries, although changes have been made in mechanical configuration and new packaging materials for lighter weight and greater durability have been used.

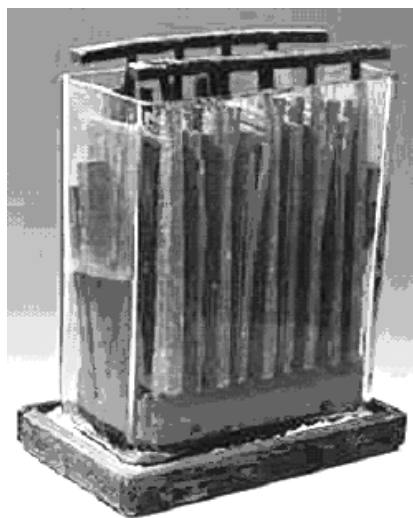


Figure I-2: Prototype of Lead-Acid Battery³

The other great breakthrough was the development of the “dry cell” battery, which used a damp paste as the electrolyte to reduce the possibility of leakage. In 1866, the French scientist Georges Leclanché patented a new “dry” battery system, “Leclanché's cell”, which was immediately successful. While it was quickly accepted by the industry, Leclanché's cell was steadily improved over the years. In 1881, J.A. Thiebaut patented the first battery with both the negative electrode and porous pot encapsulated into a zinc cup. The credit for constructing the world's first widely used battery and commercially successful “dry” battery, the zinc-carbon battery, goes to Carl Gassner. In 1901, the great inventor Thomas Edison invented the world's first alkaline storage battery, which used an alkaline or basic electrolyte. Like the “dry” battery, it had a “non-liquid” electrolyte and could be easily transported.^{3,4} These types of batteries are still commonly used today.

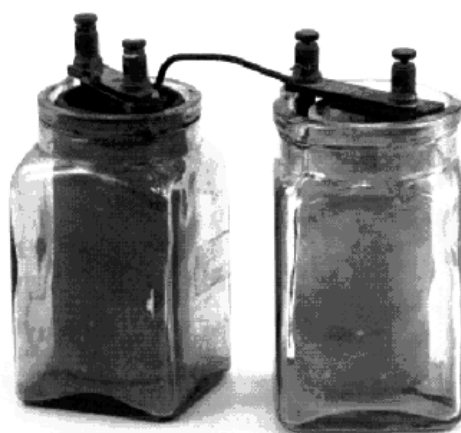


Figure I-3: Prototype of Leclanché Cell³

After World War II, many innovative batteries were invented. The development of solid state batteries has been a trend for the past forty years. Historically, batteries were based on liquid electrolytes because solid electrolytes were too resistive and could not accommodate the

volumetric changes of the cell reaction. However, with the exponential development of material science, many solid materials were found capable for battery application.⁵ Commercialization of solid state batteries has been limited due to performance and cost factors. Among the newly developed batteries, lithium batteries have made the most impact in the area of transportation, personal electronic devices, and national defense by providing a convenient, portable source of electricity.^{6,7} Since the first commercial lithium ion batteries were introduced by SONY in the 80's, the market growth of lithium ion batteries has been outpacing all other kinds of batteries. In the battery industry, "A major shift towards lithium-polymer and lithium-polymer-type batteries is taking place."⁸ Today, Japanese companies are leading the lithium ion battery industry. However, these currently commercially successful lithium ion batteries are not true solid state batteries because the 'polymer' electrolytes in these batteries consist of inert, porous polymer separators impregnated with lithium salt solutions. **Figure I-4** shows an example of the current commercialized lithium ion battery. The electrolyte system presents a leak possibility

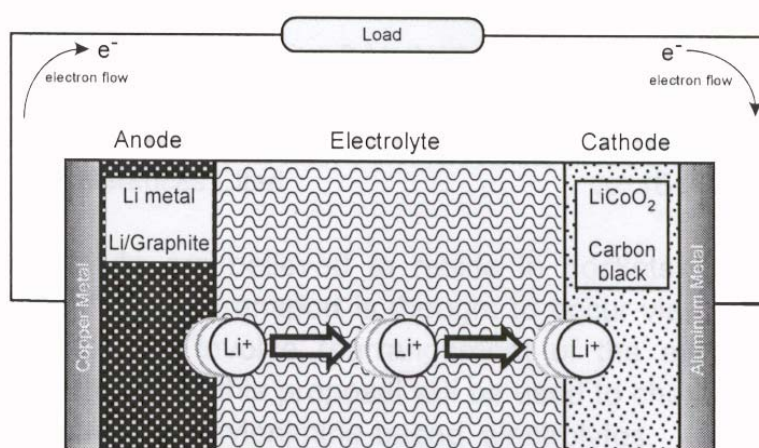


Figure I-4: Major Components of a Lithium Ion Battery

and makes it difficult to make the electrolyte ultra-thin, which is required in making high energy density batteries. All the major battery manufacturers are involved in research on new electrolytes and electrode materials that could get them in the lead in the industry. So, the race to create better batteries with smaller size, higher energy density, and leak-free construction is far from finishing and is getting more and more intense.

3. The Future of Batteries:

Over time, people have relied on various power sources. These sources have included human, animal, wind, tidal, and water energy. In modern civilization, fossil based energy sources, including petroleum, natural gas, and coal, have been the life-blood of the economy. However, not all these energy resources stored by photosynthesis are renewable. There are many arguments about when humans will reach the depletion of these resources. According to the U.S. Department of Energy, oil and natural gas will last around 100 years⁹ if we keep spending energy as we do now (see **Figure I-5**). Coal will last around 200 years¹⁰. We will not actually run out of these non-renewable resources but they will become very expensive and we will have to switch to lower-cost alternatives. The best alternatives are renewable sources, such as hydro-energy, wind-energy, and tide-energy. Other alternatives include solar energy and nuclear fission energy. However, the energy from these sources has to be transformed into electricity before it can be utilized by the end users. For applications that cannot operate by being plugged in, such as electric vehicles and portable electronic devices, the electric energy can be stored in batteries. As time passes, batteries will become more and more important as a power source for our lives.

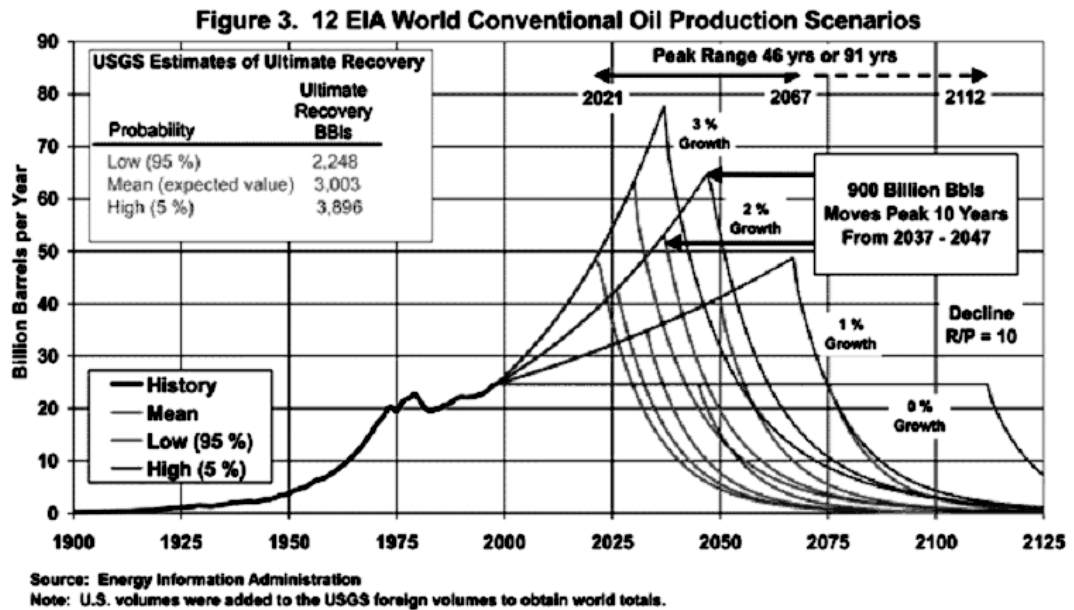


Figure I-5: World Oil and Natural Gas Estimation⁹

Battery-powered electric vehicles (EV) emerged about one century ago and were popular in Western Civilization throughout the first decade of the twentieth century. The more powerful and more reliable internal combustion engine vehicle then took over most of the market. A Renaissance of interest in EV started after the world's oil crises of 1973 and 1979. Due to rising gas prices and depleting oil reserves, EV is becoming the hottest area in the multi-billion dollar auto industry.¹¹ EV emit no CO₂ or other dangerous gases, which is an important factor in protecting the environment.

In order to provide affordable EV with acceptable performance, batteries must have the following characteristics: 1) high energy density for long driving range and less body weight, 2) high peak power for good acceleration, 3) low self discharging rates for minimizing energy lost on standing, 4) fast recharge rates for rapid refueling, 5) no leakage for low maintenance, and 6) proven safety. Many different types of batteries have been considered and attempted for use in

EV. The biggest issue that limits the utility of EV is that an affordable small size battery with enough power to drive a vehicle has not yet been developed,^{12, 13} which is why only hybrid vehicles are available now. Current commercialized hybrid powered vehicles, for example, the popular 2005 Ford Escape-Hybrid, have two engines. The Escape-Hybrid is powered by an electrical engine when the speed is less than 25 MPH. When more power is needed or the battery level is too low, the gas engine kicks in. When the gas engine is on and providing more power than needed, it will automatically recharge the battery. The battery used in an Escape-Hybrid is a Nickel-Metal Hydride battery, which consists of 250 individual cells and provides 300 amperes of current. Despite that fact that the vehicle is partially driven by electric power, the battery located under the cargo area is as big as a luggage case. If the vehicle was solely dependant on the battery, it could only cover a distance of around 20 miles. Additionally, the vehicle becomes 10% heavier and \$4000 more expensive than a conventional Ford Escape.¹⁴ Based on the successful development of lithium ion batteries and the fact that thin polymer film based electrolytes could give very high energy densities, lithium polymer batteries are the most promising candidates for use in EV from both practical and theoretical perspectives. Fuel cells are another possible source to provide enough electricity for a vehicle. However, it is just another possibility before methods of mass production and safe storage of hydrogen gas can be developed.

4. Battery Basics:

By definition, a battery is an arrangement whereby an "electrochemical" reaction can take place. The "electrical" part of the reaction proceeds via the external circuit, while the "chemical" part of the reaction occurs via ionic conduction through electrolytes. A basic battery is

composed of four components: an anode, a cathode, an electrolyte, and an electrical load⁴ (See **Figure I-6**). The basic battery is also known as a galvanic cell. When the electrons flow from anode to cathode, energy is provided to the load and this spontaneous process is discharging. The reverse process, storing chemical energy in the battery, is called charging. The theoretical cell voltage, E^0 , is directly related to the free energy change in the overall cell reaction, $\Delta G^0 = -nFE^0$ (F =Faraday constant and n =the number of electrons transferred).⁴

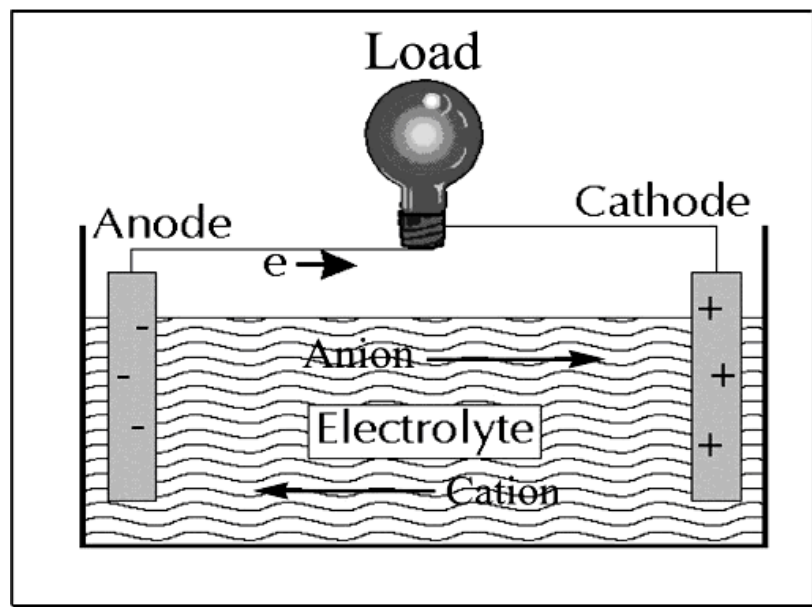
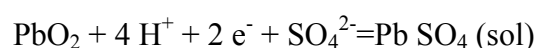


Figure I-6: A Basic Galvanic Cell

These basic cells can be connected in series or in parallel. The connection of the cells within a battery determines the output of the battery. Series connected cells multiply the voltage of a single cell. Cells connected in parallel have equal voltage to a single cell, but the current (i) is multiplied. In this way, batteries can be designed for almost any voltage or current.¹⁵ Batteries that can only be discharged once are referred to as primary batteries and rechargeable ones are secondary batteries. This is one of the common methods of battery classification.

Batteries can also be classified by the electrolytes being used. There are three classes of batteries: liquid electrolyte batteries, dry batteries and solid state batteries. Liquid electrolyte batteries use electrolytes containing ionic liquids and the ions function as the charge carriers. The lead-acid battery is a good example of a liquid electrolyte battery. Lead-acid batteries use sulfuric acid for an electrolyte, lead for the anode, and lead oxide, PbO_2 , for the cathode. The sulfuric acid can dissociate into two hydrogen ions and a sulfate group. The oxidation reaction happens at the anode with the sulfate group reacting with the lead to form lead sulfate, releasing two electrons to the external circuit. The lead oxide is reduced to lead sulfate and water at the cathode. At full discharge, both the anode and the cathode are covered with lead sulfate, and the electrolyte is mostly water. The half-cell reactions are shown in **Equation I-1**. Reversing the current flow reverses the reactions and recharges the battery.¹⁶ During the charging of the



Equation I-1: Half Reactions for the Lead Acid Battery

battery, water may be electrolyzed and produce hazardous hydrogen gas at the cathode, which is one of the disadvantages of this liquid electrolyte battery. The other disadvantages are as follows: battery orientation (a problem that stops the battery from generating current when the electrode is surrounded by the gas pockets formed from the flowing of the liquid electrolyte), relatively rapid self-discharge, material toxicity, electrolyte leakage, and the complexity of construction. However, they are backed by a well-established industry, ease of maintenance,

relatively long life cycles (500 to 1000) and the fact that no satisfactory replacement battery has been invented for automobile needs.¹²

Common “dry” batteries include Leclanchè batteries, alkaline batteries, rechargeable nickel-cadmium batteries, and many other types of batteries. “Dry” batteries actually use liquid electrolytes that are suspended in a gel or some other absorbent substance, which appears to be dry. The use of gelling materials allows for any battery orientation and helps to alleviate leakage problems. However, a “dry” electrolyte is not a true solid electrolyte.⁴ An example of a dry battery, a commercial Zinc-Manganese Dioxide battery, is shown in **Figure I-7**. It uses a moist

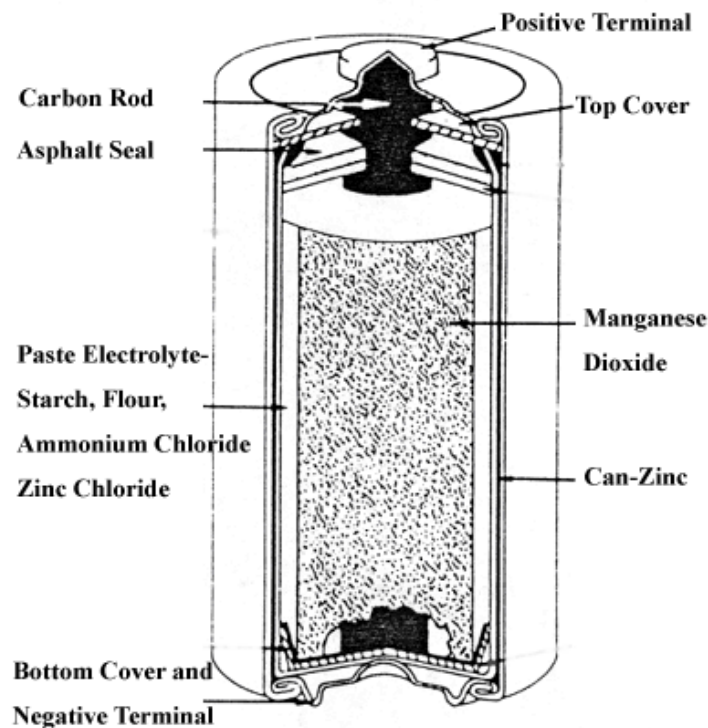


Figure I-7: Basic Construction of a Commercial Zinc Manganese Dioxide Battery

paste of ammonium chloride and zinc chloride as electrolyte. A carbon graphite rod surrounded by manganese dioxide (MnO_2) functions as a cathode. Metallic zinc serves as both anode and

container. The chemical reactions in a “dry” battery are complex, but are shown in **Equation I-2**.

The chemical process includes the oxidation of zinc at the surface of the anode. The zinc atoms



Equation I-2: Chemical Reaction for the Leclanche Battery

yield electrons and become ions with positive charge, which move away from the anode. The excess electrons on the anode flow through the circuit to the carbon rod (cathode). At the rod, the electrons combine with manganese dioxide and water. As the MnO_2 is reduced and reacts, manganese oxide is produced along with negative hydroxide ions. This reaction is accompanied by a secondary reaction. In the secondary reaction, the hydroxide ions combine with ammonium ions and form ammonium hydroxide, which can dissociate into ammonia and water. A carbon-zinc cell stops producing electricity when the manganese dioxide is used up. The battery needs to be removed right away. Otherwise, the electrolyte continues to react with the container and generates byproducts, like hydrogen gas, and will eventually create holes, which result in leaks. The electrolyte may also break the seal and leak out. In the worst scenario, it may damage the equipment in which the battery was used.

“Dry” batteries generally have higher energy densities than liquid electrolyte batteries, so, they can be made in small sizes and used in many applications such as flashlights, toys, radios, and many other portable electronic devices. No battery orientation concern is another advantage of the dry battery, because it can be placed in virtually any position. The manufacturing of the

dry battery is simple and straightforward, which makes the dry battery cheap and readily available. As mentioned above, the main problem with the dry battery is the leakage propensity, which can be caused by either the formation of byproducts or the corrosion of containers by electrolytes. The poor discharge rate is another disadvantage of the dry battery.^{3, 4} There have been many improvements made toward overcoming these disadvantages. However, the possibility of leakage cannot be eliminated due to the liquid nature of the electrolyte. Therefore, batteries that use entirely non-liquid electrolytes are more attractive.

5. Solid State Batteries:

Solid state batteries use solid state electrolytes that do not flow and, of course, will not leak. The functional temperature range of a solid state battery may be much wider than a liquid battery whose electrolytes can freeze or vaporize and make the battery nonfunctional. Because solid state electrolytes can be made very thin and into almost any shape, solid state batteries potentially have high energy densities, low internal resistances, and may be very light weight for specific applications.^{4, 17} Solid state secondary batteries perfectly fit the energy and environmental needs of the future. In order to meet the requirements for real battery applications, a solid electrolyte must have high ionic conductivity, while conducting the appropriate ions. In addition, the electronic conductivity must be negligible to attain a long shelf life.⁵

The most widely studied and utilized electrode material in solid state batteries is lithium because lithium has the lowest redox potential of all metals. As shown in **Table I-1**, the lithium half-cell reaction has a potential of -3.0 V. Other advantages of lithium include low molecular weight, low density, and having a relatively non-toxic oxidized form. Theoretically, lithium has

the highest energy density of any metal. A large disadvantage of using lithium electrodes is lithium's reactivity with water or air; requiring sealed cells.⁵ Lithium ions can also be used in

Half-reaction	V vs. SHE	Formula Weight / e ⁻
$\text{Zn}^{2+} + 2 \text{e}^- = \text{Zn}$	0.76 V	33
$\text{Cd}^{2+} + 2 \text{e}^- = \text{Cd}$	0.83 V	61
$\text{Pb}^{4+} + 2\text{e}^- = \text{Pb}^{2+}$	-1.5 V	104
$\text{Li}^+ + \text{e}^- = \text{Li}$	-3.0 V	7

Table I-1: Half Reaction Potentials of Several Metals

what are called 'swing' or 'rocking-chair' batteries because the lithium ions move back and forth between electrodes but are not present in reduced form.¹² Many lithium batteries haven been developed over the last three decades. Primary lithium cells can have voltages of nearly 4 V and practical energy densities exceeding 200 W hr / kg. Lithium cells can have very long shelf lives, and are extensively used as small cylindrical or button cells in low current rate devices, where they can operate for several years.

In the 19th century, scientists found that the ionic conductivity of solid electrolytes could be high at elevated temperatures. Further research revealed that fast ion conduction was not just a high temperature phenomenon, and many materials could have high ionic conductivity even at ambient temperatures.^{18, 19}

The three most researched types of solid electrolytes are crystalline electrolytes, vitreous electrolytes, and polymer electrolytes. In the crystalline electrolyte, one species of ions is more

mobile than the other ions, which are arranged in a crystalline skeleton. The mobile ion can migrate through interstitial sites of the skeleton when heated. There are two categories of crystalline electrolytes: anionic solid electrolytes (e.g. fluorine and oxygen conductors) and cationic solid electrolytes (e.g. silver, copper, sodium, and lithium ion conductors). Various methods have been used to enhance the ionic conductivity of crystalline electrolytes. However, a problem with crystalline electrolytes is the electrode interfacial resistance during the charge and the discharge cycles.⁵

The second class of solid state electrolyte is the vitreous or glassy electrolyte. They closely resemble liquid electrolytes because of the lack of long range ordering in these amorphous materials. Today, many ionic conductive glasses have reached conductivities of 10^{-7} Scm^{-1} . These systems function at temperatures below their glass transition temperatures and their conductivities are found to be inversely proportional to the viscosity of the materials. The charge carriers are highly decoupled from the supporting matrix, and a fraction of them can move while the rest are frozen at T_g . Traditionally, these electrolyte systems are based on oxide glasses and silver and alkali cation conductors. In the last two decades, sulphide-based glasses, borate-based glasses, and anion-conducting glasses have drawn a great deal of attention. However, there are three major concerns for the practical battery applications of glassy electrolytes: (1) relatively low conductivity, (2) chemical stability, and (3) dimensional stability at high temperature. Many models and theories have been proposed to explain these properties, and many improvements have been attempted to optimize them.⁵

The third class of solid electrolyte is polymer electrolyte, which is polymer that has metal salts dissolved in it. In these systems, the charge carriers are coupled to the supporting polymer

matrix and move cooperatively within the matrix. Polymer electrolyte batteries function best at temperatures above their T_g .⁵ Generally, the softer the matrix is, and the better the conductivity is. Compared to the so-called lithium ‘polymer’ battery and other liquid electrolyte batteries, true polymer batteries require no separators since solid polymer electrolytes can act as spacers. The polymer electrolyte itself may act as a binder with the electrodes and reduce interfacial contact problems. However, the major issue is the relatively low conductivity when the mechanical properties are sufficient for battery fabrication. Several other issues such as ion transference numbers and polarization problems need to be addressed before a polymer electrolyte system becomes commercialized.¹⁷

6. Polymer Electrolytes:

For the reasons discussed above, most polymer electrolytes use lithium ions as charge carriers. The lithium ions can move through the polymer electrolyte host. As shown in **Figure I-8**, the lithium ions are generally believed to reside in pockets forming multiple coordination bonds with surrounding heteroatoms in the polymer.²⁰ Ion transportation occurs via discrete ion

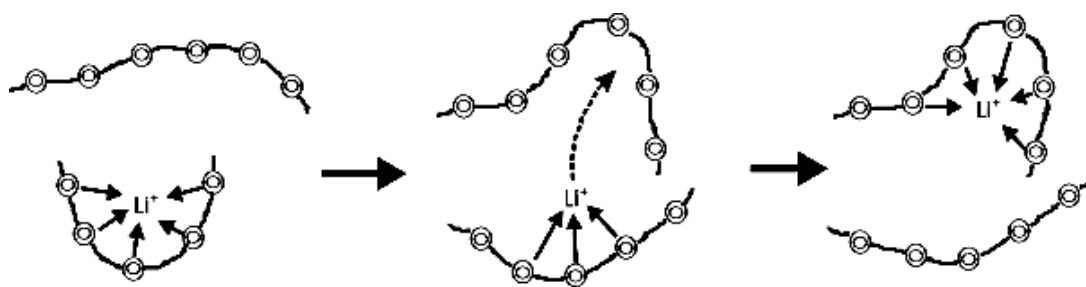


Figure I-8: Ion Jumps of Lithium Ion in Polymer Electrolyte Host

jumps from one pocket to another, involving transient bond breaking and transient bond reforming.^{21, 22} However, the lithium salts in the polymer electrolytes must first spontaneously

dissolve themselves into the host, for which the free energy of dissolution must be negative.²³ During dissolution, the ion pairs in a salt (cation and anion) typically dissociate to a certain degree and solvate with solvents. The dissociation of lithium salts in polymer electrolytes is essential because the ion-paired salts are neutral and will not carry any charge.

The actual ion transportation ability of the polymer electrolyte is the ionic conductivity, which is the magnitude of ion movement in polymer solution and measured by the electrical current transported by ions. The ionic conductivity of a homogeneous polymer electrolyte can be described by the Kohlrausch summation²⁴ (see **Equation I-3**). The ionic conductivity (σ), which is a function of temperature (T) and pressure (P), is determined by the summation of the following three factors: 1) the number of each charge-carrying species (n), 2) the charge that the each species actually carry (e), and 3) the mobility of these charge carriers (μ). When complete salt dissociation occurs, determination of charge carrier concentration and ion mobility are straightforward and the ion mobility could be directly measured by measuring the conductivity. However, the situation becomes more complicated because salts dissociate into many different species in polymer electrolytes. For example, lithium salts are known to have various coordination states when dissolved in a polymer as shown by many spectroscopic studies.^{25, 26} Theoretically, cations, anions, and many other charged species such as ion clusters in polymer electrolytes are able to carry charges. The ionic conductivity is largely determined by the most mobile ion species in the solution. Ion mobility is a key property in determining the conductivity of a polymer electrolyte.

$$\sigma_{(T,P)} = n e \mu$$

Equation I-3: Kohlrausch Summation

The mobility of the charge-carrying ions in polymer electrolyte has been shown to be related to the diffusion of the host polymer of the polymer electrolyte. The greater the polymer diffusion is, the better the ion mobility is. The polymer diffusion is related to the molecular weight of the polymer by the following relationship: $D \propto 1/M^2$ (D =diffusion coefficient, M =molecular weight). However, it is only true up to a certain molecular weight.²⁷ Ion mobility is also influenced by the morphology of the polymer electrolyte (amorphous, semi-crystalline, and crystalline). As the polymer crystallinity increases, the ordering of the polymer electrolyte increases, which limits the polymeric segmental motion. Ideally, a polymer battery would use a completely amorphous polymer electrolyte, which allows the greatest freedom of polymeric segmental motion. However, reducing of crystallinity often leads to the loss of the physical properties of polymer electrolyte. T_g is one of the often-used parameters in describing the morphological properties of a polymer. T_g s were reported as the midpoints of secondary transitions in this thesis. Above T_g , polymeric segmental motion occurs and, consequently, improves ion mobility. So in order to make a polymer electrolyte battery function well at room temperature, a T_g below room temperature is required. In crosslinked polymer electrolytes, T_g normally increases with increasing crosslink density of the polymer. Generally, a decrease of the polymer flexibility leads to lower ion mobility, and an increase of polymer flexibility leads to higher ion mobility.

In order to be considered as a preferable alternative to liquid electrolytes, the target polymer electrolyte host should have at least the following key features.^{4, 17} Firstly, the polymer should contain heteroatoms that allow for weak coordination with metal ions. Poly(ethylene oxide) (PEO), see **Figure I-9**, is one of the polymer electrolyte hosts with heteroatoms. Secondly, the energy for bond rotation should be low enough to allow for easy segmental motion. The third feature is that the coordination sites of the polymer electrolyte should be spaced out at a reasonable distance. Finally, the polymer electrolyte should have suitable mechanical properties and good stability in thermal, chemical, and electrochemical process.

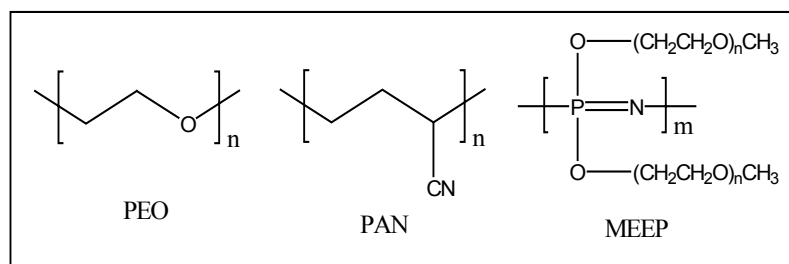


Figure I-9: Examples of Studied Polymer Electrolyte Hosts

Research to develop true solid polymer electrolytes has been going on for more than 20 years.² The conductive property of polymer electrolytes was discovered by Wright in 1973.²⁸ Armand *et al.* first recognized that polymer electrolytes were applicable for battery applications in 1978.²⁹ Many polymer electrolytes were then studied. Figure I-13 shows some of the studied polymer hosts, including poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), and poly(bis-(methoxyethoxyethoxy)phosphazine) (MEEP). Generally, polymers form complexes with salts in polymer electrolytes. The structure and morphology of these polymer electrolytes

depend on many factors: the polymer, the salt, and the actual preparation of the electrolyte. It is difficult to address the problems with polymer electrolytes because of the lack of control over the structure and morphology. Ongoing studies on different polymer electrolytes provide more insight into their fundamental nature and show how to gain more control over the morphology of polymer electrolytes.

Some of the techniques commonly used to study polymer electrolytes include infrared (IR) spectroscopy, conductivity measurements, differential scanning calorimetry (DSC), Raman spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and X-ray diffraction. IR spectroscopy and Raman spectroscopy can be used to explore the speciation of the ions in the polymer electrolytes. For example, in the PEO/lithium trifluoromethanesulfonate (LiTf), the anions (Tf) exist in different forms: as ‘free’ ions, contact ion pairs, and aggregates. Their structures are shown in **Figure I-10**. They exist in equilibrium and the equilibrium could be altered by many factors such as temperature, salt concentration, and impurities. Generally, the aggregate absorption bands are shifted to higher wavenumbers than ion pair absorption bands. The triflate ion CF_3 symmetric deformation region ($\delta_s(\text{CF}_3)$) in PEO-LiTf is shown in **Figure I-10**. The absorption is seen for ‘free’ ions at $752\text{-}3\text{ cm}^{-1}$, contact ion pairs at $756\text{-}8\text{ cm}^{-1}$, and aggregates at $761\text{-}3\text{ cm}^{-1}$.^{30, 31} DSC is commonly used to observe the thermal behavior of the polymer electrolyte. The polymer electrolyte should be functioning above the glass transition temperature (T_g) (so it has enough flexibility) and under the temperature of melting (T_m) (so it is still a solid if partly crystalline). Crystal structures help in understanding local structures of the polymer electrolytes. A thorough understanding of ion speciation, thermal behavior, local structure, and other properties could provide the foundation to make a polymer electrolyte

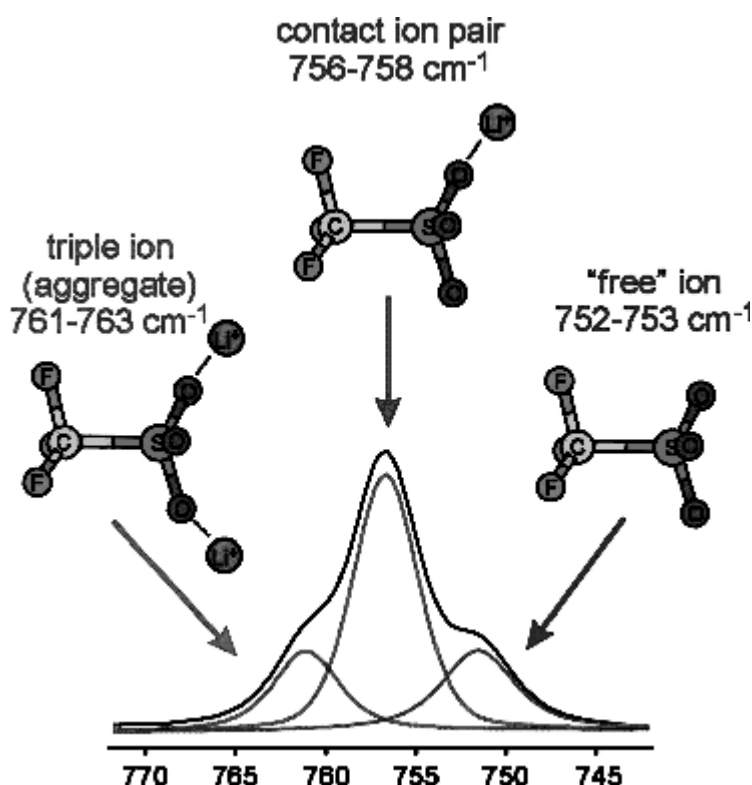


Figure I-10 Ionic Speciation of the $\delta_S(\text{CF}_3)$ in PEO-LiTf System⁶⁸

viable for use in batteries. Conductivity measurements characterize the actual performance of a polymer electrolyte. In the work discussed in this thesis, alternating current (AC) measurements are preferred over the direct current (DC) measurements. It is difficult to use DC measurements to provide an accurate conductivity because of time-dependent charge separation and polarization of the polymer electrolyte.

As mentioned before, PEO and PEO/salt complexes have been investigated in detail. PEO contains a very simple polyether backbone. PEO is generally synthesized by an anionic ring opening polymerization of ethylene oxide and is commercially available at different molecular weights. PEO forms crystalline phases with salts, and therefore, loses polymer flexibility and the mobility of the charge carrier. Non-conductive ion pairs easily form in PEO-salt systems.

Due to the unsatisfactory conductivity and poor physical properties, PEO-based solid polymer electrolytes for commercial battery applications have not been established to any great extent.^{32, 33} The physical properties of PEO can be improved by gamma radiation initiated crosslinking.³⁴ Generally, PEO is very difficult to chemically modify except for the end groups.

7. Polyamine-Based Electrolyte Hosts

In the search for a PEO alternative, a variety of oxygen-containing polymers, such as poly(propylene oxide)³⁵ and poly(ethylene succinate),³⁶ have been investigated. Poly(ethylenimine) (PEI), a PEO analog, has been studied as one of the alternatives to PEO and it provides better synthetic versatility.³⁷ Chiang *et al.* first presented the evidence that PEI could form crystalline complexes with salt and, in the case of NaI, has conductive activity.³⁸ Harris *et al.* reported the formation and conductive behavior of PEI and sodium triflate complexes.³⁹ Subsequently, Takahashi *et al.* studied the conductive activity of the polymeric complexes formed by PEI and various lithium salts, such as LiF, LiCl, LiBr, LiI, LiSCN, LiClO₄ and LiBF₄.⁴⁰ There are two types of PEI: branched PEI (BPEI) and linear PEI (LPEI). Both can be synthesized at different molecular weights. LPEI has only secondary amines and its structure is shown in **Figure I-11**. The synthesis of LPEI is not straightforward. LPEI can be synthesized from poly(2-oxazoline).⁴¹ Having only secondary nitrogens, LPEI is a suitable for fundamental studies to understand the nature of polyamine electrolyte systems. Compared to LPEI, BPEI is easy to make by a non-selective ring opening reaction of aziridine.⁴² BPEI is a very complicated system and there are three types of nitrogen atoms: primary, secondary, and tertiary, in a ratio of ca. 1:2:1, respectively.^{43, 44} The structure of BPEI is shown in **Figure I-11** and the simplified

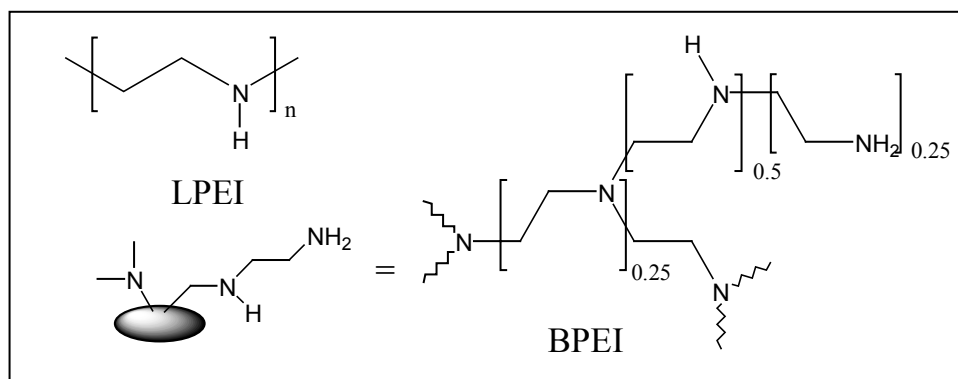


Figure I-11: LPEI and BPEI (with an empirical formula (-CH₂CH₂NH-), BPEI is shown schematically as its exact structure is variable.)

illustration that has three different nitrogen atoms will be used to represent BPEI for the rest of this thesis, but not showing the exact structure. Therefore, BPEI is unsuitable for fundamental study. However, BPEI is a convenient starting material for approaches to practical battery application because it is inexpensive and commercially available.

