DEVELOPMENT OF ION CONDUCTIVE POLYMER GEL ELECTROLYTES AND THEIR ELECTROCHEMICAL AND ELECTROMECHANICAL BEHAVIOR STUDIES

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DEVELOPMENT OF ION CONDUCTIVE POLYMER GEL ELECTROLYTES AND THEIR ELECTROCHEMICAL AND ELECTROMECHANICAL BEHAVIOR STUDIES

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The focus of this research is to develop novel polymer gel electrolytes that overcome the drawbacks of conventional polymer electrolytes involving aqueous solvents or small organic molecules. In order to reach this aim, a series of novel polymer gel electrolytes were developed using crosslinked polymer matrix as a physical container acting to form cage around electrolytes. This structure leads to high ion conductivity under the applied electric field while maintaining mechanical integrity. The following gel electrolytes were prepared by varying the polymer hosts and type of electrolytes.

The ion gels based on free radical polymerization of methylacrylate (MMA) in ionic liquid (IL), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆) were transparent, self-standing and flexible with high ambient ionic conductivity in the range of $10^{-4}$~$10^{-3}$ S/cm. The coupling effects between PMMA matrix and IL decrease with increasing the concentration of IL. The temperature dependence of ion conductivity followed Arrhenius Law, indicating a thermally activated ionic motion. Therefore, the high conductivity is considered to be due to the movement from both cations and anions to electrodes and weak polymer-ion interaction. Based on its high ion conductivity, the three layer poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT/PSS) coated electroactive actuators were also developed, which exhibited a bending behavior under electrical field.
The lithium polymer gels based on PMMA and modified siloxane (PEMPS) with LiTFSI exhibited transparency, flexibility and mechanical integrity, and remained miscible under all use conditions. This gel showed an ion conductivity $10^{-4}$ S/cm at 70 °C. The conductivity showed a maximum when the salt concentration increased for the composition of MMA/PEMPS = 30/70 and 40/60. At low concentration regime of solvent/salt (PEMPS/LiTFSI), the conductivity showed an increase with salt (LiTFSI) concentration. Beyond a critical salt concentration, the viscosity of the medium became high and this led to decrease of diffusion of ions in the medium and the decrease of conductivity. The conductivity was also increased with the decrease of PMMA/electrolyte ratio. The swelling ratio of PMMA network was also found to exhibit a maximum as the salt concentration increased. The swelling ratio increased as the PMMA/electrolyte ratio was decreased. The FTIR study indicates lithium salt was mostly dissociated by PEMPS, and had little interaction with PMMA polymer hosts.

At last, polyvinyl alcohol (PVA)/KOH and polyacrylic acid (PAA)/KOH based aqueous gels were studied for the application in Ni-Zn batteries. The crystallization and chain entanglements formed physical crosslink for the PVA/KOH gel, while the copolymerization between acrylic acid and crosslinking agent formed the chemical crosslink for the PAA/KOH based gel. Both gels showed high ambient ion conductivity around $10^{-2}$ S/cm, satisfying the mechanical and ion conductivity requirements of the membrane for successful construction of Ni-Zn batteries.
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CHAPTER I
INTRODUCTION

In the development of suitable materials in electrochemical devices, such as compact, high-efficiency batteries, fuel cell and capacitors, ion conductive polymer gels as solid state ion conductive material were found to be good candidates to replace conventional liquid electrolytes. Ion conductive polymer gels commonly consist of polymer host and electrolyte which is typically in liquid state. The polymer host has a crosslinked network structure, which serves as a container for the liquid electrolyte. The electrolyte is the embedded phase in the polymer gel comprising of salt (ion carrier) and solvent. Salt dissociates into mobile ions with the help of solvent and executes ion transfer under external potential drive, which gives the ion conduction of the polymer gel electrolyte. The aforementioned structure of ion conductive polymer gels has the advantage of high ion conductivity comparable to the liquid electrolyte, and at the same time, possessing sufficient mechanical strength and flexibility arising from the polymer host. However, conventionally ion conductive polymer gels commonly include electrolyte based on aqueous or small molecules solvents. They have serious drawbacks including volatilization loss, limited potential, poor thermal stability and mechanical properties, which limit their applications. Ion conductive gels are uniquely suited in applications such as biological sensors and artificial muscles, because they exhibit soft, wet, and stimulus responsive behavior. Among these, polyelectrolyte gels
involving aqueous solvent have been extensively studied as a polymer actuator due to their large deformation under electric field (50 % strain). However, drawbacks of these systems include:

- volatilization loss of the aqueous solvent which causes environmental hazard
- limitation of potential due to the hydrolysis of water followed by gas release (electrochemical stability)
- poor thermal stability and mechanical properties
- Slow response and weak response stress in actuation
- complex process in fabrication due to the involvement of the container of electrolyte solvent

With respect to the aforementioned facts, the objectives of this study focus on developing and designing high ion conductive and electrochemically stable ion conductive polymer gels with thermal and dimensional stability. The conventional doping method was widely used to prepare gel systems by dissolving salts in polymer (sometimes a co-solvent is needed and removed through evaporation after the mixture of polymer and ionic liquid was formed). Gray has mentioned two methods to immobilize the electrolyte liquid in the polymer network: the first is to increase the viscosity of the liquid electrolyte by adding a soluble polymer until a gel consistency is achieved; the second is to import the liquid into a microporous polymer matrix. In this study, the polymer gel electrolytes are formed by in-situ polymerization of electrolyte in monomers in the presence of a crosslinking agent. The in-situ free radical polymerization has the following advantages over the conventional method in preparing desirable polymer gel
electrolytes: first, it is convenient to control the composition of polymer and electrolyte; second, the chemically crosslinked network exhibits higher thermal stability and mechanical strength; third, more electrolyte can be embedded since the liquid phase electrolyte will be encaged in the porous network during gel formation.

After gelation, the electrolyte liquid is embedded in the three dimensional polymer network, which is composed of cages that are connected and continuous throughout the polymer gel such as the mobile ions have a spacious room to move. The polymer network was formed from monomers without polar functions so the ions transfer is not affected by the interaction between polymer chains and ions. Therefore, the consequent gel product will combine the high conductivity of the liquid electrolyte and mechanical strength of polymer. This study specifically including the following polymer gel electrolytes:

1. Ion gels based on poly(Methylmethacrylate) (PMMA) and ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF$_6$).

Polymer gel electrolyte involving ionic liquid are unique and newly developed ion conductive polymer materials.$^{5-8}$ They replace aqueous electrolyte solution by ionic liquid and show unique electrochemical properties compared with the conventional polymer gel electrolytes. The room temperature ionic liquids (RTIL) are composed of cations and ions in the state of liquid at room temperature and exhibit many favorable features as an electrolyte, including negligible vapor pressure, high ionic conductivity, non flammability, as well as good thermal and electrochemical stability.$^9$ The high ionic conductivity was contributed by the great self-dissociation and ion-transporting properties of the RTIL, as well as by the decoupling of the ion transport from polymer
segmental motion. The studies of these gels as solid state ion conductive materials are limited in recent years.

In this study, the ion gel was prepared through in-situ free radical polymerization of monomer in ionic liquid based on the concept of salt-in-polymer system. The monomer and ionic liquid were selected with respect to the miscibility of the reaction mixture and the compatibility of the system after polymerization. The ion gels with up to 90 wt% of ionic liquid were prepared. The products were transparent and flexible, exhibiting a very high conductivity at room temperature. The kinetics of gel polymerization was studied by DSC thermograms to investigate the influence of ionic liquid. The effects of polymer/ionic liquid composition on the interaction of the polymer matrix and ions in electrolyte gels were investigated, which could play a significant role in the ion transfer behavior in polymer electrolytes. The morphology study, thermal analysis, swelling ratio and ion conductivity behavior were characterized to investigate their mechanism in the application of electrochemical devices.

2. Lithium polymer gel based on lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and modified polysiloxane.

In the present study of polymer electrolytes for the application of lithium battery, the primary lithium electrolytes are made by lithium salt and small molecular organic solvents such as propylene carbonate and ethylene carbonate, which will encounter poor unstable electrochemical stability and constrain their application. In consequence, it is necessary to replace these small molecular organic solvents with a suitable solvent that is more stable and environmentally safe, and can be operated in a wide range of working conditions.
This study is aimed at developing a solid state polymer gel electrolyte that is able to improve the battery cycling life. At the same time, it should be inexpensive, commercially available and safe. With these considerations, a modified polysiloxane was used as the solvent to dissociate the LiTFSI salt so as to form the electrolyte solution. The selected polysiloxane appeared to be a good solvent for LiTFSI and miscible with MMA monomers. Therefore, the in situ polymerization could be carried out to form the crosslinked gel electrolyte. The products were synthesized with respect to the monomer/electrolyte composition and the lithium salt concentration in the electrolyte. The behavior of ion conduction was related to the interaction among the components of the gel system, the viscosity of the electrolytes, morphology of the electrolyte and gel products, as well as the structure of polymer network. The ion conductivity was found to change with the polymer/electrolyte composition and the Lithium salt concentration.

3. Polymer electrolytes for Ni-Zn batteries

It is well known that the electrolyte is at the core of the battery, and the conventional Ni-Zn battery suffers from the short circuiting and failure due to the shape change and dissolution of the zinc electrode and dendrite growth. The interest in employing solid state polymer electrolyte for Ni-Zn batteries has been renewed recently since the solid state polymer electrolyte was found to suppress the dendrite growth of Zn. In this case, the structure of crosslinked polymer gel electrolytes as mentioned previously shows a great potential in the application of Ni-Zn batteries. The chemical structure of polymer matrix will defined the type of interaction between KOH electrolyte and the polymer chain, which will, in turn, affect the conduction performance of the battery.
In the development of a suitable solid state polymer electrolyte which can efficiently suppress the dendrite growth of Zn and extend the battery lifetime, three types of solid state polymer electrolytes were designed and compared based on the electrolyte of KOH water solution. The interaction between electrolyte and polymer chains with different chemical structures such as polarized, neutralized and charged side chain was taken into consideration. This investigation is designed to help to understand the electrochemical mechanism of the KOH electrolyte in the polymer electrolyte.

4. Electroactive actuator of PEDOT coated ion gels

The studies of ionic conductivity based on IL polymer gel reveal that a higher ion conductivity relates to a larger amount of ions migration under the electric field. Since the ion transfer induced deformation is one of the main contributions of the actuation of the polymer gel system, ion gel of ionic liquid has the potential to be a solid state gel actuator that does not involve any volatile solvent and can operate in ambient conditions. However, the ionic liquid based polymer gels have been rarely studied for their electromechanical properties for actuator applications. In addition, the interaction between gel matrix and IL will influence ion transfer and result in various range of deformation under electric field. But these effects are still not well understood.

In order to have the actuation behavior, the mobile ions need to move to a certain direction under potential, which will cause the deformation of the gel due to the mass redistribution. The extent of deformation depends on the amount of mobile ions and the applied external potential. The desirable product will be a flexible solid polymer gel with maximum IL as electrolyte solution. A higher potential can also drive more ions to move towards electrode. But too high potential will cause degradation of the ion gel system
and shorten the lifetime of the actuator. Poly (3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) as a water soluble conductive polymer can be used as an ion container of the gel actuator since the ion can move in and out of its matrix due to the electrochemical reaction. In this research, the PEDOT/PSS water solution is coated on the ion gel surfaces that contacting with electrodes by film casting technology. The multilayer ion gel actuators were successfully prepared that exhibited bending behavior under direct current potential at ambient atmosphere. The actuation mechanism is proposed based on the characterization results of FTIR and morphology study.
CHAPTER II

LITERATURE REVIEW

2.1 Polymer gels

A polymer gel is a three-dimensional network with embedded liquid phase. The chemically crosslinked gel is formed by chain crosslinking during copolymerization by use of multifunctional reactants. The crosslinking reaction is carried out by the reaction of primary polymer chains with the multifunctional reactants. It is composed of all the steps of polymerization that are initiation, propagation, termination and chain transfer reactions. In the free radical crosslinking copolymerization, main reaction components include monovinyl monomers and divinyl monomers (the crosslinking agent or crosslinker). The interchain reaction and intrachain reaction will result in different network structures, leading to different properties in the final gel products. The primary chains possessing pendant double bond are mainly formed at the fast propagation step. As illustrated in Figure 2.1, the primary polymer chain first reacts with one double bond of the divinyl crosslinker, leaving the other unreacted double bond as a pendant double bond. The pendant double bond reacts with another primary polymer chain to form a crosslink structure. The continuous crosslinking finally builds up the 3-D network. It is clear that crosslinking is an inter-chain reaction which contributes to the network formation.
Some elementary reactions of a growing chain radical during the free radical copolymerization are shown in Figure 2.2, when the primary chain radicals react with the pendant double bonds on their own chains or the primary chain chemically connected with it, a cyclization reaction takes place. Thus the crosslinking copolymerization can be a very complicated set of reactions. The final gel structures and their properties will be affected by the concentration of components and synthetic conditions. For example, Scott and Peppas found the initial monomer concentration in the poly (acrylic acid) gel preparation played a significant role in the gel structure. A smaller mesh size of the network formed at a higher monomer concentration due to the decrease in the total volume of reaction solution. The increasing of monomer concentration enhanced chain interpenetration and improved the efficiency of the crosslinking reaction for the resulting gels. In addition, the extensibility of network chains was restricted because of the very limited solution volume at high monomer concentration, which resulted in less space in
the network. The above two effects could lead to an increase of the crosslink density of the network as observed and explained by Baker et al.\textsuperscript{13}

![Diagram of elementary reactions of a growing chain radical during the free radical copolymerization.](image)

Figure 2.2 Elementary reactions of a growing chain radical during the free radical copolymerization (a) Crosslinking; (b) cyclization; (c) multiple crosslinking; (d) loop formation.\textsuperscript{14} (Reproduced with permission from reference 14. Copyright John Wiley and Sons.)

One advantage of the gel electrolyte is that the formation of solid gel network from the liquid pregel mixture can be carried out simultaneously with the construction of the cell, enabling good contact between the gel electrolyte and its interfaces.

In this study, the polymer electrolytes are prepared by free radical polymerization. Equation (2.1) gives a basic expression for the rate of free radical polymerization.\textsuperscript{15}

\[
R_p = k_p[M] \sqrt{\frac{f k_d[I]}{k_t}} \quad \text{(Equation 2.1)}
\]

$[M]$ is the concentration of monomer. $[I]$ is the concentration of initiator and $f$ is the effective fraction of initiator for promoting polymerization. $k_p$, $k_t$ and $k_d$ are kinetic constants for propagation, termination, and initiation reactions. The dependence of the kinetics of radical polymerization on temperature can follow the Arrhenius relationship.
The relationship between temperature and polymerization reaction rate was shown in (Equation 2.2),

\[
R_p = \frac{k_{p0}k_{d0}}{k_{t0}^{1/2}} \left( f^2 \right)^{1/2} [M] \exp\left( -\frac{E_p - 0.5E_t + 0.5E_d}{RT} \right)
\]

(Equation 2.2)

where \(E_p, E_t, E_d\) are activation energies and \(k_{d0}, k_{p0}, k_{t0}\) are pre-exponential constants for propagation, termination, and initiation reactions, respectively. From the above formula, the polymerization rate should increase as the temperature rises because the term \(E_p - 0.5E_t + 0.5E_d\) is commonly positive for free radical polymerization. In this case, a high temperature can lead to a rapid polymerization.

Generally, copolymerization of monomer and a multifunctional crosslinker is a convenient way to synthesize gel electrolyte where all the reactants are mixed together and cast into a certain type of mold.\(^{16-21}\) Commonly used components in the free radical gel polymerization system include vinyl monomer, divinyl comonomer (crosslinker), initiator, and electrolyte solution consisting of salt and relative solvent. Reaction solution is prepared in the pregel container, and the consequent uniform and transparent solution is cast in the test tube or parallel glass plate mold. The molds are then sealed and placed in water bath at a desired temperature for a specific period of time. The gel sheet obtained from the parallel plates can be directly used or cut into a required size. The gel rods made in test tubes are often cut into thin disks before use.

2.1.1 Structure characterization

Since the crosslinked polymer gels have a 3-D network structure, they can not dissolve in solvent. This character of gel demands different methods than the linear
polymer in characterization its structure. The gel network can be described by the parameters of crosslink density and molecular weight between crosslink. A low value of these parameters indicates a loose network and a larger mesh size. Swelling ratio test is also a common method to indirectly estimate the gel network. Techniques that are generally employed to characterize structure and morphology of polymer electrolytes include optical microscopy, differential scanning calorimetry (DSC) and NMR. The general characterized parameters and their relative methods are listed as follows:

(1) Crosslink density

The crosslink density is an important parameter in defining the structure of polymer gel. It is defined as the ratio of the number of crosslinked units to the total number of reacted monomeric units that are chemically bound in primary chains. Generally, a higher crosslink density leads to a more rigid gel and lower swell capacity. Lopatin et al. qualitatively characterized the crosslink density by means of NMR and mechanical relaxation tests. In the NMR experiments, the rise in –CH concentration was related to the increase of crosslink density. A lower ability of stress relaxation and a higher elastic modulus were associated to a higher crosslink density.22

(2) Number average molecular weight between crosslinks, $\overline{M}_c$

Molecular weight between crosslinks is a central parameter in characterizing the structure of network and it can describe the crosslink density in an indirect way. It is well known that a larger value of $\overline{M}_c$ represents a longer distance between crosslinks, indicating a looser network. A simple theoretical relationship between the crosslinker dosage and the molecular weight between crosslinks is
where $\overline{M}_{c,th}$ is the molecular weight between crosslinks, $M_r$ is the molecular weight of the repeating unit, and $X$ is the crosslinking ratio which is defined as mol- crosslinker/mol- monomer. This estimation should be based on the assumptions that the conversion of the monomers is 100% and the crosslinker is all used to form a crosslink instead other side reactions.

Peppas determined $\overline{M}_c$ by means of a thermal analysis through differential scanning calorimeter DSC. This method is based on the general empirical relationship between the glass transition temperature and $\overline{M}_c$ as shown in Equation 2.4:

$$\overline{M}_c = \frac{3.9 \times 10^4}{(T_g - T_{g0})}$$

(Equation 2. 4)

where $T_g$ is the glass transition temperature of the crosslinked polymer, and $T_{g0}$ is that of the uncrosslinked polymer with the same chemical composition. Joseph et al. used equilibrium swelling ratio to calculate $\overline{M}_c$ based on the Flory-Rehner equation for the tetrafunctional network model.

3. Swelling ratio

Swelling ratio is another important parameter that gives insights into the physical structure of the gels, particularly the effective crosslink density. It can be measured by volume or weight of the swollen (at equilibrium state in a good solvent) gel to dry gel ratio. A polymer gel with a higher swelling ratio indicates a looser crosslinked network and thus a better swelling ability.
2.2 Ion conductive polymers

Based on the conduction mechanism, Osaka et al. divided conductive polymers into two categories: electron conductive polymers and ion conductive polymers. The electron conductive polymers were first reported in 1971 by Shirakawa and co-workers. The conduction in conductive polymers occurs by delocalization of their π electrons along the whole polymer chain in conjugated systems. They generally have a higher electronic conductivity than the ion conductive polymers. Ion conductive polymers, on the other hand, work by the transport of mobile ions in the system. According to Armand, ion conductive polymers can be obtained by introducing mobile ions via non-aqueous polar solvents or directly within the network of solvating macromolecules.

The ion conductive polymers have been developed mainly for electrochemical devices such as compact, high-efficiency batteries, fuel cell and capacitors. Currently, much attention has been paid to develop electrolytes to enhance the capabilities of electrochemical cells. Figure 2.3 shows the basic construction of a lithium polymer battery, where the polymer electrolyte is sandwiched by electrodes. The polymer electrolyte is in the form of thin membrane and is flexible to fit into various geometries.
The conventional material in battery industry is liquid electrolyte comprising solutions of ionic species in solvents. The electrolyte liquid dissociates into mobile ions, which enable electrochemical reactions to take place under a potential difference, with the main potential gradient focusing at the electrode interfaces.\textsuperscript{29} It has a wide application in galvanic cells and shows good conductivity. However, it suffers from several drawbacks such as corrosiveness, leakage, and no firm barrier between electrodes. Ion conductive polymers are thus introduced to overcome these problems so as to produce more advanced battery systems. Once a solid polymer electrolyte is used in the battery, no separator is needed and the electrolyte medium can be fabricated as an ultrathin film, which enables the construction of the solid state battery with high energy density.\textsuperscript{26} The developments of ion conductive polymer are briefly described by the following three stages.\textsuperscript{30}
2.2.1 Solid conductive polymer based on linear polyethers

Initially, ion conductive polymers were made by polymers containing salt with mobile ions, which is termed “salt-in-polymer” electrolyte system. The typical materials used in this case are polyethers since they have oxygen atoms with free electron pairs, which serve as electron donors to coordinate cations. Poly (ethylene oxide) (PEO) has been studied the most since Wright discovered the ionic conductivity in the complexes of PEO and alkali metal salt in 1973.\textsuperscript{31} PEO shows excellent compatibility to most alkali metals salts and exhibits good contact with electrodes in the thin film form. The transport of ions is known to mainly depend on the relaxation rate of polymer segments, so the good segmental movement leads to high ion conductivity. Linear PEO molecules tend to crystallize at room temperature, yielding rigid structures. This reduces the motion of polymer segments, leading to low ionic conductivity. Even though these materials show good mechanical properties, they exhibit a conductivity commonly under $10^{-4}$ S/cm at room temperature, which is lower than acceptable ionic conductivity $10^{-3}$ S/cm needed for practical use.

2.2.2 Polymer electrolyte based on organic plasticizers

The second generation of conductive polymers focused on using low $T_g$ polymers (such as polydimethylsiloxane (PDMS)) incorporating plasticizers (such as propylene carbonate or ethylene carbonate) to make the polymer chains flexible, so as to improve the ionic conductivity in ambient conditions.\textsuperscript{32, 33} The addition of plasticizer to solid conductive polymer decreases the $T_g$ by causing isothermal increase in the system’s
configurational entropy, which increases the chain mobility\textsuperscript{4}. But the introduction of a large amount of low $T_g$ additives generally sacrifices the mechanical properties of the material and makes them impractical.\textsuperscript{34-36}

Another method to prevent crystallization and maintain sufficient mechanical properties is to use crosslinked polymer network. In this method, the linear polymer chains form the network with the addition of crosslinking agent. The network can be easily processed into thin films and membranes so as to use as separators. Cheradame \textit{et al.}\textsuperscript{37} measured the ion conductivity of polypropylene oxide networks filled with sodium tetraphenylboride in 1980, and found that the materials did not behave like the solid electrolytes which follow an Arrhenius law. They attributed this deviation to the fact that the materials were not in the glassy state temperature range.

2.2.3 Polymer gel electrolyte

The third stage of development is the polymer gel composed of liquid electrolytes and host polymer matrix.\textsuperscript{30} Since 1990s, ionically conductive polymer gels as a novel non-aqueous ion conductive materials have been extensively studied in both electrochemical applications like batteries and electric double layer capacitors and electromechanical applications such as actuators.

Based on the structure of the polymer network, these materials can be classified into two categories: gel electrolytes and polyelectrolyte gels (see Figure 2.4 and Figure 2.5). Gel electrolytes are commonly mixed systems of polymer-electrolyte liquid, where ion conduction occurs mostly in the liquid electrolyte media.\textsuperscript{30} There is no ionic group on the polymer chain, and both the cations and the anions are mobile and contribute to
the ion conduction. Whereas, polyelectrolyte gel contains covalently bonded ionic (either cationic or anionic) groups in polymer chains and only the counterions are mobile. Therefore, the polymer matrix can either have great or little interaction with mobile ions depending on the chemical nature of polymer chains and the structure of polymer network.\textsuperscript{38, 39} In the case of little interaction, the gel system acts more like a liquid electrolyte since the ions transport mainly in the solvent medium, and the polymer matrix serves to maintain the structural integrity of the system. When the interaction becomes intense, the gel behaves more like a solid polymer electrolyte because the diffusion of ions involves strong ion-polymer-segment coupling.

![Figure 2.4 Concept structure of gel electrolyte. The polymer chains are not charged.](image-url)
The conventional composition of gel electrolyte includes a polymer, a solvent and a salt. The polymer matrix with a low to moderate crosslink density can be swollen with the solvent-salt solution to a large extent. Thus, these gel electrolytes combine the mechanical properties of polymer network with the ion conductivities of liquid electrolytes. They reduce the risk of leakage with their enhanced interfacial contact. They maintain their integrity during volumetric changes associated with charging and discharging cycles of the battery. But they also suffer from several shortcomings of the solvent like flammability and volatility, which restrict their application in large-scale devices. In addition, it is important to maintain sufficient mechanical strength under steady stresses over a temperature range that could be encountered in rechargeable cell, for application in electrically powered vehicle, the temperature range is from -20 to 60 °C.

The conductivity of gel electrolytes at room temperature (around $10^{-3}$ S/cm) is higher than that of the solid conductive polymers. To investigate the effect of the solvent
in swollen polymer network, Meyer compared the ionic conductivities between dry gels and gels that were produced by the same phosphazene-based network swollen with solvent. The compositions and chemical structures of the two systems are shown in Table 2.1, and the relative ionic conductivities as a function of temperature are illustrated in Figure 2.6. As shown in Figure 2.6, the presence of solvent in the gel network enormously increases its room temperature ionic conductivity as compared to dry state.

Table 2.1 Chemical structure and compositions of two phosphazene-based network.  

