DEVELOPMENT OF SOLID POLYMER ELECTROLYTES OF POLYURETHANE AND POLYETHER-MODIFIED POLYSILOXANE BLENDS WITH LITHIUM SALTS

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ABSTRACT

Novel flexible solid polymer electrolytes with both high ionic conductivity and good dimensional stability based on thermoplastic polyurethane (TPU)/polyether-modified polysiloxane (PEMPS) electrolytes with various lithium salts were developed. The salts used include lithium chloride (LiCl), lithium perchlorate (LiClO₄), lithium bis(trifluoromethanesulfonyl)imide (LiN(SO₂CF₃)₂ [LITFSI]). These polymer electrolytes were prepared by a solvent-free, in-situ process, instead of the conventional solution casting method. In this process, the monomer, polytetramethylene glycol (PTMG), was the solvent for dissolving lithium salts instead of a highly volatile one. This process included two steps: (a) dissolve lithium salts in PTMG and PEMPS; and (b) add 4,4’-diphenylmethane diisocyanate (MDI), 1,4 butane diol (BDO) to start polymerization of polyurethane.

The dissolution of salts in PTMG and PEMPS, the interaction of salt with PTMG and PEMPS, and the miscibility of PTMG/PEMPS were characterized using differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and optical microscopy. The structure of the anion greatly affected the solubility of salts in PTMG and PEMPS. Salts with large anions, such as ClO₄⁻ and TFSI⁻, exhibited better solubility than ones with small anions, such as Cl⁻. Salts enhanced the compatibility between PEMPS and PTMG. Kinetics studies of polyurethane polymerization using the isothermal
calorimetry indicated that the lithium salt slightly retarded the polymerization of TPU due to interaction of lithium ions with hydroxyl groups. Thermogravimetric analysis (TGA) characterization and tensile testing of TPU/PEMPS electrolytes demonstrated good thermal and dimensional stability. Morphological studies of TPU and TPU/PEMPS electrolytes were conducted using optical microscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM). TPU/PEMPS electrolytes exhibit a multiphase morphology with PEMPS dispersed in the TPU matrix. Salt improved compatibility between phases. FTIR studies indicated that lithium salts interacted strongly with the soft and hard segments of TPU as well as the PEMPS. Salt compatibilized these phases. The effects of PEMPS and lithium salts on T_m and the degree of crystallinity of TPU also were investigated by DSC. Ionic conductivity and its temperature dependence of these electrolytes were determined using an LCR meter.

A mechanism of ionic conductivity of TPU/PEMPS electrolytes was proposed. Effects of the structure of the anion, salt–polymer interaction, and multiphase morphology on the ionic conductivity were considered.
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TABLE OF CONTENTS

LIST OF TABLES ................................................................................................................................................. x

LIST OF FIGURES ................................................................................................................................................... xii

I. INTRODUCTION .................................................................................................................................................. 1

II. LITERATURE SURVEY ....................................................................................................................................... 7

2.1 Solid Polymer Electrolytes .......................................................................................................................... 7

2.1.1 Application of Solid Polymer Electrolytes ............................................................................................. 7

2.1.2 Polymer Structures in Polymer Electrolytes ........................................................................................... 9

2.1.3 Salt Solvation in Polymer Electrolytes .................................................................................................... 13

2.1.4 Effects of Preparation Methods of Polymer Electrolytes on Their Ionic Conductivity ....................... 16

2.1.5 Ionic Conduction Mechanism in Polymer Electrolytes ........................................................................ 22

2.2 Polyurethane Electrolytes .......................................................................................................................... 30

2.2.1 Basic Structure of Thermoplastic Polyurethane .................................................................................... 31

2.2.2 Kinetic of Polyurethane Polymerization ............................................................................................... 35

2.2.3 Polyurethane Electrolytes ....................................................................................................................... 37

2.3 Modified polysiloxane Electrolytes .............................................................................................................. 43

2.3.1 Modified Polysiloxane Electrolytes with Comb Structure .................................................................. 43

2.3.2 Modified Polysiloxane Electrolytes with Block Copolymer Structure .......... 46

2.3.3 Modified Polysiloxane Electrolytes with Cross-linked Structure ......................................................... 47

2.4 Polyurethane Blend and Their Electrolytes ................................................................................................ 50
2.4.1 Miscibility of Blends of Polymers with Specific Interaction .......................... 50
2.4.2 Miscibility and Morphology of Polyurethane Blends ............................... 56
2.4.3 Polyurethane Blend-Based Polymer Electrolytes and Their Ionic Conductivity ........................................................................................................ 64

2.5 The Method of Ionic Conductivity Measurement ............................................ 67

III. EXPERIMENTAL ................................................................................................. 73

3.1 Materials ............................................................................................................. 73
3.2 Preparation Procedures of Polymer Electrolyte Films .................................... 75
3.3 The Kinetics of Polymerization ........................................................................ 78

3.4 Characterization Techniques ............................................................................. 80

3.4.1 Morphological Studies ................................................................................. 80
3.4.2 Thermal Analysis ......................................................................................... 83
3.4.3 Fourier Transform Infrared Spectroscopy ...................................................... 86
3.4.4 Gel Permeation Chromatography .................................................................. 87
3.4.5 Instron Tensile Testing ................................................................................ 88
3.4.6 Ionic Conductivity Measurement .................................................................. 88

IV. RESULTS AND DISCUSSION ............................................................................. 90

4.1 Morphological Studies of PTMG and PEMPS Lithium Salt Mixtures for Solvation Studies ........................................................................................................ 91

4.1.1 PTMG/salts Mixture ..................................................................................... 92
4.1.2 PEMPS/salt Mixture ................................................................................... 104
4.1.3 PTMG/PEMPS Blends with Lithium Salts .................................................... 108

4.2 Fourier Transform Infrared Spectroscopy (FTIR) ............................................ 113
4.2.1 PTMG/salt Mixture ........................................................................................................ 113
4.2.2 PEMPS/salt Mixture ..................................................................................................... 140
4.3 Thermal Analysis By Differential Scanning Calorimetry (DSC) .................................. 153
  4.3.1 PTMG/salt Mixture .................................................................................................. 153
  4.3.2 PEMPS/salt Mixture ............................................................................................... 164

V. POLYURETHANE/POLYETHER-MODIFIED POLYSILOXANE

  ELECTROLYTES .............................................................................................................. 169

  5.1 Polymerization Kinetics of TPU .................................................................................. 169

  5.2 Morphological Studies of TPU/PEMPS Electrolytes .............................................. 186
    5.2.1 Appearance of Electrolyte Films ............................................................................ 186
    5.2.2 Optical Microscopy .............................................................................................. 190
    5.2.3 SEM ..................................................................................................................... 197
    5.2.3 AFM .................................................................................................................. 218

  5.3 Thermal Analysis of Electrolyte Films ..................................................................... 227
    5.3.1 TGA .................................................................................................................... 227
    5.3.2 DSC .................................................................................................................... 234

  5.4 FTIR of Electrolyte Films ......................................................................................... 252

  5.5 The Tensile Properties of Electrolyte Films ............................................................. 270

  5.6 Ionic Conductivity of Electrolyte Films ................................................................... 279

  5.7 Ionic Conduction Mechanisms of TPU Electrolyte and TPU/PEMPS
    Electrolytes .................................................................................................................. 319

VI. CONCLUSIONS ............................................................................................................. 337

  6.1 Conclusion of Studies on TPU/PEMPS Electrolytes .................................................. 337

  viii
6.2 Recommendations ................................................................................................ 342

REFERENCES ............................................................................................................... 344
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Basic network structure and composition of network host polymer</td>
<td>12</td>
</tr>
<tr>
<td>2.2</td>
<td>WLF parameters for Cross-linked PPO/Na B(C₆H₅)₄ electrolytes</td>
<td>28</td>
</tr>
<tr>
<td>3.1</td>
<td>Materials used in polyurethane/modified polysiloxane blend electrolytes</td>
<td>74</td>
</tr>
<tr>
<td>4.1</td>
<td>The characteristic absorption band of different polymers and salts in FTIR</td>
<td>114</td>
</tr>
<tr>
<td>4.2</td>
<td>The assignments of absorption peaks of FTIR spectra of polyethylene oxide</td>
<td>118</td>
</tr>
<tr>
<td>4.3</td>
<td>The list of glass transition (T&lt;sub&gt;g&lt;/sub&gt;), melting temperature (T&lt;sub&gt;m&lt;/sub&gt;), heat of fusion (ΔH) and total heat of fusion of different lithium salts determined by DSC</td>
<td>156</td>
</tr>
<tr>
<td>4.4</td>
<td>The list of glass transition (T&lt;sub&gt;g&lt;/sub&gt;), melting temperature (T&lt;sub&gt;m&lt;/sub&gt;), heat of fusion (ΔH) and total heat of fusion of PTMG with different salt concentrations determined by DSC</td>
<td>162</td>
</tr>
<tr>
<td>4.5</td>
<td>The list of glass transition (T&lt;sub&gt;g&lt;/sub&gt;), melting temperature (T&lt;sub&gt;m&lt;/sub&gt;), heat of fusion (ΔH) and total heat of fusion of PEMPS with different salt concentration of salts determined by DSC</td>
<td>168</td>
</tr>
<tr>
<td>5.1</td>
<td>The molecular weight of TPU/LiN(SO₂CF₃)₂ electrolytes and TPU/PEMPS/LiN(SO₂CF₃)₂ electrolytes obtained from GPC</td>
<td>185</td>
</tr>
<tr>
<td>5.2</td>
<td>TGA results of TPU, TPU/PEMPS blend and TPU/PEMPS electrolytes with different lithium salts at [O:Li]=16:1</td>
<td>229</td>
</tr>
<tr>
<td>5.3</td>
<td>The list of glass transition (T&lt;sub&gt;g&lt;/sub&gt;), melting temperature (T&lt;sub&gt;m&lt;/sub&gt;), heat of fusion (ΔH) and total heat of fusion of TPU/PEMPS blends with different blend compositions determined by DSC</td>
<td>238</td>
</tr>
<tr>
<td>5.4</td>
<td>The list of glass transition (T&lt;sub&gt;g&lt;/sub&gt;), melting temperature (T&lt;sub&gt;m&lt;/sub&gt;), heat of fusion (ΔH) and total heat of fusion in TPU electrolytes with different salt concentrations determined by DSC</td>
<td>244</td>
</tr>
</tbody>
</table>
5.5 The list of glass transition \((T_g)\), melting temperature \((T_m)\), heat of fusion \((\Delta H)\), and total heat of fusion in TPU/PEMPS electrolytes with different blend compositions at \([O:Li]=16:1\) determined by DSC .............................................. 248

5.6 Engineering tensile properties of neat TPU and TPU electrolytes with various salt concentrations ........................................................................................................ 273

5.7 Engineering tensile properties of TPU/PEMPS blend and TPU/PEMPS electrolytes with various blend compositions ..................................................................................... 278

5.8 Impedance data of some TPU electrolyte and TPU/PEMPS electrolyte .............. 302

5.9 The ionic conductivity at room temperature \(\sigma\) and activation energies \(E_a\) of TPU electrolytes with different types of salt prepared by in-situ process ............... 304

5.10 The ionic conductivity at room temperature \(\sigma\) and activation energies \(E_a\) of TPU/PEMPS electrolytes with different types of salt and various blend compositions at \([O:Li]=16:1\) prepared by the in-situ process ................................................ 304

5.11 The ionic conductivity at room temperature \(\sigma\) and activation energies \(E_a\) of TPU electrolytes with different types of salt prepared by the solution casting.. 318

5.12 The ionic conductivity at room temperature \(\sigma\) and activation energies \(E_a\) of TPU/PEMPS electrolytes with different types of salt and various blend compositions at \([O:Li]=16:1\) prepared by the solution casting ......................... 318
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Schematic diagram of basic construction of a film-like polymer electrolyte-based batteries</td>
<td>8</td>
</tr>
<tr>
<td>2.2</td>
<td>Structures of some comb branched polymers and block polymers used as host polymers</td>
<td>11</td>
</tr>
<tr>
<td>2.3</td>
<td>Phase diagram of the PEO/LiClO₄ electrolyte. The vertical boundaries represent the formation of 6:1, 3:1, 2:1, 1:1 crystalline complexes. The liquid phase is amorphous phase.</td>
<td>17</td>
</tr>
<tr>
<td>2.4</td>
<td>Phase diagram of the PEO/ZnCl₂ electrolyte. The transition temperatures were obtained using a thermo-optical analysis technique. The solid lines are calculated from the proposed model. The dotted lines are calculated from the model based on an extended Flory–Huggins equation only.</td>
<td>18</td>
</tr>
<tr>
<td>2.5</td>
<td>A helix model of the crystalline PEO/salt complex</td>
<td>24</td>
</tr>
<tr>
<td>2.6</td>
<td>Representation of cation motions in a polymer electrolyte (a) assisted by polymer chain motion only; and (b) taking account of ionic cluster contributions</td>
<td>25</td>
</tr>
<tr>
<td>2.7</td>
<td>Arrennius-Veni-type plots for logσ vs T⁻¹, for PEO/LiI and PEO/LiSCN complexes. The behavior for the larger SCN⁻ is VTF type and for the smaller I⁻ is double Arrennius-Veni type.</td>
<td>28</td>
</tr>
<tr>
<td>2.8</td>
<td>The basic units in a urethane block copolymer</td>
<td>32</td>
</tr>
<tr>
<td>2.9</td>
<td>Preparation routes for thermalplastic polyurethane (a) the prepolymer reaction route and (b) one shot sequence</td>
<td>33</td>
</tr>
<tr>
<td>2.10</td>
<td>The reaction scheme of polyurethane network</td>
<td>39</td>
</tr>
<tr>
<td>2.11</td>
<td>Schematics of the synthesis of HPa and HPb</td>
<td>39</td>
</tr>
<tr>
<td>2.12</td>
<td>Structures of two mono-comb poly(siloxane-g-ethylene oxide)</td>
<td>45</td>
</tr>
<tr>
<td>2.13</td>
<td>Schematics of the synthesis of polyether-modified polysiloxane</td>
<td>45</td>
</tr>
</tbody>
</table>
2.14 Schematics of the synthesis of double-comb polysiloxanes

2.15 Structure of acrylate end-caped polysiloxane-g-oligo(ethylene ox) cross-linker

2.16 Schematics of the synthesis of borosiloxane polymer

2.17 Schematic structures for hydrogen bond interactions between (a) PMVE-

2.18 FTIR of PEO/PMVE-Mac (60/40 wt%) blends with different concentrations

2.19 The schematic representation of formation of complex of PEO/Li+/PMVE-

2.20 (a) Schematic representation of a polymer electrolyte/blocking electrode cell,

2.21 (a) Equivalent circuit and (b) complex plane plot for Type I polymer

2.22 (a) Equivalent circuit and (b) complex plane plot for Type I polymer

2.23 The typical complex impedance plot for an amorphous and homogeneous

2.24 The complex impedance plot of Poly(butylenes adipate)-based polyurethane

3.1 Schematics of the preparation routs of the in-situ process (Lithium salts used

4.1 Cross-polarized optical micrographs of solid salts from dilute solution (a) LiCl,

4.2 Cross-polarized optical micrographs of ground salts particles (a) LiCl, (b)

xiii
4.3 Cross-polarized optical micrographs of PTMG/LiCl mixture with various LiCl concentrations; (a) Neat PTMG crystal, (b) [O:Li]=32:1 (c) [O:Li]=16:1 (d) [O:Li]=8:1 .......................................................... 95

4.4 Cross-polarized optical micrographs of PTMG/LiClO₄ complex with various salt concentrations; (a) Neat PTMG crystal, (b) [O:Li]=32:1, (c) [O:Li]=16:1, (d) [O:Li]=8:1 ............................................................................ 97

4.5 Cross-polarized optical micrographs of PTMG/Li(N(SO₂CF₃)₂ complex with various salt concentrations; (a) Neat PTMG crystal, (b) [O:Li]=32:1, (c) [O:Li]=16:1, (d) [O:Li]=8:1 ............................................................................. 98

4.6 Optical micrographs of PTMG melt with different LiCl concentrations at 60°C; (a) [O:Li]=32:1 ; (b) [O:Li]=16:1 (C) [O:Li]=8:1...................................................... 100

4.7 Optical micrographs of PTMG melt with different LiClO₄ concentrations at 60°C; (a) [O:Li]=32:1 , (b) [O:Li]=16:1, (C) [O:Li]=8:1......................................................... 101

4.8 Optical micrographs of PTMG melt with different Li(N(SO₂CF₃)₂ concentrations at 60°C; (a) [O:Li]=32:1 , (b) [O:Li]=16:1, (C) [O:Li]=8:1............. 102

4.9 Optical micrographs of PTMG melt at 60°C with different LiCl concentrations prepared by the solution casting with methanol as solvent; (a) [O:Li]=32:1, (b) [O:Li]=16:1, (C) [O:Li]=8:1 ............................................................................. 104

4.10 Optical Micrographs of PEMPS with different LiCl concentrations from melt mixing at 60°C; (a) [O:Li]=32:1 (b) [O:Li]=16:1 (C) [O:Li]=8:1 ............................................... 106

4.11 Optical Micrographs of PEMPS with different LiCl concentration from the solution casting; (a) [O:Li]=32:1 (b) [O:Li]=16:1 (C) [O:Li]=8:1 ......................... 107

4.12 Optical micrographs of PEMPS with different LiClO₄ concentrations from the solution casting; (a) [O:Li]=32:1 , (b) [O:Li]=16:1, (C) [O:Li]=8:1 ..................... 109

4.13 Optical micrographs of PEMPS with different Li(N(SO₂CF₃)₂ concentrations from the solution casting; (a) [O:Li]=32:1, (b) [O:Li]=16:1, (c) [O:Li]=8:1.............. 110

4.14 Optical Micrographs of PTMG and PEMPS blend (the ratio is calculated according to the formula of TPU/PEMPS=100/40); (a) at solid state and (b) at molten state (c) PTMG and PEMPS blend with LiClO₄ at [O:Li]=16:1......... 112

4.15 FTIR spectra of three different salts :LiCl, LiClO₄ and Li(N(SO₂CF₃)₂ ................. 117

4.16 FTIR spectra of PTMG/LiCl mixtures with various LiCl concentrations prepared by melt mixing .............................................................. 117
4.17 The deconvolution FTIR spectra of PTMG/LiCl mixtures with different LiCl concentrations in the range of 1000 cm\(^{-1}\) -1200 cm\(^{-1}\) (a) neat PTMG, (b) [O:Li]=32:1, (c) [O:Li]=16:1, (b) [O:Li]=8:1. The dotted line represents the original peak and the solid line represents the fit peaks...

4.18 The deconvolution FTIR spectra of PTMG/LiCl mixtures with different LiCl concentrations in the range of 1320 to 1400 cm\(^{-1}\) (a) neat PTMG, (b) [O:Li]=32:1, (c) [O:Li]=16:1, (b) [O:Li]=8:1. The dotted line represents the original peak and the solid line represents the fit peaks...

4.19 The deconvolution FTIR spectra of PTMG/LiCl mixtures with different LiCl concentrations in the range of 3100 to 3700 cm\(^{-1}\) (a) neat PTMG, (b) [O:Li]=32:1, (c) [O:Li]=16:1, (b) [O:Li]=8:1. The dotted line represents the original peak and the solid line represents the fit peaks...

4.20 The relative intensity of some peaks versus different LiCl concentration in PTMG/LiCl mixture prepared by melt mixing...

4.21 The relative intensity of some peaks versus different LiCl concentrations in PTMG/LiCl mixture prepared by the solution casting...

4.22 FTIR spectra of PTMG/LiClO\(_4\) melt mixture with various LiClO\(_4\) concentrations prepared by melt mixing...

4.23 The deconvolution FTIR spectra of PTMG with different LiClO\(_4\) concentration of ranging from 610 to 650 cm\(^{-1}\) (a) [O:Li]=32:1, (c) [O:Li]=16:1, (b) [O:Li]=8:1. The dotted line represents the original peak and the solid line represents the fit peaks...

4.24 The deconvolution FTIR spectra of PTMG with different LiClO\(_4\) concentration ranging from 1000 to 2000 cm\(^{-1}\) (a) neat PTMG,(b) [O:Li]=32:1, (c) [O:Li]=16:1, (b) [O:Li]=8:1...

4.25 The deconvolution FTIR spectra of PTMG with different LiClO\(_4\) concentrations ranging from 1300 to 1400 cm\(^{-1}\) (a) neat PTMG,(b) [O:Li]=32:1, (c) [O:Li]=16:1, (b) [O:Li]=8:1...

4.26 The deconvolution FTIR spectra of PTMG with different LiClO\(_4\) concentrations ranging from 3100 to 3500 cm\(^{-1}\) (a) neat PTMG,(b) [O:Li]=32:1, (c) [O:Li]=16:1, (b) [O:Li]=8:1...

4.27 The relative intensity of some peaks versus different LiClO\(_4\) concentrations in PTMG/LiClO\(_4\) mixture prepared by melt mixing...

4.28 The intensity ratio of absorption at 627 cm\(^{-1}\) to 637 cm\(^{-1}\) in FTIR of PTMG/LiClO\(_4\) mixture with different LiClO\(_4\) concentrations...
4.29 FTIR spectra of PTMG with various LiClO₄ concentrations prepared by the solution casting................................................................. 131

4.30 The relative intensity of some peaks versus different LiClO₄ concentrations in PTMG/LiClO₄ mixture prepared by the solution casting ....................... 132

4.31 FTIR spectra of PTMG with various LiN(SO₂CF₃)₂ concentrations prepared by melt mixing................................................................. 134

4.32 FTIR spectra of PTMG with various LiN(SO₂CF₃)₂ concentrations in the region of (a) 500 cm⁻¹ to 900 cm⁻¹ (b) 1000 cm⁻¹ to 1400 cm⁻¹ ....................... 135

4.33 The deconvolution FTIR spectra of PTMG with different LiN(SO₂CF₃)₂ concentrations ranging from 3100 to 3500 cm⁻¹ (a) neat PTMG , (b) [O:Li]=32:1, (c) [O:Li]=16:1, (b) [O:Li]=8:1 ......................................................... 135

4.34 The intensity ratio of absorption at 1355 cm⁻¹ to 1331 cm⁻¹ of PTMG/LiN(SO₂CF₃)₂ mixture with different LiN(SO₂CF₃)₂ concentrations .................. 136

4.35 The relative intensity of some peaks versus different LiN(SO₂CF₃)₂ concentrations in PTMG/LiN(SO₂CF₃)₂ mixture prepared by melt mixing ......... 137

4.36 FTIR spectra of PTMG with various LiN(SO₂CF₃)₂ concentrations prepared by the solution casting................................................................. 138

4.37 Relative intensity of certain peaks versus different 1/[O:Li] in PTMG/LiN(SO₂CF₃)₂ mixture prepared by the solution casting ......................... 139

4.38 FTIR spectra of PEMPS with various LiCl concentrations prepared by melt mixing................................................................. 141

4.39 FTIR spectra of PEMPS/LiCl mixture with LiCl concentrations prepared by the solution casting................................................................. 142

4.40 Relative intensity of certain peaks versus different 1/[O:Li] in PEMPS/LiCl mixture prepared by melt mixing ......................................................... 144

4.41 Relative intensity of certain peaks versus different 1/[O:Li] in PEMPS/LiCl mixture prepared by the solution casting ......................................................... 144

4.42 FTIR spectra of PEMPS/LiClO₄ complex with different LiClO₄ concentrations prepared by melt mixing ......................................................... 145

4.43 FTIR spectra of PEMPS with various LiClO₄ concentrations prepared by the solution casting ................................................................. 146
4.44 Relative intensity of certain peaks versus different \(1/[O:Li]\) in PEMPS/LiClO_4 mixture prepared by melt mixing ............................................................. 147

4.45 Relative intensity of certain peaks versus different \(1/[O:Li]\) in PEMPS/LiClO_4 mixture prepared by the solution casting ........................................................... 147

4.46 The intensity ratio of absorption at 625 cm\(^{-1}\) to 635 cm\(^{-1}\) of PEMPS/LiClO_4 mixture with different LiClO_4 concentrations .............................................................. 148

4.47 FTIR spectra of PEMPS with various Li N(SO_2CF_3)_2 concentrations prepared by melt mixing..................................................................................................... 149

4.48 FTIR spectra of PEMPS with various Li N(SO_2CF_3)_2 concentrations prepared by the solution casting.................................................................................................... 150

4.49 Relative intensity of certain peaks versus different \(1/[O:Li]\) in PEMPS/Li N(SO_2CF_3)_2 mixture prepared by melt mixing................................................................. 151

4.50 Relative intensity of certain peaks versus different \(1/[O:Li]\) in PEMPS/Li N(SO_2CF_3)_2 mixture prepared by the solution casting............................................................ 151

4.51 The intensity ratio of absorption at 1355 cm\(^{-1}\) to 1331 cm\(^{-1}\) of PEMPS/Li N(SO_2CF_3)_2 mixture with different Li N(SO_2CF_3)_2 concentrations ......... 152

4.52 DSC Thermograms of three different lithium salts: (a) LiCl (b)LiClO_4 (c)LiN(SO_2CF_3)_2 ............................................................................................................. 154

4.53 DSC Thermograms of PTMG and LiCl melt mixture prepared by melt mixing (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan ........................................ 155

4.54 DSC Thermograms of PTMG/ LiClO_4 mixture prepared by melt mixing (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan ......................................................... 159

4.55 DSC Thermograms of PTMG and LiN(SO_2CF_3)_2 melt mixture prepared by melt mixing (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan ........................................ 161

4.56 Dependence of glass transition temperature (\(T_g\)) of PTMG/salt mixtures on the salt concentration........................................................................................................ 163

4.57 Dependence of melting temperature (\(T_m\)) of PTMG/salt mixtures on the salt concentration .................................................................................................................. 163

4.58 DSC Thermograms of PEMPS/ LiCl mixture prepared by melt mixing .......... 165
4.59 DSC Thermograms of PEMPS /LiClO$_4$ mixture prepared by melt mixing........ 165

4.60 DSC Thermograms of PEMPS and LiN(SO$_2$CF$_3$)$_2$ mixture prepared by melt mixing................................................................. 167

4.61 Dependence of glass transition temperature (T$_g$) of PEMPS/salt mixtures on the salt concentration............................................................... 167

5.1 Isothermal DSC traces of neat polyurethane reactant mixtures polymerized at different temperatures............................................................ 173

5.2 Isothermal DSC traces of polyurethane reactant mixtures with LiN(SO$_2$CF$_3$)$_2$ and [O:Li]$=16:1$ polymerized at different temperatures ......................... 173

5.3 Isothermal DSC traces of polyurethane with different LiN(SO$_2$CF$_3$)$_2$ concentrations at 140$^\circ$C................................................................. 174

5.4 Isothermal DSC traces of polyurethane/PEMPS/LiN(SO$_2$CF$_3$)$_2$ reactant mixture with different blend compositions and [O:Li] $=16:1$ at 140$^\circ$C .......... 174

5.5 Isothermal DSC traces of polyurethane /PEMPS/LiN(SO$_2$CF$_3$)$_2$ reactant mixture with TPU/PEMPS=100/10 and [O:Li$^+$] $=16:1$ at different temperature 175

5.6 Experimental isothermal DSC conversion versus time profiles for neat polyurethane reactant mixture polymerized at different temperatures.......... 175

5.7 Experimental isothermal DSC conversion versus time profiles for polyurethane reactant mixtures with LiN(SO$_2$CF$_3$)$_2$ and [O:Li]$=16:1$ polymerized at different temperatures................................................................. 176

5.8 Experimental isothermal DSC conversion versus time profiles for TPU/LiN(SO$_2$CF$_3$)$_2$ reactant mixture with different LiN(SO$_2$CF$_3$)$_2$ concentrations of salts polymerized at 140$^\circ$C ........................................... 176

5.9 Experimental isothermal DSC conversion versus time profiles for TPU/PEMPS/LiN(SO$_2$CF$_3$)$_2$ reactant mixture with different blend compositions and [O:Li] $=16:1$ at 140$^\circ$C ........................................... 177

5.10 Log-log plots of DSC conversion rate versus conversion remaining for neat TPU reactant mixtures polymerized at different temperatures.................. 180

5.11 Log-log plots of DSC conversion rate versus conversion remaining for polyurethane reactant mixtures with LiN(SO$_2$CF$_3$)$_2$ at [O:Li]$=16:1$ polymerized at different temperatures........................................... 180
5.12 Log-log plots of DSC conversion rate versus conversion remaining for TPU / LiN(SO₂CF₃)₂ reactant mixture with different LiN(SO₂CF₃)₂ concentrations polymerized at 140⁰C ................................................................. 181

5.13 Log-log plots of DSC conversion rate versus conversion remaining for polyurethane / PEMPS/LiN(SO₂CF₃)₂ reactant mixture with different blend composition and [O:Li] =16:1 at 140⁰C ................................................................. 181

5.14 Log-log plots of DSC conversion rate versus conversion remaining for TPU/PEMPS/LiN(SO₂CF₃)₂ reactant mixture with PU/PEMPS=100/10 and [O:Li] =16:1 at different temperatures ......................................................... 182

5.15 Experimental reactant constant k versus 1/[O:Li] for TPU/ LiN(SO₂CF₃)₂ reactant mixture at 140⁰C ........................................................................................................ 182

5.16 Evaluation of A and Eₐ/R from semi-ln plot of k versus 1/T data for neat polyurethane polymerized at different temperatures ......................................................... 183

5.17 Experimental reactant constant k versus 1/T data for TPU/LiN(SO₂CF₃)₂ reactant mixture with [O:Li] =16:1 at different temperatures ........................................ 183

5.18 Experimental reactant constant k versus the concentration of TPU for TPU/PEMPS/LiN(SO₂CF₃)₂ reactant mixture with different blend compositions at [O:Li] =16:1 ................................................................. 183

5.19 Photos of Neat TPU, TPU/PEMPS blend, TPU/LiCl electrolyte and TPU/PEMPS/LiCl electrolyt films .................................................................................. 185

5.20 Photos of the TPU/LiClO₄ electrolyte films and the TPU/PEMPS/ LiClO₄ electrolyte films ........................................................................................................ 189

5.21 Photos of the TPU/LiN(SO₂CF₃)₂ electrolyte films and the TPU/PEMPS/ LiN(SO₂CF₃)₂ electrolyte films ................................................................................. 189

5.22 Optical micrographs of (a) neat TPU, (b)PEMPS, and (c) TPU/PEMPS blend with different blend compositions,TPU/PEMPS=100/10, (d) 100/20, (e) 100/40 191

5.23 Optical micrographs of (a) TPU/LiCl electrolyte (b)PEMPS/LiCl electrolyte and (c) TPU/PEMPS/LiCl electrolyte with different blend compositions TPU/PEMPS =100/10, (d) 100/20, (e) 100/40, at [O:Li]=16:1 ...................... 193

5.24 Optical micrographs of (a) TPU/LiClO₄ electrolyte, (b)PEMPS/ LiClO₄ electrolyte, (c) TPU/PEMPS/ LiClO₄ electrolytes with different blend compositions TPU/PEMPS =100/10, (d) 100/20, (e) 100/40, at [O:Li]=16:1 .... 195
5.25 Optical micrographs of (a) TPU/ LiN(SO$_2$CF$_3$)$_2$ electrolytes, (b) PEMPS/ LiN(SO$_2$CF$_3$)$_2$ electrolytes and (c) TPU/PEMPS/ LiN(SO$_2$CF$_3$)$_2$ electrolytes with different blend compositions TPU/PEMPS =100/10, (d) 100/20, (e) 100/40, at [O:Li]=16:1 ................................................................. 196

5.26 SEM micrographs of fracture surface of neat TPU and TPU/PEMPS blend with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40 ................................................................................................. 198

5.27 SEM micrographs of extracted fracture surface of neat TPU and TPU/PEMPS blend with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40 ................................................................................................. 200

5.28 SEM micrographs of fracture surface of TPU/LiCl electrolytes and TPU/PEMPS/LiCl electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40 ................................................................. 202

5.29 SEM micrographs of extracted fracture surface of TPU/LiCl electrolyte and TPU/PEMPS/LiCl electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40 ................................................................. 203

5.30 SEM micrograph of fracture surface of TPU/LiClO$_4$ electrolytes and TPU/PEMPS /LiClO$_4$ electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40 ................................................................. 204

5.31 SEM micrographs of extracted fracture surface of TPU/LiClO$_4$ electrolytes and TPU/PEMPS/LiClO$_4$ electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40 ................................................................. 205

5.32 SEM micrographs of fracture surface of TPU/LiTFSI electrolytes and TPU/PEMPS/ LiTFSI electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40 ................................................................. 206

5.33 SEM micrographs of extracted fracture surface of TPU/ LiTFSI electrolytes and TPU/PEMPS/LiTFSI electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40................................................................. 207

5.34 SEM micrographs of extracted film surface of neat TPU and TPU/PEMPS blend at with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40 ........................................................................................................ 210

5.35 SEM micrograph of extracted film surface of TPU/LiCl electrolyte and TPU/PEMPS/LiCl electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40 ................................................................. 211

xx
5.36 SEM micrographs of extracted film surface of TPU/LiClO$_4$ electrolyte and TPU/PEMPS/LiClO$_4$ electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d) 100/40 ........................................... 212

5.37 SEM micrographs of extracted film surface of TPU/LiTFSI electrolyte and TPU/PEMPS/LiTFSI electrolyte at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d) 100/40 ........................................... 213

5.38 SEM micrographs of film surface of solution cast TPU/ LiClO$_4$ electrolyte and TPU/PEMPS/LiClO$_4$ electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d) 100/40 ........................................... 215

5.39 SEM micrographs of the extracted film surface of solution cast TPU/LiTFSI electrolyte and TPU/PEMPS/LiTFSI electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d) 100/40. The image on the left is height image and the one on the right is phase image. (cont.) .................................................................................................................. 217

5.40 AFM topographic images of surface of (a) neat TPU, (b) TPU/LiClO$_4$ electrolytes at [O:Li]=16:1 and TPU/PEMPS/LiClO$_4$ electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (c) 100/10, (d) 100/20, (e) 100/40. The image on the left is height image and the one on the right is phase image. (cont.) .................................................................................................................. 219

5.41 AFM topographic images of surface of TPU/LiTFSI electrolytes and TPU/PEMPS/LiClO$_4$ electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/10, (b) 100/10, (c) 100/20, (d) 100/40. The image on the left is height image and the one on the right is phase image. (cont.) .................................................................................................................. 225

5.42 TGA curves of TPU electrolytes with different lithium salts at [O:Li]=16:1 ..... 228

5.43 TGA curves of TPU/PEMPS blends with various blend compositions without lithium salt .................................................................................................................................................. 228

5.44 TGA curves of TPU/PEMPS/LiCl electrolytes with different blend compositions at [O:Li]=16:1 .................................................................................................................. 231

5.45 TGA curves of TPU/PEMPS/LiClO$_4$ electrolytes with different blend compositions at [O:Li]=16:1 .................................................................................................................. 231

5.46 TGA curves of TPU/PEMPS/LiTFSI electrolytes with different blend compositions at [O:Li]=16:1 .................................................................................................................. 233

5.47 DSC Thermograms of TPU/PEMPS blends without salt at various blend compositions (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan .................................................................................................................................................. 235
5.48 Dependence of glass transition temperature ($T_g$) of TPU/PEMPS blends on the PEMPS concentration $W_{PEMPS}/(W_{PEMPS} + W_{TPU})$ ........................................ 239

5.49 Dependence of melting temperature ($T_m$) of TPU/PEMPS blends on the PEMPS concentration $W_{PEMPS}/(W_{PEMPS} + W_{TPU})$ ........................................ 239

5.50 DSC Thermograms of TPU electrolytes with various LiCl concentrations (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan ................................................................. 240

5.51 DSC Thermograms of TPU electrolytes with different LiClO$_4$ concentrations (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan ................................................................. 242

5.52 DSC Thermograms of TPU electrolytes with various LiN(SO$_2$CF$_3$)$_2$ concentrations (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan ................................................................. 243

5.53 Dependence of glass transition temperature ($T_g$) of TPU electrolytes on the salt concentrations ............................................................................................................. 245

5.54 Dependence of melting temperature ($T_m$) of TPU electrolytes on the salt concentrations ............................................................................................................. 245

5.55 DSC Thermograms of TPU/PEMPS electrolytes with various blend compositions at [O:Li]=16:1 (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan ................................................................. 246

5.56 DSC thermograms of TPU/PEMPS/LiClO$_4$ electrolytes with different blend compositions at [O:Li]=16:1 (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan ................................................................. 247

5.57 DSC Thermograms of TPU/PEMPS/LiN(SO$_2$CF$_3$)$_2$ electrolytes with different blend compositions at [O:Li]=16:1 (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan ................................................................. 248

5.58 Dependence of glass transition temperature ($T_g$) of TPU/PEMPS electrolytes on the PEMPS concentration $W_{PEMPS}/(W_{PEMPS} + W_{TPU})$ ........................................ 250

5.59 Dependence of melting temperature ($T_m$) of TPU/PEMPS electrolytes on the PEMPS concentration $W_{PEMPS}/(W_{PEMPS} + W_{TPU})$ ........................................ 250

5.60 FTIR spectra of TPU/LiCl electrolytes with different LiCl concentrations ...... 253
5.61 FTIR spectra of TPU/LiCl electrolytes with different LiCl concentrations in the range from (a) 1000-1200 cm\(^{-1}\), (b) 1660-1780 cm\(^{-1}\), (c) 3100-3500 cm\(^{-1}\) ... 253

5.62 The relative intensity of some peaks versus different LiCl concentrations in TPU/LiCl electrolytes ................................................................. 256

5.63 FTIR spectra of TPU/LiClO\(_4\) electrolytes with different LiClO\(_4\) concentrations 257

5.64 FTIR spectra of TPU/LiClO\(_4\) electrolytes with different LiClO\(_4\) concentrations in the range from (a) 1000-1200 cm\(^{-1}\), (b) 1660-1780 cm\(^{-1}\), (c) 3100-3500 cm\(^{-1}\) ... 257

5.65 The relative intensity of some peaks versus different LiClO\(_4\) concentrations in TPU/LiClO\(_4\) electrolytes ................................................................. 259

5.66 FTIR spectra of TPU/LiTFSI with different LiTFSI concentrations ........... 260

5.67 FTIR spectra of TPU/LiTFSI with different LiTFSI concentrations in the range from (a) 1000-1200 cm\(^{-1}\), (b) 1660-1780 cm\(^{-1}\), (c) 3100-3500 cm\(^{-1}\) ............... 260

5.68 The relative intensity of some peaks versus different LiTFSI concentrations in TPU/LiTFSI electrolytes ................................................................. 261

5.69 FTIR spectra of TPU/PEMPS/LiCl electrolytes with different blend compositions at [O:Li]=16:1 ................................................................. 263

5.70 FTIR spectra of TPU with different PEMPS concentrations at [O:Li]=16:1 in the range from (a) 1000-1200 cm\(^{-1}\), (b) 1660-1780 cm\(^{-1}\), (c) 3100-3500 cm\(^{-1}\) .... 263

5.71 The relative intensity of some peaks versus different PEMPS concentration in TPU/PEMPS/LiClO\(_4\) electrolytes at [O:Li]=16] ........................................ 265

5.72 FTIR spectra of TPU/PEMPS/LiClO\(_4\) electrolytes with different concentrations of PEMPS at [O:Li]=16:1 ................................................................. 266

5.73 FTIR spectra of TPU with different blend compositions at [O:Li]=16:1 in the range from (a) 1000-1200 cm\(^{-1}\), (b) 1660-1780 cm\(^{-1}\), (c) 3100-3500 cm\(^{-1}\) ............... 266

5.74 The relative intensity of some peaks versus different PEMPS concentration in TPU/PEMPS/LiClO\(_4\) electrolytes at [O:Li]=16:1 ........................................ 267

5.75 FTIR spectra of TPU/PEMPS/LiTFSI electrolytes with different concentrations of PEMPS at [O:Li]=16:1 ................................................................. 268

5.76 FTIR spectra of TPU/PEMPS electrolytes with different blend compositions at [O:Li]=16:1 in the range from (a) 1000-1200 cm\(^{-1}\), (b) 1660-1780 cm\(^{-1}\), (c) 3100-3500 cm\(^{-1}\) ................................................................. 268
5.77 The relative intensity of some peaks versus different PEMPS concentration in TPU/PEMPS/LiTFSI electrolytes at [O:Li]=16 ................................................................. 269

5.78 Typical engineering tensile stress-strain curves obtained from neat TPU film and TPU/LiClO4 electrolytes film with various LiClO4 concentrations .......... 271