PEI/salt systems do not have satisfactory conductivity, chemical stabilities, and physical properties for practical applications. The conductivity of LPEI-LiTf complexes is about an order of magnitude lower than similar PEO-LiTf systems.^{37-40, 45-47} LPEI-LiTf has an interesting conductive behavior. At low temperature, the hydrogen bonds in LPEI are disrupted by LiTf, leading to a more disordered system and higher ionic conductivity for higher LiTf compositions. However, at the temperature above the melting point of LPEI, LPEI becomes amorphous and the ionic conductivity decreases with increasing LiTf concentrations because the polymer electrolyte becomes a more locally ordered system due to the N-Li coordination.³⁷ Meanwhile, unmodified BPEI/salts systems have mediocre conductivity. The maximum conductivity of 10⁻⁶ S/cm has been reported for the salt concentration of (N:Li⁺=20:1) at 20 °C.^{48, 49} The T_g of

BPEI/salt increases steeply with the addition of salt.⁴⁸ The electrolyte becomes so stiff at room temperature that it sometimes causes contact problems with the electrodes. However, PEIs can easily be chemically modified because of the reactive nucleophilic nitrogen and their properties can be easily altered.

Our research group has been focusing on improving the physical properties and conductivity of PEI-based polymer electrolytes. Our group has developed an optimized synthesis of high molecular weight PEI,⁴⁷ has been synthetically modifying PEI using different methods, and has been studying the interaction of lithium salts with the modified PEI polymers.

The first category of modification is the functionalization of the secondary nitrogen in the PEI backbone. One of the simplest modifications is the substitution of the hydrogen atoms on the secondary nitrogen using the Eschweiler-Clarke methylation reaction, giving linear poly(N-methylethylenimine) (LPMEI) (see **Figure I-12**). Due to the elimination of hydrogen bonding, LPMEI has less crystallinity and better polymer flexibility. Therefore, better

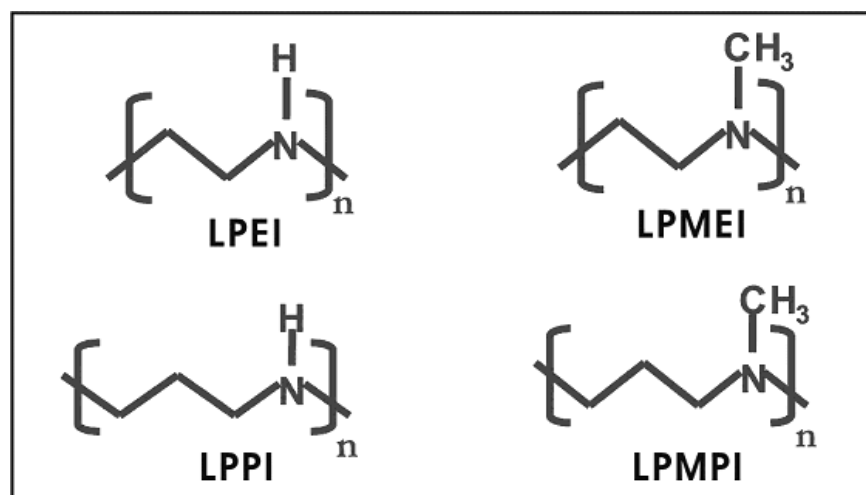


Figure I-12: Structures of LPEI, LPMEI, LPPI, and LPMPI

conductivity was observed. LPMEI still has physical property issues since the LPMEI salt complexes are viscous liquids rather than free-standing films.⁵⁰ Nonetheless, LPMEI studies provide for a further understanding of hydrogen bonding interactions and their roles in establishing crystallinity.

Further functionalization of LPEI has been made to improve conductivity. The reductive alkylation of LPEI with 2-(2-methoxyethoxy)acetic acid and sodium borohydride gives linear poly(N-2-(2-methoxyethoxy)ethylethylenimine) (LPEI-G2),⁵¹ which structurally mimics the highly conductive poly(bis-methoxyethoxyethoxyphosphazene) (MEEP).⁵² As shown in **Figure I-13**, each LPEI-G2 repeat unit contains a tertiary nitrogen atom with an ethylene oxide

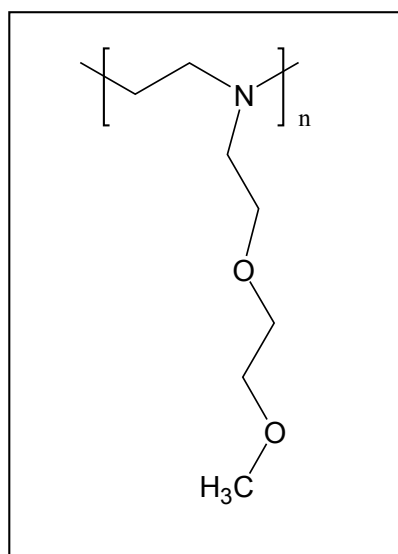


Figure I-13: Structure of LPEI-G2

side-chain. The ionic speciation in LPEI-G2-LiTf system shifts from ‘free’ ion to ion pairs with increasing salt concentration. The conductivity of a 20:1 O:Li⁺ LPEI-G2-LiTf system is about 10⁻⁵ S/cm at room temperature and increases to about 10⁻⁴ S/cm at 60 °C. By far, this is the best

conductivity in PEI-based systems. However, LPEI-G2 is still a liquid with a T_g of $-76\text{ }^{\circ}\text{C}$, which does not change significantly with the addition of salt.

The second category of modification is structural changes in the polymer backbone, which has not been really studied in polyamine-based systems. Insertion of one more carbon into the LPEI backbone gives linear poly(propyleneimine) (LPPI) (see **Figure I-12**). Even with only one more backbone carbon, LPPI may behave very differently than LPEI in many ways. As shown in **Figure I-14**, LPPI could form a six member ring with Li^+ , which may be more stable than the five member ring formed by LPEI. Therefore, LPPI may coordinate more tightly with Li^+ , which could result in lower conductivity. However, the extra backbone carbon may alter the conformational properties so as to make backbone motion easier. It is very interesting to investigate this “spacing effect”, that is the effect of the polyamine backbone insertion on the resulting polymer properties. Moreover, the backbone extended version of LPMEI, linear poly(N-methylpropylenimine) (LPMPI) could be synthesized and compared with LPMEI for further understanding of this “spacing effect” in polyamine based systems.

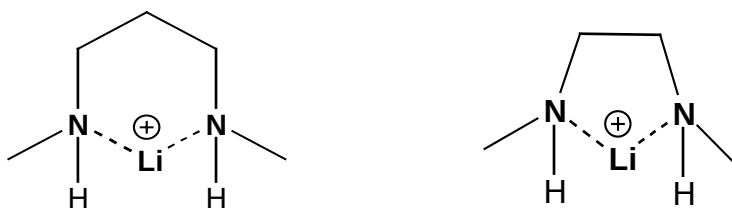


Figure I-14: Possible Local Structures of LPPI and LPEI with Li^+

The third category of modification of LPEI that our research group has investigated is crosslinking between the nucleophilic nitrogens using crosslinkers with reactive functionalities

on both ends of the molecule such as dihalide, tetraethylene glycol diacrylate, or 1,1,3,3-tetramethoxypropane.^{53, 54} Not only can LPEI be crosslinked, but LPMEI can as well. Crosslinking generates relatively robust elastomeric systems, which greatly improves the physical properties of the resulting polymer electrolytes. However, there are two important issues affecting the performance of the crosslinked PEI-based polymer electrolytes. First of all, some of these crosslinking systems result in charged ammonium moieties that affect ion speciation and transportation. Therefore, it was desirable to develop a crosslinking method, which results in neutral SPE. Radical initiated carbon-carbon bond formation may overcome the problem of the ammonium moiety formation in the conventional crosslinking method and may serve as a good means for the synthesis of a neutrally crosslinked PEI-based solid state polymer electrolyte. The incorporation of allyl groups onto the polymer nitrogen atoms would provide good precursors for radical crosslinking processes. The other critical issue is the balance between the mechanical property gain and conductivity sacrifice. Since the T_g of the polymer electrolyte increases with the crosslinking density, the mobility of charge carriers must decrease, resulting in a decrease of ionic conductivity. One way to address this issue would be by fine-tuning the crosslinking condition, compromising the conductivity loss and the physical property improvement to an acceptable level. Incorporation of some functionalized side-chains that structurally mimic some highly conductive polymer, such as MEEP, into the parent polymer is another method to overcome the conductivity loss of crosslinking. Therefore, the radical crosslinking of partially allylated, partially G2 substituted polyamine may result in brand new type of SPE with very high conductivity.

8. Project Goals:

Various groups have studied polymer electrolytes of a great diversity. The common goals for polymer electrolytes include: high ionic conductivity, negligible electronic conductivity, high stability, good mechanical properties, good physical properties, low cost, easy processing, and lithium transference numbers approaching unity.^{5, 17} Neither PEO nor PEI are satisfactory as polymer electrolyte hosts. Both are sensitive to the atmosphere and need to be processed in anhydrous environments. However, the polyamine-based polymer electrolyte hosts have more potential than polyether-based polymer electrolyte hosts because of the versatility of the nitrogen atoms in the polyamine. Polyamines can be modified in different ways to enhance conductivity and other properties. The understanding of structure-property relationships is essential for the further development of polyamine-based polymer electrolytes.

The general goal of this project is to study modified PEI-based polymer electrolyte hosts. More specifically, there will be two parts to the research in this thesis: 1) a systematic study of the relation between a polymer structural modification and the resulting property changes, and 2) semi-empirical research for the development of new solid state electrolyte materials.

In the fundamental study part of this research, LPPI was synthesized. As shown in **Figure I-13**, LPPI is a linear polyamine with three carbon atoms in the backbone and can be viewed as a backbone-modified LPEI. LPMPI was synthesized from LPPI using known synthetic routes. LPMPI can be viewed as a sidechain-modified LPPI or as a backbone-modified LPMEI (see **Figure I-13**). Although LPPI and LPMPI may not be suitable polymer electrolyte hosts, systematic studies of LPPI and LPMPI compared with the known LPEI and LPMEI data will provide a foundation for the understanding of the relation between structural modification and

properties of polyimine-based polymer electrolytes.

The semi-empirical study part of the research is based on the radical initiated crosslinking of allylic sidechains that have been synthetically grafted onto different PEIs. The goal of this part of research is to synthesize and investigate new polymer electrolyte host materials. Based on the inexpensive BPEI, branched poly(N-allylethylenimine) (BPAEI) was synthesized and crosslinked in the presence of LiTf to form solid state polymer electrolytes. As mentioned earlier, BPEI is a very complicated system, and **Figure I-15** simply illustrates that there are three types of nitrogen atoms in BPAEI, and the primary and secondary nitrogen atoms are allylated. The purpose of the crosslinked BPAEI electrolyte research is to evaluate the neutral BPEI based solid state polymer electrolytes for practical battery applications. The partially allylated PEI provides an opportunity to neutrally crosslink the polyamine with side chains that structurally mimic some highly conductive polymers such as MEEP.⁵² Based on partially allylated LPEI, linear poly(N-allylethylenimine-*co*-N-(2-(2-methoxyethoxy)ethylenimine) (LPAG2EI) was synthesized (See **Figure I-15**). The solid film resulting from radically

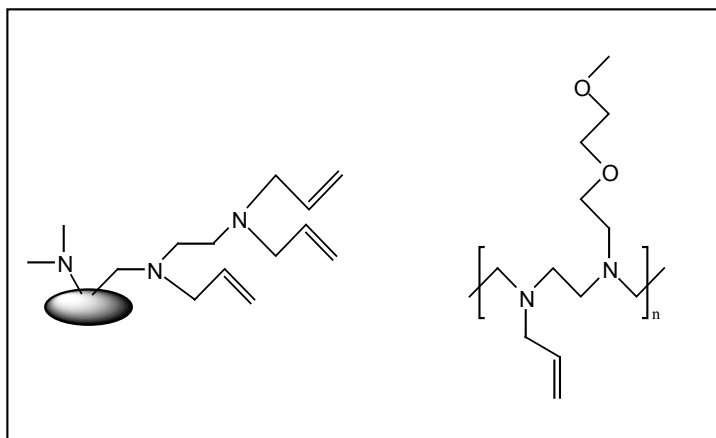


Figure I-15: Structures of BPAEI and LPAG2EI

(BPAEI is shown schematically as its exact structure is variable.)

crosslinking LPAG2PEI was studied as a polymer electrolyte host. The goal of this research on PEI/MEEP hybrid polymer electrolyte host is high conductivity performance with good physical properties. Both crosslinked materials were assembled into lithium secondary batteries as polymer electrolytes to test their actual performances in comparison with a liquid polymer electrolyte, LPMEI.

The research presented in this thesis is partly the result of collaboration with Rachel Mason. Rachel Mason and I were both responsible for the IR, DSC, and conductivity data on linear poly(propylenimine) (LPPI), linear poly(N-methylpropylenimine) (LPMPI), and linear poly(N-allylethylenimine-*co*-N-(2-(2-methoxyethoxy)ethylenimine) (LPAG2EI) systems. The linear poly(ethylenimine) (LPEI) and linear poly(N-methylethylenimine) (LPMEI) data were taken from the work of Dr. Albert Snow and Dr. Rebecca Sanders. I was responsible for the IR, DSC, and conductivity of crosslinked branched poly(N-allylethylenimine) (BPAEI) system. I was also responsible for the assembly and testing of the crosslinked BPAEI and the crosslinked LPAG2EI in lithium secondary batteries. The syntheses and characterization (NMR, IR, DSC, and GPC [if needed]) of all the polymers were conducted by me. Among these polymer electrolyte hosts, LPMPI, BPAEI, and LPAG2EI are new polymer systems except LPPI, which has been synthesized before but has not been evaluated as a polymer electrolyte host.⁴¹

CHAPTER II

LINEAR POLY(PROPYLENIMINE)

Introduction:

Many oxygen-containing polymers, such as poly(propylene oxide)³⁵ and poly(ethylene succinate),³⁶ have been investigated and compared with PEO in the search for PEO alternatives. Due to the synthetic difficulty, there are not many backbone-modified PEO polymers available. Compared to the hard-to-modify polyoxide system, polyamine-based systems are much easier to modify.³⁷ However, backbone modified PEI polymers and their performances as polymer electrolyte hosts have not been studied extensively. The relation between structural modifications and properties of polyamine-based electrolyte has not been established.

Among polyamines, linear poly(ethyleneimine) (LPEI) has drawn the most attention because of the simplicity of its structure. Since Chiang *et al.* first reported that PEI could form crystalline complexes with salts which exhibit conductive behaviors, a fair number of spectroscopic studies of PEI salt complexes have been carried out, mostly based on LPEI.³⁸⁻⁴⁰ Typically, LPEI was synthesized by an acidic or basic hydrolysis of a parent, poly(2-oxazoline).⁴¹ Different molecular weights could be obtained depending on reaction conditions. Our research group has undertaken a fundamental study of LPEI and LPEI-salt systems. LPEI was synthesized from commercially available linear poly(2-ethyl-oxazoline) (MW=200,000, Aldrich). This LPEI is a highly crystalline polymer with a molecular weight of about 86,000 g/mol and has a melting point of 65 °C.⁴⁷ LPEI is known to form different hydrates due to the extensive hydrogen bonding. Chatani *et al.* reported three different LPEI hydrates: dihydrate, sesquihydrate, and hemihydrate.^{55, 56} The comparison of nitrogen environments in

temperature has the same effect on LPEI as the addition of salt. Vibrational spectroscopic studies showed that the lithium ionic association state of LPEI-LiTf significantly shifted from the ‘free’ ion states to aggregate states with the increase of salt concentration. The conductivity of LPEI-LiTf systems was relatively low for applications as a polymer electrolyte and was about one order of magnitude lower than the corresponding PEO-LiTf system, which agreed with the previous LPEI studies.⁴⁷ This is likely due to the extensive hydrogen bonding, as well as ion coordination to the polymer, which could limit the mobility of charge carriers. A straightforward improvement is the removal of hydrogen bonding. Linear poly(N-methylethylenimine) (LPMEI) has been synthesized and investigated as an eligible candidate host for polymer electrolytes.^{37, 52} Other modifications to LPEI include backbone modification and crosslinking by difunctional crosslinkers.

Insertion of one more backbone carbon into LPEI gives the structural homolog linear poly(propylenimine) (LPPI), which has three backbone carbons. However, most PPI research has focused on PPI dendrimers, which were studied as skeletons for drug delivery polymers.^{57,58} For instance, low generation PPI dendrimers have been found to be able to efficiently deliver antisense oligonucleotides (ODNs), which target the epidermal growth factor receptor (EGFR) in A431 epidermoid carcinoma cells.⁵⁷ In the treated carcinoma cells, the growth of the cells, the expression of protein, and the transcription of mRNA were suppressed to levels comparable to those observed with oligofectamine, a cationic lipid delivery system. Tziveleka *et al.* reported a modified multifunctional PPI dendrimer for drug delivery purposes.⁵⁸ **Figure II-2** shows the preparation of this diaminobutane (DAB) PPI dendrimer-based polymer, whose surface can

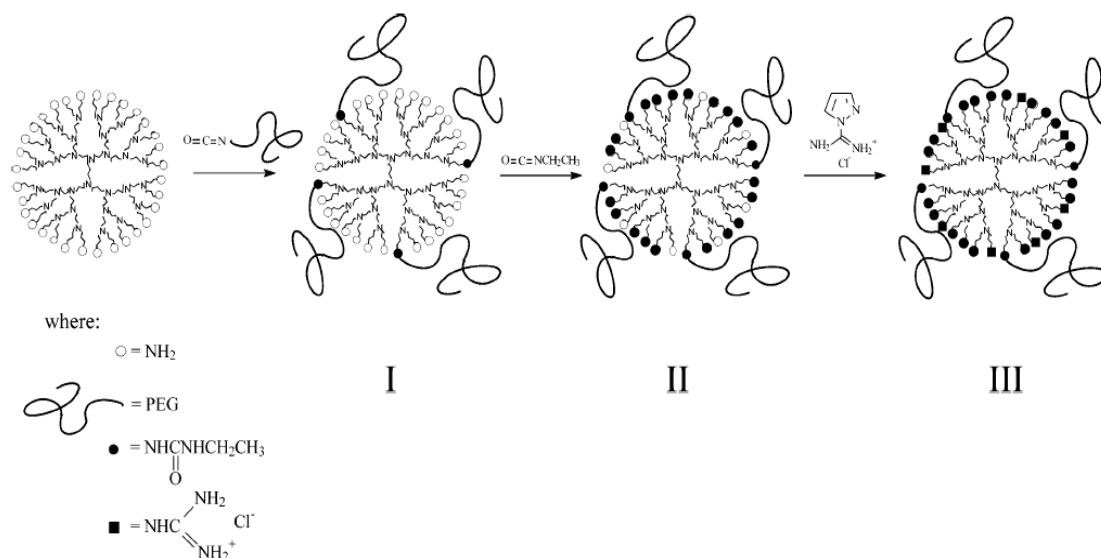


Figure II-2: Synthesis of a DAB based multifunctional dendrimer

covalently bond to different functional groups as protective and targeting ligands. Poly(ethylene glycol) chains is grafted to the dendrimer to protect it from undesired attack.⁵⁹ Guanidinium moieties is grafted to the dendrimer to secure the interaction with acidic receptors such as carboxylate and phosphate anions. The encapsulation and release of active drugs from nanocavities can be triggered by environmental changes. The study of temperature-dependent, pressure-dependent, and pH-dependent conformational changes of PPI dendrimers or PPI dendrimer-based macromolecules is another interesting field of research for drug delivery purposes. PPI dendrimers have been used as backbones for phase transfer catalysts (PTC), which do not assist bond breaking or reforming but concentrate reactive organic species into a small fraction of an aqueous mixture.⁶⁰ The PPI dendrimer-based PTC retains catalytic activity at low concentrations, whereas the low molecular weight surfactant is active only above its critical micelle concentration.

There is very limited research available on LPPI. Pioneering synthetic work on LPPI has

been done by Saegusa *et al.* and the reaction to form it is shown in **Figure II-3**.⁶¹ In the presence of a silver cyanide catalyst, 5,6-dihydro-4-H-1,3-oxazine (OZI) was synthesized from the

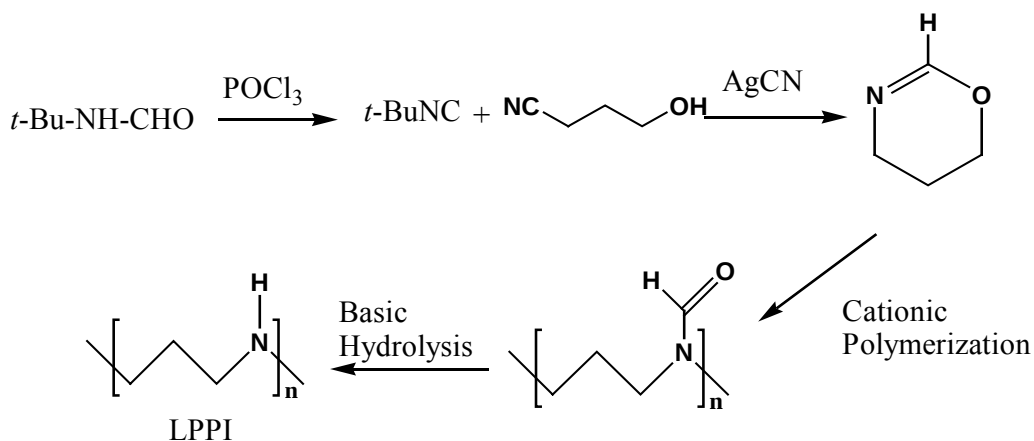


Figure II-3: Saegusa's Synthesis of LPPI

reaction of 3-amino-1-propanol and *tert*-butyl isonitrile (*t*-BuNC), which was synthesized by the dehydration of *N-tert*-butylformamide with POCl_3 . The OZI monomer was cationically polymerized to linear poly(*N*-formyltrimethylenimine) (LPOZI), which is subsequently submitted to alkaline hydrolysis. The resulting polymer, LPPI, was characterized by NMR spectroscopy, melting point, IR, and elemental analysis. The molecular weight of the parent polymer, LPOZI, ranged from 900 to 5,000 g/mol depending on the cationic initiator used. Saegusa used LPOZI with a molecular weight of 2670 g/mol to synthesize LPPI. Therefore, the resulting LPPI had a molecular weight of about 1,800 g/mol. Saegusa's LPPI exhibited a melting point of 58.5 °C. Based on the IR spectrum of Saegusa's LPPI, it contained water.

LPPI has not been reported as a polymer electrolyte host. The investigation of LPPI-salt systems and comparison with LPEI-salt systems is interesting and would be helpful toward the establishment of the relationship between structural modifications and the resulting property

changes in polyamine based polymer electrolyte hosts.

Results and Discussion:

As shown in **Figure II-4**, PPI was synthesized by the hydrolysis of linear poly (2-ethyl-5,6-dihydro-4-H-1,3-oxazine) (LPEOZ), which was obtained by a cationic ring opening polymerization of 2-ethyl-5,6-dihydro-4-H-1,3-oxazine. The monomer was prepared by a one pot cyclization reaction from 3-amino-1-propanol and propionitrile under anhydrous conditions.⁶²

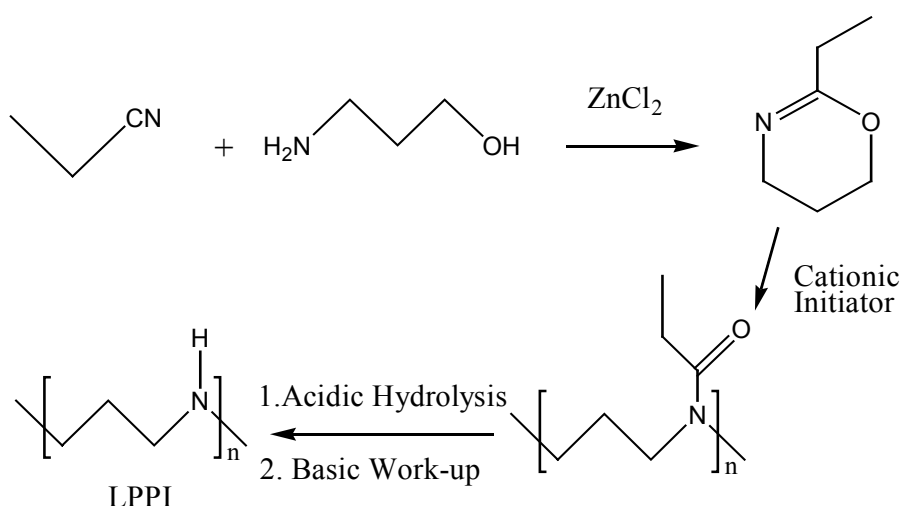


Figure II-4: Synthesis of LPPI

Compared to Saegusa's LPPI synthesis, the new route uses propionitrile and obviates the preparation of *t*-BuNC using a dangerous dehydration of a formamide. Acidic hydrolysis followed by basic work-up gave LPPI with good quality. The overall yield is greater than 60%. The resulting LPPI was characterized using NMR and IR. The NMR spectrum in d_4 -methanol possesses a triplet centered at 2.67 ppm (N-methylene protons, 4 H) and a quintet 1.75 ppm

(C-methylene protons, 2 H). The splitting patterns are very clear and reasonable (**Figure II-5**).

As shown in **Figure II-6**, a fairly symmetric N-H absorption band appears at 3218 cm^{-1} in IR spectrum. An IR spectrum of neat LPPI at a broader range is shown in the **Appendix of Spectrum I**.

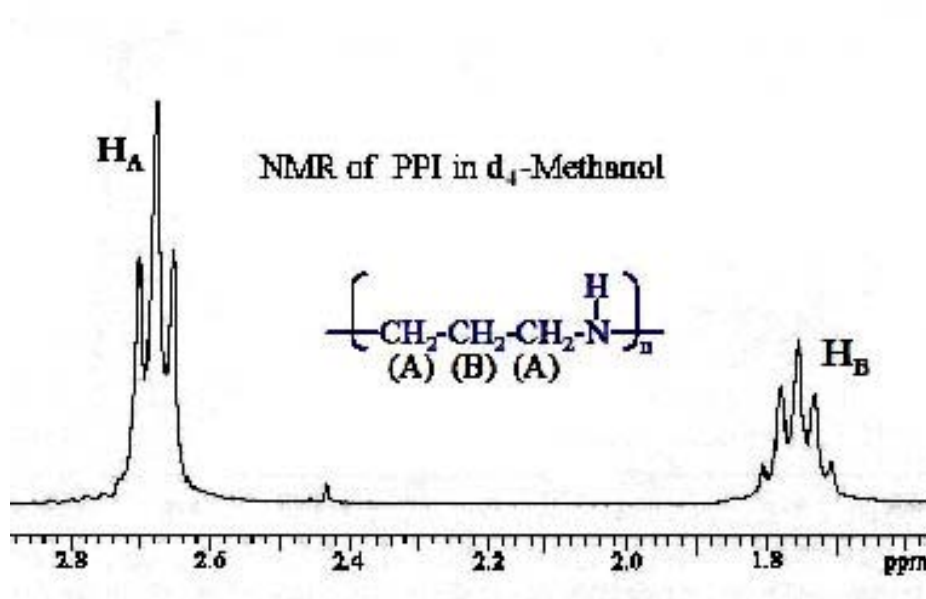


Figure II-5: 300 MHz ^1H NMR of LPPI in CD_3OD

LPPI is a brittle and highly crystalline light yellow solid. Based on the GPC measurement of the molecular weight of the parent polymer, LPEOZ, LPPI has an intermediate molecular weight. The calculated molecular weight is about 3000 g/mol. The average degree of polymerization is ca.53.

As a homolog of LPEI, there are numerous similarities between LPEI and LPPI. However, due to the extra carbon in the LPPI backbone resulting in a ‘spacing effect’, there are also significant differences in physical properties and behavior. LPEI is highly crystalline and extremely hygroscopic and will take up several waters per repeat unit, forming hard-to-remove

hydrates. In contrast, LPPI is also highly crystalline but was relatively water free; nearly identical IR spectra with no O-H absorptions were observed for both vacuum dried LPPI and “as synthesized” LPPI, as shown in **Figure II-6**. This observation could be explained by the

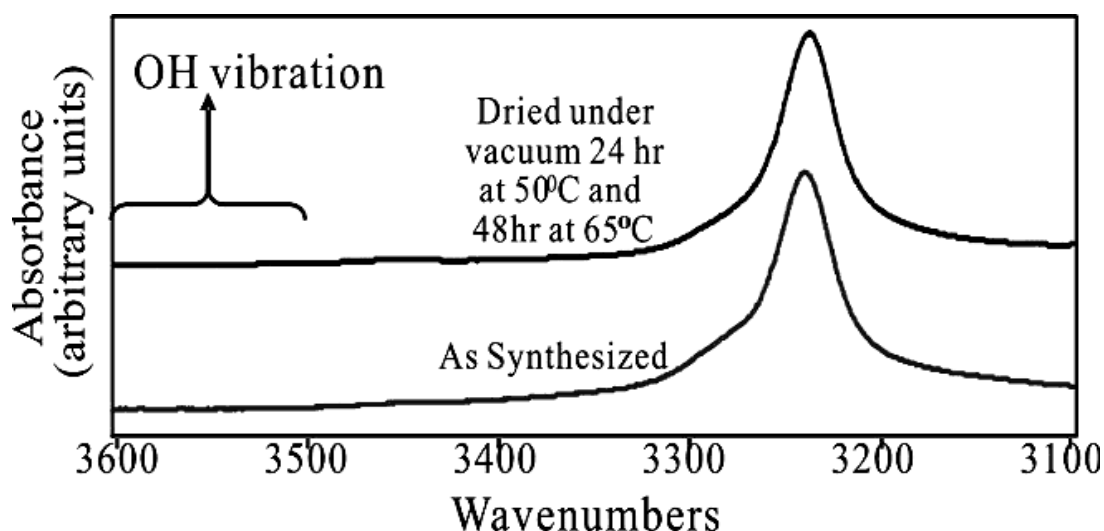


Figure II-6: IR spectra of LPPI (3100-3600 cm^{-1}): As Synthesized vs. Extensively Dried

exclusion of water during the crystallization process of LPPI, suggesting quite different inter- and intra-molecular interactions than found in LPEI. These differences in properties between LPEI and LPPI suggested that their behavior as polymer electrolyte hosts may also be significantly different.

Thermal analyses on LPPI-LiTf systems were performed. DSC data show that LPPI has a melting point temperature (T_m) of 60.5 °C, which is very close to the T_m of LPEI (ca. 65 °C).⁴⁷ **Table II-1** summarizes the T_m and the glass transition temperatures (T_g) of various LPPI-LiTf compositions. Within the range of experimental error, the T_m and T_g of PPI-LiTf do not substantially change with salt concentration. The 20:1, 15:1, and 10:1 LPPI-LiTf samples exhibit T_m s near 56 °C and T_g s near -20 °C. In the 5:1 and 3:1 samples, only a T_g (~-20 °C) is

Sample	T _g , °C	T _m , °C	Amorphous Phase	Crystalline Phase
LPPI	No T _g observed	60.5	0%	100%
LPPI/LiTf 20:1	-21.6	46.6	57%	43%
LPPI/LiTf 15:1	-20.8	45.2	69%	31%
LPPI/LiTf 10:1	-14.6	53.4	71 %	29%
LPPI/LiTf 5:1	-14.8	No T _m observed	100%	0%
LPPI/LiTf 3:1	-20.9	No T _m observed	100%	0%

Table II-1: Melting Points (T_m) and Glass Transition Temperatures (T_g) from DSC measurements on LPPI and LPPI-LiTf mixtures. The percentage of amorphous and crystalline domains were estimated from DSC measurements on LPPI and LPPI-LiTf mixtures by integration of the areas under the melting point curves and assuming LPPI is nearly 100% crystalline (as suggested by IR) to obtain an estimated ΔH_{fusion}

present. Clearly two distinct domains exist; one is a crystalline, likely neat, LPPI domain, and the other is an amorphous LPPI-LiTf complex domain, which both remain at the same composition regardless of the change in salt concentration within the range studied. The only change with varying salt concentration is the ratio between these two domains. As shown in **Table II-1**, the percentage of amorphous domain increases with the increase of the LiTf concentration, while the percentage of crystalline domain decreases accordingly. At some PPI-LiTf ratio between 10:1 and 5:1, PPI is completely transformed into the amorphous phase. After this point, the composition of the amorphous phase must be changing with added LiTf but

the increase in salt concentration has little effect on the T_g of the already highly disordered system. While this disordering phenomenon has been reported for LPEI,⁴⁷ its T_g increases monotonically with increasing LiTf over a comparable range of N:Li⁺ ratios, suggesting that LPEI and LPPI interact differently with LiTf.

IR studies on LPPI-LiTf systems were carried out. LPPI-LiTf systems and LPEI-LiTf systems were compared in the following regions: the N-H vibrational region, the conformational region, and the ionic association region.

Figure II-7 shows the temperature-dependent IR absorbance spectra of LPPI and LPEI in

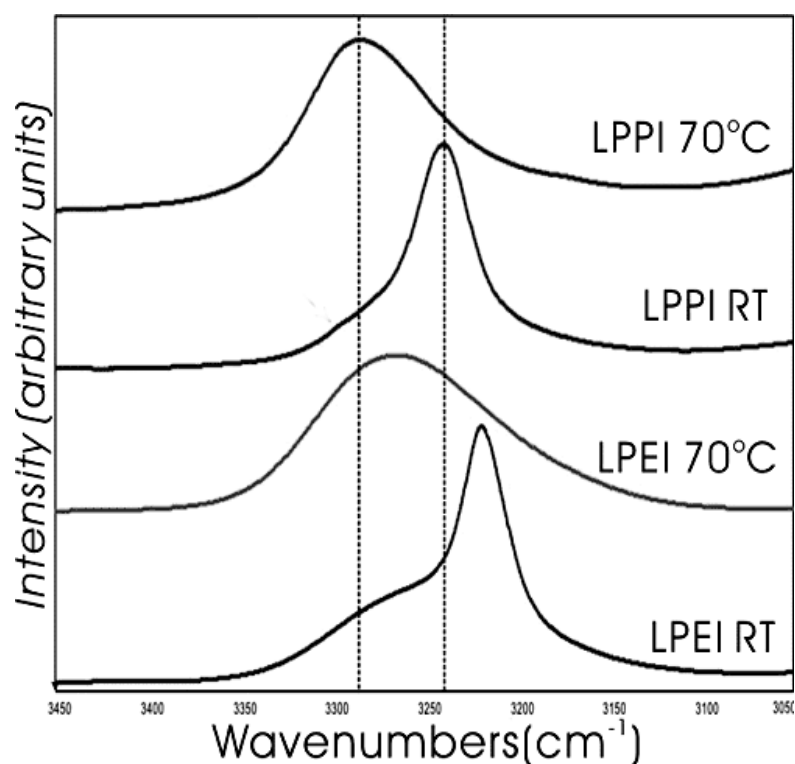


Figure II-7: IR Spectra of LPPI and LPEI (N-H region, 3100-3400 cm^{-1}), above and below their melting points. All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm^{-1} .

the region from 3050-3450 cm^{-1} . The spectrum of LPEI consists of a relatively sharp band centered at 3218 cm^{-1} and a less intense broad band around 3270 cm^{-1} . Based on previous LPEI research, the sharp band corresponds to the hydrogen-bonded domains of highly ordered crystalline LPEI. The broad band is due to more disordered regions (amorphous domains) in which hydrogen bonding still exists to a significant extent.⁴⁷ When the LPEI was heated, most of the crystallinity was destroyed and the spectrum was dominated by absorptions from amorphous domains.

The spectrum of LPPI also consists of a relatively sharp band and a broad shoulder; however, these are shifted to higher frequencies. This tells us that in LPPI there are also two domains: ordered crystalline domains and disordered amorphous domains. In both domains hydrogen bonding is weaker than their counterparts in LPEI. At both room temperature and 70 °C, the LPPI bands are narrower than those for LPEI; which may mean that LPPI has a narrower distribution of states in both the crystalline and amorphous domains. At room temperature, the LPPI shoulder band is significantly smaller than that for LPEI, suggesting that LPPI has less amorphous phase at room temperature.

When lithium triflate salt was added to LPPI and LPEI, significant differences were observed. IR spectra of neat LPEI, LPPI, and their 5:1(N:Li⁺) salt complexes are shown in **Figure II-8**. In LPEI-LiTf 5:1, two strong bands in the amorphous region were observed, while the crystalline band, present in neat LPEI, was wiped out. Two different LPEI-LiTf species were formed and in the domains where these species dominated, the system appeared to be amorphous.⁶⁸ However, when same ratio of salt was added to LPPI, there was still a significant

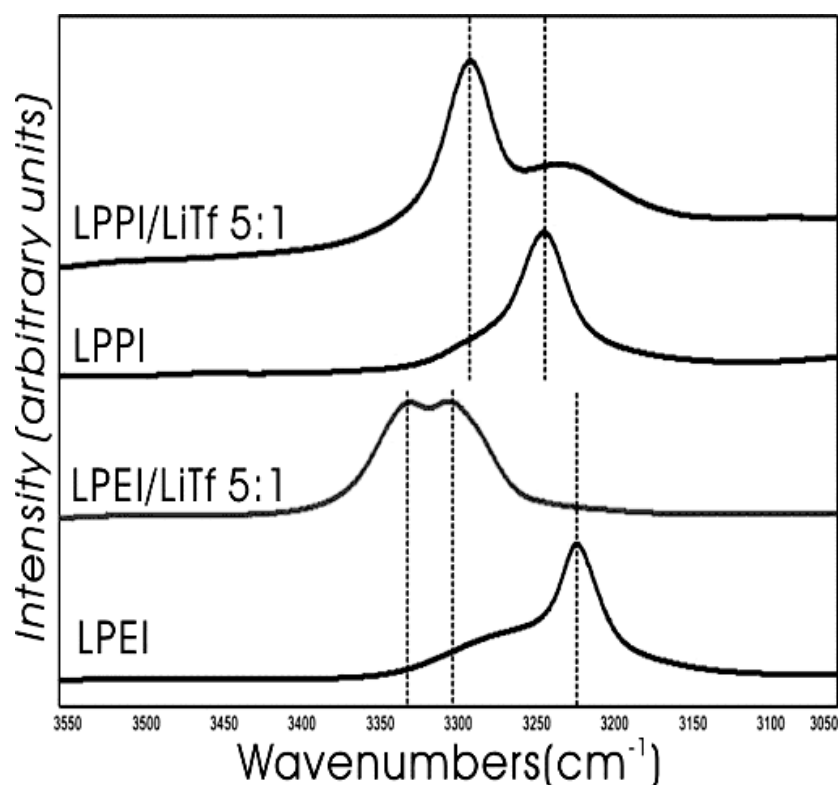


Figure II-8: IR Spectra (N-H region, 3100-3400 cm^{-1}) of LPPI and LPEI, with and without added LiTf (at an $\text{N}:\text{Li}^+$ ratio of 5:1). All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm^{-1} .

amount of the more strongly hydrogen bonded species.