<table>
<thead>
<tr>
<th>Compound</th>
<th>Basic structure</th>
<th>Crosslinker</th>
<th>Plasticizer</th>
<th>Salt</th>
<th>Salt conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>( \left[ \left( \begin{array}{c} \text{P=N} \end{array} \right) \frac{1}{2} \right] _{n} ) ( \text{OR}<em>{1} \text{OR}</em>{2} \text{OR}_{2} )</td>
<td>UV</td>
<td>none</td>
<td>LiClO(_4)</td>
<td>Li/O = 0.028</td>
</tr>
<tr>
<td></td>
<td>( R_{1} = \left( -(\text{CH}<em>{2}\text{CH}</em>{2}\text{O})<em>{7}\text{CH}</em>{3} \right) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( R_{2} = \left( -(\text{CH}<em>{2}\text{CH}</em>{2}\text{O})<em>{\gamma}\text{CH}</em>{2}\text{CH}=\text{CH}_{2} \right) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( x + y + z = n ) (random)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( R_{1}/R_{2} = 1.5 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>same as 15</td>
<td>UV</td>
<td>PC (8)</td>
<td>LiClO(_4)</td>
<td>Li/O = 0.043</td>
</tr>
</tbody>
</table>
Since 1970s, gel polymer electrolytes based on polymers with a dipole moment and organic salt solutions have been used. These materials show ambient conductivities close to $10^{-3}$ S/cm and can only work around room temperature due to the solvent volatility. Another problem was the voltage stability window of these materials was similar to that of the liquid electrolytes, which did not show any advantages in battery operation. The research in the gel electrolytes became active in 1980s. A variety of polymers, salts and solvents have been investigated to produce novel gel electrolytes. In order to investigate the effect of plasticizer/solvent on the electrochemical and mechanical properties of gel polymer electrolyte, MacFarlane and coworkers studied the effect of the addition of N,N-dimethylformamide (DMF) and propylene carbonate (PC) on increasing the concentration of charge carriers in the urethane crosslinked polyether.
network. Reiche et al. found that the extent of dissociation of the salt can be improved by the increase of the gel polarity when polar plasticizers or comonomers were introduced in the polymer network. Later they observed that polar plasticizers with low molecular weight showed high self-diffusion in the gel and resulted in high ion conductivity. The application of gel electrolyte as a battery was developed since 1997, when Tarascon et al. made the first practical rechargeable Li-ion plastic battery based on the PVDF-HFP copolymer gel electrolyte using a lithiated carbon material as the anode. The gel electrolyte battery is suitable at low temperatures (below 55 °C). Overall, in order to achieve a breakthrough with respect to practical applications, the gel electrolyte must increase its mechanical strength, while the solid polymer electrolytes need improved conductivity.

2.2.4 Polymer gel electrolyte based on ionic liquids

In recent years, a new type of polymer electrolyte involving ionic liquid has gained intensive interests in the areas of ion conductive polymer electrolytes and electroactive polymer actuators. These new materials can overcome many drawbacks of the conventional polymer gel electrolyte by the aid of electrochemical properties of the ionic liquid. Since the ionic liquid plays a crucial role in the properties of these materials, this section will start with the introduction of ionic liquid, followed by ionic liquid based polymer gel systems: ion gel.
2.2.4.1 Ionic liquid

Ionic liquids (IL) are salts in liquid state below 100 °C, which are mostly composed of ions and are highly polar yet non-coordinating solvents. Room temperature ionic liquid (RTIL) refers to an ionic liquid which is liquid at room temperature. thus, it is also called room temperature molten salts. These materials have $T_g$ and $T_m$ below room temperature. The upper temperature limit for ionic liquids is usually that of thermal decomposition instead of vaporization. These features result from the large size of the ions and low symmetry level of the cation structure, which lead to reduced lattice energy and thus lower melting point. For organic salts, their organic cations and anions have larger size compared with the inorganic ones, so they are generally favorable choices in making ionic liquid. Whereas, the contribution of anion and cation can not be solely determined in lowering the melting point, since specific interactions can increase the melting points. 47 The thermal properties along with the ionic conductivity of some well known RTILs are shown in Table 2.2. The general ionic liquid consists of organic component and the counterion group with a delocalized charge. This type of composition has the advantage to prevent the formation of a stable crystal lattice.
Table 2.2 Thermal properties and ion conductivity of some room temperature ionic liquids.²

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; / °C</th>
<th>T&lt;sub&gt;m&lt;/sub&gt; / °C</th>
<th>T&lt;sub&gt;d&lt;/sub&gt; / °C</th>
<th>σ at 30 °C /10⁻³ S cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄)</td>
<td>-89.4</td>
<td>14.6</td>
<td>391</td>
<td>20</td>
</tr>
<tr>
<td>1-butylpyridinium tetrafluoroborate (BPBF₄)</td>
<td>-66.7</td>
<td>15.5</td>
<td>342</td>
<td>3.0</td>
</tr>
<tr>
<td>1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide (EMITFSI)</td>
<td>-86.0</td>
<td>-16.0</td>
<td>444</td>
<td>8.6</td>
</tr>
</tbody>
</table>

T<sub>g</sub> and T<sub>m</sub> are the glass transition temperature, melting temperature. T<sub>d</sub> is the decomposition temperature at 10% weight loss from TGA. σ is the ion conductivity determined by complex impedance method at an AC amplitude of 10 mV.

Overall, the important features that make the ionic liquid an outstanding electrolyte compared to conventional electrolyte solutions are ⁹

- negligible vapor pressure
- high ionic conductivity
- good electrochemical stability
- non flammability
- good thermal stability

Furthermore, the composition of the ionic liquid can be adjusted by the combination of different cations and anions to achieve desired properties, thus they are also called “designer solvents”.⁴⁸ Some examples are shown in Figure 2.7. By this way, ionic liquids with desirable properties such as melting point, viscosity, and solubility can
be obtained. All the ionic liquids considered in the present study are specific to (room temperature) ionic liquid otherwise indicated.

Figure 2.7 Examples of ILs with different properties by changing the composition of ions.  

The commercially available ionic liquids are limited and expensive, which is partially due to the high cost of the precursors used for manufacturing the ionic liquids. Therefore, most ionic liquids reported in the literature were synthesized in laboratory. In fact, the lack of raw physical property data such as viscosity and density has slows the design of suitable processes on applications for ionic liquid products.  

The development history of ionic liquids can be traced back to 1914 when the organic salt ethyl ammonium nitrate ([EtNH₃][NO₃]) was found to be the first room temperature ionic liquid with a melting point of 12 °C. Since its discovery, researchers have taken great efforts in finding its applications in various areas. Now, ionic liquids have been used in many diverse fields especially as electrolyte solutions. The methylimidazolium and pyridinium cations have been proven to be good choices of the organic component in the ionic liquids. Their structures are shown in Figure 2.8. A series of organic cations can be formed based on this structure with various length of the
alkyl group R, such as [MMIM], [EMIM] (M: methyl, E: ethyl, B: butyl, IM: imidazolium). Among them, the ethylmethylimidazolium cation ([EMIM]) was generally found to exhibit the highest ionic conductivity and good stability, thus it has become the favorite choice of cation in preparing desirable ionic liquid.

![Chemical structures of (a) methylimidazolium and (b) pyridinium cations](image)

Figure 2.8 The structures of (a) methylimidazolium and (b) pyridinium cations

According to Rooney and Seddon, ionic liquids are typically developed in two stages. The first stage is chloroaluminate (III) salts. It is a mixture of [EMIM]Cl with AlCl₃ forming a series of equilibria between [EMIM][AlCl₄], [EMIM][Al₂Cl₇], and [EMIM][Al₃Cl₁₀]. The chloroaluminate ionic liquid mixtures are governed by the primary equilibrium:

$$2[\text{AlCl}_4]^- \leftrightarrow [\text{Al}_2\text{Cl}_7]^- + \text{Cl}^-; k \approx 10^{-6} \quad \text{(Equation 2.5)}$$

The disadvantage is that stage I salts are highly moisture sensitive and tends to decompose, giving off HCl by hydrolysis which is highly corrosive. The second stage is neutral and water-insoluble ionic liquids in which the air stable molten salts were developed by replacing the chloroaluminate anions. Representative anions are BF₄⁻, PF₆⁻, SBF₆⁻, CF₃SO₃⁻, and N(CF₃SO₃)₂⁻. This type of ionic liquids is much less reactive.
2.2.4.2 Ion gel based on ionic liquid

This section will focus on the polymer gel system with ionic liquid as the electrolyte. Freemantle gave the name “ion gel” to the polymer gel system when the ionic liquid and polymer matrix synergistically combined to form the gel. The ion gel in this study refers to a new type of gel polymer electrolyte based on the polymer-in-salt system prepared by in situ polymerization of vinyl monomers in room temperature ionic liquid. Ion gel is different from the previously mentioned gel electrolyte because it is a solvent free system. The increase of the number of carrier ions and their mobility can be obtained simultaneously by increasing the salt concentration for ion gels. The notion of polymer-in-salt system was put forward by Angell et al. in 1993. They considered a gel system that only a small amount of polymer can provide sufficient rubbery compliance, yet the majority of the gel system was occupied by electrolyte solution that gave a high ionic conductivity. Ion gels are an inverse concept to the solid salt-in-polymer electrolyte with respect to the weight ratio of salt to polymer. This system exhibited an improvement from the conventional polymer gel system since the content of electrolyte liquid is further increased. The introduction of this polymer-in-salt type of electrolytes has a promising future in achieving novel polymer electrolytes with high ionic conductivity and sufficient mechanical properties. The development of new polymer electrolytes with rubbery compliance and high ionic conductivity was the main target of the past studies. Ionic liquids (IL) turn out to be a favorable candidate of the electrolyte salts since they are in liquid state at ambient temperature. Besides, they contain high ionic conductivity and can be solvents for some polymers.
The polymer-in-salt electrolyte was prepared by dissolving the polymer in compatible ionic liquids, thus a rubbery electrolyte with high ionic conductivity was obtained. Sometime a co-solvent for both polymer and IL is used to embed more IL in the crosslinked polymer matrix, and is removed later via evaporation. Since chloroaluminate molten salts were found to be not environmentally friendly because of high moisture sensitivity, water-insoluble ionic liquids are preferred electrolyte salts. Carlin et al. have made rubber gel electrolytes from non-chloroaluminate ionic liquids and poly(vinylidene fluoride)-hexafluoropropylene copolymer (PVdF(HFP)). It has been reported that imidazolium salts are good plasticizers for poly(methyl methacrylate), which improved the thermal stability and reduced the $T_g$ of the system.

Nada and Watanabe were the first to produce transparent, mechanically strong, and highly conductive polymer electrolyte films by in situ free radical polymerization of vinyl monomers in room temperature liquids in 2000. The procedure of technique is illustrated in Figure 2.9. The ILs act as solvent for the polymerization and as electrolyte solution after the form of polymer gel. With the aim of achieving good ion gel systems, Watanabe and Susan varied the composition of monomer and IL in the system. The ILs they used were 1-ethyl-3-Methylimidazolium tetrafluoroborate (EMIBF$_4$) and 1-butylpyridinium tetrafluoroborate (BPBF$_4$). They determined the suitable composition of gel system by following several steps: First, the miscibility between IL and monomer was visually examined. A suitable monomer related to a specific IL is selected once the transparent and homogeneous solution was formed upon mixing. Second, the compatibility between the polymer and RTIL was visually examined. The systems that either failed in undergoing polymerization or presented phase-separation after
polymerization were abandoned. The product of selected system was transparent, self-standing, and mechanically strong electrolyte polymer films. Finally, the compatibility of selected system was investigated under DSC, where a single T_g was generally observed.

Finally, 2-hydroxyethyl methacrylate (HEMA) turned out to be the only suitable material in forming transparent and flexible film with high ion conductivity. The consequent ion gel with the composition [BPBF_4]/[HEMA] = 40/60 showed an ionic conductivity of 10^{-3} \text{ S/cm} at room temperature. The ion transport behavior of the ion gels varied depending on the composition and structure of the constituents. The high ionic conductivity was thought to be contributed by the great self-dissociation and ion-transportsing properties of the IL, as well as by the decoupling of the ion transport from polymer segmental motion. The term “decoupling” means the ion transport is independent of the segmental motion of the polymer. In other words, the ion conduction
is able to occur even at the temperature below the $T_g$ of polymer where the polymer chain is frozen. As known, in many cases the polymer is not compatible with the IL and results in phase separate. So, this technique demands compatibility between the components in the system. Other than that, the requisite degree of co-processability in subsequent fabrication and essential mechanical and chemical robustness are also important in obtaining satisfactory ion gel products\textsuperscript{58}.

Recently, Susan and coworkers reported another successful ion gel film by in situ free radical polymerization of methylmethacrylate (MMA) in the RTIL, 1-ethyl-3-methyl imidazolium bis(trifluoromethane sulfonyl)imide (EMITFSI).\textsuperscript{59} The ion gel prepared in the composition range of [EMITFSI]/[MMA] = 7/3~1/9 with a small amount of crosslinker, ethylene glycol dimethacrylate (EGDMA, 2 mol\% of MMA), formed self-standing, flexible and transparent films. The ionic conductivity reached $10^{-2}$ s/cm at room temperature. The temperature dependence of the ionic conductivity of the ion gels

\begin{align*}
\text{MMA} & \quad \text{EMITFSI} \\
\text{EGDMA} &
\end{align*}
followed the Vogel-Tamman-Fulcher (VTF) equation (Equation 2.18). The decoupling effect was enhanced by increasing the content of polymer in the ion gel system. The same ion gel system was studied by Tiyapiboonchaiya et al. \(^6\) where tetra(ethylene glycol) diacrylate (TTEDGA) was used as the crosslinker in the range of 0.5-1 wt% of the mixture of MMA and RTIL. The flexible polymer gels were obtained after polymerization even when the ratio of the [EMITFSI]/[MMA] was maintained as high as 9:1 by weight. It was observed that the \(T_g\) remained nearly constant around \(-92 \pm 2 ^\circ\text{C}\) for different concentrations of crosslinking agent, which was close to the viscous liquid electrolyte in the same polymer composition without crosslinking. This was probably due to the very small amount of crosslinker involved in the system such that the degree of crosslinking did not affect the \(T_g\) of the polymer. However, some interaction between the polymer matrix and the RTIL was observed by the disappearance of the \(T_m\) and \(T_{\text{cryst}}\) of RTIL from the thermograms of the gel system. The ionic conductivity of this gel system with various concentrations of crosslinker is shown in Figure 2.10. The ion conductivity was lower for crosslinked polymer gel than the uncrosslinked ones.
Li et al. also investigated the ion gels system based on MMA with the IL, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMP$_6$) formed by in situ polymerization.$^{60}$ The highest ionic conductivity was obtained when the mass ratio of BMIMP$_6$ to MMA
monomer is 50:50. The ionic conductivity was found to increase with the BMIMPF$_6$ concentration, but the mechanical properties suffered. The ionic conductivity followed the VTF equation, implying that there was coupling effects between the polymer matrix and IL. This interaction was analyzed by FTIR, which suggested a hydrogen bonded interaction existed between the IL and the polymer matrix. This was shown in the FTIR spectra in Figure 2.11, the characteristic peak of the stretching vibration of C=O group at the frequency 1733 cm$^{-1}$ in the pure PMMA has shifted to lower frequencies as the content of BMIMPF$_6$ increased, which was due to the hydrogen-bonded carbonyl groups.

![FTIR spectra of gel polymer electrolyte film](image)

Figure 2.11 FTIR spectra of gel polymer electrolyte film. $^{60}$ (Reproduced with permission from reference 60. Copyright Wiley.)

The kinetics of the free radical polymerization with the presence of IL by suitable monomers was investigated by other research groups.$^{47}$ These results were compared
with conventional organic solvent such as toluene. Both conversion and molecular weight increased by about a factor of 10 for the reaction taken place in IL. Furthermore, the reactions in the IL also proceeded very rapidly. According to these results, two main possible theories were put forth: the decrease of termination due to the high viscosity of the IL as the reaction medium, second, the rate constant of propagation might increase due to local environment effects.

2.2.5 Lithium polymer gel electrolyte

Presently, the rapid growth in portable electronic devices (e.g. laptop and cell phones) has generated enormous demand for compact, lightweight power supplies. In this regard, lithium battery has become one of the advanced power sources replacing the conventional battery system such as lead acid batteries. It stands out in the battery market for its high energy density. The high voltage of lithium battery is attributed to the chemistry of intercalation reactions of the most electropositive ion, lithium with electrodes. Table 2.3 lists the information of various battery systems along with their characteristics. During charging, the dendrite formation of lithium is generated from the deposition of reduced lithium on anode, which can cause a fatal problem of short circuits and damages the cell. To meet the commercial demand, the lithium cell is required to maintain a sufficient high cycling ability of the charge-recharge performance. Solid state polymer electrolyte plays an important role in achieving this objective. The solid state lithium polymer electrolytes can solve the problems of lithium dendrite formation, electrolyte leakage, flammability of the solvent and electrolytic degradation. The detailed interpretation of charge-discharge profile can be found elsewhere.
Table 2.3 Lithium battery and its electrochemical reactions

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Anode</th>
<th>Electrolyte</th>
<th>Electrolyte reactions</th>
</tr>
</thead>
</table>
| CoO₂    | C + Li| Organic electrolyte and Li salt | \[
\text{Li (C)} \leftrightarrow \text{Li}^{+} + \text{e}^{-} \quad \text{(anode)} \\
\text{Li}^{+} + \text{e}^{-} + \text{CoO}_2 \leftrightarrow \text{LiCoO}_2 \quad \text{(cathode)} \\
\text{CoO}_2 + \text{Li(C)} \leftrightarrow \text{LiCoO}_2 \quad \text{(total reaction)}
\] |

Desirable qualities for ideal electrolyte includes: high ion conductivity, good electrochemical stability, good thermal stability, good compatibility with electrodes and environmental safety. The electrolyte solution in lithium battery is commonly comprised of organic solvent and lithium salt. Some solvents are listed in Table 2.4. Among them, the most widely used solvents are PC and EC. Siloxane has also been used as a solvent for lithium salt. Since the siloxane backbone made by Si-O repeating units has poor affiliation with the lithium salt, it is modified by polyether groups to achieve better salt salvation. Inose et al. have examined the effects of poly-ether modified siloxane on the electrochemical behavior of lithium electrolyte, which was composed of 1 M LiPF₆ and ethylene carbonate/ methylethyl carbonate. They found that the lithium cycleability and electrolyte conductivity were both improved by addition of modified siloxane.

Table 2.4 Some commonly used organic solvents in lithium polymer electrolyte

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Melting point, MP (°C)</th>
<th>Boiling point, BP (°C)</th>
<th>Density, g/cm³</th>
<th>Dielectric constant, ε</th>
<th>Molecular weight</th>
<th>Solubility parameter (J cm⁻³)¹/²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl carbonate (DMC)</td>
<td>24</td>
<td>90</td>
<td>1.06</td>
<td>3.12</td>
<td>90.08</td>
<td>20.3</td>
</tr>
<tr>
<td>Diethyl carbonate (DEC)</td>
<td>-45.0</td>
<td>126</td>
<td>0.9752</td>
<td>2.82</td>
<td>118.13</td>
<td>18.0</td>
</tr>
<tr>
<td>γ-Butyrolactone (BL)</td>
<td>-43.3</td>
<td>204</td>
<td>1.1284</td>
<td>39.0</td>
<td>86.99</td>
<td>25.8</td>
</tr>
<tr>
<td>Propylene carbonate (PC)</td>
<td>-48.8</td>
<td>242</td>
<td>1.2047</td>
<td>66.14</td>
<td>102.09</td>
<td>27.2</td>
</tr>
<tr>
<td>Ethylene carbonate (EC)</td>
<td>36.4</td>
<td>248</td>
<td>1.3214</td>
<td>89.78</td>
<td>88.06</td>
<td>30.1</td>
</tr>
</tbody>
</table>
The polymer matrix of lithium polymer electrolyte has the requirements in ion conductivity, mechanical strength, transference number, thermal electrochemical stability, as well as compatibility.\textsuperscript{4,69-71} Presently, the following polymers have been widely used in preparing lithium gel polymer electrolyte for lithium batteries, such as poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), and poly(vinyl chloride) (PVdF). Table 2.5 lists several polymer hosts widely used in lithium polymer electrolyte along with their physical properties. Among them, the PMMA based lithium electrolytes were favored with respect to their high light transmittance, good chemical resistance, and good insulating properties.\textsuperscript{72} Also, PMMA is amorphous and the C=O functional group provides good affinity for the plasticizing solvent and lithium.

Table 2.5 Generally studied polymer hosts\textsuperscript{68}

<table>
<thead>
<tr>
<th>Polymer host</th>
<th>Repeat unit</th>
<th>Glass transition temperature, $T_g$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(ethylene oxide)</td>
<td>$-(\text{CH}_2\text{CH}_2\text{O})_n$</td>
<td>64</td>
</tr>
<tr>
<td>Poly(propylene oxide)</td>
<td>$-(\text{CH}_2\text{CH}_2\text{O})_n$</td>
<td>60</td>
</tr>
<tr>
<td>Poly(acrylonitrile)</td>
<td>$-(\text{CH}_2\text{CH}(-\text{CN}))_n$</td>
<td>125</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>$-(\text{CH}_2\text{C}(-\text{CH}_3)(-\text{COOCH}_3))_n$</td>
<td>105</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>$-(\text{CH}_2\text{CHCl})_n$</td>
<td>85</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td>$-(\text{CH}_2\text{CF}_2)_n$</td>
<td>40</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride-hexafluoropropylene)</td>
<td>$-(\text{CH}_2\text{CH})$</td>
<td>90</td>
</tr>
</tbody>
</table>

The room temperature conductivity of PMMA based polymer gel electrolyte was reported in the range of $10^-3$-$10^-4$ S/cm.\textsuperscript{73-75} However, these electrolytes were made by directly immobilizing electrolyte solution in the commercial PMMA in some solvent, followed by evaporating dry to remove solvent afterwards. This method commonly leads to a poor mechanical stability since the polymer matrix was only physically crosslinked.
PMMA- LiTFSI polymer electrolyte produced without the addition of any solvent was developed by Ali et al.\textsuperscript{76} The conductivity of the polymer electrolyte with 35 wt\% of LiTFSI was measured to be around 10\textsuperscript{-4} S/cm. The further addition of LiTFSI decrease the conductivity which was considered as the formation of ion pair and decrease the total number of mobile ions. Bohnke \textit{et al.} examined the conductivities and viscosities of gel electrolytes made of PMMA and 1 M LiClO\textsubscript{4}-Propylene carbonate (PC) solution.\textsuperscript{77} The authors found that the conduction behavior of electrolyte depended on the concentration of PMMA matrix. When the PMMA weight ratio was lower than 30-35\%, the electrolytes acted as a liquid state electrolyte encaged in the PMMA matrix. While a higher PMMA concentration led to a lower conductivity due to the interaction between polymer chain and lithium salt, accompanying with the rise of the activation energy of conduction. The authors also studied the effects of salt concentration on the conduction behavior of these gel electrolytes\textsuperscript{74}. The results concluded that the salt concentration exhibited a maximum conductivity in both the PC plasticizer and the PMMA gel matrix with various content of PMMA as shown in Figure 2.12. The conduction decrease at high PMMA and salt concentration was attributed to the formation of crosslinking between lithium cations and carbonyl group of PMMA, which reduces the ionic mobility and increases the activation energy of conduction.
Figure 2.12 Specific conductivity as a function of LiClO₄ concentration in PC at room temperature. Liquid electrolyte LiClO₄-PC (▲), 20w/o of PMMA gel (●), 45 w/o of PMMA gel (○).(Reproduced with permission from reference 4. Copyright The Royal Society of Chemistry)

Appetecchi *et al* ⁷⁸ reported a study on the PMMA polymer gel electrolyte with the addition of plasticizers of propylene carbonate (PC) and ethylene carbonate (EC). The preparation involved immobilization of lithium salt- plasticizer mixture in the commercially available PMMA matrix by film casting. The final product was transparent and elastic. These gel electrolytes persisted high conductivity in a wide range of temperature -20°C to 60°C, and showed a lower extent of corrosion of lithium anode than the PAN gel electrolytes. However, the consistent loss of lithium observed in the cyclic voltammetric test was still a problem limiting a long life in rechargeable lithium battery application.
The schematic principle of lithium battery is illustrated in Figure 2.13. Upon connected to the power supply, the applied voltage will launch the charge process between the anode and cathode. Consequently, the cathode will release cations into the electrolyte solution. Simultaneously, the equal amount of lithium cations will move to anode and be reduced there. For the discharge operation, the anode and cathode are connected by an external circuit. The lithium cations are oxidized at anode and move to cathode through electrolyte solution, and finally reduced in cathode.
2.2.6 Polymer electrolyte for Ni-Zn batteries

The Ni-Zn battery was invented in 1901. Even though it has been studied for over 100 years, it still remains viable and competitive in today’s battery market. Compared many commercial batteries, including today’s most popular battery-lithium battery, it has significant advantages including low cost, high energy density (55-85Wh/kg), safety, recyclability and sustainability of reserves. Equations 2.6 and 2.7 are the reactions taken place at zinc electrodes (anode). During discharging process, zinc gives out electrons and dissolves in the KOH solution to form a soluble zincate, Zn(OH)\(_2^-\). The increase in the concentration of zincate resulted in precipitation of the zincate to form ZnO. The zincate is then reduced to zinc metal during charging process. Equation 2.8 is the electrochemical reaction at Nickel oxide electrode (cathode). The overall Ni-Zn battery reaction is expressed in equation 2.9.

\[
\begin{align*}
Zn + 4 OH^- &\rightarrow Zn(OH)_4^{2-} + 2e^- \quad \text{(Equation 2.6)} \\
Zn(OH)_4^{2-} &\rightarrow ZnO + 2OH^- + H_2O \quad \text{(Equation 2.7)} \\
NiOOH + e^- + H_2O &\rightarrow Ni(OH)_2 + OH^- \quad \text{(Equation 2.8)} \\
Zn + 2NiOOH + H_2O &\rightarrow ZnO + 2Ni(OH)_2 \quad \text{(Equation 2.9)}
\end{align*}
\]

Some other electrochemical reactions in nickel-zinc batteries were demonstrated in the following equations. \(^{81,82}\) Equation 2.10 shows the zinc corrosion reaction in the presence of water. Oxygen is needed to be reduced at the zinc electrode so as to prevent the pressure rise in sealed cells as shown in equation 2.11.

\[
Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2 \quad \text{(Equation 2.10)}
\]
The conventional Ni-Zn batteries based on liquid electrolyte face big problems of dendrite growth during charging, shape change during cycling, passivation of electrodes, as well as the evolution of hydrogen on electrodes, which shorten the battery lifetime. This phenomenon is due to the shape change and dissolution of the zinc electrode, and eventually leads to short circuiting and failure. Zincate is easily to form in highly alkaline solution and this is the main reason to cause shape change of electrode and dendrites growth during charging. Figure 2.14 shows the dendrite growth of Zinc in anode.