5.79 Typical engineering tensile stress-strain curves obtained from neat TPU film and TPU/LiTFSI electrolytes film with various LiTFSI concentrations .......... 271

5.80 The elongation at break of TPU/LiClO4 and TPU/LiTFSI electrolytes vs. the salt concentration ................................................................. 273

5.81 The modulus of TPU/LiClO4 and TPU/LiTFSI electrolytes vs. the salt concentration .................................................................................. 274

5.82 Typical engineering tensile stress-strain curves obtained from TPU/PEMPS blend films with various compositions .................................................. 274

5.83 Typical engineering tensile stress-strain curves obtained from TPU/PEMPS/LiClO4 electrolyte films with various compositions ..................... 276

5.84 Typical engineering tensile stress-strain curves obtained from TPU/PEMPS/LiTFSI electrolytes with various compositions ............................ 276

5.85 The elongation at break of TPU/PEMPS/LiClO4 and TPU/PEMPS/LiTFSI electrolytes at [O:Li]=16:1 with various compositions vs. the PEMPS concentration ........................................................................... 277

5.86 The modulus of TPU/PEMPS/LiClO4 and TPU/PEMPS/LiTFSI electrolytes at [O:Li]=16:1 with various compositions vs. the PEMPS concentration .......... 277

5.87 Impedance plot of TPU/LiCl electrolytes prepared by the in-situ process with [O:Li]=32:1 at different temperatures ......................................................... 281

5.88 Impedance plot of TPU/LiCl electrolytes prepared by the in-situ process with [O:Li]=16:1 at different temperatures ......................................................... 281

5.89 Impedance plot of TPU/LiCl electrolytes prepared by the in-situ process with [O:Li]=8:1 at different temperatures ......................................................... 282

5.90 The effect of temperature on the conductivity of TPU/LiCl electrolytes prepared by the in-situ process with various salt concentrations .................. 282

5.91 Impedance plot of TPU/PEMPS/LiCl electrolytes prepared by the in-situ process with TPU/PEMPS =100/10 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C ......................................................... 284
5.92 Impedance plot of TPU/PEMPS/LiCl electrolytes prepared by the in-situ process with TPU/PEMPS =100/20 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C ......................................................... 284

5.93 Impedance plot of TPU/PEMPS/LiCl electrolytes prepared by the in-situ process with TPU/PEMPS=100/40 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C ......................................................... 286

5.94 The effect of temperature on the conductivity of TPU/PEMPS/LiCl electrolytes prepared by the in-situ process with various blend compositions at [O:Li]=16:1.................................................................................................... 286

5.95 Impedance plot of TPU/LiClO₄ electrolytes prepared by the in-situ process with [O:Li]=32:1 at different temperatures (a) from 27°C to 120°C (b) from 140°C to 180°C .................................................................................................. 288

5.96 Impedance plot of TPU/LiClO₄ electrolytes prepared by the in-situ process with [O:Li]=16:1 at different temperatures (a) from 27°C to 60°C (b) from 80°C to 100°C (c) from 120°C to 140°C .................................................................................................. 288

5.97 Impedance plot of TPU/LiClO₄ electrolytes prepared by the in-situ process with [O:Li]=8:1 at different temperatures (a) from 27°C to 60°C (b) from 80°C to 100°C (c) from 120°C to 140°C .................................................................................................. 289

5.98 The effect of temperature on the conductivity of TPU/LiClO₄ electrolytes with various salt concentrations .......................................................................................................................... 289

5.99 Impedance plot of TPU/PEMPS/LiClO₄ electrolytes prepared by the in-situ process with TPU/PEMPS=100/10 and [O:Li]=16:1 at (a) from 27°C to 80°C (b) from 100°C to 140°C (c) from 160°C to 180°C ......................................................... 291

5.100 Impedance plot of TPU/PEMPS/LiClO₄ electrolytes prepared by the in-situ process with TPU/PEMPS=100/20 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 140°C ......................................................... 292

5.101 Impedance plot of TPU/PEMPS/LiClO₄ electrolytes prepared by the in-situ process with TPU/PEMPS=100/40 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 140°C ......................................................... 292

5.102 The effect of temperature on the conductivity of TPU/PEMPS/LiClO₄ electrolytes with various blend compositions with [O:Li]=16:1................................. 293

5.103 Impedance plot of TPU/LiTFSI electrolytes prepared by the in-situ process with [O:Li]=32:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 140°C ......................................................... 295
5.104 Impedance plot of TPU/LiTFSI electrolytes prepared by the in-situ process with \([O:Li]=16:1\) at different temperatures (a) from 27°C to 80°C (b) from 100°C to 140°C........................................................................................................ 295

5.105 Impedance plot of TPU/LiTFSI electrolytes prepared by the in-situ process with \([O:Li]=8:1\) at different temperatures .................................................................................. 296

5.106 The effect of temperature on the conductivity of TPU/LiTFSI electrolytes with various salt concentrations ........................................................................................................ 296

5.107 Impedance plot of TPU/PEMPS/LiTFSI electrolytes prepared by the in-situ process with TPU/PEMPS=100/10 and \([O:Li]=16:1\) at different temperatures (a) from 27°C to 80°C (b) from 100°C to 140°C ........................................................................................................ 298

5.108 Impedance plot of TPU/PEMPS/LiTFSI electrolytes prepared by the in-situ process with TPU/PEMPS=100/20 and \([O:Li]=16:1\) at different temperatures (a) from 27°C to 80°C (b) from 100°C to 120°C ........................................................................................................ 298

5.109 Impedance plot of TPU/PEMPS/LiTFSI electrolytes prepared by the in-situ process with TPU/PEMPS=100/40 and \([O:Li]=16:1\) at different temperatures (a) from 27°C to 80°C (b) from 100°C to 140°C ........................................................................................................ 299

5.110 The effect of temperature on the conductivity of TPU/PEMPS/LiTFSI electrolytes with various PEMPS concentrations with \([O:Li]=16:1\) .......................................................... 299

5.111 The schematic representation of different region of impedance plot .................. 302

5.112 The room temperature conductivity versus salt concentrations of TPU electrolytes with three different lithium salts.......................................................................................... 305

5.113 The room temperature ionic conductivity versus PEMPS/TPU ratio for TPU/PEMPS electrolytes with different lithium salts.......................................................................................... 305

5.114 Impedance plot of TPU/LiClO₄ electrolytes prepared by the solution casting with \([O:Li]=32:1\) at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C ........................................................................................................ 310

5.115 Impedance plot of TPU/LiClO₄ electrolytes prepared by the solution casting with \([O:Li]=16:1\) at different temperatures (a) from 27°C to 80°C (b) from 100°C to 160°C ........................................................................................................ 310

5.116 Impedance plot of TPU/LiClO₄ electrolytes prepared by the solution casting with \([O:Li]=8:1\) at different temperatures (a) from 27°C to 80°C (b) from 100°C to 160°C ........................................................................................................ 311

xxvi
5.117 The effect of temperature on the conductivity of TPU/LiClO4 electrolytes with various salt concentration prepared by the solution casting................................. 311

5.118 Impedance plot of TPU/PEMPS/LiClO4 electrolytes prepared by the solution casting with TPU/PEMPS=100/10 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 160°C ................................................. 312

5.119 Impedance plot of TPU/PEMPS/LiClO4 electrolytes prepared by the solution casting with TPU/PEMPS=100/20 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 120°C (c) from 140°C to 160°C ....... 312

5.120 Impedance plot of TPU/PEMPS/LiClO4 electrolytes prepared by the solution casting with TPU/PEMPS=100/40 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 120°C (c) from 140°C to 160°C ....... 313

5.121 The effect of temperature on the conductivity of TPU/PEMPS/LiClO4 electrolytes prepared by the solution casting with various blend compositions at [O:Li]=16:1 ...................................................................................................... 314

5.122 Impedance plot of TPU/LiTFSI electrolytes prepared by the solution casting with [O:Li]=32:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C .................................................................................................... 314

5.123 Impedance plot of TPU/LiTFSI electrolytes prepared by the solution casting with [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C .................................................................................................... 314

5.124 Impedance plot of TPU/LiTFSI electrolytes prepared by the solution casting with [O:Li]=8:1 at different temperature (a) from 27°C to 80°C (b) from 100°C to 180°C .................................................................................................... 315

5.125 The effect of temperature on the conductivity of TPU/LiTFSI electrolytes with various salt concentrations prepared by the solution casting ...................... 315

5.126 Impedance plot of TPU/PEMPS/LiTFSI electrolytes prepared by the solution casting with TPU/PEMPS=100/10 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C ................................................. 316

5.127 Impedance plot of TPU/PEMPS/LiTFSI electrolytes prepared by the solution casting with TPU/PEMPS=100/20 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C ................................................. 316

5.128 Impedance plot of TPU/PEMPS/LiTFSI electrolytes prepared by the solution casting with TPU/PEMPS=100/40 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C ................................................. 317
5.129 The effect of temperature on the conductivity of TPU/PEMPS/LiTFSI electrolytes with various blend compositions at [O:Li]=16:1 ............................. 317

5.130 Schematic representation of the interaction between Li$^+$ and oxygen at different sites of PTMG: (a) ether group (b) hydroxyl group ................................. 323

5.131 Schematic representation of the network structure formed via (a) the interaction of Li$^+$ with ether oxygens from same polymer chain and (b) the interaction of Li$^+$ with different ether oxygen atoms from different polymer chains................................................................................................................... 323

5.132 Schematic representation of the interaction of lithium ions with the soft segments and the hard segments in TPU............................................................. 325

5.133 Schematic representation of (a) the morphology of TPU/PEMPS electrolyte with PEMPS Phase dispersed in TPU matrix and (b) the morphology of TPU/PEMPS electrolyte with PEMPS and TPU forming a co-continuous structure ................................................................................................. 327

5.134 Schematic representation of (a) the interaction of lithium ions with soft segments of TPU and PEMPS (c) the interaction of lithium ions with hard segments of TPU and PEMPS ..................................................................................... 329

5.135 Schematic representation of multiphase morphology of TPU/PEMPS electrolytes without salt (a) and with salts (b)................................................................. 331

5.136 Schematic representation of (a) the two possible Li$^+$ transport pathways in the morphology of TPU/PEMPS electrolyte with PEMPS Phase dispersed in TPU matrix and (b) the three possible Li$^+$ transport pathways in the morphology of TPU/PEMPS electrolyte with PEMPS and TPU forming a co-continuous structure ................................................................................................. 334
CHAPTER I

INTRODUCTION

The study of polymer–based solid electrolytes has attracted great interest in recent years due to their potential applications. The rapid development of a new generation of electronic devices such as power sources, displays, and sensors requires intensive research on solid polymer electrolytes to improve their ionic conductivity and thermal, chemical and dimensional stability as well as processability. 1

Polymer electrolytes are formed by dissolving salts in a polar polymer matrix. The most well-studied polymer electrolytes are polyethylene oxide (PEO)-based electrolytes, which were first studied by Wright in 1975. 2 PEO is a good salt solvation medium due to the strong coordination of its oxygen atom with the alkali cations, but the high degree of crystallinity of the PEO/salt complex restricts the mobility of the ions and leads to poor ionic conductivity at room temperature. Previous studies showed that the significant contribution to ionic conductivity comes from the amorphous phase in the PEO-based polymer electrolytes. 3 Therefore, it is necessary to prepare amorphous or low crystallinity materials as the host polymer for polymer electrolytes to achieve high ionic conductivity. It is reported that PEO-based polymer electrolytes possess high ionic conductivity, greater than $10^{-3}$ S/cm, above 100°C. However, their dimensional stability is poor due to the destruction of the crystalline phase above $T_m$ (60°C), which limits their application as solid electrolytes at high temperature. Various approaches have been
conducted to overcome these shortcomings, which include the development of polymer electrolytes based on linear polymers, comb-branched copolymers, block copolymers, cross-linked network polymers and polymer blends with a variety of polar groups on the chain.\textsuperscript{1} Efforts have been made to develop solvent-free polymer electrolytes by tailoring the chemical structure of the host polymers for better salt solvation of the polyether segments.

Polyether-modified polysiloxane is one of the most promising host polymers. Polysiloxanes, also known as silicones, have flexible backbones of alternating silicon and oxygen atoms, which can have a wide variety of substituents bonded to the silicon in the backbone.\textsuperscript{4} Polyether-modified polysiloxanes are prepared by incorporating the alkylene oxide containing segments into the silicones. They are good candidates for the solid polymer electrolytes with respect to their backbone flexibility. Ionic conductivity above $10^{-5}$ S/cm has been achieved using the oligo(ethylene oxide) grafted comb-shaped polysiloxane, which is close to the requirement for practical applications.\textsuperscript{5} However, their dimensional stability is poor, so they cannot function as separators in the cell.\textsuperscript{6} Chemical cross-linking between siloxane chains is employed to strengthen the dimensional stability, but it forms a rigid material and sacrifices chain flexibility, resulting in reduction of ionic conductivity.\textsuperscript{4}

Polyether-based polyurethane is an attractive candidate as matrix material for polymer electrolytes due to its unique multiphase structure. Polyurethanes are block copolymers composed of soft segments and hard segments. The hydrogen bonding between the carbonyl group and N-H group in the hard segments leads to the formation of
physically cross-linked hard domains. The interconnected or isolated hard segment domains are distributed in the soft segment matrix. The polyether-based soft segments act as polymer solvents to solvate the cations favoring the transportation of the ions and contribute to the conductivity of the polymer electrolyte. The hard segment is responsible for the dimensional stability acting as physical cross-link sites. However, the polyurethane-based polymer electrolyte usually has a much lower conductivity at room temperature due to the presence of poor ionic conductive hard domains. The majority of research on polyurethane-based polymer electrolytes is conducted on gel-type electrolytes with a polyurethane film swollen by electrolyte solutions, where polyurethane only functions as structural support.

Blending is an effective way to obtain the desired properties. Miscibility and phase morphology of the polymer blends play an important role on the ionic conductivity of polymer blend electrolytes since the paths of ion transfer originate from the high and low conductive phases as well as the interface. Some studies on polymer blend electrolytes have been reported, but there are very few studies of solvent-free polymer blend electrolytes regarding their miscibility, phase morphology and the ionic conductivity.

Salts are the source of the charge carriers in polymer electrolytes. The selection of salt is very crucial for controlling the ionic conductivity and several other properties of polymer electrolytes. The solvation of salt not only depends on the interaction between polymer and cations, but also the interaction between the cations and anions. Not all the salts are completely dissociated to form the free ions, and usually, the mobile species in
polymer electrolytes are composed of small portions of free ions and large portions of ion clusters. Size of anions can affect the size of the ion clusters and their mobility correspondingly. Salts play a critical role in the ionic conductivity not only because it is the charge carrier in the system but also because it affects the miscibility of polymer pairs as well as the morphology of the electrolytes through ion/polymer interaction. However, there are few studies on the effect of the anion size on the miscibility of polymer blends of polymer electrolytes and their properties.

The preparation methods used to form blend-based polymer electrolytes can also influence their ionic conductivity. The conventional method for preparation of polymer electrolytes used by many researchers is solution casting. The disadvantages of the solution casting method are the difficulty in removing residual solvent trapped inside the polymer electrolytes, the high processing cost, and environmental pollution, caused by the solvent. Earlier, our research group had developed an alternative novel preparation source, a solvent-free reactive processing, in which polyurethane is polymerized in-situ after mixing monomer with salts.

In this study, novel, flexible, solid polymer electrolytes based on thermoplastic polyurethane and polyether-modified polysiloxane blendd with lithium salts were developed via a solvent-free in-situ reactive process. These electrolytes are expected to have high ionic conductivity and good dimensional stability. The multiphase morphology of TPU provides the possibility to control the flexibility of the electrolytes by tailoring the architecture of the soft and hard segments of polyurethane electrolytes. The amorphous PEMPS was incorporated into TPU electrolytes to improve the ionic
conductivity. The contribution of PEMPS to the ionic conductivity of TPU/PEMPS electrolytes originates from the following hypothesis: (1) the enhancement in ionic conductivity due to the high ionic conductivity of PEMPS electrolyte itself, and (2) the enhancement in ionic conductivity due to the decrease of crystallinity of soft segments of TPU due to its interaction with PEMPS. Good dimensional stability is obtained by network formation generated by cross-linked hard segments of polyurethane and their physically interlocked phase morphology. Polymer electrolytes with three different lithium salts with various anion structures were studied: lithium chloride (LiCl), lithium perchlorate (LiClO₄), and lithium bistri fluoromethane sulfonimidate (LiN(SO₂CF₃)₂ (LITFSI)). In this in-situ reactive process, the monomer was used to dissolve the salts, instead of the volatile solvent. Thus, the in-situ process includes two steps: (a) dissolve lithium salts in PTMG and PEMPS, and (b) add MDI, BDO to start polymerization of polyurethane in the presence of PEMPS and lithium salts.

Various characterization techniques were used. First, the dissolution of salts in PTMG and PEMPS, the interaction of salt with PTMG and PEMPS, and the miscibility of PTMG/PEMPS were characterized using DSC, FTIR, and optical microscopy. Secondly, the kinetics of polyurethane polymerization was characterized using isothermal calorimetry. Thirdly, the multiphase morphology of TPU and TPU/PEMPS electrolytes were characterized using the optical microscopy, SEM and AFM. Both the fractured surfaces and the surface extracted with methanol of polymer electrolytes were studied by SEM. The thermal stability of TPU/PEMPS electrolytes was determined by TGA. The tensile properties of these polymer electrolytes were characterized by Instron tensile
testing. The interaction between the lithium salts with the soft segments and hard segments of TPU as well as the PEMPS were determined by FTIR. The effects of PEMPS and lithium salts on the thermal properties including $T_m$ and the degree of crystallinity of TPU were investigated using DSC. The ionic conductivity of these electrolytes and its temperature dependence were determined by measuring the impedance of electrolytes using an LCR meter. Finally, the results from the studies mentioned above were used to investigate the mechanism of the ionic conductivity of TPU/PEMPS electrolytes and the ion transportation in the multiphase morphology.
CHAPTER II

LITERATURE SURVEY

2.1 Solid Polymer Electrolytes

Solid polymer electrolytes have a lot of potential in their applications in various electronic devices such as solid state rechargeable batteries, fuel cells, sensors, electrochromic display devices and super capacitors.\textsuperscript{10} Extensive studies of the relationship of the structure of solid polymer electrolytes and their ionic conductivity, their ion-transport mechanism as well as the theoretical modeling of the ion-transport processes have been conducted.\textsuperscript{11}

2.1.1 Application of Solid Polymer Electrolytes

The film-like solid polymer electrolyte battery is a typical example of application of polymer electrolyte in solid state battery. Figure 2.1 illustrates the schematic structure of a film-like polymer electrolyte battery. The entire cell assembly can be produced as a laminated thin film first, and then rolled or folded into its finished shape by taking advantage of the flexible nature of polymer electrolytes.\textsuperscript{11} Song\textsuperscript{11} pointed out that the most attractive characteristics of the polymer electrolyte membrane in the cell are its great capacity to tolerate shock, vibration, and mechanical deformation, its exceptionally long shelf-lives, its wide operating temperature range, and its shape flexibility and manufacturing integrity.\textsuperscript{1}
In the last few decades, various types of polymer electrolytes have been studied. Jocob\textsuperscript{13} stated that majority of polymer electrolytes can be divided into the following categories through their composition difference according to Scrosati and Vincent\textsuperscript{12}: solvent-free solid polymer/salt complexes, plasticized polymer electrolytes, gel electrolytes and composite electrolytes et al. The most common solvent-free polymer/salt complex are PEO/salt electrolytes. Both plasticized polymer electrolytes and gel electrolytes contain great amounts of small molecular liquid plasticizer (such as propylene carbonate (PC), ethylene carbonate (EC)) to improve the mobility of ions. The incorporation of liquid plasticizers into the polymer electrolytes results in several problems including the significant reduction of the dimensional stability of the electrolyte, the releasing of volatiles and the increase of reactivity of electrolytes towards the metal electrodes.\textsuperscript{13} In order to increase the ionic conductivity, the composite polymer electrolytes have been developed where inorganic particles or in-situ particles are incorporated into polymer electrolytes.\textsuperscript{13} It was believed that these particles can reorganize polymer chains and reduce their crystallinity through the Lewis acid-base interactions between the surface of the particles and the polymer chains.\textsuperscript{14} However, there
was no significant ionic conductivity improvement reported in composite polymer electrolytes.

Overall, considering the material reactive stability, the dimensional stability and the ionic conductivity of polymer electrolytes, this research focuses on solvent-free solid polymer electrolytes.

2.1.2 Polymer Structures in Polymer Electrolytes

Polyethylene oxide-based electrolytes are the first generation of solvent-free solid polymer electrolytes. PEO is a linear polymer of ethylene oxide with a high degree of crystallinity around 70~80% due to the regularity of the unit. PEO has a $T_m$ around 65°C and a $T_g$ around 60°C. Armond stated that the oxygen atom in the ether unit of PEO has strong ability to coordinate effectively with the alkali metal cations, which makes it a good solvating medium for polymer electrolytes. Unfortunately, the high crystallinity of PEO results in its low ionic conductivity at room temperature. Cowie pointed out that the majority of the ionic conductivity come from the disordered parts of the polymer matrix (amorphous phase) and it is associated with large amplitude polymer segmental motions. They concluded that the effective method is to reduce the crystalline order and to create an amorphous polymer system within the temperature range of interest. The acceptable level of ionic conductivity of PEO electrolytes can only be achieved at temperatures above $T_m$ but the destruction of crystal at high temperature leads to the liquid state of electrolytes which cannot function as separator by itself.
It was important to develop new host polymers which have few crystalline phases and a relatively low $T_g$ for polymer electrolytes.\textsuperscript{1} In order to overcome the shortcomings of PEO electrolyte associated with its high crystallinity, a series of polymer electrolytes with diverse structures have been designed and prepared as host polymers for polymer electrolytes such as linear polymers, comb-branched copolymers, block copolymers, cross-linked network polymers as well as polymer blends with a variety of polar groups on the chain.\textsuperscript{1,17}

Cowie\textsuperscript{17} reviewed the research on the polymer electrolytes based on different structures. He pointed out that one important approach is to choose polymers with similar structure as PEO and these polymers have oxygen or nitrogen or sulphur atoms as electron donors. The classical examples are poly(propylene oxide) (PPO)\textsuperscript{18}, poly(ethylene succinate)\textsuperscript{19,20} poly(β-propiolactone) (PPL)\textsuperscript{21}, poly(ethylene adipate) (PEA)\textsuperscript{22}, poly(ethylene imine) (PEI)\textsuperscript{23}, poly(N-propylaziridine)(PNPA)\textsuperscript{24} and poly(alkylene sulphide) (P(n)S)\textsuperscript{25}. Gray\textsuperscript{1} mentioned that PPO has the similar backbone structure as PEO, and PPO electrolytes are amorphous, however, their ionic conductivities are poor because that the steric hindrance of the methyl groups along the chain limits the segmental motion required for ion motion and reduces the intensity of polymer-cation interaction.

The other approach is to modify PEO or other similar polymer by forming block copolymer, comb-branch copolymer or cross-linked networks as summaried by Gray and Cowie.\textsuperscript{1,17} The effective method to reduce the crystallinity of PEO is to replace the long chain with a short chain by preparing comb-branched polymers composed of low
molecular weight polyether chain grafted to a polymer backbone; or by preparing block copolymer to separate long polyether chain into short segment using other polymer segments. As a result, the crystallinity and flexibility of the polymer can be improved.\textsuperscript{1,17,26} The polymer backbone in comb-branched polymers or other components in block copolymers are inert and act as short chain carriers.\textsuperscript{1,17} Meyer\textsuperscript{26} summarized the structures of some comb branched polymers and block polymers used as host polymers for polymer electrolytes as listed in Figure 2.2. Most of these materials tend to show good conductivity at room temperature, but have poor dimension stability. Forming chemical or physical cross-linking in the polymer electrolytes is an optional way to improve their dimension stability.\textsuperscript{1} Table 2.1 lists some examples of the compounds of network structure summarized by Meyer.\textsuperscript{26} Gray\textsuperscript{1} pointed out that it is important to control the cross-linking in polymer electrolytes with network structures: the network is not stable at low level of cross-links; the material is very rigid at the high level of cross-links, which adversely affects ion mobility.

Figure 2.2  Structures of comb-branched and block polymers used as host polymers\textsuperscript{26}
Polymer electrolytes based on polymer blends have also been studied. Some components in polymer blends act as host polymer while other components provide structure support to maintain good dimension stability. Blending is an easier and faster way to prepare polymer electrolytes compared with the synthesis of new polymers. Examples are polymer electrolyte based on PEO/PPO\textsuperscript{34,35}, PEO/PAN\textsuperscript{36}, PEO/PMMA\textsuperscript{37}, PEO/TPU\textsuperscript{38}. Few polymer blend electrolytes have been found to show significant comprehensive properties which can reach the practical requirements.

Table 2.1 Basic network structure and composition of network host polymer\textsuperscript{26}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Basic structure</th>
<th>Cross-linker</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>( \text{\textsuperscript{1}} \text{H}_2\text{O}\text{-(CH\textsubscript{2}CH\textsubscript{2}O)\textsubscript{n}H} )\textsubscript{(n=22)}</td>
<td>( \text{H}_2\text{CO-(CH\textsubscript{2}CH\textsubscript{2}O)\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}H} )</td>
<td>39</td>
</tr>
<tr>
<td>2</td>
<td>( \text{CH}_2\text{CH}=\text{CH}_2 )\textsubscript{(n=45)}</td>
<td>( \text{CH}_3\text{H}_2\text{O-O-(CH\textsubscript{2}CH\textsubscript{2}O)\textsubscript{n}-CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}H} )</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>( \text{H}_2\text{O-(CH\textsubscript{2}CH\textsubscript{2}O)\textsubscript{n}} )\textsubscript{(n=9)}</td>
<td>( \text{OCN-Aryl-NCO} )</td>
<td>41</td>
</tr>
<tr>
<td>4</td>
<td>( \textbf{[\textbf{P-\textbf{N}]}\textbf{(P=N}(\textbf{P-N})\textbf{)}\textbf{N}]-\textbf{N} )\textsubscript{(random)} ( \text{OR}_1, \text{OR}_2, \text{OR}_3 )</td>
<td>( \text{UV} )</td>
<td>42</td>
</tr>
</tbody>
</table>
2.1.3 Salt Solvation in Polymer Electrolytes

In polymer electrolytes, metal salts are the main source of charge carriers. Gray\(^43\) summarized that the salts mostly used are salts of alkali metals, alkaline earth metals, transition metals, lanthanides and rare earth metals. These metal cations can coordinate with the oxygen atoms in polyether, polyester or the nitrogen atoms in polyaziridene resulting in their good salvation in these polymers.\(^17\) Gray\(^1\) believed that the salt affects the ionic conductivity through different aspects such as the crystalline complex formation, the intramolecular cross-linking of the polymer chains and the degree of salt dissociation.

It has been reported that PEO has great complex capacities with a series of monovalent and divalent cations such as Na\(^+\), K\(^+\), Li\(^+\), Cu\(^{2+}\) and Mg\(^{2+}\) and the complex ratio and salt solubility in polymer vary with different polymer and salt structures.\(^1,9\) The salt solubility in polymer directly determines the numbers of charge carriers and their mobility, which has a significant effect on the ionic conductive behavior. Maccallum and Vincent\(^9\) stated that salt solubility in polymers is determined by the energy and entropy changes associated with the ion transfer from the crystal lattice to their equilibrium position and that the salt could be dissolved only if the lattice energy was compensated by exothermic ion-solvent interaction. They further pointed out that there are two types of forces contributing significantly to the ion solvation: electrostatic interactions (such as ion-dipole, ion-quadrupole, dipole-dipole forces) and non-electrostatic interactions (the energy associated with the chain rotations for accommodating the coordinating groups around the ions). Gray\(^1\) gave the explanation from a different view. He pointed that the
Solvation of cations in polymer electrolytes is achieved by partial sharing of alone pair of electrons to form the coordinate bond and that the energy change in polymer electrolytes is mainly dominated by the solvation of cation and the contributions from the solvation of anions are much less due to the few interaction between host polymer with anions.

Pearson studied salt solubility in terms of the acid-base interaction between polymers and salts with the hard/soft acid base principle (HSAB). In the HSAB principle, the oxygen atom in ether group, which has the electrons hard to be polarized, is considered as hard bases; small cations without easily polarized or removed valence electrons, such as alkaline earth cations, are considered as hard cations. The strong interaction occurs by matching hard acids with hard bases or soft acids with soft bases.

Anions, as the counterpart of cations in the salt crystals, also affect the solubility of the salts. Gray mentioned that usually anions have few interactions with polymers and that large anions with delocalized charges required little solvation. Based on this theory he believed that in the aspect of the anion selection the most suitable anions for polyether-based polymer electrolytes to achieve high ionic conductivity should be in the following order:

$$\text{Cl}^- < \text{I}^- < \text{SCN}^- < \text{ClO}_4^- < \text{CF}_3\text{SO}_3^- < \text{BF}_4^- < \text{AsF}_6^-$$

In addition, he pointed out that the most appropriate salts for polymer electrolytes are expected to be those composed of a polarizing cation and a large anion of delocalized charge such as lithium superacid salts, especially the imide family salts with large and flexible anions.
Armond et al.\textsuperscript{45} reported that PEO polymer electrolyte with lithium bis(trifluoromethylsulfonyl) imide [LiN(SO$_2$CF$_3$)$_2$, LiTFSI] exhibited a high conductivity of 10$^{-5}$ S/cm at room temperature. Appetecchi et al.\textsuperscript{46} studied another imide salt, lithium bis(perfluoroethylsulfonyl) imide [LiN(SO$_2$CF$_2$CF$_3$)$_2$, LiBETI] and found that PEO electrolytes with LIBETI exhibited ionic conductivity higher than 10$^{-5}$ S/cm at 40 $^\circ$C. It was found that these lithium imides slow down the recrystallization kinetics of polymer electrolytes.\textsuperscript{1} The ab initio calculation result from Johansson et al.\textsuperscript{47} showed that both TFSI and BETI anions had small energy differences for large geometrical variations. Nie et al.\textsuperscript{48} used a branched ester-type lithium imide, lithium bis [(1,1,1,3,3,3-hexafluoro -2-propoxy) sulfonyl] imide (LiN[SO$_2$OCH(CF$_3$)$_2$]$_2$, LiHFPSI) in PEO electrolytes. They reported that the highest conductivity (10$^{-5}$ S/cm, 30 $^\circ$C) achieved was obtained when EO unit /Li$^+$ ratio was 8.

2.1.3.1 Phase diagrams

Most host polymers of polymer electrolytes are semi-crystalline polymers with both crystalline and amorphous phases. Gray\textsuperscript{1} stated that after the addition of salts into these polymers, the corresponding polymer electrolytes usually have multiphase morphology composed of stoichiometric crystalline phases, amorphous polymer electrolyte, crystalline host polymer and pure salt, etc., depending on the nature of the polymer and salt, the salt concentration, the temperature, etc.\textsuperscript{49} He reviewed the phase diagrams of polymer electrolytes obtained by researchers and summarized that it is hard to construct and interpret the phase diagrams of polymer electrolytes due to the difficulty to
approach the thermal equilibrium and the complication of various polymer/salt crystalline complexe structures and complex ratios.\textsuperscript{1} The techniques used to characterize the crystalline morphology of polymer electrolytes and construct the phase diagrams usually include optical microscopy, DSC, NMR, X-ray diffraction.\textsuperscript{1} Most studies on the phase diagram of polymer electrolytes are about PEO electrolytes. Jacobsen et al.\textsuperscript{49} proposed a shematic phase diagram of typical polymer electrolytes. Figure 2.3 shows the phase diagram of the PEO/LiClO\textsubscript{4} electrolytes reported by Gray\textsuperscript{1}. The salt rich crystals with different complex ratios( O:M =1:1, 2:1, 3:1, 6:1) in PEO/LiClO\textsubscript{4} electrolytes were identified. There were also some eutectic in the phase diagram within different composition ranges.\textsuperscript{1}

Kim and Bae\textsuperscript{50} set up a molecular thermodynamic model based on both an extended Flory-Huggins theory and a Debye-Hückel theory modified by Guggenheim to quantitatively interpret the liquid curves in the phase diagram of PEO electrolytes as shown in Figure 2.4. Later Bae and his coworker\textsuperscript{51} developed a model based on modified perturbed hard sphere chain theory and melting point depression theory to predict the liquidous curves of the PEO/PPO blend-based polymer electrolyte. However, both of these models are oversimplified and they failed in predicting the formation of various crystalline complex ratios in PEO electrolytes.

### 2.1.4 Effects of Preparation Methods of Polymer Electrolytes on Their Ionic Conductivity

Preparative techniques are important for polymer electrolyte, since the phase mophology of polymer electrolyte varies with preparation conditions. The conventional
preparation method for polymer electrolytes film is solution casting. In this method, polymer and salt are dissolved in a polar solvent and the solution is cast on a flat surface, followed by slow evaporation of solvent.¹

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Figure 2.3  Phase diagram of the PEO/LiClO₄ electrolyte. The vertical boundaries represent the formation of 6:1, 3:1, 2:1,1:1 crystalline complexes. The liquid phase is amorphous phase¹
Figure 2.4  Phase diagram of the PEO/ZnCl$_2$ electrolyte. The transition temperatures were obtained using a thermo-optical analysis technique. The solid lines are calculated from the proposed model. The dotted lines are calculated from the model based on an extended Flory–Huggins equation only.$^{50}$

Gray$^1$ pointed out that the final properties of polymer electrolytes could be significantly affected by different factors in the solution cast such as the nature of the solvent, the rate of solvent evaporation, the heating temperature because these factors change the phase morphology of the polymer crystals and the polymer salt complex crystal formation. He emphasized that the effect are especially substantial for multivalent-cation-based polymer electrolytes, because many multivalent salts are usually hydrated, the removal of these portion of water may significantly change its solvation properties.$^{1,43}$
The disadvantages of the solution casting method are (1) the difficulty of removing the traces of solvent left inside the polymer electrolyte; and (2) the high process costs and environmental pollution caused by the usage of large amounts of solvent.

Besides solution casting, Gray\textsuperscript{52} used a hot-pressing method to prepare PEO electrolytes where polymer and salt are ground together at very low temperature, and then pressed to polymer electrolyte film at high temperature. He mentioned that the polymer electrolyte film prepared by hot-pressing is usually thicker than solution cast film due to the high viscosity of polymer melt; and the non-uniform salt distribution and weak solvation of salt in polymer is also a big concern due to the absence of the vigorous mixing in melt state.\textsuperscript{1} Tandel\textsuperscript{53} and Puatrakul\textsuperscript{54} prepared the polymer electrolyte by a melt mixing method. PEO melt was mixed with various salts using internal mixer and compressed into film using compression molding. In their method, the mixing was improved but the solvation of salts in those films was still poor partially due to the high viscosity of the high molecular weight of PEO. The same research group including Jeung\textsuperscript{55} developed the in-situ polymerization of the ether and ester type polyurethane-based polymer electrolyte using monomer, polyol, as polymer solvent to dissolve salt. Polyol, chain extender and MDI were mixed with salt first and then cast onto Teflon sheet to cure in vacuum oven for 24 hours. The monomer polyol has much lower molecular weight than polymerized polyether such as PEO, which favor the solvation of the salt in polyol liquid with the absence of the common solvent like methanol. But in their work, the salt was added to polyol nearly at the same time as MDI and BDO. As a result, the salts did not have sufficient time to be completely dissolved before the
solidification initiated by the polymerization. So it is necessary to pre-dissolve the salts in polyol before the addition of the MDI and BDO.

As mentioned in Chapter 2.1.3, the solubility of a salt in the system is determined by the energy and entropy change involved. In the solution cast, the ions first dissolve into solvent from the crystal lattice, and there is a competition between solvent and polymer to interact with the ions. The strong interaction between ions and the high polarity small molecular weight solvent makes it easy to free the ions trapped in the crystal lattice. In protic solvent media, hydrogen bonding between the solvent molecular and the anion can help the dissociation between cations and anions. As the solvent is gradually removed, polymer/ions complexing is favored if there is a strong interaction between polymers and ions. However, in the solvent-free method, the polymer is a macromolecular array of Lewis bases of low polarity and extra energy is required to overcome the strained conformations in polymer backbone caused by main chain rotations. The salt crystal lattice energy is high relative to the interaction between the polymer and salt. The salt solvation process in polymer melt without any assistant of common polar solvent is quite slow and the solubility of salt in polymer melt is low. Few detailed experimental confirmations about this comparison have been reported.

The other important issue in various preparation methods is ion-pairing. Gray mentioned that ion pairing is related to the nature of the cations and anions as well as the nature of solvent used during the preparation. The small sized polar solvent can help more to separate cation from anions by isolating the cation from the anion with groups of solvent molecules than the macromolecular array. Poor salt solvation will generate a
large portion of ionic clusters which limit the mobility of the ions. Since the ionic conductivity is related to the number of the charge carrier and their mobility, the polymer electrolytes prepared by solution casting are expected to have higher ionic conductivity than the ones prepared by solvent-free method, in spite of shortcomings associated with solvents. But this conclusion is not confirmed due to the lack of studies on polymer electrolytes prepared the solvent-free method and the comparison between electrolytes prepared from various methods.

Besides the single polymer-based polymer electrolytes, many blends based on polymer electrolytes are prepared and studied. The majority of them are prepared by the solution casting method. Since most polymer pairs are immiscible, the solution cast and normal melt mixing lead to multiphase morphology with large scale phase separation driven by thermodynamic force. Interpenetrating Networks (IPNs) structures might be a possible approach to control the phase separation and generate the phase morphology with fine domain dispersion. The IPNs are a special class of polymer blends in which the polymers exist in networks that are formed when at least one of the polymers is synthesized or cross-linked in the presence of the other.\textsuperscript{56} IPNs are characterized by the presence of physical or chemical cross-links in one or both polymers. The phase morphology can be governed by the chemical process of polymerization and the physical process of phase separation.\textsuperscript{56} Phase morphology of the blend-based polymer electrolytes have significant influence on the tortuous pathway of ions motion, the ions concentration distribution in different phases, the resistance at the interface, the mobility of polymer chains, etc.\textsuperscript{1} However, few detailed studies on the effect of preparation method on the
morphology of blend-based polymer electrolyte as well as their ionic conductivity have been reported.

2.1.5 Ionic Conduction Mechanism in Polymer Electrolytes

Different ionic conduction mechanism has been proposed by researches to describe the ion motion in polymer electrolytes. The following sections briefly show the studies on the ionic conduction mechanism from the view of the ion transfer in polymer and the ionic conductivity temperature dependence.

2.1.5.1 Ion Transfer in Polymer Electrolytes

The conductivity of conducting materials with all different charge carriers can be simply represented by the following basic equation as described by Duke et al.\textsuperscript{57}

\[
\sigma = \sum_i q_i n_i \mu_i \tag{2.1}
\]

where \(\sigma\) is specific ionic conductivity, i.e. the charge transport across a unit cross-sectional area per second per unit electric field applied. Its unit is ohm\(^{-1}\)cm\(^{-1}\) or Scm\(^{-1}\). \(n_i\) and \(q_i\) are the number of each kind of carrier and its charges, respectively. The overall ionic conductivity is the total sum of the contribution from different charge carriers. All three variables on the right hand side of equation depend on the material environment.\textsuperscript{53}

In solvent-free polymer electrolytes, the charged carriers are in form of single cations, single anions, or the ion clusters. Ionic conduction is achieved by the movements of ions associated with polymer segment.\textsuperscript{1} The mobility of the charge carriers is
determined by their environment and it is function of the interaction with polymer and other ions, the nature of the charge carrier, the flexibility of polymer segment, etc.\textsuperscript{54,58}

Some studies have been done on the ion transfer mechanism inside polymer electrolytes, but there is still no clear picture of the movement of ion inside the polymer electrolyte by now. Papke et al.\textsuperscript{59} found that Na\textsuperscript{+} mostly reside inside helical PEO crystal regions and their vibrational spectroscopic showed a quasi-tetrahedral coordination of Na\textsuperscript{+} with oxygen. Greenbaum\textsuperscript{60} reported that the oxygen coordination with Na\textsuperscript{+} in PEO/NaClO\textsubscript{4} complex at -85\degree C was tetrahedral based on their NMR. Armand\textsuperscript{61} suggested a helical structure with small ions lying inside the helix of PEO/salt complex as shown in Figure 2.5. Assuming no anion motion, they proposed a hopping mechanism with only cations moving down channels within PEO helical crystalline structure. This model cannot explain the ion motion in amorphous regions.\textsuperscript{1}

Gray\textsuperscript{1} suggested another picture of the ion movement associated with the polymer segmental motions via making and breaking the co-ordination bonds between cations and polymers, resulting in more free volume for ion diffusion under the electric field. Considering the ion-ion interaction and different ionic species in polymer electrolyte, he suggested two types of ionic motions as shown in Figure 2.6. Figure 2.6 (a) illustrated the ion motion assisted by polymer chain motion. Figure 2.6 (b) illustrated the ion motion from ionic cluster to ionic cluster with polymer chains acting as anchor points. He pointed out that the detailed mechanism depends to a large extent on the concentration of salts in polymer electrolytes.
Figure 2.5  A helix model of the crystalline PEO/salt complex\textsuperscript{61}
(a) below $T_m$  (b) above $T_m$
Figure 2.6  Representation of cation motions in a polymer electrolyte (a) assisted by polymer chain motion only; and (b) taking account of ionic cluster contributions.\textsuperscript{1}
2.1.5.2 Empirical Relationships of the Conductivity Temperature Dependence

The ionic conductivity of polymer electrolytes is temperature dependent. Some empirical relationships have been developed to fit extensive ionic conductivity data of various polymer electrolytes at different temperatures, which include Arrhenius law equation, Vogel-Tamman-Fulcher (VTF) equation, Williams, Landel and Ferry (WLF) equation, etc.