In the N-H region, increasing the temperature has largely the same effect on LPEI as the addition of salt.⁴⁷ However, temperature change and salt addition to LPPI result in significantly different behavior. **Figure II-9** shows infrared spectra of various LPPI-LiTf compositions at room temperature and 70 °C in the region from 3100 cm^{-1} to 3450 cm^{-1} . At room temperature, the more weakly hydrogen bonded species grows with the increase of salt concentration. At 70 °C, the less hydrogen bonded band narrows while the more hydrogen bonded band grows with the increase of salt concentration. Based on IR bands at both temperatures, the increase of

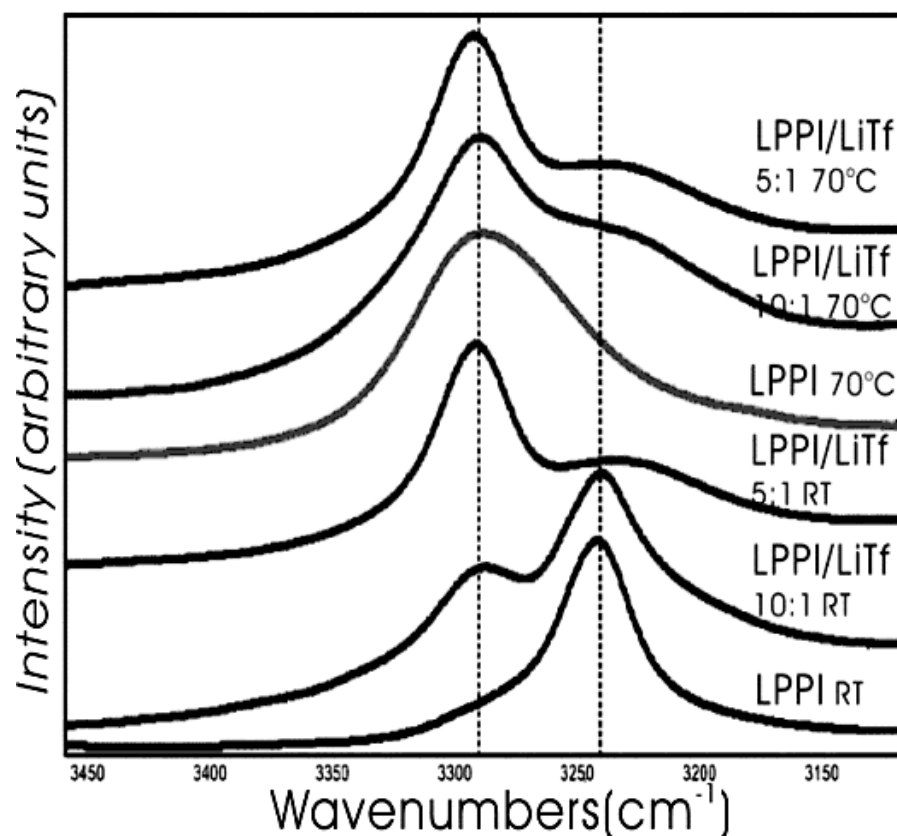


Figure II-9: IR Spectra (N-H region, 3100-3400 cm^{-1}) for LPPI, with and without added LiTf, above and below the melting point of LPPI. All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm^{-1} .

temperature has little effect on hydrogen bonding in LPPI-LiTf complexes at the concentration of 5:1(N:Li⁺). The DSC analysis in **Table II-1** shows that the LPPI is completely transformed into amorphous state by LiTf at a concentration ratio between 10:1 and 5:1 at room temperature. The IR spectra therefore imply that there are two different hydrogen-bonding environments in the amorphous LPPI-LiTf system. By comparison with the IR spectrum of neat LPPI above its T_m , the broad band centered at 3235 cm^{-1} in 5:1 LPPI-LiTf likely represents the hydrogen-bonding environment in the LPPI-LiTf species. In conjunction with N-Li⁺ coordination, the hydrogen bonds in these environments appear to be about as strong as the

hydrogen bonds in crystalline neat LPPI. Heating the samples to 70 °C appears to melt the LPPI crystalline phase but has little or no effect on the LiTf/LPPI local structure, resulting in amorphous, neat LPPI and amorphous LiTf/LPPI local structures. Consistent with the DSC data, these local structures apparently do not strongly affect segmental motion (T_g) or are not present in sufficient concentration to do so (unlikely in the 5:1 sample). The 10:1 LPPI-LiTf sample shows behavior consistent with this interpretation.

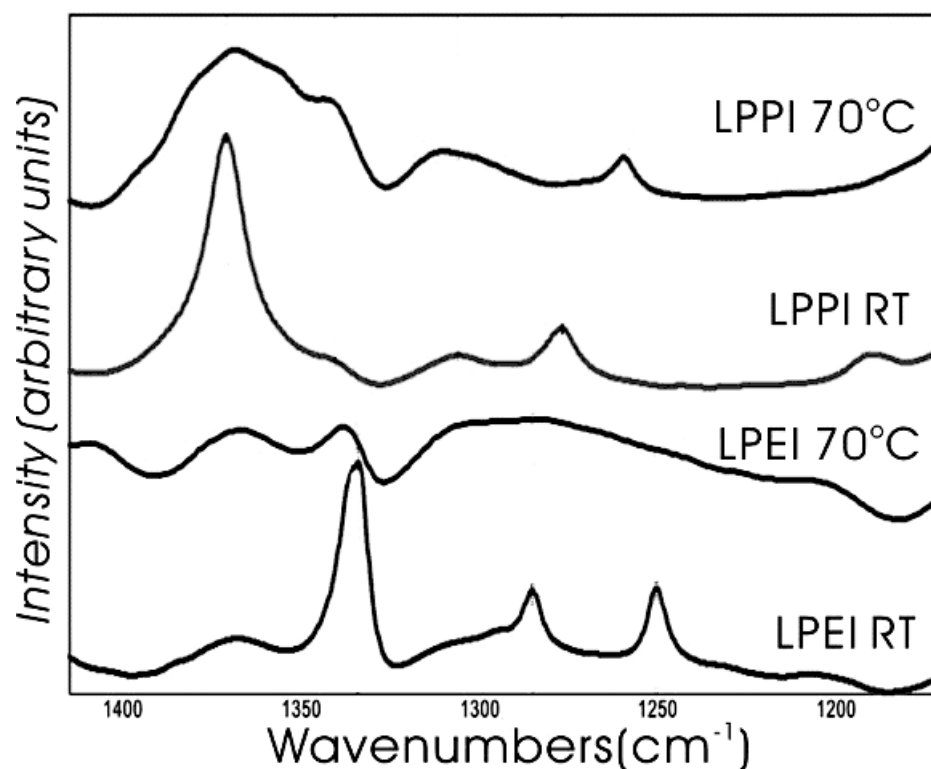


Figure II-10: IR Spectra (Conformation Region, 1150-1400 cm^{-1}) for LPEI and LPPI, above and below their melting points. All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm^{-1} .

The region from 1150 cm^{-1} to 1400 cm^{-1} is a complex mixture of C-H bending modes, C-C stretching modes, and C-N stretching modes. Out-of-plane N-H bending bands also exist in this

region and may be highly mixed with the backbone vibrational bands, which makes the pattern of this region more complicated. As shown in **Figure II-10**, LPPI has a different pattern of absorptions than LPEI due to the extra backbone carbon. When the polymers are heated, the LPPI pattern is somewhat less disrupted than the LPEI pattern is, possibly due to some relatively stable local structures resulting from the additional backbone CH_2 that is preserved in the amorphous phase. The N-H out-of-plane bending bands, which are highly mixed with backbone bands, could be another factor because it can be completely disrupted by small changes in hydrogen bonding. Since LPPI has weaker hydrogen bonds than LPEI does, the

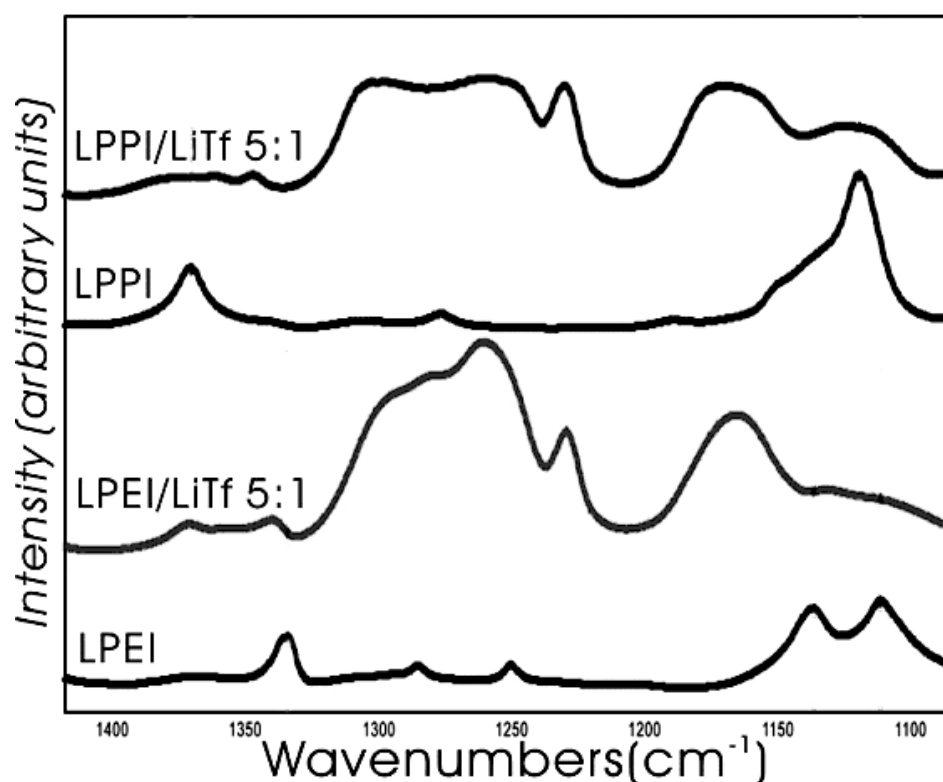


Figure II-11: IR Spectra (Conformation Region, $1150\text{--}1400\text{ cm}^{-1}$) for LPEI and LPPI, with and without added LiTf. All spectra are scaled by normalizing the intensity of the C-H bands from $2900\text{ to }3100\text{ cm}^{-1}$.

LPPI hydrogen bonds are less affected by the increase of temperature. Therefore, the backbone pattern of LPPI is less disrupted. As shown in **Figure II-11**, when lithium salts are added to the polymers, these same conformational regions of both LPPI and LPEI are similarly disrupted because the hydrogen bond strength in both systems are increased to similar level by salts. These observations are consistent with both thermal and IR N-H analysis discussed earlier.

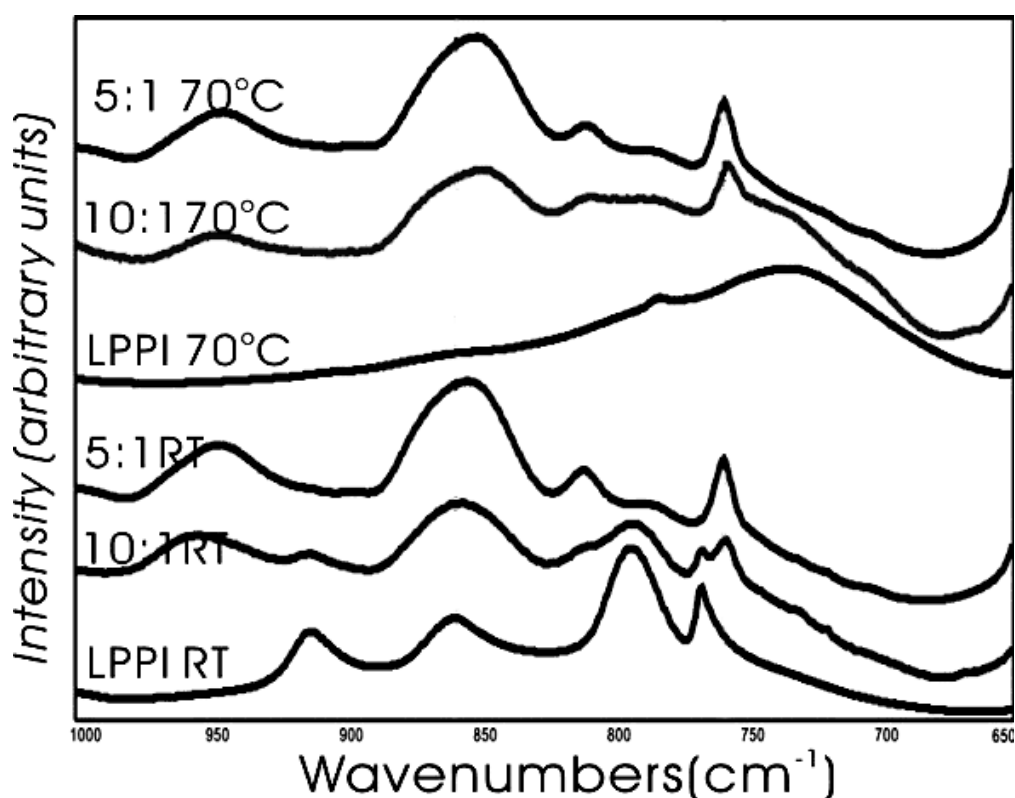


Figure II-12: IR Spectra (Conformation Region, 650-1000 cm^{-1}) for LPPI, with and without added LiTf, above and below the melting point of LPPI. All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm^{-1} .

Figure II-12 shows the conformational changes in LPPI as a function of salt concentration at room temperature and 70 °C from 650 cm^{-1} to 1000 cm^{-1} ; a region which contains C-N stretching modes, C-C stretching modes, and several triflate anion vibrations. In this region, the

polymer backbone bands were almost wiped out by heat. However, most of them could be regained by the addition of salt. This could be explained by the formation of the LPPI-LiTf local structures, which ‘lock’ the backbone into conformations that are similar to those found in LPPI at room temperature, and which are more thermally stable.

In ionic association IR studies of LPPI-LiTf systems and LPEI-LiTf systems, two key absorptions, the triflate ion CF_3 symmetric deformation mode ($\delta_s(\text{CF}_3)$) and the triflate SO_3 symmetric stretching mode ($\nu_s(\text{SO}_3)$), were investigated.

The $\delta_s(\text{CF}_3)$ has been extensively examined by our research group. Several ionically associated species previously have been assigned independent of the cation in the triflate salts in PEO. These are ‘free’ ions ($752\text{--}3\text{ cm}^{-1}$), contact ion pairs ($756\text{--}8\text{ cm}^{-1}$), and aggregate species ($761\text{--}3\text{ cm}^{-1}$).^{30,31} As shown in **Figure II-13**, the $\delta_s(\text{CF}_3)$ band first appears at 754 cm^{-1} in 20:1 LPEI-LiTf, which represents mostly free ions with some contact ion pairs. With the increasing salt concentration, this band shifts to 758 cm^{-1} , which corresponds to contact ion pairs. However, in LPPI-LiTf systems, the $\delta_s(\text{CF}_3)$ band does not shift with the increase in salt concentration and always appears at 758 cm^{-1} (see **Figure II-13**). As shown in **Figure II-12**, this band does not shift with the increase in temperature either. This observation suggests only one salt polymer coordination state exists regardless of the salt concentration in LPPI-LiTf. In the IR spectrum of LPPI/TBATf (tetrabutylammonium triflate), in which all the triflate ions are free from contact with cations, $\delta_s(\text{CF}_3)$ always appears at 753 cm^{-1} at any concentration. Combining all this information it appears that the triflate ions in LPPI-LiTf systems are not mainly free ions, but are likely contact ion pairs or aggregate species.

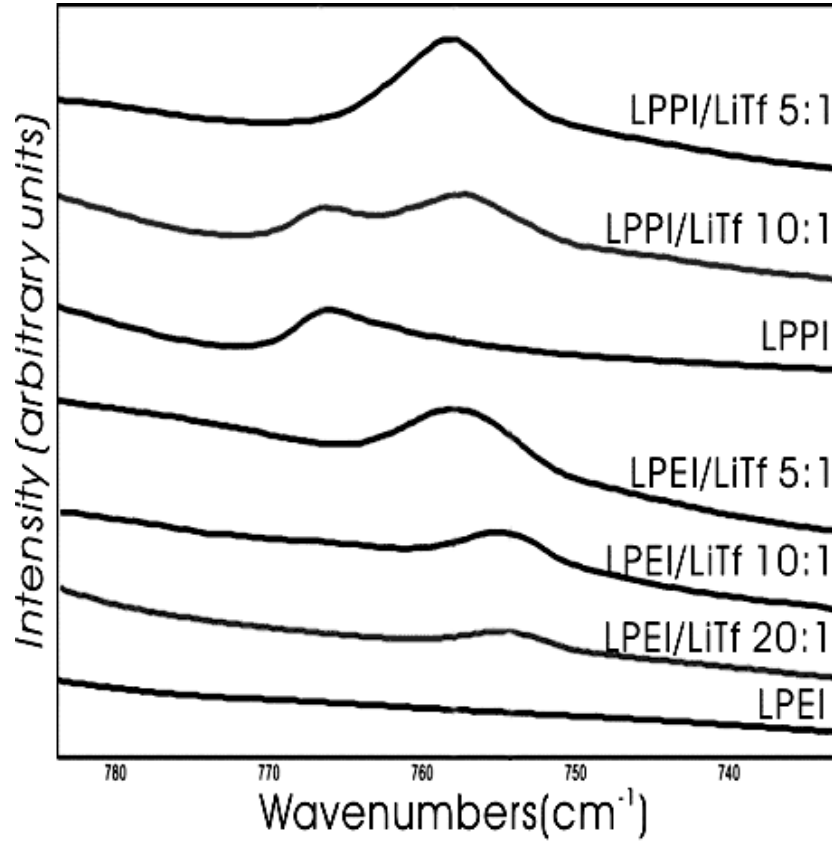


Figure II-13: IR Spectra ($\delta_s(\text{CF}_3)$, 730-780 cm^{-1}) for LPPI and LPEI, with and without added LiTf. All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm^{-1} .

Figure II-14 shows the $\nu_s(\text{SO}_3)$ bands in LPPI and LPEI at various LiTf concentrations. Based on previous PEO-LiTf research, the band at 1030-3 cm^{-1} is assigned to free ion, and the band at 1046 cm^{-1} is designated as aggregate ion. In LPEI-LiTf, there are mostly free ions. Only a small amount of ion pair appears at the 5:1 concentration. In LPPI-LiTf, two non-polymer peaks exist in this region. One is centered at 1031 cm^{-1} and the other is centered at 1039 cm^{-1} . This tells that there are ion pairs and free ions in LPPI-LiTf. This is an obvious contradiction

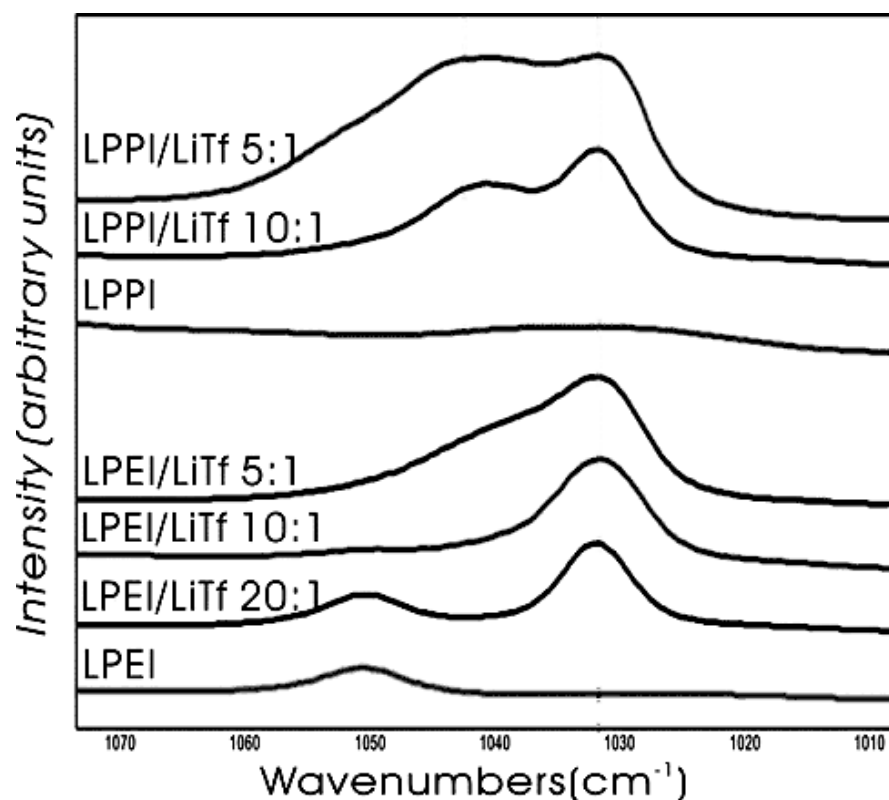


Figure II-14: IR Spectra ($\nu_s(\text{CF}_3)$, 1000-1070 cm^{-1}) for LPPI and LPEI, with and without added LiTf Salt. All spectra are scaled by normalizing the intensity of the C-H bands 2900-3100 cm^{-1} .

with the observations in the $\nu_s(\text{CF}_3)$ region. Frech *et al.* reported the similar behavior of TBATf in 2-propanol.⁶³ The $\nu_s(\text{CF}_3)$ band showed the ionic association state was aggregate, while the $\nu_s(\text{SO}_3)$ suggested it was free ion. This may be due to the formation of some relatively stable local structures by the coordination of the SO_3 part of triflate, the polymer, and the lithium cation in both LPPI-LiTf and LPEI-LiTf. As shown in **Figure II-15**, the delocalization of electrons from nitrogen across lithium to oxygen may significantly change the electronic density of SO_3 part of triflate ion.

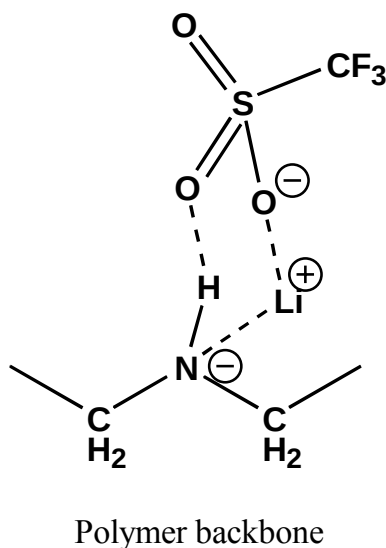


Figure II-15: Possible Local Structure in Polyamine-LiTf systems

The ionic conductivity (δ) behavior of LPPI-LiTf at various compositions was calculated from the results of the impedance measurements using the following equation: $\delta = d/RA$, where d is the thickness of the film, R is the impedance measured, and A is the area of the film. **Figure II-16** shows temperature dependent ionic conductivity data for LPPI-LiTf and LPEI-LiTf at several compositions. Generally, LPPI-LiTf systems exhibit conductivity of similar magnitude to those of LPEI-LiTf systems. As might be expected from the IR and DSC studies above, the dominating species, ion pair, possible aggregate, changes little with the addition of salt or increase in temperature, so the increase in charge carrier concentration has minor contribution to the increase of ionic conductivity with increasing LiTf concentration, which appears to be due to the increase in the amount of the amorphous domain, increasing the ionic mobility of the charge carriers that are there. Therefore, the increase in ionic conductivity with increasing salt is mainly due to the increase in ionic mobility of these charge carriers. Although the room temperature conductivities for LPPI-LiTf electrolytes are fairly low, the steep increase in

conductivity for the substantially amorphous compositions allows them to reach conductivities useful in battery applications ($>10^{-5}$ S/cm) at relatively low temperatures

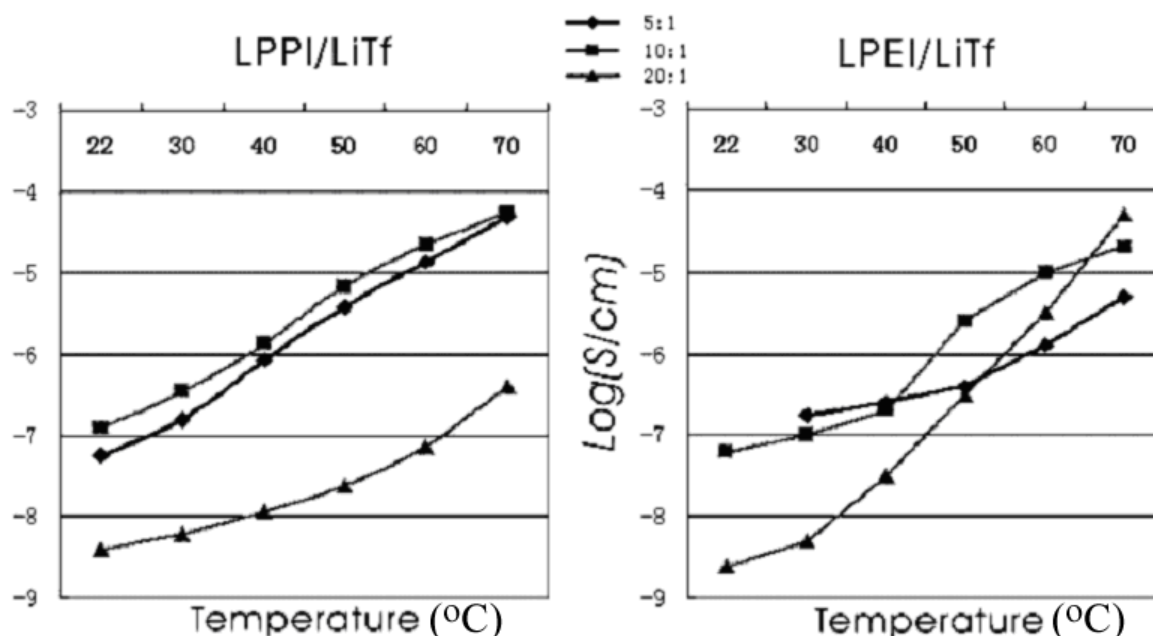


Figure II-16: Temperature Dependent Ionic Conductivities of LPPI-LiTf and LPEI-LiTf as a Function of Added LiTf

(ca. 50 °C) and can reach very high conductivities ($>10^{-3}$ S/cm) below 100 °C. In contrast, LPEI-LiTf shows very different behavior, increasing in conductivity at room temperature with increasing LiTf concentration and decreasing in conductivity with increasing LiTf at temperatures above 60 °C. This behavior in LPEI-LiTf likely results from a combination of changing speciation (charge carrier concentration) and changing ionic mobility with changing LiTf concentration.

The LPPI lithium ion concentration dependent conductivity data from 22 to 80 °C is shown in **Figure II-17**. The X-axis represents the lithium concentration in the polymer. At all

temperatures, the conductivity of the LPPI-LiTf system increases with increasing salt. At some concentration between 10:1 and 5:1, the polymer electrolyte becomes completely amorphous and the conductivity reaches a maximum concentration until it reaches a plateau, where the

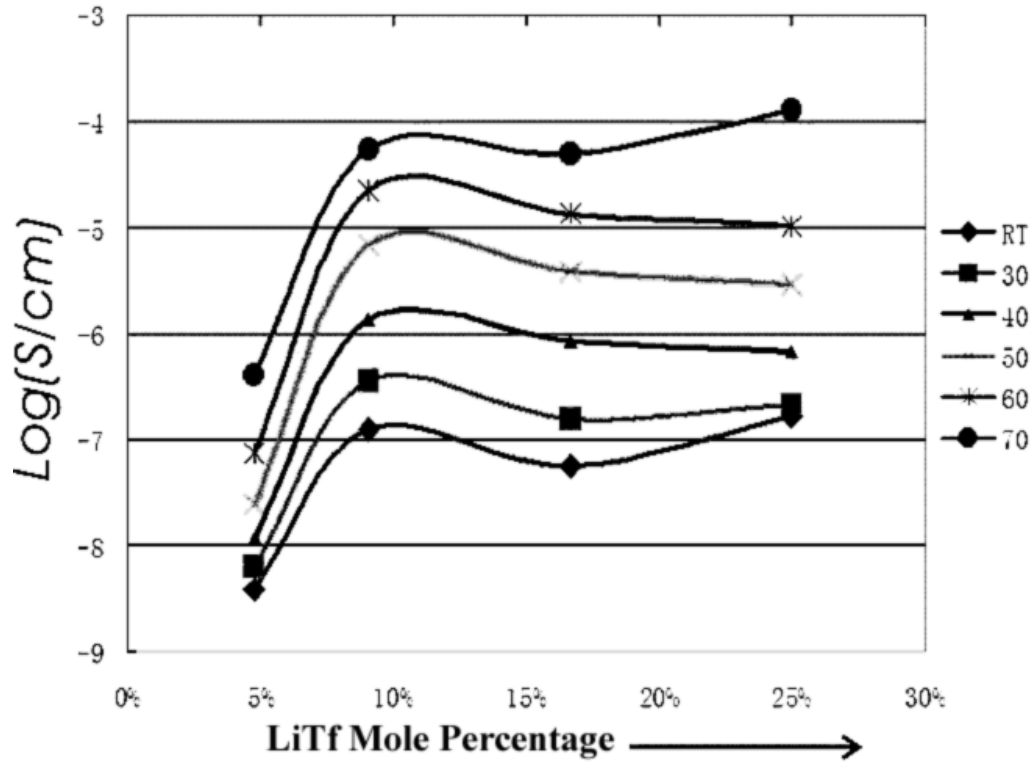


Figure II-17: Salt Concentration Dependent Ionic Conductivity of LPPI-LiTf, X-axis

represents the molar percentage between LiTf and the sum of LiTf and polymer repeat units

conductivity remains relatively stable within the experimental error. Based on the percent amorphous and crystalline domains composition data of LPPI-LiTf estimated from DSC, the initial increase of the conductivity is due to the increase in the amount of the amorphous domain. At some concentration between 10:1 and 5:1, the polymer electrolyte is completely amorphous and the conductivity reaches a maximum. When more salt is added, the conductivity decreases a little but not much due to the decrease of ionic mobility.

Conclusions and Future Directions:

A vibrational spectroscopic study and thermal analysis shows that the LPPI-LiTf electrolytes are heterogeneous, depending on the salt concentration. When there is no salt, highly ordered crystalline LPPI domains dominate. At some concentration between 0.1 mole and 0.2 mole LiTf per mole of LPPI repeat units, LPPI is completely transformed into amorphous domains and the polymer structure is disrupted into two distinct amorphous domains. As shown by the analysis of the ionic association of triflate in LPPI-LiTf, the ionic association states do not substantially change during the whole transformation process. At all temperatures, conductivities increase with salt concentration until the PE is completely transformed into amorphous phase, and then reach a plateau. After that, conductivity will decrease a little due to the decrease of ionic mobility with increasing salt concentration. Therefore, the ionic conductivity of LPPI-LiTf system likely results from a combination of relatively constant speciation (charge carrier concentration) and strongly thermally activated mobility. This conductive behavior perfectly fits the proposed domain transformation process.

In comparison with LPEI, the ionic association is the key factor behind all the behavior differences. LPEI changes coordination states with LiTf depending on salt concentration, while LPPI does not. The different ionic association is due to the extra backbone carbon of LPPI, which may allow the formation of some relatively stable local structures that stand against any change in salt concentration. Analysis (infrared and X-ray) of a crystal formed from the proper model compound and LiTf would be extremely helpful and important in understanding this unique coordination behavior of LPPI. Unfortunately, a crystal has not been grown.

Experimental:

Common reagents and solvents were commercially available and used as received unless noted. NMR was obtained using a Varian 300 spectrometer.

Synthesis of LPPI

2-Ethyl-5,6-dihydro-4-H-1,3-oxazine was prepared by a one pot cyclization reaction from 3-amino-1-propanol and propionitrile. The resulting monomer was characterized by NMR and agreed with literature.⁶¹ Freshly distilled benzyl bromide (0.009 g, 0.05 mmol) was added to 6.06 g (53.6 mmol) distilled 2-ethyl-5,6-dihydro-4-H-1,3-oxazine, which was purged with argon gas beforehand. The reaction mixture was sealed in a polymerization tube and placed in an oil bath at ~130 °C for 48 h. The resulting polymer was precipitated 2 times from a minimal amount of CH₂Cl₂ by adding the solution dropwise, and with stirring, into dry diethyl ether. The final precipitate was dried under reduced pressure (5.83 g, 96% yield). IR and ¹H-NMR of the product were consistent with literature values.⁴¹ GPC of the linear poly(2-ethyl-5,6-dihydro-4-H-1,3-oxazine) showed it to be of intermediate molecular weight: Mw 10,500, Mn 3000, PD 3.5, peak MW 13,900.

Linear poly(2-ethyl-5,6-dihydro-4-H-1,3-oxazine) (5.83, 51.6 mmol repeat units) was dissolved in 400 mL aqueous 3M HCl and heated to reflux solvent for 5 days. The solvent was removed under reduced pressure and the residue was dissolved in 200 mL hot H₂O. The resulting solution was carefully neutralized by addition of aqueous NaOH to pH >9, allowed to cool down to room temperature, and kept at room temperature for 12 h. The precipitate was collected by filtration through a glass frit and redissolved in 100 ml hot H₂O. This process was repeated several times until the filtrate was completely neutral. Air-drying of the filter cake for

24 h was followed by drying at ~65 °C for 48 h under reduced pressure. A brittle and highly crystalline light yellow solid (2.15 g, 73% yield) was obtained: IR (discussed in text) and $^1\text{H-NMR}$ (D_3COD : 2.68 (t, 4H) and 1.75 (quintet, 2H).⁴¹ Assuming no MW degradation during the hydrolysis, the resulting LPPI has an average degree of polymerization of ca. 53.

Preparation of polymer electrolytes

Anhydrous LiTf and anhydrous tetrabutylammonium triflate (TBATf), both obtained from Aldrich, were dried under reduced pressure at ~120 °C for 24 h. Anhydrous methanol was redistilled and stored over molecular sieves. LPPI was prepared as described above and verified to be water free by IR spectroscopy. All the materials were stored, and all the manipulations were conducted, in an argon-atmosphere glovebox (VAC, $\leq 1\text{ppm H}_2\text{O}$) at room temperature. Desired ratios of LPPI and LiTf were dissolved in anhydrous methanol and stirred for 24 h before casting as films. The compositions of the LPPI-LiTf samples are described as nitrogen to cation ratio (N:M^+). LPPI-LiTf samples were prepared at 3:1, 5:1, 10:1, 15:1 and 20:1 compositions.

FT-IR spectroscopy

All IR samples were directly cast onto zinc selenide windows from the solutions described above and were dried under argon purge for 24 h. Infrared spectra were recorded with a Bruker IFS66V FT-IR spectrometer under vacuum (10 mbar) over a temperature range of 20-70 °C at a 1cm^{-1} spectral resolution. Analysis of the spectral data was performed using a commercially available program (Thermo Galactic, Grams/32, version 7.0).

Differential scanning calorimetry

Samples were cast onto Teflon[®] and dried under argon for 24 h in a glove box. Samples of

10-15 mg were transferred to and sealed in an aluminum DSC pan. DSC data were collected using a Mettler DSC 820 calorimeter and were analyzed using a commercial program (STAR[®] version 6.10).

Complex impedance

LPPI-LiTf samples were cast onto a 12.5 mm stainless steel electrode from the solutions described above. The solvent was allowed to evaporate in an argon-atmosphere glovebox for 24 h and for 12 h under reduced pressure. The samples were sandwiched with another stainless steel electrode in an airtight conductivity cell, which was maintained at the desired temperature using a water bath.

Complex impedance data were recorded over a frequency range of 5 Hz to 10,000 Hz with an HP 4192A LF impedance analyzer with LABVIEW[™] 5.1 software. For all the PPI-LiTf samples, conductivity data were collected from 20 to 70 °C in 10 °C increments. All the measurements were conducted during two heating/cooling cycles to check for any significant hysteresis effects. Impedance plots were fitted using LEVM version 7.1. The ionic conductivity measurements were repeated once with freshly made samples and the statistical analysis of the error was not performed. The repeated data was generally no greater than a half order of magnitude off from the initial measurement. After the conductivity measurements were performed, IR spectroscopy was used to verify the dryness of the samples. However, samples can only be claimed to be solvent free within the detection limit of IR. Other errors include human error and instrumental error.

CHAPTER III

LINEAR POLY(N-METHYLPROPYLENIMINE)

Introduction:

LPPI, as well as LPEI, has strong hydrogen bonding interactions, which affect the morphology of the polymers and the speciation of salts within them. Methyl substitution for the hydrogen atoms on the secondary nitrogen of LPEI gives LPMEI, which has no hydrogen bonding. LPMEI was first synthesized using the Eschweiler-Clarke methylation reaction in late 1970s by different research groups.^{64, 65} Excess formalin and formic acid were heated to reflux with LPEI. The reaction mixture was acidified by HCl and the resulting LPMEI-HCl was purified by extraction, dialyses, or ion-exchange. Based on previous publications, anion exchange appears to be the most efficient method.