Figure 2.14 SEM photographs of zinc electrode after 50 discharge–charge cycles. Magnification: (a) 100; (b) 500; (c) 1000; (d) 1500. (Reproduced with permission from reference 85. Copyright Elsevier)
Many attempts have been made to suppress the dendrite growth so as to improve the battery cycle life, including modification of Zn electrodes and addition of organic additives and surfactants. The conventional electrolyte involved in Ni-Zn battery is aqueous KOH with a concentration about 30% to reach a maximum ionic conductivity. Since a high concentration of KOH leads to shape change of the Zn electrode, many studies have been carried out to modify the concentration of KOH electrolyte solution to a lower level with the addition of additives such as K₂CO₃ and KF. These additives can reduce the dendritic problem by lowering the solubility of Zn in the solution. Replacement of the liquid electrolyte with a solid state polymer electrolyte such as PEO-KOH system has been intensively studied. In 1995, Fauvarque et al. reported a solid state polymer electrolyte based on PEO and KOH water solution. The authors found that the solid electrolytes could reach 60 cycles without any dendritic growth and shape change. Solid polymer electrolytes exhibit significant improvement in overcoming the shortcomings of Ni-Zn battery. Iwakura et al. developed a polymer electrolyte from the slightly cross-linked potassium poly(acrylate) (PAAK) and KOH aqueous solution. This polymer electrolyte dramatically improved the cyclic performance of the battery compared with conventional aqueous solution. Dendritic growth on the zinc electrode was minimal during the charge-discharge operation as shown in Figure 2.15.
2.3 Ion conductivity of gel electrolytes

The fundamental principles and parameters of ion conductivity will be described in this section.

2.3.1 Mechanism of ion conduction

The study of the ionic conductivity requires the elemental knowledge of mobility and transfer number of the mobile ions.

The ion conductivity $\sigma$ can be estimated by the following equation:\textsuperscript{103}

$$\sigma = \sum n_m q_m \mu_m$$  
(Equation 2.12)
Where \( n_m, q_m \) and \( \mu_m \) are the concentration, charge and mobility of charge carrier \( m \), respectively. The ion conductivity here is also a function of temperature and pressure, and this equation is suitable for a homogeneous polymer electrolyte\(^{103} \). With the assumption that the dissolved salt completely dissociates into cations and anions in the electrolyte system, the determination of ion conductivity depends only on the evaluation of ion mobility.

The ionic mobility \( \mu \) can be calculated by the Stokes-Einstein equation

\[
\mu = \frac{q}{6\pi \eta r_s}
\]  
(Equation 2. 13)

Here \( q \) is the electronic charge on each charge carrier, \( \eta \) is the solution viscosity, \( r_s \) is the effective hydrodynamic (Stokes) radius. Ionic diffusion coefficient \( D \) is assumed to relate to the Stokes-Einstein (Equation 2.12) and can also be used to evaluate the ionic mobility. This is Nernst-Einstein relationship between the ionic diffusion coefficient and the ionic mobility\(^{104} \)

\[
\mu = \frac{qD}{KT}
\]  
(Equation 2. 14)

where \( K \) is the Boltzmann constant. Ionic conductivity from Nernst-Einstein equation is then described as following\(^{105} \)

\[
\sigma_{\text{diff}} = \frac{Nq^2}{kT}(D_+ + D_-)
\]  
(Equation 2. 15)

where \( N \) is the number of charge carriers per cm\(^3 \) on the assumption of complete dissociation, and \( D_+ \) and \( D_- \) are the diffusion coefficient of the cation and anion,
respectively. The ionic transfer (transport) number is an important parameter in describing the mechanism of ion conduction in polymer electrolyte as well as its application\textsuperscript{29}. It represents the fraction of the total current carried by the mobile ions. The ionic transfer number of cation, \( t^+ \), can be estimated by the equation as follows\textsuperscript{105}

\[
\frac{\mu^+}{\mu^+ + \mu^-} = \frac{q_+ D_+}{q_+ D_+ + q_- D_-}
\]

(Equation 2.16)

where \( \mu^+ (\mu^-) \) and \( q^+ (q^-) \) are ionic mobility and electronic charge on the cation (anion), respectively.

There is a dearth of the reports on ion conduction mechanism for gel polymer electrolytes (also called GPE), but it is observed that the conduction mechanism is somewhere between the liquid electrolytes and solid polymer electrolytes (also called SPE).\textsuperscript{38, 39} Ward \textit{et al.}\textsuperscript{106} believed that the similarities are more than the differences for gel and liquid systems in the behavior of conduction mechanism, but polymers in some way interact with the electrolyte components to modify the properties of gel electrolyte. Based on the extensive research on PAN and PMMA gels,\textsuperscript{107, 108} conductivity seems to be associated with the dynamics of the whole gel system rather than with the individual components of the gel, such as polar solvent and polymer matrix.\textsuperscript{4} Saito \textit{et al.} investigated the PVDF based lithium gel electrolytes prepared by the phase inversion method.\textsuperscript{104, 109} They found the diffusion coefficients of some gels were composed of two components which responded to different phases: the trapped solvent in the cavities in the membrane and the swollen polymer chains.

The migration in the trapped solvent is faster than that in the swollen chains because of the block arising from the crosslinking network and chemical interaction. The
The migration in the trapped solvent is faster than that in the swollen chains because of the block arising from the crosslinking network and chemical interaction. The swollen polymer network was thought to be the dominant phase contributing to the total conductivity of the gel electrolytes. They also pointed out that a high conductivity can be achieved when the gel exhibited a homogeneous structure and a single component of the diffusion process, because the charge carrier migrated smoothly in the polymer through the cavities. Aihara et al. measured the individual self diffusion coefficient of the components in the PEO based gel electrolyte, and compared with the ionic conductivities to explore the ionic conduction mechanism. The ion dissociation in the gel electrolyte was found to be better than in the bulk liquid electrolyte, but the ionic conductivity of the gel electrolyte was lower. The authors attributed this to the slower diffusion of the cations in the gel electrolyte because the cations were trapped in the polymer matrix.

2.3.2 Temperature dependence of ionic conductivity

Generally, the ionic conductivity increases with temperature. The chemical structure of the host polymer plays a crucial role in picturing the ion conduction. Hodge et al. found that there was a positive correlation between the amount of conducting phase and free volume in the gel when investigated the poly (2-hydroxyethyl methacrylate) gel. The difference of GPE from SPE lies in the fact that the ion transport in the gel system couples with the movement of solvent.

The motion of mobile ions in GPE can be reflected from the temperature dependence of the ionic conductivity. Among the various models in describing the
migration of charge carrier in the polymer gel electrolyte, Arrhenius equation is the simplest one. 39

\[
\sigma = A \exp\left(\frac{-\Delta E}{RT}\right)
\]  
(Equation 2.17)

where \(A\) is the prefactor contains many terms, \(\Delta E\) is the activation energy for conduction, and \(R\) is the ideal gas constant. This relationship fits the thermally activated ionic motion the best. Some GPE materials with inert polymer matrixes obey this relationship. Examples are \(\beta\)-cyclodextrin/dimethylacetamide gels.112

Armand reported ion conduction as a function of temperature for GPE follows a free volume law.28 The studies on PEO based gel and PAN, PMMA based gels exhibit a single phase behavior, where the conductivity follows a free volume model

\[
\sigma = AT^{-1/2} \exp\left\{\frac{-E_a}{K(T - T_0)}\right\}
\]  
(Equation 2.18)

Here \(T_0\) is the ideal glass transition temperature, \(T_0 \approx T_g - 20\), and \(E_a\) is the pseudo activation energy. This equation is also called Vogel-Tam-Mann-Fulcher (VTF) empirical equation.113 The temperature dependence exhibits a bending deviation from the Arrhenius equation

For amorphous polymer electrolytes, Arrheniums plots normally do not follow a straight line, but a positively curved line, which is describing by the well known Williams-Landel-Ferry (WLF) equation.29

\[
\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)}
\]  
(Equation 2.19)
where \( \sigma(T) \) is the ionic conductivity as a function of temperature \( T \), \( C_1 \) and \( C_2 \) are constant that can be determined experimentally. A fit of experimental data to WLF equation implies that the change in ionic conductivity with temperature is mainly caused by the mobile charge which is influenced by the local segmental motion.\(^{29} \) A comprehensive review of the theoretical basis of WLF equation are given by Bruce and Gray.\(^{103} \)

Arrhenius plot is the logarithmic plot of ionic conductivity against the reciprocal temperature. Kubota et al. claimed that the mechanism of ionic conduction can also be evaluated from the shape of Arrhenius plots.\(^{38, 39} \) They believed that if the curve was almost linear, meaning the conduction is thermally activated and the migration of the mobile ions did not associate with the thermal relaxation of the polymer chains\(^{114} \). Thus the solvent is the main conduction medium, while the polymer matrix only serves to provide structural integrity. At the same time, a nonlinear such as a positive curved line indicates segmental motion dependant ion conduction, which generally happens to amorphous solid polymer electrolyte.

2.3.3 Factors of the gel components

The ionic conductivity of polymer electrolytes varies with temperature. However, as a GPE material, the ionic conductivity also depends on its unique components in this system such as polymer matrix (host), solvent, and salt. These important factors in determining the ionic conduction behavior of GPE materials will be discussed in detailed as follows.
2.3.2.1 Polymer matrix

The main role of polymer matrix in electrolyte gels is to provide sufficient mechanical strength, even though the solvating effects on salts can not be neglected in some cases.\textsuperscript{4} Due to the sparseness of reports concerning the ion transport mechanism in a gel electrolyte, there is a great demand to disclose the relationship between the ionic conduction mechanism and the molecular structure of the host polymer.\textsuperscript{30, 107, 115} There are several factors that can control the structure of the host polymer: porosity, pore size, crosslinking density, and the degree of polymerization.\textsuperscript{104} The role of matrix in acting with ion transport can be influenced by the chemical nature of gel, for instance, if there are ionic groups along the polymer chains. It can also be controlled by the degree of crosslinking for the polymer network through varying the crosslinking ratio.\textsuperscript{38, 39}

2.3.2.2 Solvent

The small molecules in the gel systems serve as a plasticizer for the host polymer to increase its chain flexibility and a solvent for the salts to weaken the ion association. The aprotic liquid behaves in different ways from water or other hydrogen-bonded solvents in dissolving salts\textsuperscript{4}. The latter can solvate both cations and anions. Whereas the former can only solvate cations by coordinating bond between solvent molecules and cations, and scarcely solvate the anions. Polymer solvent and some organic solvent belong to this category. Among the many types of small molecule solvent/plasticizers engaged in gel electrolytes, EC and PC are the most widely used ones primarily because
they possess high dielectric constants, good compatibility with many salts and polymers, as well as relatively low volatility.

Gray mentioned some currently popular solvents that are used to improve the ion pair dissociation effects of PEO based gel electrolyte system. These include modified carbonate, dioctyl sebacate (DOS), and diethyl phthalate (DEP) based on the same design idea: Providing more oxygen sites for cation co-ordination. Besides, DOS and DEP also persist high boiling temperature.
2.3.2.3 Salt

Salts play a central role in ion conduction of gel electrolytes since they are the charge carriers, which provide mobile ions for ion conduction to take place. The extensively studied salts include lithium and sodium salts of $\Gamma^-$, $\text{ClO}_4^-$, $\text{CF}_3\text{SO}_3^-$ and $\text{AsF}_6^-$.\textsuperscript{118} In general, there is a maximum of ionic conductivity with the increase of the salt concentration. Tokuda \textit{et al.} explained that the increase of conductivity at low salt concentrations is due to the increase in the number of charge carriers; whereas at high salt concentration, the intense ion-ion interaction leads to ionic association leading to substantial solution viscosity increases suppressing the mobility.\textsuperscript{105}

2.3.4 Measurement methods

A comprehensive characterization of the electrical properties of polymer electrolyte commonly requires the knowledge of: (1) the conductivity of polymer electrolyte as a function of temperature; (2) the transport number of each charged component as a function of temperature; (3) identification of the conduction offered by different charged components.\textsuperscript{119} Generally, the electrochemical properties of the cells and the gel polymer electrolyte were examined through complex plane frequency analysis of alternating current (AC) impedance and cyclic voltammetry. The former method is conducted especially to investigate the ionic conductivity of polymer electrolyte as well as transport number.\textsuperscript{120} The cyclic voltammetric measurements are used to determine the stable potential windows of the polymer electrolyte with certain electrode.\textsuperscript{2} The measurement of ionic conductivity demands the construction of a cell in which the
interested sample is sandwiched by two electrodes, and the electrodes connect the polymer electrolyte with the apparatus.\textsuperscript{121,122}

Complex plane frequency analysis of AC impedance will be introduced here. AC impedance spectroscopy has been a traditional technique to examine the properties of electrochemical systems. It is the preferable method in measuring the ionic conductivity of polymer electrolyte through a simple electrochemical cell, where the polymer samples, especially in the form of films, are sandwiched between electrodes, and the bulk electrical properties can be conveniently determined. This method can characterize both the long-range migration and the polarization of ions. The frequency range involved in this technique is from 100 Hz to 1 MHz. In the AC measurements, the impedance, $Z$ is represented by a vector consisting of two parameters: one is the magnitude of the impedance determined from the ratio of voltage and current maxima, $|Z| = \frac{V_{\text{max}}}{I_{\text{max}}}$, and the other is the phase angle $\theta$, which is the phase difference between the voltage and current.\textsuperscript{119} Both the magnitude and the phase angle vary with applied frequency. Since the expression of the impedance by a vector is analogous to a complex number in the complex plane, it is thus also called complex impedance. In this way, the impedance expressed by the symbol $Z^*$ can be represented by the real part $Z'$ and imaginary part $Z''$ by the following equation

$$Z^* = Z' - jZ''$$  \hspace{1cm} (Equation 2.20)

Here $j$ is the complex number operator. The complex form of impedance enables the calculation of impedance by the aid of complex algebra once the individual components impedance in the circuits are available.\textsuperscript{119}
The AC experiment involves two steps: to determine the complex impedance of a cell as a function of the frequency and to express the results in the form of a complex number in a complex plane, which is also called Cole-Cole plot. The magnitude of complex impedance $|Z|$ can be directly read along with its phase angle $\Theta$. In the Cole-Cole plot, imaginary component of the impedance $Z''$ (equals to $|Z|\cdot\sin\Theta$) is plotted versus real component $Z'$ (equals to $|Z|\cdot\cos\Theta$). A typical scheme of complex plane response is shown next to its equivalent circuit in Figure 2.16. This represents an ideal polymer electrolyte cell containing blocking electrodes.

![Figure 2.16 A typical complex impedance plot with respect to its ideal circuit. The capacitance of the electrode, $C_e$ is in series with the parallel combination of the bulk resistance, $R_b$ and the bulk capacitance, $C_b$.](image)

Based on the circuit, the equation used to describe the respective Cole-Cole plot is represented by Equation (2.21).

$$Z_{total}^* = R_b \left[ \frac{1}{(1 + \omega R_b C_b)^2} \right] - j \left( R_b \left[ \frac{\omega R_b C_b}{1 + (\omega R_b C_b)^2} \right] + \frac{1}{\omega C_e} \right) \quad \text{(Equation 2.21)}$$

where $Z_{total}^*$ is the total impedance and $\omega$ is angular frequency, $C_e$ is the capacitance of the electrode, $R_b$ is the bulk resistance, and $C_b$ is the bulk capacitance.
A plot of complex impedance spectra for a polyethylene oxide polymer electrolyte film with Ni as the electrode substrate is shown in Figure 2.17.\textsuperscript{123} The plot composes of two distinct regions: the semi-circle at high frequency attributed to the bulk conductivity of the electrolyte; the inclined line at low frequencies is related to the electrical capacitance of the film. The intercept on the $Z'$ axis shows the value of the bulk electrical resistance $R_b$. The shape of the colo subjects to the material of electrodes.

![Complex impedance spectra](image)

Figure 2.17 A typical plot for PEO electrolyte film.\textsuperscript{123} (Reproduced with permission from reference 123. Copyright Elsevier.)

After the bulk resistance, $R_b$ is obtained according to Cole-Cole plot, and then the ionic conductivity can be calculated from the following equation.\textsuperscript{124, 125}

$$\sigma = \frac{d}{R_b S}$$  \hspace{1cm} (Equation 2.22)

here, $d$ and $s$ are the thickness and the area of sample, respectively.
2.4 Electroactive polymer gels and their actuation

Ion conductive polymer gels have been extensively investigated as electroactive polymers in the application of actuators since 1990’s. Because of their superior features such as soft, wet, flexible, and stimulus responsive behaviors, ion conductive polymer gels begin to replace some of the conventional hard mechanical materials like metal and ceramics in many areas. Progress in biological and polymer technology requires great development in the study of gel electrolyte.

Polymer gels exhibiting environmentally responsive volume change are called responsive gels. They also have the interchangeable name as “smart” and “actuated” gels. The volume change of these responsive gels is performed by the transfer of swollen solvent in the gel, which can be induced by environmental stimuli such as temperature, pH, ion strength, and electric field. From this point of view, responsive gels are also considered as intelligent materials since they possess three characteristic functions: sensing, processing, and response.

Polymer gels possessing the function of deformation under the environmental stimuli are potential materials in the application of actuators. Among various stimuli that can drive the deformation of gel actuators, electric field turns out to be an efficient and convenient one. Gel actuators commonly exhibit larger strains and lower forces compared with actuators made from conducting polymers. Hamlen et al. originally declared the electrically driven deformation of polyelectrolyte gels in 1965. The study was based on poly(vinylalcohol) (PVA) gel, which exhibited volume shrinking near the anode under a DC electric field and recovered its original volume once the power was shut down. The Authors attributed this phenomenon to the change of polymer network
structure due to pH variation near the anode side. Fragala et al. produced an electrically activated artificial muscle system in 1972.\textsuperscript{128} The applications of polymer gels as sensor and actuator materials were later studied by many researchers.\textsuperscript{129-133}

The unique properties of polymer gels receive especially intensive attentions in the area of biomedical technology. Presently, soft actuators in the field of biomedical such as controlled drug release and artificial sphincter have been realized for biomedical use. Even though gel actuators exhibit superior advantages including compactness, simplicity, light weight, small power driven, and low material costs,\textsuperscript{134} they also suffer some drawbacks like long response time, poor mechanical strength, requirement of solvent bath container and volatile solvent. According to Mazzoldi et al.,\textsuperscript{135} in order to imitate biological muscles possessing both the features of force generators and motion generators, the actuator material has to behave like a spring with tunable elastic parameters. A comprehensive statement of the requirements for artificial materials was reported by De Rossi et al. including larger displacement, high stability, fast response, and environmental safe.\textsuperscript{136}

Studies in this area have shown that the actuation deformation under the electric field can be varied by changing the chemical nature of the polymer matrix and the content of the embedded solution. Based on the nature of polymer matrix, it can be ionized or neutral, or even electrically conductive, depending on the chemical structure of the backbone and the function group on the side chain. On the other hand, the solvent inside the matrix can be either ionic conductive or non ionic conductive. The following section will discuss the characteristics of several generally studied gel systems along with their advantages and drawbacks in the use of actuators.
2.4.1 Polyelectrolyte gels

Polymer gels with ionic groups on the backbone, namely polyelectrolyte gels or ionic gels, were observed to show higher order of volume change than neutral polymer gels. Consequently, polyelectrolyte gels attract the broadest interest in the study of gel actors. With respect to the type of ion distribution and deformation in electric field, electroactive polyelectrolyte gels as actuator materials can be classified into three types: anionic, cationic and amphoteric gel as indicated by Table 2.6. The schemes of cationic gel and amphoteric gel and their behavior under electric field are illustrated in Figure 2.18. In the case of (a) Cationic gel, electric field attracts the mobile anions towards right side, which results in a heterogeneous ion distribution. In the case of (b) Amphoteric gel, the same amount of mobile cations and the anions are attracted towards opposite direction, which results in a homogeneous ion distribution in terms of macroscopic view even under electric field. Generally, the preferable gels as actuator materials are amphoteric gels since they exhibit homogeneous deformation. Tamagawa and Taya expatiated on the ions distribution of different type of polyelectrolyte gels and theoretically predicted the potential in amphoteric gels.\textsuperscript{137}

Nevertheless, the polyelectrolyte gels as actuator materials are known to confront insurmountable difficulties: the slow response due to diffusion controlled process, the volatility of solvent, the hydrolysis of water under high voltage followed by the release of gases, as well as weak responsive stress.
Table 2.6 Classification of electroactive polymer gels

<table>
<thead>
<tr>
<th>Gel type</th>
<th>Anionic</th>
<th>Cationic</th>
<th>Amphoteric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ions (immobile) fixed on network</td>
<td>anions</td>
<td>cations</td>
<td>both cations and anions</td>
</tr>
<tr>
<td>Deformation</td>
<td>heterogeneous</td>
<td>heterogeneous</td>
<td>homogeneous</td>
</tr>
<tr>
<td>Ion distribution without electric potential</td>
<td>immobile anions and mobile cations homogeneously distributed</td>
<td>immobile cations and mobile anions homogeneously distributed</td>
<td>cations and anions distributed homogeneously</td>
</tr>
<tr>
<td>Ion distribution under electric potential</td>
<td>asymmetric</td>
<td>asymmetric</td>
<td>symmetric</td>
</tr>
</tbody>
</table>

58
2.4.2 Non-ionic neutral gel

Non-ionic-conductive but electroactive polymer gels have been investigated as potential gel actuator materials that can overcome some disadvantages of conventional polyelectrolyte gels. These systems involve non-ionic gel matrix with non-ionic organic solvents. A representative system is poly(vinyl alcohol) (PVA) in dimethyl sulfoxide (DMSO) which can deform under direct current electric field. The non-ionic solvent DMSO with a dielectric constant of 40 can exhibit orientation because the S=O bond and S=C bond orientate in different direction under electric field. This orientation induces the
deformation of gel matrix. Hirai and coworkers have investigated PVA-DMSO gel systems as an actuator material since 1990s.\textsuperscript{138,139} The maximum strain in length was reported to be 8\% under an electric field of $2.5 \times 10^5$ v/m within 20 milliseconds (ms).\textsuperscript{138} Recently, the bending as much as $90^\circ$ under 400V/mm within 60ms was observed.\textsuperscript{139} Overall, these materials show fast response deformation and no leakage in work that are better than the conventional polyelectrolyte gels, but they exhibit smaller strain which leads to some restrictions in the applications.

2.4.3 Ionomeric polymers

The ionic polymer is the polyelectrolyte containing ionized groups on side chains. The actuation mechanism is the transfer of selective ions to the polymer chain under electric stimulus.\textsuperscript{140,141} The most famous ionic polymer is Nafion\textsuperscript{®}. The Nafion\textsuperscript{®} membrane is a copolymer of tetrafluoroethylene and a perfluoro vinyl ether.\textsuperscript{142}

\[
\begin{array}{c}
\text{CF}_2\text{CF}_2 \\
\text{CF}_2\text{CF}_2 \\
\text{CF}_2\text{CF}_2 \\
\text{CF}_2\text{CF}_2 \\
\text{CF}_2\text{CF}_2 \\
\text{SO}_3\text{H}
\end{array}
\]  

Figure 2.19 Chemical Structure of Nafion
These materials are known to exhibit good cationic conductivity when swollen with water. The ionic polymer based actuators are attractive since they show high strain output (>9 %) and require low operation voltage (<5 V). However, some drawbacks of ionic polymers limit their application as actuator materials. The membrane materials are limited to few perfluorinated ionic polymers due to the issues of synthetic convenience and the chemical stability. The water involvement generates lifetime problem because both the conductivity and the stability of the ion-change membrane strongly depend on the water content which will change with time. Finally, the high cost of the material is also a crucial problem.

2.4.4 Conductive polymer gels

The use of ionic liquids as the electrolyte media in polymer actuators has been actively studied in recent years because of the realization of its unique electrochemical features. The actuation mechanism was the reversible transport of ions and solvent molecules between the polymer and electrolytes during the electrochemical oxidation and reduction. As illustrated in Figure 2.20, the conductive polymer polypyrrole (PPy) executes oxidation and reduction in ionic liquid, accompanying with the intercalation and de-intercalation of ions (cations in this case) from the polymer.
In 2002, Lu et al. reported electrochemical mechanical actuators by using ionic liquid and π-conjugated polymers such as polyaniline, polypyrrole, and polythiophene. They found these actuators showed long lifetime without electroactivity loss when worked in ambient condition. They also compared the actuation behavior of PPy in ionic liquid and in PC-TBA PF₆ (tetrabutylammonium hexafluorophosphate) as shown in Figure 2.21. The results showed that the PPy and ionic liquid system gave more stable displacement in the cycling test. While the displacement in PC-TBA PF₆ decreased after certain cycles presumably due to the decomposition of PC with a narrow potential window.
Zhou et al. formed the gel electrolyte by conducting in situ polymerization of MMA and IL inside the porous PVDF,\textsuperscript{147} which has been platinised with platinum through sputter-coating, followed by electrochemical deposition of poly(pyrrole) (Figure 2.22). The authors observed a strain of 2 % under the potential range $\pm$ 2 V. The bending took about 30-60 s to reach the maximum value, which is longer than the actuator where PC-TBA-PF$_6$ as the electrolyte media.
Later, Vidal et al. synthesized a semi-interpenetrating polymer actuator from 3,4-ethylenedioxythiophene (EDOT) and (polybutadiene/polyethylene oxide) as shown in Figure 2.23). The polybutadiene/polyethylene oxide films were first synthesized and then immersed in PEDOT, followed by the polymerization using FeCl₃. The ionic liquid/CH₂Cl₂ was then introduced into the polymer films to form the gel actuator. The authors found this method allowed for a gradient decrease of the PEDOT content from the surface to the center of the polybutadiene/polyethylene oxide films. They used the following figure (2.23) to show the difference between the layered actuator and the one piece actuator obtained in their study. The two working potential ranges ± 2 V and ± 5 V were used to stimulate the actuation. The displacement rate was found to increase with a higher potential, but a high potential like 5 V caused the degradation of conducting polymer films and resulted in less reversible bending actions.