Arrhenius law equation as shown in equation (2.2) is a basic relationship, which describes the linear relationship of \( \ln \sigma \) with \( \frac{1}{T} \).

\[
\sigma = \sigma_0 \exp\left( -\frac{E_a}{RT} \right)
\]  

(2.2)

where \( \sigma_0 \) is conductivity at the absolute temperature \( T=0 \) K, \( E_a \) is the activation energies, and \( R \) is the gas constant. Muller\(^62\) studied the PEO\(_8\)-LiCF\(_3\)SO\(_3\) polymer electrolyte and fitted the data with Arrhenius law. The activation energy was 2.0 eV at temperature below 55\(^0\)C and it turned to 0.6eV at temperature above 55\(^0\)C. Similar trends were also observed in other polymer electrolytes such as PEO/NaSCN, PEO/NaCF\(_3\)SO\(_3\), PEO/NaI and PEO/LiCF\(_3\)SO\(_3\).\(^63\)

The Vogel-Tamman-Fulcher (VTF) equation is in the following form:

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

(2.3)

where \( T_0 \) is a reference temperature corresponding to an ideal glass transition temperature at the thermodynamic equilibrium; \( A \) is a pre-exponential factor, which is determined by the transport coefficient and proportional to the number of carrier ions, \( B \) is a constant with the dimensions of energy, \( k \) is the Boltzmann constant.\(^63\) Chabogno\(^64\) studied the conductivity temperature dependence of PEO/LiI and PEO/LiSCN electrolytes and found
that the one with smaller anion $I^-$ behaved as the double-Arrhenius type but one with larger anion SCN$^-$ fits VTF type as showed in Figure 2.7. 63

The ionic conductivity behavior of some polymer electrolytes was found to fit Williams, Landel and Ferry (WLF) equation well. The WLF equation is described in the following equation:

$$\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T - T_g)}{(C_2 + (T - T_g))}$$  \hspace{1cm} (2.4)

where $\sigma(T)$ and $\sigma(T_g)$ are ionic conductivity at T and Tg respectively, $C_1$ and $C_2$ are constant. WLF equation incorporates the relaxation processes of polymers into the relationship using shift factor, $a_T$. The shift factor is the ratio of any mechanical relaxation process at temperature to its value at some reference temperature. 1,63 Killis et al 65 found that the ionic conductivity temperature dependence of PPO network/NaB(C6H5)4 complex could be expressed using WLF equation with the parameters as listed in Table 2.2.

2.1.5.3 Theoretical Model of the Temperature Dependence

Theoretical models have been developed to describe the conductivity dependence on temperature. Among them the free volume approach is one of the simplest ways to understand polymer segmental mobility. Free volume models have been extensively used in polymer electrolyte studies. In the free volume model, motion is assumed to be a non-thermally activated process but occurs as a result of redistribution of the free volume. 1,66
Figure 2.7   Arrhenius-type plots for log\(\sigma\) vs T\(^{-1}\), for PEO/LiI and PEO/LiSCN complexes. The behavior for the larger SCN is VTF type and for the small I is double arrhenius type\(^{63,64}\)

Table 2.2     WLF parameters for cross-linked PPO/Na B(C\(_6\)H\(_5\))\(_4\) electrolytes\(^{63,65}\)

<table>
<thead>
<tr>
<th>Na(^+)/PO unit</th>
<th>(T_g) ((^0)C)</th>
<th>(C_1)</th>
<th>(C_2)</th>
<th>(\sigma(T_g)) (S/cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>40</td>
<td>5.6</td>
<td>56.7</td>
<td>1.3x10(^{-11})</td>
</tr>
<tr>
<td>0.010</td>
<td>46</td>
<td>5.2</td>
<td>61</td>
<td>1.5x10(^{-10})</td>
</tr>
<tr>
<td>0.017</td>
<td>57</td>
<td>6.1</td>
<td>79.5</td>
<td>7.1x10(^{-10})</td>
</tr>
<tr>
<td>0.034</td>
<td>65</td>
<td>6.5</td>
<td>84.5</td>
<td>2.7x10(^{-9})</td>
</tr>
<tr>
<td>0.051</td>
<td>69</td>
<td>6.8</td>
<td>80.5</td>
<td>8.1x10(^{-9})</td>
</tr>
</tbody>
</table>
Miyamoto and Shibayama\textsuperscript{67} proposed a model based on the extension of free volume theory, which allows explicitly for the energy requirements of ion motion relative to counter ions and polymer host. Later Cheradame \textsuperscript{68} elaborated this model and he combined the Arrhenius and free volume behavior together in the following form:

\[
\sigma \propto \exp\left( -\frac{\gamma v^*}{v_f} - \frac{\Delta E}{RT} \right) \tag{2.5}
\]

Where \( v_f \) is the free volume, \( v^* \) is the critical free volume of the polymer, \( \gamma \) is the Lagrange parameter and \( \Delta E \) is the activation energy taken as the following form:

\[
\Delta E = E_a + E_b + \Delta W/\epsilon_s \tag{2.6}
\]

where \( E_a \) is the potential energy barrier for displacement of the polymer segment, and \( E_b \) is the activation energy which the ion requires to jump. Bruce\textsuperscript{69} pointed out that a free volume expression of the ionic conductivity on temperature can be derived into a similar form of VTF or WLF, but VTF and WLF are empirical and their validity do not depend on free volume theory.

Bruce\textsuperscript{69} stated that free volume models can describe the conductivity behavior to some extent, but they ignored the kinetic effects associated with macromolecules and also the models were not directly related to the microscopic picture. He further pointed out that as a result, these models did not predict straightforwardly how such variables such as ion size, polarisability, ion pairing, solvation strength, ion concentration etc., affect the conduction process.

Adam and Gibbs\textsuperscript{70} proposed another approach, the configuration entropy model, by introducing two parameters (the number of lattice site and number of distorted bonds) into the free volume theory. The mass transportation mechanism in this model is assumed
to be a group cooperative rearrangement of the chain with the probability $W$, as expressed in the following equation:

$$W = A \exp\left(-\frac{\Delta \mu \nu_c^*}{kT S_c}\right)$$

(2.7)

where $A$ is a coefficient, $\nu_c^*$ is the minimum configuration entropy required for rearrangement, $S_c$ is the configurationally entropy at temperature $T$, and $\Delta \mu$ is the free energy barrier per mole which impedes the rearrangement.$^{1,55}$ Bruce$^{69}$ mentioned that both VTF and WLF equation can be derived from the configurationally entropy model.

More models based on the modification of the free volume theory and configuration entropy theory or dynamic bond percolation has been propered.$^{71}$ None of them can precisely predict the conductivity of polymer electrolytes due to their complexity.

2.2 Polyurethane Electrolytes

Thermal plastic thermoplastic polyurethane (TPU) is a linear block copolymer with alternating sequences of hard segments and soft segments. It has multi-phase morphology with interconnected or isolated hard segment domains formed by strong hydrogen bonding of the urethane units distributed in the soft segment. The hydrogen bonding in the hard domains forms a physical network to enhance the properties of polyurethane.$^{72}$ The polyether-based polyurethane is good polymer matrix candidate for polymer electrolytes. The ether-based soft segment complexed with salt can give ionic conductivity and the network structure formed by hard segments can provide dimension stability.$^{55}$
2.2.1 Basic Structure of Thermoplastic Polyurethane

Polyurethanes (PUs) are one of most popular commercial polymers, which include versatile materials with various composition and properties. All complex reaction products of isocyanates and polyhydroxy compound are considered as polyurethane. The polymer chains of polyurethane can be either linear or slightly branched (thermoplastic polyurthane) or cross-linked (thermosetting polyurethane). The history of polyurethanes can go back to 1937 when O.Bayer reacted diisocyanates with aliphatic diols to make fiber. After the Second World War the polyurethane elastomers and foams were developed.

Polyurethane is synthesized by the reaction of isocyanate function group with function group bearing hydrogen like hydroxyl as illustrated in equation 2.8. It is composed by the three basic building units: polyol, diisocyanate and chain extender as shown in Figure 2.8. The desired properties of polyurethane such as strength and stiffness can be obtained by tailoring its three basic units.

\[
R_1 \text{N} \equiv \text{C} \equiv \text{O} + R_2 \text{OH} \rightarrow H_2\text{C} \equiv \text{NH} \equiv \text{O} \equiv R_2
\]  
(2.8)

The selection of isocyanates and polyl is based on the target properties of polyurethane products. The most well known isocyanates include Toluene diisocyanate (TDI), 4,4’-diphenylmethane diisocyanate (MDI) and Polymeric diphenylmethane diisocyanate (PMDI), etc. The main polyols used are polyether or polyester or their copolymer. Although Chain extenders are minor components in the formulations of polyurethane, they not only contribute to the nature and the density of chemical cross-links but also control the nature and size of the hard segments that are
responsible for physical cross-links in linear thermoplastic polyurethanes. The commonly used chain extenders are aromatic diamines and aliphatic or aromatic hydroxy compounds. Many classes of compounds have been investigated as catalysts but only tertiary amines and some tin, mercury and bismuth compounds have acquired practical importance.

The typical preparation procedures of polyurethane can be classified into two basic techniques according to the sequence: the prepolymer route and the one-shot route. In the prepolymer technique, the polyol is reacted with excess of isocyanate first, resulting in the isocyanate capped prepolymer and the prepolymer is then mixed and reacted with the chain extender in the second step. In the one-shot technique, all the reactants are mixed together simultaneously. Figure 2.9 illustrates the two different preparation routes for polyurethane.

![Diagram of urethane block copolymer]

Figure 2.8 The basic units in a urethane block copolymer
Figure 2.9 Prepartion routes for polyurethane: (a) the prepolymer reaction route and (b) one shot route \(^{75}\) (cont.)
Figure 2.9  Prepartion routes for polyurethane: (a) the prepolymer reaction route and (b) one shot route.\textsuperscript{75}
2.2.2 Kinetic of Polyurethane Polymerization

The elemental kinetic mechanisms of urethane formation from active hydrogen bearing compounds and isocyanates are very complex and are still under studied. For convenience, an Arrhenius type phenomenological rate law as described below has been widely used in most studies with success.\(^\text{76,77,78}\)

\[
\frac{d[NCO]}{dt} = -k[R\,NCO]^a[R\,OH]^b = -k[NCO]^a[OH]^b
\]

\(k = Ae^{-Ea/RT}\)  \hspace{1cm} (2.9)

Where \([NCO]\) and \([OH]\) are the concentrations of the isocyanate and the active hydroxyl group in reaction, respectively. The parameters, \(a\) and \(b\), represent the order of reaction with respect to isocyanate and active hydroxyl group. In equation (2.10), \(k\) is rate constant, \(A\) is an Arrhenius coefficient, \(Ea\) is activation energy, \(R\) is the gas constant and \(T\) is temperature in Kelvin unit. When catalysts are used in reaction, the rate constant also depends on catalyst concentration and can be expressed in the following expression:

\[
k = [Cat.]^c A e^{-Ea/RT}
\]

where \([Cat.]\) is catalyst concentration and \(c\) is the order of the reaction with respect to catalyst.\(^\text{132}\) Parnell\(^\text{76}\) found that in reactions with minimal catalyst concentration the order of reaction is close to that of uncatalyzed urethane reaction. For simplicity, the rates of reaction in equation (2.10) can be expressed as addition of catalyzed and uncatalyzed urethane reaction as following equation.\(^\text{76,77,78}\)

\[
k = k_1 + k_2 = A_1 e^{-Ea_1/RT} + [Cat.]^c A_2 e^{-Ea_2/RT}
\]

\hspace{1cm} (2.12)
where \( k_1 \) is the rate constant of uncatalyzed reaction and \( k_2 \) is the rate constant of catalyzed reaction. Equation (2.9) can be simplified as equation (2.13), when the reaction occurs at the equal stoichiometry \([C]=[NCO]=[OH]\):

\[
\frac{d[C]}{dt} = -k[C]^n
\]  

(2.13)

where \( n=a+b \), is the overall order of reaction. This equation also can be rewritten with conversion term, \( \alpha \), and initial isocyanate concentration, \([C]_0\), since \([C] = [C]_0(1-\alpha)\).^{76,132}

\[
\frac{d\alpha}{dt} = -k[C]_0^{1-n}(1-\alpha)^n
\]  

(2.14)

Macosko\(^{77}\) pointed out that the methods used to study the kinetics can fall into two categories: directly monitoring the concentration of the unreacted end groups and measuring the physical properties related to the extent of the reaction such as the modulus, viscosity, conductivity and heat evolution. They used the adiabatic reaction method studied the kinetics of polyurethane with various composition.\(^{78}\) Parnell\(^{76}\) used the Roman spectroscopy and DSC method to study the polymerization kinetics of polyurethane synthesized by polybutylene adipate (PBA), 1,4 butanediol (BDO) and 4,4’ diphenylmethane diisocynate (MDI). He reported \( n \) value of 1.7 in his study, which showed the agreement with Macosko et al.\(^{77}\) He investigated kinetic behavior of TPU in reactive extrusion process of TPU/PVC blend as well as the effect of catalyst on the kinetics. A kinetic model was proposed based on the Arrhenius type phenomenological rate law as described in equation (2.14) to predict the experimental data well over a certain range of catalyst levels and polymerization temperatures. It was found that the
TPU polymerization in-situ with PVC also obeyed the same nth order, phenomenological kinetic rate law followed by neat TPU and that the overall rate constant employed in the rate law increased in the presence of PVC due to the catalyst effect of the stabilizer of PVA on the polymerization of polyurethane.\textsuperscript{132}

Jeung\textsuperscript{55} investigated the effect of alkali metal salt on the kinetics of polyurethane with the same method as the one used by Parnell\textsuperscript{76}. Polyurethane was in-situ reacted by (PTMG), 1,4 butandiol (BDO) and 4,4’ diphenylmethane diisocynate (MDI) in the presence of salts. Salts were believed to act as catalysts accelerating or decelerating the reaction, depending on their concentration. The kinetic model of polyurethane with minimal catalyst was used to predict the kinetic behavior of urethane reaction in this system. Average value of n of 1.2 was obtained from the different polymerization temperatures and LiClO\textsubscript{4} mole concentrations.

2.2.3 Polyurethane Electrolytes

Polyurethane is used as an alternative candidate as the host polymer for polymer electrolyte because of their good chemical stability, excellent mechanical properties and low glass-transition temperature of soft segments.\textsuperscript{79,80,81,82,83,84,85} Significant advances have been made in both the study of the material properties and the understanding of their structure and ionic conduction relationship.

Kilis et al.\textsuperscript{86} studied a series of polyether and polyester-based polyurethane electrolytes. They described the polyurethane network electrolytes as self-ionizable networks. Carvalho\textsuperscript{87} studied the ionic conductivity of polymer electrolytes based on a
polyurethane network with LiN(CF$_3$SO$_3$)$_2$ (LiTFSI) as shown in Figure 2.10. The cross-linking density of polyurethane was controlled by using the PEO chain with different lengths.

Yang et al.\textsuperscript{88} synthesized a novel salt oligo-ether sulfate (SPEG) and prepared a series of PU/SPEG polymer electrolytes. SPEG showed a significant effect on polyurethane morphology. The ionic conductivity of PU electrolytes increased as the SPEG content increased. The PU electrolyte with SPEG-600 (oligo-ether sulfate prepared with PEG-600) had a higher ionic conductivity than the one with SPEG-400 (oligo-ether sulfate prepared with PEG-400).

Kuo et al.\textsuperscript{89} studied the effect of the hard segment content in PEG-based polyurethane on their ionic conductivity. The variation of the ratio of hard segments to soft segments in polyurethane electrolytes was achieved by controlling the mole ratio of polyethylene glycol to chain extender. It was found that the conductivity decreased with increasing hard segment concentration due to segmental motion restriction of the polymer chain resulted from the decrease in the free volume.

Hong et al.\textsuperscript{90} synthesized hyperbranched polyurethane with AB$_x$ macromonomers containing linear units as the host polymer. Two types of novel hyperbranched polyurethanes, HP$_a$ and HP$_b$, were synthesized as shown in Figure 2.11. They pointed out that the ionic conductivity can be achieved by using longer ethylene glycol chains and higher concentrations of LiClO$_4$ in the HP materials.
Figure 2.10  The reaction scheme of polyurethane network\textsuperscript{87}

Figure 2.11  Schematic diagram of the synthesis of HPa and HPb\textsuperscript{90}
Huang et al. synthesized polyurethane with three different structures: linear, hyperbranched and comb-cross-linked structures, as host polymers for polymer electrolytes. They found that salt concentration significantly influenced the morphology as well as their ionic conductivity. When [O:Li] were controlled to be 12, 4 and 4 for linear, hyper-branched and comb cross-linking polyurethane, respectively, the electrolytes displayed micro-phase separated morphology and the ionic conductivity reached maxima respectively at $2.2 \times 10^{-7}$ S/cm, $2.8 \times 10^{-6}$ S/cm and $2.8 \times 10^{-5}$ S/cm at room temperature.

Digar et al. cross-linked polyurethane by radiation curing the vinyl group incorporated on the side chain prior to reaction. The cross-linking process was carried out by irradiating linear polyurethane with reactive diluents (such as triphenyl glycol diacrylate (TPGDA), methyl methacrylate (MMA), acrylonitrile (AN), ethyl acrylate (EA)) in the presence of LiClO$_4$. The conductivity of the prepared electrolytes followed the VTF relationship. The $T_g$ of the hard segment decreased with the increase of the salt concentration, which was explained as the result of the phase mixing between hard and soft segments in the presence of LiClO$_4$.

Jeung proposed a solvent-free method to prepare the polyurethane electrolytes via the in-situ polymerization of polyurethane in the present of salts. Both polyether-based polyurethane electrolytes and polyester-based polyurethane electrolytes with salts containing various cation were studied. The $T_g$ and the crystallinity of the soft segments decreased with the addition of salts while the $T_m$ of the soft segment increased due to the formation of polymer/salt complex crystal. Polyether-based polyurethane were found has
a higher ionic conductivity than polyester-based polyurethane electrolytes. That was explained as that the polyether chain was more flexible than polyester chain, resulting in more ion mobility. The temperature dependence of ionic conductivity of all the prepared polyurethane followed the Arrhenius behaviors. The phase mixing between the hard segments and soft segments initiated by the interaction of cation with both soft segment and hard segment were found by the evidences that the $T_m$ and degree of the crystallinity of hard segment decreased and that the typical absorbing peaks in FTIR analysis shifted. It was consistent with the results of other researchers.$^{89,92}$

The interaction between salt and polyurethane plays an important role on the final properties of polymer electrolytes. They can contribute to the salt solvation in polymer, the morphology of electrolytes, ionic conductivity, etc.$^{1,55}$ A series of technology including IR spectroscopy, DSC, AFM, etc. have been used to investigate their relationship.

McLennaghan et al.$^{93}$ conducted H$^1$ and $^{13}$C-NMR studies on the interactions of salt with polyurethane. The absorbance wavelength shifts of urethane protons were identified. Heumen et al.$^{94,95}$ studied the IR spectrum of PTMG-based polyurethane electrolytes with LiCF$_3$SO$_3$ and Li(CF$_3$SO$_2$)$_2$N. They pointed out that the H-bonded N-H band was shifted from its original 3310 cm$^{-1}$ to 3300cm$^{-1}$ at high salt concentration due to the coordination of the Li$^+$ with ether oxygen atoms which used to be hydrogen-bonded with the N-H group. Based on the intensity changes and shifts of the peaks in the IR spectra, they believed that Li$^+$ not only interacted with the electron-rich oxygen atoms of
the soft segment but also interacted with the electron-rich nitrogen atoms of the hard segments.

Zhu et al. investigated a series of PEG-based polyurethane electrolytes with NaClO₄ and reported that the oxygen atoms of carbonyl and ether oxygen groups had different activities to cations according to the IR analysis. The absorption peak intensity of Na⁺ coordinated C-O-C increased with the addition of NaClO₄ first, then plateaued at high salt concentrations. They explained that this indicated that the coordination of C-O-C with sodium cations reached the saturated level. At the same time, the peak intensity of the Na⁺ coordinated C=O increased slightly at low salt concentration first and then increased sharply at high salt concentrations. They suggested that there was selective coordination of Na⁺ with ether oxygen and carbonyl oxygen: Na⁺ prefers to interact with the ether groups rather than carbonyl groups at low salt concentrations; and the interaction between carbonyl groups with cations is favored only after the coordination between Li⁺ with ether oxygen turns saturated. They also noticed that the hard segments aggregation decreased after the addition of the salts in the AFM studies and explained it as the result of the competition between hydrogen bonding and cation coordination, with the hard segments. Coordination between cations with carbonyl groups weakened the hydrogen bonding of the hard segments, resulting the phase mixing of the soft segments and hard segments.

Huang et al. studied the ion state in polyurethane electrolytes using the Raman spectroscopy. The ClO₄⁻ stretching band became broad and shifted to higher wave numbers after the salt was mixed with polyurethane. They studied the relative proportion
of free ion, ion pair and ion aggregation in the electrolytes by resolving these bands using Lorentzian lines to obtain peak deconvolution. They believed that the component at 631 cm\(^{-1}\) should be assigned to free-ions and the component at 638 cm\(^{-1}\) should be attributed ion pair Li\(^+\)ClO\(_4^-\). The appearance of new bands at higher frequencies indicated the presence of aggregates of the salts in the samples.

2.3 Modified polysiloxane Electrolytes

Modified polysiloxane is an alternative polymer structure to PEO in the respect of decreasing crystallinity and increasing flexibility of polymer electrolytes. Polysiloxanes, due to the very low \(T_g\) (The \(T_g\) of poly(dimethylsiloxanes) is around \(-123^\circ C\)) and chemical inertness, are good candidates for backbones of host polymers.\(^{17}\) Gray\(^1\) mentioned that the backbone of the alternating silicon and oxygen atoms (-Si-O-) is a poor media for salt solvation because the Si-O bond tends to suppress the oxygen donor numbers, therefore polysiloxanes have to be modified with polyether to achieve good ion coordination characteristics.

2.3.1 Modified Polysiloxane Electrolytes with Comb Structure

A variety of polyether short chains can be bound to silicon.\(^{97}\) Bannister et al.\(^{98,99}\) synthesized polysiloxane with comb structure for their potential application in cryobiology and also investigated the conducting properties of their salt complexes.\(^{100}\) Kohama et al.\(^{101}\) synthesized polysiloxanes with comb structure by reacting poly(methylsioxane) (PHMS) with low molecular weight alcohols under catalysts. Smid
et al. synthesized a comb polysiloxane, poly((ω-methoxyoligo-(oxyethylene) ethoxy) methylsiloxane)s (PMMS-n), with oligo(oxyethylene) side chains from poly(methylsiloxane) with zinc octanoate as catalyst. They found that the number of oxygen atoms in the oligo(oxyethylene) side chain has an effect on the properties. The PMMS-5, PMMS-8, PMMS-12 (the number referring to average number of oxygen atoms in the oligo(oxyethylene) side chain of the comb polymer) were clear, viscous liquids at room temperature, and PMMS-16 and PMMS-22 were waxy solid. They concluded that modified comb polysiloxane was no longer amorphous at the room temperature when the length of the side chain reached a certain value.

Oh et al. developed two types of mono-comb poly(siloxane-g-ethylene oxide)s electrolytes: PMHSnC-A and PMHSnC-B as shown in Figure 2.12. These electrolytes with LiTFSI showed ionic conductivities above $10^{-4}$ S/cm at room temperature. B type electrolytes showed higher ionic conductivity than A type. They explained that Si–O bond had more ionic characteristics and less rotation barriers than Si–C, which makes PMHSnC-B structure to be more flexible and polar than PMHSnC-A structure.

Hooper et al. synthesized a series of double-comb structured polysiloxane polymers containing oligo(ethylene oxide) in the side chains as shown in Figure 2.13. It was found that the ionic conductivity of these electrolytes with LiN(SO$_2$CF$_3$)$_2$ increased with n ( n is the number of the repeat ethylene oxide unit on the branch.) first and then decreased. Later they synthesized another series of double–comb polysiloxanes with two oligo(ethylene oxide) groups on each silicon as shown in Figure 2.14. It was found that
polymer electrolytes based double-comb polysiloxanes displayed higher ionic conductivity than the mono-comb ones.

Figure 2.12  Structures of two mono-comb poly(siloxane-g-ethylene oxide) (a) PMHSnC-A and (b)PMHSnC-B\textsuperscript{97}

Figure 2.13  Schematics of the synthesis of polyether-modified polysiloxane\textsuperscript{105}
2.3.2 Modified Polysiloxane Electrolytes with Block Copolymer Structure

Besides of polysiloxanes with comb structure, polysiloxanes with block copolymer structures have also been synthesized. Sun\textsuperscript{107} reacted dimethoxy/diethoxysilane, or tetramethoxysilane with hydroxyl group-containing components to prepare diepoxy silane for the synthesis of silacrown ethers and mono-exchanged aloxysilane. Nagaoka et al.\textsuperscript{108} used dimethyl dichlorosilane and mono-, di-, tetra-, and nonaethylene glycol to synthesize PDMS-PEO copolymers \((-\text{SiMe}_2\text{O(CH}_2\text{CH}_2\text{O})_n\text{m}}\text{ (n=1,2,4,9))}. They investigated the relationship among $T_g$ of these polymers and the copolymer composition, as well as their ionic conductivity. The highest conductivity observed in the PDMS-PEO copolymer/LiClO$_4$ at room temperature was $1.5 \times 10^{-4}$ Scm$^{-1}$ when $n=4$. Mei et al.\textsuperscript{109} synthesized a phenyl siloxane-PEO network using phenyl trichlorosilane and PEO.
Sun et al.\textsuperscript{110} studied the relationship of the n value (the number of the repeating ethylene oxide unit in the PEO segment) and the ionic conductivity of the PDMS-PEO copolymers electrolytes. The ionic conductivity exhibited the minimum value around n=9. They pointed out that n affected the conductivity of these polymer electrolytes via its influence on two factors (1) the flexibility of the copolymer; and (2) the relative amount of oxyethylene available for solvation of the ions. If n>9, the influence on the first factor dominates; and if n<9, the influence on second factor dominates.

2.3.3 Modified Polysiloxane Electrolytes with Cross-linked Structure

Polymer electrolytes based on uncross-linked polysiloxanes have shown good conductivity, but they have poor dimension stability. So polysiloxane electrolytes are cross-linked to some extent in order to improve their dimension stability. However, cross-linking between polysiloxane chains directly results the loss of flexibility of polysiloxane chains, which decreases the ions mobility.\textsuperscript{111,112} The new approaches such as constructing semi-IPNs structures with polysiloxane or incorporating plastizer into cross-linked polysiloxane have been employed.

Oh et al.\textsuperscript{97,113} studied semi-IPNs poly(siloxane-g-ethylene oxide)s electrolytes with poly(siloxane-g-ethylene oxide)s entrapped inside the network formed by the cross-linking agent, poly(ethylene glycol) dimethacrylate (PEGDMA). They found the ionic conductivity of this semi-IPN type polysiloxane could approach to 10\textsuperscript{-4} S/cm at 37 \degree C. Their ionic conductivity depended on the ratio between the mono-comb poly(siloxane-g-ethylene oxide) and the cross-linking agent.
Kang et al. synthesized a cross-linker based on the oligo(ethylene oxide) grafted polysiloxane with acrylate functional end group as shown in Figure 2.15. The cross-linked solid polymer electrolytes were prepared by UV-radiation or thermal curing a homogeneous solution of the above acrylate end-caped polysiloxane cross-linker, LiCF$_3$SO$_3$, an initiator and plastilizer poly(ethylene glycol) dimethyl ether (PEGDME). The obtained polymer electrolytes were transparent and amorphous at room temperature. The dimensional stability of the prepared polymer electrolyte film depended on the side chain ethylene oxide length (y), the number of the repeating unit of the main chain (x) and the content of PEGDME. The conductivity of the polymers without the addition of PEGDME was in the range from 1.6 x10$^{-5}$ to 5.8x10$^{-5}$S/cm at 30 °C. Their ionic conductivity gradually increased with increasing the PEGDME content.

Some study has been reported on single ion conducting polymer, in which the anion is immobilized on the polymer backbone to overcome problems associated with strong ion pairing. Kurono et al. prepared a series of polymer electrolytes based on borosiloxane with trapped anions as shown in Figure 2.16. The anion trapping was realized by anion interaction with the Lewis acidic boron in the polymer backbone. However, due to the high rigidity of the borosiloxane polymer their ionic conductivity is low.
Figure 2.15  Structure of acrylate end-caped polysiloxane-g-oligo(ethylene oxid) cross-linker

Figure 2.16  Schematics of the synthesis of borosiloxane polymer
2.4 Polyurethane Blend and Their Electrolytes

Polymer blending is an economical way to produce materials with tailor-made properties without synthesizing new materials.\textsuperscript{116} Polymer electrolytes based on polyurethane blends have also been studied. A second polymer is blended with polyurethane to improve the ionic conductivity or enhance the dimension stability. The miscibility of blends and their morphology have significant impact on the ionic conductivity of polymer electrolytes based on polyurethane blend.

2.4.1 Miscibility of Blends of Polymers with Specific Interaction

The miscibility of polymer blend is an important factor for obtaining the desired properties. There are several specific factors contributing to the miscibility of polymer blends, such as polarity, specific group attraction, molecular weight, blend ratio and crystallinity of the components.\textsuperscript{116}

Theoretical predictions of the miscibility of polymer blends have already been studied by many researchers in academics and industries. The Flory-Huggins theory of polymer blend is one of the basic and well known theories of the thermodynamics of polymer blends using mean field theory. In the original Flory-Huggins theory, the interaction parameter, $\chi$, is proportional to $1/T$. The modified Flory-Huggins theory replaced $\chi$ with a more general function $\chi(T, \phi, P)$, where $T, \phi, P$ are the temperature, component ratio and pressure respectively. So $\chi$ depends on temperature, pressure, and concentration, which allows for describing various phase diagrams.\textsuperscript{117,118}
However the expression of $\chi$ is still a semi-empirical form. Moreover, they cannot be used to predict the miscibility of blend of polar polymers with specific strong interaction between polar groups. The interaction between polar groups cannot be expressed by the Van der Waals type interaction. Few theories can precisely describe the miscibility of polymer blend with specific interaction like hydrogen bonding, dipole-dipole interaction, ionic interaction, metal coordination, and other strong interactions between the electron donor and electron acceptor. Painter et al. developed association models to describe the free energy changes related to hydrogen-bonding between components of binary polymer blends. As mentioned in chapter 2.3.3.1, Kim and Bae proposed a molecular thermodynamic model based on both an extended Flory-Huggins theory and a Debye-Hückel theory modified by Guggenheim to quantitatively interpret the liquidous curves in the resulting phase diagram of polymer electrolytes composed of polyethylene oxide and different salts. Later Bae and his coworker developed a model based on modified perturbed hard sphere chain theory and melting point depression theory to describe the phase behaviours of the blend-based polymer electrolyte composed of polyethylene oxide, polypropylene and salts. Unfortunately, these models only described the phase diagram between the polymer and salt, and did not give any suggestion on the miscibility of polymers in polymer blend in the presence of salts (such as the miscibility of PEO and PPO). For polymer blend based electrolytes, the addition of salt into polymer blend can influence the miscibility of the polymer blend via forming multi polymer/cation coordination. However, there are no thermodynamic models to describe miscibility for polymer blend electrolytes with salts.
Experimentaly, the techniques used in the study of the miscibility and morphology of polymer blends include optical microscopy, DSC, FTIR, SAXS, WAXDS, SEM, TEM and AFM. Among them, optical microscopy, SEM, TEM and AFM can directly provide the observation of the phase morphology of the immiscible or miscible blends. They are selectively used depending on the phase separation scales. In DSC, the $T_g$ shift, melt temperature depression and heat of fusion of the blends can indicate the interaction between polymer pairs. If they are completely miscible, only one $T_g$ can be found, which is between the $T_g$ of the each parent component. In FTIR, the shift and relative intensity change of characteristic absorbing peak associated with certain functional group from the unblended state can provide the information about the interaction existed in the blend if the blend is miscible.

Mani et al. and Li et al. found the salts had compatibilizing effect on polymer pairs. Kim et al. reported that the addition of salt facilitated the miscibility of polymer pairs in their study of the polymer electrolytes based on PEO/poly(oligo[oxyethylene]oxysebacoyl) blend. Their evidence was that the DSC results showed two melting peaks of the blend without LiClO$_4$ when PES/PEO is 60:40; but only one melting peaks was observed after the addition of 10% of LiClO$_4$. They attributed this change to the result of the simultaneous interaction of Li$^+$ with the oxygen atoms of the PEO and ether oxygen or ester oxygen of the PES. Tandel reported that TEM micrographs of the morphology of PEO/PPO electrolytes indicated that the addition of the salt favored the miscibility of PEO and PPO blend.
Rocco et al.\textsuperscript{127,128} investigated the miscibility of polymer electrolyte based on blend of polyethylene oxide (PEO) and poly(methyl vinyl ether-maleic acid) (PMVE-Mac). They pointed out that the observation of only one $T_g$ in DSC of PEO/PMVE-Mac blends with various compositions indicated their miscibility over the entire studied composition range. They explained that the miscibility was attributed to the intermolecular hydrogen bonding between the polymer pairs. FTIR showed that after blending the intensity of the peak from 1600 to 1650 cm\(^{-1}\) decreased and its peak maximum shifted to higher wavenumbers; at the same time the peak originally at 3460 cm\(^{-1}\) shifted gradually to lower wavenumbers. They stated that the O-H groups of PMVE-Mac formed hydrogen bonds with the oxygen atoms of PEO, freeing bonded C=O groups and that the amount of free and self-associated O-H groups decreased to form the inter-associated hydrogen bonds with the PEO oxygen as illustrated in Figure 2.17. They further studied the PEO/PMVE-Mac-based polymer electrolytes with LiClO\(_4\).\textsuperscript{128} Only one $T_g$ is observed in all blend compositions after the addition of LiClO\(_4\). The $T_g$ increased first as the LiClO\(_4\) concentration increased up to 10 wt% and then decreased as more LiClO\(_4\) was added. In the FTIR of blends with LiClO\(_4\) as shown in Figure 2.18, a decrease in the wavenumber from 3447 to 3421 cm\(^{-1}\) as well as the peak shape change was observed with the LiClO\(_4\) concentration increasing from 2.5 to 20 wt%. It was explained as the interaction between the acid group and Li\(^+\). They pointed out that the ion-dipole interaction was stronger than a dipole-dipole interaction therefore a negative shift in the wavenumber happened. It was found that there was a higher fraction of bonded C=O groups than free C=O groups when LiClO\(_4\) concentrations below 5 wt%
based on the relative intensity ratio of each corresponding peak. From the FTIR and DSC results, they suggested there was a preferential formation of complex of PEO/Li+/PMVE-Mac as shown in Figure 2.19.\textsuperscript{128} Later they studied the miscibility of polymer electrolytes based on PEO and poly(bisphenol A-co-epichlorohydrin) (PBE) blend and found the miscibility varied with the salt concentration.\textsuperscript{129}

Gnanaraj et al.\textsuperscript{130} synthesized a comb-like polymer by grafting poly(ethylene oxide) chain onto the macromer poly(ethylene glycol) ethyl ether methacrylate (PEGEEM) and blended this comb-like polymer with PEO to use as host polymer for polymer electrolytes. DSC studies showed one $T_g$ for both the polymer blend and their corresponding electrolytes.

Fonseca et al.\textsuperscript{131} added LiClO$_4$ into the poly(dimethylsiloxane-co-ethylene oxide) P(DMS-co-EO)/poly(epichlorohydrin-co-ethylene oxide) P(EPI-co-Eo) blend. DSC results showed that P(DMS-co-EO) was miscible with P(EPI-co-EO) and formed amorphous blend when the P(DMS-co-EO) content was lower than 15%; and phase separation occurred when extra P(DMS-co-EO) was added. Only one $T_g$ in DSC was observed in the blend with 20% P(DMS-co-EO) after the addition of salt. They suggested that this indicated that the salt enhanced the miscibility of P(DMS-co-EO) with P(EPI-co-Eo). However, the result was inconclusive due to the limited composition ranged studied and the overlapping in DSC pattern.
Figure 2.17  The schematic structures for hydrogen bond interactions between (a) PMVE-MAc/PMVE-Mac and (b) PEO/PMVE-MAc molecules\textsuperscript{127,128}
Figure 2.18  FTIR of PEO/PMVE-Mac (60/40 wt%) blends with different concentration of LiClO₄ in (a) the ether region (b) the carbonyl group region and (c) hydroxyl group region¹²⁷,¹²⁸

Figure 2.19  The schematic representation of formation of complex of PEO/Li⁺/PMVE-Mac¹²⁷,¹²⁸

2.4.2 Miscibility and Morphology of Polyurethane Blends

Technology for blending polyurethane with other polymers has developed over the past years as a means of improving final properties and reducing manufacturing
Polyurethanes are widely used in form of blends with polyvinyl chloride, polyamide, polycarbonate, ABS plastic, polyolefin, etc. They are also important ingredients in paints, adhesives and sealants.

Direct physical mixing of polyurethane with other polymers is the easiest blending way. Guo et al. studied blends of poly(ethylene oxide) and an amorphous copolyester polyurethane. All the blends showed a single $T_g$. The crystallization of PEO was identified in the blends with PEO content higher than 10 wt%. They calculated the interaction parameter for these blends using the melting temperature depression and obtained a value of -3.42 cal/cm$^3$. Wen et al. studied similar blends as the polymer matrix for gel polymer electrolytes. They found that PTMG based polyurethane was immiscible with PEO whereas PEG based polyurethane was partially miscible with PEO.

Most polyurethane blends are not miscible, which leads to the morphology with large scale phase separation. One approach to control the morphology is to enhance their miscibility. In general, the introduction of the specific interaction between parent polymers into blends is an effective way to enhance their miscibility, such as formation of covalent bonds, hydrogen bonds, ionic interaction and other strong interactions between the functional groups of parent polymers. Yong et al. mixed sulfonated polystyrene with a polyurethane with special structure. They incorporated N-methyl diethanolamine into polyurethane as chain extender together with butanediol. After blending, the proton in the sulfonic acid was transferred to tertiary amine and formed amine cation, which had strong interaction with the sulfonic anion. As a result, the miscibility of the polymer blends was improved. They pointed out that the morphology of
the blend was controlled by adjusting the concentration of sulfonic acid and tertiary amine. Another important approach to control the morphology can be accomplished through the reactive process to form interpenetrating polymer network with network morphology via physical cross-linking or chemical cross-linking. The work on IPNs of polyurethane blends is briefly reviewed in the following section.

3.4.2.1 IPNs of Polyurethane blends

As described previously, many polyurethane blends exhibit immiscibility and complicated morphology or phase separation without specific interaction. However, the use of phase separated morphology lead us to develop novel morphology for improving their properties. One of the methods to form different morphologies is in-situ polyurethane polymerization, which can generate polyurethane blend with kinetically controlled morphology.\textsuperscript{132} Parnell\textsuperscript{132} stated that the high reaction activity of isocynate with hydrogen bearing component and the versatility in the formulation of polyurethane make it possible to blend polyurethane with a second polymer through the in-situ polyurethane polymerization and tailor their miscibility to meet the desired morphology-property specification.