LPMEI has been investigated and characterized as a polymer electrolyte host.^{37, 52, 66} LPMEI is a light brown, viscous liquid which exhibits poor mechanical properties, even at the molecular weight of 114,000. LPMEI is reported to be hygroscopic and soluble in many solvents such as methanol, ethanol, chloroform, acetonitrile, dimethylformamide, tetrahydrofuran, and benzene.⁵¹ LPMEI forms a solid hydrate, which has one H₂O per four repeat units.⁶⁸ Previous research on LPMEI is limited. Tanaka *et al.* studied LPMEI-LiTf and LPMEI/lithium perchlorate (LiClO₄) systems and reported that LPMEI-LiTf was more conductive than LPMEI/ LiClO₄ by about an order of magnitude. However, LPMEI-LiTf was less conductive than the corresponding LPEI at low salt concentration (~15:1, N:Li⁺).^{52, 66}

Our research group has synthesized high molecular weight LPMEI (ca. 115,000 MW) and investigated LPMEI-LiTf systems.³⁷ This research showed that LPMEI-LiTf had a higher

conductivity than LPEI-LiTf at low salt concentration and LPEI-LiTf had a higher conductivity than LPMEI-LiTf at moderate to high salt concentrations. Evidence was presented that cation-anion interaction was a key factor in the conductive behavior of LPMEI-LiTf systems, resulting in aggregate formation and local ordering of the system at moderate to high salt concentrations.³⁷ Because of conductivity and mechanical property issues, LPMEI does not perform as well as needed for a solid state polymer electrolyte. There is room for improvement on LPMEI-based systems. For instance, LPMEI can be crosslinked by a di-halides or bis-triflates to form materials that do not melt up to 100 °C.⁶⁷

Similarly, linear poly(N-methylpropylenimine) (LPMPI) could be synthesized using the Eschweiler-Clarke methylation reaction. LPMPI can be viewed as either a sidechain-modified LPPI or as a backbone-modified LPMEI. However, the synthesis of LPMPI has never been reported and thus has not been studied as a polymer electrolyte host. In this chapter, the synthesis of LPMPI and its performance as a polymer electrolyte host in comparison with LPMEI, particularly focusing on changes in polymer backbone conformation and the differences in ionic speciation, will be discussed.

Results and Discussions:

LPMEI was synthesized from LPPI, following the route shown in **Figure III-1**. LPPI prepared in Chapter II (ca. 3,000 MW) was heated with excess formic acid and formalin to reflux for 12 h. Concentrated HCl was added to the reaction mixture to break down paraformaldehyde and to protonate LPMPI. The resulting LPMPI ammonium chloride salt was neutralized by ion exchange. Removal of solvent gave LPMPI, a highly viscous pale yellow

liquid. The yield is almost quantitative.

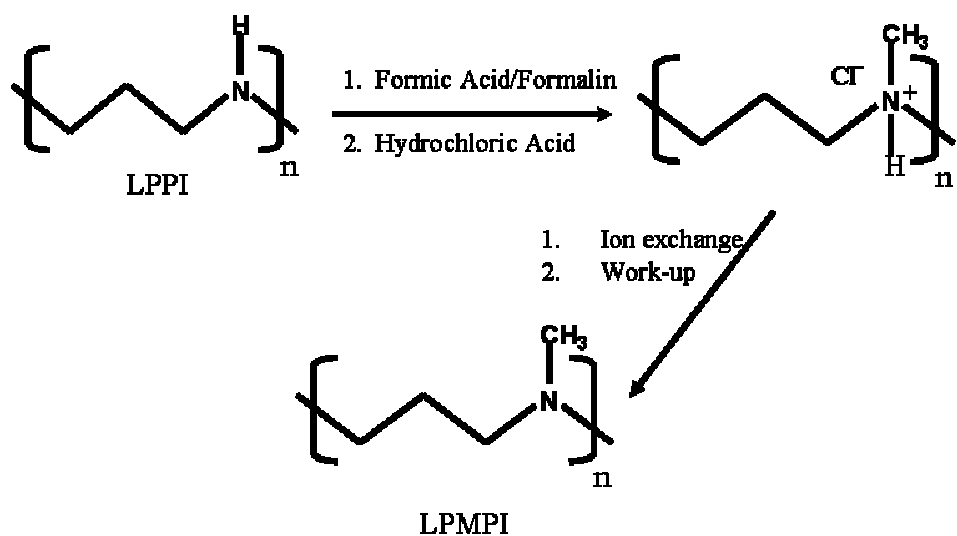


Figure III-1: Synthesis of LPMPI

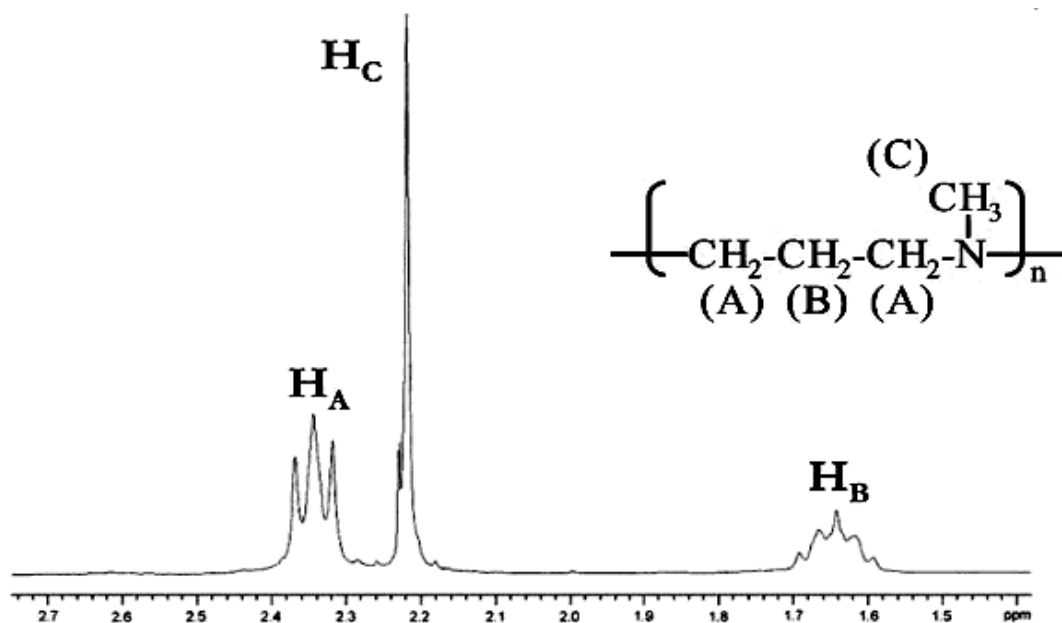


Figure III-2: 300 MHz ^1H NMR of LPMPI in CDCl_3

The ^1H NMR spectrum of LPMPI possesses a triplet centered at 2.34 ppm (N-methylene protons, 4 H), a singlet centered at 2.21 ppm (N-methyl protons, 3H), and a quintet 1.64 ppm

(C-methylene protons, 2 H). The splitting patterns are very clear and reasonable (**Figure III-2**).

The absence of N-H stretching bands in the IR spectrum ($3200\text{--}3300\text{ cm}^{-1}$) of LPMPI indicates complete methylation of the backbone nitrogen. IR spectra of neat LPMPI and LPMEI are shown in **Figure III-3**. Since neither system is able to hydrogen bond on its own, there is a great deal of similarity between the IR spectra of the two, except in a few regions.

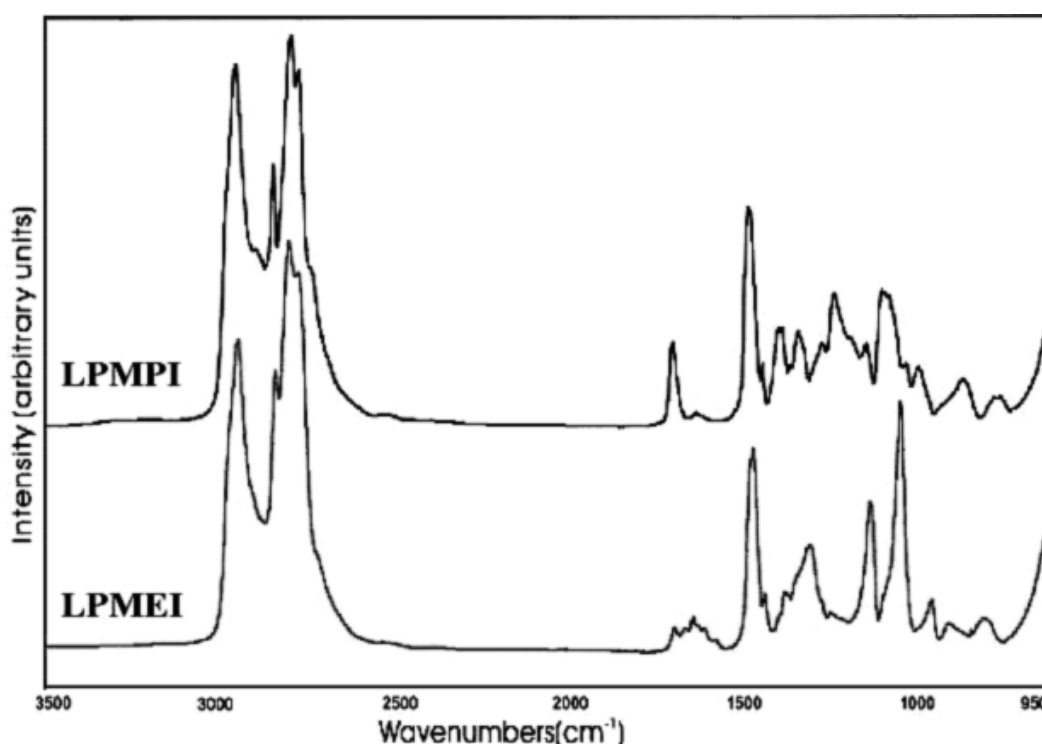


Figure III-3: IR Spectra of Neat LPMPI and Neat LPMEI

DSC data indicate the behavior of the LPMPI and LPMEI systems is similar. Neat LPMPI has a glass transition temperature (T_g) of $-88\text{ }^{\circ}\text{C}$, while neat LPMEI displays a T_g of $-93\text{ }^{\circ}\text{C}$. A melting point (T_m) was not observed for either system above the $-150\text{ }^{\circ}\text{C}$. As shown in **Figure III-4**, with the addition of lithium triflate salt, the T_g of LPMEI-LiTf system increases gradually with salt concentration, shifting nearly $80\text{ }^{\circ}\text{C}$ to $-14\text{ }^{\circ}\text{C}$ at the 5:1 N:Li⁺ composition, while the

LPMPI-LiTf system changes only about 60 °C to -28 °C at the same salt concentration. In either system, the change of T_g is relatively small and suggests that, for the most part, these methylated polyamine systems are amorphous domains and do not change dramatically with salt concentration. Since neither of the two systems form freestanding solids, they both have physical property issues as polymer electrolytes unless crosslinked.

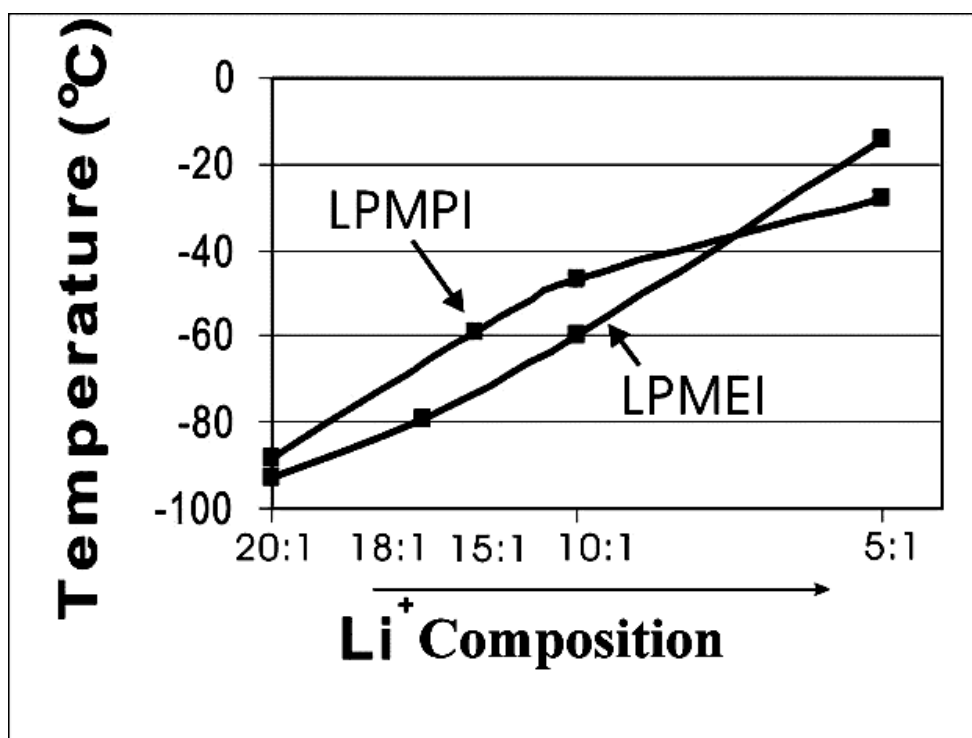


Figure III-4: Glass transition temperatures LPMEI and LPMPI as a function of LiTf concentration

Temperature dependent IR scans were performed on LPMPI samples at elevated temperatures. **Figure III-5** shows the region (1150-1550 cm^{-1}) of the IR spectra of neat LPMPI at room temperature and at ten-degree intervals from 30 °C to 80 °C. The uppermost spectrum of the figure was collected at room temperature after allowing the sample to cool from

80 °C. Below 40 °C, there are almost no changes in the spectrum of the neat material. From 40 °C to 60 °C, the spectra indicate notable changes. By 60 °C these shifts appear to be

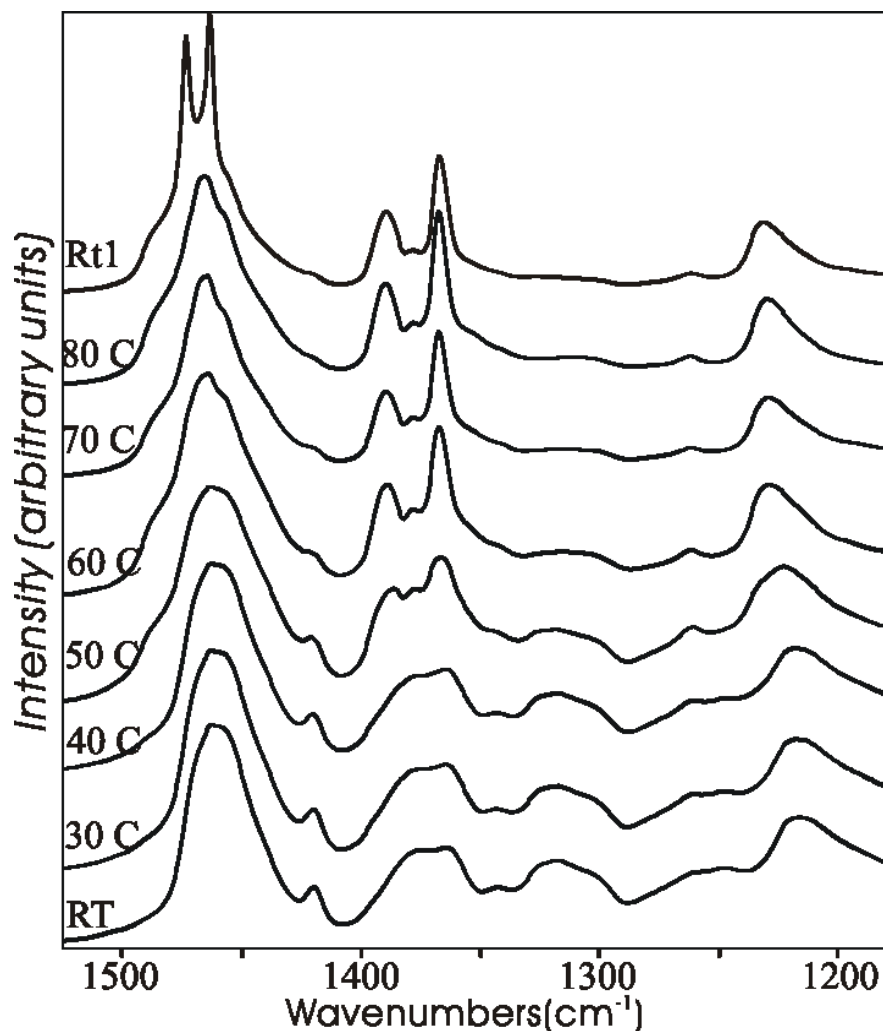


Figure III-5: IR spectra of LPMPI-LiTf in region ($1150\text{--}1550\text{ cm}^{-1}$) as a function of temperature. All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm^{-1} .

stabilized. Upon cooling, some areas of the spectrum return to their initial room temperature states. However, some of the changes experienced at higher temperatures are retained.

The addition of salt to PMPI, effectively removes all IR temperature dependence up to $80\text{ }^{\circ}\text{C}$.

In each salt composition, 20:1, 10:1, and 5:1, the initial room temperature spectrum shows virtually no change with the addition of heat or with cooling back to room temperature. This suggests that some energetically favorable local structure are obtained with the addition of salt and effectively locked into place, so that heating does not result in a significant change in structure. This behavior is not unexpected, since LPMEI also shows negligible temperature dependence with salt addition.³⁷

The IR regions for the symmetric SO_3 bend ($\delta_s\text{SO}_3$) around $630\text{-}650\text{ cm}^{-1}$, the symmetric CF_3 deformation ($\delta_s\text{CF}_3$) around $750\text{-}760\text{ cm}^{-1}$, the symmetric SO_3 stretch ($\nu_s\text{SO}_3$) around 1050 cm^{-1} , and the asymmetric CF_3 stretch ($\nu_{as}\text{CF}_3$) around 1170 cm^{-1} were studied for the salt concentration dependent ionic speciation in LPMPI-LiTf systems and were compared to those in the LPMEI-LiTf systems.

Figure III-6 shows the comparison between LPMPI-LiTf and LPMEI-LiTf in the region of the $\delta_s(\text{CF}_3)$ (triflate ion CF_3 symmetric deformation mode). In the LPMPI-LiTf system, the presence of a band at 762 cm^{-1} suggests an aggregated species. That the band does not move toward a lower frequency with increasing salt concentration further substantiates the aggregation claim. Increase of salt concentration sharpens the band and results in a slight shoulder at 751 cm^{-1} , indicating that while free ion never constitutes majority specie, aggregate specie is strongly favored with salt addition. The LPMPI-LiTf system is overall more aggregated than the LPMEI-LiTf system in this region. In the LPMEI-LiTf, no speciation changes are evident in this region since the $\delta_s\text{CF}_3$ band appears narrow and symmetric at 758 cm^{-1} in the 20:1 system and remains so up to 5:1. Oddly enough, from the results of curve fitting, the ionic speciation slightly shifts to higher wave numbers, indicating the shift to more

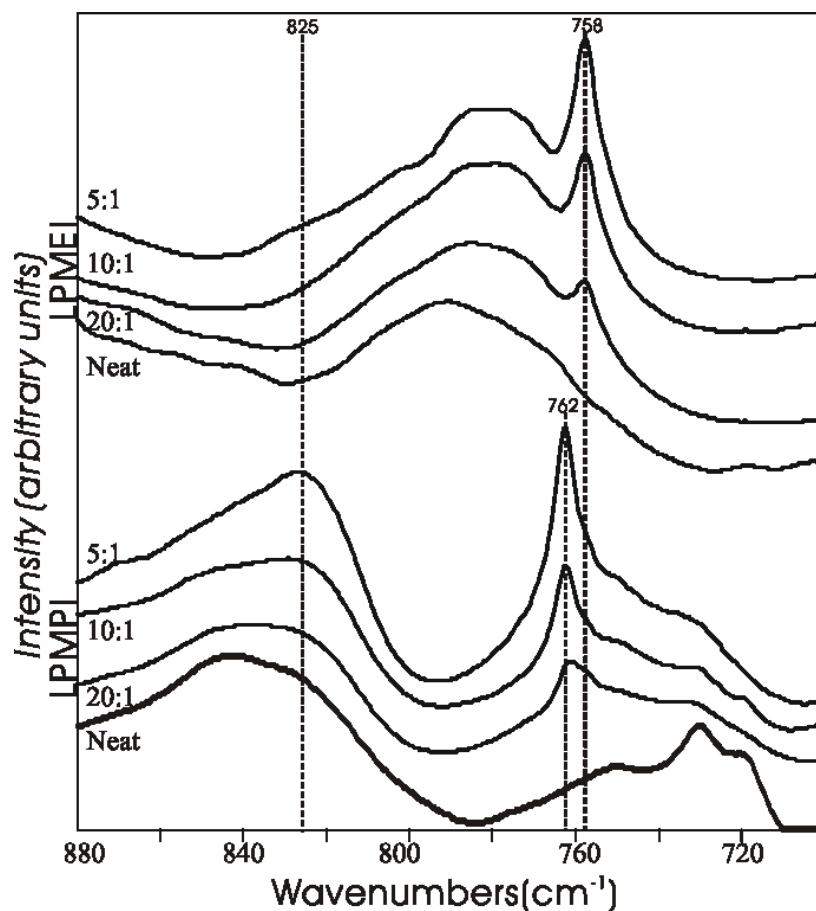


Figure III-6: IR spectra of LPMEI-LiTf and LPMPI-LiTf in $\delta_s(\text{CF}_3)$ region ($700\text{--}880\text{ cm}^{-1}$). All spectra are scaled by normalizing the intensity of the C-H bands from $2900\text{ to }3100\text{ cm}^{-1}$.

aggregated species with increasing salt concentration.⁶⁸ Also in **Figure III-6**, the polymer backbones of both LPMPI and LPMEI appear to be affected by the interaction with Li^+ as indicated by the changes in the regions around 825 cm^{-1} and 785 cm^{-1} , respectively.

As shown in **Figure III-7**, the $\delta_s(\text{SO}_3)$ (triflate SO_3 symmetric deformation mode) region also indicates large independence of salt concentration in ionic speciation in the LPMEI-LiTf system. Here, the band appears at 638 cm^{-1} with a shoulder at 630 cm^{-1} , both of which steadily grow with increasing salt concentration. However, the ionic speciation of the LPMPI-LiTf

system appears to have some salt concentration dependence. The $\delta_s(\text{SO}_3)$ band appears narrow and mostly symmetric at 639 cm^{-1} and grows in both intensity and breadth with added salt stretching to 645 cm^{-1} by 5:1, indicating an increase in the more aggregated species. Again, the LPMPI-LiTf system seems to display a higher degree of ionic aggregation than the LPMEI-LiTf system.

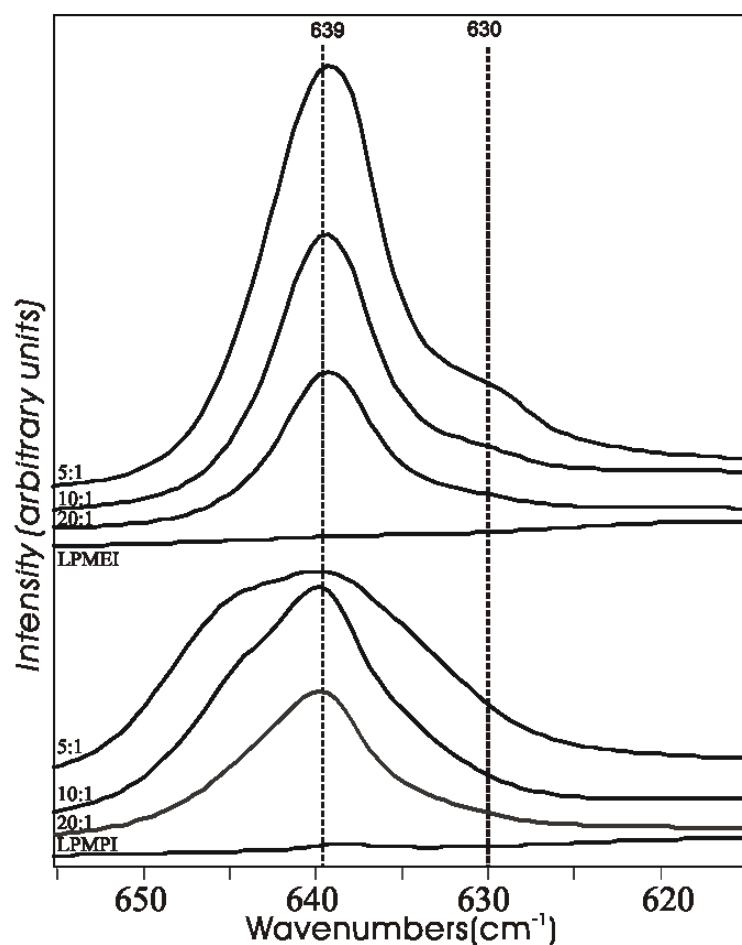


Figure III-7: IR spectra of LPMEI-LiTf and LPMPI-LiTf in $\delta_s(\text{SO}_3)$ region ($600\text{--}660\text{ cm}^{-1}$). All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm^{-1} .

This trend is reinforced the comparison between LPMPI-LiTf and LPMEI-LiTf in the $\nu_s(\text{SO}_3)$ (triflate ion SO_3 stretching mode) and $\nu_{\text{as}}(\text{CF}_3)$ (triflate ion CF_3 asymmetric stretching

mode) absorption regions (**Figure III-8**). In the $\nu_{as}(\text{CF}_3)$ region, neither system exhibits concentration dependent speciation, but the LPMPI-LiTf system with a band centered at 1172

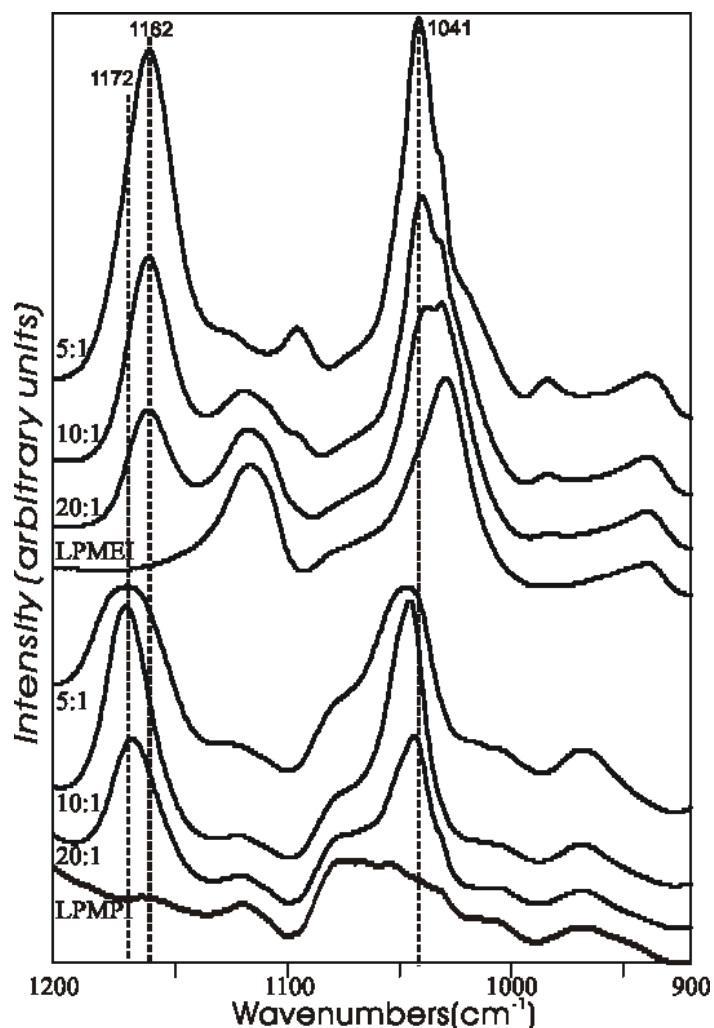


Figure III-8: IR spectra of LPMEI-LiTf and LPMPI-LiTf in $\nu_s(\text{SO}_3)$ & $\nu_{as}(\text{CF}_3)$ regions (1000-1200 cm^{-1}). All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm^{-1} .

cm^{-1} appears to contain more highly aggregated species than the LPMEI-LiTf system with a band at 1162 cm^{-1} . This is also observed in the $\nu_s(\text{SO}_3)$ region. While the LPMEI-LiTf systems display no obvious concentration dependence of ionic speciation, it does seem to contain overall

less aggregated species than the LPMPI-LiTf system. The $\nu_s(\text{SO}_3)$ band of LPMEI-LiTf at 1041 cm^{-1} indicates contact ion pair while the higher frequency of the same band in LPMPI-LiTf suggests higher aggregation. In the LPMPI-LiTf system, this band first appears narrow and peaking at 1043 cm^{-1} in the 20:1 sample. It steadily increases in intensity and breadth with increasing salt concentration, peaking at 1045 cm^{-1} and 1046 cm^{-1} in the 10:1 and 5:1 samples respectively.

An interesting, possible polymer backbone band is found in the region from 1550 cm^{-1} to 1750 cm^{-1} . **Figure III-9** shows this IR region of neat LPMPI and LPMPI-LiTf complexes at

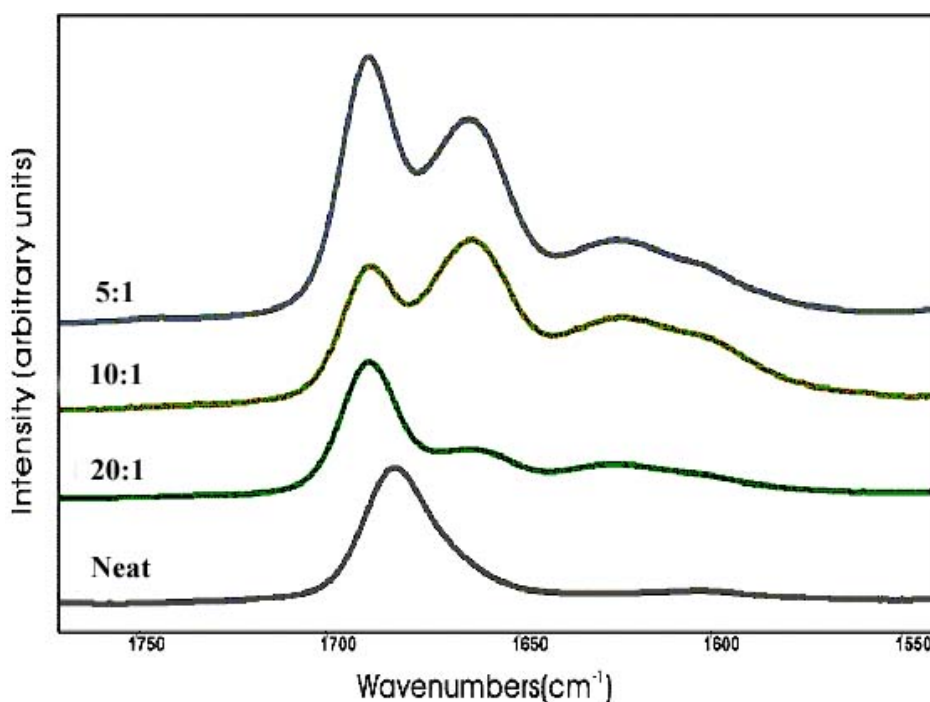


Figure III-9: Unidentified LiTf sensitive IR bands in LPMPI-LiTf IR spectra at various LiTf compositions

20:1, 10:1, and 5:1. In this region, the IR pattern is very sensitive to the LiTf concentration. This vibrational band has never been studied. The exact assignment of this band is not available.

However, it must be a result of the addition of methyl groups to the backbone nitrogen because this band is absent in the LPPI IR spectra. This band is highly unlikely caused by the carbonyl groups in the residual formalin from Eschweiler-Clarke reaction because neither the formalin hydrogen signal in ^1H -NMR nor the carbonyl carbon signal in ^{13}C -NMR is detected. Therefore, it is possibly a side-chain N-CH_3 band and the interesting splitting pattern may be caused by the inductive effect of lithium to nitrogen. In the IR of LPMEI-LiTf, there is also a small band in the same region. However, the splitting pattern is not sensitive to LiTf concentration as that of LPMPI-LiTf system.

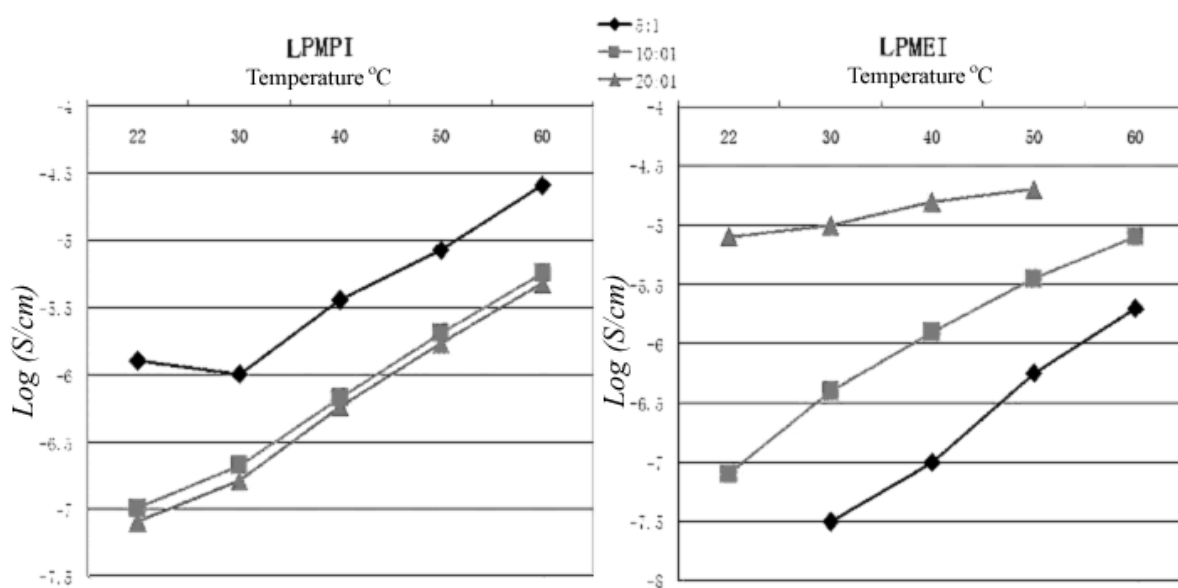


Figure III-10: Ionic conductivity of LPMPI-LiTf and LPMEI-LiTf as a function of LiTf composition and temperature.

A preliminary study of the conductivity of the LPMPI-LiTf system at various salt concentrations: 20:1, 10:1, and 5:1 were conducted, but the measurements have not been repeated. Comparison of the conductive behavior of LPMPI-LiTf to LPMEI-LiTf is laying the

groundwork for further investigation. The preliminary conductivity results of LPMPI-LiTf and LPMEI-LiTf are shown in **Figure III-10**. Similar magnitudes of conductivity, but opposing behaviors are observed for the two systems. The LPMEI-LiTf conductivity decreases with increasing LiTf concentration, while the conductivity of LPMPI-LiTf increases. In the LPMEI-LiTf system, as shown by DSC data, the addition of salt makes the backbone stiffer by the coordination between backbone nitrogen and lithium cation, which consequentially decreases the ion mobility. The ion speciation also suggests the decrease of ionic mobility. As a result, conductivity of LPMEI-LiTf system decreases with increasing salt concentration. In the LPMPI-LiTf system, the ionic mobility should decrease with increasing salt concentration by an amount close to that of LPMEI-LiTf system as indicated by thermal analysis. However, the 20:1 and 10:1 composition sample seems to have conductivity of same magnitude while the 5:1 sample has conductivity about two orders of magnitude higher. This result is surprising and further conductivity measurement and investigation are undergoing by my collaborator: Rachel Mason.