Figure 2.23  Dry system actuators made by (a) three-layer actuator where the solid polymer electrolyte (SPE) is sandwiched between two electronic conducting polymer and (b) Gradient one piece actuator where the electronic conducting polymer is selectively embedded towards the outside faces of the SPE IPN matrix. Reproduced with permission from reference 148. Copyright Elsevier.)
Cho et al. reported an electroactive polymer actuator made by Nitrile rubber (NBR) and IL with poly(3,4-ethylenedioxythiophene) (PEDOT) as electrodes. The PEDOT was synthesized on the NBR surface, and then soaked in the IL. By applying various BMIM(1-Butyl-3-methyl imidazolium )X based on the anion X size, the authors found that the displacement increase with a larger anion size. The bending action was quicker and larger in the ionic liquid than in the conventional electrolyte LiCLO₄/PC. Even though the enhancement of actuation in ionic liquid was still not clear, but the authors considered the mobility and the concentration as two main factors contributing to the actuation.

Recently, Mukai et al. have developed polymer actuators by using electrodes including single-wall carbon nanotubes (SWNTs). The gel electrolyte and electrodes were both prepared by film casting. The electrolyte layers were sandwiched with two electrodes layers and followed by hot pressing to form the gel actuator. The actuation mechanism is shown in Figure 2.24.
2.4.5 Deformation measurement

In this section, some typical experimental setups are illustrated with respect to different types of deformation test. The material and size of specimen are addressed.

2.4.5.1 Bending

Figure 2.25 shows the apparatus of bending test for PAAm gels under a DC. electric field. The specimen was immersed in ionic solution, and was placed separately from the two electrodes with complete freedom to deform. In this case, the gel specimen will bend semicircularly under the electric field.
Another type of set up to check the bending property of gel under a.c. electric field was illustrated in Figure 2.26,\textsuperscript{133} where one end of the gel film was fixed and the rest was immersed in Na$_2$CO$_3$ solution. The PVA-PAA gel film was 0.41 mm in thickness and its cross-section was 10 mm $\times$ 40 mm. The relative deflection curves in electric fields increased as the applied frequency decreased.
Figure 2.26 (a) Set up of deformation measurement of gel film in electric field. (b) Deflection curves of gel film under sinusoidally varied electric field \(^{133}\) (Reproduced with permission from reference 133. Copyright Springer.)

The geometric illustration of deformation in bending test by Akle was shown in Figure 2.27, who used rectangular samples of 3 mm \(\times\) 3 0 mm with the thickness around 68
Based on this illustration, the bending strain as a function of time was computed by Equation (Equation 2.23), assuming a constant curvature of bending.

\[ \varepsilon(t) = \frac{\delta(t)d}{L^2} \]  

(Equation 2.23)

where \( L_f \) is the free length of the transducer, \( T \) is the thickness, \( \delta(t) \) is the free deflection, \( \varepsilon(t) \) is the strain.

In addition, the angle of bending is another way to describe the bending of electroactive gels. By using a scale in angle degree, the angle of bending under an electric stimulus was obtained by directly reading the deviated angle from the off-electric field position.\(^{150,151}\)
2.4.5.2 Contraction and extension

A typical set up of axial deformation measurement was schemed as Figure 2.28. According to the report of Popvic\textsuperscript{152}, the size of gel sample is 5 mm $\times$ 5 mm $\times$ t mm (t is the thickness =1~4 mm). The images captured by PC were analyzed for strain.

![Figure 2.28 Experimental set up of axial deformation measurement](image)

The gel shape changes with time under electric field and its relative setup for measuring the contraction is illustrated in Figure 2.29 according to Gong et al.\textsuperscript{153} The anionic gel sandwiched by a pair of planar electrodes performed anisotropic contraction under a DC voltage, accompanying with fluid exudation.
Figure 2.29 Measurement of gel contraction and the shape change of the gel with time under electric field.

The range of deformation and relative method to capture depend on the type of polymer gels. In examining the contraction of gels under electric field, a CCD camera with magnifying lens is generally employed to record the length changes with time. The deformation changes in Popovic’s work\textsuperscript{152} were about 0.5 mm for a 3 mm long region of Polyacrylamide based gel. A laser displacement meter is used to measure the bending
displacements when they are within 1 mm. Akle used a non-contact laser vibrometer to measure the displacement in an ac induced bending test where the bending strain varied in the range of $1 \times 10^{-4}$ to $1 \times 10^{-5}$ per volt.\textsuperscript{143} When the deformation is too tiny to be characterized by direct displacement measurement, the force measurements are performed instead. This is likely to occur when the extension of thin films is measured. According to Akle,\textsuperscript{143} the data obtained through direct displacement is generally noisy and minute due to the stiffness in the thickness direction and the nature of the thin film. For instance, a typical deformation generated by a 300 μm strain is only 60 nm. Thus, instead of the direct displacement measurements, the force measurement is carried out in this case. A tensile force of 1g/0.0025 cm\textsuperscript{2} was reported in the form of force density by Fragala et al., which corresponded to a change in length about 10% under 1.8 V and 10 mA/cm\textsuperscript{2} electric field.\textsuperscript{128} Other related reference can be found in literatures.\textsuperscript{154}
CHAPTER III

EXPERIMENTAL

In this section, chemicals and the preparation methods with respect to different gel system will be introduced.

3.1 Materials and preparation

The materials used in preparing different systems of polymer gel electrolytes will be presented in this section along with their synthetic techniques.

3.1.1 Ion gel based on ionic liquid

In situ free radical polymerization of the compatible vinyl monomers in ionic liquids is carried out to form a transparent, mechanically strong, and highly conductive ion gel. The materials for preparation of ion gels are shown in Table 3.1. All materials are used as received. The IL [BMIM][PF₆] is a colorless liquid at room temperature, with $T_g = -78$ °C and two melting points at $T_m = -7.4$ and 8.0 °C, respectively.¹⁵⁵
Table 3.1 Materials used in ion gels

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Structure</th>
<th>Mn</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylmethacrylate (MMA)</td>
<td><img src="image1.png" alt="Structure of MMA" /></td>
<td>100.1</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Tetra(ethylene glycol) diacrylate (TTEGDA)</td>
<td><img src="image2.png" alt="Structure of TTEGDA" /></td>
<td>302.3</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Benzoyl peroxide (BPO)</td>
<td><img src="image3.png" alt="Structure of BPO" /></td>
<td>242.2</td>
<td>Aldrich</td>
</tr>
<tr>
<td>1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆)</td>
<td><img src="image4.png" alt="Structure of BMIMPF₆" /></td>
<td>284.2</td>
<td>AK SCI</td>
</tr>
<tr>
<td>Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT/PSS)</td>
<td><img src="image5.png" alt="Structure of PEDOT/PSS" /></td>
<td></td>
<td>Aldrich</td>
</tr>
</tbody>
</table>

The synthetic route for ion gels is illustrated in Figure 3.1. MMA (99%), TTEGDA (technical grade) and Benzoyl peroxide (BPO) (reagent grade, 97%) were received from Aldrich. The RTIL, BMIMPF₆ (98%) was received from AK Scientific.
The mixture of MMA and BMIMPF₆ according to the designed weight ratio was placed in a vial. The initiator, BPO (5 wt% of MMA) and the crosslinking agent, TTEGDA (5 wt% of MMA) were then added and the reaction solution was stirred at room temperature. After the reactants were well mixed and dissolved, the reaction solution was poured between two Petri dishes with 1 mm thick PTFE spacers. The radical polymerization was carried out at 70 °C for 24 hours. The gel product was then placed in the vacuum oven for 3 days before use. In addition, bulk PMMA films without ILs will be prepared as a reference material by using the same polymerization technique of an ion gel.

```
CH₂=C—C—OCH₃     +   IL(BMIPF₆)
CH₃

MMA

a) Crosslinker, TEGDA
b) Initiator, BPO

Mix

Mold

a) React at 70 °C for 24 hours
b) Vacuum dry at 65 °C for 3 days

Product
```

Figure 3.1 The synthetic route for ion gels in the PMMA-IL system.

The ion gel actuators were prepared by casting a layer of 1.3 wt% PEDOT water solution on the both sides of the gel surface, followed by vacuum dry for 24 hours at room temperature. The thickness of PEDOT film can be justified by coating multiple
layers of PEDOT on the gel surface. After coating, the edges of the gel sample were cut, so as the PEDOT films only cover the top and bottom surface of the gel sample.

3.1.2 Lithium polymer gel electrolyte

The materials in preparing lithium polymer gel electrolytes are listed in Table 3.2. All materials are used as received.
Table 3.2 Materials used in Lithium polymer gel electrolyte

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Structure</th>
<th>Mn</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylmethacrylate (MMA)</td>
<td>![MMA structure]</td>
<td>100.1</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Tetra(ethylene glycol) diacrylate (TTEGDA)</td>
<td>![TTEGDA structure]</td>
<td>302.3</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Benzoyl peroxide (BPO)</td>
<td>![BPO structure]</td>
<td>242.2</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Polyethyleneoxide modified polysiloxane (PEMPS)</td>
<td>![PEMPS structure]</td>
<td>3400</td>
<td>Gelest</td>
</tr>
<tr>
<td>Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI)</td>
<td>![LiTFSI structure]</td>
<td>287</td>
<td>Aldrich</td>
</tr>
</tbody>
</table>

The synthetic route for lithium polymer electrolyte is illustrated in Figure 3.2. The two mixtures of MMA reaction and electrolyte of LiTFSI and PEMPS were prepared separately, and then mixed together. The synthesis procedure is similar to that of ion gels.
The samples are prepared with respect to different MMA to PEMPS weight ratios and [O]:[Li] molar ratios. The latter parameter is interpreted by the following relationship.

\[
[O]:[Li] = \frac{\text{Mole of O on CH}_2\text{CH}_2\text{O in PEMPS}}{\text{Mole of Li in LiTFSI}}
\]

The recipe in the lithium polymer electrolyte synthesis is listed in Table 3.3. LITFSI weight ratio of the sample is illustrated in Table 3.4 and Figure 3.3.
Table 3.3 Synthesis recipe of lithium polymer electrolyte

<table>
<thead>
<tr>
<th>[PMMA]:[PEMPS] by weight</th>
<th>r = [O]:[Li] molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8:1</td>
</tr>
<tr>
<td>30:70</td>
<td>IGMS37-r8</td>
</tr>
<tr>
<td>40:60</td>
<td>IGMS46-r8</td>
</tr>
<tr>
<td>50:50</td>
<td>IGMS55-r8</td>
</tr>
<tr>
<td></td>
<td>16:1</td>
</tr>
<tr>
<td></td>
<td>IGMS37-r16</td>
</tr>
<tr>
<td></td>
<td>IGMS46-r16</td>
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<td></td>
<td>IGMS55-r16</td>
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<td></td>
<td>26:1</td>
</tr>
<tr>
<td></td>
<td>IGMS37-r26</td>
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<td></td>
<td>IGMS46-r26</td>
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<tr>
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<td>IGMS55-r26</td>
</tr>
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<td></td>
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<tr>
<td></td>
<td>IGMS46-r32</td>
</tr>
<tr>
<td></td>
<td>IGMS55-r32</td>
</tr>
</tbody>
</table>

Table 3.4 LiTFSI weight ratio of lithium polymer electrolyte

<table>
<thead>
<tr>
<th>Sample</th>
<th>LiTFSI wt% in Gels</th>
</tr>
</thead>
<tbody>
<tr>
<td>r = [O/Li]</td>
<td>8</td>
</tr>
<tr>
<td>IGMS55</td>
<td>33</td>
</tr>
<tr>
<td>IGMS46</td>
<td>39</td>
</tr>
<tr>
<td>IGMS37</td>
<td>46</td>
</tr>
</tbody>
</table>

Figure 3.3 LiTFSI weight ratio in lithium polymer electrolytes with various [O/Li].
3.1.3 Polymer electrolyte for Ni-Zn battery

Three polymer electrolyte systems were prepared for the application of Ni-Zn battery based on PVA, PAA and PMMA. KOH water solution was used as the electrolyte for all the electrolyte systems. The materials are listed in Figure 3.6. PVA was used as received. 50 % KOH solution was diluted to 25% by addition of distilled water and maintained in a volumetric flask.
Table 3.5 Materials used in preparing polymer electrolytes for Ni-Zn battery

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Structure</th>
<th>Mn</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl alcohol) (PVA)</td>
<td><img src="image" alt="Structure" /></td>
<td>85000</td>
<td>aldrich</td>
</tr>
<tr>
<td>50 wt% KOH solution</td>
<td>KOH in H₂O</td>
<td>56</td>
<td>aldrich</td>
</tr>
<tr>
<td>DI water</td>
<td>H₂O</td>
<td>18</td>
<td>lab</td>
</tr>
<tr>
<td>Acrylic Acid (AA)</td>
<td><img src="image" alt="Structure" /></td>
<td>86.1</td>
<td>aldrich</td>
</tr>
<tr>
<td>Ammonium Persulfate (APS)</td>
<td><img src="image" alt="Structure" /></td>
<td>228.2</td>
<td>aldrich</td>
</tr>
<tr>
<td>Methylmethacrylate (MMA)</td>
<td><img src="image" alt="Structure" /></td>
<td>100.1</td>
<td>Aldrich</td>
</tr>
<tr>
<td>N,N′-Methylenebisacrylamide (BIS)</td>
<td><img src="image" alt="Structure" /></td>
<td>154.2</td>
<td>Aldrich</td>
</tr>
<tr>
<td>1-Hydroxycyclohexyl phenyl ketone (HPK)</td>
<td><img src="image" alt="Structure" /></td>
<td>204.3</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Tetra(ethylene glycol) diacrylate (TTEGDA)</td>
<td><img src="image" alt="Structure" /></td>
<td>302.3</td>
<td>Aldrich</td>
</tr>
</tbody>
</table>
For PVA based electrolytes, PVA water solution was first prepared. 2.5 g PVA was added to 75 ml water and the solution was heated on a hot stage around 70 °C under stirring. After PVA was completely dissolved, 20 ml 25% KOH was added dropwise. The mixture was stirred to obtain a homogeneous and viscous solution. The solution was then poured in glass Petri dishes and cooled at room temperature. The weight of the solution was measured. Another weight was measured after the water is evaporated at room temperature when the white and smooth gels were formed.

PAA based electrolytes have been prepared by two ways: thermal synthesis and UV curing, as shown in Figure 3.4 and Figure 3.5, respectively.
PMMA based polymer electrolytes were also prepared by free-radical copolymerization of MMA and TEGDA in the mixture of PEMPS and KOH water solution. The reaction mixture was stirred at room temperature until reached a homogeneous solution. The solution was poured into test tubes and heated at 70 °C for 24 hour to achieve gel products.
3.2 Characterization techniques

The characterization techniques and their general operating conditions are listed in this section. However, the characterization procedure needs to be specific for different polymer electrolyte systems, which will be addressed in detail later in Chapter IV.

3.2.1 Morphological studies

OM (Lietz Laborlux polarized optical microscopy) was used to study the phase separation of reaction components in the mixture of synthesis and the corresponding films after film casting. Hitachi S-2150 Scanning Electron Microscopy (SEM) was also used to characterize the morphology of polymer electrolytes. The sample was held by an aluminum sample support and sputter coated with silver.

3.2.2 Swelling ratio test

Polymer gels with crosslinked network were swelled in suitable solvents. For example THF is a good solvent to swell PMMA. In order to conduct swelling ratio test, the polymer electrolytes were firstly etched in certain solvents such as methanol to remove the salt from the polymer network. The sample then swelled in solvent like THF until reach swelling equilibrium.

3.2.3 FTIR spectroscopy

The interaction between the ionic liquid molecule and the polymer network was explored by Thermo Scientific Nicolet 380 Fourier Transform Infrared (FTIR). FTIR
spectroscopy is known to be very useful in analyzing the formation of complexation and interaction as a result of various compositions of the polymer electrolytes. The FTIR spectra of polymer gels involving various weight ratios of electrolytes were compared. The shifts in the wave number of absorption bands are ascribed to the interactions between the polymer matrix and corresponding electrolytes. The infrared spectra were recorded under nitrogen atmosphere in the range of 4400–400 cm⁻¹ with a resolution of 4 cm⁻¹.

3.2.4 Solution viscosity measurements

The electrolyte solution with different composition of PEMPS and LiTFSI was characterized by Bohlin Gemi nano viscometer to determine the shear viscosity. The viscosity data was obtained at shear rate in the range of 0.01 s⁻¹ to 1000 s⁻¹ at 25 °C, with the logarithm stepwise shear rate increment. The 4/40 cone-plate fixture was used.

3.2.5 Kinetics of polymerization

**Differential scanning calorimetry (DSC) analysis**

The Thermal Advantage 2920 DSC was used to investigate the kinetics of polymerization of ion gels. The reaction enthalpy of the polymerization of MMA, ΔH° was reported to be -26 KJ/mol in the literature. Since the amount of crosslinker in the mixture of reaction was very small (only 5 wt% of MMA), it was assumed that all the heat generation was caused by the reaction of double bond from MMA.

After the solution of reaction mixture was prepared at room temperature, 5-10 mg of the solution was placed in a hermetically sealed aluminum pan. An empty pan served
as the reference pan. The cell was then heated to the desired reaction temperature and the isothermal reaction was carried out. The heat flow as a function of time was calculated by DSC from the area under the peak of exotherm. A liner baseline reflecting the heat flow at the end of reaction was obtained. The heat flow due to the reaction at any time is considered as the difference between the measured heat flow and the baseline heat flow. The heat flow is then related to the heat generation from the polymerization reaction of monomers by the following formula,

\[ \alpha = \frac{\Delta H(t)}{\Delta_r(H)} \]  

(Equation 3.1)

where \( \alpha \) is the conversion of monomer at the specific time \( t \), \( \Delta H(t) \) is the molar heat flow of reaction at time \( t \), and \( \Delta_r(H) \) is the molar theoretical reaction enthalpy. The conversion of monomer as a function of time is then estimated in this way.

**Thermogravimetric Trace (TGA)**

TGA analysis was used to monitor the weight loss of material upon any reaction involving the change of composition as the temperature rises, such as dehydration, volatile removal and decomposition. Since the ionic liquid has essentially zero vapor pressure, for ion gels where the ionic liquid is the solvent, the mass loss of volatiles resulting from unreacted monomers can be detected by TGA. The conversion of MMA monomer for the ion gel products can be estimated by this way.

According to the previous studies, PMMA ion gels with ILs such as BMIMPF\(_6\) and EMITFSI remain stable at a temperature higher than 300 °C. The decomposition temperature of bulk PMMA without IL is around 250 °C. The corresponding ion gels were reported to present decomposition temperatures somewhere
in between, depending on the content of IL. On the other hand, the boiling point of MMA is about 100 ºC at ambient environment, which is far lower than the decomposition temperature of the ion gel.

3.2.6 Thermal analysis

Thermal Advantage 2920 DSC was carried out at a heating rate of 10 ºC/min under nitrogen atmosphere to detect $T_g$ and miscibility of polymer electrolytes. Thermal Advantage Q500 modulated thermogravimetric analyzer (TGA) was performed from room temperature to 475 ºC at a heating rate of 20 ºC/min under nitrogen atmosphere.

3.2.7 Ion conductivity measurement

The ionic conductivity of electrolytes and relative polymer gels were measured by complex plane frequency analysis of alternating current impedance as shown in Figure 3.6. The measurement was performed in a homemade cell using a multi-frequency LCR meter (Hewlett Packard 4274A). The cell is made of two stainless steel disks as electrodes separated by a Teflon spacer ring. The samples are then filled in the cell and sealed in a Teflon bag.
A HCS302 hot stage with sample chamber was used to control the temperature in the range from room temperature to 70 °C, with a heating temperature interval of 10 °C. The samples of known area were thermally equilibrated at each temperature for at least 15 min before measurements. The ionic conductivity as a function of temperature was measured at frequencies from 1 Hz to 1MHz, using AC amplitude of 1V. The ionic conductivity is calculated from the measured resistance when the imaginary component at high frequency falls to zero. Sample thickness, $d$, is determined by the difference between caliper measurements of the end-to-end length of the stainless steel rods with and without the polymer gel between them. The bulk resistance of the polymer electrolyte, $R_b$, is obtained from the impedance spectrum. Thus, the ionic conductivity, $\sigma$, is calculated according to Equation (3.2).

$$\sigma = \frac{d}{R_b S} \quad \text{(Equation 3.2)}$$
The temperature dependence of ionic conductivity for the polymer gels and that of bulk ILs is depicted in the Arrhenius plots. The accuracy of all of the results is checked by replicate measurements under identical experimental conditions.

3.2.8 Actuation measurement

In order to characterize electroactive deformation, specific devices were constructed with respect to different type of deformation test. Agilent U8002A Single Output DC Power Supplies was used as the actuation stimulus. The operating potential was varied between 0 V to 5V. In bending test, the bending displacements of the free end of the gel strip were measured in the application of DC electric field. In contraction test, the axial deformation between electrodes was measured.

The experimental setup for bending test of IL polymer is shown in Figure 3.7. The setup is horizontally laid on the table. The sample was cut into strips with a cross section 10 mm × 40 mm, and 0.5-1 mm in thickness. One end of the sample was contacted with stainless steel electrodes and fixed by a plastic clip which connected to dc power supply. The other end of the sample was free to move under the electric field. The displacement of bending was recorded by camera from the top.
The bending displacement, \( \delta \), is the moving distance of the gel end from the off-electric field position upon electric field. According to Alke\textsuperscript{143}, the bending strain \( \varepsilon(t) \) as a function of time, is calculated from (Equation 3.3)

\[
\varepsilon(t) = \frac{\delta(t)d}{L^2} \tag{Equation 3.3}
\]

where \( \delta(t) \) is read from the camera. The equation can be used as far as a constant curvature is assumed.
CHAPTER IV

RESULTS AND DISCUSSION

4.1 Ion Gel based on ionic liquid

As mentioned in previous sections, ion gels using room temperature ionic liquid (RTIL) as the solvent are promising substitutes of the polymer electrolyte involving aqueous electrolyte solution. However, the synthesis procedure of in situ polymerization of monomer in ionic liquid requires a suitable combination of the two components.\textsuperscript{2, 59} First, the initial reaction mixture of monomer and IL should be miscible to form a homogeneous solution. Second, the IL and polymer should be compatible so as to avoid phase separation after gelation takes place.\textsuperscript{160, 161} This means the liquid phase electrolyte can be uniformly dispersed in the solid phase of polymer matrix without seeping out. The morphological development will play a key role in forming applications such as batteries and actuation devices.

Based on these above requirements, there are a limited number of combinations of RTIL and polymer available. 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF\textsubscript{6}) is a good RTIL with a $T_m$ around 10 °C. It is widely used since it is highly ion conductive, environmentally friendly, electrochemically stable, and compatible with some commonly used crosslinked polymer networks. The polymer matrix including PMMA was synthesized using appropriate crosslinker and initiator. The vinyl
monomer for in-situ polymerization is selected with respect to the predetermined RTIL. Another feature of the PMMA polymer matrix is it exhibits minimum association and high swelling ability with RTIL, while maintaining good flexibility at ambient conditions. Methylmethacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) and the responsive polymers were reported to be compatible with several ILs and can form transparent and flexible ion gels when tetra(ethylene glycol) diacrylate (TTEDGA) was used as the crosslinker for a suitable content.\(^6\) Besides serving as the electrolyte, IL is also a good plasticizer in PMMA matrix.

In this study, ion gels were produced in the presence of crosslinking agent, tetra(ethylene glycol) diacrylate (TTEDGA) by in situ polymerization of methylmethacrylate (MMA) in hexafluorophosphate (BMIMPF\(_6\)). Since the decomposition temperature of the initiator BPO is in the range of 60 °C ~ 80 °C (\(t_{1/2} = 10\) hours at temperature = 73 °C), the reaction temperature in this study was set at 70 °C. A series of compositions of ion gels were prepared in 50/50 to 10/90 MMA / IL weight ratios.

In this chapter, the effect of ionic liquid concentration on the ion gel polymerization was investigated using DSC kinetics study under isothermal reaction condition followed by temperature scan. The resulting gel products were characterized using FTIR, thermal analysis, ion conductivity as well as their morphology to assess the gel network and its conduction mechanism.
4.1.1 Ion gel polymerization

The in situ polymerization of MMA in ionic liquid in the presence of divinyl crosslinking agent leads to crosslinking of the polymer chain and formation of polymer gel. The gel point is referred to the formation of a three-dimensional network with infinitely large molecular size by three dimensional linking of the molecules into a long range network.\textsuperscript{162} Walling studied the kinetics of gel formation of PMMA-ethylene dimethacrylate with various crosslinking agent concentrations.\textsuperscript{163} The experimental data showed a 4.4\% conversion at the gel point, when the divinyl monomer was 1.0 mol\% of the MMA monomer. Thus the gel point occurred at a very early stage of the reaction. Chern and Poehlein\textsuperscript{164} derived a model of the cure kinetics based on diffusion-controlled mechanisms and achieved reasonable agreements for the MMA-EGDMA system. The authors assumed equal reactivity of the two reaction components.