In the in-situ blending process, polyurethane monomer, polyol and chain extender or prepolymer are first mixed uniformly with the second polymer, then the mixture is cured after the addition of components with isocynate function group. After complete curing, polyurethane can form a physical network or chemical network in the blend depending on the functionality of the reactants.\textsuperscript{75,132} The in-situ polymerization process
optimizes the mixing of polymer blend and offers an effective way to control the morphology of the polymer blend. Usually, the polyurethane blend prepared by this process can be classified as IPNs according to its definition stated in section 2.1.4, since the blending process initiates the in-situ formation of the polyurethane network structure in the presence of the second polymer. In-situ formed polyurethane blends with some polymers cross-linked and others uncross-linked are termed semi-IPNs; and ones with all the polymers cross-linked are termed full-IPNs. According to Kempner\textsuperscript{56,135}, the cross-linking in the IPNs has a broad definition: it can be physical or chemical cross-linking; the chemical cross-linking can be formed by the covalent bond while the physical cross-linking can be the crystalline of semicrystalline polymers, ionic portion of the ionomers, hydrogen bonding etc. The physical cross-linked IPNs are called thermoplastic IPNs.\textsuperscript{56,135}

A variety of the IPNs of polyurethane blends have been studied, such as IPNs of polyurethanes with poly(methyl methacrylate)\textsuperscript{136,137}, Poly(ethyl methacrylate)\textsuperscript{138}, polystyrene\textsuperscript{139}, poly(vinyl acetate)\textsuperscript{140}, poly(vinyl chloride)\textsuperscript{141}, Poly(vinyl alcohol)\textsuperscript{142} and ploy(vinyl Pyrrolidone)\textsuperscript{143} etc. The morphology of the IPNs structures is controlled by the two competitive processes: the phase separation and the formation of cross-links.\textsuperscript{144,145} The phase separation is resulted from the poor miscibility between different components due to the weak interaction. It is achieved by polymer chain diffusion through a viscous media to form phase domains. Oppositely the formation of cross-links restricts the diffusion and freezes the present morphology.\textsuperscript{144,145} The techniques used to
examine the morphology of these IPNs are same as the ones used on normal blends, such as DSC, TDMA, SEM, TEM and SAXS.\textsuperscript{145}

Cassagnau et al.\textsuperscript{146} synthesized a polyethylene/polyurethane blend via in situ polymerization of monomers or prepolymer dispersed in a molten polyethylene matrix in an internal mixer. They found the solubility difference between isocyanate monomers and polyol in molten PE induced an imbalanced stoichiometry, which limited the degree of polymerization during the blending process.

Parnell et al\textsuperscript{132,147} developed a reactive blending process for producing Poly(vinyl chloride) /thermoplastic polyurethane (PVC/TPU) blends with twin screw extruder. This process includes two fundamental stages: (1) the compounding and plasticization of PVC with the polyol and chain extender of the TPU; and (2) the subsequent polymerization of TPU in-situ with PVC to produce a PVC/TPU blend after adding the diisocyanate. They studied the intermolecular interaction in both stages of the reactive blending process by the Raman spectroscopy. It was found that the reaction induced the PVC/TPU blend phase separation accompanied with in-situ polyurethane polymerization. In the first stage, the TEM studies of the PVC/PBA blend showed a relatively homogeneous morphology with PVC content up to 50\%. Also DSC trace of the fast quenched sample of PVC/PBA/BDO blend with high PVC content displayed one broad glass transition intermediate between those of pure PVC and PBA. For the samples with low PVC blends, they pointed out that the result was inconclusive because the rapid quenching failed to yield a completely amorphous blend as evidenced by a broad PBA melting endotherm. They believed that the broad glass transitions in these samples might suggest
some degree of heterogeneity. In the second stages, the TEM of PVC/TPU exhibited heterogeneous, multiphase blend morphologies with significant phase mixing. By comparing the phase morphology of PVC/TPU reactive blend with PVC/TPU melt blend, it was noticed that the melt blends showed less diffuse interfaces between phases than analogous reactive blends. The PVC/TPU melt blend with blend ratio equal to 44/56 wt% showed a dispersion of TPU rich phases approximately 500nm in diameter in a PVC rich continuous phase. However, the corresponding reactive blend showed phase inversion with a dispersion of PVC rich phases in a TPU rich continuous phase.

Hourston et al.\textsuperscript{144} prepared polyetherurethane/Polyethylmethacrylate IPNs by simultaneous polymerization of both poly(propylene glycol) based polyurethane and polyethylmethacrylate from monomers. The morphology and phase continuity of the blends with various blend ratios were studied using TDMA, M-TDSC, TEM and SAXS. They stated that the tan$\delta$ vs. temperature plots of the neat polymers and the polymer blends with 90:10, 80:20, 30:70, 20:80, 10:90 IPN compositions showed a single-transition peak; while the intermediate compositions exhibited a shoulder at the second transition and IPNs with 50:50 composition showed three transitions. They concluded that the blend was semi-miscible over the entire composition range and there were multiphase morphology, which was also confirmed by M-TDSC data. No gross phase separation was observed in TEM images of all compositions. They pointed out that the phase domains were not well defined, but still gradual change can be observed in compositions. SAXS results implied that the domain size distribution of these IPNs were quite broad.\textsuperscript{148}
Zhang et al.\textsuperscript{149} prepared a series of semi-IPNs biodegradable materials via in-situ polyurethane polymerization. Polyurethane networks were in-situ formed in the presence of different natural polymer derivatives, such as nitrocellulose\textsuperscript{150}, nitrokonjac glucomannan\textsuperscript{151} and benzyl konjac glucomannan(B-KGM)\textsuperscript{152,153}. In their work on the blend of benzyl starch (BS) with TPU, they found there was strong hydrogen bonding between the BS and PU network based on the absorbing intensity decrease of unbonded carbonyl group and intensity increase of bonded N-H in FITR with addition of BS. Their morphology study showed the BS domain became a dual continuity phase with increasing the BS concentration. They pointed out that ESR implied that BS stuck tightly to PU and led to the mobility of the PU network being restricted, resulting in their good mechanical properties.

Some work has been done on polyurethane/polysiloxane IPNs. Klepner et al\textsuperscript{154} prepared polyurethane/polysiloxanes IPNs by mixing polymers in aqueous emulsions together with their cross-linking agents and stabilizers. Schurb and Evans\textsuperscript{155} prepared IPNs using various diisocyanate prepolymerms and an amine-modifed polydimethylsioxane. However, no detailed studies on the morphology of these blends were reported. Vlad et al\textsuperscript{156} prepared a series of polyurethane/polydimethysiloxane IPNs in sequent procedure. The PU network was synthesized from 2,4-TDI and castor oil with glycerol as cross-linked agent. The polysiloxane network was synthesized from a $\sigma,\omega$-dihydroxypolydimethylsiloxane. TEM images of the PU/PDMS IPNs showed different heterogeneous phase morphology with various compositions. They reported that It exhibited the discontinuous morphology when composition ratio reached unity.
Attractive groups between the polyurethane and other components were introduced to improve the miscibility in the IPNs by various researchers\textsuperscript{157,158}. The incorporation of relatively small number of ionic moieties into polyurethane backbone significantly alters the properties of the materials\textsuperscript{159,160}.

Yu et al.\textsuperscript{158} incorporated a positive charge group –N(CH\textsubscript{3})\textsubscript{2} into a series of polyurethane/polyacrylates IPNs to enhance the interaction between phases. The positive charge group was added to polyacrylates by polymerization N,N-Dimethylethanolamolamic ethacrylate DMA with other acrylate monomer. A negative charge group (–CN) was incorporated into polyurethane from hydroxyl group-terminated butadiene-acrylonitrile copolymer. The molar ratio of the –N(CH\textsubscript{3})\textsubscript{2} group to the –CN group was controlled to unity. They investigated the effect of the interaction of positive charge group and negative charge group on the morphology of IPNs by SAXS and SEM. They found that the data such as short-range correlation distance, the transverse length of domain, the interfacial area etc. indicated the miscibility between two components increased due to the interaction of the charged groups.

Jaisankar et al.\textsuperscript{161} prepared ionomeric IPNs with PVC and PU anionomers using sequential polymerization. The ionomer, 2,4-dihydroxy benzoic acid (DHBA) was used to incorporate –COOH group in polyurethane chain. Quaternization of the –COOH groups was realized by the addition of triethylamine (TEA). It was found that viscosity increased during formation of the ionomeric IPNs. SEM images showed that more equal dual phase continuity after ionomer formation and the miscibility of the IPNs was improved. They suggested that the ionic interaction can be used to control the IPN miscibility to obtain a
semi-miscible morphology. Also as a result of ionic group interaction, the thermal stability and mechanical properties were enhanced.

2.4.3 Polyurethane Blend-Based Polymer Electrolytes and Their Ionic Conductivity

Due to the limitation of the low ionic conductivity of polyurethane/salt electrolytes, the majority of the studied polyurethane blend-based polymer electrolytes are gel polymer electrolytes which are swollen by a large amount of plasticizer such as PC or EC. Few works on polyurethane based solvent-free polymer electrolytes have been reported. Most of these works mainly focus on achieving high ionic conductivity. The effects of factors such as salt type, preparation method, cross-linking and morphology on the properties of polyurethane blend electrolytes are still understudied.

Shibata et al.\textsuperscript{162} studied polymer electrolytes based on blends of polyurethane and two different types of modified polysiloxane, poly(dimethylsiloxane-co-methyl phenylsiloxane)s and polyether-modified polysiloxane, prepared by solution casting. The poly(dimethylsiloxane-co-methylphenylsiloxane)s showed poor miscibility with TPU. It was found that their ionic conductivity decreased with the excess addition of poly(dimethylsiloxane-co-methylphenylsiloxane)s into the polyurethane electrolytes due to its poor salt solvation. Polyether-modified polysiloxane decreased the $T_g$ of the soft segment of TPU and showed better compatibility with TPU. The maximum ionic conductivity of the polyurethane/polyether-modified polysiloxane blend with LiClO$_4$ can approach $10^{-6}$ S/cm.
Xie et al.\textsuperscript{163} reported a polymer electrolyte based on (castor oil-polyethylene glycol) polyurethane/poly(alkymethacrylate) IPNs. They reported that the ionic conductivity of IPNs with LiClO\textsubscript{4} was in the range of $10^{-5}$ to $10^{-4}$ S/cm. It exhibited high ionic conductivity at room temperature when the EO/Li molar ratio reached 20/1. The ionic conductivity increased with increasing polyethylene glycol content, especially when the content was larger than 65%. They suggested that in this case the polyethylene glycol segments occurred in a continuous phase, which provided a continuous pathway for transportation of Li\textsuperscript{+} cation. The molecular weight of the polyethylene glycol also exhibited an effect on the ionic conductivity. The conductivity of the IPNs electrolytes decreased with the increase of the molecular weight of the polyethylene glycol from 2000 to 3350, if the content of polyethylene glycol content in IPNs kept constant. They explained that this was due to the increase of crystallinity of polyethylene glycol in IPNs with the molecular weight of polyethylene glycol. In addition, they studied the effect of chemical structure of the poly(alky methacrylate) on the ionic conductivity of the PINs. Different monomers: methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA), ethyl acrylate(EA), butyl acrylate (BA), and vinyl acetate (VAc) were used to synthesize poly(alkyl methacrylate). The conductivity of IPNs increased in the following order when the above monomers were used to synthesize poly(alkymethacrylate): EA<VAc<MMA<BA<EMA<BMA. They found that the order was almost the same as that of increasing difference of solubility parameters between the alky methacrylate unite and PEG, i.e. the decreasing order of the compatibility between the two components, except PVAc. They suggested a possible explanation that the
interaction of the graft group with PEG lowered the ability of PEG to complex with LiClO₄. No detailed information about the morphology of these electrolytes was reported.

Basak et al. studied polymer electrolyte system based on semi-IPNs of poly(ethylene oxide) based polyurethane(PEO-PU) and poly(acrylonitrile) (PAN) with lithium trifluoromethanesulfonate (LiCF₃SO₃). They found that the room temperature FTIR analysis indicated a salt solvation process occurred predominantly in the polyether segments of the semi-IPNs and the salt induced a morphological transition of the polymer matrix from semi-crystalline to amorphous phase. It was noticed there was a transition of their temperature dependence of conductivity: it followed the Arrhenius behavior at low temperatures and VTF dependence at higher temperatures. In their study on the PEO-PU/PAN with LiClO₄, they found this transition became more prominent with increasing the salt content. By correlation the trends in DSC and XRD, they suggested that this crossover in temperature dependent conductivity was attributed to the phase morphology change of semi-IPNs above the T_m of the polyether segments.

In polymer electrolytes, ions have strong interaction with polymers. The salt has a significant impact on the miscibility and morphology of the polymer blends and therefore affects the ionic conductivity. However, the relationship of the effect of ions on the miscibility and morphology of the polymer blends as well as the ionic conductivity is still understudied.
2.5 The Method of Ionic Conductivity Measurement

The principle of the ionic conductivity measurement of polymer electrolyte is to apply voltage to a cell assembly containing a polymer electrolyte sandwiched between the two electrodes and determine its impedance. The ionic conductivity of the polymer electrolyte can be determined by direct current measurements and the alternating current measurements. Alternation current measurement method is the more popular approach because ionic conducting polymers possess both the bulk conductivity, $R_b$, and capacitance capability, $C_p$. Bruce gave a detailed explanation on the fundamentals of the ionic conductivity measurement such as the various schematic circuit models of cell assembly with different polymer electrolytes and the different nature of electrodes, the interpretation of the impedance plot, the factors influencing the obtained A.C. response, etc. These theories are selectively illustrated in the following section.

The response of any cell contained polymer electrolytes to an A.C. signal can be represented by an equivalent electrical circuit consisting of resistors and capacitors. Polymer electrolyte systems are usually quite complicated because they are heterogeneous with both amorphous and crystalline regions and non-uniform salt concentration distribution. Bruce pointed out that some factors have to be considered: the effective pathway of the current is a tortuous pathway, which is longer than the distance between the two electrodes; higher resistance barriers may exist between the interfaces of the different phases; and the potentially mobile ions are not completely dissociated from each other and free to migrate. All these factors make it difficult to interpret the A.C. measurement data. He made an ideal simplification of real polymer
electrolyte and developed a systematic model under the assumption that the polymer electrolytes systems were homogeneous and all the mobile ions were assumed to be free to migrate, which did not intimately interact with each other. Since the A.C. response of polymer electrolytes varied with mobile species in polymer electrolyte and electrodes used in the experiment, Bruce\textsuperscript{166} divided the polymer electrolytes into two types according to the mobile species: type I, only one kind of ionic species was mobile; type II, more than one kind of ionic species were mobile. Also He classified the electrodes used in the measurement into two types: blocking electrodes (the mobile species do not participate in any electrode reaction, such as the platinum electrodes); and non-blocking electrodes (there is finite electrode reaction, such as the lithium electrodes).\textsuperscript{166}

The following are some typical A.C responses of idealized polymer electrolyte under the above assumption. The migration of the ions and the dielectric polarization of the polymer chain can be represented by a resistor, $R_b$ and a capacitor, $C_b$, respectively. Each electrode is somewhat like a parallel-plate capacitor, so it can be represented by a capacitor, $C_e$. For the cells with type I or type II polymer electrolyte sandwiched between two blocking, the equivalent circuit can be simplified as shown in Figure 2.20(a). The total impedance of the cell can be expressed as following equation:

$$Z_{total}^* = \frac{1}{R_b \left[\frac{\omega R_b C_b}{1 + (\omega R_b C_b)^2}\right]} \left(\frac{\omega R_b C_b}{1 + (\omega R_b C_b)^2}\right) + \frac{1}{\omega C_e}$$ \hspace{1cm} (2.15)

Figure 2.20 (b) illustrates the impedance plot from the low frequencies to the high frequencies. At high frequencies, the circuit can be reduced to a parallel $R_b \cdot C_b$
combination and the impedance plot is a semicircle in the complex plane. At low frequencies, the circuit can be reduced to a series combination of \( R_b \) and \( C_b \) and the impedance plot is a vertical spike displaced a distance \( R_b \) along the real axis. At very low frequency, the circuit can be simplified to the electrode capacitance \( C_e \) only.\(^{166}\)

All the fundamental electrical properties of the polymer electrolytes and the cell such as \( R_b \), \( C_b \) and \( C_e \), can be obtained via the following calculations based on the impedance data: \( R_b \) is determined from the intersection point of the impedance curve with the x axis except the origin; \( C_b \) is calculated from \( R_b = \frac{1}{\omega_{\text{max}} C_b} \), at the maximum of the semicircle in impedance plot; \( C_e \) is obtained through \( C_e = \frac{1}{Z \sigma} \). from any point on the spike. \( R_b \) is a geometry dependent physical term. The specific ionic conductivity \( \sigma \) is dimensionally irrelevalve and describes the material properties. The relationship of the specific ionic conductivity \( \sigma \) with \( R_b \) can be represented by a simple form as equation (2.16) for the measurement setup with polymer electrolytes film sandwiched between two electrolytes.

\[
\sigma = \frac{L}{R_b A} \quad (2.16)
\]

where \( L \) represents the separation distance of the electrodes and \( A \) is the area of the electrode.\(^{166}\)

Bruce\(^{166}\) explained that if the mobile species adsorption occurs in the blocking electrodes, the equivalent circuit and complex impedance plot should be like that shown
in Figure 2.21; and if the electrodes are non-blocking, the appropriate equivalent circuit as shown in Figure 2.22 should be used.

The above interpretations are all derived from the idealized polymer electrolytes. However, in the impedance spectrum of the real polymer electrolytes, semicircles are significantly broadened and electrode spikes are distinctly non-vertical. According to Bruce\textsuperscript{166}, the departure of the real A.C. response from the idealized models is attributed to the following factors: surface layers on the electrodes; dielectric relaxation and ion trapping; inhomogeneities in polymer electrolytes; ion and ion interaction; rough electrodes, et al. Figure 2.23 shows the typical complex impedance plot for an amorphous and homogeneous PPO/LiClO\textsubscript{4} polymer electrolyte based on a network polymer with blocking electrode (a) and non-blocking electrode (b).\textsuperscript{167} Figure 2.24 shows the complex impedance plot of poly(butylenes adipate) based polyurethane electrolyte with different salt concentration with blocking electrode.\textsuperscript{55}

Figure 2.20 (a) Schematic representation of a polymer electrolyte/blocking electrode cell, $R_b$, electrolyte resistance; $C_b$, electrolyte capacitance; $C_e$, electrode capacitance. (b) Complex impedance plot for the circuit in (a)\textsuperscript{166}
Figure 2.21  (a) Equivalent circuit and (b) complex plane plot for Type I polymer electrolyte sandwiched between blocking electrodes with absorption on electrode surface. $R_b$, $C_b$, bulk resistance and capacitance; $C_e$, electrode resistance, $C_{ad}$, $R_{ad}$, adsorption capacitance and resistance.\textsuperscript{166}

Figure 2.22  (a) Equivalent circuit and (b) complex plane plot for Type I polymer electrolyte sandwiched between non-blocking electrodes. $R_b$, $C_b$, bulk resistance and capacitance; $R_e$, $C_e$, electrode resistance, and capacitance.\textsuperscript{166}
Figure 2.23  The typical complex impedance plot for an amorphous and homogeneous PPO/LiClO₄ polymer electrolyte based on a network polymer with (a) blocking electrode and (b) non-blocking electrode.\textsuperscript{167}

Figure 2.24  The complex impedance plot of Polybu(butylenes adipate) based polyurethane electrolyte with; ♦ - 0.0156 mole; ■ -0.0078 mole; ▲ - 0.0039 mole NaClO₂.\textsuperscript{55}
CHAPTER III
EXPERIMENTAL

3.1 Materials

The thermoplastic polyurethane (TPU) used in this study was formulated with a low hard segment content and high soft segment content. The polyol used was polytetramethylene glycol (PTMG) with a molecular weight of 2000g/mol purchased from sigma-aldrich chemical company. The chain extender, 1,4 butanediol, was purchased from ARCO and diisocyanate, 4,4’ diphenylmethane diisocynate (MDI), was supplied by Bayer. Polyether-modified polysiloxane (PEMPS) was purchased from Gelest, Inc. Three different lithium salts with various types of anions were used: lithium chloride LiCl, lithium perchlorate LiClO₄, lithium bistrifluoromethanesulfonimidate LiN(SO₂CF₃)₂ (LITFSI). They were all from Aldrich. Table 3.1 lists a detailed description of the used materials.

The formulation of the polyurethane component in the electrolytes or in the blend contained 68.26%PTMG, 6.14% BDO and 25.60% MDI by mass when the stoichiometric ratio of hydroxyl to isocyanate functionality was maintained at unity. In this experiment, 2% excess of stoichiometry of MDI was used to compensate for trace amounts of residual water in the salt, and reactants. Regardless of the polymerization environment, the TPU component inside the polymer system was synthesized via one-shot reaction. PTMG, PEMPS, salts or premixed monomer/salts mixture were dried under a vacuum at 80°C for
1 day before polymerization of polyurethane. DBO was dried in a vacuum oven first and
demoistured over 3 Å molecular sieves at room temperature for 2 weeks prior to
synthesis. MDI was stored under vacuum at 0°C before usages.

Table 3.1 Materials used in polyurethane/modified polysiloxane blend electrolytes

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Chemical Structure</th>
<th>Mn</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyether polyol</td>
<td>Poly(tetrahydrofuran/polytetramethylene glycol)</td>
<td>2000</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Chain Extender</td>
<td>1,4 butane diol</td>
<td>90</td>
<td>ARCO</td>
</tr>
<tr>
<td>MDI</td>
<td>4,4’-diphenylmethane diisocyanate</td>
<td>250</td>
<td>Bayer</td>
</tr>
<tr>
<td>Cross-linking regent</td>
<td>1,1,1-Tris(hydroxymethyl)propane (TM P)</td>
<td>134</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Polyether-modified polysiloxane</td>
<td>Dimethylsiloxane-(60%propylene oxide-40%ethylene oxide) block/graft copolymer</td>
<td>20,000</td>
<td>Gelest</td>
</tr>
<tr>
<td>Salt</td>
<td>Lithium chloride</td>
<td>42</td>
<td>Aldrich</td>
</tr>
<tr>
<td></td>
<td>Lithium perchlorate</td>
<td>106</td>
<td>Alfa aesar</td>
</tr>
<tr>
<td></td>
<td>Lithium bistri fluoromethanesulfonimide</td>
<td>287</td>
<td>Aldrich</td>
</tr>
</tbody>
</table>
3.2 Preparation procedures of Polymer Electrolyte Films

It is an unique and novel method to prepare polymer electrolytes using solvent-free in-situ process as follows. Polyurethane electrolytes and Polyurethane (PU)/Polyether-modified polysiloxane (PEMPS) electrolytes studied in this research were prepared by the solvent-free in-situ process. In particular, the effect of the preparation method on the properties of the final products of electrolytes was studied. In comparison to this solvent-free in-situ process, the conventional solution cast method was also investigated.

3.2.1 In-situ process

PTMG, PEMPS and salt were directly mixed together with a magnetic stirrer at 60°C for 1 day to ensure the salts completely dissolved without adding any volatile solvent. Then the mixture was dried under vacuum at 80°C for 1 day. Four kinds of different melt mixtures with various compositions including PTMG/salt, PEMPS/salt, PTMG/PEMPS, and PTMG/PEMPS/salts were prepared for characterization prior to the polymerization. The dried PTMG/PEMPS/salt mixture was poured into an aluminum pan on a hot stage and then mixed with BDO and MDI at 80°C using a stirrer. After that, the reactive mixture was poured in a sheet and put into a vacuum oven for 24 hours at 100°C for further curing. The lithium salt concentration in the polymer electrolytes was represented by the stoichiometry ratio of the ether unit in the polymer to Lithium in the lithium salt, [O:Li]. The PEMPS concentration is represented by the weight ratio of TPU to PEMPS, \( W_{TPU} / W_{PEMPS} \). The polymer electrolytes with [O:Li] equal to 8:1, 16:1, 32:1 and \( W_{TPU} / W_{PEMPS} \) equal to 100/10, 100/20, 100/40 respectively were prepared. In order to
study the effect of PEMPS on the properties of TPU electrolytes, TPU electrolytes with
different salts were also prepared using the similar procedure but without adding PEMPS.
The chemical cross-linked PU/PEMPS electrolytes were prepared by a similar procedure
with the formula, 68.26%PTMG, 5.12% BDO, 1.02% TMP and 25.60% MDI by mass.
However, it was found that the chemical cross-linked PU/PEMPS electrolytes prepared
cannot form a good film. Therefore in this study we only focused on the study of polymer
electrolytes based on the thermoplastic polyurethane. The preparation routes of polymer
electrolytes are illustrated in Figure 3.1.

3.2.2 Solution casting

The neat TPU used to prepare solution cast blend electrolytes was synthesized via
one shot reaction. The procedure is similar to the one used for the in-situ process stated
above. The TPU, PEMPS and salt were dissolved in tetrahydrofuran (THF) separately.
The solutions were mixed together and stirred with a magnetic stirrer in a covered flask
for 5 hours at 50°C to be well mixed. Then they were poured on a Teflon coated
aluminum sheet. The solvent was slowly removed at 40°C in the hood and then the film
was dried in a vacuum oven at 80°C for one day. All the films were stored in the
desiccator. Four different mixtures with various compositions including PTMG/salt,
PEMPS/salt, PTMG/PEMPS, and PTMG/PEMPS/salts were also prepared using
conventional solution cast with methanol as solvent.
Figure 3.1  Schematic of the preparation routes of the in-situ process (lithium salts used in the above preparations are LiCl, LiClO₄ and LiN(SO₂CF₃)₂ respectively)
3.3 The Kinetics of Polymerization

The kinetics of the in-situ process was investigated using the isothermal DSC method. The heat generated during the reaction was determined as a function of time. The effects of the addition of ions and PEMPS on the kinetics were studied.

The method used to study the kinetics of polyurethane in this research is same as the one used by Parnell\textsuperscript{132}. Reactant mixtures were quenched with dry ice after vigorous mixing. Then mixtures were carefully weighted to 10 ± 2 mg and sealed in aluminum hermetic pans. The sealed sample was preheated to a specific isothermal temperature and heat flow resulting from the exothermic TPU polymerization reaction was measured as a function of time. After 30 minutes of isothermal polymerization, samples were immediately quenched to 0°C and then temperature scanned from 0°C to 200°C at a heating rate of 20°C/min. Any residual heat of reaction remaining after isothermal polymerization was determined to ensure complete TPU polymerization. A second non-isothermal scan was conducted immediately after the first temperature scan in order to determine the baseline for future residual heat of reaction calculations.

This study assumed a constant enthalpic heat of reaction, no significant interference from side reactions, and heat evolved during polymerization was proportional to the extent of polymerization. Conversion as a function of time can be calculated from the following equation

$$\alpha(t) = \frac{\Delta H_1 + \Delta H(t)}{-\left(\Delta H_{\text{rxn}}\right)}$$

(3.1)
where \( \Delta H_1 \) is the molar heat of reaction lost during sample preparation, sample loading, and DSC stabilization, \( \Delta H(t) \) is the measured molar heat of polymerization as a function of polymerization time, and \( \Delta H_{\text{rxn}} \) is the total molar enthalpic heat of reaction for TPU step growth polyaddition which is assumed constant for all isothermal polymerization temperatures. Macosko et al.\textsuperscript{77} and Parnell\textsuperscript{132} reported that \( \Delta H_{\text{rxn}} \) had a value of approximately -90kJ/mole equivalent isocyanate from their adiabatic temperature rise experiment.

The measured molar heat of polymerization, \( H(t) \), was obtained from integrating the area underneath the isothermal traces in the isothermal specific heat flow versus time profiles according to the following equation:

\[
H(t) = \frac{1000}{[C_0]} \int_0^t \frac{\partial H}{\partial t} dt
\]

(3.2)

where \([C_0]\) is initial isocyanate molality and \(\partial H/\partial t\) is specific heat flow. The following equation was used to calculate \( \Delta H_1 \).

\[
\Delta H_1 = -(\Delta H_{\text{rxn}}) - \Delta H_m - \Delta H_r
\]

(3.3)

\( \Delta H_m \) is calculated from equation (3.3) at a final polymerization time of 30 minutes. \( \Delta H_r \) is calculated from the area underneath the exothermal trace of specific heat flow versus temperature profiles obtained from temperature scan experiments performed subsequently to each isothermal trace.

Applying the conversion versus time data into the equations in section 2.2.2 in chapter II, the kinetic parameters K and n were determined from log-log plots of conversion rate versus fractional conversion.
3.4 Characterization Techniques

The solvent-free in-situ polymerization process in this study includes two steps. In the first step PTMG or PEMPS was mixed with lithium salts and then the polymerization of PTMG occurred. The interaction between the reactant and the salts, the miscibility of the salts with monomer as well as the effect of salts effect on the kinetics of polyurethane polymerization, all play an important role on the feasibility of this process. The morphology of the TPU/PEMPS electrolytes significantly affects their ionic conductivity and dimension stability. The ionic conductivity, the dimensional stability and the thermal properties are the major factors determining the application of the polymer electrolytes. Therefore, the PTMG/salt, PEMPS/salt and PTMG/PEMPS mixtures were characterized by the DSC, FTIR, and optical microscopy before polymerization to study the interaction between PTMG with various salts and the solubility of various salts in PTMG without the addition of volatile solvent. The polymer electrolytes films with various compositions prepared after polymerization were characterized using the TGA, DSC, FTIR, Optical microscopy, SEM, TEM and impedance measurements. Also the selected polymer electrolytes prepared by solution cast were characterized by the similar techniques in order to compare with the ones made by the in-situ process.

3.4.1 Morphological Studies

The morphological studies of PTMG/salt mixture, PEMPS/salt mixture, TPU electrolytes and TPU/PEMPS electrolytes are conducted using different technique
including optical microscopy (OM), scanning electronic microscopy (SEM) and atomic force microscopy (AFM), respectively.

3.4.1.1 Optical microscopy (OM)

A Lietz Laborlux polarized optical microscope equipped with a video camera and hot stage were used to study the salt solvation, the miscibility of PTMG and PEMPS, and the effects of the salts on the miscibility by observing the morphology of the PTMG/salt melt mixtures, PEMPS salt melt mixtures and the PTMG/PEMPS melt mixtures. The molten melt mixtures were cast on a glass slide. The sample was cooled down to room temperature slowly to crystallize for 2 days and then heated to 60°C (above T_m of PTMG) at a heat rate of 5°C/min. The morphology changes of the mixtures during this whole cooling and heating course were observed through the computer connected to the optical microscopy equipped with HCS302 hot stage (INSTEC inc) and video camera.

Since the melting points of all the salts used in this study are all above 80°C (the T_m of LiCl, LiClO_4 and LiN(SO_2CF_3)_2 are 240°C, 334°C and 274°C respectively), the undissolved salts in the form of crystals were distinguished from the optical microscopy images of the molten PTMPG/salt mixture at 60°C if the crystals size is visible in the range of magnification. In order to compare the lithium salt solvation behavior in the in-situ process with the one in solution cast, the PTMG/salt mixtures and the PEMPS/salt mixtures prepared by the solution cast using methanol as solvent were also characterized by optical microscopy.
3.4.1.2 Scanning Electron Microscopy (SEM)

The morphology of polymer electrolytes were investigated using a Hitachi S-2150 SEM. Samples were immersed in liquid nitrogen and cryogenically fractured. The fractured samples were mounted to aluminum sample holder and sputter coated with silver by a sputter coating machine.

The neat TPU, TPU electrolytes, TPU/PTMPS blend and TPU/PEMPS electrolytes samples were pretreated by two different processes before observation: (1) the fractured surface as it is and (2) the fractured surface in which the PEMPS was extracted in methanol for 2 days and washed by methanol and dried in a hood overnight. This extraction procedure led to an easier examination of the dispersion of the PEMPS phase in the blends and blend electrolytes. The surfaces of polymer electrolyte films prepared by solution cast were also examined by SEM.

The SEM was used to examine the miscibility and morphology of PU/PEMPS blends and their electrolytes. The dispersed size of PEMPS phase, the phase mixing between PEMPS and the soft segments or hard segments of PU and the interfaces between different phases were observed. Comparison of the SEM micrographs of TPU/PEMPS blends with neat TPU samples provided the information about the miscibility of TPU with PEMPS as well as their morphology. Comparison of SEM micrographs of TPU/PEMPS/salt blends with TPU/salt samples provided the information about the effect of salts on the blend morphology. In particular, the effects of the different types of anion on their miscibility and crystalline morphology were investigated. In addition, the effects of preparation methods such as the in-situ process and the solution cast method on their
morphology were also studied.

3.4.1.3 Atomic Force Microscopy (AFM)

The DI MultiMode Scanning Probe Microscopy (SMP) with the tapping mode Atomic Force Microscopy (AFM) technique was used to examine the topography of surface of polymer electrolytes films prepared by solution cast. The original electrolytes films were cut into small pieces and glued on the top of a metallic sample holder. Both the height and phase images of the surface of polymer electrolytes were obtained. The canning size were around 30µm.

3.4.2 Thermal Analysis

The TPU electrolytes and TPU/PEMPS electrolytes with various compositions were characterized using TGA to study their thermal stability. The thermal transition of PTMG/salt mixture, PEMPS/salt mixture and polymer electrolytes were studied using DSC.

3.4.2.1 Thermogravimetric analysis (TGA)

The thermal stabilities of polymer electrolytes were studied by a Thermal Advantage Q500 modulated thermogravimetric analyzer. Samples were carefully weighed to about 10 ± 2 mg in a platinum pan. TGA scans were recorded at a rate 20°C/min under a nitrogen atmosphere from room temperature to 500°C.

TGA analysis determines the degradation temperature of polymers based on the
mass loss. The TGA data of polymer electrolytes with various compositions were analyzed regarding to the following two aspects: (1) the effects of PEMPS, various salts and their concentrations on the degradation temperature of polymer electrolytes; and (2) the application temperature ranges of these polymer electrolytes. This also provided some indirect information about the polymer/polymer interaction and polymer/salt interaction.

3.4.2.2 Differential Scanning Calorimetry (DSC)

Thermal transition temperature and crystalline melting behavior of the PTMG/salt mixture, PEMPS salt mixture and polymer electrolytes were investigated using a Thermal Advantage 2920 differential scanning calorimeter operating with non-isothermal mode. Samples were scanned in the range of -120 to 200°C. All the DSC thermograms were recorded at a scan rate of 20°C/min. All the samples were run twice. After first thermal scanning, samples were quenched to -120°C using liquid nitrogen and immediately the second thermal scan was performed with the same temperature range as the first run. The purpose of the second run was to characterize the glass transition temperature of samples with minimal effect of crystallization. Glass transition temperature ($T_g$) was estimated from the extrapolated midpoint of an endothermic shift while melting temperature ($T_m$) was estimated from the extrapolated midpoint of melting endothermic peak.

Our previous research group applied the melting point depression analysis analogously to evaluate the interaction between salts and polymers.\cite{55}
The melting point depressions in polymer blends can be calculated by interaction parameter as in the research work of Nishi et al.\textsuperscript{168,169} The interaction parameter $\chi_{12}$ was assumed to be of the form:

$$\chi_{12} = \frac{BV_1}{RT}$$  \hspace{1cm} (3.4)

where $B$ is the polymer-polymer interaction energy density. The following equation can be derived based on the Flory-Huggins-Scott approximation applied on polymer mixture:

$$\frac{1}{V_1} \left[ \frac{1}{T_m} - \frac{1}{T_m^0} \right] = - \frac{BV_{2u}}{\Delta H_{2u}} \frac{V_1}{T_m}$$  \hspace{1cm} (3.5)

where $V_{2u}$ and $\Delta H_{2u}$ is the molar volume of the repeating units and the enthalpy of the repeating unit, respectively. Plotting $(1/T_m - 1/T_{m0})/\phi_1$ versus $\phi_1/T_m$, the value of $B$ can be calculated from the slope of these variables. The negative value of $\chi_{12}$ means that the polymer pair can form a thermodynamically stable mixture above the melting point and the positive value of $\chi_{12}$ means the reverse. Analogous to the change of $T_m$ in polymer blend, the interaction and miscibility of TPU/PEMPS blend can be examined. In polymer electrolytes, salt can get into the crystal phase of polymer and form polymer/salt complex crystals, given high salt concentration, $[O:M]<4$. However, at the salt concentrations used in this research ($[O:M]>4$), the interaction of salt ions with polymers might reduce the ordered structure of polymer crystals and lead to imperfect crystals and more amorphous portions.

The thermal transition temperature such as $T_g$ can also been used to determine the miscibility of polymer blends and mixtures with salts etc. The change of $T_g$ also provides the information of interaction and miscibility of polymer blends as mentioned in various
monographs. For immiscible polymer blends, there are two separate $T_g$s with values close to the $T_g$s of corresponding polymer components. For partial miscible polymer blends, the $T_g$s of the two components shift inwards due to the interaction. These two $T_g$s merge into one $T_g$ in completely miscible blends. In this case, according to the Gordon-Taylor equation as shown in equation (3.6), the strength of specific intermolecular interactions can be evaluated by the $k$ parameters. Physically, values of $k$ less than unity are attributed to the positive free volume deviations from simple linear additively upon mixing two polymers.

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2}$$ (3.6)

where $T_g$ and $T_{gi}$ are the glass transition temperatures of the blend and component $i$, respectively, and $w_i$ is the weight fraction of component $i$. The $T_g$ of polymer electrolytes at different salt concentrations and blend ratios were plotted to study the interaction between salt and polymers or the interaction between TPU and PEMPS.

3.4.3 Fourier Transform Infrared Spectroscopy

PTMG/salt mixtures, PEMPS/salt mixtures and polymer electrolytes with various compositions were characterized using Mattson Genesis Series FTIR at room temperature to study the salt solvation, the interaction between polymer and salt, and the interaction between polymer and polymer associated with salts. Liquid samples of PTMG/salt mixtures or PEMPS/salt mixtures were directly cast on the KBr Plate and the solid samples of polymer electrolytes were dissolved into THF and cast on the KBr plate. After
the sample was dried, the plates cast with samples were scanned over the range 4000-400 cm\(^{-1}\).

The FTIR of TPU components were examined in the following regions: (1) The hydrogen bonded N-H stretching mode and the free N-H stretch (3600-3100 cm\(^{-1}\)); (2) the carbonyl symmetric stretching vibration or amide band (1750-1650 cm\(^{-1}\)); and (3) The C-O-C stretch for the soft segment and C(O)-O-C stretch of the hard phase (1150-1000 cm\(^{-1}\)). The FTIR of PEMPS were focused on the following regions: (1) the two peaks around 1264 cm\(^{-1}\) and 803 cm\(^{-1}\), which are ascribed to the CH\(_3\)-Si symmetric deformation; and (2) Si-O-Si asymmetric stretch of polysiloxane main chain and C-O-C stretching of ether side chain (1150 cm\(^{-1}\) to 1000 cm\(^{-1}\)).\(^{171}\) The FTIR of PTMG were examined on the C-O-C stretching (1150 cm\(^{-1}\) to 1000 cm\(^{-1}\)) and –OH group stretching (3500 cm\(^{-1}\)-3100 cm\(^{-1}\)). The interactions between ions and polymers and between the different functional groups in polymer were studied by determining the wavenumber shift and absorption intensity change of the interested peaks. Usually, the CH\(_2\) absorbance occurring at 2970 cm\(^{-1}\) is not influenced by the interactions as mentioned above. It was used to normalize the absorbance intensity of the interested peaks. The relative intensity of different interested peaks was obtained by dividing the absorbance intensity of the corresponding peaks with the absorbance intensity at 2970 cm\(^{-1}\) in the same spectra.

3.4.4 Gel Permeation Chromatography (GPC)

A Waters 150-C gel permeation chromatography (GPC) was used to study the effect of lithium salts and PEMPS on the molecular weight and its distribution of TPU
prepared by the in-situ process. THF was used as solvent to dissolve the TPU electrolytes and TPU/PEMPS electrolytes. The GPC component utilized five ultrastyra gel columns with THF as the carrier solvent. Polystyrene standards were used as calibration curves.

3.4.5 Instron Tensile Testing

The tensile properties of polymer electrolyte films were characterized by Monsanto D 2000 tensile tester with 1000N load. The gauge length was controlled to be 2 cm. The films were cut into a 5mm x 30mm rectangular strip samples. The crosshead speed was 15mm/min.