Similar to the comparison between the LPMEI-LiTf system and LPEI-LiTf system, the LPMPI-LiTf system has less crystallinity than the LPPI-LiTf system because of the elimination of hydrogen bonding. As expected, the non-hydrogen bonded polyamine systems are observed to have greater conductivities than the corresponding hydrogen bonded polyamine systems at room temperature. However, they exhibit different trends at higher temperature. **Figure III-11** and **Figure III-12** show the conductivity data of LPPI-LiTf, LPMPI-LiTf, LPEI-LiTf, and LPMEI-LiTf at room temperature and 50 °C, respectively. At room temperature, the conductivities of LPPI-LiTf and LPEI-LiTf initially increase with salt concentration and then

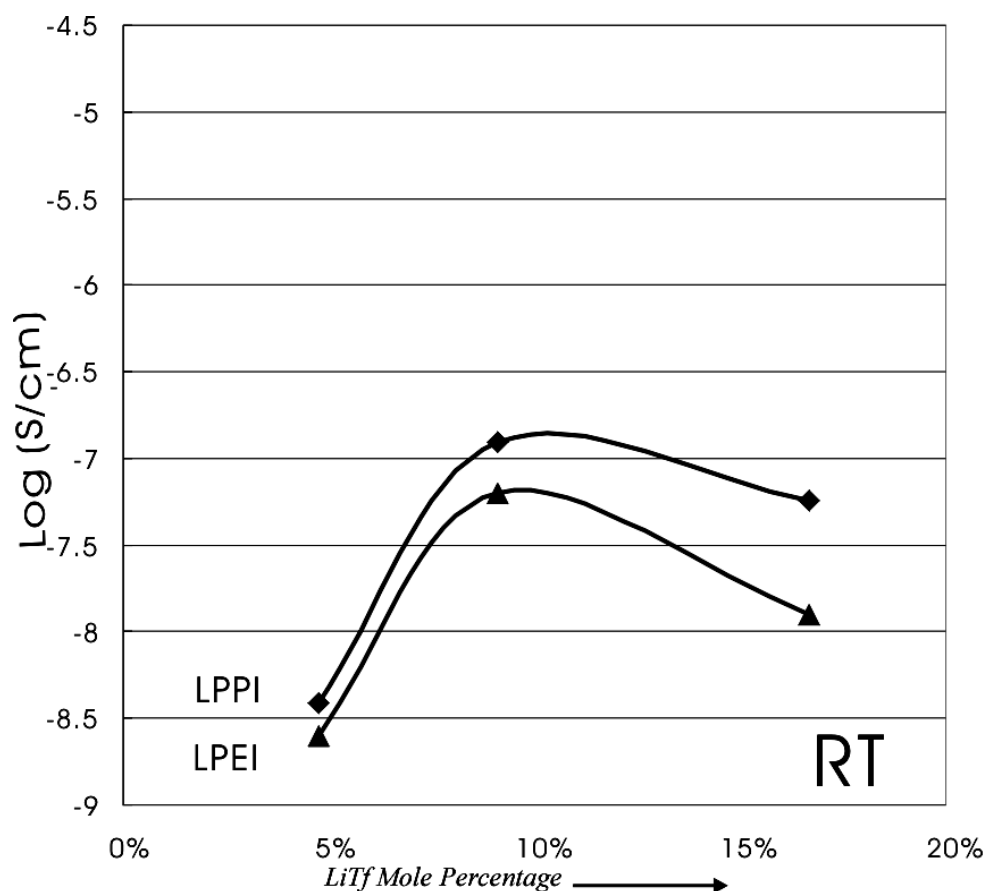


Figure III-11: Conductivity of LPPI-LiTf, LPMPI-LiTf, LPEI-LiTf, and LPMEI-LiTf as a function of LiTf concentration at room temperature

reach their maximum conductivity, followed by conductivity decrease, possibly due to the formation of more aggregate species, which are either non-conductive (ion pair) or have poor ionic mobility (aggregate). The conductivity behaviors of LPMPI-LiTf and LPMEI-LiTf are different. The shape of the LPMEI-LiTf the room temperature salt-dependent conductivity curve is like an upside-down bell, indicating better conductivity at both higher and lower salt concentration. The conductivity of LPMPI-LiTf increases with salt concentration. However, at 50 °C, the conductivity of LPMEI-LiTf decreases almost linearly with increasing salt

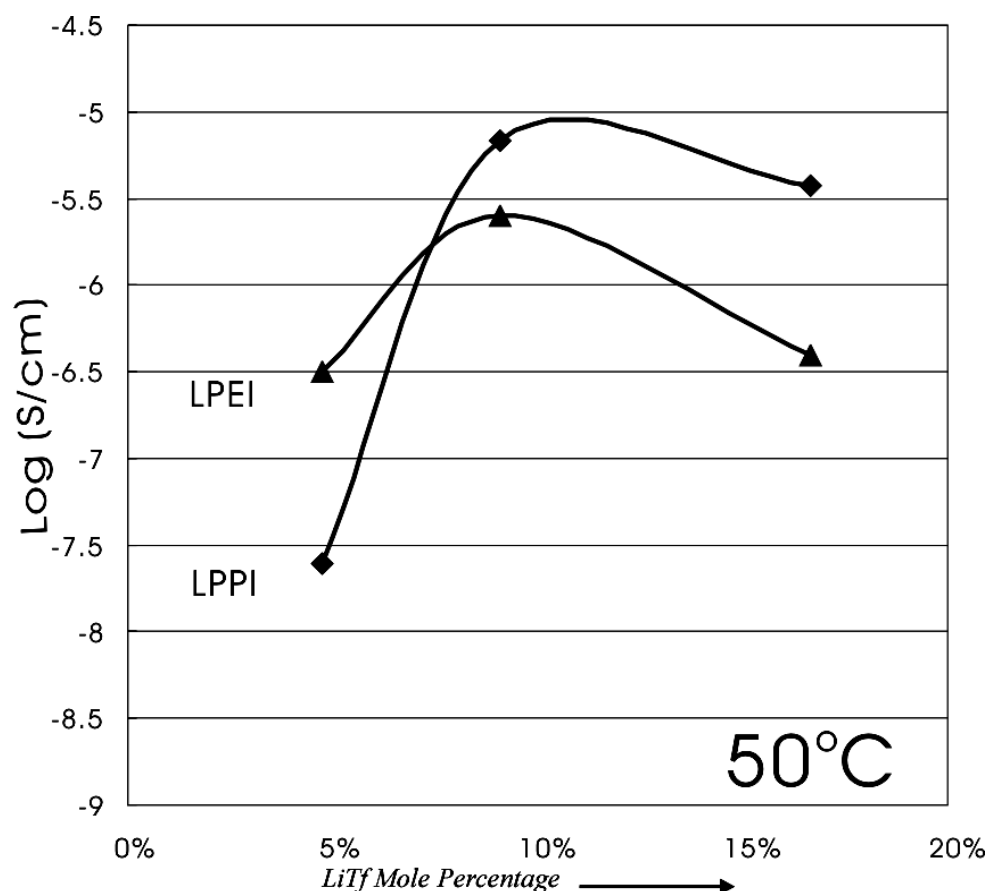


Figure III-12: Conductivity of LPPI-LiTf, LPMPI-LiTf, LPEI-LiTf, and LPMEI-LiTf as a function of LiTf concentration at 50 °C

concentration, while the conductivities of LPPI-LiTf, LPMPI-LiTf, and LPEI-LiTf have almost the same salt dependent conductivity trends. The complete comparison of conductivity above the melting temperatures of the polyamines, which is about 60 °C, is unavailable because of the lack of LPMEI conductivity data in this temperature range. The salt concentration dependent conductivities of LPPI-LiTf, LPMPI-LiTf, and LPEI-LiTf at 70 °C are shown in **Figure III-13**. At this temperature, the LPEI-LiTf system behaves as the LPMEI-LiTf system does at 50 °C, indicating that the hydrogen bonding in LPEI is totally disrupted and has no effect on ionic

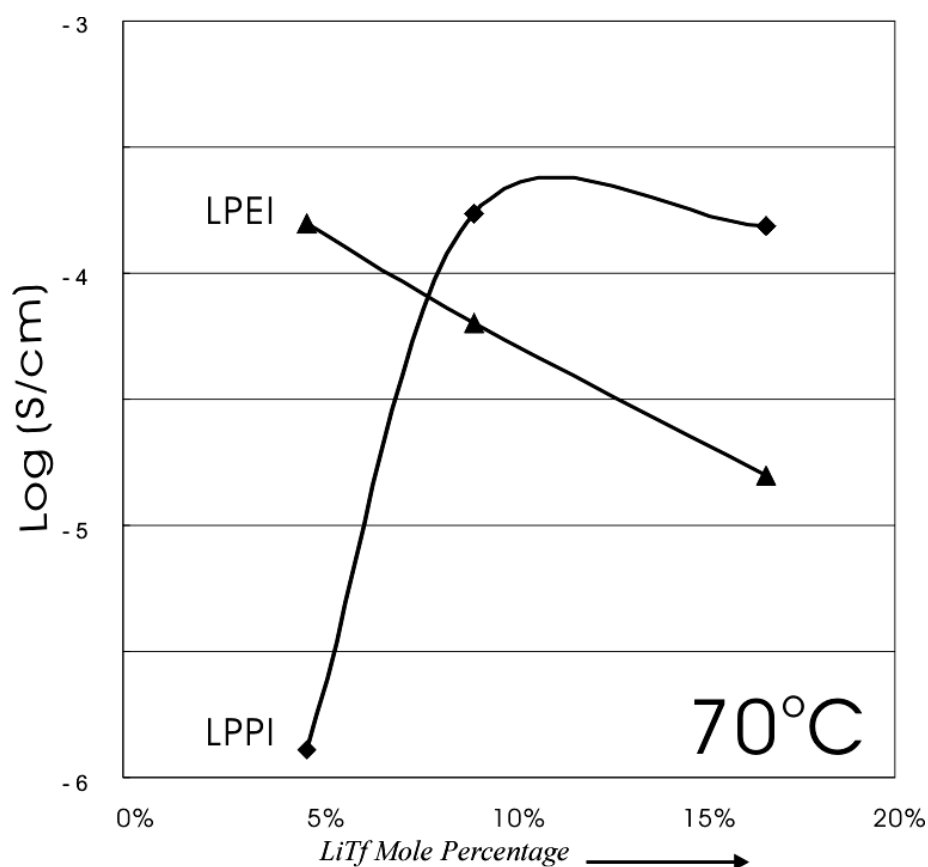


Figure III-13: Conductivity of LPPI-LiTf, LPMPI-LiTf, and LPEI-LiTf at a function of LiTf concentration at 70 °C

conductivity. However, the LPPI-LiTf and LPMPI-LiTf systems still behave as they do at room temperature and 50 °C, suggesting the possible six-member-ring local structures formed by the polymer backbone and Li^+ are fairly stable against heat, thus limiting the ionic mobility.

Conclusions and Future Directions:

LPMPi was successfully synthesized, as proven by NMR. The LPMPi-LiTf system was spectroscopically compared to the LPMEI-LiTf system. The LPMPi-LiTf system is non-crystalline over a wide temperature range. The T_g of LPMPi based system ranges from -88

$^{\circ}\text{C}$ for neat polymer to -28°C for 5:1 N:Li $^{+}$. In LPMPI-LiTf complexes, Li $^{+}$ appears to interact with the polymer backbone and most ionic speciation bands indicate more aggregated species than LPMEI-LiTf system. Both LPMPI-LiTf and LPMEI-LiTf systems have similar thermal behavior. Their conductivity are in the same magnitude. Contrary to the decrease of LPMEI-LiTf conductivity with increasing LiTf concentration, the conductivity of LPMPI-LiTf increases with increasing LiTf concentration.

The LPMPI-LiTf system is still under investigation by our research group. In order to obtain a better understanding of the relationship between polymer electrolyte performance and structural modification in polyamine system, the conductivity, the salt concentration dependent IR, and temperature dependent IR should be examined in greater detail and be compared with the LPEI, LPPI, and LPMEI data. Meanwhile, a further spectroscopic study of LPMPI based system using RAMAN technique could be very helpful in understanding the LiTf sensitive band in the region from 1550 cm^{-1} to 1750 cm^{-1} . A future comprehensive study of the complexes formed by proper model compounds and salts could provide more insight into local structures in the LPMPI-LiTf system. A possible model compound for LPMPI, N,N,N',N'-tetramethylpropyldiamine, is shown in **Figure III-14**. Also, the physical properties of the

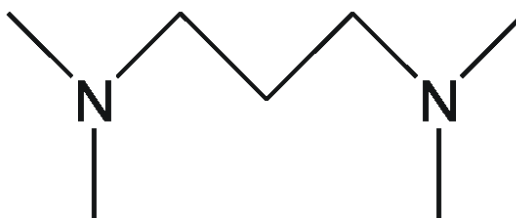


Figure III-14: A Possible Model Compound for LPMPI

LPMPI based systems could be improved by future crosslink experiments using various crosslinkers.

Experimental:

Common reagents and solvents were commercially available and used as received unless noted. NMR was obtained using a Varian 300 spectrometer.

Synthesis of LPMPI

LPPI (around 3.02 g, 0.0530 mol repeat units) was dissolved in 50 mL distilled water. 200 mL of formic acid (88% solution, Aldrich) and 125 mL of formaldehyde (37% solution, Aldrich) were added to the reaction vessel. The solution was heated to reflux solvent for 24 h. The reaction mixture was allowed to cool to room temperature before the addition of 150 mL of concentrated HCl. The solvent, as well as acids and formaldehyde, was removed under reduced pressure. The resulting LPMPI ammonium chloride salt was dissolved in a minimal amount of distilled water. The solution was neutralized by passing through an OH⁻ ion exchange column (DOWEX-2 400). The removal of solvent under reduced pressure gave LPMPI, a highly viscous reddish brown liquid (3.57 g, 0.0503mol). This procedure gave a 95% yield. ¹H-NMR (CDCl₃: 2.34 (t, 4H), 2.21 (s, 3H), and 1.64 (quintet, 2H). Assuming no MW degradation during the Eschweiler-Clarke methylation, the resulting LPMPI has a degree of polymerization of ca. 53.

Preparation of polymer electrolytes

Anhydrous LiTf (Aldrich) was dried under reduced pressure at ~120 °C for 24 h. Anhydrous methanol was redistilled and stored over molecular sieves. LPMPI was prepared as

described above and verified to be water free by IR spectroscopy. All the materials were stored, and all the manipulations were conducted, in an argon-atmosphere glovebox (VAC, ≤ 1 ppm H₂O) at room temperature. Desired ratios of LPMPI and LiTf were dissolved in anhydrous methanol and stirred for 24 h before casting as films. The compositions of the LPMPI-LiTf samples are described as nitrogen to cation ratios (N:Li⁺).

FT-IR spectroscopy

All IR samples were cast directly onto zinc selenide windows from the solutions described above and were dried under argon purge for 24 h. Infrared spectra were recorded with a Bruker IFS66V FT-IR spectrometer under vacuum (10 mbar) over a temperature range of 20-70 °C at a 1 cm⁻¹ spectral resolution. Analysis of the spectral data was performed using a commercially available program (Thermo Galactic, Grams/32, version 7.0).

Differential scanning calorimetry

Samples of 10-15 mg were cast into aluminum DSC pan and dried under argon for 24 h in a glove box. Samples were then placed under vacuum at room temperature for 12 h before being sealed. DSC data were collected using a Mettler DSC 820 calorimeter and were analyzed using a commercial program (STAR[®] version 6.10).

Complex impedance

LPMPI-LiTf samples were cast onto 12.5 mm stainless steel electrodes from the solutions described above. The solvent was allowed to evaporate in an argon-atmosphere glovebox for 24 h and for 12 h under reduced pressure. The samples were sandwiched with another stainless steel electrode in an airtight conductivity cell, which was maintained at the desired temperature using a water bath.

Complex impedance data were recorded over a frequency range of 5 Hz to 10,000 Hz with an HP 4192A LF impedance analyzer with LABVIEWTM 5.1 software. Data were collected from 20 to 70 °C in 10 °C increments. Impedance plots were fitted using LEVM version 7.1. The ionic conductivity measurements were not repeated. After the conductivity measurements were performed, IR spectroscopy was used to verify the dryness of the samples. However, samples can only be claimed to be solvent free within the detection limit of IR. Other errors include human error and instrumental error.

CHAPTER IV

CROSSLINKED BRANCHED POLY(N-ALLYETHYENIMINE)

Introduction:

As discussed in Chapter One, many heteroatom-containing polymers have been studied in the research on solid state polymer electrolytes (SPE), which can be used to construct highly flexible and leak-free batteries. These polymers need to be modified to improve their performance. In polyimine based polymer electrolyte research, branched poly(ethylenimine) (BPEI) is a convenient starting material because it is commercially available and inexpensive. However, as mentioned introduction chapter, BPEI is a complicated system with three different categories of nitrogen and not suitable for fundamental study. BPEI is synthesized in large scale by a simple, non-selective ring opening reaction of aziridine.⁴² **Figure IV-1** shows the initiation and propagation steps in BPEI polymerization.

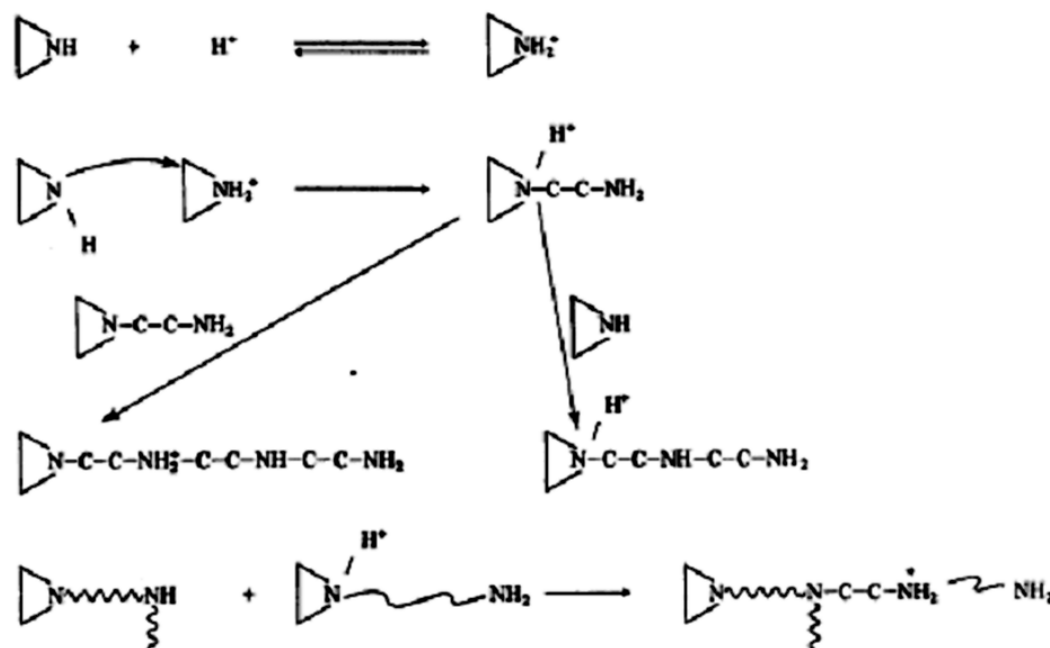


Figure IV-1: Synthesis of BPEI

Although BPEI has a low T_g , the glass transition temperature markedly increases with the addition of salt from (~ -50 °C (neat) to ~ 50 °C (N:Li⁺=4:1))⁴⁸, along with concomitant significant decreases in ionic conductivity. Sometimes, the crystalline complexes formed by BPEI and salt could cause contact problems with the electrodes. A maximum conductivity of 10^{-6} S/cm at 20 °C has been reported for BPEI:LiTf at a 20:1 (N:Li⁺) composition.^{48, 49} Chemically modified BPEI-type dendrimers, poly(propyleneimine) tetrahexacontaamine (DAB-AM-64) and poly(amidoamine) (PAMAM), have been reported by Dillon *et al.*²⁰. The optimum conductivity of complexes formed by these dendrimers and Li[(CF₃SO₂)₂N] ranges from 6.3×10^{-7} S/cm at room temperature to 1.0×10^{-4} S/cm at 100 °C.²⁰ Attempts have been made to improve the physical properties of PEI by chemical modification of the nitrogen and crosslinking through the backbone nitrogen atoms.^{37, 69} Crosslinking by substitution reactions using bifunctional crosslinkers with leaving groups on both ends is one method to improve polymer physical properties;²² however, this method creates charged ammonium moieties that affect ion transportation and ion speciation, that is, the complex equilibrium between various ionic species that may exist in the polymer electrolyte. Therefore, it was desirable to develop a neutral crosslinked SPE host based on commercially available BPEI.

Radical initiated carbon-carbon bond formation may serve as the best means for the synthesis of a neutrally crosslinked BPEI. Allylation of the amine groups in BPEI with allyl bromide, followed by neutralization, gave branched poly(N-allylethylenimine) (BPAEI) (**Figure IV-2**). Effective radical initiated crosslink conditions were determined for this material. Initially, subjective empirical observations of physical properties and dissolution tests were used to evaluate crosslinking of the resulting films. Infrared spectroscopy(IR) and differential

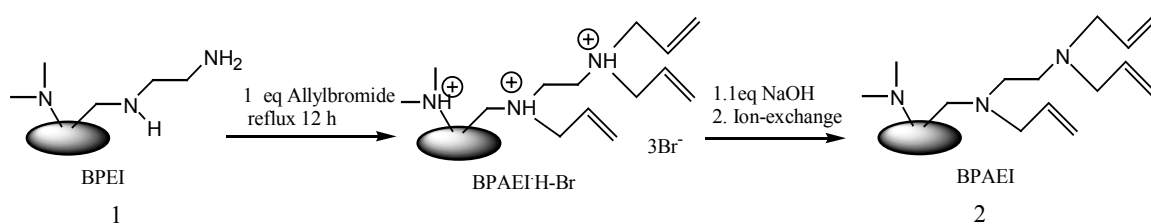


Figure IV-2: Synthesis of BPAEI (with an empirical formula $(-\text{CH}_2\text{CH}_2\text{NH}-)$, BPEI is shown schematically as its exact structure is variable.).

scanning calorimetry (DSC) spectroscopy were used to study crosslinking. IR and conductivity studies of BPAEI-LiTf electrolytes prepared using the effective conditions were performed.

Results and Discussions:

BPEI is a complicated system with primary, secondary and tertiary nitrogen atoms in a ratio of ca. 1:2:1, respectively.^{44, 70, 71} Although its empirical formula is $(-\text{CH}_2\text{CH}_2\text{NH}-)$, BPEI is shown in **Figure IV-2** schematically as its exact structure is variable. **Figure IV-2** does not show the exact structure of BPEI but simply illustrate that there are three types of nitrogen atoms in BPEI. One equivalent of allyl bromide was used to allylate BPEI. The disappearance of the N-H signals in

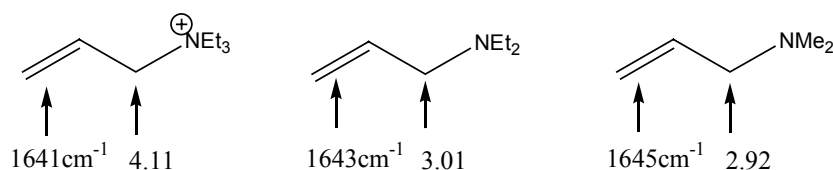


Figure IV-3: ^1H NMR chemical shifts and IR absorption frequencies for model compounds.¹³

BPAEI NMR and IR shows that the substitution is essentially complete. As shown in **Figure IV-3**, the NMR shift of an allyl methylene group α to a tri-substituted nitrogen such as in N,N-diethylallylamine and N,N-dimethylallylamine is around 3.0 ppm, while that of the allyl methylene group α to a tetra-substituted, cationic nitrogen as in allyltriethylammonium iodide is around 4.1 ppm.⁷² The NMR of our BPAEI does not have any signal around 4.1 ppm (see **Figure IV-4**), which is consistent with tetra-substitution of the nitrogen being negligible.

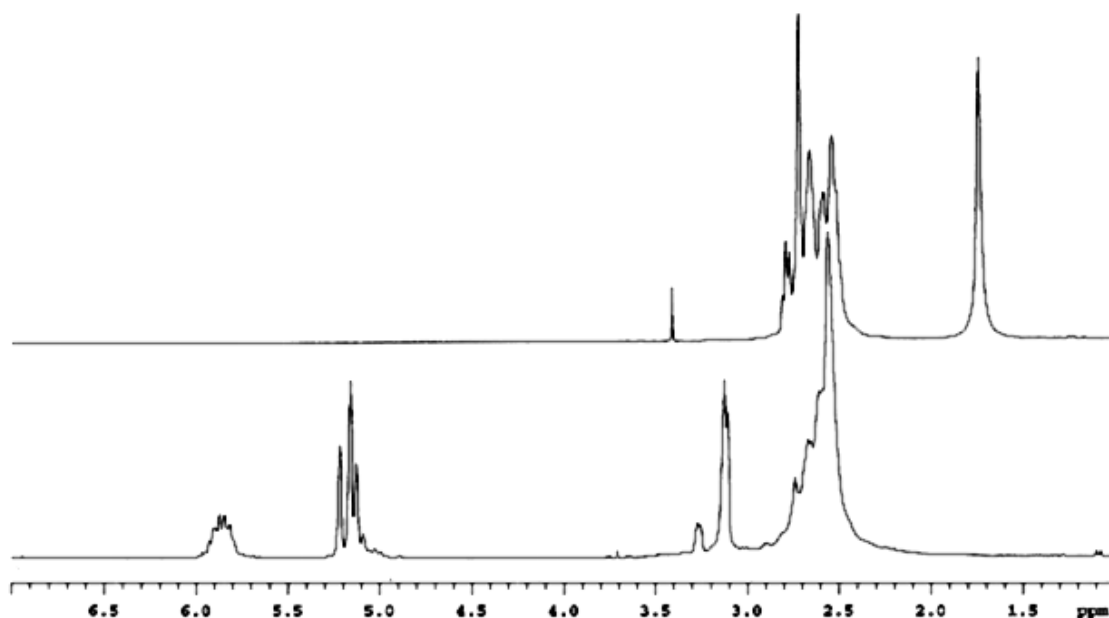


Figure IV-4: 300 MHz ^1H NMR of BPEI (upper) and BPAEI (lower) in CDCl_3 .

As shown in **Figure IV-5**, the more structurally accessible primary nitrogen likely reacts with allyl bromide first. Eventually the original secondary nitrogens are allylated as well. One of the hydrogen atoms on the mono-allylated primary nitrogen could be transferred to the more steric-hindered tertiary nitrogen forming ammonium cations. The resulting primary nitrogen could react with allyl bromide again and form di-allylated amine. The species in this process are

in equilibrium. All the nitrogen atoms are tri-alkylated and protonated at the end of the process. Once neutralized, there are only tertiary nitrogens in BPAEI.

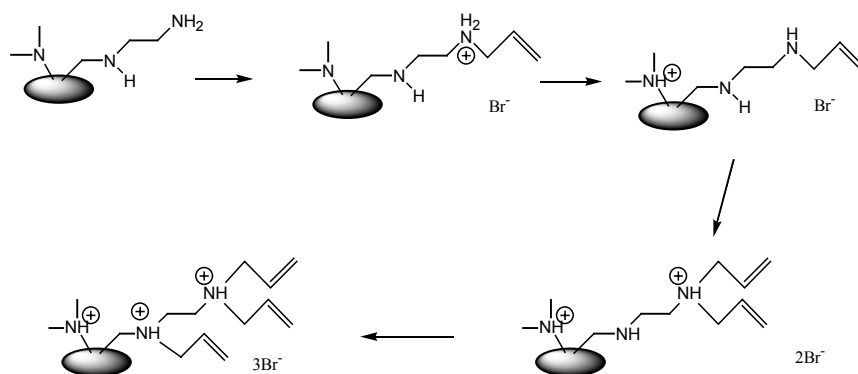


Figure IV-5: Generalized reaction pathway for allylation of BPEI.

BPAEI is an extremely viscous liquid with a light brown color and is soluble in many solvents such as water, benzene, methanol, and chloroform. Measurement of the IR spectrum ($3200\text{--}3600\text{ cm}^{-1}$) of the sample being stored under ambient conditions over a period of a week indicated that BPAEI does not appear to be hygroscopic. Therefore it is possible to manipulate and store BPAEI in the atmosphere. When BPAEI is radically crosslinked, it becomes a light brown, shiny, transparent solid film. Crosslinked BPAEI forms flexible freestanding polymer films with moderate physical strength. The average thickness of the crosslinked BPAEI films was 0.15 mm. Crosslinked BPAEI is not soluble in common solvents. Measurement of the IR spectrum ($3200\text{--}3600\text{ cm}^{-1}$) of the sample being stored under ambient conditions over a period of a week established that the crosslinked BPAEI does not take up water from the atmosphere. Crosslinked BPAEI-LiTf slowly absorbs water that could be removed by heating under reduced pressure. Generally, this method of making the BPEI-based neutral crosslinked polymer electrolyte requires no stringent conditions and, in our experience, can be easily scaled up with

virtually 100% yield.

To optimize the crosslinking of BPAEI, the following initiators were investigated at a 30:1 (N: initiator, molar ratio) initiator composition, a temperature of 80 °C, and times ranging from 12 h to 60 h: VA-061 (dimethyl 2,2-azobisisobutyrate), V-50 (2,2-azobis(2-amidinopropane) dihydrochloride), VA-044 (2,2-azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride), VA-086 (2,2'-azobis [2-methyl-N-(2-hydroxyethyl) propionamide]), AIBN (α,α' -Azobis(isobutyronitrile)), benzoyl peroxide, and V-501 (4,4'-azobis(4-cyanopentanoic acid). Crosslinking attempts in the condensed phase showed that V-50, VA044, V-501, and AIBN gave positive results based on dissolution tests while VA-086 gave very poor results and VA-061 did not work at all. Crosslinking studies in the presence of salt were conducted. The conditions described in the experimental section were used, and the salt (LiTf) concentration was maintained at 10% by weight. The V-50, VA-044, V-501, and AIBN initiators that were successful in crosslinking without salt were used. AIBN needed more than 72 h to form a crosslinked film, while V-501 and VA-044 took 48 h to form crosslinked films. However, V-50 needed only 12 h to form a well-crosslinked film with good physical properties and which could be easily peeled from the glass. None of the other three films could be easily peeled off without being broken into pieces. Therefore, V-50 was used as the initiator for further studies.

The crosslinked films were studied using IR, DSC and conductivity measurements. There was no obvious difference between BPAEI and crosslinked BPAEI in the IR spectrum except in the region from 850 cm^{-1} to 1050 cm^{-1} and the region from 1500 cm^{-1} to 1720 cm^{-1} . **Figure IV-6** shows the V50 concentration dependent IR of crosslinked BPAEI films from 850-1050 cm^{-1} .

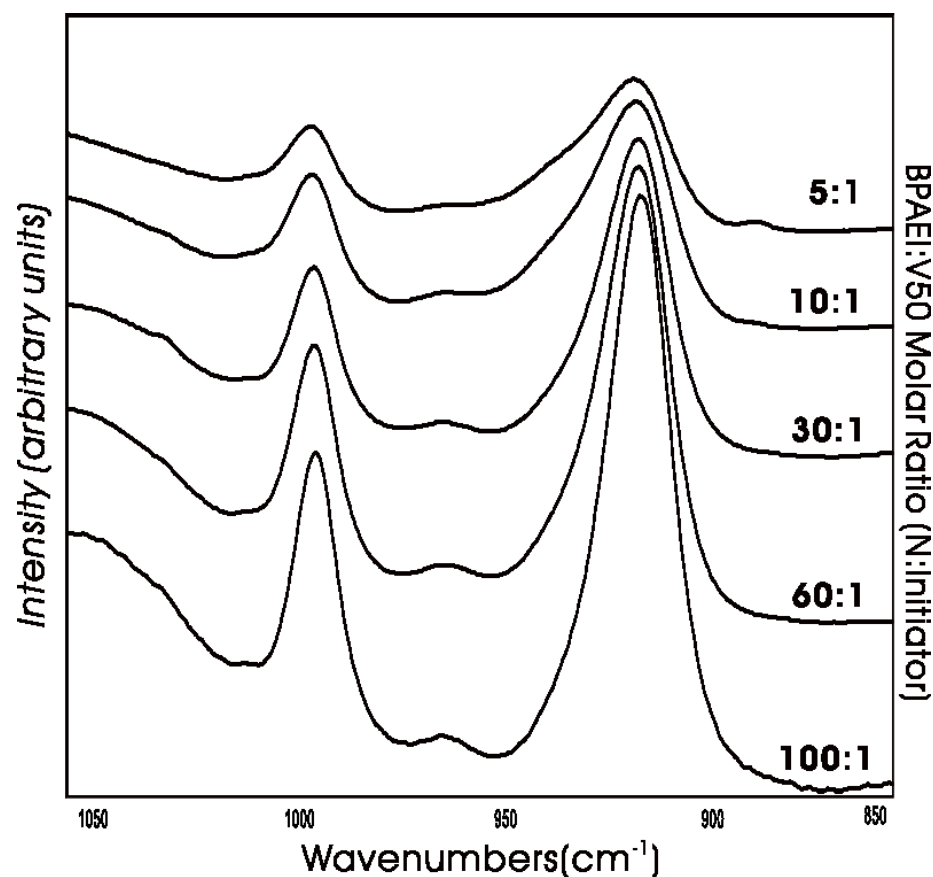


Figure IV-6: IR spectra of crosslinked BPAEI films ($850\text{--}1050\text{ cm}^{-1}$) as a function of V-50 crosslinker composition. All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm^{-1} .

The alkene C-H bending vibration bands⁷³ centered at 995 cm^{-1} and 916 cm^{-1} gradually decrease with the increase of V-50 concentration, although the changes are not as significant as those in the region from 1500 cm^{-1} to 1720 cm^{-1} , which is shown in Figure IV-7.

Figure IV-7 shows the IR spectra of BPEI, V50, BPAEI, and Crosslinked BPAEI with various concentration of V50 in the region from 1500 cm^{-1} to 1720 cm^{-1} . In this region, the band at 1642 cm^{-1} is assigned to the C=C stretching vibration of unconjugated linear alkenes^{16, 17} according to literature⁷³ and the data shown in Figure IV-3,⁷² while the band at 1673 cm^{-1} is

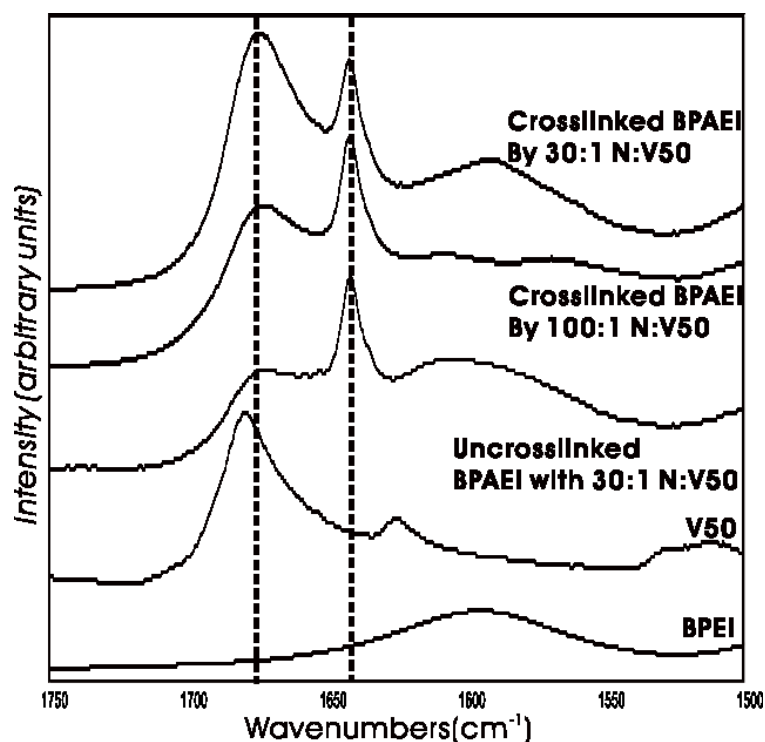


Figure IV-7: IR Comparison of BPEI, neat V-50, BPAEI, and BPAEI films crosslinked using various amounts of V-50. All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm⁻¹.

unidentified. The band at 1673 cm⁻¹ exists intrinsically in the uncrosslinked BPAEI without V-50 present and grows significantly after crosslinking while the initiator concentration is kept constant. The intensity increase of the band at 1673 cm⁻¹ must be related to crosslinking. However, the initiator (V-50) has an IR absorption centered at 1680 cm⁻¹. Due to the small concentration of initiator used in crosslinking, the V-50 band at 1680 cm⁻¹ is unlikely to be observed in the crosslinked BPAEI IR spectrum. Further, the frequency and the intensity of this band do not change when neat V-50 was subjected to the same reaction conditions used to crosslink BPAEI. Therefore, the intensity increase of the band at 1673 cm⁻¹ is not due to the initiator and must come from some structural changes in the polymer during the crosslinking

process. However, at this time it is not possible to assign this band. Therefore, this band may qualitatively indicate presence of crosslinking but cannot quantitatively indicate the crosslink density. The crosslink densities are unknown since there are unreacted C=C bonds after crosslinking as indicated by the presence of alkene vibration bands in Figures IV-6 and IV-7. However, the strength of these films increases with initiator concentration while the swelling decreases, as expected.

Although, the exact crosslink mechanism is unknown, some possible crosslink pathways are discussed below. At first, the free radical is generated by heat and most of it either adds to the double bond⁷⁴ or abstracts an allylic hydrogen, generating an allylic radical. The radical can be rearranged along the sidechain and transferred among the sidechains. Thus, many different radicals could be formed in BPAEI, and only a few possible intermediate radicals are shown in **Figure IV-8**. Finally, intramolecular or intermolecular couplings of these radicals terminate the crosslink reaction. The whole crosslinking process is complex, and unreacted C=C bonds are

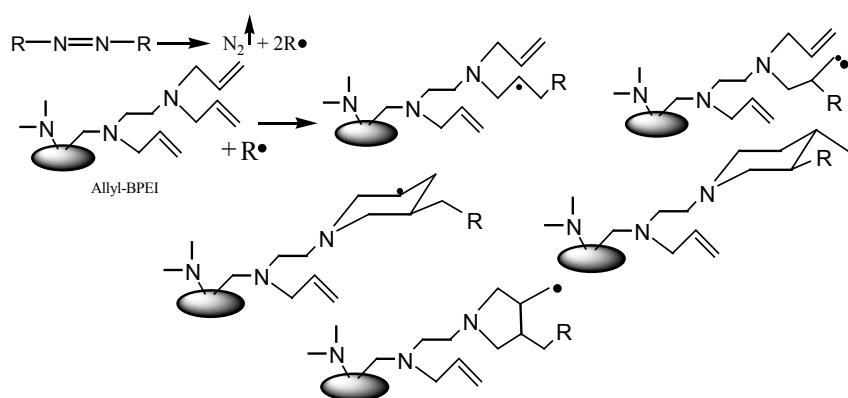


Figure IV-8: Possible radical intermediates in the crosslinking mechanism

(R-N=N-R represents V-50)

still present after crosslinking. In the presence of LiTf, the situation becomes more complicated because LiTf could affect the crosslinking in many different ways. For example,

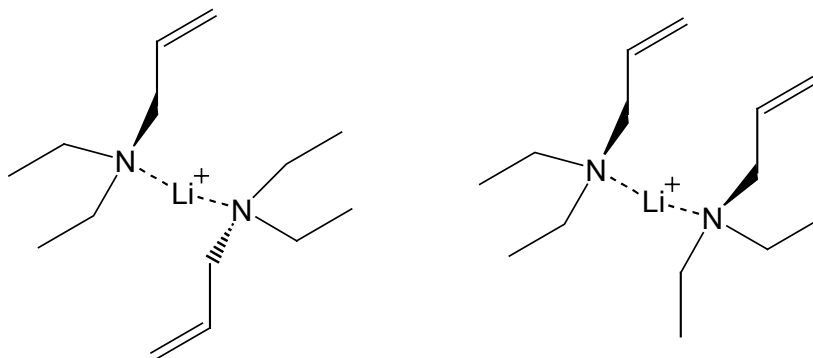


Figure IV-9: Possible local conformational structures in BPAEI-LiTf prior to crosslinking.