In order to study the ion gel polymerization, the reactive solutions of ion gel synthesis with selected MMA/BMIMPF\textsubscript{6} compositions were carried out isothermally using differential scanning calorimetry. First the reaction was isothermally carried out at a desired temperature for long enough time until the exothermic peak return back to the original baseline before the start of the reaction. Subsequently, the samples were quickly cooled down to room temperature and subjected to a temperature scan at a heating rate of 10 °C/min to 200 °C to quantify the residual heat due to incomplete polymerization from isothermal reaction.
The overall heat of reaction ($\Delta H$) was defined as the sum of the isothermal reaction ($\Delta h_i$), the subsequent residual heat ($\Delta h_r$) obtained during the temperature sweep up for each sample, and the heat loss ($\Delta h_l$) due to sample loading and stabilization\(^{165}\).

\[
\Delta H = \Delta h_l + \Delta h_i + \Delta h_r
\]  
(Equation 4. 1)

The conversion of the isothermal reaction $\alpha$, was then calculated by

\[
\alpha = 1 - \frac{\Delta h_r}{\Delta H}
\]  
(Equation 4. 2)

The total heat of reaction ($\Delta H$) was measured through independent adiabatic temperature rise experiments by DSC\(^{166, 167}\) where the reactant mixture was heated to 200 °C with a heating rate of 10 °C/min. This calculation method assumed a constant enthalpy of reaction and neglected the side reactions. Thus the heat release during reaction was only attributed to polymerization.

First, the independent adiabatic temperature rise reactions were conducted by DSC from 0 °C to 200 °C, with a heating rate 10 °C/min. The resulting thermograms are shown in Figure 4.1. The reaction heat for each ion gel composition can be used to calculated the total heat of reaction, $\Delta H$. 


Table 4.1 Reaction heat from ion gel adiabatic reaction

<table>
<thead>
<tr>
<th>MMA%</th>
<th>Onset temperature °C</th>
<th>Peak temperature °C</th>
<th>Reaction heat J/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>92.29</td>
<td>116.58</td>
<td>475.20</td>
</tr>
<tr>
<td>30%</td>
<td>84.49</td>
<td>108.41</td>
<td>355.67</td>
</tr>
<tr>
<td>50%</td>
<td>101.44</td>
<td>115.88</td>
<td>330.80</td>
</tr>
</tbody>
</table>

The isothermal DSC thermograms at 70 °C for a series of compositions are shown in Figure 4.2. Ion gels with MMA weight ratio of 10 wt%, 30 wt%, and 50 wt% are compared with the bulk polymerization of 100 wt% MMA. The ion gels with 10 wt%
and 30 wt% MMA show no obvious exothermic peak during the 40 min scanning period. Ion gel with 50 wt% of MMA shows a small and broad exothermic peak starting around 26 minutes, while the bulk polymerization of MMA with crosslinking agent exhibits a sharp peak between 30-35 minutes. It can be seen that the polymerization of a lower MMA concentration leads to a slower polymerization and delay in the initiation of polymerization. This is attributed to two effects: when the ionic liquid is major phase (90/10-70/30 IL/MMA) the systems obtained were found to exhibit high viscosity. This, in turn, leads to reduction in diffusion of MMA and reduced the reaction rate. Second, in this composition range, the low concentration of MMA leads to slow polymerization rate described by equation (2.1).

Immediately following the isothermal reaction, samples were heated from room temperature to 200 °C. The results of temperature scan are shown in Figure 4.3. Ion gels with 10 wt% and 30 wt% of MMA exhibit clear exothermic peaks between 70 °C and 140 °C. Ion gel with 50 wt% of MMA shows a smaller and narrower peak in the range of 100 °C – 160 °C, which is comparable to that of the bulk polymerization of MMA. For ion gels with small concentration of MMA, most of the polymerization took place at a higher temperature. However, the completion of the polymerization containing 10-30% MMA fraction, occurred earlier than the compositions containing 50 wt % MMA. At higher reaction temperatures, the compositions containing higher ionic liquid polymerize at higher rate leading to higher conversion rate for a given reaction time. These conclusions are in accord with the literature where other researchers also concluded that the delay of termination is primarily due to the higher viscosity, and thus lower diffusion, in the presence of ionic liquid. The conversion of each ion gel composition were
calculated using DSC scans and are shown in Table 4.2. The conversion increased as the MMA concentration increased.

Figure 4.2 DSC thermograms for ion gel isothermal reaction at 70 °C
Figure 4.3 DSC thermograms for ion gel temperature scan subsequently after isothermal test at 70 °C

Table 4.2 Conversion of isothermal reaction at 70 °C based on residual temperature scan

<table>
<thead>
<tr>
<th>MMA%</th>
<th>Peak Area J/g</th>
<th>Conversion %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>29.87</td>
<td>37%</td>
</tr>
<tr>
<td>30%</td>
<td>59.79</td>
<td>44%</td>
</tr>
<tr>
<td>50%</td>
<td>28.51</td>
<td>84%</td>
</tr>
<tr>
<td>100%</td>
<td>48.06</td>
<td>86%</td>
</tr>
</tbody>
</table>

At 70 °C the reaction rate is too slow to be detected by DSC in the experimental time chosen (Figure 4.2 top line). Therefore, the isothermal experiment for each sample in Figure 4.2 was repeated at 80 °C for a longer reaction time, followed by a temperature scan from room temperature to 200 °C. The results were shown in Figure 4.4 and Figure 4.5. As mentioned earlier, the polymerization with a lower MMA weight ratio leads to a slower polymerization. The characteristic point and peak area for Figure 4.4 and Figure 98
4.5 are given in Table 4.3 and Table 4.4, respectively. The conversions of isothermal test at 80 °C are compared with those at 70 °C in Table 4.2. The results show that the use of higher temperature leads to increased polymerization rate and a higher conversion. The larger increase in conversion for the low MMA% system is ascribed to the significant viscosity drop of ionic liquid at higher temperature.

Figure 4.4 DSC thermograms for ion gel isothermal reaction at 80 °C
Figure 4.5 DSC thermograms for ion gel temperature scan subsequently after isothermal test at 80 °C

<table>
<thead>
<tr>
<th>PMMA%</th>
<th>Start time</th>
<th>Onset time</th>
<th>Maximum time</th>
<th>Stop time</th>
<th>Peak Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>30%</td>
<td>5.25</td>
<td>5.91</td>
<td>18.51</td>
<td>51.01</td>
<td>55.58</td>
</tr>
<tr>
<td>50%</td>
<td>1.78</td>
<td>16</td>
<td>20.32</td>
<td>28.43</td>
<td>303.2</td>
</tr>
<tr>
<td>100%</td>
<td>5.55</td>
<td>13.82</td>
<td>14.83</td>
<td>18.05</td>
<td>161.5</td>
</tr>
</tbody>
</table>

Table 4.4 DSC data for temperature scan subsequently after isothermal test at 80 °C

<table>
<thead>
<tr>
<th>PMMA%</th>
<th>Start temperature</th>
<th>Onset temperature</th>
<th>Maximum temperature</th>
<th>Stop temperature</th>
<th>Peak Area</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>90.52</td>
<td>111.14</td>
<td>134.67</td>
<td>139.24</td>
<td>11.38</td>
<td>68%</td>
</tr>
<tr>
<td>30%</td>
<td>88.20</td>
<td>130.45</td>
<td>144.39</td>
<td>171.19</td>
<td>34.24</td>
<td>68%</td>
</tr>
<tr>
<td>50%</td>
<td>91.13</td>
<td>112.22</td>
<td>138.67</td>
<td>167.95</td>
<td>22.70</td>
<td>87%</td>
</tr>
<tr>
<td>100%</td>
<td>97.30</td>
<td>108.44</td>
<td>144.36</td>
<td>176.44</td>
<td>46.01</td>
<td>87%</td>
</tr>
</tbody>
</table>
To investigate the kinetics of ion gels at broad range of temperatures and times, the ion gel with 10% MMA was picked. The DSC thermograms of isothermal reaction at different temperature are shown in Figure 4.6. It shows that a higher temperature leads to an earlier occurrence of polymerization peak. Figure 4.7 shows DSC thermograms for temperature scan for ion gel 10% MMA following isothermal test at various temperatures. At each temperature, the heat of polymerization, $\Delta h_i$ was calculated based on the isothermal reaction, and the residual heat, $\Delta h_r$ was obtained from the heat release in temperature scan tests.

Figure 4.6 DSC thermograms for isothermal reaction of ion gel 10% MMA at different temperature
In Table 4.5, the temperature dependency of conversion ($\alpha$) of 10 % MMA ion gel calculated by equation 4.2 is shown. Here, the overall heat was calculated based on the adiabatic temperature scan test, using the reaction enthalpy 355.67 J/g referring to Table 4.1. $\Delta h_i$ and $\Delta h_r$ are enthalpy of isothermal polymerization and residual heat from the subsequent temperature scan, respectively. Gonzalez-Romero and Casillas$^{169}$ reported conversion of bulk PMMA polymerization varied from 0.87 to 0.91 in the temperature range from 70 °C to 80 °C, where the overall heat was considered as the sum of $\Delta h_i$ and $\Delta h_r$. 

Figure 4.7 DSC thermograms for temperature scan of ion gel 10 % MMA subsequently after isothermal test at various temperature
Table 4.5 Conversion of isothermal reaction for ion gel of 10% MMA at various temperatures

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$\Delta h_i$, J/g</th>
<th>$\Delta h_r$, J/g</th>
<th>Conversion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>39.57</td>
<td>6.535</td>
<td>82%</td>
</tr>
<tr>
<td>80</td>
<td>34.74</td>
<td>5.559</td>
<td>84%</td>
</tr>
<tr>
<td>90</td>
<td>21.81</td>
<td>1.989</td>
<td>94%</td>
</tr>
</tbody>
</table>

These results show that 100% conversion of free radical polymerization was hard to achieve primarily due to increased viscosity at the late stage of polymerization, when the movement of monomer becomes diffusion limited.\textsuperscript{164}

Some part of the residual unreacted monomers can be estimated by a temperature scan to the point above the synthesis temperature. The conversion is calculated based on the adiabatic reaction heat of PMMA at 70 °C. For ion gel samples synthesized at 70 °C for 24 hours, DSC temperature scan from room temperature to 200 °C with a ramp rate 10 °C/min were conducted. The results are shown in Figure 4.8. The exothermic peaks due to the heat release from the polymerization of residual monomers become stronger and sharper as MMA% increases. The exothermic peak for 10 % MMA ion gel is not very clear, instead, the curve presents several small peaks between 90 °C to 120 °C. This is because the amount of MMA in the system was so small, that the reaction heat of polymerization is hard to identify by the DSC test. For each composition, the onset and peak temperature of the exothermic peak, as well as the integrated peak area were analyzed by TA universal analysis software. Conversion and characteristic temperature of ion gels in DSC temperature scan are shown in Table 4.6. It shows that the high conversations were achieved in the MMA% range 20%–40%, with the highest value 98.04 % at 40 % MMA. The conversions are relatively low at higher and lower MMA%.
This result is different from the previous observation presented earlier in Figure 4.2 and Figure 4.4, where the reaction of higher MMA concentration system achieved a higher conversion within 60 minutes. It should be noted that the reactions in Figure 4.8 were carried out for 24 hours. Even though the polymerization at early stage was faster for higher MMA% system, the reaction rate reduced at the late stage due to vitrification essentially stopping the reaction. For moderate MMA% (20%~40%) systems, the ionic liquid plays a positive role as a plasticizer for the diffusion of the free radical at the late stage of the polymerization, which leads to a more complete polymerization.

Figure 4.8 DSC temperature scan for the residual heat of ion gels synthesized at 70 °C
Table 4.6 Conversion and characteristic temperature of ion gels in DSC temperature scan

<table>
<thead>
<tr>
<th>MMA%</th>
<th>Onset Temperature, °C</th>
<th>Peak Temp, °C</th>
<th>Residual Heat, J/g</th>
<th>Conversion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%</td>
<td>124.75</td>
<td>145.18</td>
<td>36.17</td>
<td>90%</td>
</tr>
<tr>
<td>50%</td>
<td>117.32</td>
<td>137.04</td>
<td>18.65</td>
<td>90%</td>
</tr>
<tr>
<td>40%</td>
<td>123.69</td>
<td>142.35</td>
<td>2.783</td>
<td>98%</td>
</tr>
<tr>
<td>30%</td>
<td>106.84</td>
<td>133.42</td>
<td>5.383</td>
<td>95%</td>
</tr>
<tr>
<td>20%</td>
<td>131.36</td>
<td>142.94</td>
<td>2.431</td>
<td>97%</td>
</tr>
<tr>
<td>10%</td>
<td>99.48</td>
<td>100.41</td>
<td>2.954</td>
<td>92%</td>
</tr>
</tbody>
</table>

4.1.2 Thermal analysis

Figure 4.9 shows the DSC curves of the ion gels containing various amounts of BMIMPF$_6$ as well as bulk PMMA and BMIMPF$_6$. The $T_g$s of ion gels and two parent components are shown in Table 4.7. The PMMA bulk exhibits a $T_g$ at 92 °C, and the neat RTIL of BMIMPF$_6$ shows a $T_g$ at -75 °C. The ionic liquid also exhibits a crystallization peak at -20 °C and a melting peak around 10 °C. Consequently, it is in liquid state at room temperature. Ion gels with different weight fraction of BMIMPF$_6$ have single $T_g$ located between PMMA and RTIL, which indicate that the ion gels exhibit a single phase. As the weight ratio of PMMA to BMIMPF$_6$ decreases from 50/50 to 10/90, the crystallization and melting peaks disappear, and the $T_g$ decreases, exhibiting the dramatic effect of ionic liquid in decreasing the overall $T_g$ of the ion gel system. This is reasonable and in agreement with prior literature.$^{6,59,60}$
Figure 4.9 DSC thermograms of PMMA polymer network with different weight fractions of BMIMPf$_6$.

Table 4.7 Glass transition temperature as a function of PMMA to BMIMPf$_6$ weight ratio.

<table>
<thead>
<tr>
<th>PMMA/BMIMPf$_6$</th>
<th>0/100</th>
<th>10/90</th>
<th>20/80</th>
<th>30/70</th>
<th>40/60</th>
<th>50/50</th>
<th>10/0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g$ ($^\circ$C)</td>
<td>-78.2</td>
<td>-73.2</td>
<td>-69.0</td>
<td>-59.5</td>
<td>-45.2</td>
<td>-22.7</td>
<td>98.6</td>
</tr>
</tbody>
</table>

To analyze the effect of crosslinking agents, the glass transition temperatures of ion gels with and without crosslinking reaction were studied by DSC and were compared as a function of ionic liquid concentration in Figure 4.10. For ion gels with ionic liquid, the uncrosslinked gel exhibited a lower $T_g$ than the crosslinked one. As the content of
As the ionic liquid concentration increases, the $T_g$'s of both crosslinked and uncrosslinked approach that of the neat ionic liquid.

Figure 4.10 Glass transition temperature of crosslinked and not crosslinked ion gels as a function of BMIMPF$_6$ weight ratio.
The relation between $T_g$ and the composition of ion gel was also compared with the well known Fox equation\textsuperscript{170} and the simplified Couchman-Karasz\textsuperscript{171} equation based on Simha-Boyer rule,\textsuperscript{172} which are interpreted as follows:

Cortazar 	extit{et al.} studied the glass transition temperatures of plasticized polyarylates by comparing the experimental data obtained by DSC to the data predicted by different equations based on Couchman-Karasz equation and its simplified versions.\textsuperscript{173} Couchman and Karasz\textsuperscript{171} equation shown in Equation 4.3 is based on the continuity of mixture entropy at $T_g$. But it requires the $\Delta C_p$ in the $T_g$, which is not easily available in the literature.

\begin{equation}
\ln\left(\frac{T_{g2}}{T_{g1}}\right) = \frac{w_2 \Delta C_{p2} \ln\left(\frac{T_{g2}}{T_{g1}}\right)}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}}
\end{equation}

(Equation 4.3)

However, under certain conditions, the term of $\Delta C_p$ can be neglected and Couchman-Karasz equation can be simplified further.

By applying Simha-Boyer empiric rule\textsuperscript{172} which assuming $T_g \Delta C_p$ kept constants for many polymers, the equation is simplified as:

\begin{equation}
\ln\left(\frac{T_{g2}}{T_{g1}}\right) = \frac{w_2 \ln\left(\frac{T_{g2}}{T_{g1}}\right)}{w_1 \left(\frac{T_{g2}}{T_{g1}}\right) + w_2}
\end{equation}

(Equation 4.4)

where $T_{g1}<T_{g2}$. When $T_{g1}\approx T_{g2}$, the above equation can be further simplified to Fox equation.\textsuperscript{170}
\[ \frac{1}{T_g} = \frac{w_1 T_{g1}}{w_2 T_{g2}} \]  

(Equation 4. 5)

This equation is used to predict the glass transition temperatures for random copolymers. From Figure 4.10, the ion gel \( T_g \) were more closer to the data predicated by Simha-Boyer empiric rule. Since the degree of crosslinking is known to change of the polymer \( T_g \), the values in Table 4.6 were used to empirically estimate the molecular weight between crosslinks shown in Equation 2.4. This equation is only valid for the polymers

\[ M_c = \frac{3.9 \times 10^4}{(T_g - T_{g0})} \]  

(Equation 2.4)

with \( T_g \) shift due to crosslinking effects. The calculated molecular weights between crosslinks as a function of ion gel composition are shown in Figure 4.11. As IL varied from 50% to 90% of weight, \( M_c \) increased from 3000 to 10000 g/mol, which indicates long chains between crosslinks and looser network as mentioned previously in Section 2.1.1. The Am Ende and Peppas also used this empirical equation to characterize PAA/EGDMA crosslinked polymers in the presence of 40% solvent of water or ethanol. According to their reports, \( M_c \) varied in the range of 4200 to 1550 g/mol when the crosslinking agent, ethylene glycol dimethacrylate (EGDMA), changed from 0.01 to 0.02 as a molar ratio to AA monomer. In this study, the molar ratio of TTEGDA to MMA was kept at 0.01656 that is between 0.01 and 0.02 as mentioned above. \( M_c \) was 2867 g/mol at 50% IL, which was comparable to the reported value by Am Ende and Peppas involving 40% solvent.
In addition, the simple theoretical relationship between the molecular weight between crosslinks and the crosslinking ratio (mol-crosslinking agent/ mol-monomer) (Equation 2.3) was also applied to estimate the molecular weight between crosslinks.

\[
\overline{M_c} = \frac{M_r}{2X}
\]

(Equation 2.3)

Since the crosslinking ratio in our study was kept as 0.01656 for all the ion gel samples, it does not change with the gel composition. Consequently, the theoretical molecular weight between crosslinks is 3022 g/mol for all ion gels that is close to the values for ion gels with 50% and 60% IL obtained by Equation 2.4.

Figure 4.11 Molecular weight between crosslinks for ion gels with various BMIMPF₆ %
The thermal stability of ion gels was characterized by TGA. The samples were heated from room temperature to 450 °C with a heating rate of 20 °C/min under nitrogen atmosphere. Figure 4.12 shows the TGA curves of the ion gels with varying amount of BMIMPF$_6$. The onset weight loss points for each composition of ion gels were detected by TA universal analysis software and displayed in Figure 4.13. As seen in Figure 4.13, no noticeable weight loss was observed for both the ion gel samples and bulk PMMA until around 130 °C. The weight loss of bulk PMMA started to show at 130 °C, and became rapid after 260 °C, which is consistent with the well known decomposition temperature of PMMA.$^{60}$ For ion gels, as the content of ionic liquid varied from 50 % to 100 % for neat BMIMPF$_6$, the initial weight loss temperature was slightly increased. However, the presence of ionic liquid dramatically increase the thermal stability of ion gels compared with bulk PMMA. As the weight ratio of ionic liquid increases, the decomposition points of ion gels become close to the decomposition temperature ($T_d$) of neat BMIMPF$_6$ around 350 °C. In addition, all the ion gels exhibit one step weight loss and display good combination between ionic liquid phase and the solid polymer matrix, which was different from the PMMA/IL ion gel without crosslinking agent.$^{60}$ This may be due to the fact that only small amount of PMMA was involved in the ion gel compared with BMIMPF$_6$, so that the weight loss corresponding to PMMA decomposition is not significant. Furthermore, the crosslinked polymer matrix also played a positive role in improving the mechanical strength and compatibility of the ion gels due to the one step weight loss. As mentioned before in section 3.2.5, the TGA was also a useful method to monitor the kinetics and conversion of the polymerization reaction of ion gel involving no volatile substrates. Figure 4.14 indicates the conversions of all the ion gels with
various amount of ionic liquid resulted from the DSC residual scan (Figure 4.8) and TGA weight loss at decomposition temperature (shown in Figure 4.13). From TGA, all the conversions were in the range of 88 % to 92 %, which are very close to the data from DSC for ion gels with 10% and 50% IL, but lower for the ion gels with 20%~40% IL. The difference can be ascribed to the fact that the weight loss products at TGA decomposition temperature is not only water and unreacted monomer but also due to the decomposition of PMMA and ionic liquid. Therefore, the conversions from TGA are lower than from DSC tests. Overall, the ion gels with ionic liquid from 50% to 90% showed good compatibility between the ionic and PMMA polymer matrix, and exhibited increased stability over a wide temperature range.
Figure 4.12 TGA curves for PMMA polymer gels with different weight fraction of BMIMPF$_6$. 

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Figure 4.13 The onset decomposition temperature and weight% from TGA curves for ion gels as a function of PMMA%.

Figure 4.14 Conversions of ion gel with various composition based on DSC and TGA tests.
4.1.3 FTIR spectroscopy

The molecular structure and the intermolecular interaction of ionic liquid BMIMPF$_6$ have been studied by Meng$^{176}$ and Antony$^{177}$. Meng et al. reported the formation of hydrogen bonding between F on the anion PF$^-\$ with either the H from imidazolium ring (C-H) and from the side alkyl chain attached to the imidazolium ring.$^{176}$ Figure 4.15 shows the molecular structure of BMIMPF$_6$, where the hydrogen bond is formed by F and H from the position 2 (C2) on the ring (F····H-C). This hydrogen bonding exhibited the lowest formation energy among others (other H on the ring or from the side alkyl chains). The authors also found that the C-H bond at position 2 in the ring has lengthened and the distance between C-H and F was shortened. This H on C2 located between the two nitrogen atoms on the ring was very active, which was reported to have acidic properties, so it is easy to form hydrogen bonding in ionic liquids.$^{178, 179}$
Figure 4.15 Molecular structure and interaction illustration of BMIM$^+$ and PF$_6^-$ of the ionic liquid$^{176}$

The interaction between the PMMA network and ionic liquid was investigated by FTIR. Figure 4.16 shows the FTIR spectra of the ion gels. The important peaks and their assignments for BMIMPF$_6$ and PMMA are listed in Table 4.8.$^{60}$$^{180}$
Table 4.8 Assignments of characteristic peaks in ion gel system

<table>
<thead>
<tr>
<th>Component</th>
<th>Wave number(cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMIMPF₆</td>
<td>3172 and 3126</td>
<td>C-H for the cyclic ring</td>
</tr>
<tr>
<td></td>
<td>1577</td>
<td>C-C and C-N stretching of imidazole ring</td>
</tr>
<tr>
<td></td>
<td>1387 and 1469</td>
<td>CH₃ stretching vibration on the side chain</td>
</tr>
<tr>
<td></td>
<td>838 and 890</td>
<td>stretching vibration of PF₆⁻ and the P-F bond</td>
</tr>
<tr>
<td></td>
<td>1168</td>
<td>P-H bending vibration</td>
</tr>
<tr>
<td>PMMA</td>
<td>1730</td>
<td>stretching vibration of free C=O</td>
</tr>
<tr>
<td></td>
<td>1718–1725</td>
<td>hydrogen bonded C=O</td>
</tr>
<tr>
<td></td>
<td>2994 and 2952</td>
<td>stretching of CH₃</td>
</tr>
<tr>
<td></td>
<td>966 and 911</td>
<td>bending vibration of CH₃</td>
</tr>
<tr>
<td></td>
<td>1485–1365</td>
<td>deformed vibration of C–H</td>
</tr>
<tr>
<td></td>
<td>2925, 2853, 845</td>
<td>stretching vibration of CH₂</td>
</tr>
<tr>
<td></td>
<td>1274, 1243, 1193, 1151</td>
<td>stretching vibration of C–O–C</td>
</tr>
<tr>
<td></td>
<td>989</td>
<td>stretching vibration of CH₃–O</td>
</tr>
</tbody>
</table>

The characteristic peaks of interest for this study is the stretching vibrations of C=O in PMMA as illustrated in Figure 4.16 (a). The pure PMMA exhibited two peaks of C=O: a small shoulder at 1737 cm⁻¹ due to the free C=O group and a strong peak at 1722 cm⁻¹ due to the hydrogen bonded C=O with water. As the amount of BMIMPF₆ increases from 50% to 90%, the peak of hydrogen bonded C=O at 1722 cm⁻¹ move to higher wave numbers (1726 cm⁻¹, 1727 cm⁻¹, 1729 cm⁻¹) and flattens. This movement to higher wave number suggests a decreasing hydrogen bonding between PMMA and water. As the PMMA% decreases in the ion gel, the C=O peak flattens. This wave number shift can also be attributed to the interaction of H in BMIMPF₆ associated with C=O and form other types of hydrogen bonds⁶⁰ which is weaker than the hydrogen bonding with water. At the same time, the peak at 1737 cm⁻¹ for free C=O groups does not show obvious change as PMMA% decrease from 50% to 30% in the ion gel, and slightly shifts to lower
frequency position (1735 cm\(^{-1}\) and 1733 cm\(^{-1}\)) as the concentration of PMMA further decreases to 10\%, which indicates the interaction between PMMA and IL increases, such as C=O with C-H group of BMIMPF\(_6\). Figure 4.16(b) shows the characteristic stretching vibration of C-H in the cyclic BMIM\(^+\) group of RTIL. The neat BMIMPF\(_6\) exhibits a C-H vibration at 3172 cm\(^{-1}\). As the weight fraction of PMMA increased from 10 \% to 50 \%, the C-H vibration slightly moves to lower wave numbers, indicating a weak interaction between PMMA matrix and RTIL, BMIMPF\(_6\). Overall, no significant interaction was observed between C=O group of PMMA and C-H group of BMIMPF\(_6\). In Figure 4.16(c), PF\(^-\) from BMIMPF\(_6\) shows a peak around 820 cm\(^{-1}\). After adding PMMA, the peaks at 820 cm\(^{-1}\) become broader and slightly shift to higher wave number at 50\% PMMA composition. The small peak at 1151 cm\(^{-1}\) is for stretching vibration of C-O group from bulk PMMA. A small peak at 1168 cm\(^{-1}\) is observed next to the vibration at 1151 cm\(^{-1}\), which is for the P-H hydrogen bond between the anion and cation of IL. For the ion gels with 50 \% to 30 \% PMMA, the curves in the range of 1200~1100 cm\(^{-1}\) show double peak due to the coexistence of the C-O group and P-H group in the system. As PMMA\% varies from 30 \% to 10 \% in the ion gels, the peak arising from C-O disappears and only P-H peak is observed. Thus, as the concentration of ionic liquid increases, most ions decouple from the PMMA network and contribute to the conduction instead of associating with polymer network.
4.1.4 Morphology study of ion gel structure

The gel products were transparent, soft, flexible and mechanically self-standing, as shown in Figure 4.17. The thickness of the gel film was maintained around 1 mm.
The ion gel surface was observed under optical microscope as shown in Figure 4.18. For the ion gel surface with 10% PMMA, it is clear to see some liquid phases on the gel surface, indicating the ionic liquid has seeped out from the gel matrix. This may be due to the fact that the weight fraction of PMMA is only 10 wt%, so the gel matrix is not enough to hold all the ionic liquid that is nine times of its weight. As a consequence, some ionic liquid remains outside of the network after gelation. The liquid phase can also be found for the ion gels with 20% and 30% PMMA. However, as the PMMA content increased, the liquid phase decreased, which means more ionic liquid could be trapped inside the polymer gels as PMMA is increased. Figure 4.8 (d) shows the structure of ion gels with 50 wt% PMMA. There was no visible liquid phase on the surfaces. The network was distributed all around the gel, with a mesh size around 50 μm. Many air bubbles were also found on the gel surface with a diameter less than 10 μm. The air trapped in the solution tried to release from the system during the heating of reaction solution and the polymerization, but the solution became more and more viscous.
as the reaction progressed, which restrained the release of air bubbles. Since the reaction was taken place in a sealed container, the air bubbles were finally trapped at the interface between the mold and the gel solution.