3.4.6 Ionic Conductivity Measurement

The ionic conductivities of the polymer electrolytes in this research were measured by a multi-frequency LCR meter (Hewlett Packard 4274A). The magnitude of complex impedance $|Z|$ and the phase angle $\theta$ of polymer electrolytes were read directly from the instruments. The samples were sandwiched between stainless steel electrodes. The cell impedance was measured at various frequencies ranging from 100 Hz to 100 kHz. The voltage applied on the sample was fixed at 5V throughout the experiments. The complex impedance plot was obtained by plotting $Z'' = |Z|\sin \theta$ against $Z' = |Z|\cos \theta$. Then the A.C. ionic conductivity was calculated from the bulk resistance obtained from the complex impedance plot. The bulk resistance was defined as the resistance value on the impedance plot where the spike and semi-circle extrapolated to intercept at the real axis.
The temperature dependence of the ionic conductivity was studied with the aid of HCS302 hot stage (Instec, inc.) connected with the heating and temperature control system. The films sandwiched between stainless steel electrodes were placed in the sample chamber of the hot stage. The ionic conductivity measurements were recorded at room temperature and 20°C intervals from 40°C to 160°C. The cell was kept at the desired temperature for at least 10 minutes to reach the equilibrium temperature of the sample prior to reading the data. The bulk resistance of the sample at different temperatures was obtained and used to calculate its ionic conductivity. The results of ionic conductivity (S/cm) vs. the reciprocal of absolute temperature (100/T(K)) were plotted to exhibit the temperature dependence of the ionic conductivity.
CHAPTER IV
RESULTS AND DISCUSSION

In this research, TPU/PEMPS electrolytes were prepared by a solvent-free in-situ process in which the polyurethane polymerization occurred in the presence of lithium salts and PEMPS. The advantage of this process is that it does not use volatile solvents. Instead, the PTMG acts as a common solvent to dissolve the lithium salt by the interaction of salt with ether oxygen atom during melt mixing. In order to ensure good salt solvation in PTMG, the PTMG/salt mixture, PEMPS salt mixture, and PTMG/PEMPS/salts mixture were premixed and then followed by polymerizing polyurethane after adding MDI and BDO.

The discussion section in this research is divided into two separate chapters. In the first section, the salt solvation in PTMG, PEMPS, PTMG/PEMPS blend for lithium salts with three different anions as well as the interaction of salt with polymer are discussed. The discussion in the second section includes the kinetics of polyurethane polymerization in the presence of lithium salts and PEMPS, the morphology of TPU electrolytes and TPU/PEMPS electrolytes, their thermal stability and thermal behavior, their ionic conductivity behavior as well as the various polymer/polymer interactions and polymer/ions interactions. A proposed ionic conduction mechanism of TPU/PEMPS electrolytes is discussed.
The complete dissolution of salt in PTMG and PEMPS respectively is an important step in the proposed solvent-free process. The dissolution of salts in PTMG without the aid of polar volatile solvent depends on the interaction between PTMG and salts, and the interaction between cations and anions. The effect of the anion structure significantly influences the strength of interaction between cation and anion, therefore controlling their solvation in polymers. The amount of salt dissociated in the polymer matrix directly controls the number of the charge carrier and determines the ionic conductivity of polymer electrolytes. In this section, the salt solvation in PTMG and PEMPS, the effect of salts on the crystal morphology of PTMG, the miscibility of PTMG and PEMPS, the effect of the salt on their miscibility as well as the interaction of PTMG and PEMPS with salts were studied by different characterization techniques including optical microscopy, DSC and FTIR.

4.1 Morphological studies of PTMG and PEMPS lithium salt mixtures for solvation studies

PTMG/salt mixtures and PEMPS/salt mixtures with various salt concentrations were prepared by directly mixing salt with PTMG melt or PEMPS at 60°C. The salt concentration is represented by the mole ratio of ether oxygen atoms to lithium ions, [O:Li], which was controlled to be 32:1, 16:1 and 8:1 ratio respectively in this experiment. PTMPS/salt mixtures were observed by both by cross-polarized optical microscopy for observing their crystalline morphology and by non-polarized optical microscopy for their morphology at molten state respectively. Since PEMPS is an
amorphous liquid at room temperature, the PEMPS/salt mixtures were only observed with non-polarized optical microscopy.

4.1.1 PTMG/salts Mixture

Figure 4.1 shows the three different lithium salt crystals (LiCl, LiClO₄ and LiN(SO₂CF₃)₂) obtained by solution cast of the dilute salt methanol solution on glass slides. Each salt forms its characteristic crystal structure: LiCl forms small densely packed crystals; LiClO₄ forms a certain needle shape; and LiN(SO₂CF₃)₂ forms spherulites with maltese crosses as shown in Figure 4.1. In order to make the salts dissolve easily, the salts used to prepare the PTMG/salt complex were ground into powder before mixing with PTMG melt. The morphology of these salt powders was obtained by directly observing the powder mounted on the surface of glass slides. As shown in Figure 4.2, unlike the solution cast samples, the salts powder exhibits lumps of small crystals. Due to the stacking, it is hard to tell the shape of the small crystals.

The PTMG/salt mixtures were cast on a glass slides and covered with another glass slide. By pressing the top glass slide, a very thin layer of melt was sandwiched between two glass slides. The film was observed after crystallization at room temperature for over 2 days. This procedure minimized the overlapped spherulites. Figure 4.3 shows the PTMG spherulites in the PTMG/LiCl melt mixture. The size of the PTMG spherulites shows little change as the LiCl concentration increases. However, the size of PTMG spherulites of both PTMG/LiClO₄ mixture and PTMG/LiN(SO₂CF₃)₂ mixture changes
Figure 4.1  Cross-polarized optical micrographs of solid salts from dilute solution (a) LiCl, (b) LiClO₄, (c) LiN(SO₂CF₃)₂
Figure 4.2  Cross-polarized optical micrographs of ground salts particles (a) LiCl , (b) LiClO₄ , (c) LiN(SO₂CF₃)₂
Figure 4.3  Cross-polarized optical micrographs of PTMG/LiCl mixture with various LiCl concentrations; (a) Neat PTMG crystal, (b) [O:Li]=32:1 (c) [O:Li]=16:1 (d) [O:Li]=8:1
dramatically with the salt concentration as shown in Figure 4.4 and Figure 4.5. Especially, when the ratio of [O:Li] reaches 8, the large spherulites form much smaller crystals as shown in Figure 4.4(d) and Figure 4.5(d). Also, it was noticed that the dark area increases as the salt concentration increases, which indicates that more amorphous phase is induced by the incorporation of salts. The effect of the lithium salts on the morphology of PTMG/salt mixture implies a different level of retardation or crystallization kinetics change due to the different interactions between PTMG and various lithium salts used in this study. This observation suggests that there is a weaker interaction between PTMG and LiCl than between PTMG and LiClO₄ or between PTMG and LiN(SO₂CF₃)₂. This conclusion is based on the fact that in the LiCl crystal there is a strong interaction between Li⁺ and Cl⁻, which results the weak interaction between PTMG and Li⁺, compared to the case of LiClO₄.

There are few reports on the effect of salts on the crystallization of PTMG, but similar studies have been conducted by previous researches on PEO/salt systems. The spherulitical morphology of PEO-LiBF₄ complex has been reported by Wright and Payne¹⁵. The PEO-LiBF₄ films were prepared by solution cast with polar solvent. They pointed out that PEO/salt complex had some local-range order in the ionic lattice but the long-range order was limited by the chain entanglement and frequent irregularities in helical structures. The molecular weight of PTMG used in this research is only 2000 and this value is far below the critical molecular weight of the chain entanglement. However, PTMG/salt mixtures in Figure 4.4 and Figure 4.5 have similar morphological structures to ones of films of high molecular weight PEO complex observed by Wright and Payne¹⁵.
Figure 4.4  Cross-polarized optical micrographs of PTMG/LiClO$_4$ complex with various salt concentrations; (a) Neat PTMG crystal, (b) [O:Li]=32:1, (c) [O:Li]=16:1, (d) [O:Li]=8:1
Figure 4.5 Cross-polarized optical micrographs of PTMG/ LiN(SO$_2$CF$_3$)$_2$ complex with various salt concentrations; (a) Neat PTMG crystal, (b) [O:Li]=32:1, (c) [O:Li]=16:1, (d) [O:Li]=8:1
It is possible that in the PTMG salt mixture prepared by melt mixing the cations interact with the ether oxygens on PTMG and act as anchors to connect different PTMG chains together and form physical network structures. The folding of PTMG segments to form crystal is impeded by the entanglement caused by the network structures. So the crystal size decreases and the degree of the crystallinity also decreases as the salt concentration increases. The physical cross-link effect of ions on polymers has been reported by previous researchers on the study of the polyelectrolytes and ionomers.\textsuperscript{126,127,128} Lundberg and his coworkers\textsuperscript{172} reported that there was a dramatic increase in viscosity as salts were added into the PEO solutions. Similar phenomena are also observed in the PTMG/salt mixture prepared by melt mixing in this experiment, where the PTMG/salt melt mixture is much more viscous than neat PTMG melt.

The PTMG/salt mixtures at melt state were also observed for residue using a non-cross polarized optical microscopy. Since the melting points of all the salts used in this research are all above 60\textdegree{C}, the undissolved salts in the PTMG/salt mixtures are in the form of crystals at 60\textdegree{C}. The undissolved salt should appear in the clear background of PTMG/salt. The undissolved LiCl particles were observed in PTMG/LiCl melt mixture as shown in Figure 4.6 and its amount increases as the salt concentration increases. At a high LiCl concentration of [O:Li]=8:1, the undissolved LiCl crystal particles form a larger agglomeration. However, no undissolved salt crystal is observed in the PTMG/LiClO\textsubscript{4} melt mixture as shown in Figure 4.7 and PTMG/LiTFSI melt mixture in Figure 4.8. These photographs indicate that both LiClO\textsubscript{4} and LiTFSI are dissolved in PTMG even without polar solvent. The different dissolution behavior of lithium salts with
Figure 4.6  Optical micrographs of PTMG melt with different LiCl concentrations at 60°C; (a) [O:Li]=32:1; (b) [O:Li]=16:1; (c) [O:Li]=8:1
Figure 4.7  Optical micrographs of PTMG melt with different LiClO$_4$ concentrations at 60$^\circ$C; (a) [O:Li]=32:1 , (b) [O:Li]=16:1, (C) [O:Li]=8:1
Figure 4.8  Optical micrographs of PTMG melt with different LiN(SO$_2$CF$_3$)$_2$ concentrations at 60$^0$C; (a) [O:Li]=32:1 , (b) [O:Li]=16:1, (C) [O:Li]=8:1
different anions can be attributed to the structural differences of these anions. Cl\(^-\) is a small monatomic anion with concentrated charge distribution, which has strong interaction with small size Li\(^+\) and can easily form well-packed crystal lattice. ClO\(_4\)\(^-\) and TFSI\(^-\) are large polyatomic anions with dislocated charge, which weakens their interaction with Li\(^+\), and the large size difference between anion and Li\(^+\) leads to the loosely packed crystal lattice. Therefore, compared with LiCl, the other two lithium salts with large anions such as LiClO\(_4\) and LiTFSI, are more easily dissociated.

Pearson\(^{44}\) used the hard/soft acid base principle (HSAB) to explain the interaction between polymers and cations and the interaction between cations and anions. According to HSAB theory as mentioned in chapter 2.1.3, Li\(^+\) is a hard acid and the oxygen in ether (such as PTMG) should be a hard base, while Cl\(^-\) should be classified as a hard base and ClO\(_4\)\(^-\) and TFSI\(^-\) are soft bases. In HSAB theory, the strong interaction occurs by matching hard acids with hard bases and soft acids with soft bases. Therefore, Li\(^+\) may interact more strongly with oxygen in PTMG than with ClO\(_4\)\(^-\) and TFSI\(^-\). Although both ether oxygen and Cl\(^-\) are hard bases, Li\(^+\) interacts more strongly with Cl\(^-\) than ether oxygen. This explains the dissolution difference of these three lithium salts in PTMG.

In order to investigate whether the presence of polar solvent such as methanol can induce significant difference in dissolution of LiCl in PTMG, the PTMG/LiCl mixtures were also prepared using a solution cast method with methanol as solvent. After the vaporization of methanol, the melted PTMG/LiCl mixture was cast on the glass slide for observation using optical microscopy. Compared with the micrograph of the PTMG/LiCl mixture prepared by direct melt mixing as shown in Figure 4.6, the undissolved LiCl
particles still exist and the undissolved particles are dispersed more uniformly and less large agglomerates as shown in Figure 4.9. Thus, it can be concluded that the usage of methanol does not significantly change the solubility of LiCl in PTMG. Wright\textsuperscript{173} pointed out that in the solution cast process salt was solvated by the solvent and dissociated into free ions surrounded by solvent molecular first, and as solvent was removed, solvent was ready to surrender ions to polymer. However, in this research due to the strong interaction between Li\textsuperscript{+} and Cl\textsuperscript{-}, Li\textsuperscript{+} tends to go back to Cl\textsuperscript{-} and form LiCl crystal or large ion clusters instead of forming complex with PTMG after the removal of solvent.

![Optical micrographs of PTMG melt at 60\textdegree C with different LiCl concentrations prepared by solution cast with methanol as solvent; (a) [O:Li]=32:1, (b) [O:Li]=16:1, (C) [O:Li]=8:1](Figure 4.9)
4.1.2 PEMPS/Salt Mixture

Figure 4.10 shows the optical micrographs of PEMPS/LiCl prepared by direct melt mixing. The undissolved LiCl particles were identified in the melt mixture with [O:Li] from 32:1 to 8:1. Especially, at [O:Li] =8:1, there are large agglomerates of LiCl, which indicates the poor solvation of LiCl in PEMPS. However, in the PEMPS/LiCl prepared by solution cast with methanol as solvent, nearly no LiCl crystal was observed at low salt concentration, [O:Li]=32:1, as shown in Figure 4.11(a). By comparing Figure 4.10(c) with Figure 4.11(c), it was found that at high salt concentration, [O:Li]=8:1, PEMPS/LiCl mixtures prepared by solution cast shows better dispersion of salt particles than the one prepared by melt mixing. This difference in dispersion can be attributed to the use of polar solvent, methanol. As mentioned in the previous section, LiCl crystal experienced two sequent preparations in the solution cast procedure: the first one is the complete dissolution of LiCl in methanol; the other is the formation of the agglomerates after the drying of methanol. In first step, the large salt aggregation as shown in Figure 4.2 completely disappears. In the second step, LiCl crystal nucleuses are formed and LiCl agglomerates start to grow gradually as the evaporation of methanol because of the poor interaction between LiCl and PEMPS. However, only small LiCl agglomerates are formed in the second step because the existence of the high viscosity PEMPS impedes the growth of large LiCl agglomerates as results of diffusion restriction. However in the melt mixing the dissociation of the large aggregation is achieved only by the interaction of LiCl with ether oxygen on PEMPS. Due to the high lattice crystal energy of LiCl, the
Figure 4.10 Optical Micrographs of PEMPS with different LiCl concentrations from melt mixing at 60°C; (a) [O:Li]=32:1 (b) [O:Li]=16:1 (C) [O:Li]=8:1
Figure 4.11  Optical micrographs of PEMPS with different LiCl concentration from solution cast; (a) [O:Li]=32:1 (b) [O:Li]=16:1 (C) [O:Li]=8:1
agglomerates cannot be completely dissociated, so they remain as big particles shown in Figure 4.11(c).

The optical micrographs of PEMPS/ LiClO₄ and PEMPS/LiTFSI melt mixture are shown in Figure 4.12 and Figure 4.13, respectively. Similarly, no undissolved salt is found in the field, which indicates the good salt solvation in PEMPS. It is worthwhile to point out that PEMPS has similar ether branches as PTMG. The effective solvation media in both materials is ether oxygen, which explains their similar salt solvation behavior.

4.1.3 PTMG/PEMPS Blends with Lithium Salts

PTMG/PEMPS blend with lithium salts are the precursor of TPU/PEMPS electrolytes. Their morphology, especially the miscibility, is important for the phase morphology of TPU/PEMPS electrolytes. The morphology of PTMG/PEMPS blends without salt was observed using optical microscopy. Figure 4.14(a) and Figure 4.14 (b) show the morphology of PTMG/PEMPS blend at both room temperature and elevated temperature (> 60°C). At room temperature, PTMG exhibits the spherulite morphology and the size of PTMG crystal spherilite is much smaller compared with that of neat PTMG. Also it was noticed that there was some spherical inclusion in the crystals. Since PEMPS is in an amorphous state at the room temperature, the spherical phases are believed to be the separated PEMPS phase, which is also further confirmed from the phase morphology of the blend in the molten state as shown in Figure 4.14 (b). Since PTMG is the major component and PEMPS is the minor component in the blends, the small droplets in the phase morphology of their blend in molten states will be PEMPS
Figure 4.12  Optical micrographs of PEMPS with different LiClO₄ concentrations from solution cast; (a) [O:Li]=32:1 , (b) [O:Li]=16:1, (C) [O:Li]=8:1
Figure 4.13  Optical micrographs of PEMPS with different LiN(SO$_2$CF$_3$)$_2$ concentrations from solution cast; (a) [O:Li]=32:1, (b) [O:Li]=16:1, (c) [O:Li]=8:1.
phase. The sharp boundary between PEMPS phase and the matrix PTMG phases indicates the poor miscibility between these two components. There are a number of specific factors that can contribute to the miscibility of polymer blends, such as polarity, specific group attraction, molecular weight, blend ratio and crystallinity of the components. In this study, PTMG is a semi-crystalline polymer and PEMPS is an amorphous polymer. Although the PEMPS is the polysiloxane grafted with ether chain which has similar structures with PTMG, the spacious barrier is a major factor determining their miscibility just as the cause of the poor miscibility between PEO with PPO. Tandel in our research group used the PEO/PPO blend as polymer matrix for polymer electrolytes. In his study, it was found that PEO/PPO blend was immiscible at higher concentration of PPO and showed phase separation at 50% of PPO. He believed that the steric hindrance of methyl group in PPO restrict the miscibility between PEO and PPO.

After the addition of salts in PTMG/PEMPS blends, the interface between two phases became blurred and the separated domain size reduced as shown in Figure 4.14 (c). This indicates that the addition of salt on the immiscible blends of PTMG/PEMPS improved the compatibility between PEMPS phase and PTMG phase. This might be attributed to the binder function of Li$^+$ ions on both PTMG and PEMPS via the interaction between Li$^+$ with PEMPS and the interaction between Li$^+$ and PEMPS. Similar results have been reported by other researchers on different polymer systems. Mani et al. and Li et al. found the salts had compatibilizing effects on polymer pairs. Kim et al. also indicated that the addition of salt probably facilitated the miscibility of
polymer pairs in their study of the polymer electrolytes based on PEO/poly(oligo[oxyethylene]oxysebacoyl) (PES) blend.

Figure 4.14  Optical Micrographs of PTMG and PEMPS blend (the ratio is calculated according to the formula of TPU/PEMPS=100/40); (a) at solid state and (b) at molten state (c) PTMG and PEMPS blend with LiClO₄ at [O:Li]=16:1
4.2 Fourier Transform Infrared Spectroscopy (FTIR)

The interaction of salts with polymers plays an important role on the salt dissolution in PTMG and PEMPS as well the miscibility of these two components. The characteristic absorption peaks of ether group, carbonyl group and amine groups etc. associated with the interaction are expected to be shifted or broadened and their intensities are expected to be depressed or enhanced.

The characteristic peaks of PTMG of interest are in two regions: the C-O-C stretching (1150 cm\(^{-1}\) to 1000 cm\(^{-1}\)) and –OH group stretching (3500 cm\(^{-1}\)-3100 cm\(^{-1}\)). These peaks indicate possible salt solvation sites on PTMG.\(^{174}\) In PEMPS, two regions of interests are mainly focused: (1) the two peaks around 1264 cm\(^{-1}\) and 803 cm\(^{-1}\), which are ascribed to the CH\(_3\)-Si symmetric deformation; (2) Si-O-Si asymmetric stretch of polysiloxane main chain and C-O-C stretching of ether side chain (1150 cm\(^{-1}\) to 1000 cm\(^{-1}\)).\(^{175}\) The characteristic absorption band of different polymers and salts are listed in Table 4.1. In this research, the interested regions of TTIR spectra stated above were analyzed using peak separation FITYK software for peak deconvolution of overlapped peaks. The Gaussian–Loreinze analysis was used in this study.

4.2.1 PTMG/Salt Mixture

Figure 4.15 shows the FTIR spectra of the three different kinds of lithium salts used in this study including, LiCl, LiClO\(_4\) and LiN(SO\(_2\)CF\(_3\))\(_2\). LiCl has a broad absorption band ranging from 500-700 cm\(^{-1}\) because of overlapping different vibration modes of
Table 4.1 The characteristic absorption band of different polymers and salts in FTIR\textsuperscript{171,174}

<table>
<thead>
<tr>
<th>Materials</th>
<th>Chemical group</th>
<th>Wavenumber of the absorption band (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMG</td>
<td>C-O-C stretching</td>
<td>1150 cm\textsuperscript{-1} to 1000 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td></td>
<td>O-H group stretching</td>
<td>3500 cm\textsuperscript{-1} to 3100 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>PEMPS</td>
<td>CH\textsubscript{3}-Si symmetric deformation</td>
<td>1264 cm\textsuperscript{-1}, 803 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td></td>
<td>Si-O-Si asymmetric stretch</td>
<td>1080 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td></td>
<td>C-O-C stretching</td>
<td>1100 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>LiCl</td>
<td>Vibration of Li\textsuperscript{+}Cl\textsuperscript{-} ion pair</td>
<td>500-700 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>LiCl\textsubscript{O\textsubscript{4}}</td>
<td>free anions ClO\textsubscript{4}\textsuperscript{-}</td>
<td>623 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td></td>
<td>ion pair formation of anion ClO\textsubscript{4}\textsuperscript{-}</td>
<td>635 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>LiN(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2}</td>
<td>the antisymmetric SO\textsubscript{2} stretching mode ((\nu(SO\textsubscript{2})\textsubscript{a}))</td>
<td>1350 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td></td>
<td>symmetric CF\textsubscript{3} stretching mode</td>
<td>1200 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td></td>
<td>((\nu(CF\textsubscript{3})\textsubscript{s}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S-N stretching</td>
<td>740 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td></td>
<td>combined C-S stretching and C-F stretching</td>
<td>760 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td></td>
<td>the combined C-S and S-N stretching</td>
<td>785 cm\textsuperscript{-1}</td>
</tr>
</tbody>
</table>
Li⁺Cl⁻ ion pairs. The absorption peaks located around 1630 cm⁻¹ comes from the impurity or moisture residue in the form of crystal water according to Nakajima et al.¹⁷⁶ They pointed out the water molecule had a H-O-H bending vibration band and a O-H stretching vibration band of water around 1645 cm⁻¹ and 3618 cm⁻¹ respectively.¹⁷⁷ In their FTIR study of molten LiCl, they stated that the decrease of the inter-ionic distance could cause a shift of the vibration modes of the Li-Cl interaction to higher wavenumber.¹⁷⁶ The distance of Li-Cl is expected to change as LiCl is dissolved in polymer. Therefore, the shift of absorption peaks can be used to interpret the degree of ion dissociation. However, since the absorption peaks located around 500-700 cm⁻¹ as shown in Figure 4.15, are hard to be deconvolved, it is impossible to predict the ion dissociation by analyzing that region. On the other hand, the absorption peak located at 1670 cm⁻¹ also appeared in the FTIR of other salts.

In Figure 4.15, LiClO₄ has an absorption peak at 635 cm⁻¹. Wieczorek et al.¹⁷⁸ and Salmon et al.¹⁷⁹ assigned the 623 cm⁻¹ band to free anions ClO₄⁻ and the peak located at 635 cm⁻¹ to ion pair formation of the anion ClO₄⁻. In the LiClO₄, most of the ClO₄⁻ is in the form of ion pairs and thus the overlapped peaks at 623 cm⁻¹ and 635 cm⁻¹ generate the strong absorption peak around 635 cm⁻¹. In the FTIR spectra of LiN(SO₂CF₃)₂, there are several characteristic absorption peaks in the region of 1100-1400 cm⁻¹ and 500-800 cm⁻¹. According to Wen et al.¹⁸⁰, the peaks around 1350 cm⁻¹ and 1200 cm⁻¹ are attributed to the antisymmetric SO₂ stretching mode (ν(SO₂)ₐ) and symmetric CF₃ stretching mode (ν(CF₃)ₙ) respectively. And the peaks located in the region of 730-800 cm⁻¹ are assigned
as follows: 740 cm\(^{-1}\) for S-N stretching, 760 cm\(^{-1}\) for the combined C-S stretching and C-F stretching, and 785 cm\(^{-1}\) for the combined C-S and S-N stretching.\(^{181}\)

Figure 4.16 shows the FTIR spectra of PTMG/LiCl melt mixture with the different ratio of [O:Li]. PTMG has a similar structure as PEO except for the hydroxyl groups at both ends of chain. Detailed assignments of each absorption peak of PEO are listed in Table 4.2. The 844 cm\(^{-1}\) peak and 963 cm\(^{-1}\) peak in the neat PTMG is attributed to the CH\(_2\) rock/C-C stretch and CH\(_2\)-rock/CH\(_2\) twist, respectively.\(^{55}\) The peak around 1100 cm\(^{-1}\) is related to the C-O stretching. The peaks located around 1283 cm\(^{-1}\) and 1364 cm\(^{-1}\) are assigned as the asymmetric wagging vibrations of the CH\(_2\) group with respect to the C-C axis of the OCH\(_2\)-CH\(_2\) sequence. Peaks located in the range from 2860 cm\(^{-1}\) to 2950 cm\(^{-1}\) are assigned as the CH\(_2\) symmetric stretch and ant-symmetric stretch. The strong absorption in the range of 3300 to 3500 cm\(^{-1}\) is assigned as the terminal hydroxyl group. According to Zhang et al.\(^{182}\), the peak of hydrogen bonded O-H stretching band in neat PTMG was centered at 3482 cm\(^{-1}\). The appearance of a peak around 3380 cm\(^{-1}\) in Figure 4.16 is attributed as the O-H bonded with Li\(^+\). It is noticed that the intensity of this peak increases as the salt concentration increases. The 1100 cm\(^{-1}\) peak of neat PTMG has been reported to shift to the lower frequency and the additional peak appears at 1085 cm\(^{-1}\) after the addition of salts. Ferry et al.\(^{174}\) believed that it was caused by the weakening of the C-O-C bond by cation coordinations. By tracing the intensity change and wavenumber shift of the peak around 1110 cm\(^{-1}\), the interaction between ether oxygen and lithium salts will be determined. Due to the overlapping between the original peaks corresponding to undoped ether group and the shifted peaks corresponding to Li\(^+\) doped
Figure 4.15  FTIR spectra of three different salts: LiCl, LiClO₄, and LiN(SO₂CF₃)₂

Figure 4.16  FTIR spectra of PTMG/LiCl mixtures with various LiCl concentrations prepared by melt mixing
Table 4.2 The assignments of absorption peaks of FTIR spectra of polyethylene oxide

<table>
<thead>
<tr>
<th>Wavelength, cm(^{-1})</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2950m</td>
<td>CH(_2) antisymmetric stretch</td>
</tr>
<tr>
<td>2890s</td>
<td>CH(_2) symmetric stretch</td>
</tr>
<tr>
<td>2885s</td>
<td>CH(_2) symmetric stretch</td>
</tr>
<tr>
<td>2865s</td>
<td>CH(_2) symmetric stretch</td>
</tr>
<tr>
<td>1470m</td>
<td>CH(_2) scissor</td>
</tr>
<tr>
<td>1463m</td>
<td>CH(_2) scissor</td>
</tr>
<tr>
<td>1457m</td>
<td>CH(_2) scissor</td>
</tr>
<tr>
<td>1453w</td>
<td>CH(_2) scissor</td>
</tr>
<tr>
<td>1415w</td>
<td>CH(_2) wag</td>
</tr>
<tr>
<td>1364m</td>
<td>CH(_2) wag</td>
</tr>
<tr>
<td>1345s</td>
<td>CH(_2) wag</td>
</tr>
<tr>
<td>1283m</td>
<td>CH(_2) twist</td>
</tr>
<tr>
<td>1244</td>
<td>CH(_2) twist</td>
</tr>
<tr>
<td>1149s</td>
<td>C=*O stretch, CH(_2) rock</td>
</tr>
<tr>
<td>1119s</td>
<td>C–C, C–O stretch</td>
</tr>
<tr>
<td>1102 vs</td>
<td>C=*O stretch</td>
</tr>
<tr>
<td>1062m</td>
<td>C –O, C–C stretch, CH(_2) rock</td>
</tr>
<tr>
<td>963s</td>
<td>CH(_2) rock, CH(_2) twist</td>
</tr>
<tr>
<td>947m</td>
<td>CH(_2) rock(gauche), C –C stretch</td>
</tr>
<tr>
<td>844s</td>
<td>CH(_2) rock(gauche), C –C stretch</td>
</tr>
</tbody>
</table>
ether group, the peak at 1110 cm\(^{-1}\) is broadened. Figure 4.17 shows peak deconvolution results in the range of 1000 to 1200 cm\(^{-1}\), the overlapped broad peak can be separated to three different peaks including 1110 cm\(^{-1}\), 1102 cm\(^{-1}\) and 1054 cm\(^{-1}\). As the salt concentration increases, the intensity of the peak around 1110 cm\(^{-1}\) decreases and the 1102 cm\(^{-1}\) peak shifts to the low frequency to 1095 cm\(^{-1}\) and its intensity increases due to the interaction Li\(^+\) to ether oxygen atom, which is in agreement with reports on the complex of PEO and cations.\(^{174, 178, 180}\). The intensity of 1374 cm\(^{-1}\) peak increases as the concentration of LiCl increases as reported by Golodnitsky et al.\(^{183}\). Figure 4.18 shows the deconvolved peaks in the –OH region (3100 to 3700 cm\(^{-1}\)). The centered of –OH peak is shifted to the lower frequency as the salt concentration increases.

In order to compare the interaction between salt and PTMG with and without the polar solvents, PTMG/LiCl mixtures prepared by the solution cast were also characterized. The CH\(_2\) absorbance peak located at 2970 cm\(^{-1}\) does not change before or after the addition of the salt. It is used as an internal standard to normalize the absorbance intensity of the peaks of interests. The relative intensity of the specific peak is equal to the ratio of the intensity of the interested absorbance peak to the 2970 cm\(^{-1}\) peak. Figure 4.20 and Figure 4.21 show the variation of relative intensity of different characteristic peaks with the LiCl salt concentration in melt mixing process and solution process, respectively. The intensity of the peak of the mixture prepared by the solution process is expected to be more sensitive to the salt concentration than that of the mixture prepared by melt process because of the slightly better dissolution of LiCl in PTMG with
Figure 4.17  The deconvolution FTIR spectra of PTMG/LiCl mixtures with different LiCl concentrations in the range of 1000 cm\(^{-1}\) - 1200 cm\(^{-1}\) (a) neat PTMG, (b) [O:Li]=32:1, (c) [O:Li]=16:1, (b) [O:Li]=8:1. The dotted line represents the original peak and the solid line represents the fit peaks.

Figure 4.18  The deconvolution FTIR spectra of PTMG/LiCl mixtures with different LiCl concentrations in the range of 1320 to 1400 cm\(^{-1}\) (a) neat PTMG, (b) [O:Li]=32:1, (c) [O:Li]=16:1, (b) [O:Li]=8:1. The dotted line represents the original peak and the solid line represents the fit peaks.
Figure 4. The deconvolution FTIR spectra of PTMG/LiCl mixtures with different LiCl concentrations in the range of 3100 to 3700 cm\(^{-1}\): (a) neat PTMG, (b) [O:Li]=32:1, (c) [O:Li]=16:1, (d) [O:Li]=8:1. The dotted line represents the original peak and the solid line represents the fit peaks.
Figure 4.20 The relative intensity of some peaks versus different LiCl concentration in PTMG/LiCl mixture prepared by melt mixing
Figure 4.21  The relative intensity of some peaks versus different LiCl concentrations in PTMG/LiCl mixture prepared by solution cast
solvent. However, no significant difference is observed. This is because there is only a very small amount of LiCl dissolved in PTMG in both methods.

The FTIR spectra of PTMG/LiClO₄ mixtures with different LiClO₄ concentrations and their deconvolution results of different peaks are shown from Figure 4.22 to Figure 4.26. The peak around 630 cm⁻¹ with a broad shoulder can be separated into two peaks: 627 cm⁻¹ and 637 cm⁻¹, which are associated with the free Li⁺ and ion contacted Li⁺ according to Wieczorek et al. The relative intensity of both peaks increases as the LiClO₄ concentration increases while the intensity ratio between two peaks $I_{627}/I_{637}$ decreases as LiClO₄ concentration increases as shown in Figure 4.28. This indicates that more Li⁺ ions tend to form ion clusters at high LiClO₄ concentration. Similar as the FTIR of PTMG/LiCl, the 1121 cm⁻¹ peak intensity decrease and 1100 cm⁻¹ peak shifts to low frequency as shown in Figure 4.24. The intensity of 1379 cm⁻¹ peak increases with the salt concentration in Figure 4.25. The appearance of the 3264 cm⁻¹ peak is due to the interaction of Li⁺ with the –OH group and its intensity increases. The bonded –OH vibration around 3433 cm⁻¹ shifts to the lower frequency in Figure 4.26 due to the interaction of Li⁺ with hydrogen bonded O atom. While the free –OH stretching around 3480 cm⁻¹ is shifted to higher frequency around 3550 cm⁻¹. The FTIR spectra of PTMG/LiClO₄ mixture with different LiClO₄ concentrations prepared by the solution cast and their relative intensity of some peaks of interest are shown in Figure 4.29 and Figure 4.30 respectively. Comparing Figure 4.27 with Figure 4.30, no noticeable difference was observed.
Figure 4.31 shows the FTIR spectra of PTMG/LiN(SO$_2$CF$_3$)$_2$ melt mixture with different [O:Li]. The strong absorption band in PTMG at 1105 cm$^{-1}$ (asymmetric COC stretching) is strongly affected by cation complexation. Wen et al.$^{180}$ studied the FTIR spectra of PEO/ LiN(SO$_2$CF$_3$)$_2$ electrolytes, finding that the intensity of C-O-C peak at 1104 cm$^{-1}$ in the pure PEO was strongly influenced by the addition of Li$^+$. In their research, they considered that in very dilute LiN(SO$_2$CF$_3$)$_2$ water solution the N(SO$_2$CF$_3$)$_2^-$ was in the form of free N(SO$_2$CF$_3$)$_2^-$ and so the spectrum of N(SO$_2$CF$_3$)$_2^-$ obtained in that solution was analogous to the spectrum of free N(SO$_2$CF$_3$)$_2^-$.

It was found that in very dilute LiN(SO$_2$CF$_3$)$_2$ water solution, the peaks appeared at 1347, 1204, 1138 and 1057 cm$^{-1}$ and the additional new peaks at 1322 and 1229 cm$^{-1}$ appeared in high concentration. As the concentration increases, the peaks at 1236 and 1143 cm$^{-1}$ associated with the aggregate formation appeared. The peaks of dried LiN(SO$_2$CF$_3$)$_2$ can be split into three peaks including 1351 cm$^{-1}$, 1241 cm$^{-1}$ and 1066 cm$^{-1}$. Deepa et al.$^{184}$ believed that the absorption peak at 1355 cm$^{-1}$ was assigned to free imide ions and it splits into two components at 1337 and 1359 cm$^{-1}$ when there exist contact–ion pairs. Similar conclusion was also made by Bakker et al.$^{185}$

As shown in Figure 4.32, the peaks at 575 cm$^{-1}$ and 799 cm$^{-1}$ of neat LiN(SO$_2$CF$_3$)$_2$ are shifted to lower frequency as salt concentration increases due to the interaction between the anion and ether group of PTMG. The 1331 cm$^{-1}$ peak splits into
Figure 4.22 FTIR spectra of PTMG/ LiClO$_4$ melt mixture with various LiClO$_4$ concentrations prepared by melt mixing.
Figure 4.23  The deconvolution FTIR spectra of PTMG with different LiClO₄ concentration of ranging from 610 to 650 cm⁻¹, (a) [O:Li]=32:1, (c) [O:Li]=16:1, (b) [O:Li]=8:1. The dotted line represents the original peak and the solid line represents the fit peaks.

Figure 4.24  The deconvolution FTIR spectra of PTMG with different LiClO₄ concentration ranging from 1000 to 2000 cm⁻¹ (a) neat PTMG, (b) [O:Li]=32:1, (c) [O:Li]=16:1, (b) [O:Li]=8:1.
Figure 4.25  The deconvolution FTIR spectra of PTMG with different LiClO$_4$ concentrations ranging from 1300 to 1400 cm$^{-1}$ (a) neat PTMG, (b) [O:Li]=32:1, (c) [O:Li]=16:1, (b) [O:Li]=8:1.

Figure 4.26  The deconvolution FTIR spectra of PTMG with different LiClO$_4$ concentrations ranging from 3100 to 3500 cm$^{-1}$ (a) neat PTMG, (b) [O:Li]=32:1, (c) [O:Li]=16:1, (b) [O:Li]=8:1.
Figure 4.27  The relative intensity of some peaks versus different LiClO$_4$ concentrations in PTMG/LiClO$_4$ mixture prepared by melt mixing
Figure 4.28  The intensity ratio of absorption at 627 cm\(^{-1}\) to 637 cm\(^{-1}\) in FTIR of PTMG/LiClO\(_4\) mixture with different LiClO\(_4\) concentrations

The intensity ratio of absorption at 627 cm\(^{-1}\) to 637 cm\(^{-1}\) in FTIR of PTMG/LiClO\(_4\) mixture with different LiClO\(_4\) concentrations.
Figure 4.29 FTIR spectra of PTMG with various LiClO₄ concentrations prepared by solution cast
Figure 4.30  The relative intensity of some peaks versus different LiClO$_4$ concentrations in PTMG/LiClO$_4$ mixture prepared by solution cast.
two peak around 1331 cm$^{-1}$ (contact anion ion) and 1350 cm$^{-1}$ (free anion). The relative intensity ratio of $I_{1350}/I_{1331}$ cm$^{-1}$ decreases as the salt concentration increases as shown in Figure 4.34, which indicates that more N(SO$_2$CF$_3$)$_2^-$ is in the form of contact-anion ions as more salt is added.

The deconvolution FTIR spectra of –OH region is shown in Figure 4.33. There might exist different kinds of interaction in this region: free –OH stretching, hydrogen bonded –OH, Li$^+$ bonded –OH and N(SO$_2$CF$_3$)$_2^-$ bonded –OH. The peak around 3282 cm$^{-1}$ is assigned as hydrogen bonded –OH associated with Li$^+$ and the peak around 3350-3380 cm$^{-1}$ is assigned as hydrogen bonded –OH and N(SO$_2$CF$_3$)$_2^-$ bonded –OH. In Figure 4.33, it is observed that at [O:Li]=32:1, the area corresponding the hydrogen bonded -OH associated with Li$^+$ is much larger than the area of the one corresponding to the associated with ion cluster. However, as more salt is added, the absorption peak area of the latter one becomes dominant, which implies that the Li$^+$ bonded hydroxyl coexists with and hydrogen bonded hydroxyl. However, Li$^+$ bonded hydroxyl is more favored after the salts are added.
Figure 4.31 FTIR spectra of PTMG with various LiN(SO$_2$CF$_3$)$_2$ concentrations prepared by melt mixing
Figure 4.32  FTIR spectra of PTMG with various LiN(SO$_2$CF$_3$)$_2$ concentrations in the region of (a) 500 cm$^{-1}$ to 900 cm$^{-1}$ (b) 1000 cm$^{-1}$ to 1400 cm$^{-1}$

Figure 4.33  The deconvolution FTIR spectra of PTMG with different LiN(SO$_2$CF$_3$)$_2$ concentrations ranging from 3100 to 3500 cm$^{-1}$ (a) neat PTMG , (b) [O:Li]=32:1, (c) [O:Li]=16:1, (b) [O:Li]=8:1
Figure 4.34  The intensity ratio of absorption at 1355 cm$^{-1}$ to 1331 cm$^{-1}$ of PTMG/LiN(SO$_2$CF$_3$)$_2$ mixture with different LiN(SO$_2$CF$_3$)$_2$ concentrations
Figure 4.35 The relative intensity of some peaks versus different LiN(SO$_2$CF$_3$)$_2$ concentrations in PTMG/ LiN(SO$_2$CF$_3$)$_2$ mixture prepared by melt mixing
Figure 4.36 FTIR spectra of PTMG with various LiN(SO₂CF₃)₂ concentrations prepared by solution cast.
Figure 4.37 Relative intensity of certain peaks versus different $1/[O:Li]$ in PTMG/LiN(SO$_2$CF$_3$)$_2$ mixture prepared by solution cast.
4.2.2 PEMPS/salt Mixture

The FTIR of PEMPS/LiCl mixture prepared by melt mixing and the relative intensity of their characteristic peaks are shown in Figure 4.38 and Figure 4.40. According to Fan et al.\(^\text{186}\), the peak at 803 cm\(^{-1}\) and 1264 cm\(^{-1}\) are assigned to the CH\(_3\)-Si rocking and CH\(_3\) in Si-CH\(_3\) symmetric bending. The Si-o-Si asymmetric stretching is in the range of 1100 cm\(^{-1}\) to 1028 cm\(^{-1}\). The C-O-C stretching of the ether group on the side chain of polysiloxane is around 1110 cm\(^{-1}\), which is at the same location as the ether group in PTMG. The appearance of an absorption band around 1660 cm\(^{-1}\) is introduced by the impurity in LiCl salts as discussed in previous section.