Anions are omitted for clarity.

the Li^+ could coordinate to nitrogen atoms in the polymer backbone and form some relatively stable local structures prior to crosslinking. These structures could possibly position the $\text{C}=\text{C}$ bonds on these nitrogen atoms further away from each other or closer to each other (see **Figure IV-9**), thus help or hinder the crosslinking process.

However, IR showed that the band at 1673 cm^{-1} gradually decreased with the increase of LiTf concentration with constant initiator composition (30:1 N:V-50). **Figure IV-10** shows the LiTf concentration dependent IR (the region from 1550cm^{-1} to 1750cm^{-1}) of crosslinked BPAEI-LiTf Films. It is likely that LiTf somewhat suppresses the BPAEI radical crosslinking process.

BPAEI has a glass transition temperature T_g of $-65\text{ }^\circ\text{C}$, which is somewhat lower than the T_g of BPEI ($-50\text{ }^\circ\text{C}$), likely as a result of decreased H-bonding. When BPAEI was crosslinked, the T_g gradually increased with crosslinking initiator concentration, as shown in **Figure IV-11**.

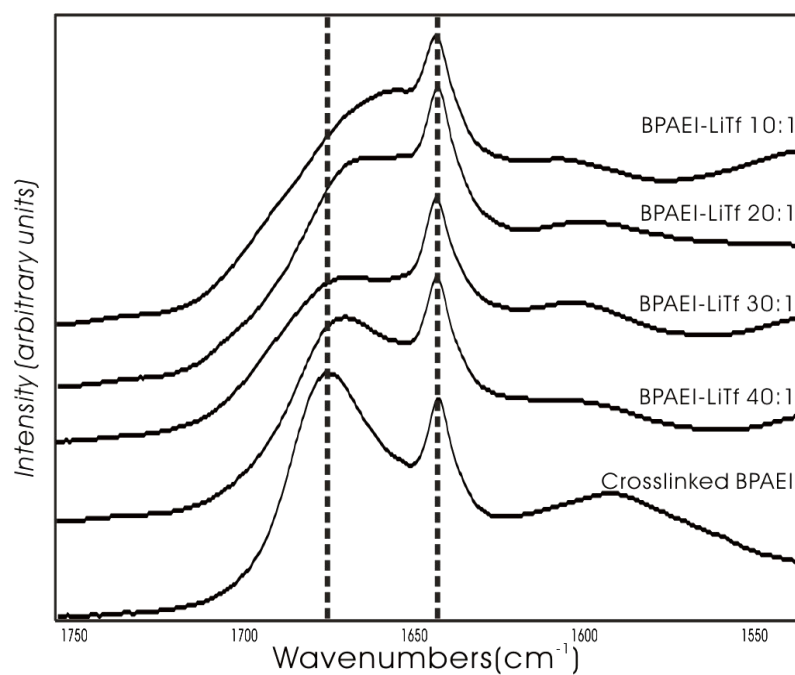


Figure IV-10: Infrared spectra of crosslinked BPAEI-LiTf films with 30:1 N:V-50 at various salt compositions (1550 cm^{-1} - 1750 cm^{-1}). All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm^{-1} .

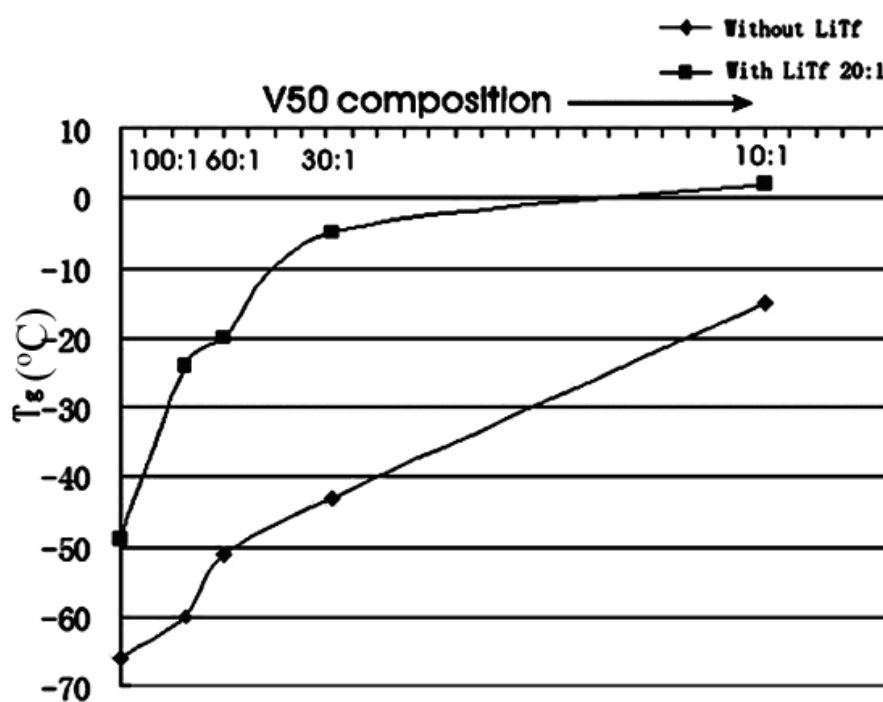


Figure IV-11: Glass transition temperatures of BPAEI and crosslinked BPAEI films as a function of V-50 crosslinker concentration, with and without 20:1 N:LiTf present.

Upon the addition of LiTf, the crosslinked BPAEI films with different V-50 concentration exhibited higher T_g s than the films without LiTf. **Figure IV-12** shows the DSC curves of the crosslinked BPAEI films crosslinked using different amounts of radical initiators while LiTf composition is kept as 20:1. There are two factors likely contributing to the loss of polymer flexibility during the crosslinking process: crosslinking of the polymer chains, which restricts polymer motion, and the coordination between Li^+ and nitrogen atoms in the polymer. In **Figure IV-11**, the lower line represents the T_g of crosslinked BPAEI at different initiator concentration and the top line represents the T_g of crosslinked BPAEI-LiTf (20:1 N: Li^+) at different initiator compositions. In the uncrosslinked BPAEI-LiTf 20:1 (N: Li^+) sample, there

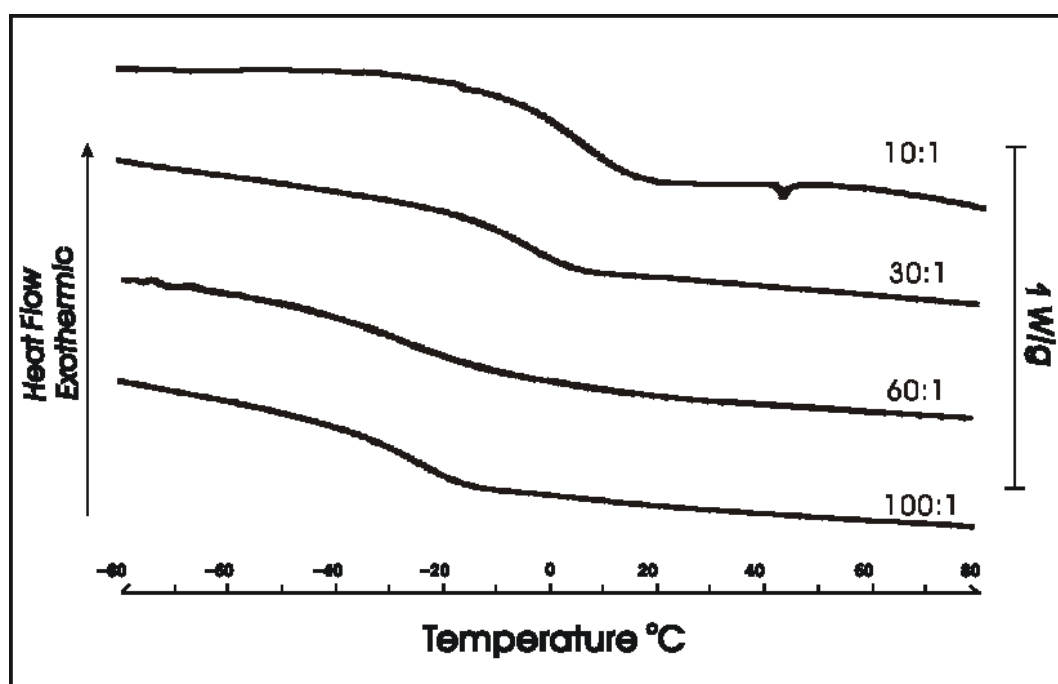


Figure IV-12: DSC curves of crosslinked BPAEI films with 20:1 N:LiTf as a function of V-50 crosslinker composition (100:1, 60:1, 30:1, and 10:1)

is only a contribution from the N-Li⁺ coordination, which causes a T_g increase of 17 °C. In the presence of LiTf, the crosslinking of polymer chains and N-Li⁺ coordination combine synergistically to contribute to the increase of T_g. At the compositions near 60:1 (N:Initiator), unusual changes in the rates of T_g's increasing were observed both with and without LiTf. These samples were remade fresh and same phenomenon was observed reproducibly. This suggests some undefined morphological changes occur in the crosslinked polymer electrolyte around these initiator concentrations.

Figure IV-13 shows the triflate ion SO₃ symmetric stretching ($\nu_s(\text{SO}_3)$) bands at the LiTf concentration from 40:1 to 10:1. This vibrational mode has been extensively examined based in PEO and PEI mixtures with LiTf.^{30, 47} In PEO electrolytes containing LiTf, the bands in the $\nu_s(\text{SO}_3)$ region have been assigned as free ions (1032-1034 cm⁻¹), contact ion pairs (1037-1042 cm⁻¹), and aggregate species (1047-1054 cm⁻¹).^{30, 31} Prior to and after crosslinking, the $\nu_s(\text{SO}_3)$ band appeared at 1030 cm⁻¹. In the crosslinked BPAEI-LiTf films, the $\nu_s(\text{SO}_3)$ band was observed at 1030 cm⁻¹ at all LiTf concentrations, suggesting that most of the triflate ions in crosslinked BPAEI were 'free' ions. At higher salt concentrations, a shoulder at 1040 cm⁻¹ grew, suggesting the existence of small amount of contact ion pairs at higher salt concentrations. The relative concentrations of the various triflate ion species present were fairly independent of salt concentration. IR spectra of BPAEI-LiTf before and after crosslinking showed that the $\nu_s(\text{SO}_3)$ band for the BPAEI-LiTf complexes appeared at 1030 cm⁻¹ and the relative concentrations of the triflate species were unchanged before and after crosslinking. IR spectra of BPAEI-LiTf crosslinked using various initiator concentrations showed that the relative concentrations of the triflate species appeared to be independent of crosslink density.

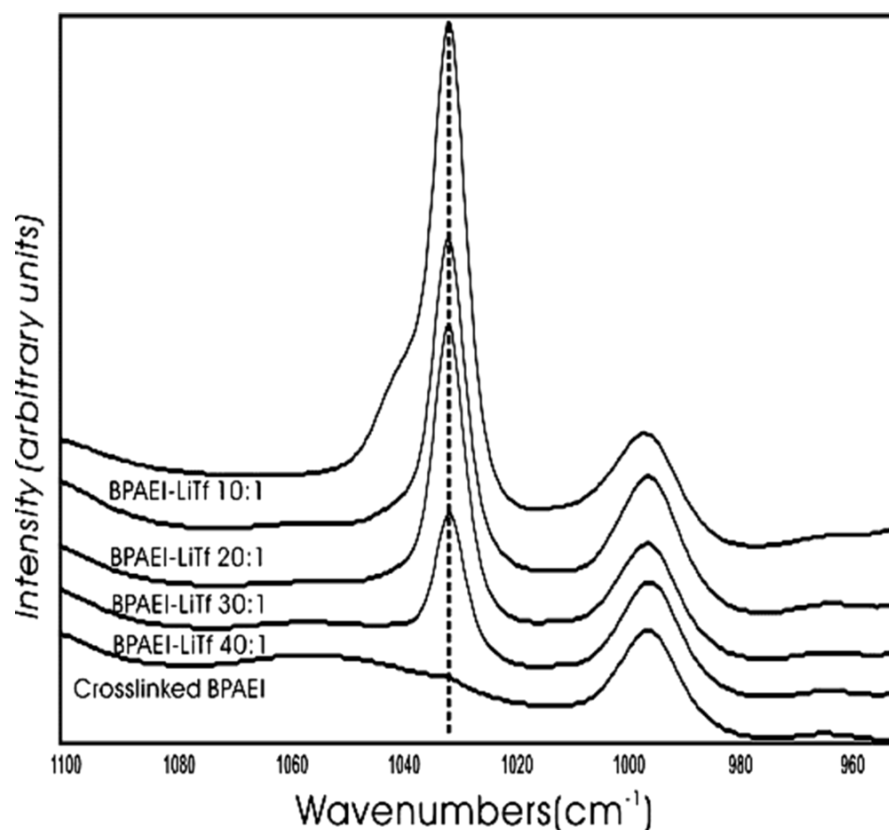


Figure IV-13: LiTf composition dependent IR spectra of BPAEI and BPAEI-LiTf films crosslinked using 60:1 N:V-50. All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm^{-1} .

A preliminary ionic conductivity study at compositions from 40:1 to 10:1 (N:Li⁺) with the polymer repeat unit to initiator ratio kept at 30:1 showed that the 20:1 (N:Li⁺) sample had the best conductivity. Ionic conductivities were measured as a function of initiator concentration to determine the optimum concentration of initiator. In this series of measurements, the LiTf composition was 20:1 (N:Li⁺). For each initiator composition, conductivity samples were individually prepared twice. For each sample, three temperature dependent cycles of measurements were undertaken. After the measurements were performed, IR spectroscopy was

used to verify the dryness of the samples. As shown in **Figure IV-14**, the 60:1 (N:Initiator) sample performed the best reproducibly. The fact that the ionic speciation did not change significantly with crosslink density implies that the number of charge carriers was reasonably constant. Therefore, the decrease of polymer segmental motion due to the formation of crosslinks (as related to the T_g of the films) is expected to decrease the ionic mobility, in turn decreasing the ionic conductivity. This trend was observed in every sample except the 60:1 (N: Initiator) sample. It should be noted that this sample exhibited an unusual thermal behavior in the DSC analysis. It is possible that in this sample there is a change in the morphology of the polymer electrolyte that causes the unusual increase of ion mobility even when the general trend of T_g is still increasing.

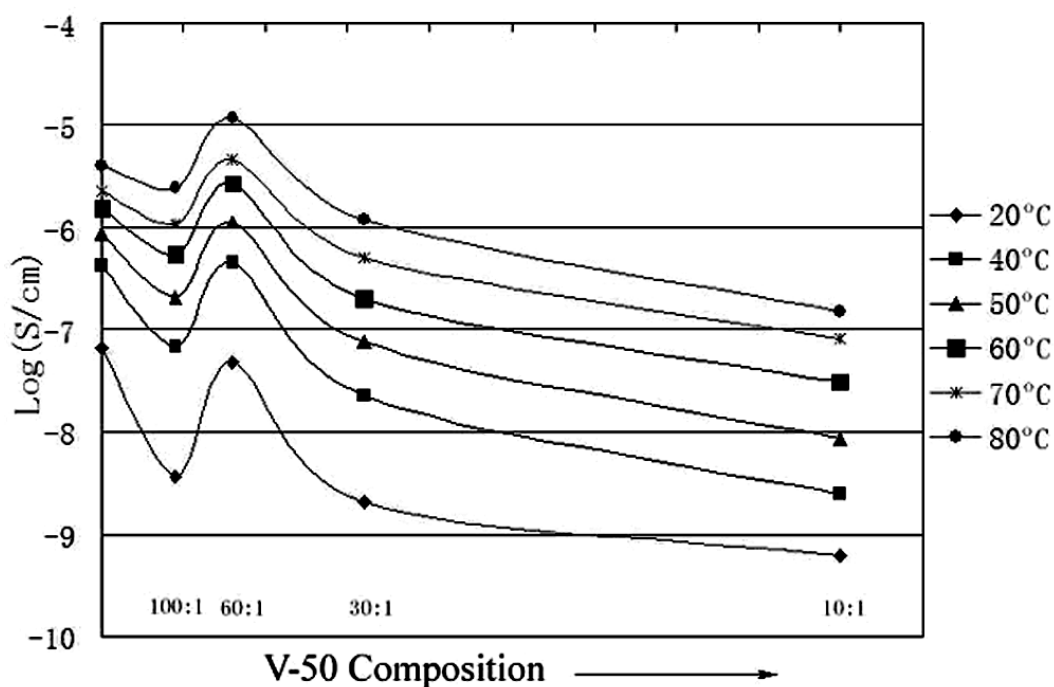


Figure IV-14: Ionic conductivity of crosslinked BPAEI-LiTf films as a function of V-50 concentration and temperature with 20:1(N:Li⁺) LiTf.

Conductivity measurements at temperatures between 20 °C and 80 °C of a series of samples in which the LiTf composition was varied while maintaining the optimum initiator composition (60:1) demonstrated that 20:1 was still the optimum salt composition (**Figure IV-15**). The number density of “free” ions, the primary charge carriers, should increase with increasing salt concentration, and conductivity should increase accordingly. Indeed this is observed at low salt concentration. However, as the salt concentration increases, the increasing number of N-Li coordination interaction decreases the segmental motion of the polymer chains between covalent crosslink sites. This decrease then decreases the ionic conductivity. At some composition between 30:1 and 20:1 these two factors balanced each other and the optimum conductivity is achieved.

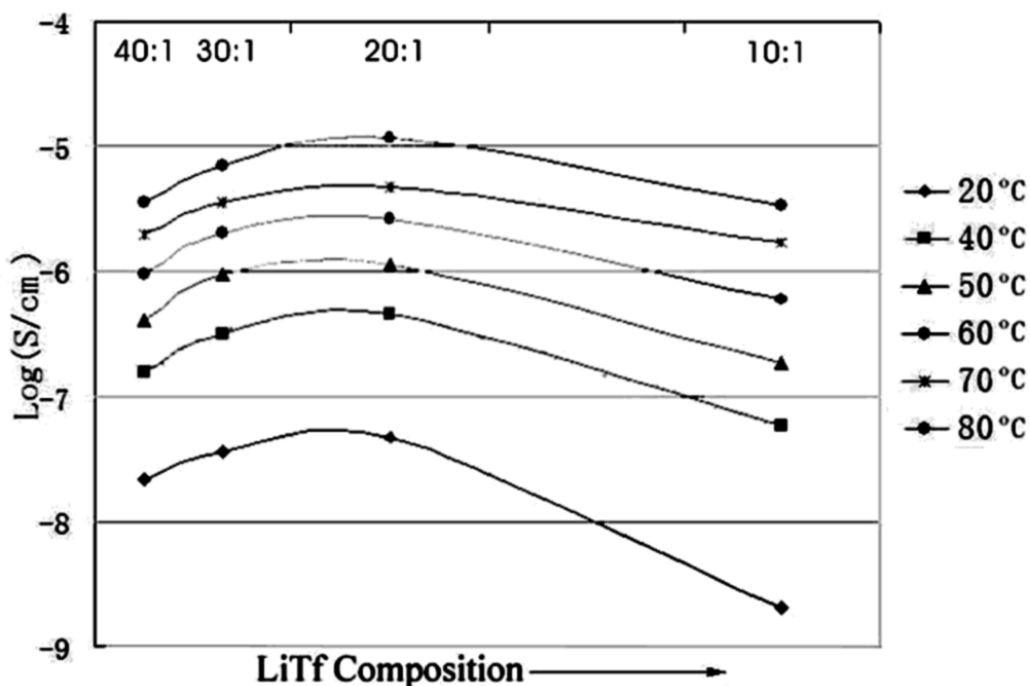


Figure IV-15: Ionic conductivity of BPAEI-LiTf films crosslinked using 60:1 (N:Initiator) V-50 as a function of LiTf concentration and temperature.

At a fixed N:V-50 ratio of 60:1, apparent energies of activation calculated from the temperature dependent conductivity data increased monotonically from 17.8 to 25.8 kcal/mole as a function of increasing LiTf concentration (40:1 to 10:1 N:Li, respectively). The IR data for these samples shows speciation to remain relatively constant as a function of LiTf concentration and temperature (data not shown). Therefore, the increase in the apparent energy of activation is likely due mostly to decreases in ion mobility stemming from morphological changes induced by the presence of LiTf as reflected in the increasing T_g for the samples. At a fixed N:Li ratio of 20:1, apparent energies of activation calculated from the temperature dependent conductivity data 15.7, 22.1, 18.5, 22.0, and 19.9 kcal/mole as a function of increasing cross-linker (V-50) concentration (none, 100, 60, 30, and 10:1 N:V-50, respectively). The IR data for these samples also shows speciation to remain relatively constant as a function of LiTf concentration and temperature. Therefore, the variability in the apparent energy of activation is again likely due mostly to changes in ion mobility stemming from a combination of morphological changes on cross-linking as reflected in the variable T_g for the samples, including the unusual minimum for the 60:1 N:V-50 sample.

In our research, LiTf is commonly used because the speciation signals of triflate anion are well identified based on PEO-LiTf studies.^{30, 31} However, lithium bis(trifluoromethanesulfonyl) imide (LiTfsi) is often used in battery trials because LiTfsi is more stable during the charge and discharge process. Therefore, the conductivity of a crosslinked BPAEI-LiTfsi (N:Li⁺=20:1, N:Initiator=60:1) sample was measured to get an idea of the conductive ability of this new polymer salt combination for the future battery trial. As shown in **Figure IV-16**, crosslinked BPAEI-LiTfsi exhibits lower conductivity than comparably prepared BPAEI-LiTf

from room temperature to 100 °C.

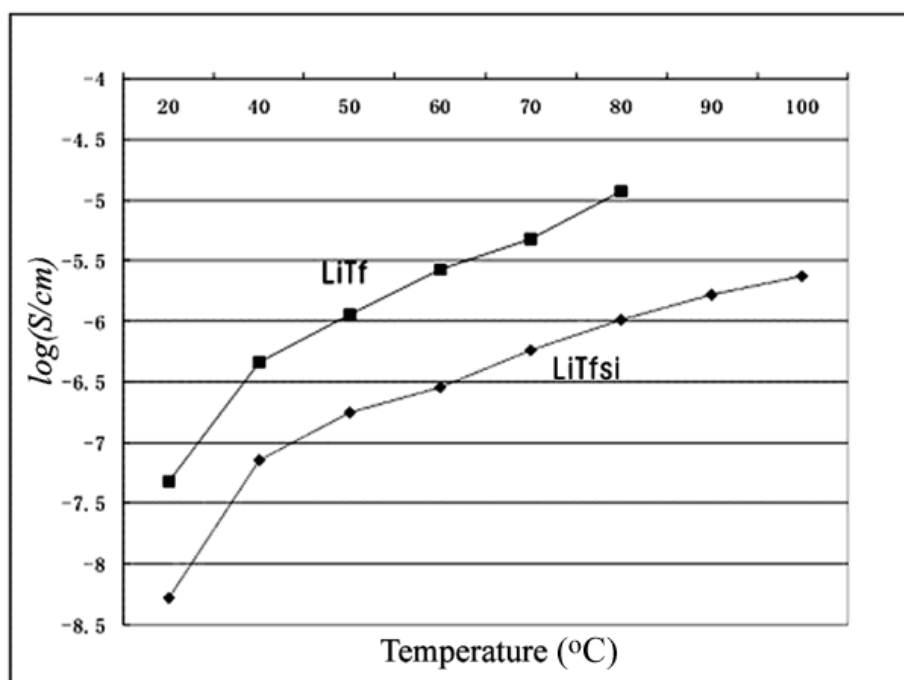


Figure IV-16: Ionic conductivity of BPAEI-LiTf (N:Li⁺=20:1) film and BPAEI-LiTfsi (N:Li⁺=20:1) film crosslinked using 60:1 (N:Initiator) V-50 as a function of temperature.

Conclusions and Future Directions:

BPEI may be allylated to give a polyamine that can be radically cross-linked to form mechanically coherent, freestanding films. With LiTf present during cross-linking, solid polymer electrolytes (SPEs) were formed. Ionic conductivity of these SPEs was a strong function of temperature and morphology resulting from the cross-linking and, to a lesser extent, lithium salt concentration. The conductivity measurements were consistent with spectroscopic studies, which showed that ionic speciation is relatively invariant with cross-link or salt concentration. Thermal studies suggesting that T_g , and therefore ion mobility, is very dependent on both cross-linking and LiTf concentration. Although the salt was present as mostly ‘free’

triflate ions and presumably ‘free’ lithium ions, the overall conductivity was not very good due to the very large increase of the polymer electrolyte rigidity with salt concentration, which is a characteristic of the parent polymer BPEI⁴⁸ and many other polymer electrolyte hosts. However, these SPEs showed a maximum conductivity of ca. 10^{-5} S/cm at 80 °C, the minimum conductivity needed for fabrication of functioning lithium batteries. Cross-linking of allylated PEI-based polymers that have been modified to increase ion mobility is therefore a viable strategy for the formation of useful SPEs.

Construction of a lithium coin cell using crosslinked BPAEI/salt as electrolyte would be an interesting but not very difficult experiment to do. By measuring whether the crosslinked BPAEI based cell is working or how well it is working would provide a practical perspective of this material. Crosslinking the partially allylated BPEI, on which has other functional side-chains grafted, would provide another method of preparing neutral solid state polymers with different functionalities at large scale.

Experimental:

Common reagents and solvents were commercially available and used as received unless noted. NMR was obtained using a Varian 300 spectrometer.

Synthesis of BPAEI

BPEI **1** (10.0 g, 0.233 equivalents, avg. MW ca. 10000, Aldrich) was added to 100 mL HPLC grade methanol, and the reaction vessel was cooled using an ice bath. Allyl bromide (28.2 g, 0.233 moles) was added dropwise while stirring. After warming up to room temperature slowly, the system was heated to reflux solvent for 12 h. Solvent and any excess allyl bromide

were removed under reduced pressure. The residue was redissolved in 100 mL methanol. Sodium hydroxide (9.32 g, 0.233 moles) was added as pellets while stirring and the solvent was heated to reflux for 1 h. After methanol was removed, benzene (100 mL, 50 mL and 50 mL) was used to extract the polymer from inorganic sodium bromide. The benzene was removed under reduced pressure and the polymer was dissolved in 50 mL H₂O. The resulting solution was passed through an OH⁻ ion-exchange column (DOWEX-2 400). Removal of water under reduced pressure gave neutral BPAEI **2** (18.4 g, 0.221 moles). This procedure gave a 95% yield. ¹H-NMR (CDCl₃) δ(ppm) 2.4-2.8 (br, 4 H, backbone CH₂), 3.1 (d, 2 H, sidechain CH₂), 5.3 (t, 2 H, =CH₂), 6.0 (m, 1 H, -CH=). IR (3072cm⁻¹(=CH₂), 1642cm⁻¹(C=C), no N-H absorption from 3300 cm⁻¹ to 3500 cm⁻¹).

Syntheses of Solid State Polymer Electrolytes:

In order to prepare the polymer electrolyte (crosslinked BPAEI-LiTf), BPAEI **2** was dissolved in a minimum amount of methanol with a desired amount of initiator (Wako Chemicals, USA) and LiTf (Aldrich) and stirred for 1h. LiTf was dried under vacuum at 120 °C over night prior to use. The resulting homogenous solution was cast onto a glass slide and the methanol was allowed to evaporate in air for 2 h. The cast films were positioned in an oven at 80 °C for 12 h. The films were then removed from the glass slides using a razor blade and dried in a vacuum oven at 70 °C for 48 h. All the films were stored *in vacuo* prior to measurements. The compositions of the BPAEI-LiTf samples are described as nitrogen to cation molar ratio (N:M⁺).

FT-IR Spectroscopy

The BPEI and BPAEI IR samples were directly cast onto NaCl windows from methanol

solution and dried in an argon-atmosphere glovebox. All the polymer electrolyte IR samples were directly cast onto NaCl windows from the homogenous BPAEI-LiTf-Initiator solutions described in the materials section and were dried under ambient conditions. The materials on these windows were crosslinked and dried using the same procedure described for crosslinking thicker films. Infrared spectra were recorded at a 1 cm^{-1} spectral resolution using a Bruker IFS66V FT-IR spectrometer with the samples under vacuum (10 mbar). Analysis of the spectral data was performed using a commercially available program (Thermo Galactic, Grams/32, version 7.0).

Differential scanning calorimetry

The pure BPEI and BPAEI samples were directly transferred into aluminum DSC pans and dried in a vacuum oven at room temperature for 24 h before being sealed. Pre-dried crosslinked, BPAEI and crosslinked BPAEI-LiTf films were cut into small pieces before being sealed in aluminum pans. DSC data were collected with a Mettler DSC 820 calorimeter and were analyzed using a commercial program (STAR[®] version 6.10).

Complex impedance

Predried polymer electrolyte films were sandwiched between two 12.5 mm stainless steel electrodes in an airtight conductivity cell in a desiccator. The cell was maintained at the desired temperature by placing it in a metal container wrapped with heating tape. A K-type thermocouple was used to monitor the cell temperature. Complex impedance data were recorded over a frequency range of 5 Hz to 10,000 Hz using an HP 4192A LF impedance analyzer with LABVIEW[™] 5.1 software. Conductivity data were collected from 20 to 80 °C in 10 °C increments under a dry nitrogen purge. All the measurements were conducted throughout

three heating/cooling cycles. Impedance plots were fitted using LEVM version 7.1. The ionic conductivity measurements were repeated once with freshly made samples and the statistical analysis of the error was not performed. The repeated data was generally no greater than a half order of magnitude off from the initial measurement. After the conductivity measurements were performed, IR spectroscopy was used to verify the dryness of the samples. However, samples can only be claimed to be solvent free within the detection limit of IR. Other errors include human error and instrumental error.

CHAPTER V: CROSSLINKED LINEAR

POLY(N-ALLYLETHYLENIMINE-CO-N-(2-(2-METHOXYETHOXY)ETHYL) ETHYLENIMINE)

Introduction:

To date, no SPE with satisfactory performance has been found. As discussed in Chapter I, the major issue is the relatively low conductivity when the physical properties are sufficient for battery fabrication.¹⁷ It is difficult to address these problems because of the lack of control over the polymer electrolyte's structure and morphology, which depend on many factors: the polymer, the salt, and the actual preparation of polymer electrolyte. Scientists have studied poly(ethylene oxide) (PEO) as a polymer electrolyte host. However, it has poor physical properties.^{32,33} Linear poly(ethylenimine) (LPEI) has been studied as a PEO analog.³⁸ Previous research shows that LPEI/salt electrolytes do not have sufficient ionic conductivity or mechanical properties needed for practical applications. However, polyamine based PE host can be synthetically modified to address these problems because of the synthetic versatility of nitrogen.³⁷ Several side-chain modified LPEI-based polymer electrolyte hosts such as linear poly(N-methylethylenimine),^{37,64} linear poly(N-2-cyanoethylenimine),⁷⁵ and linear poly(N-2-(2-methoxyethoxy)ethyl)-ethylenimine (LPEI-G2)⁷⁷ have been reported.

Modification of polymers using tethered ethoxy (-CH₂CH₂O-) side-chains gives the polymers PEO-like features, which may enhance the ionic conductivity. Poly(bis-methoxyethoxyethoxyphosphazene) (MEEP), a liquid with a T_g well below room temperature (-84 °C), has been studied by Allcock *et al.*⁷⁷ The optimum room temperature conductivity of MEEP-LiTf is 2.7 x 10⁻⁵ S cm⁻¹ (O:Li⁺ at 24:1). Another oligo-(ethylene oxide)

side-chain containing polymer electrolyte host, linear poly(N-(2-(2-methoxyethoxy)ethyl)ethylenimine) (LPEI-G2), was reported by Snow *et al.*⁷⁶ LPEI-G2 is also a viscous liquid with a T_g of -76 °C. The T_g of the LPEI-G2-LiTf system increase rapidly with the addition of salt to 16 °C at 5:1 (O:Li⁺). The 10:1 N:Li⁺ sample had a conductivity of $5 \times 10^{-6} \text{ S cm}^{-1}$ at 25 °C and $7 \times 10^{-5} \text{ S cm}^{-1}$ at 60 °C. The conductivity of the LPEI-G2-LiTf drops at higher salt concentration. Neither polymer electrolyte is a useful SPE because of their poor mechanical properties. As discussed in Chapter IV, radical initialized crosslinking of allylated polyamine is one method of forming neutral polyamine based SPE without generating charged ammonium moieties that effect ion speciation and transport. Therefore, it is desirable to develop a neutral crosslinked LPEI based solid polymer electrolyte with 2-(2-methoxyethoxy)ethyl (G2) side-chains, whose local structure mimics MEEP.

Incorporation of both allyl side-chains and G2 side-chains onto LPEI will result in a new copolymer, which can be radically crosslinked to solid state polymer electrolyte. At first, we conducted a series of allylation reactions to prove that we could control the degree of allylation by reactant quantities. The structure of resulting polymer linear poly(N-allylethylenimine-*-co*-ethylenimine) (LPAEI) is shown in **Figure V-1**. Subsequently, we synthesized the linear poly(N-allylethylenimine-*-co*-N-methylethylenimine) (LPAMEI) (**Figure V-3**), indicating that the unreacted nitrogen atoms remaining after allylation can be successfully functionalized. LPAMEI was crosslinked with salt present to form the polymer electrolyte, and conductivity was measured. These experiments demonstrated that the di-functionalized LPEI-based polymer prepared using this method could be crosslinked to form SPEs and the resulting SPEs were conducting. Finally, the incorporation of allyl side-chains onto about half of the nitrogens in the

LPEI backbone and G2 side-chains onto the rest gave a new polymer electrolyte host, linear poly(N-allylethylenimine- *-co*-N-(2-(2-methoxyethoxy)ethylenimine) (LPAG2EI), which has not only the conductive features of polyethers and polyamines but also the capability of being neutrally crosslinked to form SPEs. LPAG2EI was radically crosslinked with various concentrations of LiTf present to form polymer electrolytes. The resulting films were investigated by initial empirical observation of physical properties and dissolution tests, followed by infrared spectroscopy (IR), differential scanning calorimetry (DSC), and complex impedance measurements. Further more, some crosslinked LPAG2EI electrolytes based secondary lithium batteries were assembled and submitted to battery recycling tests, which will be discussed in Chapter VI.

Results and Discussions:

The syntheses of a series of partially allylated LPEI, 10%, 25%, 50%, 80%, and 100% are shown in **Figure V-1**. The starting polymer LPEI was synthesized using literature procedures⁴⁷ from commercially available 200,000 MW linear poly(2-ethyloxazoline) (LPEOZ). Allylation was conducted in the presence of potassium carbonate salt at 1:1 (allylbromide: K₂CO₃) ratio, which neutralized ammonium cations generated by *SN*₂ substitution. The entire series of syntheses share the same procedure except the amount of allylbromide used, which ranged from 0.1 to 1 equivalent.

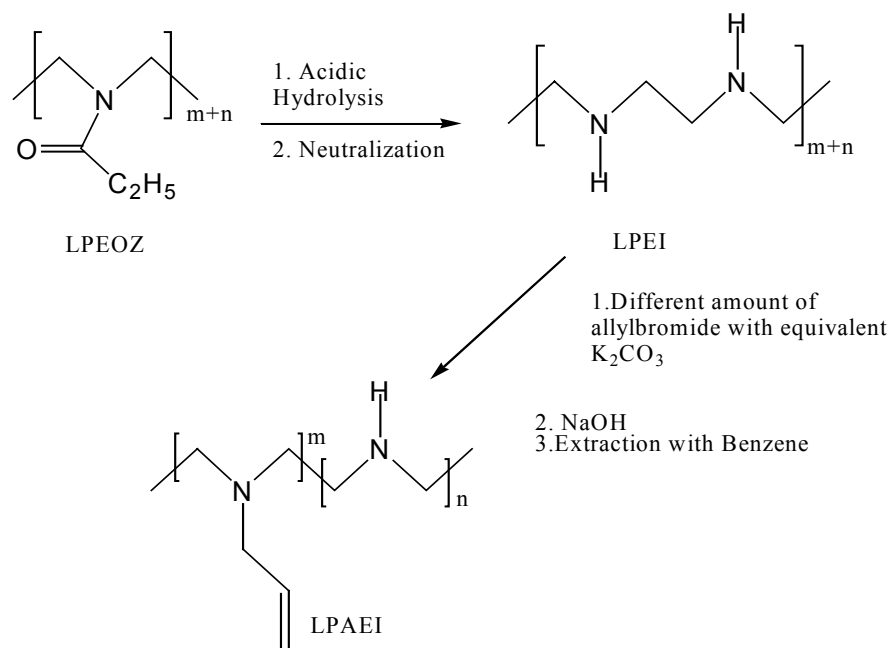


Figure V-1: Synthesis of Partially Allylated LPEI from LPEOZ with an empirical formula $(-\text{CH}_2\text{CH}_2\text{NCOCH}_2\text{CH}_3-)$

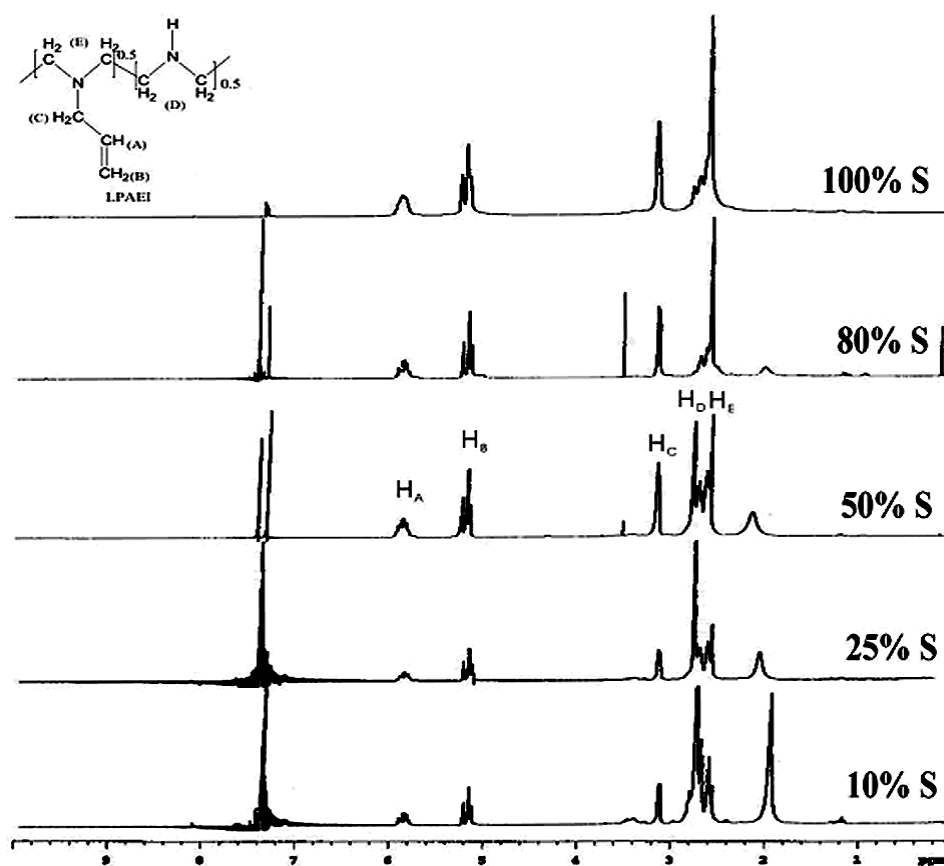


Figure V-2: 300 MHz ^1H NMR of Allylated LPAEI Series

^1H NMR spectra of the resulting polymers are shown as a stack plot in **Figure V-2**. The methylene singlet centered at 3.12 ppm (H_c) increases gradually with the amount of allylbromide used. Meanwhile, the integration ratio between the methylated backbone methylene groups and the unreacted backbone methylene groups changes accordingly, indicating that the percentage of allylated nitrogen atoms could be controlled by reactant quantities.