![Image](image1)

(a)  
(b)

![Image](image2)

(c)  
(d)

Figure 4.18 Ion gel surface with various weight ratio of PMMA:IL: (a) 10:90, (b) 20:80, (c) 30:70, (d) 50:50

Since the structure of ion gel surface was greatly affected by the contacted mold surface, it is worthy to study the inside structure from the cross section perpendicular to the gel surface. Therefore, ion gels have been cut from the surface, and the cross section was observed under microscope. The image of the cross section of ion gel with 20 wt% PMMA is shown in Figure 4.19. The mesh size ranges from 10 μm to 60 μm. Some
meshes are not shown clearly because of the cutting and the flowing out of the ionic liquid. More meshes from the network were seen from the cross section view of ion gel with 45 wt% and 50wt% PMMA in Figure 4.20, respectively.

Figure 4.19 Cross section view of ion gel with weight ratio of PMMA: IL = 20:80

Figure 4.20 Cross section view of ion gel with weight ratio of PMMA: IL = 40:60
In order to obtain a better view of the network structure inside the ion gels, the ionic liquid on the surface needs to be removed. With this consideration, ion gels of 10 wt% PMMA were immersed in water to etch out ionic liquid before observation. As seen in Figure 4.22, the network structure is much clearer compared with the untreated gel products in Figure 4.19. The network had a general mesh size about 50 μm, and these meshes in different size were all connected to form continuous paths. Besides, the meshes were found to be filled with small bubbles. This may arise from the high viscosity of the reaction solution, which prevented air from moving to the surface, as seen in Figure 4.18.
4.1.5 Swelling ratio test

The role of TTEGDA (tetra(ethylene glycol)diacrylate) as a crosslinking agent on the formation of crosslinked network can be confirmed by determining the swelling ratio of consequent ion gels in a good solvent for PMMA. The crosslinked network will not dissolve but swell upon exposure to the solvent. The swelling ratio test was carried out in THF for ion gels with various compositions of PMMA and ionic liquid, as shown in Figure 4.23. As the MMA content increases, the swelling ratio of ion gel decreases, indicating a higher crosslinking density of the gel network. The crosslinking density decreases with higher ionic liquid content even as the molar ratio of MMA to crosslinking agent, TTEGDA remains constant. This suggests that the presence of ionic liquid plays a role in the crosslinking reaction between MMA and TTEGDA. This can be explained by two facts: First, at a higher monomer concentration, the total solvent volume is decreased, and thus a larger number of crosslinks are formed in the final gel
product. Second, the higher concentration of monomer also enhance the chain interpenetration so as to improve the crosslinking reaction instead of the side reactions like cycling, which is favored when the mobility of pendant double bonds is high. This fact will finally result a smaller mesh size at the higher concentration of monomer. The various reactions in crosslinking copolymerization are illustration in Figure 4.24. The formation of cycling reactions does not contribute to the ultimate network structure, leading to a decrease of the crosslinking density. This relationship of PMMA composition and the swelling ratio is also in consistence with the literature observations\textsuperscript{13} as previously mentioned in section 2.1.1.

![Figure 4.23 Swelling ratio of ion gels with various MMA wt%](image)

Figure 4.23 Swelling ratio of ion gels with various MMA wt%
4.1.6 Ion conductivity

The ion conductivity as a function of temperature for ion gels was measured with various compositions of MMA and ionic liquid. The measurements were conducted in air. Gel samples with known thickness and surface area were sandwiched between electrodes made of stainless steel. The cell consisted of gel sample and electrodes was connected to the multi-frequency LCR meter and placed in the hot stage chamber, whose temperature could be controlled by a computer. Each sample was tested from 30 °C to 70 °C with a temperature interval of 10 °C. The plots of complex impedance of ion gels are shown in Figure 4.25 to Figure 4.29, where the imaginary component of the impedance, $Z''$ is plotted against the real component, $Z'$. The bulk electrical resistance, $R_b$ is represented by the $Z'$ value at the minimum $Z''$. For the ion gel with 50 % PMMA shown
in Figure 4.25, the impedance spectra at 30 °C and 40 °C exhibit part of the semi-circle at high frequency, followed by inclined line at low frequency. As the temperature rise ultimately to 70 °C, the part of semi-circle generally disappeared, and the Z' value at the minimum Z" (R_b) shifts to a lower number, which corresponded to a decrease in the ion gel impedance. In Figure 4.26, for ion gel with 40 % PMMA, the part of semi-circle disappeared at a lower temperature. As PMMA decreased from 30 % to 10 % (Figure 4.27-Figure 4.29), the semi-circle parts no longer exist, only the inclined lines are present. It is also found that as the PMMA decreased, R_b at the same temperature moved to a lower number. The lowest R_b was obtained for ion gel with 10% PMMA at 70 °C in Figure 4.29.
Figure 4.25 Impedance plot of ion gel with 50 % PMMA at various temperatures
Figure 4.26 Impedance plot of ion gel with 40 % PMMA at various temperatures

Figure 4.27 Impedance plot of ion gel with 30 % PMMA at various temperatures
Figure 4.28 Impedance plot of ion gel with 20% PMMA at various temperatures

Figure 4.29 Impedance plot of ion gel with 10% PMMA at various temperatures
The $R_b$ found in the aforementioned plots of complex impedance was used to calculate the ion conductivity of ion gels through equation (2.21). The temperature dependence of conductivity for each ion gel is depicted in Figure 4.30. The ion conductivity was found to increase as the content of BMIMPF$_6$ increased. For each ion gel, the ion conductivity increased as the temperature increased. The increase of the ion conductivity as BMIMPF$_6$ increases is due to the fact that the introduction of more RTIL in the ion gel decreases the $T_g$ of ion gel matrix, and weakens the interaction between RTIL and polymer matrix, thus resulting in more mobile ions. The highest room temperature of ion gel with weight ratio of [PMMA]/[BMIMPF$_6$] = 10/90 is $3.38 \times 10^{-3}$ S/cm. This ion gel exhibited ion conductivity as high as $9.72 \times 10^{-3}$ S/cm at 70 °C. This phenomenon agrees with the results of FTIR and DSC mentioned in the previous sections. In addition, the lines of different ion gels exhibit almost linear temperature dependence of the ion conductivity, which fits the Arrhenius law as previously mentioned in equation (2.16), indicating the decoupling of the ion transfer from the PMMA matrix and a thermally activated ionic motion.
4.1.7 Conclusions

Ion gels were successfully prepared by in-situ polymerization of MMA with TTEDGA in the RTIL of BMIMPF$_6$. All the ion gels are self-standing, flexible and transparent, exhibiting very high thermal stabilities. The room temperature ion conductivity is in the range of $10^{-4}$~$10^{-3}$ S/cm. In addition, the dependence of ion conductivity fits Arrhenius law well. The crosslinked network structure with a mesh size around 20 µm-50 µm was observed by microscope and confirmed by swelling ratio measurements. Our findings indicate that the interaction between PMMA matrix and RTIL decrease with increasing the content of BMIMPF$_6$, which enhances ion conductivity. IL polymer gel systems show a high ionic conductivity indicating that a
larger amount of ions migrate under the electric field. Based on the experimental observations, the mechanism of ion conduction in ion gel is illustrated in Figure 4.31. Most of the ions of ionic liquid are decoupled from the PMMA network, and randomly distributed in the gel. After application of electric field, anions and cations move towards the anode and cathode respectively and both contribute to the final high conductivity. Polymer network serves as a physical container of ionic liquid. The meshes in crosslinked PMMA form continuous paths for the ions to move between electrodes. Since the ion transfer induced deformation is one of the main contributions of the actuation of the polymer gel system, the high ion conductivity leads to propose an actuation property of the gel system under electric field.

Figure 4.31 Schematic illustration of ion conduction of ion gel
4.2 Electroactive ion gel based on ionic liquid

In order to be used in actuation devices, the body of the gel needs to be flexible and exhibits good mechanical stability. Actuation properties are improved with increased IL concentrations in the gel. IL ion transport is the main factor for the volume change. The crosslinked polymer network primarily serves as a physical container to hold the IL. In this section, the conventional polyacrylic acid (PAA) aqueous actuator was first prepared according to the previous studies in this area. The electromechanical measurements were then carried out for the PAA gel and ion gel. Then a three layer poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT/PSS) coated ion gel actuator is introduced to overcome the problems of ion gels in use as an actuator. The bending test and morphology and FTIR experiments were used to characterize the ion gel actuators.

4.2.1 Electromechanical measurement

The poly(acrylic acid) gels were synthesized by free radical copolymerization of acrylic acid with the crosslinking agent, N,N'-methylenebisacrylamide in KOH water solution. Then, the equilibrium swelled crosslinked poly(acrylic acid) gels were used as a reference to analyze the actuation behavior and compared to that of ion gels. The PAA gel strip was immersed in DI water solution and execute bending test under DC. power supply. The measurements were made according to Figure 3.6 in Chapter III. As shown in Figure 4.32, the gel strip exhibits a bending strain of 0.017 toward cathode within 8 s under a 6 V DC voltage. The sample was observed to bend toward the anode after
switching the voltage to -6V. This phenomenon is in consistent with the literature reports as mentioned in 2.4.1. Under the electric field, the $K^+$ cations move out from the gel system toward cathode accompanying with water. At the same time, the local pH is lower near anode. The $H^+$ will neutralized the negatively charged poly(acrylic acid) network. Therefore, the network shrinks and bends towards anode due to the release of the repulsive force between the polymer chains and the effluence of the counter ions ($K^+$).  

Figure 4.32 Bending of PAA gel in water under d.c. power supply.

The ion gel based on ionic liquid and PMMA was then tested its actuation behavior under DC voltage. As shown in Figure 4.33, the gel strip was sandwiched by stainless steel electrodes and fixed by a polypropylene clip. The assembling is then connected to a DC power supply with the voltage change from 0~ 30 V. However, no visible displacement of bending under the range of testing was found. The contact
Surface of ion gel with electrode was observed as shown in Figure 4.34. Both the ion gel and the electrodes show liquid on the contacting surface. The thickness of the contacting area of ion gel exhibited a contraction strain of 1.11%, which is primarily due to the seeping out of ionic liquid and the pressure of clip. These observations indicate that the ion gel itself can not execute actuation because the ionic liquid directly seeping out the polymer under electric field and the neutral PMMA polymer matrix does not respond to the electric field. Therefore, the ion gel needed to be modified in order to show actuation behavior.
The conducting polymer was then considered to be a good candidate to overcome the problems of ion gel, because it can both serve as an ion carrier by carrying out electrochemical reactions with the mobile ions and at the same time, as a responsive polymer to the electric field since it is conductive. Since Poly (3, 4-ethylenedioxythiophene) PEDOT/PSS is a commonly used conducting polymer. Comparing with other commercial conducting polymers, PEDOT/PSS is suspended in aqueous solution and easy for the film casting process. In this research, the IL-PMMA ion gel surface was coated multiple layers of PEDOT/PSS by film casting. These PEDOT/PSS layers play crucial roles as both ion container and electrode. Under electric field, there will be reversible transport of ions between the PEDOT/PSS polymer and the ion gel electrolyte during electrochemical oxidation and reduction. Incorporation and withdraw movement of cations from the PEDOT/PSS polymer are expected as the polymer exhibited negative and positive potentials, respectively.

The samples of PEDOT/PSS coated ion gel were cut into strips with dimension of 3 mm × 50 mm. The gel strips were fixed horizontally by stainless steel and plastic clips.
The tip displacements as a function of time (0-60 s) at various voltages were recorded by a camera. As shown in Figure 4.35, the ion gel strips with 90 % ionic liquid was subjected to a direct current potential with voltage varying from 0 to 3 volts. (a) Shows the initial position of the sample before test. (b) shows the sample position after 1 min under 2 volts. The bending strain was calculated to be 0.0113. (c) shows the sample after 1 min under 3 volts. The strain has been increased to 0.0142 in this case. It is also worth to notice that the gel sample was very thin and soft that the bending at the end collapsed to some extent, so the bending angle might be a little larger than what it should be. Overall, the bending strain increased as the potential increased, which is reasonable because the higher potential can cause more ions to move into the PEDOT/PSS layer, leading to a higher bending strain. However, there is a limit of potential due to the degradation of polymer under higher potential. Ion gels subjected to a potential higher than 5 Volts was observed to degrade and leaded to an irreversible bending. This phenomenon is consistent with the observation of other researchers,\textsuperscript{148} who concluded that higher voltage can degrade the conducting polymer even though the initial rate of bending increases. Another important observation of the bending test is that the sample bends towards cathode under electric field. This is believed to be due to the movement of cations towards cathode and consequent accumulation in the PEDOT/PSS layer. In addition, the amount of bending strain of PEDOT/PSS coated ion gel is comparable to the strain of PAA aqueous system. Therefore, the ion gel shows a great potential as a non aqueous gel actuator replacing the traditional water based gel systems. This ion gel actuator also exhibits a unique advantage since it can operate in air without any inert atmosphere protection, which is a common precaution for ion conducting electrolytes.
Figure 4.35 Bending actuation for ion gel with IL/PMMA=90/10. Film thickness is 0.31 mm. (a) Voltage = 0 V, (b) Voltage = 2 V last 1 min with strain $\varepsilon_b = 0.0113$, (c) Voltage = 3V last 1 min with strain $\varepsilon_c = 0.0142$

4.2.2 Morphology of PEDOT/PSS layer

The cross-section of the PEDOT/PSS coated ion gels was observed by optical microscope. In Figure 4.36, the highlighted dark edge was the PEDOT/PSS layer, whose thickness was 0.0422 mm.

Figure 4.36 Cross-section view of PEDOT/PSS coated ion gel
SEM observations were carried out for PEDOT/PSS coated ion gels on both the surface and cross-section. Figure 4.37 shows the surface of PEDOT/PSS layer deposited on the ion gel. The coating area was mostly uniform, but some small cracks were observed. The circles may due to the evaporation of water during drying. Figure 4.38 shows the cross-section of the sample. The PEDOT/PSS layer was shown on the left edge with a thickness around 20 μm. Next to the PEDOT/PSS layer is the ion gel network with porous meshes. The cracks on the surface can be modified by casting multiple layers of PEDOT/PSS, so the conducting polymer can be distributed continuously and uniformly for better actuation behavior.

Figure 4.37 SEM picture of the PEDOT/PSS coated ion gel surface
4.2.3 FTIR study of PEDOT/PSS films

FTIR spectroscopy of the PEDOT/PSS film on ion gels before and after the bending test under electric field was used to analyze the movement of the mobile ions in the PEDOT/PSS film. Figure 4.39 shows the spectroscopy of PEDOT/PSS film after bending compared with that of original PEDOT/PSS film and neat BMIMPF$_6$. The frequencies of characteristic peaks with their assignments were listed in Table 4.8. It has been reported in the literatures,$^{181, 180}$ for BMIMPF$_6$, the characteristic peaks at 3172 cm$^{-1}$ and 3126 cm$^{-1}$ are assigned to the C-H vibration of cyclic BMIM$^+$, 1575 cm$^{-1}$ is for the bending of C-C, 1468 cm$^{-1}$ and 1387 cm$^{-1}$ are for the stretching of CH$_3$ group, while the peak at 817 cm$^{-1}$ is for the stretching of PF$_6^−$. The peak at 1170 cm$^{-1}$ is due to the ring stretching vibration of BMIM cation.$^{182}$ From Figure 4.39, comparing with the IR of original PEDOT/PSS layer, the PEDOT/PSS layer shows new peaks after bending due to
the incorporation and association with BMIMPF$_6$. The presence of peak at 817 cm$^{-1}$ is due to the introduction of PF$_6^-$.

The new peaks at 1171 cm$^{-1}$ and 1575 cm$^{-1}$ is for the C-C ring stretching, 3171 cm$^{-1}$ and 3137 cm$^{-1}$ is for the C-H vibration, 1469 cm$^{-1}$ is assigned to the CH$_3$ group on the side chain of BMIM$^+$, respectively. Therefore, these new peaks proved the transfer of ions to the PEDOT/PSS layer under electric field, which consequently leads to bending actuation of PEDOT/PSS coated ion gel.

Table 4.9 IR characteristic frequency and its assignment of BMIMPF$_6$

<table>
<thead>
<tr>
<th>Wave number, cm$^{-1}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>817</td>
<td>PF$_6^-$</td>
</tr>
<tr>
<td>1171</td>
<td>ring stretching of BMIM</td>
</tr>
<tr>
<td>1469</td>
<td>CH$_3$</td>
</tr>
<tr>
<td>1575</td>
<td>C-C in cyclic BMIM</td>
</tr>
<tr>
<td>3174, 3137</td>
<td>C-H in cyclic BMIM</td>
</tr>
<tr>
<td>3674</td>
<td>N-H</td>
</tr>
</tbody>
</table>
4.2.4 Conclusions

A three-layer PEDOT/PSS coated ion gel actuator was developed that exhibits reversible bending under DC. The deformation strain was operated in air and was comparable to PAA based aqueous polyelectrolyte gels. The bending toward anode was due to the accumulation of the large size BMIM$^+$ cations in PEDOT/PSS layer as cartooned in Figure 4.40.
Figure 4.40 Actuation mechanism of PEDOT/PSS coated ion gel
CHAPTER V

LITHIUM POLYMER GEL BASED ON PMMA AND MODIFIED POLYSILOXANE

The polymer gel electrolyte based on PMMA and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) was developed with polyethyleneoxide modified polysiloxane (PEMPS). The two reasons for PEMPS to be used as a solvent in this study: it has a good compatibility with both the polymer matrix PMMA and LiTFSI salt, and it can improve the cycleability of the lithium cell by inhibiting the dendrite formation of lithium through constraining the reduction of electrolyte solutions. The gel electrolytes were prepared by in-situ polymerization of MMA in the solution of LiTFSI and PEMPS as a function of MMA/PEMPS weight ratio and [O/Li] value. The [O/Li] value is defined as the molar ratio of PEMPS ether oxygen to LiTFSI as previously mentioned in 3.1.2. The effects of polymer/solvent composition and salt concentration on the ion transfer behavior were studied by the following characterization techniques.

5.1 Electrolyte solution- mixture of lithium salt and modified polysiloxane

The mixture of LiTFSI and PEMPS forms the electrolyte in the polymer gel. It is the mobile phase for ion conduction, and does not participate in MMA polymerization. As the electrolyte solution, the interaction between LiTFSI salt and PEMPS plays a crucial role in the ion transport of the polymer gels. Here, optical microscope, FTIR, and
viscosity measurement were used to investigate LiTFSI and PEMPS electrolyte solutions.

5.1.1 Morphology study of electrolyte miscibility

The miscibility of LiTFSI and PEMPS electrolyte were analyzed by optical microscopy. Samples of LiTFSI salt crystals were investigated under cross polarized light. Figure 5.1 shows the picture of neat LiTFSI in air under non polarized and polarized light to see the crystal structure. From (a) and (b), the LiTFSI salt are in the form of small densely packed crystals. Since it is very sensitive to moisture, it absorbed the water in air and quickly turned into an aqueous LiTFSI solution as shown in (c). Figure 5.2 shows the photograph of neat PEMPS, which was a clear liquid in air. LiTFSI and PEMPS were then mixed to form a uniform electrolyte solution with various [O/Li] value as shown in Figure 5.3. As [O/Li] decreased from 32 to 8, the concentration of lithium salt increased. Consequently, the size of the undissolved LiTFSI crystal increased. This was due to the fact that the amount of PEMPS was not enough to dissolve all the LiTFSI as the concentration of Lithium salt increased. As a result, the undissolved lithium salt remained solid crystals. This also suggests that even though the high lithium concentration is desired to reach high conductivity, there is a critical content of lithium salt beyond which it is insoluble.
Figure 5.1 microscope picture of Neat LITFSI in air. (a) under non polarized light, (b) under polarized light, and (c) LiTFSI dissolved in atmospheric water.

Figure 5.2 Neat PEMPS in air
Figure 5.3 PEMPS and Li salt Solution with various [O/Li]. Photographs in left column were under non polarized light, right column under polarized light.
5.1.2 FTIR Analysis

The miscibility of lithium salt in PEMPS is associated with the extent of salt dissociation in the solvent. It is related to the interaction between these two components. FTIR is an efficient method to characterize this salt-solvent interaction. The characteristic peaks and their assignments of the components are listed in Table 5.1. The peaks at 1351 cm\(^{-1}\), 1187 cm\(^{-1}\) and 1056 cm\(^{-1}\) are assigned to the C-SO\(_2\)-N asymmetric stretch, C-F stretch and S=O bonding of LiTFSI, respectively.\(^{184}\) For PEMPS, the peaks appear at 1021 cm\(^{-1}\) and 1099 cm\(^{-1}\) are assigned to Si-O-Si group and C-O-C group.\(^{185}\) These two groups (C-O-C and Si-O-Si) are related to the salt dissociation of lithium salt. Consequently, the characteristic peaks of these chemical groups are expected to change as the composition of LiTFSI and PEMPS changes.

<table>
<thead>
<tr>
<th>LiTFSI</th>
<th>PEMPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wave number, cm(^{-1})</td>
<td>Assignments</td>
</tr>
<tr>
<td>-----------------</td>
<td>--------------</td>
</tr>
<tr>
<td>1351</td>
<td>C-SO(_2)-N</td>
</tr>
<tr>
<td>1197</td>
<td>C-F</td>
</tr>
<tr>
<td>1056</td>
<td>S=O</td>
</tr>
<tr>
<td>785</td>
<td>C-S and S-N</td>
</tr>
<tr>
<td>760</td>
<td>C-S and C-F</td>
</tr>
<tr>
<td>740</td>
<td>S-N</td>
</tr>
</tbody>
</table>

In Figure 5.4, mixtures of PEMPS-LiTFSI with different [O/Li] are investigated by FTIR to study their interaction. A new intense peak occurred at 1056 cm\(^{-1}\) after the addition of LiTFSI to pure PEMPS, which is due to the S=O bonding of LiTFSI. This
peak becomes sharper as $r = [O/Li]$ changes from 32 to 8. The presence of new peaks are also observed at 1187 cm$^{-1}$ and 1351 cm$^{-1}$ due to the C-F stretch and S=O bonding of LiTFSI. At the same time, the peak of C-O-C at 1099 cm$^{-1}$ becomes flat as $r = [O/Li]$ decreases from 32 to 8. This observation is reasonable since concentration of PEMPS decreases as $[O/Li]$ decreases. It also indicates an intense interaction between S=O in LiTFSI and C-O-C in PEMPS. The Si-CH$_3$ of PEMPS at 803 cm$^{-1}$ is overlapped with the two peaks in 760–800 cm$^{-1}$ due to C-S of Lithium salt.