The 620 cm\(^{-1}\) peak disappeared after the addition of the salts. A similar trend as the one in PTMG/LiCl mixture has been found that the relative intensity of peak in 1110 cm\(^{-1}\) decrease as the salt concentration increases first and then reach a plateau at [O:Li\(^+\)]=16:1. This indicates that PEMPS is already saturated by LiCl when [O:Li\(^+\)]=16:1, and the further addition of LiCl can not be dissociated by PEMPS. This agrees well with the optical microscopy results. The fact that LiCl reaches the saturation level at same concentration of both PTMG and PEMPS mixtures implies that the dissolution of LiCl in PEMPS are mainly controlled by the grafting ether chain. Few are contributed by the oxygen in the silicone backbone chains. Cowie et al.\(^\text{30}\) pointed out that the siloxanes –Si-O- were poor media for the ionic conduction in spite of the low T\(_g\) normally associated with these polymers because the characteristics of the Si-O-bond itself which tends to the suppress the oxygen donor number. It was found that the ionic conductivity of polydimethylsiloxane (DPMS) is low due to the poor salt solvation ability.
Figure 4.38  FTIR spectra of PEMPS with various LiCl concentrations prepared by melt mixing
Figure 4.39  FTIR spectra of PEMPS/LiCl mixture with LiCl concentrations prepared by solution cast
although it has very flexible chains. By taking advantage of the flexiblility of Si-O-bond and the good salt salvation of polyether such as PEO, the polyether-modified polysiloxane with various structures has been developed as the host polymer for polymer electrolytes and shows good ionic conductivity. 102,103,105,106 Oh et al. 97 reported that a mono-comb polyether grafted polysiloxane electrolytes with LiTFSI showed ionic conductivity above $10^{-4}$ S/cm.

Comparing the FTIR results of PEMPS prepared by melt mixing with the ones prepared by solution cast, it is found that the intensity of $1110\text{cm}^{-1}$ peak is more depressed in the case of solution cast than the one in melt mixing. Interestingly, the intensity of $1110\text{cm}^{-1}$ peak in the PEMPS/LiClO$_4$ and PEMPS/Li N(SO$_2$CF$_3$)$_2$ mixture increases after the addition of salts as shown in Figure 4.42 and Figure 4.49. These results are opposite to the results obtained in PEMPS/LiCl complex and PTMG complexed with different salts. The possible explanation is that Li$^+$ not only interacts with ether oxygen but also interacts with the oxygen in the Si-O and the intensity of the peak centered at $1110\text{cm}^{-1}$ is the result of vibrations of combined interactions. The $620 \text{cm}^{-1}$ peak of PEMPS disappears and the intensity of the $627\text{cm}^{-1}$ peak and $635 \text{cm}^{-1}$ peak of LiClO$_4$ increases with the addition of salt as shown in Figure 4.42. The decrease of the intensity ratio of $627\text{cm}^{-1}$ to $635 \text{cm}^{-1}$ indicates that more ClO$_4^-$ exists in the form of ion cluster as more salt is added. This intensity ratio shows higher values in samples prepared by solution cast than the one prepared by melt mixing as in Figure 4.46, which indicates that more free ions exist in the sample prepared by solution cast. However, for PEMPS with Li N(SO$_2$CF$_3$)$_2$ in Figure 4.51, the two curves illustrates that there is not significant
Figure 4.40 Relative intensity of certain peaks versus different $\frac{1}{[\text{O:Li}^+]}$ in PEMPS/LiCl mixture prepared by melt mixing

Figure 4.41 Relative intensity of certain peaks versus different $\frac{1}{[\text{O:Li}^+]}$ in PEMPS/LiCl mixture prepared by solution cast
Figure 4.42 FTIR spectra of PEMPS/LiClO₄ complex with different LiClO₄ concentrations prepared by melt mixing
Figure 4.43  FTIR spectra of PEMPS with various LiClO₄ concentrations prepared by solution cast
Figure 4.44  Relative intensity of certain peaks versus different $1/[O:Li]$ in PEMPS/LiClO$_4$ mixture prepared by melt mixing

Figure 4.45  Relative intensity of certain peaks versus different $1/[O:Li]$ in PEMPS/LiClO$_4$ mixture prepared by solution cast
Figure 4.46  The intensity ratio of absorption at 625 cm\(^{-1}\) to 635 cm\(^{-1}\) of PEMPS/ LiClO\(_4\) mixture with different LiClO\(_4\) concentrations
Figure 4.47 FTIR spectra of PEMPS with various Li N(SO$_2$CF$_3$)$_2$ concentrations prepared by melt mixing
Figure 4.48 FTIR spectra of PEMPS with various Li N(SO$_2$CF$_3$)$_2$ concentrations prepared by solution cast.
Figure 4.49   Relative intensity of certain peaks versus different $1/[O:Li]$ in PEMPS/ Li $N(SO_2CF_3)_2$ mixture prepared by melt mixing

Figure 4.50   Relative intensity of certain peaks versus different $1/[O:Li]$ in PEMPS/ Li $N(SO_2CF_3)_2$ mixture prepared by solution cast
difference on the ratio of free ion to ion cluster. The similar Li N(SO$_2$CF$_3$)$_2$ dissociation behavior in PEMPS with and without methanol can be attributed to the weak interaction between Li$^+$ and TFSI$^-$.  

Figure 4.51 The intensity ratio of absorption at 1355 cm$^{-1}$ to 1331 cm$^{-1}$ of PEMPS/ Li N(SO$_2$CF$_3$)$_2$ mixture with different Li N(SO$_2$CF$_3$)$_2$ concentrations
4.3 Thermal Analysis By Differential Scanning Calorimetry (DSC)

The presence of salt in PTMG and PEMPS changes their thermal behavior due to the interaction between salts and polymers. DSC results of monomer/salt or polymer/salts complex can provide valuable information on salt solvation and their miscibility.

4.3.1 PTMG/salt Mixture

Figure 4.52 shows the DSC thermogram of three different salts used in this study. LiCl has two distinct endothermic peaks at 98.9°C and 240.6°C. LiCl has another peak at a very high temperature around 605°C. The DSC scan in Figure 4.52 is in the range of room temperature to 400°C. Therefore the peak above 400°C is not shown in Figure 4.52. LiClO₄ has four endothermic peaks at 133°C, 157°C, 334°C and 369°C respectively. The endothermic peaks of LiTFSI are around 51°C, 121°C and 274°C. The lowest endothermic peaks in the DSC of all the three salts are associated with the losing of crystal water. The detailed data is summarized in Table 4.3.

The DSC results of neat PTMG and PTMG/LiCl complex with different salt concentrations are shown in Figure 4.53. Neat PTMG shows an endothermic peak at 40°C in the DSC thermogram of the first run. Due to the high degree of crystallinity of PTMG, it is difficult to identify the glass transition of PTMG. So PTMG is quenched after the first scan to minimize the crystallinity and then subjected to the second scan to obtain the glass transition temperature. The second run of the DSC thermogram exhibits a
Figure 4.52  DSC Thermograms of three different lithium salts: (a) LiCl  (b)LiClO₄  
(c)LiN(SO₂CF₃)₂
Figure 4.53  DSC Thermograms of PTMG and LiCl melt mixture prepared by melt mixing (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan
Table 4.3 The list of glass transition ($T_g$), melting temperature ($T_m$), heat of fusion ($\Delta H$) and total heat of fusion of different lithium salts determined by DSC

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<th>$T_{m3}$</th>
<th>$T_{m4}$</th>
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transition at $-66^\circ$C. The PTMG/LiCl mixture exhibits two endothermic peaks and one of the peaks appears below $40^\circ$C and the other is at around $40^\circ$C, which suggests two crystalline phases. Shriver and coworkers$^{187}$ studied the phase diagram of PEO/NH$_4$SCN and found that PEO complex of NH$_4$SCN showed the mixture of amorphous phase and crystalline phases. The phase diagram contained a eutectic phase at NH$_4$SCN mole fraction around 0.1. When salt concentration is below that value there is crystalline phase of PEO/ NH$_4$SCN complex and neat crystalline phase of neat PEO. The stoichiometry of PEO/ NH$_4$SCN complex is 4:1 oxygen to salt. Lee and Crist$^{188}$ also found a similar result on PEO/salt complex. Therefore, it is possible that the one below $40^\circ$C in Figure 4.53 is related to the melting of crystalline PTMG/LiCl complex phase and the one around $40^\circ$C can be attributed to the pure PTMG crystal phase. At \([O:Li]=16:1\) and \(8:1\) an endothermic peak is observed at around $98^\circ$C, which also is shown in the DSC thermogram of neat LiCl crystal. This suggests that that peak is attributed to the undissolved LiCl in the PTMG/LiCl mixtures. The undissolved LiCl in PTMG/LiCl melt mixture is also observed in the optical micrographs shown in the previous section.
The $T_g$ at -66°C of neat PTMG is slightly shifted to the higher temperature at $[O:Li]=32:1$ and then decreased to the lower temperature at $[O:Li]=16:1$ and $[O:Li]=8:1$. The $T_g$ elevation after the addition of salts has also been observed by researchers in the study of PEO electrolytes. Puatrakul et al.\textsuperscript{54} believed that it was due to the reduction of the free volume of the polymer matrix by adding the salts and the salt-polymer interaction reducing the average segmental mobility of polymer chain. The interaction of Li$^+$ with oxygen makes Li$^+$ function as binder to connect different segments together and decrease the flexibility of PTMG segments. The fact that $T_g$ decreases at higher salt concentration in PTMG/LiCl melt mixtures might be associated with the undissolved LiCl which acts as plasticizer and dissociates the interaction between PTMG segments. The cross-linking structures initiated by the interaction of Li$^+$ and PTMG can also cause the reduction of the degree of crystallinity. The heat of fusion in PTMG and PTMG/LiCl mixture is listed Table 4.3. The heat of fusion values of the PTMG phase decreases as the salt concentration increases while the heat of fusion value of the PTMG/LiCl phase increases correspondingly. It indicates that LiCl tends to form crystal with PTMG after the excessive LiCl is introduced into the mixture.

Figure 4.54 shows the DSC traces of PTMG with LiClO$_4$. The second endothermic peak appears around 20°C after the addition of LiClO$_4$. Its location varies with the LiClO$_4$ concentration. The endothermic peaks are associated with the melting of the PTMG/LiClO$_4$ crystalline phase. Similarly, it is found that in PTMG/LiCl, the melting temperature of the PTMG/LiClO$_4$ crystalline phase increases as salt concentration increases. The finding in these results is that the heat of fusion decreases as
salt concentration increases. The more salt is added, the more PTMG/LiClO₄ is in the form of amorphous state. On the contrary, the overall heat of fusion of PTMG/LiClO₄ decreases dramatically as [O:Li] changes from 16:1 to 8:1. A recrystalization peak appears. The reason is that the strong interaction of Li⁺ with PTMG limits the flexibility of polymer chain and will inhibit the chain folding to form crystal.

Jeung⁵⁵ studied the thermal behavior of PEO electrolytes with four different salts, LiClO₄, NaClO₄, CuCl₂ and KI. The Tₘ depression was observed in all the PEO electrolyte studied in her research after the addition of salts. After the addition of LiClO₄, the Tₘ of the original neat PEO decreases from 73°C to around 48°C which depends on the salt concentration. The T₉ of PEO was also elevated from -60 to higher values as the salts were added. In the PEO electrolytes with 0.125 mole of NaClO₂, the T₉ was increased to -3.3°C. The Tₘ elevation in PEO electrolytes has also been reported in electrolytes with high salt concentration, especially [O:M]>3. Wright et al.¹⁷₃ pointed out that the DSC of PEO-alkali salt complexes, in general, showed two distinct endothermic regions. The low endothermic was centered near 60-70°C and higher endothermic occurred at the transition to the isotropic melts at temperature higher than 150°C. In salt-deficient samples only the lower endotherm was observed, which was related to the melting of the lower-melting complexed PEO/salt form. At high salt concentrations, the additional higher endothermic appeared due to the formation of high melting PEO/salt complex with the low stoichiometry such as PEO-NaSCN 3:1 complex. Minier et al.¹⁸⁹ reported an endothermic peak at around 160°C in PEO electrolyte with high
Figure 4.54  DSC Thermograms of PTMG/ LiClO₄ mixture prepared by melt mixing (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan
concentration of LiCF$_3$SO$_3$. In our research, the salt concentration is limited relatively low in order to prevent formation of high melting polymer/salt complex in which ions have low mobility. The high melting endothermic peak is not observed in the DSC thermograms of all the PTMG/salt mixture.

In comparison with the $T_g$ data of PTMG/LiCl, the $T_g$ of PTMG/LiClO$_4$ keeps continuously increasing as LiClO$_4$ concentration increases. This result implies that all the LiClO$_4$ are dissolved in PTMG. The absence of melting peaks of LiClO$_4$ crystal in DSC results together with results obtained by optical microscopy and FTIR, confirms the good dissolution of LiClO$_4$ in PTMG.

Figure 4.55 shows the DSC results of PTMG/LiTFSI. PTMG/LiTFSI exhibits two $T_g$s at [O:Li]=8:1. One $T_g$ appears around -55$^\circ$C and the other appears around -14$^\circ$C. The $T_g$ at a higher temperature might be associated to the transition of PTMG/LiTFSI complex with different stoichiometry. Also it was found that the $T_m$ of PTMG/ LiTFSI crystalline phase decreased as the salt concentration increased. These $T_m$ values are lower than the values of PTMG/ LiClO$_4$. The values of $T_g$, $T_m$ and the heat of fusion of each PTMG/salt mixture are listed in Table 4.4. Nearly all the PTMG/salt mixtures exhibit the increase in $T_g$ and decrease of $T_m$ as well as the reduction in the crystallinity after the addition of salt into PTMG. The DSC results correspond well with the results obtained from optical microscopy and FTIR regarding with the fact that LiCl is partially dissolved in PTMG while LiClO$_4$ and LiTFSI are completely dissolved in PTMG.
Figure 4.55  DSC Thermograms of PTMG and LiN(SO$_2$CF$_3$)$_2$ melt mixture prepared by melt mixing (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan
Table 4.4  The list of glass transition ($T_g$), melting temperature ($T_m$), heat of fusion ($\Delta H$) and total heat of fusion of PTMG with different salt concentrations determined by DSC

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Figure 4.56 Dependence of glass transition temperature ($T_g$) of PTMG/salt mixtures on the salt concentration

Figure 4.57 Dependence of melting temperature ($T_m$) of PTMG/salt mixtures on the salt concentration
4.3.2 PEMPS/salt Mixture

PEMPS has polyether branches grafted on the siloxane backbone chain. The branched architecture and the flexible polysiloxane backbone chain result in the amorphous property of PEMPS. Figure 4.58 shows the DSC results of PEMPS/LiCl mixtures. The neat PEMPS has a glass transition temperature at -78\(^0\)C. The \(T_g\) decreases with the addition of LiCl to PEMPS. The addition of LiCl to PEMPS shows a similar behavior as the addition of LiCl to PTMG so that \(T_g\) increases as the salt concentration increases first and then decreases due to the plasticizer effect of undissolved LiCl crystal. The DSC thermogram of PEMPS/LiCl mixtures with high LiCl concentration ([O:Li]=8:1) clearly shows the endothermic peak associated with LiCl crystal at around 95\(^0\)C. This means that there is still some undissolved LiCl crystal in the mixture. This phenomenon agrees with the DSC and FTIR results. The neat PEMPS shows a broad, shallow endothermic peak centered at -11\(^0\)C, which is contributed from the dissociation of small amounts of ordered ether side chain. Kang et al.\(^{190}\) pointed out that such an endothermic peak is very common for the comb-like polyether-modified polysiloxane. DSC thermogram in Figure 4.58 shows the peak shifts to higher temperature at high salt concentration.

Hooper et al.\(^{106}\) found that \(T_g\) polymer electrolytes based on polyether branched double comb polysiloxanes increases with the salt concentration increases. In Figure 4.59, no peaks related the LiClO\(_4\) are observed and \(T_g\) increases with salt concentration.
Figure 4.58  DSC Thermograms of PEMPS/ LiCl mixture prepared by melt mixing

Figure 4.59  DSC Thermograms of PEMPS /LiClO$_4$ mixture prepared by melt mixing
At [O:Li]=8:1 there is a substantial jump of $T_g$, the value increases to $-27^\circ C$ from $-78^\circ C$, which indicates that the interaction of Li$^+$ with PEMPS significantly confined the mobility of flexible PEMPS. It is possible that a network structure with Li$^+$ acting as cross-linker to connect different ether segment is formed, which leads the dramatic change of mobility. Watanabe et al.\textsuperscript{191} investigated the elevation in the $T_g$ of both high molecular weight and low molecular weight PPO and concluded that it was caused by the intermolecular and intramolecular cross-linking resulting from the formation of three chelate rings from three polymer chains, involving two ether oxygens from each other.

In PEMPS/LiClO$_4$ mixture, the endothermic peak associated with the dissociation of the ordered polyether branches almost disappears as shown in Figure 4.59. The reason is that the formation of the ordered structures was hindered by interaction of polymer and ions. Furthermore, a transition appears at around $10^\circ C$ instead of an endothermic peak for PEMPS/LiClO$_4$ mixture with [O:Li]=8:1. This might be associated with the dissociation of the polymer-ion network. Figure 4.60 illustrates the DSC of PEMPS/LiTFSI. The $T_g$ elevation is also found by the addition of LiTFSI. No endothermic peaks corresponding to melt of salt crystal peaks and the ordered polyether branches are shown in the DSC thermogram. This suggests that the ordered polyether branched structure might be destroyed by interacting with ions. The study in the previous section shows that the LiTFSI seem have the strongest interaction with polymer among the three lithium salts. Therefore, PEMPS/LiTFSI will have the higher $T_g$ elevation in comparison with PEMPS/LiClO$_4$ mixture. However, it is found that PEMPS/LiClO$_4$ shows the highest $T_g$, then PEMPS/LiTFSI, and PEMPS/LiCl least. This phenomenon
Figure 4.60  DSC Thermograms of PEMPS and LiN(SO$_2$CF$_3$)$_2$ mixture prepared by melt mixing

Figure 4.61  Dependence of glass transition temperature ($T_g$) of PEMPS/salt mixtures on the salt concentration
might be attributed to the formation of large ion clusters due to the high lattice energy of LiClO4 crystal. The LiClO4 crystal cannot be completely dissociated as free ions. Some of them exist in the form of big ion clusters. Charged ion clusters can interact with more polyether branch chains, thus greatly limiting the freedom of the polyether branches. However, due to the low lattice energy of LiTFSI salts, more LiTFSI is dissociated into free ions.

Table 4.5 The list of glass transition (Tg), melting temperature (Tm), heat of fusion (ΔH) and total heat of fusion of PEMPS with different salt concentration of salts determined by DSC

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CHAPTER V

POLYURETHANE/POLYETHER-MODIFIED POLYSILOXANE ELECTROLYTES

5.1 Polymerization Kinetics of TPU

One of goals in this study was to develop a novel solvent-free in-situ process for the preparation of the thermoplastic polyurethane (TPU)/polyether-modified polysiloxane (PEMPS) electrolytes. In the in-situ process, polyol, isocyanate and chain extender were polymerized in the presence of different salts and PEMPS. The monomer, polyol, played the role of common solvent to solvate the lithium salts first, then became the soft segments of polyurethane after polymerization. No volatile solvent was used so there were no concerns about material instability, environmental hazards, and high process costs due to the usage of large a mount of solvent. In the previous sections, it was concluded from the FTIR results of PTMG/salt mixtures that cations can interact with ether oxygen of hydroxyl group. However, the interaction of cations or anions with hydroxyl group might affect the activity of reactive hydroxyl group, interfering the polyurethane reaction.

Little work has been reported on the effect of salt on the kinetic of polyurethane polymerization in the presence of salts. Jeung$^{55}$ studied the polymerization kinetics of polyurethane in-situ with LiClO$_4$, CuCl$_2$, NaClO$_2$ respectively, for two kinds of polyurethane: poly(butylene adipate) based polyurethane (PBA-PU) and Poly(tetra methylene glycol) (PTMG-PU) based polyurethane. In her study, it was found that salts
had different effects on polymerization: LiClO₄ activated the polymerization of PBA-PU while CuCl₂ retarded the reactions; CuCl₂ and NaClO₂ slowed the polymerization of PTMG-PU but LiClO₄ slowed the reaction below 140°C and fasten the reaction above 140°C.

The kinetics of polyurethane in PTMG based PU with LiN(SO₂CF₃)₂ are studied in this section. The kinetics of this in-situ process was studied using isothermal DSC. The heat generated as a function of time was determined. The same method was used by Parnell⁷⁶ on the study of the kinetics of reactive blending of polyurethane with PVC. The detailed experimental procedure is described in section 3.3. This study assumed a constant enthalpic heat of reaction, no significant interference from side reactions, and heat evolved during polymerization is proportional to the extent of polymerization. The total molar enthalpic heat of reaction for TPU polymerization $\Delta H_{rxn}$ was assumed constant for all isothermal polymerization temperatures, which was obtained from their adiabatic temperature rise experiment (ATR). The $\Delta H_{rxn}$ of PTMG based polyurethane polymerization in this research was calculated to be -87 kJ/mole equivalent isocyanate from the data obtained in the adiabatic temperature rise of the polymerization of PTMG, MDI and BDO. Parnell⁷⁶ reported that $\Delta H_{rxn}$ of poly(butylenes adipate)-based polyurethane was approximately value -90 kJ/mole equivalent isocyanate. A value of $\Delta H_{rxn}$ = 63 kJ/mole equive NCO was obtained by Macosko et al⁷⁷. Lovering and Laidler¹⁹² obtained values between 77.5 and 104.7 kJ/mole equivalent NCO reacted for aromatic isocyanates and diisocyanates. Macosko et al.⁷⁷ stated that the heat of reaction depended mainly on the type of isocyanate; but variations in the results of the heat of
reaction were observed for different types of polyols. In this research, it was found that the structure difference of PTMG and PBA negligibly influences the value of the heat of reaction in comparison with the data obtained by Parnell\textsuperscript{76}.

Equation (2.12) in section 2.2.2 is based on the assumption that the order of the polyurethane reaction under both the catalyzed and non-catalyzed conditions is same. For polyurethane reactions in which the non-catalyzed reaction and the catalyzed reaction have different orders of reaction, the simplified empirical model described in equation (2.12) does not apply. In Parnell’s\textsuperscript{76} study, the n value of non-catalyzed polyurethane was very close to the one of catalyzed polyurethane reaction and it has a average value of 1.7.

The plots of heat flow vs. polymerization time for polyurethane electrolytes with different salt concentration and PEMPS concentration at various temperatures are shown from Figure 5.1 to Figure 5.5. The exothermic heat flow for the neat polyurethane decreases with the polymerization time significantly at temperatures ranging from 100\textdegree C and 140\textdegree C. The heat flow reaches almost zero after 10 minutes, which indicates that the reaction is nearly completed within a short time. The exothermic heat flow of polyurethane/LiN(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2} electrolytes with certain salt concentrations increases with temperature at the beginning of the reaction as shown in Figure 5.2. While the heat flow of polyurethane/LiN(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2} electrolytes with different salt concentrations decreases with decreasing of the values of [O:Li], i.e. the salt concentration increase, as shown in Figure 5.3. This implies that the incorporation of LiN(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2} into the polyurethane reactant retards the polymerization reaction. The retardation might be caused by the interaction of free Li\textsuperscript{+} or Li\textsuperscript{+} ion clusters with reactive hydroxyl groups which impede its
reaction with isocyanate. It is possible that the interaction of salts with the isocyanate can also contribute since it is found that Li\(^+\) can interact with the carbonyl group on the hard segment of TPU. The heat flow of polymerization decreases after the addition of PEMPS, as shown in Figure 5.4. The polyurethane reactant is diluted by the presence of the non-reactive component so that the reaction is slowed down due to the decrease of effective reactant concentration. Figure 5.5 shows the plot of heat flow vs. polymerization time for TPU/PEMPS/LiN(SO\(_2\)CF\(_3\))\(_2\) electrolyte with PU/PEMPS=100/10 and \([\text{O:Li}] = 16\) at various temperatures. The temperature dependence is similar to that of TPU/LiN(SO\(_2\)CF\(_3\))\(_2\) electrolyte.

The non-isothermal DSC scan of the reactant mixture from room temperature to \(200^\circ\)C is conducted following the isothermal polymerization to calculate the heat residue. For most samples, the reaction was already completed after the 30 min isothermal scan. The heat residue calculated is usually negligible. As mentioned before, the conversion and conversion rate were calculated by applying equations (3.1)-(3.3). The plots of convention vs. polymerization time were drawn in Figure 5.6, Figure 5.7, Figure 5.8 and Figure 5.9. The symbols represent the data calculated by using the equations (3.1)-(3.3). From the log-log plots of conversion rate vs. conversion remaining, the kinetic parameters for neat polyurethane can be obtained by fitting into the kinetic law model stated in section 2.2.2 with least squares linear regression techniques. The \(k\) and \(n\) values were determined from the intercept and slop of the plot respectively.
Figure 5.1   Isothermal DSC traces of neat polyurethane reactant mixtures polymerized at different temperatures

Figure 5.2   Isothermal DSC traces of polyurethane reactant mixtures with LiN(SO₂CF₃)₂ and [O:Li]=16:1 polymerized at different temperatures
Figure 5.3  Isothermal DSC traces of polyurethane with different LiN(SO$_2$CF$_3$)$_2$ concentrations at 140$^\circ$C

Figure 5.4  Isothermal DSC traces of polyurethane/PEMPS/LiN(SO$_2$CF$_3$)$_2$ reactant mixture with different blend compositions and [O:Li] =16:1 at 140$^\circ$C
Figure 5.5  Isothermal DSC traces of polyurethane /PEMPS/LiN(SO₂CF₃)₂ reactant mixture with TPU/PEMPS=100/10 and [O:Li] =16:1 at different temperature

Figure 5.6  Experimental isothermal DSC conversion versus time profiles for neat polyurethane reactant mixture polymerized at different temperatures
Figure 5.7  Experimental isothermal DSC conversion versus time profiles for polyurethane reactant mixtures with LiN(SO$_2$CF$_3$)$_2$ and [O:Li]=16:1 polymerized at different temperatures.

Figure 5.8  Experimental isothermal DSC conversion versus time profiles for TPU/LiN(SO$_2$CF$_3$)$_2$ reactant mixture with different LiN(SO$_2$CF$_3$)$_2$ concentrations of salts polymerized at 140°C.
Figure 5.9  Experimental isothermal DSC conversion versus time profiles for TPU/PEMPS/LiN(SO$_2$CF$_3$)$_2$ reactant mixture with different blend compositions and [O:Li] =16:1 at 140°C
It was found that the polyurethane reactions with different salts, PEMPS concentrations at different isothermal conditions almost followed the same nth order and the average of n value was approximately 1.2 ± 0.2, which is similar to the results obtained by Jueng\textsuperscript{55} on the study of the kinetics of polyurethane electrolytes with LiClO\textsubscript{4}.

The k values of neat TPU at different temperatures were obtained in Figure 5.10. The k values of TPU/Li(N(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2} electrolytes at [O:Li]=16:1 and TPU/PEMPS/Li(N(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2} electrolytes at [O:Li]=16:1 with \(W_{TPU}/W_{PEMPS} =100/10\) at different temperatures were obtained from Figure 5.11 and Figure 5.14, respectively. The k values of TPU/Li(N(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2} electrolytes with various salt concentrations and TPU/PEMPS/Li(N(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2} electrolytes with various blend compositions were obtained from Figure 5.12 and Figure 5.13. These k values were used to study the effect of salt concentration, temperature and PEMPS concentration on the reaction. It was found that k values decrease as the salt concentration increases as shown in Figure 5.15. This indicates that the presence of LiTFSI retards the reaction of polyurethane polymerization. In Jeung's\textsuperscript{55} study, it is found that the LiClO\textsubscript{4} acts as a catalyst and accelerated the polyurethane reaction at very low salt concentrations ([O:Li]>64:1). The effect of LiClO\textsubscript{4} on the reaction constant was described in the form of \(k_2\) in the equation (2.12). However, in case of LiN(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2}, \(k_2\) will be a negative value if the equation (2.12) is used, which does not have any physical meaning with respect to the fundamental reaction steps. Equation (2.12) cannot properly represent the hinder effect of LiN(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2} on the reaction. The possible explanation for the different effect of LiClO\textsubscript{4} in her study and LiTFSI in this study is that in the lithium concentration used in this study is much higher.
than the one in Jeung’s study. At high lithium salt concentrations, the large counter ions, TFSI−, might also influence the reaction. The detailed mechanism of the effect of LiTFSI on polyurethane reaction is not clear.

For the polymerization of neat TPU, the value of k can be described by equation (2.10). According to the kinetic model, a semi-ln plot of k versus 1/T can be a straight line with its slope equal to −Ea/R and y-intercept equal to ln[A]. Using a linear least squares regression method, a fit line satisfying the following equation was obtained for neat polyurethane polymerization in Figure 5.16 with a least squares r² value of 0.85 and the standard derivation of A and Ea/R, +1.88x10² and +2.497x10² respectively.

\[
\frac{d\alpha}{dt} = (787*e^{-4705/T}) \left[ C_0 \right]^{0.2} (1-\alpha)^{1.2}
\]  

The experimental data of k for TPU/ LiN(SO₂CF₃)₂ reactant mixture with [O:Li]=16:1 at various temperatures are plotted in Figure 5.17. The k value increases as temperature increases. It is hard to determine whether k can still be represented by the simple form as described in equation (2.10), since the interaction mechanism is not clear. Figure 5.18 shows the variation of k with the different TPU concentrations for the TPU/ PEMPS/LiN(SO₂CF₃)₂ reactant mixture with [O:Li]=16:1. The k value was found to decrease as PEMPS concentration increases. As mentioned before, a possible effect of PEMPS on the reaction is that PEMPS dilutes the concentration of isocynate and hydroxyl group. Also PEMPS can be bonded with the hydroxyl group via the anchor effect of lithium ions, therefore it hinders the isocynate attacking the hydroxyl group spacially.
Figure 5.10  Log-log plots of DSC conversion rate versus conversion remaining for neat TPU reactant mixtures polymerized at different temperatures

Figure 5.11  Log-log plots of DSC conversion rate versus conversion remaining for polyurethane reactant mixtures with LiN(SO$_2$CF$_3$)$_2$ at [O:Li]=16:1 polymerized at different temperatures
Figure 5.12 Log-log plots of DSC conversion rate versus conversion remaining for TPU/LiN(SO₂CF₃)₂ reactant mixture with different LiN(SO₂CF₃)₂ concentrations polymerized at 140°C.

Figure 5.13 Log-log plots of DSC conversion rate versus conversion remaining for polyurethane/PEMPS/LiN(SO₂CF₃)₂ reactant mixture with different blend composition and [O:Li] = 16:1 at 140°C.
Figure 5.14  Log-log plots of DSC conversion rate versus conversion remaining for TPU/PEMPS/LiN(SO₂CF₃)₂ reactant mixture with PU/PEMPS=100/10 and [O:Li] =16:1 at different temperatures

Figure 5.15  Experimental reactant constant k vs. versus 1/[O:Li] for TPU/LiN(SO₂CF₃)₂ reactant mixture at 140°C
Figure 5.16 Evaluation of A and Ea/R from semi-ln plot of k₁ versus 1/T data for neat polyurethane polymerized at different temperatures

Figure 5.17 Experimental reactant constant k versus 1/T for TPU/LiN(SO₂CF₃)₂ reactant mixture with [O:Li] =16:1 at different temperatures
The effect of salts and PEMPS on the kinetics of polymerization of polyurethane can result in the variation of the molecular weight of polyurethane. The neat TPU, TPU/LiN(SO₂CF₃)₂ electrolytes and TPU/PEMPS/ LiN(SO₂CF₃)₂ electrolytes prepared by the in-situ process were subjected to GPC characterization. It was found that there was a small amount very high molecular weight TPU in all these samples, which might be identified as the slightly cross-linked TPU. This phenomenon is very common in bulk polymerized polyurethane. Due to the existence of this portion of polyurethane, the weight average molecular weight, $M_w$, is very high and cannot be used to explain the effect of the salts and PEMPS. Therefore, the peak molecular weight in the GPC results was used in this study. The results of molecular weight obtained from GPC are listed in Table 5.1.

The molecular weight of TPU electrolyte is slightly lower that of neat TPU. The peak molecular weight of TPU decreases from its original value of 50,701 to 33,182 at [O:Li]=8:1 The molecular weight of TPU/PEMPS/ electrolytes was higher than that of the neat TPU at low PEMPS concentration such as TPU/PEMPS=100/20 and lower than that of the neat TPU at high PEMPS content such as TPU/PEMPS=100/40. Based on Table 5.1, it was concluded that the presence of lithium salt in the polyurethane reactant decreases the molecular weight of polyurethane slightly due to the interaction of lithium ions with the reactive functional groups. However, the molecular weight variation originated from the addition of salt and PEMPS was not substantial.
Figure 5.18  Experimental reactant constant $k$ vs. the concentration of TPU for TPU/PEMPS/LiN(SO$_2$CF$_3$)$_2$ reactant mixture with and different blend compositions at [O:Li] = 16:1

Table 5.1  The molecular weight of TPU/LiN(SO$_2$CF$_3$)$_2$ electrolytes and TPU/PEMPS/LiN(SO$_2$CF$_3$)$_2$ electrolytes obtained from GPC

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<td>8:1</td>
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5.2 Morphological Studies of TPU/PEMPS Electrolytes

The morphology of TPU/PEMPS electrolytes plays an important role in their ionic conductivity and the dimension stability. The TPU electrolytes and TPU/PEMPS electrolytes films with various compositions were characterized by Optical microscopy, SEM and AFM to study the miscibility of TPU and PEMPS and the morphological structure of polymer electrolytes.

5.2.1 Appearance of Electrolyte Films

Figure 5.19 shows the photos of electrolyte films. The photos were taken with the electrolyte films layered on top of a paper with the University of Akron logo to examine their transparency and appearance. The thickness of the film is around 0.3-0.1mm. The film in first row in Figure 5.19 is the neat TPU film and the ones on second row are TPU/PEMPS blend films with various blend compositions. The films of TPU/LiCl electrolytes with various salt concentrations and the films of TPU/PEMPS/LiCl electrolytes with various blend compositions are displayed in the third and fourth column. Neat TPU film is in the form of semi-transparent film, which is believed to be the result of micro-scale phase separation of soft segments and hard segments. TPU/PEMPS blend films look similar to the neat TPU films, but more opaque. This might result from the poor compatibility between PEMPS and TPU. After the addition of LiCl into the TPU, TPU electrolyte films with different salt concentrations still showed semi-transparent.

The addition of PEMPS into TPU in the presence of LiCl made the film slightly brownish. A similar effect was observed in the TPU/PEMPS electrolytes with LiClO₄.
Figure 5.19  Photos of Neat TPU, TPU/PEMPS blend, TPU/LiCl electrolyte and TPU/PEMPS/LiCl electrolyte films
and LiTFSI as shown in Figure 5. 20 and Figure 5. 21, respectively. The initial color of neat TPU film was slightly yellow. The color change might be related to the interaction of salts with the hard segments which contains the benzene groups. These conjugated functional groups are sensitive to the surrounding chemical environments. The different interactions result the shifts of the visible absorbing bands. Usually polyurethane tends to show a yellowish color.

From the above figures, it was noted that TPU film became more transparent after the addition of salts and more opaque after the addition of PEMPS. This phenomenon suggests the multiphase morphology structure of TPU electrolyte and TPU/PEMPS electrolytes. The detailed morphological study using optical microscopy, SEM and AFM was conducted in the following sections.
Figure 5. 20 Photos of the TPU/LiClO$_4$ electrolyte films and the TPU/PEMPS/LiClO$_4$ electrolyte films

Figure 5. 21 Photos of the TPU/LiN(SO$_2$CF$_3$)$_2$ electrolyte films and the TPU/PEMPS/LiN(SO$_2$CF$_3$)$_2$ electrolyte films
5.2.2 Optical Microscopy

Figure 5.22 shows the optical micrographs of the neat TPU film and the TPU/PEMPS blend films with different blend compositions. Neat TPU film demonstrates phase separation with small domains dispersed in the matrix. This originates from the phase separation of hard domain and soft domain of TPU. The morphology of TPU depends on the ratio of hard segment to soft segment. The TPU used in this study was formulated with low hard segments content, so the phase separation is not easy to identify. The PEMPS itself is transparent due to its uniform amorphous nature. However, the blends of TPU and PEMPS at various blend compositions are immiscible and form large phase separation morphology. The separation scale is several to tenth µm. The PEMPS forms droplets dispersed into the TPU matrix. The crystalline phase of TPU could not be identified by optical microscopy due to small size and low degree of crystallinity.

By comparing Figure 5.22(a) with Figure 5.22(d) and Figure 5.22(e), it was noticed that the sizes of PEMPS domains in the TPU/PEMPS blends were larger than the size of hard domains of TPU. As the concentration of PEMPS increased, more separated PEMPS domains were dispersed in the TPU matrix. Especially, as shown in Figure 5.22(e), the PEMPS phase dispersed in the TPU phase can be easily identified. The immiscibility of TPU with PEMPS can be explained by the following reason. First, although 80% PEMPS is the polyether branch chain which has similar chemical structure as the soft segments of TPU, the steric barrier caused by the branch structure inhibits the effective interaction.
Figure 5.22  Optical micrographs of (a) neat TPU, (b) PEMPS, and (c) TPU/PEMPS blend with different blend compositions, TPU/PEMPS=100/10, (d) 100/20, (e) 100/40
between linear soft segment of TPU and the branched polyether chain of PEMPS. Tandel\textsuperscript{53} reported the immiscibility of PEO with PPO was due to the steric barrier caused by the methyl group of PPO. Kim et al.\textsuperscript{193} reported the phase separation of PEO/poly(oligo[oxyethylene]oxysebacoyl) (PES) blend in their study on polymer electrolytes based on the fact that the DSC results showed two melting peaks. In this study, it was noted that the morphology of TPU/PEMPS blend was changed greatly by the addition of salts. Figure 5.23 (a) illustrates the phase morphology of TPU with LiCl at [O:Li]=16:1. The phase separation between soft domain and hard domain cannot be recognized using the optical microscopy. This means the compatibility of different phases is improved. In the other words, the salts induce the phase compatibility between TPU and PEMPS. Wen et al.\textsuperscript{7} studied the polyurethane electrolytes with different polyurethane structures and found that the interaction of salt with polyurethane caused the phase mixing between hard segments and soft segments. Jeung\textsuperscript{55} studied the polyurethane electrolytes with salts composed of different cations and anions. In her study, similar phase mixing behavior was observed. The undissolved particles in the background are undissolved LiCl, which was also seen in the optical micrographs of the PEMPS/LiCl mixtures and the PTMG/LiCl mixtures.

Comparing Figure 5.23 (c) (d) (e) with Figure 5.22 (c) (d) (e), it is also revealed that after the addition of salt the miscibility of PEMPS and TPU matrix is improved, based on the observation that the boundary of the different phase domain blurred although the phase separation still existed. This indicates the compatibility enhancement of PEMPS phase and TPU phase induced by salts. In Tandel’s study\textsuperscript{53} on PEO/PPO
Figure 5.23  Optical micrographs of (a) TPU/LiCl electrolyte (b) PEMPS/LiCl electrolyte and (c) TPU/PEMPS/LiCl electrolytes with different blend compositions TPU/PEMPS =100/10, (d) 100/20, (e) 100/40, at [O:Li]=16:1
based electrolytes, the TEM micrograms showed that the addition of the salt favored the miscibility of PEO and PPO blend. In Kim et al.’s work\textsuperscript{193}, only one melting peak was observed after the addition of 10\% of LiClO\textsubscript{4}. They explained that as the result of the simultaneous interaction of Li\textsuperscript{+} with the oxygen atoms of the PEO and ether oxygen or ester oxygen of the PES.