Given that these experiments were successful, we did not study this series of polymers as polymer electrolyte hosts but moved on to study the functionalization of the non-allylated nitrogen atoms in 50% allylated LPEI, LPAEI-50, which was chosen to be the starting polymer for the subsequent side-chain modification research as the 1:1 ratio provides a balance between crosslink density and ethylene oxide chain density.

As shown in **Figure V-3**, LPAMEI was synthesized using Eschweiler-Clarke methylation on the 50% allylated LPEI (LPAEI-50). The overall yield was greater than 90%. The resulting LPAMEI was characterized using IR and NMR. The absence of N-H stretching bands in the IR spectrum ($3200\text{--}3300\text{ cm}^{-1}$) indicated the complete methylation of the non-allylated backbone nitrogen atoms. An IR spectrum of neat LPAMEI is shown in the **Appendix of Spectrum II**.

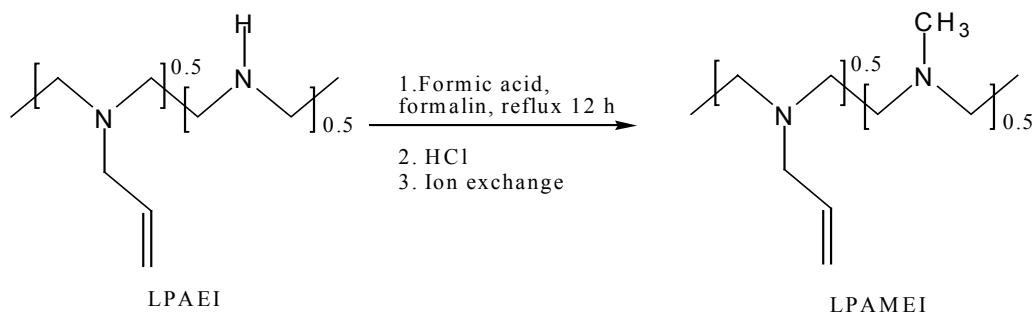


Figure V-3: Synthesis of LPAMEI from LPAEI-50

As shown in **Figure V-4**, The NMR spectrum of LPAMEI possesses a multiplet centered at 5.83 ppm (vinyl methine proton, 1 H), a doublet centered at 5.18 ppm (vinyl methylene protons,

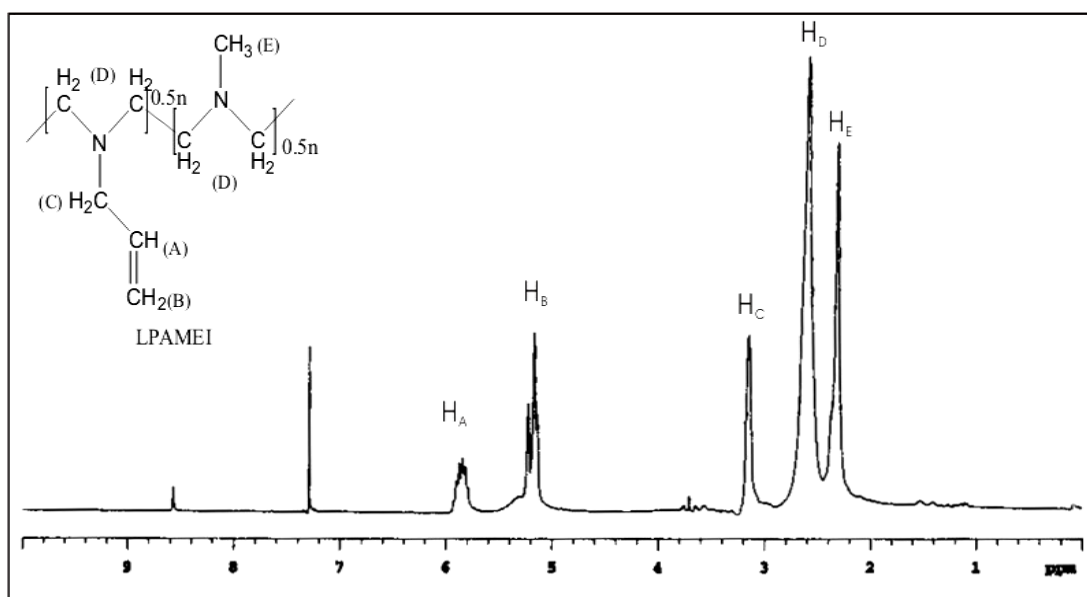


Figure V-4: 300 MHz ^1H NMR of LPAMEI

2 H), a singlet centered at 3.08 ppm (side-chain N-methylene protons, 2 H), a broad band centered at 2.58 ppm (backbone methylene protons, 8 H), and a singlet centered 2.35 ppm (N-methyl protons, 3 H). The splitting patterns are clear although the H_C protons, which should be a doublet, appear as a broadened singlet. LPAMEI was crosslinked with 20:1 (N: Li^+) LiTf to form an SPE. Although detailed study of this system was not the purpose of this research, preliminary impedance measurement of a 20:1 crosslinked LPAMEI-LiTf sample ($3 \times 10^{-9} \text{ S cm}^{-1}$ at room temperature and $4.0 \times 10^{-6} \text{ S cm}^{-1}$ at 100°C) shows that crosslinked LPAMEI is capable of functioning as an SPE host. LPAMEI based SPE systems are interesting and worth of further study. Given these experiments successfully demonstrated that the polymer prepared

covalently crosslinked to form a solid film at $\sim 105^\circ\text{C}$ using a radical initiator, 2,2-azobis(2-amidinopropane) dihydrochloride (V-50). LPAG2EI based SPEs were prepared by crosslinking the host polymer with various amounts of LiTf present. The choice of initiator and initiator concentration were based on previous crosslinked BPAEI research and were not optimized for LPAG2EI based system.

The NMR spectrum of the resulting LPAG2EI possesses a multiplet centered at 5.83 ppm (vinyl methine proton, 1 H), a triplet centered at 5.17 ppm (vinyl methylene protons, 2 H), a broad multiplet from 3.51 ppm to 3.65 ppm, (side-chain O-methylene protons, 6 H), a singlet centered at 3.38 ppm (O-methyl protons, 3 H), a doublet centered at 3.12 ppm (allylic side-chain N-methylene protons, 2 H), a triplet centered at 2.70 ppm (G2 side-chain N-methylene protons, 2 H), and two overlapped singlets ranging from 2.42 ppm to 2.68 ppm (backbone methylene protons, 8 H) (see **Figure V-6**). The splitting patterns are clear. The analysis of NMR integration

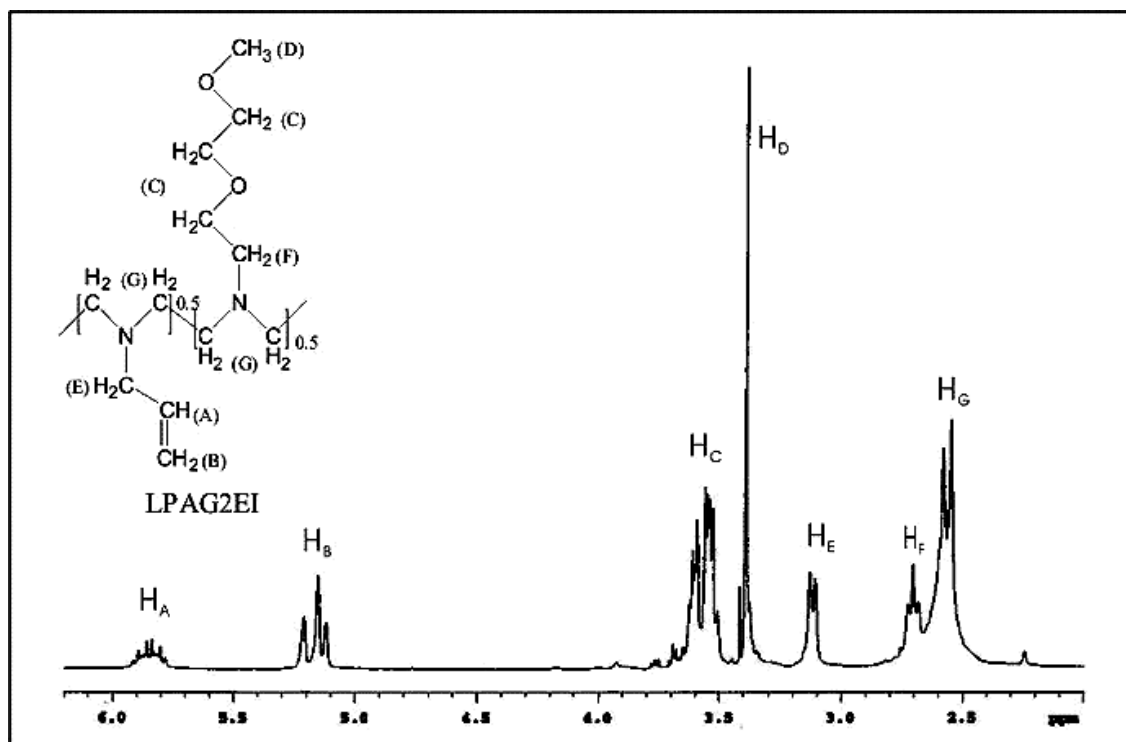


Figure V-6: 300 MHz ^1H NMR of LPAG2EI

of H_D (3.38) and H_E (3.12) also proves that the ratio between the allylic side-chain and G2 side-chain is roughly 1:1.

Since the ratio between allylic side chains and G2 side chains was roughly 1:1, there are, on average, two nitrogen atoms and two oxygen atoms in every two backbone repeat units (see **Figure V-6**). The average chemical formula for every two backbone repeat units is $C_{12}H_{24}N_2O_2$. The salt concentration of LPAG2EI based SPE is defined as $N:M^+$. For example, there are ten allyl side-chains and ten G2 side-chains for each Li^+ in a 20:1 sample.

LPAG2EI is a highly viscous liquid with a light brown color. The T_g of LPAG2EI is $-83\text{ }^\circ\text{C}$, which is about the same as for MEEP ($-84\text{ }^\circ\text{C}$)⁷⁷ and slightly lower than LPEI-G2 ($-76\text{ }^\circ\text{C}$)⁷⁶. With LiTf present, LPAGEI was heated with 30:1 (N: V50) at $\sim 105\text{ }^\circ\text{C}$ for 48 h to form

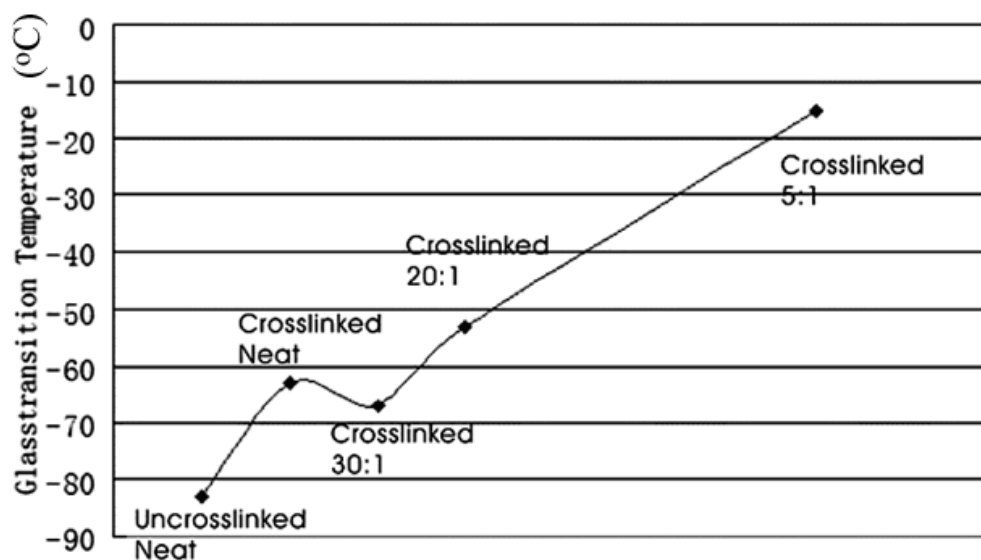


Figure V-7: Glass transition temperatures of uncrosslinked LPAG2EI, crosslinked LPAG2EI, and crosslinked LPAG2EI films using 30:1 V-50 as a function of LiTf concentration.

crosslinked LPAG2EI-LiTf, which is a dark-colored solid. The resulting SPE has moderate physical properties but is not as robust as the crosslinked BPAEI-based SPE discussed in Chapter IV. Crosslinked LPAG2EI has a T_g of $-63\text{ }^{\circ}\text{C}$. As shown in **Figure V-7**, the T_g of LPAG2EI based SPEs increases with salt concentration from $-67\text{ }^{\circ}\text{C}$ (30:1) through $-53\text{ }^{\circ}\text{C}$ (20:1) to $-15\text{ }^{\circ}\text{C}$ (5:1). Interestingly, the T_g of 30:1 composition is slightly lower than crosslinked LPAG2EI without salt, suggesting that salt may interfere with the crosslinking process. In comparison, the T_g of LPEI-G2 based polymer electrolytes increases from $-76\text{ }^{\circ}\text{C}$ (neat), through $-60\text{ }^{\circ}\text{C}$ (10:1), to $16\text{ }^{\circ}\text{C}$ (2.5:1).⁷⁶

IR samples of LPAG2EI based SPE with various amounts of LiTf were cast from homogeneous solutions onto zinc selenide IR windows and crosslinked under the conditions described in the experimental section. The IR spectra of LPAG2EI based SPE samples (neat, 30:1, 20:1, and 5:1) in the region from 800 cm^{-1} to 1020 cm^{-1} are shown in **Figure V-8**. The IR signature in this region mostly represents the interaction between the Li^+ and the tethered G2 side-chains and the resulting structural changes. The vibrational modes in this region have been shown to consist mostly of mixed CH_2 rocking, $\rho(\text{CH}_2)$, and C-O stretching, $\nu(\text{C-O})$, in the studies of both PEO and diglyme.⁷⁸ The frequencies and intensities of these bands are sensitive to the interaction between Li^+ and the oxygen atoms in the polymer and the local conformation of the oxygen containing polymer chain.⁷⁹ In this IR region, the polymer absorption of LPAG2EI consists of a medium intensity band centered at 918 cm^{-1} and three weak bands centered at 852 cm^{-1} , 963 cm^{-1} , and 996 cm^{-1} . At low salt concentration (20:1 and 30:1), no noticeable change is observed. However, in the 5:1 sample, a medium intensity band centered

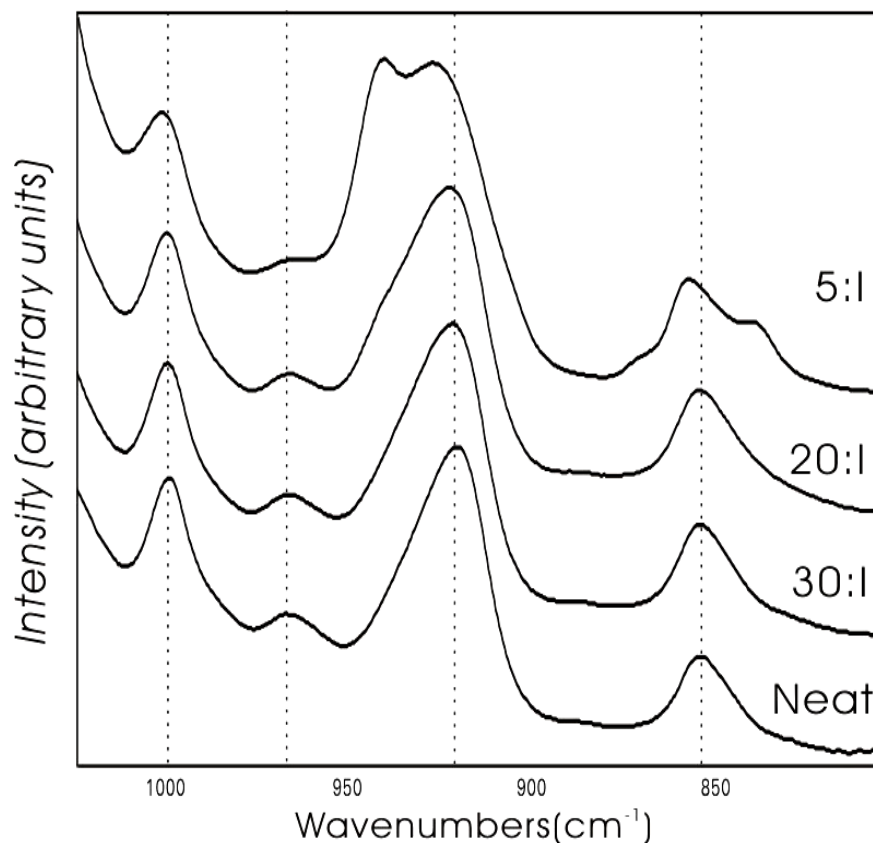


Figure V-8: IR spectra of crosslinked LPAG2EI films using 30:1 N:V-50 at various salt compositions (800 cm^{-1} - 1020 cm^{-1}). All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm^{-1} .

at 938 cm^{-1} and a weak band centered at 836 cm^{-1} appear while the other four bands slightly shift to higher wavenumbers. These changes indicate that the most of the polymer G2 side-chain structure is not disrupted at a low salt concentration. At a high salt concentration, some G2 side-chains may form complexes with LiTf that significantly change their local structures, leading to the appearance of the new IR bands at 938 cm^{-1} and 836 cm^{-1} . Generally, the backbone conformations of the LPAG2EI-based SPEs are reasonably stable against the addition of salt because of their structural stability from the covalent crosslinking. Unlike the crosslinked LPAG2EI/LiTf system, this backbone region in diglyme/LiTf and PEO/LiTf systems was

significantly disrupted at compositions of 10:1 ($\text{O}:\text{Li}^+$) and higher.^{80, 81} This backbone IR region in LPEI-G2/LiTf system is more sensitive to LiTf addition and drastic changes at high LiTf concentrations are observed.⁷⁶ Studies to assign these bands by the use of model compounds are ongoing.

The IR spectra of 30:1 and 5:1 LPAG2EI based SPE at room temperature and 100 °C are shown in **Figure V-9** in the tethered G2 side-chain backbone region from 800 cm^{-1} to 1020 cm^{-1} . In the 30:1 sample, there is no noticeable difference between room temperature and 100 °C, at which temperature the crosslinked LPAG2EI-based lithium battery will be tested. In the

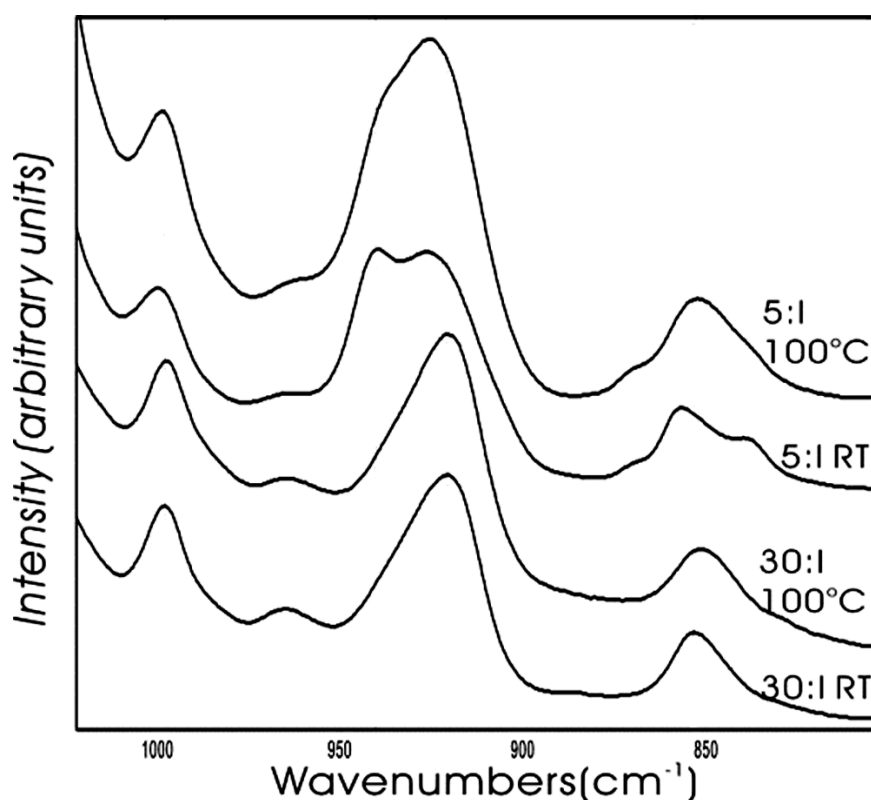


Figure V-9: IR spectra of crosslinked LPAG2EI films using 30:1 N:V-50 with 30:1 and 5:1 N:LiTf at room temperature and 100 °C (800 cm^{-1} -1020 cm^{-1}). All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm^{-1} .

5:1 sample, however, the intensity of the band centered at 938 cm^{-1} appears to decrease with increasing temperature, indicating that the new local structures induced by high concentrations of salt are greatly reduced by heat.

The triflate SO_3 symmetric stretching mode, $\nu_s(\text{SO}_3)$, and the CF_3 symmetric deformation mode, $\delta_s(\text{CF}_3)$, are the most distinct IR absorptions indicating ionic speciation. They contain multiple bands due to different ionic species, which have been assigned, in case of $\nu_s(\text{SO}_3)$, as ‘free’ ions at $1032\text{--}1034\text{ cm}^{-1}$, contact ion pairs at $1037\text{--}1042\text{ cm}^{-1}$, and aggregates at $1047\text{--}1054\text{ cm}^{-1}$

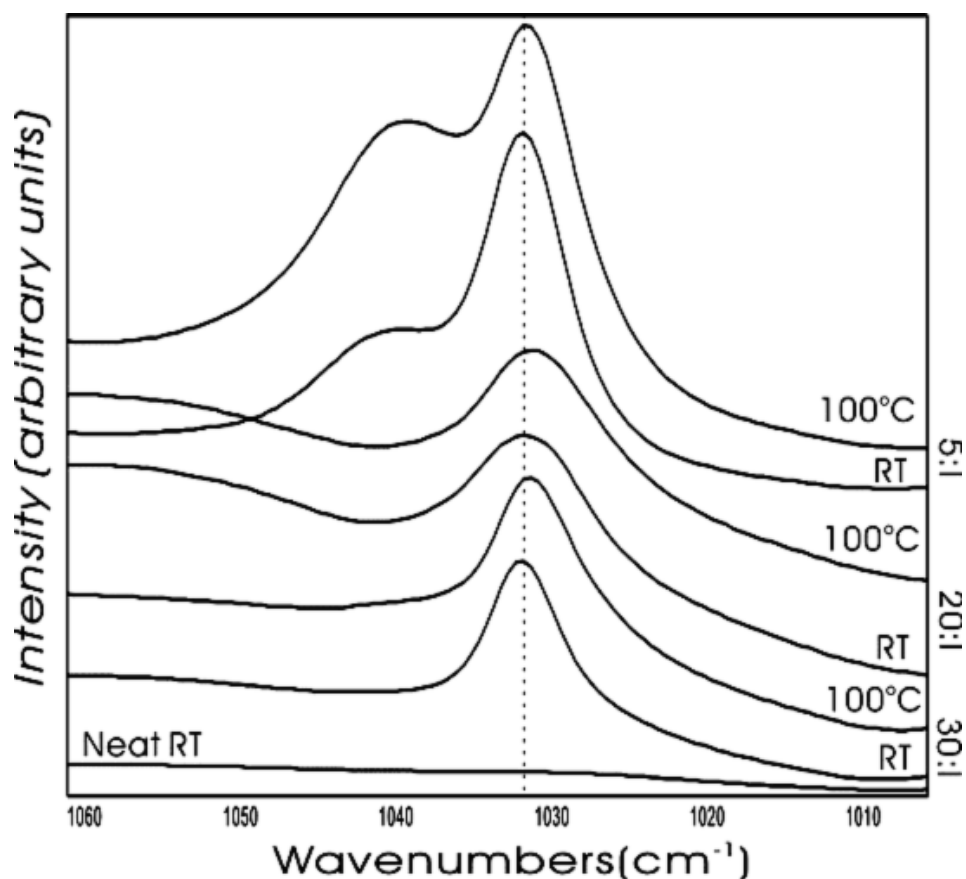


Figure V-10: IR spectra of crosslinked LPAG2EI films ($\nu_s(\text{SO}_3)$ region) using 30:1 N:V-50 with various amounts of salt at room temperature and 100°C . All spectra are scaled by normalizing the intensity of the C-H bands from 2900 to 3100 cm^{-1} .

cm⁻¹ based on previous PEO research.^{30, 31} As shown in **Figure V-10**, the ionic association state appears to be mainly the ‘free’ ion state and does not change significantly with temperature at lower salt concentration. Addition of more salt decreases the relative amount of ‘free’ ions, but the ‘free’ ion is still a significant portion of the total ionic species even in the 5:1 sample. At high salt concentration, increasing temperature appears to increase the amount of ion pairs and aggregate species significantly. Deconvolution of the bands in this region give the percentage integrated band intensity of each species to total integrated band intensity of all species, which can be used to estimate the relative concentration of each species. The deconvolution results of $\nu_s(\text{SO}_3)$ are reported in **Table V-1** and are consistent with the above empirical observations. This temperature-dependent IR measurement has been carried out over two cycles and the observed changes of ionic species appear to be reversible. The same ionic association trend is observed in the region of the $\delta_s(\text{CF}_3)$ band, which is in the region from 750 cm⁻¹ to 760 cm⁻¹.

Wave Number \ N:Li ⁺ %	30:1		20:1		5:1	
	RT	100 °C	RT	100 °C	RT	100 °C
1031 cm ⁻¹	100	100	100	99	72	52
1039 cm ⁻¹	0	0	0	0.5	24	40
1051 cm ⁻¹	0	0	0	0	4	8

Table V-1: Percent of triflate species in LPAG2EI based SPE from curve fitting of $\nu_s(\text{SO}_3)$

The temperature-dependent ionic conductivities of LPAG2EI based SPEs at various salt concentrations (30:1, 20:1, and 5:1) are shown in **Figure V-11**. The ionic conductivity of

LPEI-G2 (10:1) is also shown as a reference. For each concentration, conductivity samples were individually prepared twice. For each sample, three temperature-dependent cycles of measurements were undertaken. After the measurements were performed, IR spectroscopy was used to verify the dryness of the samples. When compared to PEO based polymer electrolyte, which can achieve reasonable conductivity about 10^{-5} S/cm at ~ 100 °C when its crystalline phase melt,⁸² the crosslinked LPAG2EI based SPE has outstanding ionic conductivity. When compared to the LPEI-G2/LiTf system, the LPEI-G2-LiTf system has a greater ionic

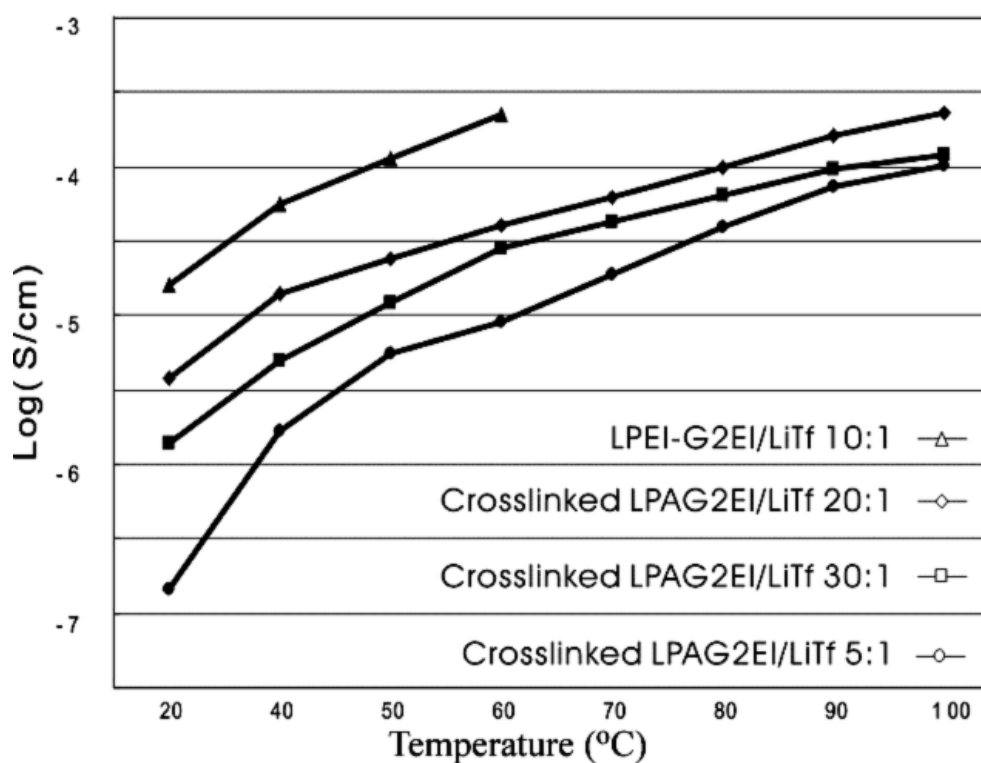


Figure V-11: Conductivity of LPAG2EI based SPE (30:1, 20:1 and 5:1)
and LPEI-G2-LiTf 10:1

conductivity about one order of magnitude from room temperature to 60 °C. This is expected because LPEI-G2 is a liquid. The crosslinked 20:1 N:Li⁺ LPAG2EI sample has a conductivity of

$1.3 \times 10^{-6} \text{ S cm}^{-1}$ at room temperature and $7.1 \times 10^{-4} \text{ S cm}^{-1}$ at 100°C , which are better than the other two concentrations. Over the temperature range of the measurements, the ionic conductivities of the different samples appear to start from different levels at room temperature and converge toward each other with increasing temperatures. At low salt concentrations, where almost all the ions exist as ‘free’ ions at both temperatures, the increase of ionic mobility with temperature only raises the ionic conductivity less than two orders of magnitude from room temperature to 100°C . However, at high salt concentration, the increase of ionic mobility plays a more important role in determining ionic conductivity. Despite a 20 % loss of ‘free’ ion from room temperature to 100°C , the ionic conductivity of the 5:1 sample is increased about three orders of magnitude by the gain in ionic mobility as temperature increases.

Conclusions and Future Directions:

LPAG2EI was successfully synthesized and characterized. Free-standing polymer electrolytes were prepared by radical crosslinking of LAG2EI and LiTf at various compositions and were investigated by means of vibrational, thermal and impedance spectroscopies. These crosslinked SPEs are true solid films with low T_g s. As indicated by IR, the dominant triflate species in these SPE are ‘free’ ions and do not significantly change with LiTf concentration. Therefore, outstanding ionic conductivities were observed in these SPEs. The minimum conductivity needed for functioning lithium batteries, which is ca. 10^{-4} S/cm , was achieved at the temperature as low as 40°C . Compared to MEEP and LPEI-G2, LPAG2EI-based polymer electrolytes have better physical properties and good ionic conductivities. Therefore, the formation of useful neutral SPEs from cross-linking of partial allylated LPEI-based polymers

with oxygen-containing side-chains, which can greatly enhance the ionic conductivity, is a viable strategy.

As a continuation of this research, some secondary lithium batteries using the LPAG2EI-based polymer electrolytes were assembled and tested for their actual performance, which are discussed in detail in the next chapter. Aside from the battery trial, other possible improvements on this PEO/PEI hybrid system include optimizing the crosslink conditions and fine-tuning the ratio between allylic side-chains and G2 side-chains for a better compromise between the conductivity loss and the physical property improvement. Furthermore, other types of side-chains can be grafted onto the LPAEI instead of G2 side-chains.

Experimental:

Common reagents and solvents were commercially available and used as received unless noted. NMR spectra were obtained using a 300 Hz Varian spectrometer.

Synthesis of LPAEI

LPEI (avg. MW ca. 86,000) was synthesized by the acidic hydrolysis of linear poly(2-ethyl-2-oxazoline) (Aldrich, avg. MW 200,000) as in literature.⁴⁷ LPEI **1** (2.01 g, 46.5 *mmoles repeat unit*) and K₂CO₃ (3.21 g, 23.3 *mmoles*) were added to 100 mL HPLC grade methanol and the reaction vessel was cooled using an ice bath. Allyl bromide (2.81 g, 23.3 *mmoles*) was added dropwise while stirring. After warming up to room temperature slowly, the system was heated to reflux solvent for 12 h. Solvent and any excess allyl bromides were removed under reduced pressure. The residue was redissolved in 100 mL methanol. Sodium hydroxide (NaOH) (0.932 g, 23.3 *mmoles*) was added as pellets while stirring and the solvent was

heated to reflux for 1 h. After methanol was removed, benzene (100 mL, 50 mL and 50 mL) was used to extract the polymer from inorganic sodium bromide. Removal of benzene under reduced pressure gave neutral LPAEI-50% **2** (2.75 g, 43.7 mmol *repeat unit*). $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 2.5-2.8 (br, 8 H), 3.1 (d, 2 H₂), 5.2 (t, 2 H), 5.9 (m, 1 H) (**Figure V-2**)

Synthesis of LPAMEI

Previously synthesized LPAEI (0.501 g, 7.94 mmol *repeat unit*), 23 mL of formic acid (88% solution, Aldrich), and 15 mL of formaldehyde (37% solution, Aldrich) were added to the reaction vessel. The solution was heated to reflux solvent for 24 h. The reaction mixture was allowed to cool to room temperature before the addition of 18 mL of concentrated HCl. The solvent, as well as acids and formaldehyde were removed under reduced pressure. The resulting LPAMEI ammonium chloride salt was dissolved in a minimal amount of distilled water. The solution was neutralized by passing through an OH^- ion exchange column (DOWEX-2 400). The removal of solvent under reduced pressure gave LPAMEI (0.581 g, 7.54 mmol *repeat unit*). This procedure gave a 95% yield. $^1\text{H-NMR}$ (CDCl_3): 2.3 (s, 3 H), 2.4-2.7 (br, 8 H), 3.1 (s, 2 H), 5.2 (d, 2 H), 5.8 (m, 1 H) (**Figure V-4**)

Synthesis of LPAG2EI

1.02 g (16.2 mmol *repeat unit*) of LPAEI-50% was dissolved in 2-(2-(methoxyethoxy)acetic acid (30 mL, Aldrich). The reaction mixture was stirred by a mechanical stirrer and cooled by an ice bath. 20 mL tetrahydrofuran was added to insure homogeneity. Excess NaBH_4 (~3 g, Aldrich) was added slowly in the form of small pellets. Because the side reaction between NaBH_4 and acid is very exothermic and the other side product is a highly flammable gas, H_2 , one should pay special safety attention to keep the

reaction vessel at low temperature at this step. Also, the less reactive pellet-form NaBH_4 is preferred over the more reactive powder-form NaBH_4 . The reaction mixture was then allowed to warm to room temperature, followed by 5 days of heating at $55\text{ }^\circ\text{C}$. The reaction mixture was allowed to cool to room temperature and 35 mL distilled water was added. The resulting solution was cooled by an ice bath. Pellets of NaOH were added with mechanical stirring until the pH of solution was much greater than 12. The solution was extracted with CH_2Cl_2 (5 x 50 mL, Fisher). After being washed with aqueous NaOH solution ($\text{pH} \gg 12$), the organic portion was dried over Na_2SO_4 . The removal of solvent gave 1.50 g (13.5 mmol *repeat unit*) of LPAG2EI. This procedure gave an 83 % yield. ^1H -NMR (CDCl_3 δ (ppm) 2.4-2.7 (br, 8 H), 2.7 (t, 2 H), 3.1 (d, 2 H), 3.4 (s, 3 H), 3.5-3.7 (m, 6 H), 5.2 (t, 2 H), 5.8 (m, 1 H)) (**Figure V-6**), IR. (3072 cm^{-1} ($=\text{CH}_2$), 1642 cm^{-1} ($\text{C}=\text{C}$), no N-H absorption from 3300 cm^{-1} to 3500 cm^{-1}).