Figure 5.4 IR Spectra of PEMPS and LITFSI mixtures with various $r = [O/Li]$
Since the peaks of S=O and C-F in lithium salt are clearly present in the picture without significant overlap with other noise, their relative intensities at various composition can be compared based on the intensity of an inert group. The relative intensity was calculated by the ratio of peak heights between the interested group and the inert group. In this case, CH₂ is thought to be inert of the interaction between salt and PEMPS. So its peak height at 2870 cm⁻¹ was used as the inert peak height. As shown in Figure 5.5, the peak intensity of both S=O and C-F decreases as [O/Li] increases, because of the decreasing salt concentration. However, the intensities at [O/Li] = 8 for both S=O and C-F are much higher compared to other [O/Li] values at 16, 24 and 32. This suggests that the dissociation of lithium salt at [O/Li] = 8 is less efficient at higher [O/Li] values.

Figure 5.5 Relative intensity of characteristic peaks in Lithium salt as a function of [O/Li]
For the peaks of C-O-C and Si-O-Si in PEMPS, the position changes of their wave numbers according to various [O/Li] are shown in Figure 5.6. As [O/Li] decreases from 32 to 8, the wave number of C-O-C peak generally decreases, while the wave number of Si-O-Si peak decreases only at [O/Li] = 8. This observation reveals that the lithium salts favor the interaction with C-O-C, and are dissociated from Si-O-Si only at higher salt concentration.

![Figure 5.6 Wave number of characteristic peaks of PEMPS as a function of [O/Li]](image)

5.1.3 Viscometry Measurement

The viscosity of PEMPS and LiTFSI mixtures with respect to different [O/Li] was measured at room temperature, with a shear rate between 0.01 s\(^{-1}\) and 1000 s\(^{-1}\). From Figure 5.7, the viscosity dramatically decreases as [O/Li] increase from 8 to 16 and...
become flat when [O/Li] further increases to 26 and beyond. This phenomenon is in accord with the FTIR results in Figure 5.5 and the miscibility morphology in Figure 5.3. In summary, lithium salt does not completely dissolve in PEMPS at [O/Li] = 8 due to the high salt concentration. As more PEMPS is added, salt was dissolved more into the electrolyte solution. So the viscosity drop is due to better dissociation and miscibility of LiTFSI in PEMPS as the concentration of LiTFSI decreases.

![Figure 5.7 Viscosity of PEMPS and LiTFSI mixture as a function of [O/Li].](image)

5.2 Lithium polymer gel electrolyte

The characterization and analysis of the obtained lithium/PEMPS/PMMA polymer gels will be addressed in this section. All lithium polymer gels were prepared by in situ polymerization of methylmethacrylate (MMA) in PEMPS-LiTFSI electrolyte in the presence of crosslinking agent, TTEDGA. The effect of LiTFSI-PEMPS electrolyte
on the reaction of gel polymerization was investigated through DSC kinetics study of isothermal polymerization and temperature scan after polymerization. The gel products were analyzed by microscopy, FTIR, thermal analysis, swelling ratio test and ion conductivity measurement. The gel network and its conduction mechanism were studied with respect to MMA/PEMPS weight ratio and [O/Li] (ether group in PEMPS/ Li in LiTFSI) molar ratio of the electrolyte.

5.2.1 Lithium polymer electrolyte polymerization

This section focuses on the polymerization reaction of PEMPS and PMMA in the presence of initiator and crosslinking agent, respectively. The reaction was characterized by DSC first isothermally for desired period followed by upsweep of temperature. The conversion is related to the area of exothermic peak. The method was described in detail in section 4.1.1.

The possible side reactions of PEMPS with initiator and crosslink agent were first investigated at room temperature. The mixture of reactants was stirred until completely dissolved and cast in glass vial for observation. The solution of PEMPS and BPO was still transparent liquid after remaining in room temperature for a couple of days. However, the solution of PEMPS, BPO and TEGDA became a white sticky liquid after several days at room temperature. This sticky liquid, after mixing with water, decomposed into small white particles suspended in the water. This observation is thought due to the polymerization of TEGDA in the presence of BPO. Since the TEGDA molecules have two functional double bonds, it can perform both polymerization and crosslinking reaction. However, the content of TEGDA in the solution was too small to
form a network throughout the whole material since it is only 5 wt% of PEMPS. The sticky liquid was believed to be the partially crosslinked TEGDA polymers dissolved in PEMPS. To further characterize the polymerization of PEMPS and TTEGDA, isothermal reactions of PEMPS and BPO with and without TTEGDA were conducted at 70 °C by DSC. In Figure 5.8, both solutions exhibit a small curve in about 2 to 3 minute into polymerization. These small curves might be the noise due to the heat fluctuation along with the temperature change at the beginning of polymerization. For solution composed of PEMPS and BPO, no discernible exothermic peak was found. While for the solution with PEMPS, BPO and TEGDA, a slight and broad convex curve is found between 15 and 38 minutes. This is related to the reaction of TTEGDA. As the reaction mixture combines a very small amount of TEGDA, the polymerization reaction was slow, leading to a broad exothermic curve. The isothermal DSC tests were subsequently followed by a temperature scan from room temperature to 220 °C to measure the residual heat. In Figure 5.9, both reaction solutions exhibit an exothermic curve at around 120 °C. The solution with TEGDA shows a higher peak, which is thought to correspond to both the reaction of unsaturated double bonds of TEGDA and polymerization of PEMPS. The results indicate that there is no polymerization of PEMPS takes place at the experimental temperature around 70 °C, so the isothermal reaction at this temperature can be negligible.
Figure 5.8 DSC isothermal reactions of PEMPS and TEGDA polymerization reaction at 70°C

Figure 5.9 Temperature scan following PEMPS and TEGDA isothermal reaction

The reactions of MMA polymerization and crosslinking in PEMPS were studied by DSC. First, the effects of lithium salt on the gelation were determined. Figure 5.10 shows the exothermic curves of isothermal reactions for the reaction solution with and without LiTFSI. For the reaction solution without LiTFSI, except a small exothermic
peak occurred at the beginning, within 3 minutes of polymerization, no obvious heat release was found in the experimental period. While for the reaction solution involving LiTFSI, a very broad convex curve was presented starting from 20 minute to 40 minute. This exhibits a slow polymerization took place in this period. The temperature scans of the two reactions were carried out subsequently following the isothermal reaction, and the results are shown in Figure 5.11. Both samples exhibit an exothermic curve in the 120 °C to 140 °C range. The curve of the sample without LiTFSI is broader and occurs a little later than the curve of the sample involving LiTFSI. This indicates the former solution generates more heat from polymerization. Consequently, the former solution has a lower reaction conversion during isothermal test shown in Figure 5.10. Therefore, the presence of LiTFSI can increase the polymerization rate and conversion of MMA, which is consistent with the observation of ionic liquid based ion gels and the literature.47

![Graph showing isothermal polymerization of MMA in PEMPS at 70°C. MMA/PEMPS weight ratio = 40/60. Dashed line is for polymer gel with [O/Li] = 16, and the solid line is for polymer gel without Lithium salt.]

Figure 5.10 Isothermal polymerization of MMA in PEMPS at 70°C. MMA/PEMPS weight ratio = 40/60. Dashed line is for polymer gel with [O/Li] = 16, and the solid line is for polymer gel without Lithium salt.
Figure 5.11 Temperature scan following Polymerization of MMA in PEMPS isothermal reaction. MMA/PEMPS weight ratio = 40/60. Dashed line is for polymer gel with [O/Li] = 16 and the solid line is for polymer gel without Lithium salt.

The effect of TEGDA on the polymerization of MMA in PEMPS and LiTFSI was also examined by DSC. Figure 5.12 demonstrates the curves of isothermal reaction of MMA in the presence of PEMPS and LiTFSI at 70°C. The [O/Li] ratio is maintained at 16. The reaction system involving TEGDA shows a clear exothermic curve during 20~40 minutes, while the reaction system without TEGDA does not show noticeable exothermic heat within the experimental time. Since the crosslinking agent, TEGDA, only takes 5wt % of MMA, most reaction heat is attributed to MMA polymerization. In this case, the reaction of MMA involving TEGDA is faster. The temperature scans of these products are exhibited in Figure 5.13.
Figure 5.12 Isothermal polymerization of MMA in PEMPS (MMA/PEMPS =4/6) with $r ([O/Li]) = 16$ at 70 °C. Dashed line is for polymer gel with crosslinking agent (CRX), and the solid line is for polymer gel without crosslinking agent (NCRX).

Figure 5.13 Temperature scan following Polymerization of MMA in PEMPS with $r =16$ isothermal reaction. The lighter dashed line is for polymer gel with crosslinking agent, and the solid line is for polymer gel without crosslinking agent.
Lithium polymer gels in this research were allowed to cure at 70 °C over 20 hours. In order to analyze their conversion with respect to the effects of PMMA/PEMPS composition and [O/Li], the residual heat due to unreacted monomer was characterized by DSC temperature scan from room temperature to 200 °C with a heating rate 10 °C/min. Figure 5.14 and Figure 5.15 show the DSC thermograms of lithium polymer gel as a function of [O/Li] and PMMA/PEMPS, respectively. In Figure 5.14, the exothermic peaks due to residual heat for various [O/Li] are located in the 95 °C ~ 170 °C range. The gel sample without lithium salt exhibits a sharper exothermic peak than others. As shown in Table 5.2, the conversion increases as [O/Li] decreases to 16, and then decreases exhibiting maximum in conversion as lithium salt content increases. This phenomenon indicates an increase in lithium salt in a moderate range leads to a higher conversion of the polymerization probably due to local effects. However, too much lithium salt can cause a dramatic rise in viscosity of the reaction solution as shown in Figure 5.7 in section 5.1.3, where the viscosity increased 3 times as [O/Li] decreased from 16 to 8. As discussed before for ionic liquid based ion gels polymerization in 4.1.1, a high viscosity will result in a low conversion due to the diffusion limitation of the radicals and monomers.
Figure 5.14 Residual heat scan of lithium polymer gel (PMMA/PEMPS = 40/60) as a function of [O/Li].

Table 5.2 Conversion of lithium gel in DSC residual heat scan as a function of [O/Li]

<table>
<thead>
<tr>
<th>[O/Li]</th>
<th>Residual Heat $\Delta h_r$, J/g</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>no Li</td>
<td>30.73</td>
<td>83%</td>
</tr>
<tr>
<td>32</td>
<td>12.33</td>
<td>90%</td>
</tr>
<tr>
<td>16</td>
<td>8.572</td>
<td>93%</td>
</tr>
<tr>
<td>8</td>
<td>8.948</td>
<td>90%</td>
</tr>
</tbody>
</table>

Table 5.3 shows the conversion of lithium gels with different PMMA/PEMPS composition at [O/Li] = 16. The residual heat was analyzed by TA Universal analysis software according to Figure 5.15. The conversion increases as PMMA/PEMPS...
increases from 30/70 to 40/60, and then decreased as it reached PMMA/PEMPS = 50/50. This observation is similar to the conversions of PMMA/ionic liquid polymer gels described in Table 4.6, where ion gels also showed a maximum conversion of 98.04% at PMMA/BMIMPF$_6$ = 40/60. Therefore, the increase of conversion with MMA% is due to the fast polymerization rate at the early stage, and the decrease of conversion is attributed to the vitrification effects after the gelation take place for higher MMA%. Overall, the results from above analyses indicate that the conversion exhibited a maximum as [O/Li] and PMMA/PEMPS increases. The highest conversion was found to be 92.51% for lithium gels with PMMA/PEMPS = 40/60, and [O/Li] =16.

![Residual heat scan of lithium polymer gels with various PMMA/PEMPS weight ratio. [O/Li] =16 for all the gel samples.](image)
Table 5.3 Conversion of lithium gel in DSC residual heat scan as a function of PMMA/PEMPS

<table>
<thead>
<tr>
<th>PMMA/PEMPS</th>
<th>Residual Heat $\Delta h$, J/g</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>30/70</td>
<td>14.96</td>
<td>82%</td>
</tr>
<tr>
<td>40/60</td>
<td>8.572</td>
<td>93%</td>
</tr>
<tr>
<td>50/50</td>
<td>22.73</td>
<td>85%</td>
</tr>
</tbody>
</table>

5.2.2 Morphology study

The obtained gel electrolytes in the forms of polymer film with about 1 mm thickness are shown in Figure 5.16. The pictures of samples at various compositions of MMA/PEMPS are demonstrated with respect to [O/Li]. All the samples are flexible and transparent with a sufficient mechanical strength to be self-standing.
Figure 5.16 Pictures of lithium polymer gel films with various MMA/PEMPS weight ratio and [O/Li]. The pictures in the three columns are for gels with [O/Li], from left to right, 16, 26, 32, respectively.

The cross section of the gel was observed under the microscope. From Figure 5.17, the mesh size of the network is in the range of 10~ 30 μm. Even though some gel part is collapsed and deformed due to cutting, it is still clear to see the porous network composed of network of meshes forming continuous paths for ion transfer.
Figure 5.17 Cross section view of lithium polymer gel under microscope. The sample has a weight ratio MMA/PEMPS = 50/50 and [O/Li] = 26.

5.2.3 FTIR spectroscopy

The interaction of LiTFSI and PEMPS of various concentrations of salt was analyzed by FTIR. The [O/Li] effects was analyzed for polymer electrolytes when MMA/PEMPS weight ratio keeps constant at 30/70, 40/60, and 50/50, respectively, as shown in Figure 5.18. The characteristic peaks of LiTFSI and PEMPS as well as their interaction were addressed previously in section 5.1.2. For pure PMMA, the IR studies of vibrational assignments were available in the literature.\textsuperscript{187-190} The characteristic peaks at wavenumber 1726 cm\(^{-1}\) is due to C=O asymmetric stretching from the carbonyl group. The bands at 1420 cm\(^{-1}\) and 1350 cm\(^{-1}\) are due to CH\(_2\) group. The band near 1357 cm\(^{-1}\) is due to the O-CH\(_3\) asymmetric bending. The interaction of the lithium cation and the C=O group has been observed by previous studies.\textsuperscript{60, 188, 189, 191, 192}
In Figure 5.18 (a) PMMA/PEMPS=30/70, the peaks at 1351 cm\(^{-1}\) and 1187 cm\(^{-1}\) of LiTFSI become sharp and intense as the [O/Li] decreases, while the C=O peak of PMMA at wavenumber 1726 cm\(^{-1}\) stays at the same wavenumber position as [O/Li] changes. This means the interaction between PMMA and LiTFSI becomes weak when the MMA/PEMPS weight ratio is lowered to 30/70. In this case, since the ether group of PEMPS is more abundant, the lithium salt has increased interaction with PEMPS instead of PMMA. From Figure 5.16 (b) PMMA/PEMPS=40/60, C=O peak of PMMA at wavenumber 1726 cm\(^{-1}\) moves to a higher position of wave number and becomes broad and flat as [O/Li] decreases. This indicates an increase in the interaction between lithium salt and PMMA chain. Therefore, the interaction between MMA and LiTFSI increasing as r decreases. In Figure 5.16 (c), as the weight ratio of MMA/PEMPS increases to 50/50, the peak of S=O bonding from LiTFSI at 1056 cm\(^{-1}\) becomes less intense compared with that in polymer electrolytes with lower MMA/PEMPS. This indicates the lithium salt has less interaction with ether groups due to the decrease of PEMPS in the gel system. On the other hand, the C=O peak from PMMA does not change much as [O/Li] changes. This reveals that PEMPS plays a more important role in dissociation with lithium salt compared with PMMA. This is primarily due to the fact that PEMPS is in a liquid state which has more access to reach the lithium salt, while the C=O group in PMMA side chain is immobilized by the crosslinked network and can not move easily to coordinate with the lithium salt.
(a) MMA/PEMPS = 30/70

(b) MMA/PEMPS = 40/60
Figure 5.18 IR Spectra of lithium polymer electrolyte with various $r = [O/Li]$.

5.2.4 Thermal analysis

The thermal analysis of the lithium polymer electrolytes were conducted by DSC and TGA. Figure 5.19 (a)-(c) show the DCS spectra of samples with various [O/Li] values and constant PMMA/PEMPS. The crosslinked PMMA was mentioned before (section 4.1.2) shows a $T_g$ of 99 °C. The glass transition temperatures as a function of $r$ for lithium gels with various PMMA and PEMPS composition are shown in Figure 5.20. As the lithium salt increase and [O/Li] decreases, the glass transition temperature of the gel sample generally increases. $T_g$ is maximal at -37 °C for $r = 8$ then becomes slowly reduces as $r$ decreases. The increase of $T_g$ at higher salt concentration is partially due to the interaction between LiTFSI and the PMMA network to form a coupling complex.
structure through C=O and Li ion, which was confirmed by FTIR previously in section 5.2.3. The glass transition temperatures for lithium polymers and bulk PEMPS as well as bulk PMMA are listed in Table 5.4.
Figure 5.19 DSC spectra of Lithium polymer electrolytes as a function of [O/Li] value.

(c) PMMA/PEMPS = 50/50

Figure 5.20 Glass transition temperature of lithium polymer electrolytes as functions of PMMA/PEMPS weight ratio and [O/Li] value
Table 5.4 Glass transition temperature as functions of MMA/PEMPS weight ratio and [O/Li] value

<table>
<thead>
<tr>
<th>MMA/PEMPS</th>
<th>[O/Li]</th>
<th>T_g, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50</td>
<td>32</td>
<td>-62.5</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>-63.6</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>-49.5</td>
</tr>
<tr>
<td>40/60</td>
<td>32</td>
<td>-65.4</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>-63.8</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>-59.1</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>-52.6</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>-36.9</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>-66.7</td>
</tr>
<tr>
<td>30/70</td>
<td>32</td>
<td>-61.3</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>-61.6</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>-55.0</td>
</tr>
<tr>
<td>Bulk PMMA</td>
<td>N/A</td>
<td>98.6</td>
</tr>
<tr>
<td>Bulk PEMPS</td>
<td>N/A</td>
<td>-82.0</td>
</tr>
<tr>
<td>PEMPS/LiTFSI</td>
<td>26</td>
<td>-72.7</td>
</tr>
<tr>
<td>PMMA/LiTFSI</td>
<td>N/A</td>
<td>87.3</td>
</tr>
<tr>
<td>PMMA/PEMPS=40/60</td>
<td>N/A</td>
<td>-66.7</td>
</tr>
</tbody>
</table>

The thermal stability of lithium polymer electrolytes with respect to PMMA/PEMPS weight ratio and various $r = [O/Li]$ was analyzed by TGA, and shown in Figure 5.21-Figure 5.23. For each composition of PMMA/PEMPS, the decomposition temperature increases with $r$, which can be attributed to the enhancing coupling effects of lithium salt and PMMA matrix.
Figure 5.21 TGA curves of lithium polymer electrolytes with PMMA/PEMPS = 30/70
Figure 5.22 TGA curves of lithium polymer electrolytes with PMMA/PEMPS = 40/60
The effects of PMMA/PEMPS composition on the thermal stability of lithium polymer electrolytes are demonstrated by Figure 5.24, where [O/Li] is kept at 16 for each PMMA and PEMPS composition. A higher PMMA/PEMPS composition leads to a higher decomposition temperature of the polymers, which is reasonable since PMMA matrix is the physical container of the polymer gels. However, all the samples exhibit noticeable decomposition (5 % weight loss) until 170 °C.
Figure 5.24 TGA curves of lithium polymer electrolytes as a function of PMMA/PEMPS composition. [O/Li] = 16 for all samples.

5.2.5 Ion conductivity of Lithium polymer gels

The ion conductivity of Lithium polymer gels with various compositions of MMA, PEMPS and LiTFSI were measured. (a)-(c) in Figure 5.25 show the ion conductivity change as a function of $r = \frac{[O/Li]}{}$ for polymer gels with certain weight ratio of MMA to PEMPS. For each composition of MMA and PEMPS, the highest ion conductivity of the polymer gel occurs at $r = 26$, while the lowest at $r = 32$. This is believed to be due to the trade off of high viscosity when high loadings of salt and low concentration of salt at low salt loadings. The conductivity is maximized in the intermediate level.
(a) PMMA/PEMPS = 30/70
(b) PMMA/PEMPS = 40/60
Figure 5.25 Conductivity as a function of temperature with respect to $r = \frac{[O/Li]}{r}$ for gels with weight ratio: (a) PMMA/PEMPS = 30/70, (b) PMMA/PEMPS = 40/60, (c) PMMA/PEMPS = 50/50

To investigate the effect of weight ratio of MMA to PEMPS, the gels are compared at the same ratio of $[O/Li] = 26$, and their ion conductivities are showed in Figure 5.26. The ion conductivity for every gel increases as temperature rises. The ion conductivities of MMA/PEMPS = 30/70 overlap with that of MMA/PEMPS = 40/60 in the measured temperature range. The ion conductivities of MMA/PEMPS = 30/70 and MMA/PEMPS = 40/60 are also higher than that of MMA/PEMPS = 50/50. But this difference of ion conductivity decreases as temperature rises. The dependence of ion
conductivity on temperature is not linear. Therefore, the ion transfer is considered to be coupled with PMMA polymer matrix to some extent.

![Graph showing conductivity of gels with different PMMA to PEMPS weight ratio.](image)

**Figure 5.26** Conductivity of gels with different PMMA to PEMPS weight ratio but same [O/Li] = 26 as a function of temperature

5.2.6 Swelling ratio test

Since the PEMPS/LiTFSI electrolyte is soluble in water, the gel samples were first immersed in water to extract the electrolyte from the PMMA network before the swelling test. Then the gel is swollen in THF to reach an equilibrium swelling. The weight of dry gel after water extraction and that of gel at equilibrium swelling were used to calculate the swelling ratio. The effect of MMA concentration on the swelling ratio of
lithium gel is demonstrated and compared with the swelling ratio of ionic liquid based gel in Figure 5.27. For lithium gels based on PMMA-PEMPS, a smaller MMA concentration gives a higher swelling ratio when the [O/Li] ratio remains constant. It is also observed that the MMA-PEMPS based lithium gels exhibit higher swelling ratio than that of MMA-IL gels for the same MMA weight ratio. As a result, the polymer network of MMA-PEMPS-Lithium gel has a larger mesh size. This can be due to the fact that the electrolyte of LiTFSI-PEMPS takes a larger volume in the polymer gels than ionic liquid. This is because in the lithium gels, the weight ratio of PMMA is relative to the weight of PEMPS, and lithium salt was not counted in the total weight calculation. In fact, the introduction of Lithium salt into PEMPS increases the volume of PEMPS itself.

![Swelling Ratio vs MMA Concentration](image)

Figure 5.27 swelling ratio of lithium polymer gel as a function of MMA weight concentration. The [O/Li] ratio was kept constant at 16 for all the gel samples.

As the weight ratio of PMMA to PEMPS remains constant at 40/60, the effect of $r = [O/Li]$ ratio on the swelling ratio is illustrated in Figure 5.28. Swelling ratio exhibits a
maximum (at 26) when [O/Li] increases from 0 to 32. This result can be related to the observation in Figure 5.25 (a) and (b), where [O/Li] = 26 exhibits a maximum ion conductivity. The high conductivity can be attributed to the larger mesh size of the polymer matrix which can form free and continuous path with larger space for the ion to transfer, so as to achieve high ion conductivity.

Figure 5.28 Swelling ratio of lithium polymer gel as a function of [O/Li] ratio. The MMA to PEMPS weight ratio was kept constant at 40/60 for all the gel samples.

5.2.7 Conclusions

The transparent, flexible and self-standing lithium polymer gels based on PMMA-PEMPS were developed with the PMMA/PEMPS weight ratio ranges from 30/70 to 50/50. The electrolyte of lithium-PEMPS was characterized with respect to [O/Li].
solubility of lithium in PEMPS tends to decrease as [O/Li] increases as observed in optical microscopy. The viscosity of the electrolyte is dramatically increased with high loadings of LiTFSI. This is ascribed to reaching the solubility limit of LiTFSI in PEMPS. The kinetics of the in-situ polymerization indicates that no PEMPS polymerization takes place at the temperature investigated. Most of the heat evolved was attributed to the polymerization of MMA. Lithium salt was found to accelerate the MMA polymerization rate and yield higher conversions. The conversion of the lithium gel samples were analyzed by residual temperature scan, and a higher conversion is found for the composition of PMMA/PEMPS = 40/60, and [O/Li] at 16~32. The FTIR results of the interaction between lithium salt and PEMPS and PMMA indicated that lithium salt was mostly dissociated from PEMPS. The T_g of lithium gels was found to increase as lithium or PMMA is increased. In addition, lithium gels with a higher salt concentration exhibited a higher decomposition temperature, indicating a higher thermal stability. The porous structure with a mesh size around 20 μm was observed. The crosslinked network is analyzed by swelling ratio test, which reveals a maximum at [O/Li] = 26. The same materials also showed the highest ion conductivity.
CHAPTER VI

POLYMER ELECTROLYTES FOR Ni-Zn BATTERIES

Three polymer electrolyte systems were studied for the application of Ni-Zn battery based on PVA, PAA and PMMA. The polymer electrolytes were formed by saturating the polymer matrix with a KOH solution. Based on the chemical nature of the polymer matrix, the KOH salt will exhibit different extent of interaction with the polar side group of polymer chains. Among these three polymers, PVA and PAA are hydrophilic materials. PAA has the strongest interaction with KOH since its acid group will be neutralized with the alkaline, KOH and form potassium carbonylate salts. At the same time, PAA side chains are ionized. The alcohol group on PVA will hydrogen bond with aqueous KOH, but the polymer chain will not be charged. Therefore, the presence of water is important in this system, and PVA itself can not dissolve the KOH salt. On the other hand, PMMA is hydrophobic because the ester group and does not dissolve in water. So it has the weakest interaction with the KOH salt. In order to have the salt dissolve in PMMA network, the system has to involve water, and at the same time, a cosolvent that can dissolve both water and the hydrophobic polymer chain. The solid polymer electrolytes were obtained by film casting method. The conductivity behavior of each electrolyte was measured and compared.
6.1 PVA and KOH based polymer electrolytes

The mixture of PVA and KOH water solution were cast in a Petri dish, followed by drying at room temperature to form an electrolyte film. Polymer electrolyte films were prepared from different $M_n$ of PVA, and their appearances were shown in Figure 6.1. It was observed that sample (a) revealed a smoother film than sample (b), which has a lower $M_n$. This may suggest that the larger molecular weight is more suitable to form uniform film. This is possibly due to the fact that long polymer chains lead to physical crosslinks through the entanglements of polymer chains, which can trap more electrolyte solution in the crosslinked network.