It is interesting to notice that, in Figure 5.24 (a) and Figure 5.25(a), the droplets caused by phase separation of hard domain and soft domain disappeared with the addition of LiClO\textsubscript{4} and LiN(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2}, respectively. Similar to the observation in Figure 5.23 (c) (d) (e), the addition of LiClO\textsubscript{4} and LiN(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2} also improved the compatibility of PEMPS and TPU as shown in Figure 5.24 (c) (d) (e) and Figure 5.25(c) (d) (e). In the case of PEMPS/TPU/LiN(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2} electrolytes, the phase separation morphology can barely be seen at low PEMPS concentration. It can be concluded that among these three lithium salts, LiN(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2} greatly enhances the compatibility of PEMPS and TPU due to the strong interaction of Li\textsuperscript{+} with both ether oxygen of PEMPS and the ether oxygen of soft segment of TPU or the nitrogen atom on the hard segments of TPU.
Figure 5.24 Optical micrographs of (a) TPU/LiCO₄ electrolyte, (b) PEMPS/ LiCO₄ electrolyte, (c) TPU/PEMPS/ LiCO₄ electrolytes with different blend compositions TPU/PEMPS =100/10, (d) 100/20, (e) 100/40, at [O:Li]=16:1
Figure 5.25 Optical micrographs of (a) TPU/ LiN(SO₂CF₃)₂ electrolytes, (b) PEMPS/ 
LiN(SO₂CF₃)₂ electrolytes and (c) TPU/PEMPS/ LiN(SO₂CF₃)₂ 
electrolytes with different blend compositions TPU/PEMPS 
=100/10, (d) 100/20, (e) 100/40, at [O:Li]=16:1
5.2.3 SEM

TPU/PEMPS electrolyte films may exhibit different morphology from the surface to interior of the films. In this section, two types of SEM studies were discussed. The first one is to observe the fracture surface of the polymer electrolyte, which shows the information of the morphology of the interior of electrolytes film. The second one is to observe the electrolyte film surface to obtain their surface morphology. Due to the similarity of PEMPS with the soft segments of polyurethane, the contrast of PEMPS phase with TPU phase in SEM is not sufficient enough to identify the distribution of the different phases. Therefore, the film surface was etched by methanol to enhance the contrast. Hence, not only the fracture surface and the original film surface of polymer electrolytes but also their corresponding surfaces treated with methanol were observed using SEM in this study. PEMPS can dissolve in methanol and TPU is nearly undissolvable in methanol, the cavities occupied by PEMPS in TPU matrix can be exposed in the extracted surface.

Figure 5.26 shows the SEM micrographs of the fractured surface of neat TPU and TPU/PEMPS blends. Due to the small amount of hard segments and irregular paracrystal formation of the hard segments, it is expected that the phase morphology of TPU cannot be observed even though the neat TPU have a separated domain structure composed of hard segments and soft segments. Neat TPU showed a smooth homogenous surface whereas TPU/PEMPS blends exhibited a two-phase morphology. The separated domain is around 1-10 µm in size and the size of the domain varied with the concentration of PEMPS.
Figure 5.26  SEM micrographs of fracture surface of neat TPU and TPU/PEMPS blend with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d) 100/40
In comparison of Figure 5.26(b) with Figure 5.26(c), it was observed that domain size of the two-phase morphology increased greatly when the composition TPU/PEMPS reached 100/40. The dispersed domain is TPU phase and the matrix with the darker color is PEMPS. It seems that the two-phase morphology become co-continuous or modulated structure at the high PEMPS concentration. In order to investigate the level of distribution and dispersion of PEMPS phase in TPU, the PEMPS phase was extracted from fracture surfaces of TPU/PEMPS blends with using methanol. The morphology of the extracted fracture surfaces of neat TPU and TPU/PEMPS blend is shown in Figure 5.27. Neat TPU showed a slightly rough surface after extraction as shown in Figure 5.27(a). This can be explained as the result of removal of small molecular weight of TPU, which causes small dents on the surface. Figure 5.27 (b) and Figure 5.27 (c) show empty holes due to the extraction of PEMPS phases as well as small amounts of isolated TPU phases. When the blend composition TPU/PEMPS increased to 100/20, the modulated structure was revealed as shown in Figure 5.27(c). For the TPU/PEMPS blend with TPU/PEMPS=100/40, Figure 5.27(d) shows a porous structure caused by the removal of the dispersed PEMPS phase. The dimension of these pores is in the range of 1-10 µm. The pores seem to be connected with each other and form co-continuous structure.

Although TPU is undissovable in methanol, it can be slightly swollen by methanol. The swelling of TPU by methanol during extraction and the removal of the methanol during the drying can deform the cavity left by PEMPS phases, therefore the extracted surface obtained by this method does not exactly reflect the domain size or
Figure 5.27 SEM micrographs of extracted fracture surface of neat TPU and TPU/PEMPS blend with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40
shape of the dispersed PEMP phase. However, it still can provide valuable information of the morphology of TPU/PEMPS blend.

The morphology of the fracture surfaces of TPU/PEMPS electrolytes with three different lithium salts are shown in Figure 5.28, Figure 5.30 and Figure 5.32 respectively. Their corresponding extracted surfaces are shown in Figure 5.29, Figure 5.31 and Figure 5.33. The salt concentration is fixed at [O:Li]=16:1. In comparison of Figure 5.28 with Figure 5.27, it was noted that the roughness of the fracture surface of TPU/PEMPS blend decreased after the addition of LiCl. The phase boundary of the phases in Figure 5.28(c) is less clear than the one in Figure 5.27(c). For TPU/PEMPS/LiCl electrolytes with TPU/PEMPS=100/40, the phase separation is visible but the size of the dispersed phases is much smaller than the one without LiCl.

The changes in the morphology are attributed to the interaction of Li⁺ with both phases. Li⁺ ions act as anchors between the boundary interfaces of different phases and improves the compatibility between PEMPS phase and TPU. The phase compatibility between PEMPS phase and TPU was also observed from the extracted fracture surface as shown in Figure 5.29. When TPU/PEMPS=100/10, the cavity generated from the removal of PEMPS phase can barely be seen. The cracks shown in the extracted fracture surfaces originate from uneven shrinkage of TPU film by drying. As the PEMPS content increases, the number of cavity increases. For TPU/PEMPS/LiCl electrolytes with TPU/PEMPS=100/40, the cavities of PEMPS phase become much larger as shown in Figure 5.29(d). The white particles resting on the extracted fracture surfaces shown in Figure 5.29 are believed to be the TPU phase dispersed in the PEMPS matrix. They are
Figure 5.28  SEM micrographs of fracture surface of TPU/LiCl electrolytes and TPU/PEMPS/LiCl electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d) 100/40
Figure 5.29  SEM micrographs of extracted fracture surface of TPU/LiCl electrolyte and TPU/PEMPS/LiCl electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d) 100/40
Figure 5.30 SEM micrograph of fracture surface of TPU/LiClO$_4$ electrolytes and TPU/PEMPS/LiClO$_4$ electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d) 100/40
Figure 5.31  SEM micrographs of extracted fracture surface of TPU/LiClO₄ electrolytes and TPU/PEMPS/LiClO₄ electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40
Figure 5.32 SEM micrographs of fracture surface of TPU/LiTFSI electrolytes and TPU/PEMPS/ LiTFSI electrolytes at \([O:Li]=16:1\) with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d) 100/40
Figure 5.33 SEM micrographs of extracted fracture surface of TPU/ LiTFSI electrolytes and TPU/PEMPS/LiTFSI electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40
part of the TPU matrix surrounded by PEMPS phase on the fracture surface before extraction. They fell out from the surface to form an isolated particle after the surrounding matrix of the PEMPS phases are extracted. Small amount of particles were left due to the insufficient washing or partial attachment to the TPU matrix.

Similarly, the morphology of fracture surface of TPU/PEMPS electrolytes after the addition of LiClO$_4$ or LiTFSI are shown Figure 5.30 and Figure 5.32, respectively. No phase separation of PEMPS and TPU was observed after the addition of LiClO$_4$ up to TPU/PEMPS=100/40. In comparison of Figure 5.28 with Figure 5.30, it was found that the phase compatibility between PEMPS phase and TPU for TPU/PEMPS/LiClO$_4$ electrolytes is better than that for TPU/PEMPS/LiCl electrolytes, at equal blend composition. No phase separation of PEMPS and TPU was observed after LiTFSI is added as shown in Figure 5.32. The different effects of three different lithium salts on the TPU/PEMPS blend morphology are associated with the interaction strength with polymer as mentioned in the FTIR and DSC studies of the PTMG/PEMPS mixtures. Although a smooth fracture surface was observed in TPU/PEMPS electrolytes with LiTFSI, the two-phase morphology was observed after the extraction as shown in Figure 5.33.

The morphology study of the fracture surface TPU/PEMPS blends with different lithium salts indicates that TPU/PEMPS has a two-phase morphology. The interaction of salt with polymer improves their compatibility. The roughness of the extracted fracture surface came from two sources: the roughness of fracture surface before extraction and the cavities generated from the removal of the dispersed phase. The overlapping leads the difficulty to identify the roughness caused by the latter source. The fracture surface
studies discussed above are only on the morphology observed in the cross-section area of the polymer electrolytes. In the following sections, the extracted surfaces of electrolytes are discussed.

The morphology of the original TPU/PEMP blend and TPU/PEMPS electrolytes films surface was flat and smooth. However, a certain level of roughness was observed on the extracted surface. Figure 5.35 shows the extracted surface of neat TPU and TPU/PEMPS blend films. The relatively smooth surface with a few small particles on the extracted surface of neat TPU film in Figure 5.35(a) came from the removal of methanol from the swollen TPU matrix. At TPU/PEMP =100/10, some small cavities generated by the removal of PEMPS phases are shown in Figure 5.35(b). The extracted surface of TPU/PEMPS film with TPU/PEMP =100/20 seems rough since more the PEMPS phase is removed as shown in Figure 5.35(c). A powdery surface was observed at the high concentration of PEMPS as shown in Figure 5.35(d).

In comparison of Figure 5.35 with Figure 5.27, it is worth mentioning that the morphology of extracted fracture surface of TPU/PEMPS blend is much rougher than that of the extracted film surface. On the original surface of the film, some PEMPS phases are embeded deep inside the TPU phases, thus resulting in preventing the extraction by methanol. However, due to poor adhesion between PEMPS phase and TPU phase more PEMPS phase is exposed out on the facture surface of the cross-section area of the blend film.

The morphology of the extracted surface of TPU/PEMPS electrolyte films with different lithium salts are shown in Figure 5.35, Figure 5.36 and Figure 5.37 respectively.
Figure 5.34  SEM micrographs of extracted film surface of neat TPU and TPU/PEMPS blend with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d) 100/40
Figure 5.35 SEM micrograph of extracted film surface of TPU/LiCl electrolyte and TPU/PEMPS/LiCl electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d) 100/40
Figure 5.36  SEM micrographs of extracted film surfaces of TPU/LiClO$_4$ electrolyte and TPU/PEMPS/LiClO$_4$ electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40
Figure 5.37  SEM micrographs of extracted film surfaces of TPU/LiTFSI electrolyte and TPU/PEMPS/LiTFSI electrolyte at [O:Li]=16:1 with different compositions, TPU/PEMPS  (a) 100/0  (b) 100/10  (c) 100/20  (d)100/40
The extracted surfaces of TPU/LiCl electrolytes film and TPU/PEMPS/LiCl electrolyte film with TPU/PEMPS =100/10 were relatively smooth. As the PEMPS content increases, it became rough. Particularly, at TPU/PEMPS =100/40, a large amount of particles was exposed out on the extracted surface as shown in Figure 5.35 (d). This indicates a large size of surface area of the electrolytes film is occupied by PEMPS phase at high PEMPS concentration.

A similar trend was observed for TPU/PEMPS/LiClO$_4$ electrolyte films and TPU/PEMPS/LiTFSI electrolyte films. In comparison of Figure 5.35 (d) with Figure 5.36 (d) and Figure 5.37(d), the morphology of the extracted surface of TPU/PEMPS electrolytes with LiClO$_4$ or LiTFSI is much smoother than the one of TPU/PEMPS electrolytes with LiCl. This difference is due to the different effect of lithium salts on the compatibility of PEMPS phase and TPU.

Besides the type of salts, the preparation method will influence the morphology of the surface of TPU/PEMPS electrolytes. In this study, the morphology of the extracted surface of TPU/PEMPS/LiClO$_4$ electrolyte films prepared by solution cast was compared with that prepared by the in-situ process. Figure 5.38 shows the original surface of TPU/PEMPS/LiClO$_4$ electrolyte films. They were very uniform and no phase separation was observed. The layered structures in Figure 5.38 were originated from the results of the gradual removal of THF. In the solvent evaporation process of viscous polymer electrolyte solution, the solvent on the edge of the film was dried first and then the dry front gradually approached the center. The lined structures shown in Figure 5.38 were
Figure 5.38 SEM micrographs of film surface of solution cast TPU/ LiClO$_4$ electrolyte and TPU/PEMPS/LiClO$_4$ electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d)100/40
formed at interfaces of the dried part and wet part. After extraction with methanol, the cavities with the size of around 1-5 µm appeared on the extracted surfaces of TPU/PEMPS/LiClO4 electrolytes films as shown in Figure 5.39.

In comparison of Figure 5.39 with Figure 5.36, it can be concluded that the surface of polymer electrolytes prepared by solution cast is smoother than the one by the in-situ process. Also, by comparing the cavity area in Figure 5.36 (c) with Figure 5.39 (c), it seems that slightly more PEMPS phases exist on the film surface for TPU/PEMPS electrolytes prepared by solution cast. The explanation is as follows. The miscibility of PEMPS with TPU is poor. In the solution cast, as solvent vaporizes, the phase separation takes place and due to the coexistence of the small amount of solvent the separated PEMPS phases tends to gradually migrate to the surface during the long time drying as the results of its high surface energy. However, in the in-situ process, the polyurethane polymerization progresses immediately after the vigorous mixing of the reactants and results in the solidification of electrolyte in short time. The migration of PEMPS to the surface is significantly restricted in the in-situ process.
Figure 5.39    SEM micrographs of the extracted film surfaces of solution cast TPU/LiTFSI electrolytes and TPU/PEMPS/LiTFSI electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/0 (b) 100/10 (c) 100/20 (d) 100/40
5.2.3 AFM

As discussed in the previous sections, the surface characteristics of a series of TPU/PEMPS electrolytes will give more insight of understanding phase separation and their properties of final film products. In particular, the surface structure of electrolytes films will influence their ionic conductivity. The phase contrast of PEMPS with TPU in SEM is not large enough to see the phase separation on the original polymer electrolytes film surface. Although the morphology of the extracted surface of TPU/PEMPS electrolytes films can provide useful information, this obtained morphology is still slightly deformed by the swelling of TPU and drying of methanol. Therefore, AFM topographic image scan was used to characterize the original surface morphology of TPU/PEMPS electrolytes film.

The electrolytes films prepared by the in-situ process had rough surfaces as indicated by the SEM results. This made it hard to obtain high quality AFM images. In this section, only AFM results of the solution cast films are discussed. Figure 5.40 (a) illustrates the AFM topographic images of neat TPU film. The left side image is the height image, which shows the roughness of the sample surface and the right side images is the phase image. The phase image of neat TPU shows the white dots with the size of 0.1 to 1 µm uniformly distributed in the whole field. These dots represent the hard domain of TPU and the darker matrix represents the soft domain of TPU. The domain size of hard segments of TPU is usually around the range of several hundred nm and the size varies with the ratio of the hard segment and soft segments and the chemical
Figure 5.40   AFM topographic images of surface of (a) neat TPU, (b) TPU/LiClO$_4$ electrolytes at [O:Li]=16:1 and TPU/PEMPS/LiClO$_4$ electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (c) 100/10, (d) 100/20, (e) 100/40. The image on the left is height image and the one on the right is phase image. (cont.)
structures of these segments. The phase separation pattern in the Figure 5.40 (a) indicates that hard domains are dispersed in the matrix of the soft domains.

It is interesting to note that after the addition of LiClO₄, the white dots disappeared as shown in Figure 5.40 (b). This is attributed to the interaction between soft segments and hard segments associated with Li⁺, which leads to the phase mixing. TPU itself is a block polymer with multiphase morphology, which includes the soft domain composed of soft segments, the hard domain composed of hard segments via the hydrogen bonding between hard segments, and the soft-hard domain composed of soft segment and hard segments interacted via the hydrogen bonding between hard segments and soft segments. The interaction of Li⁺ with both the soft segments and hard segments can induce the formation of more soft-hard domains and reduce hard domains. So the size of the hard domain is much smaller and the boundary of soft domain and hard domain as well as soft-hard domain became vague after the addition of salt. This phenomenon was also observed in the optical microscopy studies of TPU electrolytes as discussed in section 5.2.1.

The phase mixing of hard and soft segments of TPU caused by the addition of salt has also been reported by previous researchers. Zhu et al. studied a series of PEG based polyurethane electrolytes with NaClO₄ and found that the AFM images showed the hard segment aggregation decreased after the addition of the salts. There exists a competition between hydrogen bonding and cation coordination. The coordination between cations with carbonyl groups decreased the hydrogen bonding between hard segments and resulted the phase mixing. The phase mixing was also
confirmed by Wen et al\textsuperscript{38} in their studies on the FTIR characterization of polyurethane electrolytes. However, Furtado\textsuperscript{194} and his coworkers found that the phase separation of hard segments and soft segments in polyurethane is more visible as the salt concentration increased, which was supported by the thermal analysis data. The possible explanation of the different phase separation phenomena is due to the fact that in Furtado’s investigation, very high salt concentration was used. Therefore, undissociated salts might play a role of enhancing the phase separation.

Huang et al\textsuperscript{195} studied morphology of solid polymer electrolytes based on polyurethanes with linear, branched and comb-cross-linked structures with LiClO\textsubscript{4} using AFM. They noticed that the salt concentration had significant influences on the morphology. The AFM topographic images of linear polyurethane/LiClO\textsubscript{4} electrolytes with [O:Li]=24 revealed a typical phase-segregated morphology with bright aggregate as the hard-segment-rich regions and dark background as soft-segment-rich matrix. The dimension of the bright aggregation was around 0.1~0.5µm. As the salt concentration increased, the size of hard-segment-rich regions reduced. When [O:Li] reached 12, the minimum size of the hard-segment-rich region was obtained. With the further increase of the salt concentration, a different kind of aggregate appeared because of the precipitation of alkali metal salt. They believed that the inter-ionic electrostatic forces as well as the incompatibility between the incorporated salt and non-polar polymer matrix induced the salts to aggregate. Also the formation of large ion pairs at high concentration above the critical value, leads to the salt precipitation.
Figure 5.40 (c), Figure 5.40 (d) and Figure 5.40 (e) show the TPU/PEMPS/LiClO$_4$ films with different compositions at [O:Li]=16:1. The soft-hard segments phase separation of TPU is invisible after the addition of the LiClO$_4$ as mentioned above. So the spherical dots in these figures are believed to be PEMPS phase. At low PEMPS content, the PEMPS phase can barely be distinguished from the AFM topographic images. However, with the increase of PEMPS concentration, the PEMPS phase gradually appeared. In particular, as $W_{TPU}/W_{PEMPS}$ reaches 100/40, the PEMPS phase was easily identified and it formed a spherical domain with size around 1 $\mu$m. The similar color of the PEMPS phase to that of soft segments of TPU in the phase images of the AFM topographic images in Figure 5.40 indicates the similar modulus of these phases since the tapping mode is used in AFM study.

The AFM topographic images of TPU/PEMPS/LiTFSI electrolyte films are shown in Figure 5.41. Similarly, the hard-soft segment phase mixing caused by the addition of Li salts was observed in Figure 5.41(a). The separated PEMPS phases were observed in samples of all blend compositions with $W_{TPU}/W_{PEMPS}$ from 100/10 to 100/40. The size of separated domains was around 1-5 $\mu$m. The distribution density of these domains increased as the concentration of PEMP increased. It was found from the AFM images that PEMPS formed the droplet trapped in the TPU matrix on the surface of the electrolytes, which agrees well with the results obtained from the SEM images of the extracted surfaces.
AFM topographic images of surface of (a) neat TPU, (b) TPU/LiClO$_4$ electrolytes at [O:Li]=16:1 and TPU/PEMPS/LiClO$_4$ electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (c) 100/10, (d) 100/20, (e) 100/40. The image on the left is height image and the one on the right is phase image. (cont.)
Figure 5.40  AFM topographic images of surface of (a) neat TPU, (b) TPU/LiClO₄ electrolytes at [O:Li]=16:1 and TPU/PEMPS/LiClO₄ electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (c) 100/10, (d) 100/20, (e) 100/40. The image on the left is height image and the one on the right is phase image.
Figure 5.41  AFM topographic images of surface of TPU/LiTFSI electrolytes and TPU/PEMPS/LiClO₄ electrolytes at \([\text{O:Li}]=16:1\) with different compositions, TPU/PEMPS (a) 100/10, (b) 100/10, (c) 100/20, (d) 100/40. The image on the left is height image and the one on the right is phase image. (cont.)
Figure 5.41  AFM topographic images of surface of TPU/LiTFSI electrolytes and TPU/PEMPS/LiClO₄ electrolytes at [O:Li]=16:1 with different compositions, TPU/PEMPS (a) 100/10, (b) 100/10, (c) 100/20, (d) 100/40. The image on the left is height image and the one on the right is phase image.
5.3 Thermal Analysis of Electrolyte Films

The thermal stability of polymer electrolyte films is an important aspect for their application in electronic devices. In this section, the thermal stability of TPU/PEMPS electrolytes was characterized using TGA and the thermal transition of these electrolytes films were studied using DSC. The effect of salt and PEMPS on the degradation temperature of electrolytes films and their $T_g$, $T_m$ and crystallinity were investigated.

5.3.1 TGA

It has been reported that the interaction of salt with polymer causes the degradation of polymer electrolytes at lower temperature. Jeung\textsuperscript{55} pointed out that the addition of different inorganic salts, LiClO$_4$, NaClO$_4$, CuCl$_2$ and KI into PEO decreased the thermal stability of neat PEO. Yang and Farrington’s study\textsuperscript{196} on PEO electrolyte with ZnCl$_2$ indicated that the ether bond in PEO might be weakened by the interaction between Zn$^{2+}$ and the ether oxygen and that the anion type was not a main origin of the thermal stability of PEO electrolytes.

The TGA curves of TPU electrolytes with different lithium salts are shown in Figure 5.42. The addition of lithium salts influences the weight loss of TPU at lower temperature than that of neat TPU. The 5% weight loss temperature of TPU electrolytes are listed in Table 5.2. The addition of LiTFSI to the neat TPU has a significant effect on the thermal stability of TPU. The temperature at 5% weight loss of TPU/LiTFSI electrolytes decreases to 241\degree C from the value of neat TPU at 314\degree C. Neat TPU exhibited
Figure 5.42  TGA curves of TPU electrolytes with different lithium salts at [O:Li]=16:1

Figure 5.43  TGA curves of TPU/PEMPS blends with various blend compositions without lithium salt
Table 5.2  TGA results of neat TPU, TPU/PEMPS blends and TPU/PEMPS electrolytes with different lithium salts at \([O:Li]=16:1\)

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two steps thermal degradation. The first step is attributed to the degradation of soft segments and the second step is related to the degradation of hard segments. TPU electrolytes of all three lithium salts showed three steps of thermal degradation. In the soft segment of TPU electrolytes, ether groups are in two different forms: one without interaction with salts and the other one interacted with salts. Since the ether bond is weakened by the interaction between ether oxygen with salts, the thermal degradation of salt complexed ether group occurs in the first step. Later thermal degradation of uncomplexed ether group takes place in the second step. After the first two steps, the degradation of hard segments of TPU proceeds. It was observed that TPU/LiTFSI electrolytes undergo thermal degradation at lower temperature than TPU electrolytes with other lithium salts. This is because among the three lithium salts with different anion, LiTFSI has the strongest interaction with polymer, as discussed in previous sections. Therefore the bond strength of the ether group in soft segment of TPU/LiTFSI significantly decreases, which results in the more decrease of its degradation temperature.

Figure 5.43 shows the TGA of TPU/PEMPS blends at different blend ratio without any lithium salts. Neat PEMPS exhibited a temperature at 5% weight loss around 275 °C and only one-step thermal degradation was observed, which is associated with the degradation of polymer ether branches on the polysiloxane. TPU/PEMPS blends showed 5% weight loss at a temperature between the value of neat TPU and PEMPS. Two-step thermal degradation was observed in these blends, in which the first one belongs to the degradation of the ether group in soft segments and PEMPS and the second one is due to the degradation of the hard segments.
Figure 5.44  TGA curves of TPU/PEMPS/LiCl electrolytes with different blend compositions at [O:Li]=16:1

Figure 5.45  TGA curves of TPU/PEMPS/LiClO₄ electrolytes with different blend compositions at [O:Li]=16:1
Vlad et al.\textsuperscript{156} studied the thermal stability of IPNs of PU and polydimethylsiloxane (PDMS). TGA showed PDMS has better thermal stability than polyurethane. The IPNs of PU/PDMS are very stable up to 200\textdegree{}C and lose weight rapidly around 350-450\textdegree{}C. The IPNs with higher content of PDMS undergo 5\% weight loss at higher temperatures. In this study, PEMPS show lower thermal stability than TPU because the unstable ether branches on polysiloxane chain. The –Si-O- is much stronger than –C-O-, which provides the high temperature application of silicone rubber.

TGA of TPU/PEMPS electrolytes with different lithium salts at different blend compositions are shown in Figure 5.44, Figure 5.45 and Figure 5.46 respectively. Their temperatures at 5\% weight loss are also listed in Table 5.2. It was noticed that as the concentration of PEMPS increased, the degradation temperature of blend electrolytes decreased. This is same conclusion for all the TPU/PEMPS electrolytes with different lithium salts. Compared with TPU/PEMPS/LiCl electrolytes and TPU/PEMPS/LiClO\textsubscript{4}, the TPU/PEMPS/ LiTFSI electrolytes showed the poorest thermal stability due to the strong salt/polymer interaction. However, since the general operation temperature of devices with solid polymer electrolytes such as solid battery is under 120\textdegree{}C, the polymer electrolytes prepared in this study is sufficient to meet the application requirement.
Figure 5.46  TGA curves of TPU/PEMPS/LiTFSI electrolytes with different blend compositions at [O:Li]=16:1
5.3.2 DSC

The DSC behavior of TPU is complicated because the co-existence of different phases of hard and soft segments. Hepburn\textsuperscript{75} reported that generally the observed transitions of polyurethane in DSC were categorized into three main groups: those below -30\textdegree C associated with the glass transition temperature of the soft segments, transition in the region 80-150\textdegree C and those above 160\textdegree C associated with the thermal dissociation of the hard block aggregates which may be crystalline or paracrystalline. The multiple endothermic peaks appearing in the region around 80\textdegree C are usually ascribed to the dissociation of the urethane soft segment hydrogen bonds and those in the region of 150\textdegree C to the break-up of urethane hydrogen bonds. Cooper et al\textsuperscript{197} stated the T\textsubscript{g} of the soft segment was influenced by the restricted movement imposed at the hard segment-soft segment junction and at phase boundaries where the hard domain acts as a filler particles. They explained the endothermic peak around 10 to 20\textdegree C as the crystalline melting of the soft segment, and the endotherm in the region of 30-60\textdegree C as the breakup of short-range ordering in the hard micro-segment. The endotherm peaks between 120\textdegree C-190\textdegree C are associated with the disruption of long-range order of hard domain and the enotherm peaks above 200\textdegree C corresponds to microcrystalline order of the hard microdomains.

Figure 5.47 shows the DSC thermograms of neat TPU and TPU/PEMPS blend at various blend ratios. Neat TPU showed a glass transition temperature of soft segment around -62\textdegree C and the melting temperature of soft segment around 14\textdegree C. The transition shift around 52\textdegree C is related to the glass transition temperature of hard segments and the
Figure 5.47  DSC Thermograms of TPU/PEMPS blends without salt at various blend compositions (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan
endothermic peak at 189°C results from the dissociation of the hydrogen bonding of hard segments. Due to the high soft segment content in the formula of TPU, the above two regions associated with hard segment was not visible. The $T_g$ of PEMPS is around -78°C. All the TPU/PEMPS blend with at various compositions show only one glass transition shift. Based on the morphology studies of TPU/PEMPS blends in previous sections, it was concluded that all the blends exhibit multi-phase morphology. Therefore, the existence of one $T_g$ in the DSC thermogram cannot be interpreted as the evidence of the miscibility between soft segment of TPU and PEMPS. In the DSC thermogram of TPU/PEMPS blends, it is hard to separate the $T_g$ of PEMPS and the $T_g$ of soft segments since they are very close to each other. The broad transition shifts were considered as the results of the overlapping two $T_g$s and shifts of each $T_g$ caused by the interaction of the soft segment and PEMPS. The dependence of $T_g$ of TPU/PEMPS blend on the PEMPS concentration, $W_{PEMPS}/(W_{PEMPS} + W_{TPU})$ is plotted in Figure 5.48. It was noticed that $T_g$ decreased as PEMPS concentration increased.

The endotherm associated with the dissociation of the hydrogen bonding of the hard segments was also shifted to lower temperatures as the PEMPS concentration increased and they were hard to detect when the blend ratio reached to 100/40. This is because that the interaction between PEMPS and hard segments slightly hindered the formation of the highly ordered structure via hydrogen bonding of hard segments and that the effective hard segments concentration in the blend is greatly diluted by the addition of large amounts of PEMPS.
A small endothermic peak at around 3°C appeared prior to the melting temperature of crystalline structure of soft segments after the addition of PEMPS. This peak might be associated with the breakup of short range ordered soft segments. The presence of high viscous PEMPS prevents some soft segments forming crystalline structures and results the formation of short range ordered structures. The \( T_g \), \( T_m \) and the heat of fusion of neat TPU and TPU blends are summarized in Table 5.3. The dependence of \( T_m \)s of the soft segments and the hard segments on the PEMPS concentration is plotted in Figure 5.49. The \( T_m \) of the soft segment increased and \( T_m \) of the hard segments decreased with increasing the PEMPS concentration.

Figure 5.50 shows the DSC thermograms of TPU electrolytes with different LiCl concentrations. The dependence of \( T_g \) and \( T_m \) on the LiCl concentration are plotted in Figure 5.53 and Figure 5.54. The \( T_g \) of the soft segment seems does not change significantly with varying the concentration of LiCl as shown in Figure 5.53. The \( T_m \) of the soft segment decreases and the degree of crystallinity of the soft segments decreases as the salt concentration increases as shown in Figure 5.50. An endothermic peak appeared around 102°C. A similar endothermic peak also appeared in the DSC traces of PTMG/LiCl mixture. This peak did not come from neat TPU. It was generated from the undissolved LiCl salts. The heat of fusion of the endothermic associated with the breakup of the hydrogen bonding of the hard segments around 180°C increases after the addition of LiCl, which indicates that LiCl helps the aggregation of the hard segments. The \( T_g \) of soft segment slightly decreases after the addition of LiClO₄ as shown in Figure 5.50. The crystallinity of soft segments is greatly depressed by the addition of LiClO₄.
Table 5.3 The list of glass transition ($T_g$), melting temperature ($T_m$), heat of fusion ($\Delta H$) and total heat of fusion of TPU/PEMPS blends with different blend compositions determined by DSC.

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<th>$T_{g2}$</th>
<th>$T_{g3}$</th>
<th>$T_{m1}$</th>
<th>$T_{m2}$</th>
<th>$\Delta H_1$</th>
<th>$\Delta H_2$</th>
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Figure 5.48  Dependence of glass transition temperature ($T_g$) of TPU/PEMPS blends on the PEMPS concentration $W_{PEMPS}/(W_{PEMPS}+W_{TPU})$

Figure 5.49  Dependence of melting temperature ($T_m$) of TPU/PEMPS blends on the PEMPS concentration $W_{PEMPS}/(W_{PEMPS}+W_{TPU})$
Figure 5.50  DSC Thermograms of TPU electrolytes with various LiCl concentrations (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan
Chen et al.\textsuperscript{198} studied the polyurethane gel electrolytes with soft segment based on PEG, PTMG and PEG/PTMG mixtures doped with various LiClO\textsubscript{4}. They pointed out that the \(T_g\) of PEG based TPU electrolytes are higher than that of PTMG based TPU electrolytes, and the \(T_g\) of TPU basing on the mixture of PEG and PTMG was between them. The \(T_g\) of the soft segments of TPU doped with LiClO\textsubscript{4} increased. The \(T_g\) of PTMG based TPU electrolytes increased from \(-60.6^\circ\text{C}\) to \(-53.5^\circ\text{C}\) as the LiClO\textsubscript{4} concentration increased from 0.5 to 1.5mmol of LiClO\textsubscript{4}/g TPU. The TPU formula in their experiment is that the molar ratio between the hard segment and soft segment is 1:4.

The behavior of \(T_g\) of soft segments in TPU electrolytes with LiTFSI shown in Figure 5.51 is different from that of the TPU electrolytes with LiClO\textsubscript{4} or LiCl. From Figure 5.49, It is revealed that the LiTFSI increases their \(T_g\) up over \(10^\circ\text{C}\). Especially when \([\text{O}:\text{Li}]=8:1\), the \(T_g\) increases around \(20^\circ\text{C}\) more than the original \(T_g\) without salt. The large increase of \(T_g\) of soft segments indicates the strong interaction between LiTFSI and ether group in soft segments, which agrees with the DSC results of PTMG/LiTFSI mixture. The \(T_m\) of soft segments decreases below \(10^\circ\text{C}\) and the heat of fusion of hard segments dissociation also decrease. At the high LiTFSI concentration, where \([\text{O}:\text{Li}]=8:1\), no endothermic peak of the hard segments dissociation is observed. The \(T_g\), \(T_m\) and heat of fusion of the neat TPU and TPU blends are summarized in Table 5.4.

The DSC thermograms of TPU/PEMPS electrolytes with different lithium salts are shown in Figure 5.55, Figure 5.56, and Figure 5.57 respectively. Their \(T_g\), \(T_m\) and the heat of fusion are summarized in Table 5.5. The dependence of \(T_g\) and \(T_m\) of their soft segments on the PEMPS concentration is plotted in Figure 5.58 and Figure 5.59.
Figure 5.51  DSC Thermograms of TPU electrolytes with different LiClO₄ concentrations (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan
Figure 5.52 DSC Thermograms of TPU electrolytes with various LiN(SO$_2$CF$_3$)$_2$ concentrations (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan
Table 5.4  The list of glass transition ($T_{g}$), melting temperature ($T_{m}$), heat of fusion ($\Delta H$) and total heat of fusion in TPU electrolytes with different salt concentrations determined by DSC

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<th>$T_{g3}$ (°C)</th>
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<th>$T_{m3}$ (°C)</th>
<th>$\Delta H_1$ (J/g)</th>
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Figure 5.53  Dependence of glass transition temperature ($T_g$) of TPU electrolytes on the salt concentrations

Figure 5.54  Dependence of melting temperature ($T_m$) of TPU electrolytes on the salt concentrations
Figure 5.55  DSC Thermograms of TPU/PEMPS electrolytes with various blend compositions at [O:Li]=16:1  (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan
Figure 5.56  DSC thermograms of TPU/PEMPS/LiClO₄ electrolytes with different blend compositions at [O:Li]=16:1  (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan.
Figure 5.57  DSC Thermograms of TPU/PEMPS/LiN(SO₂CF₃)₂ electrolytes with different blend compositions at [O:Li]=16:1  (a) first thermal scan and (b) second thermal scan of quenched sample after first thermal scan
Table 5.5 The list of glass transition ($T_{g}$), melting temperature ($T_{m}$), heat of fusion ($\Delta H$) and total heat of fusion in TPU/PEMPS electrolytes with different blend compositions at [O:Li]=16:1 determined by DSC

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Figure 5.58  Dependence of glass transition temperature ($T_g$) of TPU/PEMPS electrolytes on the PEMPS concentration $W_{PEMPS}/(W_{PEMPS} + W_{TPU})$.

Figure 5.59  Dependence of melting temperature ($T_m$) of TPU/PEMPS electrolytes on the PEMPS concentration $W_{PEMPS}/(W_{PEMPS} + W_{TPU})$. 
respectively. The $T_g$ of the soft segments of different electrolytes are all in the range of $-71^0C$ to $-64^0C$. This temperature range is slightly below the $T_g$ of TPU electrolytes without PEMPS, which implies that the addition of PEMPS decreases the $T_g$ of the blend electrolytes. It is known that the mobility of polymer chain plays an important role on the ionic conductivity of polymer electrolytes. The decrease of $T_g$ of the soft segments implies that the their chain flexibility is improved. In Figure 5.55, the endothermic peaks associated with the incompletely dissolved LiCl appears in the range from $90^0C$ to $97^0C$. Also an endothermic peak appears around $68^0C$ to $75^0C$ after the addition of PEMPS. Both neat PEMPS and TPU/LiCl electrolytes do not have endothermic peak around this range. According to Cooper\textsuperscript{197}, this peak might be related to the disruption of the short range order of the hard segments. Thus, the appearance of this peak indicates that the addition of PEMPS to TPU/LiCl favor the formation of hard segment aggregation. The $T_m$ of the soft segments of TPU/PEMPS/LiCl electrolytes increases with the addition of PEMPS as shown in Figure 5.59. In the DSC thermograms of TPU/PEMPS/ LiTFSI electrolytes, a second $T_g$ around $-30^0C$ to $-40^0C$ is observed. This is attributed to $T_g$ of the soft segment interacting with hard segments as the results of the mixing of soft domain and hard domain caused by the interaction of LiTFSI with both soft segments and hard segments.
5.4 FTIR of Electrolyte Films

In this study, FTIR is used to study the interaction of salts with TPU and PEMPS as well as the hard-hard segment hydrogen bond and soft–hard segment hydrogen bond in TPU by the weave number shifts of the characteristic absorption peak and their intensity changes. This interaction will lead the blends of TPU and PEMPS to improve their miscibility.

According to Heumen and Stevens\textsuperscript{94,95}, the following three region in the FTIR of TPU are very important for information of the phase morphology of TPU and the interactions of salts with each component of polymer electrolytes: (1) The hydrogen bonded N-H stretching mode and the free N-H stretch (3600-3100 cm\textsuperscript{-1}); (2) the carbonyl symmetric stretching vibration or amide band (1750-1650 cm\textsuperscript{-1}); and (3) The C-O-C stretch for the soft segment and C(O)-O-C stretch of the hard phase (1150-1000 cm\textsuperscript{-1}). Hence, three functional groups including ether group, carbonyl and N-H are examined to study the interaction of salts with different functional groups and the effect of salts and PEMPS on the phase morphology of TPU.

Figure 5.60 and Figure 5.61 show the FTIR of TPU with different LiCl concentrations and the enlargement of three regions corresponding to C-O-C, C=O, and N-H respectively. In the region of 1000-1200 cm\textsuperscript{-1}, both the intensity and location of the peaks exhibit few changes after the addition of LiCl. This result indicates the weak interaction between LiCl and the ether oxygen in soft segments. This is consistent with the results obtained in the FTIR of PTMG/LiCl. In the region of 1600-1800 cm\textsuperscript{-1}, the peak at 1732 cm\textsuperscript{-1} is assigned to the free bonded carbonyl and the peak at 1700 cm\textsuperscript{-1} is associated
Figure 5.60  FTIR spectra of TPU/LiCl electrolytes with different LiCl concentrations

Figure 5.61  FTIR spectra of TPU/LiCl electrolytes with different LiCl concentrations in the range from (a) 1000-1200 cm\(^{-1}\), (b) 1660-1780 cm\(^{-1}\), (c) 3100-3500 cm\(^{-1}\)
to the bonded carbonyl groups. As shown in Figure 5.61(b), the peak at 1700 cm\(^{-1}\) shifted to the lower frequency and exhibits a much broader band with the addition of LiCl than the one without LiCl. This might be caused by the interaction of Li\(^+\) with carbonyl oxygen. According to Ferry et al\(^{174}\), in the region of 3100 to 3500 cm\(^{-1}\), TPU exhibits three different absorption peaks: the peak at 3435 to 3450 cm\(^{-1}\) is assigned to the free N-H; the peak at 3309-3316 cm\(^{-1}\) is assigned to the NH groups hydrogen bonded to the carbonyl oxygen of the hard segment; the peak at 3257 to 3262 cm\(^{-1}\) is assigned to the N-H groups bonded to the ether oxygen of PTMG soft segments. In Figure 5.61(c), only a broad peak appears in this region with and without the addition of LiCl, as the result of overlapping of absorption peaks of N-H in different forms. In neat TPU there is a very strong peak around 3310 cm\(^{-1}\), which implies large portion of N-H is bonded to hard segments. However, the width of the peak becomes broader and the center of this peak shifts to low wavenumbers as the LiCl is added. This indicates that more of N-H group is bonded to soft segments after the addition of LiCl. In other words, the LiCl induces phase mixing of TPU. The variation of relative intensity of some specific peaks with the concentration of salts are plotted in Figure 5.62. At [O:Li]=16:1, the changes in the relative intensity are significant for the peaks at 1112 cm\(^{-1}\), 3327 cm\(^{-1}\) and 3494 cm\(^{-1}\) as discussed above. This indicates that more salts interacted with the soft segments and hard segments of TPU at [O:Li]=16:1.