Preparation of polymer electrolytes

To prepare the polymer electrolyte (crosslinked LPAG2EI-LiTf), LPAG2EI was dissolved in a minimum amount of anhydrous methanol with a desired amount of initiator (Wako Chemicals, USA) and LiTf (Aldrich) and stirred for 1h. The resulting homogenous solution was cast onto a film carrier (glass slide, IR window, DSC pan, or impedance measurement cell) and the methanol was allowed to evaporate in air for 2 h in an argon-atmosphere glove-box. The cast films were positioned in an oven under vacuum at room temperature for 1 h before 48 h of crosslinking at $\sim 105\text{ }^\circ\text{C}$. The resulting films were dried under vacuum at room temperature for 24 h. All the manipulations were conducted in an argon-atmosphere glove-box. All samples were stored *in vacuo* prior to measurements. The compositions of the LPAG2EI-LiTf samples are described by their nitrogen to cation ratio ($\text{N}:\text{Li}^+$)

FT-IR Spectroscopy and Differential scanning calorimetry

The LPAEI-50% and LPAG2EI IR samples were directly cast onto NaCl windows from methanol solution and dried in argon-atmosphere glove-box. The neat LPAG2EI was directly transferred into aluminum DSC pans and dried in a vacuum oven at 50 °C for 24 h before being sealed. The polymer electrolyte samples for IR and DSC were prepared as described above. Infrared spectra at room temperature, 50 °C, and 100 °C were recorded with a Bruker IFS66V FT-IR spectrometer under vacuum (11 mbar) at a 1 cm⁻¹ spectral resolution. Analysis of the spectral data was performed using a commercially available program (Thermo Galactic, Grams/32, version 7.0). DSC data were collected with a Mettler DSC 820 calorimeter and were analyzed using a commercial program (STAR[®] version 6.10).

Complex impedance

The polymer electrolyte films were prepared as described in the polymer electrolytes preparation section and sandwiched between two 12.5 mm stainless steel electrodes in an airtight conductivity cell, which was maintained at the desired temperature using a vacuum heating oven. A thermocouple was used to monitor the cell temperature. A dry nitrogen purge was maintained during the measurements. Complex impedance data were recorded over a frequency range of 5 Hz to 10,000 Hz using an HP 4192A LF impedance analyzer with LABVIEW[™] 5.1 software. Conductivity data were collected from room temperature to 100 °C in 10 °C increments. All the measurements were conducted throughout three heating/cooling cycles. Impedance plots were fitted using LEVM version 7.1. The ionic conductivity measurements were repeated once with freshly made samples and the statistical analysis of the error was not performed. The repeated data was generally no greater than a half order of

magnitude off from the initial measurement. After the conductivity measurements were performed, these samples in the conductivity cell were smeared onto IR windows and IR was conducted to verify the dryness of the polymer electrolytes. However, samples can only be claimed to be solvent free within the detection limit of IR. Other errors include human error and instrumental error.

CHAPTER VI

BATTERY TRIALS OF CROSSLINKED POLYMER ELECTROLYTES

Introduction:

Construction of lithium polymer batteries using the polyamine-based electrolytes we have developed followed by cycling provides a direct evaluation of the performance of the material. In this chapter, crosslinked BPAEI/salt and crosslinked LPAG2EI/salt will be incorporated into secondary cells as the electrolyte and separator. The discharge-charge cycling performance of these cells will be discussed and compared to a LPMEI based cell, whose performance has been reproducibly measured by our research group.

Polymer electrolyte research often focuses on thermal behavior, ionic speciation, and ionic conductivity instead of the actual performance of these polymer electrolytes due to the difficulty in preparing and testing SPE-based batteries. Battery trials require an appropriate cell design, selection of compatible electrode materials, and the equipment to characterize cell performance. Several high-molecular-weight PEO-LiTf based cells, composed of metallic lithium as the anode, lithium vanadium oxide (LiV_3O_8) as the cathode, and PEO-LiTf as the electrolyte, have been reported in literature. These cells were cycled between 80 and 120 °C.⁸³⁻⁸⁶

Based on these previous cell designs, a standardized method of preparing lithium coin cells with polymer electrolytes was developed by our research group. In our research, lithium bis(trifluoromethanesulfonyl)imide (LiTfSi) is used as the salt in the polymer electrolyte instead of LiTf because of its superior electrochemical stability.⁸⁷ The construction of a coin cell is shown in **Figure VI-1**. In the cell, a layer of metallic lithium (as anode), a layer of LiV_3O_8 paste (87% LiV_3O_8 , 5% KS6 graphite, 5% SLP graphite, and 3% Teflon[®] shred, as cathode), and a

layer of polymer electrolyte (polymer host and various amount of LiTfsi) are sandwiched between two stainless steel disks, which function as both current collectors and spacers. When a liquid electrolyte is used, an inert porous polyethylene/polypropylene separator is needed. The cell is sealed by a pair of special pans, obtained from Kerr-McGee Corporation. These pans have special construction, which allow the formation of an airtight seal when compressed using the proper equipment. All the materials used are either prepared in an argon glove-box or dried under vacuum at elevated temperature. The cell is assembled in an argon glove-box so that the interior of the coin cell is air-free and humidity free.

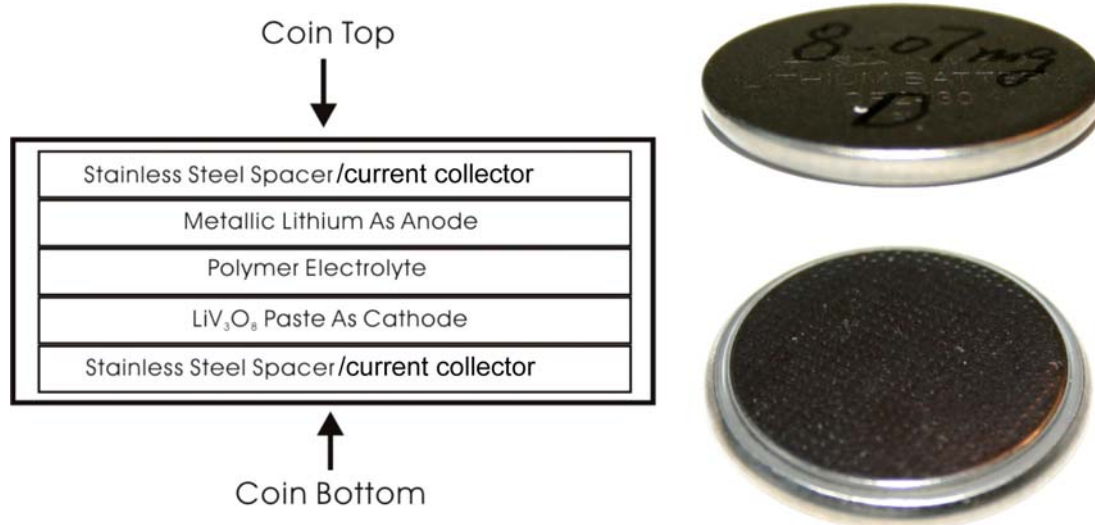


Figure IV-1: Diagram of a Secondary Lithium Coin Cell and an Assembled Cell

The electrochemical reaction of the lithium coin cell is shown in **Figure IV-2**. In the discharge cycle, vanadium is reduced from V^{5+} to V^{4+} . Metallic lithium is oxidized to Li^+ ion, which is transported to cathode through polymer electrolyte. LiV_3O_8 is a high energy density

cathode material, which has a layer structure that allows fast lithium ion intercalation and de-intercalation while maintaining its conformation. The theoretical capacity of LiV_3O_8 is 280 mAh/g. With charging, vanadium is oxidized back to V^{5+} . Lithium ion de-intercalated from vanadium oxide matrix and is transported back to the anode, at where it is reduced to Li^0 .⁸³

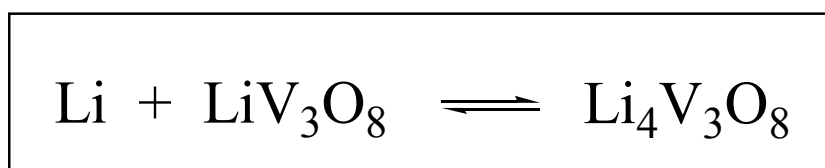


Figure IV-2: Cell Reaction of $\text{Li}|\text{Polymer Electrolyte}|\text{LiV}_3\text{O}_8$

Results and Discussions:

During the development of our lithium coin battery protocol, my colleagues were able to prepare $\text{Li}|\text{PEO}_9:\text{LiTfsi}|\text{LiV}_3\text{O}_8$ batteries, whose capacity and recycling performance matched literature values.⁶⁷ In their evaluation of the LPMEI/LiTfsi electrolyte based batteries, which is still under investigation, they were able to obtain two excellent cycles of discharge-charge capacities, followed by subsequent significant fade in capacities. Since LPMEI is a viscous liquid, the use of a Celgard separator was required. The sources of the fade behavior were speculated as resulting from factors in two areas: 1) possible Celgard breakdown or porosity loss and 2) polymer electrolyte breakdown or oxidation on the surface of cathode. I was able to assemble a $\text{Li}|\text{LPMEI}_{20}:\text{LiTfsi}|\text{LiV}_3\text{O}_8$ battery following the protocol, reproducing the battery recycling result to set a baseline for the evaluations of the crosslinked BPAEI and the crosslinked LPAG2EI-based battery trials.

The $\text{Li}|\text{LPMEI}_{20}:\text{LiTfsi}|\text{LiV}_3\text{O}_8$ battery that I prepared was tested at 100 °C, while the

current density was set at $\pm 10 \mu\text{A}/\text{cm}^2$ and the voltage window was set from 1.9 to 3.0 V. A plot of voltage versus time for my $\text{Li}|\text{LPMEI}_{20}:\text{LiTfsi}|\text{LiV}_3\text{O}_8$ battery is shown in **Figure VI-3**. Two discharge voltage plateaus from 2.3V to 2.7V appear in the discharge cycle, indicating two steps of the reduction of vanadium. The highest current is generated in this period. In the following charge cycle, this plateau occurs between 2.75 V and 3.0 V. However, for unknown

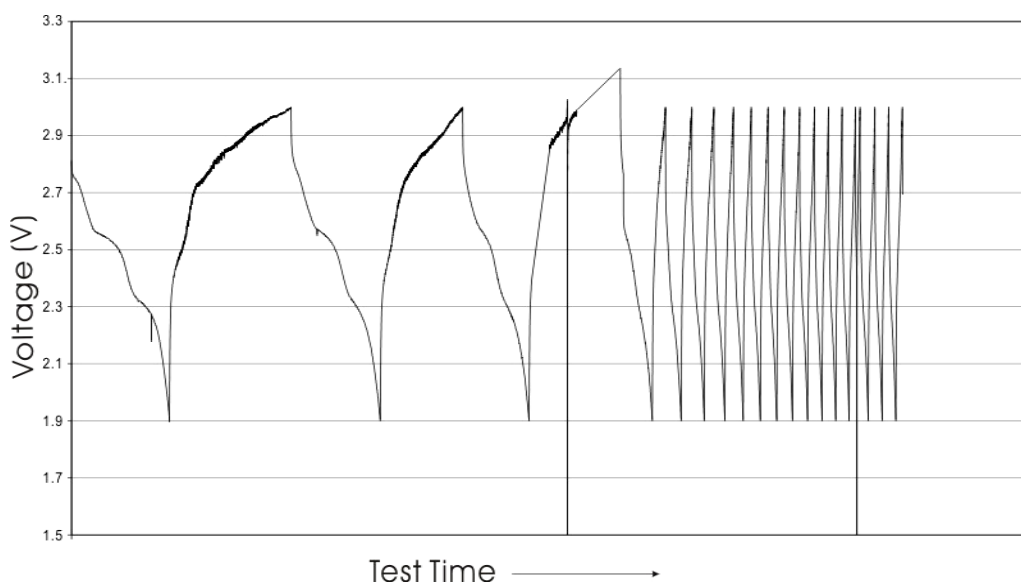


Figure VI-3: Voltage vs. Time Plot of a $\text{Li}|\text{LPMEI}_{20}:\text{LiTfsi}|\text{LiV}_3\text{O}_8$ battery at 100 °C, Current set at $\pm 10 \mu\text{A}/\text{cm}^2$ and Voltage window from 1.9 to 3.0 V

reason, the charge curve did not mirror the discharge curve as it should. This battery was able to be recharged till cycle number four, when the controlling computer of the recycler crashed and stopped measuring for an unknown amount of time. In **Figure VI-3**, there is a spike touching the test time axis. After the experiment was restarted, the battery quickly lost its capacity.

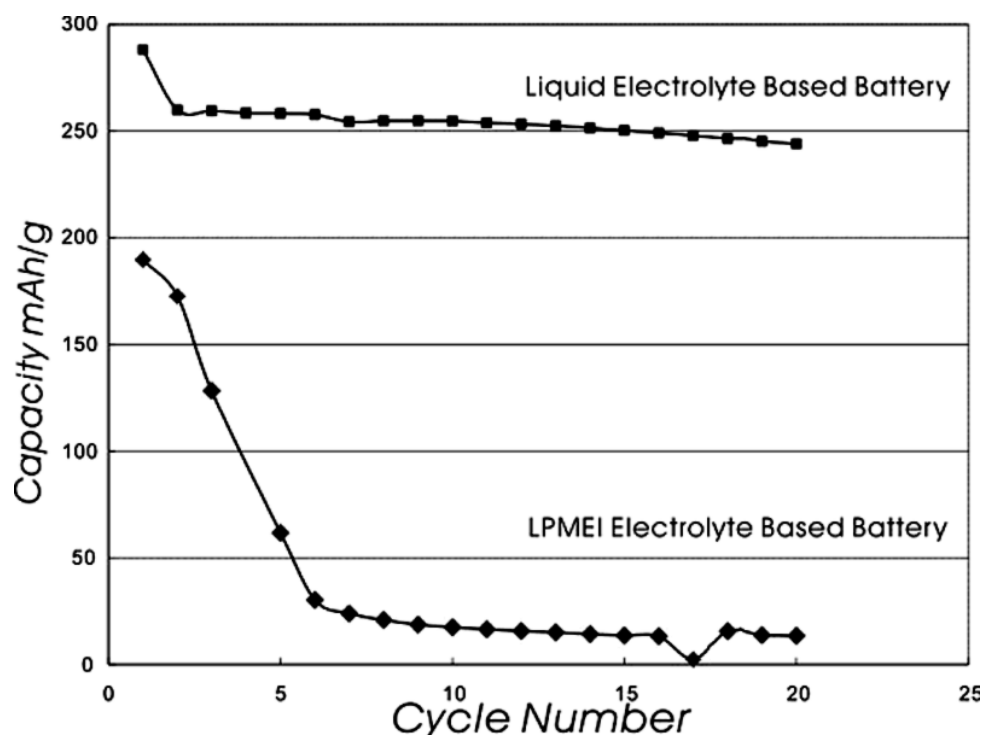


Figure VI-4: Typical discharge and Charge capacities of a cell composed of Li|LPMEI₂₀LiTfsi|LiV₃O₈ with minimum pressure, current set at $\pm 10 \mu\text{A}/\text{cm}^2$, and a voltage range of 1.9 to 3.0 V at 100 °C and a Typical Liquid Electrolyte Based Battery

Figure VI-4 shows the plots between the capacities and cycle numbers of the Li|LPMEI₂₀:LiTfsi|LiV₃O₈ battery and a typical liquid electrolyte-based battery. Liquid electrolyte-based batteries can be recycled many times while maintaining the capacity about 20 mAh/g lower than the theoretical capacity of LiV₃O₈, which is about 280 mAh/g. The LPMEI electrolyte based battery fades out fairly quickly after five cycles. However, the results show that the Li|LPMEI₂₀:LiTfsi|LiV₃O₈ battery was functioning as a secondary battery, just not as well as those commercial liquid electrolyte based batteries.

Two Li|crosslinked BPAEI₂₀:LiTfsi|LiV₃O₈ batteries were prepared following the protocol with some modifications. Since the crosslinked BPAEI₂₀:LiTfsi electrolyte is a solid, no

Celgard is needed. In one battery, the pre-crosslinked polymer electrolyte methanol solution was cast and crosslinked on a glass slide. In the other battery, the electrolyte was directly cast onto the cathode and crosslinked with the cathode. In either case, the exact thickness of SPE is unknown because the SPE is elastic and will undergo dimensional change under the pressure during the battery sealing process. As discussed in Chapter IV, crosslinked BPAEI₂₀:LiTfsi film has a low conductivity. Therefore, poor performance is expected. The first battery barely worked due to the possible interfacial problems. The second battery was functioning as a battery. Its capacity is significantly lower than the capacity of the Li|LPMEI₂₀:LiTfsi|LiV₃O₈ battery, not to mention the theoretical capacity of LiV₃O₈. The batteries do not hold the voltage plateaus very long, indicating that they are unable to produce much current. Because the crosslinked BPAEI electrolytes have low ionic conductivities, the resulting polarization may make it function as a capacitor.

Subsequently, a Li|Crosslinked LPAMEI₂₀:LiTfsi|LiV₃O₈ battery was assembled to observe the effect of crosslinking on battery performance relative to uncrosslinked LPMEI batteries. As shown in **Table VI-1**, it recycled at lower temperature although using a very low charge/discharge density. After we increased the test temperature to 100 °C, we were able to recycle it more than three hundred cycles until we thought it was not meaningful to keep recycling. (See **Figure VI-5**) The recycling behavior of this battery is very interesting and strange. After ninety cycles, it looked like the equilibrium between discharge and charge was established when the recycling test was stopped. After several days of resting, I restarted the recycling. Surprisingly, the discharge capacity had been almost doubled while the charge

Temperature (°C)	Cycle Number	Drain Rate ($\mu\text{A}/\text{cm}^2$) Discharge/Charge	Discharge Capacity (mAh/g)	Charge Capacity (mAh/g)	Recycle Efficiency %
RT	1	1/1	0.2	0.23	115
35	9	1/1	0.8	0.92	115
45	12	1/1	1.9	N/A	N/A
	14	5/2.5	0.35	0.36	103
55	17	5/2.5	1	1.1	110
65	20	5/2.5	1.9	1.9	100
75	22	5/2.5	3.2	7.4	231
85	24	5/2.5	3.9	3.8	97
100	25	5/5	75	17	23

Table VI-1: Typical discharge and Charge capacities of a cell composed of Li|Crosslinked LPMEI₂₀LiTfsi|LiV₃O₈ with minimum contact pressure, at various temperatures, various current densities, and a voltage range of 1.9 to 3.0 V

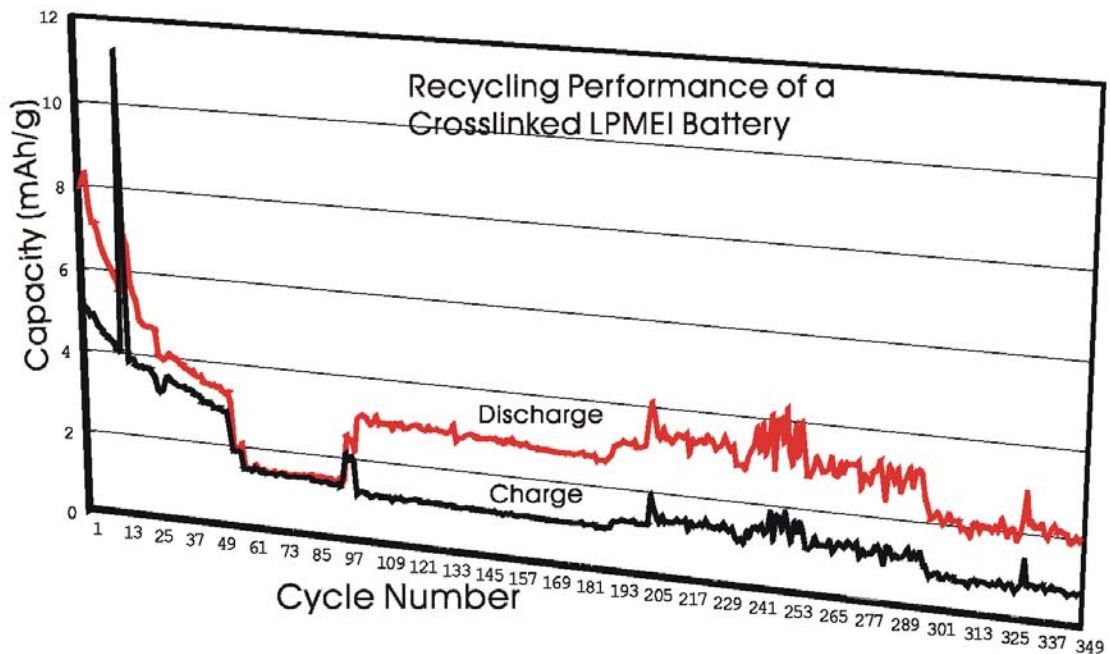


Figure VI-5: Typical discharge and Charge capacities of a cell composed of Li|Crosslinked LPMEI₂₀LiTfsi|LiV₃O₈ with minimum pressure, current set at + 5 $\mu\text{A}/\text{cm}^2$ and -10 $\mu\text{A}/\text{cm}^2$, and a voltage range of 1.9 to 3.0 V at 100 °C

capacity stayed the same since cycle number ninety-seven. Apparently, this discharge boost was related to the long resting time but no battery could discharge more than charge all the time. When compared with the Li|LPMEI₂₀:LiTfsi|LiV₃O₈ battery that I prepared, the crosslinked LPAMEI based battery is inferior in specific capacity, which is expected, and has lower operation temperature and better recycling ability.

Finally, some Li|crosslinked LPAG2EI₂₀:LiTfsi|LiV₃O₈ batteries were prepared and investigated. We were able to successfully reproduce batteries that function as secondary batteries but were unable to reproduce their specific recycling capacity due to the variability of our battery fabrication process. The average of the open-circuit voltage (OCV) of these batteries is about 2.7 V and these batteries can produce currents of about 10 micro amperes at room temperature. One battery had been successfully recycled at room temperature and a temperature dependent recycling performance test was carried out up to 100 °C. During these measurements, the drain rate was increased up to +10 μ A/cm² and -20 μ A/cm² and the capacities increased rapidly with increasing temperatures. The results are shown in **Table VI-2**. Although the specific recycle capacity of this battery at lower temperatures (<70 °C) were poor, it demonstrated great potentials because PEO-based batteries did not function at all at these temperatures. Finally, this battery was submitted to a current density-dependent recycling performance test at 100 °C. Unfortunately, this test was started at a high discharge current density 100 μ A/cm² and this battery was irreversibly damaged. As shown in **Table VI-3**, it was unable to show reproducible capacity at the same discharge current density. However, this battery was still recycled 100 more cycles until we thought it was not meaningful to keep recycling. Compared with the crosslinked LPAMEI based battery, the crosslinked LPAG2EI

Temperature (°C)	Cycle Number	Drain Rate ($\mu\text{A}/\text{cm}^2$) Discharge/Charge	Discharge Capacity (mAh/g)	Charge Capacity (mAh/g)	Recycle Efficiency %
RT	1	5/5	0.3	0.2	67
	11	1/1	2.3	1.6	70
35	18	1/1	20.1	N/A	N/A
	19	5/5	2.6	2	77
45	23	5/5	8.9	5.3	60
	25	10/10	4.1	2.8	68
55	29	10/10	7.7	4.5	58
65	32	10/10	13.5	6.4	47
75	35	10/10	24.5	7.4	30
	37	20/10	7.1	5.5	77
85	38	20/8	21.3	21.2	100
100	40	20/10	75	97	129

Table VI-2: Typical discharge and Charge capacities of a cell composed of Li|Crosslinked LPAG2EI₂₀LiTfsi|LiV₃O₈ with minimum pressure, at various temperatures, various current densities, and a voltage range of 1.9 to 3.0 V

Cycle Number	Drain Rate ($\mu\text{A}/\text{cm}^2$) Discharge/Charge	Discharge Capacity (mAh/g)	Charge Capacity (mAh/g)	Recycle Efficiency %
42	100/9	7.8	12.7	163
44	85/9	9.1	11.2	123
46	70/9	10.5	12.4	118
48	55/9	11.8	10.3	87
50	40/9	12.8	10.5	82
52	20/9	20.7	16.8	81

Table VI-3: Typical discharge and Charge capacities of a cell composed of Li|Crosslinked LPAG2EI₂₀LiTfsi|LiV₃O₈ with minimum pressure, at 100°C, various current densities, and a voltage range of 1.9 to 3.0 V

based battery showed much better performance due to the more flexible G2 side-chains. Compared with the well studied PEO electrolyte-based batteries, which are normally recycled from 80 to 120 °C,⁸³⁻⁸⁶ the crosslinked LPAG2EI electrolyte-based battery has lower operational temperatures but is inferior in specific capacity. However, this system is totally non-optimized and there is a great deal of improvement which could be done to improve the performance of the

crosslinked LPAG2EI-based battery. Because the crosslinked LPAG2EI polymer electrolyte does not have a crystalline phase and PEO polymer electrolyte does, the PEO polymer electrolyte needs to be heated to melt part of the crystalline phase to make the battery functional and the crosslinked LPAG2EI polymer electrolyte does not need to be heated. This is one of the major advantages of the crosslinked LPAG2EI polymer electrolyte over PEO polymer electrolytes.

The roles of the radical crosslinking initiator in the battery are worthy of studying. Apparently, the residue of V-50 after crosslinking is relatively stable in the lower current density electrochemical process because these batteries can be recycled a couple hundred of times in our experiments. However, the Cl^- that comes with the initiator could seriously affect the performance of these batteries. These chlorides could migrate under the electric field to the interfacial area of the battery and form layers of lithium chloride, affecting the ionic conductivity of the electrolyte and blocking the ion transport in and out of the cathode lattice.

A crosslinked LPAG2EI polymer electrolyte (20:1 N: Li^+) was prepared using VA-061 (dimethyl 2,2-azobisisobutyrate) (30:1 N:VA-061), a radical initiator without chloride, under similar crosslinking conditions to understand the possible effect of chloride in LPAG2EI based systems. Longer time (>72 h) was needed to form a solid film and the resulting electrolyte had less physical strength than the electrolyte prepared using V-50. Based on IR (data not shown), the ionic speciation of the polymer electrolyte was found not to change with the different initiators. The conductivity of polymer electrolyte prepared using VA-061 was of the same magnitude as that using V-50 (data not shown). Crosslinked LPAG2EI-based batteries using VA-061 have been prepared and found to be functioning as secondary batteries and further

recycling tests are ongoing.

Conclusions and Future Directions:

Initial battery tests showed that both the crosslinked LPAMEI electrolyte-based battery and crosslinked LPAG2EI electrolyte-based batteries function at low temperatures and had reasonable performance as a solid state battery, especially the latter case. In the future, greater quantities of LPAG2EI need to be synthesized to continue this research. As mentioned in Chapter V, other types of conductivity enhancing side-chains can be grafted onto the LPAEI instead of G2 side-chains and crosslinked to solid state polymer electrolytes. This type of PEO/PEI hybrid polymer electrolyte not only shows great potential itself but also provide a new method that may lead to the future commercializeable solid state battery.

Experimental:

Synthesis of LPMEI:

LPMEI was synthesized using the Eschweiler-Clarke methylation reaction from LPEI,⁵⁰ which was synthesized as referenced.⁴⁷

Synthesis of BPAEI:

BPAEI was synthesized as described in chapter IV.

Synthesis of LPAMEI:

LPAMEI was synthesized as described in Chapter V.

Synthesis of LPAG2EI:

LPAG2EI was synthesized as described in Chapter V.

Preparation of Li|Polymer Electrolyte| LiV₃O₈Coin Cell:

The cathode material, LiV₃O₈ paste, was first prepared by mixing and grinding LiV₃O₈ (87%, by weight), KS6 graphite (5%), SLP graphite (5%), and Teflon[®] (3%). The resulting cohesive solid was rolled into a thin and flat film. A 1.5 cm diameter disk of this film weighing about 10 mg was cut out with a circular template and the actual mass was recorded. After the LiV₃O₈ paste was dried under reduced pressure at 150 °C for 24 h, it was placed in the middle of a stainless steel plate positioned in a coin cell bottom. A solution of polymer electrolyte (0.05 g polymer host, corresponding amount of lithium salt, and 1 ml solvent) was prepared in a dry air purge glove-box and cast onto the cathode part of the cell until the metal plate was completely covered. The casting process was repeated three times every 30 minutes to ensure enough material on cathode. In the case of BPAEI based cell, LiTfsi was used as salt and monoglyme was used as solvent. In the case of LPAG2 based cell, LiTf was used as salt and methanol was used as solvent. After the solvent was allowed to evaporate for an hour, the cell was transferred to a vacuum oven, where the crosslinking reaction was carried out as described in Chapter IV and Chapter V. A slightly different method was applied in preparing the liquid polymer electrolyte (LPMEI) based cell. After the LPMEI-LiTfsi/methanol solution was first cast onto the cathode and allowed to evaporate, a 2.2 cm circular sheet of Celgard[®] separator membrane was placed on top of the cathode. More LPMEI-LiTfsi/Methanol solution was added until the Celgard was saturated. After 30 minutes of drying, the casting process was repeated twice. The cell was then dried under vacuum at 60 °C for 24 h. After crosslinking or drying, a metallic lithium disk with a diameter of 1.5 cm was placed on top of the cell in an argon atmosphere glove. After another stainless steel plate was placed on the lithium disk, the cell was finally

sealed by carefully positioning the top of the coin cell, which was crimped with the lip of the bottom lid.

Cell Recycling Test:

The assembled coin cell was transferred to an oven, where the cell was maintained at a desired temperature. The cell was connected to an Arbin Electrochemical Analyzer and tested according to programmed schedules. A typical program started with one hour of pre-rest, followed by a discharge at the desired current density. After 15 minutes of rest, the cell was charged at a desired current density. Upon the completion of charging, the cell rested for 15 minutes. The charge-discharge cycle was repeated the desired number of times before the end of test.

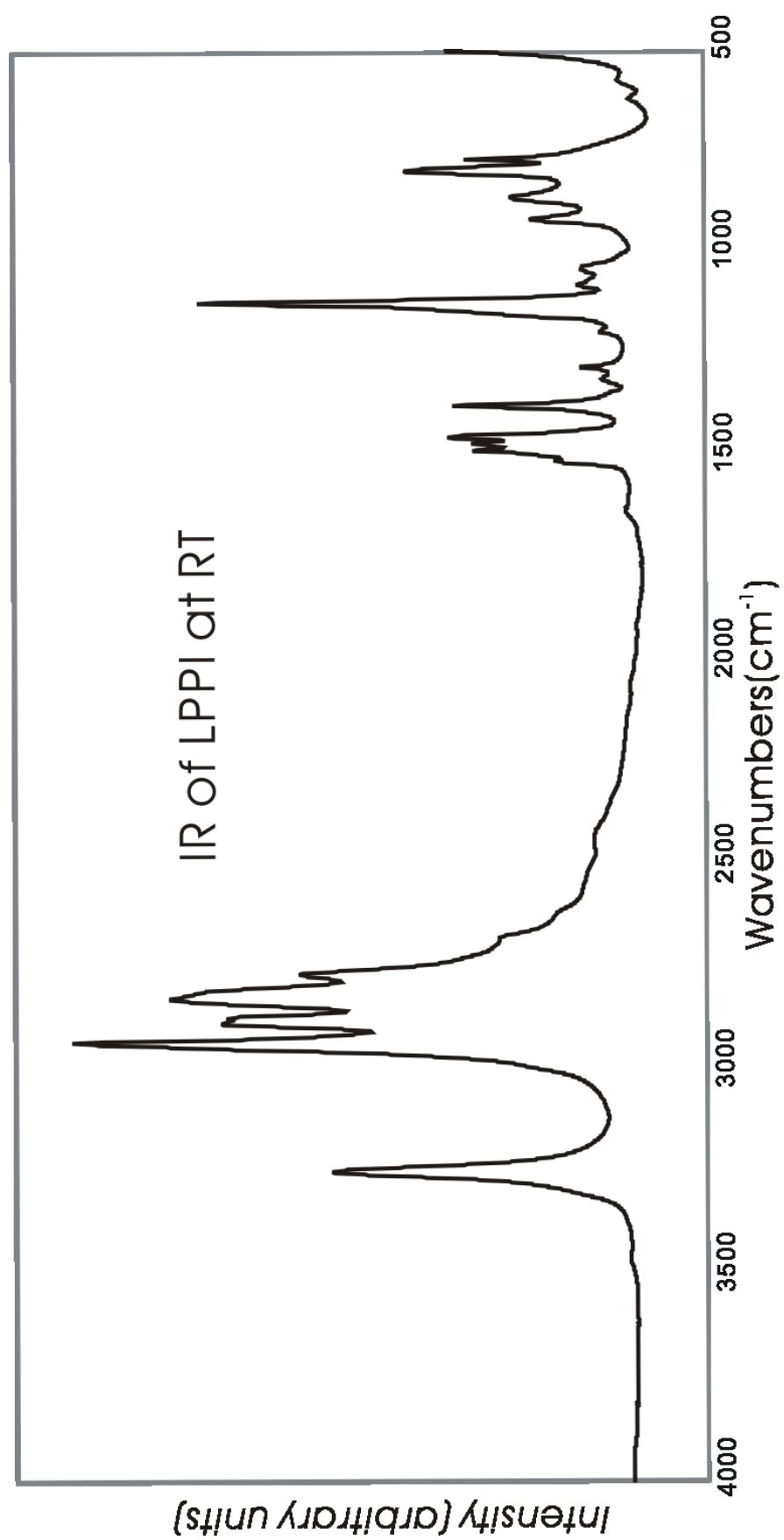
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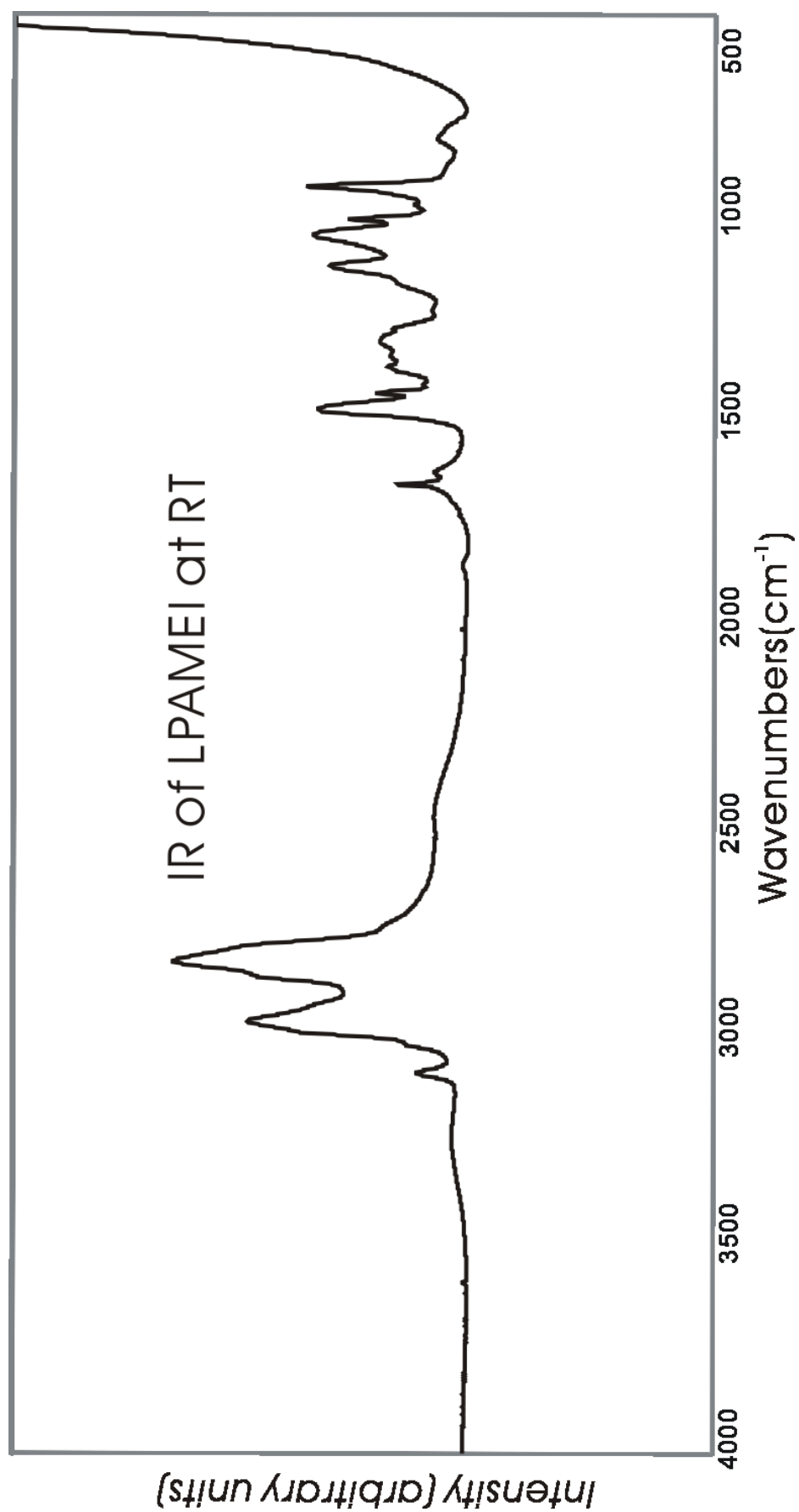
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Appendix of Spectrum I



Appendix of Spectrum II



Appendix of Spectrum III