![Figure 6.1 Pictures of Polymer electrolytes based on PVA and KOH. (a) PVA $M_n = 85,000$–146,000 g/mol, (b) PVA $M_n = 31,000$–50,000 g/mol](image)

The ion conductivity of the two polymer electrolytes and their composition are measured and listed in Table 6.1. The PVA-(a) with a larger molecular weight shows very high ion conductivity on the order of $10^{-2}$ S/cm at room temperature, while PVA-(b)
exhibits a much lower conductivity, only on the order of $10^4$ S/cm at the same condition. Since water content and the composition of other components were very close for the two PVA polymer electrolytes, the only reason for the 100 times difference in ion conductivity is the molecular weight of PVA. As previously stated, the longer polymer chains lead to more entanglements to form a network efficient enough to contain more solvent, while the shorter chain leads to a less entangled network to trap enough electrolyte solution. This effect shows a phase separation of electrolyte solution from the PVA network. Therefore, the following study of these polymer electrolytes was focused on films of PVA-(a) with a larger molecular weight.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PVA, Mw</th>
<th>Ω, S/cm</th>
<th>Water</th>
<th>PVA</th>
<th>KOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA-(a)</td>
<td>85,000-146,000</td>
<td>0.0396</td>
<td>30.66%</td>
<td>23.11%</td>
<td>46.23%</td>
</tr>
<tr>
<td>PVA-(b)</td>
<td>31,000-50,000</td>
<td>0.000165</td>
<td>31.62%</td>
<td>22.79%</td>
<td>45.59%</td>
</tr>
</tbody>
</table>

The picture of the dried PVA film is shown in Figure 6.2. The film was placed on the top of a paper with blue grid. It is very thin and transparent. The weight of casting solution was recorded. After the solution was dried over night, it was weighed again. The water content of the dried PVA film was calculated to be 22.21% by weight.
The PVA film dried from PVA-water solution was observed under optical microscope as shown in Figure 6.3. The right picture captured under polarized light shows only very few crystals of PVA exist in the system. The crystal size is less than 0.1 mm. The crystal structure of 25 % KOH water solution dry at room temperature is shown in Figure 6.4. The needle like crystals grew from the mixture: likely KOH. The PVA and KOH polymer electrolyte was also prepared on glass slides to form a thin film and observe under microscope. In Figure 6.5, the electrolyte films were observed under non polarized light and polarized light. In both cases, the branched dendritic crystals of PVA were observed. These leaf shape crystals, formed during casting and subsequent heating the pregel solution at 70 °C, lead to the white opaque appearance of the film. In addition, no KOH crystals were seen in the electrolyte films by microscope. So KOH was completely dissolved in the formed polymer films and no visible crystallization was found due to KOH.
Figure 6.1 Microscope pictures of PVA film after film casting from PVA water solution.

Figure 6.2 Microscope picture of 25 % KOH water solution under polarized light.
Figure 6.3 Microscope pictures of crystal structures from PVA and KOH based polymer electrolytes. (a) under non polarized light, (b) under polarized light

The thermal properties of neat PVA (commercial product without any treatment) and the film cast from PVA water solution (same sample as in Figure 6.2 and Figure 6.3) were also analyzed by DSC as shown in Figure 6.6. The sample was heated from room temperature to 110 °C at 10 °C /min to remove the heat history, and then quickly cooled to –20 °C, and ramped to 300 °C with a heating rate 10 °C /min. The thermogram was analyzed by the TA universal analysis software to determine the glass transition temperature, peaks, as well as the integrated area relative to each peak. The glass transition temperature was 41.7 °C. The endothermic peaks were found around 220 °C, primarily due to the decomposition of PVA.
The PVA and KOH mixtures and their dried polymer electrolyte films were analyzed by FTIR. In Figure 6.7, the broad band at 3200-3400 cm\(^{-1}\) is due to the O-H stretching. For PVA, 1059 cm\(^{-1}\) is for C-O stretching, 1438.4 cm\(^{-1}\), 1353 cm\(^{-1}\) and 1645 cm\(^{-1}\) are for the -CH\(_2\) vibration, 2997 cm\(^{-1}\) is for –CH stretching, and 850 for the C-C stretching, respectively\(^{193}\). After the formation of PVA-KOH film, the –OH band at 3200-3400 cm\(^{-1}\) for PVA-KOH water solution moved to lower wave number, which is due to the evaporation of water, so as the KOH salt has more intense interactions with PVA instead of with water. At the same time, the characteristic peaks of PVA appeared as the solidified PVA polymer, such as the frequencies at wave number of 1438.4 cm\(^{-1}\).
for C-O, 1353 cm\(^{-1}\) and 1438 cm\(^{-1}\) for –CH\(_2\). The peak of –CH stretching at 2997 cm\(^{-1}\) has some extent of overlap with the –OH vibration at 3122 cm\(^{-1}\), which resulted in the two shoulders near 3000 cm\(^{-1}\) for the PVA film. The –CH\(_2\) peak at 1645 cm\(^{-1}\) moved to 1735 cm\(^{-1}\) as the film solidified from solution, which is an indication of the reduced interaction between PVA and water.

![FTIR spectroscopy of PVA-KOH water solution and polymer electrolyte.](image)

Figure 6.7 FTIR spectroscopy of PVA-KOH water solution and polymer electrolyte.

6.2 PAA and KOH based polymer electrolytes

Polymer gel electrolytes based on poly (acrylic acid) (PAA)and KOH solution were also prepared by thermally initiated polymerization and UV curing. Figure 6.8 shows the schematic structure of the PAA/KOH gel electrolyte. As the polymerization of acrylic acid proceeds in aqueous KOH, the –COOH group on its side chain executes neutralization reaction with KOH. Thus, certain amount of –COOH groups are ionized to
be negative charged –COO\(^-\), and the extent of neutralization of –COOH group depends on the concentration of KOH solution. After the gelation, the mobile ions of OH\(^-\), H\(^+\) and K\(^+\) remain in the embedded liquid phase in the crosslinked PAA matrix.

![Schematic structure of PAA gels with KOH solution](image)

Figure 6.8 Schematic structure of PAA gels with KOH solution

The gel products prepared through thermal initiation in test tubes were transparent gel rods with a diameter of 10 mm. They were then cut into 1 mm thick disks for characterization. The gel disks are shown in Figure 6.9, and their conductivity were measured by complex impedance analysis under an AC electric field. The complex plot is shown in Figure 6.10. The conductivity was calculated to be 3.19×10\(^{-2}\) S/cm at room temperature.
Figure 6.9 Picture of PAA-KOH gel electrolyte disks

Figure 6.10 Cole-cole plot of thermal initiated PAA-KOH polymer gels

The PAA-KOH polymer gel electrolyte was also prepared by UV curing. The reaction solution was cast into a glass vial with flat bottom, and then exposed to 312 nm UV light with a power of 3 W/cm² for 6 s. The obtained gel film is shown in Figure 6.11. Ion conductivity measurement was run on a film cut from the center area. The
conductivity at room temperature was calculated to be $2.49 \times 10^{-2}$ S/cm according to the cole-cole plot in Figure 6.12.

Figure 6.11 Picture of PAA-KOH gel electrolytes prepared by UV curing method.

Figure 6.12 Cole-cole plot of PAA-KOH polymer gel prepared by UV curing method.
6.3 PMMA and KOH based polymer electrolytes

Polymer electrolytes based on PMMA and PEMPS-KOH electrolyte solution were formed. The material chosen for polymer electrolyte is similar to that in developing the lithium polymer electrolyte as mentioned previously in 2.2.5 and Chapter V. The liquid phase electrolyte was expected to be embedded in the network of crosslinked PMMA, and be able to exhibit high ion conductivity without strong coupling effect from the polymer chain. But it is worth to note that PEMPS in the current study for Ni-Zn batteries has another important role, which serves as a co-solvent for the MMA monomer and KOH water solution for the in situ polymerization methodology. The polymer electrolytes with PMMA/PEMPS/25% KOH = 5/5/2 exhibited an ion conductivity of 2.0 ×10⁻⁴ S/cm at room temperature.

6.3.1 Miscibility of reaction mixtures

MMA is not miscible with KOH water solution, thus it leads to phase separation of the reaction mixture. This can be explained by solubility parameter, which is a measure of the attractive strength between molecules of the materials, and is widely used to predict miscibility. Generally, a small difference of solubility parameters between the components will lead to good miscibility. According to the literature, the solubility parameter of MMA is 9.5, while 23.4 for water. So there is a large difference between these two materials.¹⁹⁴ Therefore, a co-solvent may be needed to form a miscible solution. PEMPS was found to be soluble with MMA from previous study in section 4.2. In addition, it can also dissolve the aqueous KOH very well. Different mixtures made by
the reaction components are shown in Figure 6.13. Vial a and b are mixtures of PEMPS with 25% KOH water solution and with MMA, respectively. Both mixtures leaded to transparent solutions. Vial c has the mixture of solutions from vial a and vial b without any stirring. It is clear to see the layer separation between two phases involving KOH water solution and MMA. After stirring at room temperature, the mixture became a uniform and transparent solution. Finally, it turned colorless with the addition of initiator and crosslinking agent, as shown in vial d. Thus, addition of PEMPS yields single phase transparent pregel solution.

![Figure 6.13 Picture of component mixtures in reaction solutions. a. KOH solution + PEMPS, b. MMA+PEMPS, c. MMA+PEMPS+KOH solution, d.MMA+PEMPS+KOH+BPO+TEGDA](image)

6.3.2 Phase separation phenomena of reaction mixtures and gel products

Figure 6.14 shows the polymerized product after being cut into disks. The products with a composition of PMMA/PEMPS/25% KOH = 5/5/2 were opaque, flexible and self-standing.
When the polymerization reaction mixture was prepared in ice water bath, a phase separation was produced as shown in Figure 6.1. The upper phase in the test tube appeared clear solution of a single phase, while the lower phase was opaque. Following polymerization of the multiphase material, the products were found to consist two phases: the solid PMMA and the liquid electrolytes. This observation indicates that there is a competition of the rate between the phase separation and the polymerization. Since the ice bath prevents pre-polymerization before heating to desired polymerization temperature, the polymerization rate of MMA will be slower than that prepared in room temperature. It is well known in the chapter 2.1 (equation 2.2) that the rate of polymerization increases with temperature (above the initiation temperature). In this case, the phase separation appears faster than the crosslinking polymerization of PMMA, allowing the aqueous KOH enough time to flow out from the MMA domain prior to network formation.
Figure 6.2 Phase separation of reaction solution after stirred in ice bath.

A chemical analysis of gel products and their liquid phase mixture formed in room temperature and ice bath were conducted by FTIR. The characteristic peaks of PMMA and PEMPS were described previously in section 5.2. For PEMPS, the peaks appear at 1021 cm\(^{-1}\), 1099 cm\(^{-1}\) and 2864 cm\(^{-1}\) are assigned to Si-O-Si group, C-O-C stretching and C-H stretching, respectively. For PMMA, the characteristic peaks at wavenumber 1726 cm\(^{-1}\) and 2954 cm\(^{-1}\) are due to C=O asymmetric stretching from the carbonyl group and the C-H stretching. The bands at 1420 cm\(^{-1}\) and 1350 cm\(^{-1}\) are due to the CH\(_2\) group. The band near 1357 cm\(^{-1}\) is due to the O-CH\(_3\) asymmetric bending. After room temperature polymerization, the peaks for Si-O-Si and C-O-C for PEMPS at 1021 cm\(^{-1}\) and 1099 cm\(^{-1}\), C=O for PMMA at 1726 cm\(^{-1}\), as well as the broad band of O-H stretching for KOH at at 3200-3400 cm\(^{-1}\) are observed as shown in Figure 6.16. The double shoulders at 2864 cm\(^{-1}\) and 2954 cm\(^{-1}\) are due to the C-H stretching of PEMPS and PMMA, respectively. This result revealed that KOH-PEMPS electrolytes were contained in PMMA polymer matrix. It is also noticed that the peak of Si-O-Si became smaller and
the peak of –C-O- moved to a lower wave number compared with those of the bulk PEMPS. The C=O peak of PMMA did not show any change. It indicates that the KOH water solution has more interaction with PEMPS, namely, most of the KOH solution was dissolved in PEMPS. This can also be found for the liquid phase. For the products prepared in ice bath, the peaks of C=O and –CH for PMMA became broader, but the peaks of Si-O-Si and C-O-C for PEMPS became sharper. Besides, the peak of –OH group is very strong. These results indicate that the liquid phase consists of siloxane, KOH, and very small amount of MMA. On the other hand, the solid phase consists mostly of PMMA, some siloxane, and very small amount of KOH. Therefore, the liquid phase of KOH water solution with PEMPS separated from the MMA and PEMPS phase during the polymerization, which resulted in the solid phase of PMMA while liquid phase of KOH water solution after polymerization.
6.3.3 Morphology study of phase separation in the reaction mixtures

Cross-polarized microscope was used to better understand the phase separation phenomena during polymerization by morphology studies of the phase changes in reaction mixture.

First, the KOH solid and its aqueous solution were observed under microscope to study the structure of KOH crystal. Figure 6.17 shows the morphology of neat KOH solid powder under polarized light, and its crystals are in the shapes of irregular polygons. Figure 6.18 show the pictures of 25% KOH water solution heating at different temperatures. In picture (a), the KOH crystals in the initial solution were in the shape of needle with a thickness 0.06 mm. Upon heating for 4 s at 70 °C (picture (b)), more KOH
crystals were formed, and some crystals appeared deformed. After the temperature was increased to 90 °C, the KOH crystals became thicker and accumulated denser in the center (c), while the edge part shows the densest crystallization because of the fast evaporation of water in this area. Thus, the water evaporation speeds up with temperature rise, resulting in deformation and a dense accumulation of needle like KOH crystals.

Figure 6.17 Microscope picture of solid KOH particles under cross polar light.
Figure 6.18 Microscope pictures of 25% KOH solution at different heating temperature. (a) 0 second at 70 °C, (b) 4 s at 70 °C, (c) the center part at 90 °C, (d) the edge at 90 °C

Figure 6.19 shows the optical micrograph of PMEPS-KOH electrolyte solution with the composition of PEMPS/25% KOH water solution = 3/1. The mixture is a uniform and transparent solution without any phase separation, so PEMPS seems to be a good solvent at this composition for KOH water solution. To study the phase separation phenomena as a function of temperature, a small drop of this mixture of PEMPS and KOH was cast on a glass slide and then heated from room temperature to 70 °C. As shown in Figure 6.20, when heated from (a) to (d), the observation of the mixture were
conducted under both non polarized light and cross-polarized light microscopy. The phase separation occurred from a small scale as seen at 30 °C, the droplets with diameter size less than 0.03 mm were formed, which were considered to be the water separated from PEMPS phase. As water evaporated in air, it moved to the surface of the mixture solution since it has a lower density than PEMPS. As the temperature increased to 40 °C, some of the droplets start to coalesce to form larger droplets with a diameter of about 0.07 mm. The aqueous droplets continued to grow as the temperature increased to 50 °C. Many droplets were observed in the size of 0.14 mm. Some of the droplets became dark was due to the nucleation and growth of KOH crystals induced by the loss of water. The crystallization was confirmed by the bright circles in the photograph under polarized light. Continued increase of temperature to 60 °C caused more water droplets turn dark. KOH crystallization continued with the increased temperature to 70 °C. The larger crystals grow by coalescing with their neighbor droplets and the rest still stay in the small
size around 0.01 mm or less. Phase separation occurred by this movement of water droplets and formation of KOH crystals due to the evaporation of water at higher temperature. Ultimately, the KOH separated from the mixture. In conclusion, the KOH can only be dissolved in the presence of water, and as the water evaporates, KOH forms crystals.
Figure 6.20 Microscope pictures of mixture of PEMPS: 25% KOH = 3:1 heated from 30 °C to 70 °C. Pictures in left column were taken under non polarized light and pictures in right column were taken under cross-polarized light except 30 °C and 40 °C.
With this consideration, if the polymerization of MMA is carried out quickly, the crosslinked network may form prior to phase separation. The polymer electrolytes prepared at room temperature as shown in Figure 6.14 might be due to these effects since no obvious phase separation was observed during polymerization. However, the microscale phase separation may exist for the gel products after polymerization due their opaque appearance. This hypothesis was tested by observing the phase separation phenomenon of reaction mixture during polymerization under microscope. The mixture with weight ratio MMA: PEMPS: 25% KOH = 5:5:2 was cast on a glass slide and heated at 70 °C. Figure 6.21 shows the morphology of the reaction mixture changes as time increases from a to d. Since the mixture was open to air, water evaporated with time. This could result in phase separation of KOH from PEMPS as observed in Figure 6.20. However, the phase separation of electrolyte solution made by PEMPS and KOH water solution was redistributed due to MMA polymerization and crosslinking, which finally encaged the electrolyte solution in the meshes of PMMA network. Thus, the fast gelation due to MMA crosslinking can efficiently prevent the phase separation of KOH water solution from PEMPS and polymer phase.
Figure 6.21 Microscope Pictures of reaction mixture of PMMA and KOH heated at 70°C. PMMA /PEMPS/ 25% KOH = 5/5/2. Pictures were taken every 2 minutes and put in order from (a) to (d).

The polymerized film of PMMA/PEMPS/ 25% KOH = 5/5/2 was observed under polarized light to see the formation of KOH crystals on the glass slide. As shown in Figure 6.22, KOH crystals are distributed in the film. The crystals in left edge were smaller and denser than that in the right part which was in the center part of the film. The dark domains represented the amorphous polymer matrix of PMMA.
6.3.4 Morphology study of phase separation in the PMMA-KOH polymer gels

The PMMA-KOH polymer electrolytes prepared in sealed test tubes were analyzed by microscope under polarized light. Figure 6.23 shows the morphology varied in different parts. Dark lines are observed in picture (a) and they are connected to each other and formed a network structure. Some crystals are observed imbedded under the surface of polymer. Picture (b) shows flower-shape crystals densely appeared on the surface, which is similar to the KOH crystals at high temperature in (d) of Figure 6.18. This pattern was due to the loss of water on the surface of the polymer electrolytes.
Figure 6.23 Microscope picture of PMMA-KOH polymer electrolytes under polarized light.

PEMPS-KOH electrolytes were removed by water soaking to see the PMMA morphology. In Figure 6.24, it was clear to see the crosslinked network of PMMA on the cross sections that were cut along the length of test tubes and along the diameter of test
tubes. The mesh size of the network is around 0.30 μm. In addition, the picture also shows dark boundaries distributed inside the material and connected with each other. The distance between these dark boundaries was comparable to the network mesh size formed by the dark lines in previous photograph Figure 6.23 (a), which were considered to be the water channel. These water channels could be formed during the polymerization induced phase separation and became dark boundaries after water evaporated.
Figure 6.24 Microscope picture of polymer electrolyte with PMMA/PEMPS/KOH = 5/5/3 after immersed in water. (a) Cross section parallel to the length of the test tube, (b) cross section perpendicular to the length of the test tube.

The polymer electrolytes were characterized by SEM to analyze the morphology of the surface that is open to air and inside. Figure 6.25 and Figure 6.26 show the surface of the polymer film that was open to air. In this case, the evaporation of water was fast. As a result, the KOH crystals were observed in these two SEM pictures. Figure 6.26 shows the flower like crystals formed in larger scale, which has a diameter size of 5 μm.
Along with the crystals, some white lines in the shape of webs were also seen from the photograph, which could be the dark lines found in previous optical microscope pictures (Figure 6.23(a) and Figure 6.24 (a)).

Figure 6.25 SEM picture of the surface of PMMA-KOH polymer electrolyte that contacts with air
The surface formed from contact with the glass during polymerization was also observed by SEM. As shown in Figure 6.27, the morphology is different from that in Figure 6.25. There was no obvious domain of crystals on the surface. Instead, some dark holes less than 10 μm were observed, which might be due to the air bubbles generated during polymerization heating. The root-like structure might be due to the stretch during peeling of the sample from a mold. Figure 6.28 shows the side view of the polymer electrolyte sample. Layered web structure was observed, which was considered to be associated with the crosslinked PMMA network.
Figure 6.27 SEM pictures of PMMA-KOH polymer electrolyte for the surface contact with glass

Figure 6.28 SEM picture of side view of PMMA-KOH polymer electrolyte
6.4 Conclusions

The conductivity of polymer electrolytes based on PAA-KOH and PVA-KOH showed very high room temperature ion conductivities of $3.19 \times 10^{-2}$ and $3.96 \times 10^{-2}$ S/cm, respectively. From the morphology study, the higher molecular weight PVA (85,000~146,000 g/mol) lead to formation of a uniform film with high conductivity, while the PVA with a lower $M_w$ resulted in cracked films. The formation of PVA network is due to physical crosslinking due to crystallization and chain entanglements. The PAA-KOH based polymer electrolyte was also successfully prepared by UV curing within 10 seconds, which allows its continuous rapid manufacturability. The high conductivity is due to the mobile $K^+$, $H^+$ and $OH^-$ ions.

However, the acid group of PAA can consume $OH^-$ of the KOH salt by neutralization, which is an essential element in the electrochemical reaction of the Ni-Zn battery. Therefore, the high conductivity does not indicate a high concentration of the hydroxide.

For PMMA-KOH based polymer electrolytes, PEMPS showed as a good co-solvent for MMA monomer and KOH water solution in the mixture for in situ polymerization. But phase separation still easy to take place during polymerization due to the polymerization of MMA and water evaporation. The polymerization of MMA induced a solid and liquid phase separation, while the water evaporation resulted in KOH salt crystal formation. The latter effect resulted in a low conductivity of $2 \times 10^{-4}$ S/cm at room temperature. The phase separation of KOH from the PEMPS solvent and/or polymer matrix in the state of solid crystals was observed by the microscope and SEM characterization. The crosslinked PMMA network structure was also observed. These
analyses suggest that the dark lines in the polymers could be water channels formed during the polymerization induced phase separation.
CHAPTER VII

SUMMARY AND FUTURE STUDY

Three types of polymer gel electrolytes were developed and characterized for specific applications in electrochemical devices. The in situ polymerization of monomer in electrolyte leaded to good miscibility among the components in the system before and after polymerization. The polymer-in-salt system was obtained so as the majority part (50% - 90% by weight) of the polymer electrolyte was occupied by electrolyte. In consequence, the high ion concentration contributed to the high ion conductivity. The polymer gel electrolytes, at the same time, provide mechanical integrity that enables the material to have flexible and elastic properties. The solid state polymer gel electrolytes are promising as replacements for the conventional liquid state electrolytes. They overcome severe shortcomings inherent with the aqueous or small organic solvents, such as leakage, evaporation, hazard, and pollution.

The PMMA/BMIPF$_6$ ion gels were clear, flexible and exhibited high thermal stability above 130 °C. Their high ion conductivity is comparable to liquid state electrolyte around $10^{-3}$S/cm at room temperature. The system is solvent free and stable to operate in air. The movement of mobile ions in PMMA/ BMIPF$_6$ ion gels was further used to develop a three layer PEDOT/PSS coated ion gel actuator. The deformation strain is comparable to PAA based aqueous polyelectrolyte gels and is driven by the
incorporation and withdraw movement of cations from the polymer accompany negative and positive potentials, respectively.

The lithium polymer gels based on PMMA-PEMPS with LiTFSI were also clear, flexible and self-standing and show good compatibility between the components. The ion conductivity in order of $10^{-4}$ S/cm was achieved at 70 °C. The ion conductivity exhibits a maximum at 26 as [O/Li] increased from 8 to 32, which is consistent to the trend of swelling ratio of the gel as [O/Li] varies, and corresponds to the extent of the dissoluble and dissociated Li salt in the gels.

For the polymer electrolytes for Ni-Zn batteries, the PVA/KOH and PAA/KOH polyelectrolyte gels showed high ambient ion conductivity around $10^{-2}$ S/cm. The PVA/KOH gel films were opaque due to the crystallization of PVA during drying. The PAA/KOH films were transparent and were also formed through UV curing. PEMPS was observed to be a good co-solvent of MMA and KOH aqueous solution in the reaction mixture. However, phase separation still easy to take place during gelation. The PMMA/PEMPS/KOH based gel electrolytes showed much lower ion conductivity comparing with the former two electrolytes, which is due to the high viscosity of PEMPS and low concentration of mobile ions in the system.

Based on the observations and results of this research, the following recommendations are suggested for the future study of the polymer electrolytes:

1. Mechanical strength of the material can be measured by tensile test. Since the gel sample is soft and easy to break in the contacting area of grips under pressure, a special design of sample is needed to prevent the crack in the contacting area during the tensile test. In this case a frame made of
paper board may be useful to fix the gel specimen and help to extend soft gel sample completely and prevent the crack during test.

2. The microstructure such as the micro-scale phase separation of the electrolyte from polymer matrix can be investigated by dynamic mechanical analysis (DMA). The presence of single peak for the temperature dependence of loss tangent (tanδ) will real a compatible system. The value of tanδ is defined by the ratio of the loss modulus over the storage modulus.

3. The durability of gel actuator can be studied by cycling test as a function of voltage and temperature.

4. The efficiency of the lithium polymer electrolyte on improving the life time of the cell can be characterized by cycling test of repeating charge and discharge operation.

5. The electrochemical stability can be analyzed by cyclic voltammetric measurement. By this way, the potential limit leading to irreversible oxidation will be captured.
REFERENCES


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