The FTIR of TPU electrolytes with LiClO\(_4\) are plotted in Figure 5.63 and Figure 5.64. The FTIR of the TPU/ LiClO\(_4\) electrolytes in the ether region is different from the results of the TPU/LiCl electrolytes. The peak around 1110 cm\(^{-1}\) shifts to the lower
frequency with the addition of LiClO⁴ and the frequency decrement increases as the concentration of LiClO⁴ increases. Also it is noticed that the intensity of free carbonyl peak around 1730cm⁻¹ significantly decreased while the intensity of bonded carbonyl peak around 1700cm⁻¹ increases as the LiClO⁴ concentration increases as shown in Figure 5.65, which means that some portion of free carbonyl turns into bonded state after the addition of salts. The bonded carbonyl peak with LiClO⁴ around 1700m⁻¹ shifts to a lower frequency than the one of neat TPU. The shift is related to the interaction of Li⁺ with bonded carbonyl group. This interaction decreases the strength of the carbonyl bond and causes the shift of absorption frequency to a lower value. In the N-H region, TPU electrolytes with LiClO⁴ shows a higher frequency shifts from 3320cm⁻¹ to 3350cm⁻¹ because the interaction of Li⁺ with carbonyl releases some bonded N-H into free bonded N-H. This trend is also observed in Jeung’s study on the FTIR of TPU/LiClO⁴ electrolyes. The different interaction between TPU with LiCl from TPU with LiClO⁴ is caused by the different interaction strength of ether oxygen with LiCl from LiClO⁴.

The results of TPU/ LiTFSI shown in Figure 5.66 and Figure 5.67 are similar to that of TPU/LiClO⁴ electrolytes. The peak at 3320cm⁻¹ shifts to high frequency, which means more free N-H is generated. The peak at 1700cm⁻¹ of the bonded carbonyl is stretched broader and with multi-splitting shape peaks due to the existence of LiFTSI. The peak around 1100cm⁻¹ almost becomes a plateau due to the overlapped three peaks contributed from the Li⁺ bonded ether, free bonded ether and hydrogen bonded ether. The absorption frequency decrease of ether group and bonded carbonyl groups is associated
Figure 5.62  The relative intensity of some peaks versus different LiCl concentrations in TPU/LiCl electrolytes
Figure 5.63  FTIR spectra of TPU/LiClO₄ electrolytes with different LiClO₄ concentrations

Figure 5.64  FTIR spectra of TPU/LiClO₄ electrolytes with different LiClO₄ concentrations in the range from (a) 1000-1200 cm⁻¹ (b) 1660-1780 cm⁻¹ (c) 3100-3500 cm⁻¹
with the weakening of the bond strength in TPU electrolytes with the three different lithium salts. This explains the phenomenon that the thermal stability decrease depending on the salt concentration of TPU electrolytes discussed in section 5.2.1. The relative intensity of the interested peaks is plotted in Figure 5.68. The intensity of the peak at 3484 cm\(^{-1}\) related to the free N-H slightly decreases as the LiTFSI concentration increase. The one at 1703 cm\(^{-1}\) is nearly unchanged with the LiTFSI.

Wen et al\(^7\) examined the –NH stretching region of TPU/LiClO\(_4\) electrolytes with various hard segment concentrations. They found that the N-H peak displayed very little shifting with varying hard and soft segments composition while the free –NH stretching band is shifted to higher frequency by means of adding LiClO\(_4\) to TPU. The shift was maximum at lower salt concentrations because of the plasticizing efect of the associated ions on TPU at high salt concentrations. They proposed that the shifting of the free -NH peak position caused by the salt might be explained on the basis of interaction of Li\(^+\) ions with the N atoms in the free –NH group, thus resulting in the reducing of N-H bond length and its shift to lower frequency.

In order to study the interaction between TPU and PEMPS in the TPU/PEMPS electrolytes, TPU/PEMPS electrolytes with different lithium salts and various blend compositions were also characterizaed by FTIR. The FTIR of TPU/PEMPS/LiCl electrolytes with various blend compositions is shown in Figure 5.69 and Figure 5.70. The frequency of the peak of ether group remains unchanged after the addition of PEMPS because the ether branch of PEMPS has a similar stucture as the soft segment. But the peaks become broader, which indicates the formation of the interaction between
Figure 5.65  The relative intensity of some peaks versus different LiClO₄ concentrations in TPU/LiClO₄ electrolytes
Figure 5.66  FTIR spectra of TPU/LiTFSI with different LiTFSI concentrations

Figure 5.67  FTIR spectra of TPU/LiTFSI with different LiTFSI concentrations in the range from (a) 1000-1200 cm\(^{-1}\), (b) 1660-1780 cm\(^{-1}\), (c) 3100-3500 cm\(^{-1}\)
Figure 5.68 The relative intensity of some peaks versus different LiTFSI concentrations in TPU/ LiTFSI electrolytes
the ether oxygen in soft segments and the ether oxygen in PEMPS via their interaction with \( \text{Li}^+ \). The intensity of the peaks of interest of TPU/PEMPS/LiCl electrolytes at [O:Li]=16:1 with varying blend composition vs. \( W_{\text{PEMPS}} / W_{\text{TPU}} \) is plotted in Figure 5.71. The intensity of the free bonded carbonyl peak at 1730cm\(^{-1}\) increases and the intensity of the bonded carbonyl peak at 1700cm\(^{-1}\) decreases as the PEMPS concentration increases till \( W_{\text{PEMPS}} / W_{\text{TPU}} = 0.2 \), then reaches a plateau as shown in Figure 5.71. This result indicates that PEMPS has the opposite effect on TPU in this region in comparison with lithium salts as discussed above. Also the intensity of the hard segment bonded N-H absorption at 3310cm\(^{-1}\) increases and the frequency of the center of the overlapped broad band of N-H group shifts to higher frequency as the concentration of PEMPS increases.

Zhu et al\(^{96}\) studied a series of polyether based polyurethane electrolytes with NaClO\(_4\) and pointed out that the oxygen atoms of carbonyl and ether oxygen groups had different activity to cations according to their FTIR results. The relative absorption intensity of the peak corresponding to the coordinative C-O-C increased with the addition of NaClO\(_4\) first. Then it reached a plateau at high salt concentrations, which implied that the coordination of C-O-C with sodium cations reached the saturated level. On the contrary, the coordination degree of the C=O with sodium cation increased slightly at low salt concentration and then increased sharply at high salt concentration. They concluded that there was selective coordination of Na\(^+\) with ether oxygen and carbonyl oxygen and Na\(^+\) interacted preferentially with the ether groups rather than carbonyl groups at low salt concentrations.
Figure 5.69  FTIR spectra of TPU/PEMPS/LiCl electrolytes with different blend compositions at [O:Li]=16:1

Figure 5.70  FTIR spectra of TPU with different blend compositions at [O:Li]=16:1 in the range from (a)1000-1200 cm\(^{-1}\), (b) 1660-1780 cm\(^{-1}\), (c) 3100-3500cm\(^{-1}\)
A possible explanation for the results of TPU/PEMPS/LiCl electrolytes in this study is due to the fact that the ether part of PEMPS is competing with the carbonayl group in interacting with LiCl. However, LiCl favors the ether oxygen on PEMPS more than carbonyl group of the hard segments, resulting in separating the Li⁺ interacted with carbonyl group and forming better hard-hard segment interaction.

The FTIRs of TPU/PEMPS/LiClO₄ electrolytes and TPU/PEMPS/LiFSI with different blend compositions are shown in Figure 5.72 and Figure 5.75. And their relationship of intensity and the peaks of interest are plotted in Figure 5.74 and Figure 5.77 respectively. The results of TPU/PEMPS/LiClO₄ electrolytes and TPU/PEMPS/LiTFSI are similar to that of TPU/PEMPS/LiCl electrolytes. The peak originally at 1110 cm⁻¹ becomes much boarder with the addition of salts. The intensity ratio of the free bonded carbonyl group to the bonded carbonyl group increases as the PEMPS concentration increases as shown in Figure 5.74 and Figure 5.77. The intensity of peak at 3327 cm⁻¹ is slightly increased. These results indicate that the addition of PEMPS reduced the interaction of Li⁺ with the hard segment and enhanced the hard-hard segments interaction in TPU/PEMPS/LiClO₄ electrolytes. However, comparing the curves of peak at 1112 cm⁻¹ in Figure 5.74 with the one in Figure 5.77, it is noticed that in TPU/PEMPS/ LiClO₄ electrolytes, the intensity of peak at 1112 cm⁻¹ decreases and its minimum occurs at \( W_{PEMPS} / W_{TPU} = 0.1 \). This difference is caused by the variation of the interaction strength between TPU and these two salts.
Figure 5.71 The relative intensity of some peaks versus different blend composition in TPU/PEMPS/LiClO₄ electrolytes at [O:Li]=16:1
Figure 5.72  FTIR spectra of TPU/PEMPS/LiClO$_4$ electrolytes with different concentrations of PEMPS at [O:Li]=16:1

Figure 5.73  FTIR spectra of TPU with different blend compositions at [O:Li]=16:1 in the range from (a) 1000-1200 cm$^{-1}$ (b) 1660-1780 cm$^{-1}$ (c) 3100-3500 cm$^{-1}$
Figure 5.74  The relative intensity of some peaks versus different blend composition in TPU/PEMPS/LiClO₄ electrolytes at [O:Li]=16:1
Figure 5.75  FTIR spectra of TPU/PEMPS/LiTFSI electrolytes with different concentrations of PEMPS at [O:Li]=16:1

Figure 5.76  FTIR spectra of TPU/PEMPS electrolytes with different blend compositions at [O:Li]=16:1 in the range from (a) 1000-1200 cm$^{-1}$ (b) 1660-1780 cm$^{-1}$ (c) 3100-3500 cm$^{-1}$
Figure 5.77  The relative intensity of some peaks versus different PEMPS concentration in TPU/PEMPS/LiTFSI electrolytes at [O:Li]=16:1
5.5 The Tensile Properties of Electrolyte Films

The important characteristics of solid polymer electrolytes over liquid electrolytes are their solid nature, flexibility and easy processability. As the separator in the battery, the solid polymer electrolyte itself has to produce a solid thin film and possess good mechanical properties. The gel polymer electrolytes or plasticized polymer electrolytes can achieve very high ionic conductivity \((10^{-2} \text{ S/cm})\) at very high solvent content, but the mechanical properties are poor due to the inclusion of the large amount of volatile solvent or plasticizer. Their properties are also unstable due to the evaporation of volatile solvent or plasticizer. In this study the multi-phase hard domain-soft domain morphology of TPU makes it possible that TPU electrolytes not only can have considerable ionic conductivity, but also exhibit good dimension stability. From the morphological studies of TPU electrolytes and TPU/PEMPS electrolytes, it is found that the addition of lithium salts in TPU induces the phase mixing between soft segments and hard segments, and the addition of PEMPS in TPU results in the phase separation. Therefore, it is possible that the salt and PEMPS can also influence their mechanical properties in this study. In this section, the tensile properties of TPU electrolytes and TPU/PEMPS electrolytes were characterized by tensile testing measurement.

The stress-strain curves of neat TPU, TPU/LiClO\(_4\) electrolytes and TPU/LiTFSI electrolytes with various salt concentrations are illustrated in Figure 5.78 and Figure 5.79. Their tensile properties are summarized in Table 5.6. The TPU used in this study is formulated with high soft segments content, so that the neat TPU film exhibits good elasticity. It can be stretched up to 1200% as shown in Figure 5.78. However, the
Figure 5.78  Typical engineering tensile stress-strain curves obtained from neat TPU film and TPU/LiClO$_4$ electrolytes film with various LiClO$_4$ concentrations

Figure 5.79  Typical engineering tensile stress-strain curves obtained from neat TPU film and TPU/LiTFSI electrolytes film with various LiTFSI concentrations
elongation at break of TPU/LiClO₄ electrolytes decreases even at low LiClO₄ concentration, [O:Li]=32:1. As more LiClO₄ is added, their elongation at break gradually decreases. A similar trend is also observed in TPU/LiTFSI electrolytes. The elongation at break of both TPU/ LiClO₄ electrolytes and TPU/LiTFSI electrolytes with various salt concentrations are plotted in Figure 5.80. At equal salt concentrations, the TPU electrolytes with LiTFSI can be stretched longer than the one with LiClO₄. For both TPU/ LiClO₄ electrolytes and TPU/LiTFSI electrolytes, the modulus decreases almost linearly with increasing the salt concentration as shown in Figure 5.81. The modulus of TPU TPU/LiTFSI electrolytes is slightly higher than the corresponding TPU/LiTFSI electrolytes when [O:Li] is below 8:1. However, at [O:Li]=8:1, the trend is reversed. It is noticed that the tensile properties of TPU electrolyte is slightly deteriorated by the addition of lithium salts. This is due to the morphology change of TPU including the level of the phase mixing caused by the interaction of lithium ions with soft–hard segments of TPU. The high modulus of TPU is mainly contributed from the existence of the hard domains and the network structure formed by physical cross-linking of the hard domains via hydrogen bonding. Some of the hydrogen bonding is destroyed by the lithium ions in TPU electrolytes as mentioned in previous sections. As a result, the mechanical properties of TPU electrolyte are influenced correspondingly. However, the tensile properties of these TPU electrolytes are still very promising compared with the mechanical properties of other polymer electrolytes which exhibit similar ionic conductivity.
Table 5.6  Engineering tensile properties of neat TPU and TPU electrolytes with various salt concentrations

<table>
<thead>
<tr>
<th>Materials</th>
<th>[O : Li ]</th>
<th>Modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat TPU</td>
<td></td>
<td>12.6</td>
<td>19.9</td>
<td>1100</td>
</tr>
<tr>
<td>TPU/LiClO₄</td>
<td>32</td>
<td>8.4</td>
<td>6.6</td>
<td>482</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>5.7</td>
<td>3.3</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>4.2</td>
<td>3.6</td>
<td>222</td>
</tr>
<tr>
<td>TPU/LiTFSI</td>
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<td>10.6</td>
<td>12.0</td>
<td>666</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>7.1</td>
<td>5.7</td>
<td>571</td>
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<td></td>
<td>8</td>
<td>1.8</td>
<td>1.3</td>
<td>350</td>
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</tbody>
</table>

Figure 5.80  The elongation at break of TPU/LiClO₄ and TPU/LiTFSI electrolytes vs. the salt concentration
Figure 5.81 The modulus of TPU/LiClO$_4$ and TPU/LiTFSI electrolytes vs. the salt concentration

Figure 5.82 Typical engineering tensile stress-strain curves obtained from TPU/PEMPS blend films with various compositions
Figure 5.82 shows the stress-stain curves of TPU/PEMPS blend without lithium salts. The tensile properties of TPU/PEMPS blend become inferior to ones of the blends with low PEMPS content such as the blend composition TPU/PEMPS= 100/10. The film was no longer an elastomer and it was easily breaks under stretching. This is contributed from the poor compatibility between TPU and PEMPS as discussed in morphological studies of TPU/PEMPS blend in section 3.1. Interestingly, by comparing the stress-strain curves of TPU/PEMPS blend without salts with the ones of with lithium salts shown in Figure 5.83 and Figure 5.84, it is observed that the addition of lithium salts in TPU/PEMPS blend improves the tensile properties. Prior to adding lithium salts, the TPU/PEMPS film can only be stretched to about 8 to 40 %, while they can reach high up to 1200% after the addition of lithium salts as listed in Table 5.7. This indicates that the lithium salts enhance the compatibility of these blends, which agrees well with the morphological study.

In order to study the effect of PEMPS on the mechanical properties of TPU in the presence of lithium salts, the modulus and elongation at break of TPU/PEMPS/LiClO$_4$ electrolytes and TPU/PEMPS/LiTFSI electrolytes at [O:Li]=16:1 with various blend compositions versus the PEMPS concentration, $W_{TPU}/(W_{TPU}+W_{PEMPS})$, are plotted in Figure 5.85 and Figure 5.86. The addition of PEMPS increases the elongation at break of TPU electrolyte but decreases the modulus of TPU electrolytes slightly, at constant ratio of [O:Li]. The elongation at break of TPU/PEMPS/LiTFSI varies with the PEMPS content more than that of TPU/PEMPS/LiClO$_4$. The increase of elongation at break resulted from the addition
Figure 5.83 Typical engineering tensile stress-strain curves obtained from TPU/PEMPS/LiClO$_4$ electrolyte films with various compositions.

Figure 5.84 Typical engineering tensile stress-strain curves obtained from TPU/PEMPS/LiTFSI electrolytes with various compositions.
Figure 5.85 The elongation at break of TPU/PEMPS/LiClO$_4$ and TPU/PEMPS/LiTFSI electrolytes at [O:Li]=16:1 with various compositions vs. the PEMPS concentration.

Figure 5.86 The modulus of TPU/PEMPS/LiClO$_4$ and TPU/PEMPS/LiTFSI electrolytes at [O:Li]=16:1 with various compositions vs. the PEMPS concentration.
of PEMPS in TPU/PEMPS electrolytes might be associated with the contribution of the flexibility of the PEMPS phases.

From the aforementioned results, it can be concluded that the change of mechanical properties of TPU/PEMPS electrolytes after the addition of lithium salts and PEMPS is related to the change of morphology originated from the interaction of lithium ions with each phase of the blends. Although the mechanical properties such as modulus and elongation at break are slightly affected by the above factors, the desired dimensional stability can still be achieved by selecting a particular composition such as TPU/PEMPS/LiTFSI with [O:Li]=16:1 and blend composition TPU/PEMPS=100/20.

Table 5.7  Engineering tensile properties of TPU/PEMPS blends and TPU/PEMPS electrolytes with various blend compositions

<table>
<thead>
<tr>
<th>Materials</th>
<th>TPU/PEMPS</th>
<th>Modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat TPU</td>
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<td>12.6</td>
<td>19.9</td>
<td>1100</td>
</tr>
<tr>
<td>TPU/PEMPS</td>
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<td>18.0</td>
<td>2.1</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>100/20</td>
<td>15.0</td>
<td>1.3</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>100/40</td>
<td>11.4</td>
<td>0.1</td>
<td>8</td>
</tr>
<tr>
<td>TPU/PEMPS/LiClO₄</td>
<td>100/10</td>
<td>6.4</td>
<td>6.1</td>
<td>541</td>
</tr>
<tr>
<td>[O:Li]=16:1</td>
<td>100/20</td>
<td>5.4</td>
<td>9.2</td>
<td>559</td>
</tr>
<tr>
<td></td>
<td>100/40</td>
<td>3.5</td>
<td>2.1</td>
<td>330</td>
</tr>
<tr>
<td>TPU/PEMPS/LiTFSI</td>
<td>100/10</td>
<td>6.8</td>
<td>4.8</td>
<td>577</td>
</tr>
<tr>
<td>[O:Li]=16:1</td>
<td>100/20</td>
<td>5.0</td>
<td>14.5</td>
<td>1237</td>
</tr>
<tr>
<td></td>
<td>100/40</td>
<td>2.1</td>
<td>4.6</td>
<td>667</td>
</tr>
</tbody>
</table>
5.6 Ionic Conductivity of Electrolyte Films

The ionic conductivity of polymer electrolytes is very important for their application. The principle of the ionic conductivity measurement of polymer electrolyte is to apply a voltage to a cell assembly containing a polymer electrolyte film sandwiched between two electrodes and determine its impedance. The properties of the polymer electrolytes can be determined by a direct current measurement or a alternating current measurement. In our research, the alternating current measurement was used and the ionic conductivity of solid polymer electrolyte was determined by measuring the bulk resistance via A.C. impedance measurement. The sample was sandwiched between two stainless steel electrodes. The cell impedance was measured at various frequencies ranging from 100 Hz to 100 kHz. The voltage applied on the sample was fixed at 5V throughout the experiments. The magnitude of complex impedance $|Z|$ and its phase angle $\theta$ of polymer electrolytes were read directly from the instrument. The impedance plot of electrolytes was obtained by plotting $|Z| \cos \theta$ versus $|Z| \sin \theta$. Usually, the impedance plot consists of a spike and semi-circle. The bulk resistance $R_b$ was determined by extrapolating the complex impedance plot curve to intercept at the real axis. Then the ionic conductivity can be calculated from bulk resistance with the dimension of polymer electrolyte sample.

The ionic conductivity of TPU electrolytes and TPU/PEMPS electrolytes with various lithium salts prepared by the in-situ process were determined to study the effect of the structure of the anion and the addition of the high ionic conductive component PEMPS on the ionic conductivity. The polymer electrolytes prepared by solution cast are
selectively examined to study the effect of different preparation methods on the ionic conductivity of polymer electrolytes.

The impedance plot of TPU electrolytes prepared by the in-situ process with various LiCl concentrations at different temperatures are plotted in Figure 5.87 to Figure 5.89. \( Z' = |Z|\cos \theta \) and \( Z'' = |Z|\sin \theta \). The typical impedance curve of the polymer electrolyte shows a semi-circle followed by a spike from the left side of the \( Z' \) axis to its right side. The impedance plot of TPU/LiCl only exhibited a part of semi-circle in the studied frequency ranges and no spike was observed. Interestingly, as the temperature increases, more portion of the semi-circle appears. When \([O:Li]=32:1\), only a very small portion of semi-circle is shown in the plot at the room temperature and a nearly half of semi-circle appears at \(80^\circ\)C. As the temperature continuously increases, more portion of the semi-circle is observed. A nearly full semi-circle appears at \(180^\circ\)C. Increasing the LiCl concentration gradually from \([O:Li]=32:1\) to \([O:Li]=8:1\), more of the semi-circle appears at lower temperatures. The complete semi-circle appears at \(140^\circ\)C when \([O:Li]=16:1\) and appears at \(120^\circ\)C when \([O:Li]=8:1\).

Extrapolation is necessary for the incomplete semi-circle pattern for interpreting the intercept of the imaginary semi-circle with the \( Z' \) axis, so that its bulk resistance can be determined. The bulk resistance of TPU/LiCl electrolytes with \([O:Li]=32:1\) at the low temperatures is hard to determined because only a very small portion of semi-circle is shown. The ionic conductivity data at the lower temperatures cannot be obtained. The ionic conductivity data of TPU/LiCl electrolytes obtained by calculating from bulk
Figure 5.87  Impedance plot of TPU/LiCl electrolytes prepared by the in-situ process with [O:Li]=32:1 at different temperatures

Figure 5.88  Impedance plot of TPU/LiCl electrolytes prepared by the in-situ process with [O:Li]=16:1 at different temperatures
Figure 5.89  Impedance plot of TPU/LiCl electrolytes prepared by the in-situ process with [O:Li]=8:1 at different temperatures

Figure 5.90  The effect of temperature on the conductivity of TPU/LiCl electrolytes prepared by the in-situ process with various salt concentrations
resistance at different temperatures is plotted in Figure 5.77. It can be seen that the log $\sigma$ increases linearly with $1/T$ for TPU/LiCl electrolytes with various LiCl concentration, which indicates that the ionic conductivity temperature dependence follows the Arrhenius law. The activation energy of the ionic conductivity temperature dependence is calculated from the slope, which is around 0.017 eV as listed in Table 5.8. The ionic conductivity increases as the LiCl concentration increases. This is because more LiCl leads to more charge carriers and results in the ionic conductivity increasing. Jeung\textsuperscript{55} reported that in her study the activation energy of the ionic conductivity of TPU electrolytes with various inorganic was in the range of 0.02 to 0.012 eV, which varied from salt species and salt concentration.

Figure 5.91 to Figure 5.93 are the impedance plots of TPU/PEMPS/LiCl electrolytes with various blend compositions at [O:Li] =16:1. When TPU/PEMPS ratio is 100/10, it is noticeable that over half of the semi-circle is shown in the impedance plot even at the room temperature and the full part of the semi-circle appears at the temperatures from 60$^\circ$C up. As the temperature approaches 100$^\circ$C, some of the left part of the semi-circle is missing. The higher the tested temperature, the more of the left side is missing. When the temperature is around 140$^\circ$C, only the right part of the semi-circle is shown. As the temperature continues going up, only a small portion of the right side of the semi-circle is left. When TPU/PEMPS ratio is 100/20, a small portion on the left side of semi-circle is gone and a small tail shows up at the right side at the room temperature. The full semi-circle appears at 40$^\circ$C. A similar trend like the impedance plot of
Figure 5.91  Impedance plot of TPU/PEMPS/LiCl electrolytes prepared by the in-situ process with TPU/PEMPS =100/10 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C

Figure 5.92  Impedance plot of TPU/PEMPS/LiCl electrolytes prepared by the in-situ process with TPU/PEMPS =100/20 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C
TPU/PEMPS/LiCl electrolytes with TPU/PEMPS =100/20, is also observed when TPU/PEMPS blend ratio reaches to 100/40. Figure 5.93 shows the impedance plot with TPU/PEMPS = 100/40. The whole part of the semi-circle appeared at room temperature. As the temperature increases, the pattern of the impedance plot changes sequentially: at low temperatures, only a small portion on the left part of the semicircle disappears; as the temperature increases, more portion disappears and gradually only a small portion of the right side of the semicircle is left; at high temperatures, the impedance plot shows a small portion of the right side of semicircle followed by a small tilted straight line.

The ionic conductivity of TPU/PEMPS/LiCl electrolytes with various blend compositions at various temperatures is plotted in Figure 5.94. As mentioned before, the ionic conductivity of TPU/LiCl electrolyte with [O:Li]=16:1 at room temperature is out of the measurement range. However, the addition of PEMPS into these electrolytes makes a more complete shape of the impedance semi-circle plot measured and the bulk resistance fall into the measurement range. As the concentration of PEMPS increases the ionic conductivity of corresponding TPU/PEMPS/LiCl electrolyte increases up to around $2 \times 10^{-7} \text{S/cm}$ till TPU/PEMPS blend ratio reaches 100/20. The ionic conductivity of TPU/PEMPS/LiCl electrolyte with TPU/PEMPS=100/20 is very close to that of TPU/PEMPS=100/40 in the lower temperature region and slightly higher than that of the latter at the temperatures higher than 120$^0$C. This indicates that the extra addition of PEMPS into TPU/PEMPS/LiCl electrolyte does not change the ionic conductivity at lower temperatures after the blend composition reaches to 100/20, but it improves the ionic conductivity at higher temperatures. This can be explained by that the interaction of
Figure 5.93 Impedance plot of TPU/PEMPS/LiCl electrolytes prepared by the in-situ process with TPU/PEMPS=100/40 and \([O:Li]=16:1\) at different temperatures (a) from 27°C to 100°C (b) from 120°C to 180°C

Figure 5.94 The effect of temperature on the conductivity of TPU/PEMPS/LiCl electrolytes prepared by the in-situ process with various blend compositions at \([O:Li]=16:1\)
LiCl with polymer is not sufficiently strong, which makes LiCl only interact with a small amount of PEMPS and TPU. As the extra amount of PEMPS is added to the TPU matrix, the interfacial adhesion between TPU and PEMPS becomes poor. While with increasing the temperature, since the solubility of salts in polymer has a temperature dependence, more undissolved LiCl particle can be dissociated into ions or ion clusters providing extra binders between PEMPS and TPU, thereby enhancing their interface. The ionic conductivity temperature dependence of TPU/PEMPS/LiCl electrolyte follows Arrhenius law. The ionic conductivity curve of TPU/PEMPS/LiCl electrolytes is shifted upwards to higher value when PEMPS is added.

Figure 5.95 to Figure 5.97 shows the impedance plot of TPU/LiClO$_4$ electrolytes at various temperatures. At the lower LiClO$_4$ concentration where [O:Li]=32:1, the low $Z''$ area of the semi-circle is shown at temperature below 100$^\circ$C, then the right portion of semi-circle at high $Z''$ area appears when the temperature increases, finally the full portion of the semi-circle appears when temperature is in the range between 100$^\circ$C to 140$^\circ$C. At [O:Li]=16:1, only the right portion of the semi-circle at high $Z''$ area is shown till the temperature reaches 60$^\circ$C, and then a tilted spike appears after the right part of the semi-circle at high $Z''$ area at temperature above 60$^\circ$C. Interestingly more of the tilted spike and less of the semi-circle at high $Z''$ area appear with increasing the temperature gradually and the impedance plot exhibits a V shape at high temperatures. At [O:Li]=8:1, a similar trend is seen in the low temperature region. Only a spike appears at the temperatures above 80$^\circ$C. The obtained ionic conductivity at various temperatures for
Figure 5.95  Impedance plot of TPU/LiClO₄ electrolytes prepared by the in-situ process with [O:Li]=32:1 at different temperatures (a) from 27°C to 120°C (b) from 140°C to 180°C

Figure 5.96  Impedance plot of TPU/LiClO₄ electrolytes prepared by the in-situ process with [O:Li]=16:1 at different temperatures (a) from 27°C to 60°C (b) from 80°C to 100°C (c) from 120°C to 140°C
Figure 5.97  Impedance plot of TPU/LiClO₄ electrolytes prepared by the in-situ process with [O:Li]=8:1 at different temperatures (a) from 27°C to 60°C (b) from 80°C to 100°C (c) from 120°C to 140°C

Figure 5.98  The effect of temperature on the conductivity of TPU/LiClO₄ electrolytes with various salt concentrations
TPU/LiClO$_4$ electrolytes is plotted in Figure 5.98. The logarithm of the ionic conductivity of TPU/LiClO$_4$ electrolytes increases linearly with increasing the reciprocal of temperature, which indicates the ionic conductivity behavior follow Arrhenius law. The linear curve is shifted to higher ionic conductivity values as the salt concentration increases. The ionic conductivity nearly increases by one order of magnitude as the salt concentration doubles. The room temperature conductivity of TPU/LiClO$_4$ electrolytes increases from $2 \times 10^{-9}\, S/cm$ to $2 \times 10^{-7}\, S/cm$.

Figure 5.99 to Figure 5.101 illustrates the impedance plot of TPU/PEMPS/LiClO$_4$ with different concentrations of PEMPS. Similarly, the impedance plot shows different patterns in different temperature regions. When only a small amount of PEMPS is added, the curve composed of a semi-circle and a tilted spike is shown at the room temperature, then a nearly full semi-circle appears at the temperatures in the range of $40^0\text{C}$ to $80^0\text{C}$; after that the impedance plot is in the form of a combination of a portion of semi-circle and a spike at the temperatures above $80^0\text{C}$, finally a V shaped plot appears at the temperatures above $160^0\text{C}$. A similar trend is observed for the TPU/PEMPS/LiClO$_4$ electrolytes with TPU/PEMPS=100/20 and 100/40. Figure 5.102 shows the ionic conductivity determined at various temperatures for TPU/PEMPS/LiClO$_4$ electrolytes. The ionic conductivity of TPU/LiClO$_4$ increases greatly with the addition of a small amount of PEMPS, then the difference increases linearly with the PEMPS concentration.

The impedance plots of TPU electrolytes with lithium salt with a large anion, LiTFSI, are represented from Figure 5.103 to Figure 5.105. At the low salt concentration, [O:Li]=32:1, the impedance curves are in the form of a full portion of semi-circle
Figure 5.99  Impedance plot of TPU/PEMPS/LiClO₄ electrolytes prepared by the in-situ process with TPU/PEMPS=100/10 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 140°C (c) from 160°C to 180°C
Figure 5.100 Impedance plot of TPU/PEMPS/LiClO₄ electrolytes prepared by the in-situ process with TPU/PEMPS=100/20 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 140°C

Figure 5.101 Impedance plot of TPU/PEMPS/LiClO₄ electrolytes prepared by the in-situ process with TPU/PEMPS=100/40 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 140°C
Figure 5.102  The effect of temperature on the conductivity of TPU/PEMPS/LiClO$_4$ electrolytes with various blend compositions with [O:Li]=16:1
followed by a tilted small spike at temperature below 60°C; and at the higher temperatures the impedance curve becomes a partial semi-circle with a tilted spike which intercepts with Z’ axis at the joint between the semi-circle and the spikes. When [O:Li] increases to 16:1, the impedance curve shows a small portion of semi-circle and a tilted spike at the temperatures below 100°C. Only the tilted spike is observed in the impedance plot at temperatures above 100°C. At [O:Li] = 8:1, the impedance pattern with only a tilted spike appears at 60°C, which is lower than the corresponding temperature in case of [O:Li]=16:1. The ionic conductivity data of the electrolytes at temperature above 60°C is not obtained. The dimensional stability of TPU/LiTFSI electrolytes at the high temperatures becomes poor at [O:Li]=8:1, the pressure applied between the two electrodes make the thickness of the electrolyte film become thinner and causes a short circuit between the electrodes. The dimensional stability deterioration of TPU/ LiTFSI electrolytes at higher salt concentrations is generated by the soft segment/hard segment phase mixing association with the strong interaction between Li⁺ and those segments.

In Figure 5.106, it is noticed that the ionic conductivity curves of TPU/LiTFSI at various temperatures shift to higher values as the salt concentration increases. The room temperature ionic conductivity of TPU/LiTFSI can reach to $1.25 \times 10^{-5} \text{ S/cm}$ when [O:Li] is controlled to 8:1. The curves in Figure 5.106 have different slopes, which indicate that the activation energy of the TPU/LiTFSI electrolytes varies with the salt concentration. The possible explanation is that the phase mixing induced by the interaction of LiTFSI with the soft segments and hard segments of TPU makes the
Figure 5.103 Impedance plot of TPU/LiTFSI electrolytes prepared by the in-situ process with [O:Li]=32:1 at different temperatures (a) from 270°C to 800°C (b) from 1000°C to 1400°C

Figure 5.104 Impedance plot of TPU/LiTFSI electrolytes prepared by the in-situ process with [O:Li]=16:1 at different temperatures (a) from 270°C to 800°C (b) from 1000°C to 1400°C
Figure 5.105    Impedance plot of TPU/LiTFSI electrolytes prepared by the in-situ process with [O:Li]=8:1 at different temperatures

Figure 5.106    The effect of temperature on the conductivity of TPU/LiTFSI electrolytes with various salt concentrations
hydrogen bonding dissociated at lower temperatures, and resulting in the better flexibility of TPU and higher ionic conductivity.

The impedance plots of TPU/PEMPS/LiTFSI electrolytes with various blend compositions at different temperatures are plotted in Figure 5.107 to Figure 5.109. At TPU/PEMPS = 100/10, the impedance plot exhibit partial semi-circle and a tilted spike at the temperatures below 80°C; the curve changes into a V-shape as the temperature increases. A similar trend is observed for TPU/PEMPS/LiTFSI electrolytes with TPU/PEMPS= 100/10. The difference is that the Z’ value where the plot intercepts with Z’ axis is smaller, which indicates small bulk resistance. When TPU/PEMPS=100/40, a V-shaped curve is formed at room temperature and as the temperature increases the left part of the V curve gradually disappears and the right part shows more till only a tilted line appears in the impedance plot above 100°C.

The ionic conductivity data of TPU/PEMPS/LiTFSI is plotted in Figure 5.110. It can be seen that the addition of PEMPS makes the ionic conductivity curve of TPU/LiTFSI electrolytes shift upwards. Their ionic conductivity increases nearly one order of magnitude when TPU/PEMPS is up to 100/40. It is found that their ionic conductivity has a non-linear relationship with the PEMPS concentration. Regarding its temperature dependence, the ionic conductivity of TPU/PEMPS/LiTFSI electrolytes increases more at higher temperatures than at lower temperatures when TPU/PEMPS=100/10. Overall, the incorporation of PEMPS into TPU enhances the ionic conductivity of TPU/LiTFSI electrolytes.
Figure 5.107  Impedance plot of TPU/PEMPS/LiTFSI electrolytes prepared by the in-situ process with TPU/PEMPS=100/10 and [O:Li]=16:1 at different temperatures (a) from 270°C to 800°C (b) from 1000°C to 1400°C

Figure 5.108  Impedance plot of TPU/PEMPS/LiTFSI electrolytes prepared by the in-situ process with TPU/PEMPS=100/20 and [O:Li]=16:1 at different temperatures (a) from 270°C to 800°C (b) from 1000°C to 1200°C
Figure 5.109  Impedance plot of TPU/PEMPS/LiTFSI electrolytes prepared by the in-situ process with TPU/PEMPS=100/40 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 140°C

Figure 5.110  The effect of temperature on the conductivity of TPU/PEMPS/LiTFSI electrolytes with various blend compositions with [O:Li]=16:1
It is worth mentioning that from the impedance plots of polymer electrolytes with various compositions, the electrolyte with a very high resistance exhibits only the left part of the semi-circle using the instrument used in this research; as the temperature gradually increases, more of the semi-circle is shown from the half to the whole; and then the impedance curve shows a semi-circle followed by a small portion of a tilted spike; the further temperature increase leads to showing more of the tilted spike; the impedance plot in form of a tilted spike is shown at higher temperatures. The change of the semi-circle pattern associated with the temperature is related to the bulk resistance variation caused by the temperature difference. The bulk resistance of the sample increases with increasing the temperature.

The impedance measurement range of LCR meter used in this research is $0.01\Omega < |Z| < 20M\Omega$ and the frequencies are eleven discrete points with $100Hz \leq \omega \leq 100Hz$. For TPU electrolytes and TPU/PEMPS electrolytes, this frequency range is not sufficiently wide to construct the whole impedance plot. (i.e. given the frequency range is broad enough, the impedance plots of all the samples will show a deformed semi-circle and a tilted spikes or more complicated patterns.) The obtained impedance and phase angle data of TPU/LiCl electrolytes with [O:Li]=32:1 is shown in Table 5.8. It is noticed that at low frequency range of the LCR meter, the impedance is too high, which is out of the measurement range. For low ionic conductive electrolytes, only a small part of the semi-circle is constructed by the obtained experimental data. However, for TPU/PEMPS/LiTFSI electrolytes with TPU/PEMPS=100/40 as listed in Table 5.8, even the test frequency increases to the highest frequency range of the LCR
meter, all the eleven data points are only distributed on the tilted spikes. This indicates that a much higher frequency is needed to obtain the data to construct the semi-circle part, i.e. the high frequency range of the LCR meter used in this experiment can only fall into the low frequency region category of the whole frequency region where both the semi-circle and the tilted spike is constructed. For the low ionic conductivity electrolytes, the low frequency range of the LCR meter used in this experiment falls in the high frequency region of the whole plot. The impedance data of TPU or TPU blend electrolytes obtained using the LCR meter in this research falls in different regions of the typical impedent plot as shown in Figure 5.111 depending on the resistance of the sample. As the ionic conductivity of electrolytes increases, i.e. its resistance decreases, the plot obtained in the experiment shifts from the lower numbered region to the high numbered region. This explains the diversity of impedance plot shape obtained in this experiment.

Similar phenomena are reported by Fonseca et al. in their study of the ionic conductivity behavior of polymer electrolytes based on poly(dimethyl siloxane-co-ethylene oxide) (P(DMS-EO)). At low temperatures, in the impedance plots of P(DMS-EO)/LiCO₄ electrolytes with 20 wt% of LiClO₄, a semi-circle and a spike were observed. With increasing temperature, this semi-circle gradually disappears and shifts to a lower resistance value. They also found that the ionic conductivity of P(DMS-EO) increased greatly with the LiClO₄ concentration at low LiClO₄ concentration such as 2.5%wt or 5.0 wt%, then it reached a plateau level with the further increase of the LiClO₄ concentration.
Table 5.8 Impedance data of some TPU electrolyte and TPU/PEMPS electrolyte

<table>
<thead>
<tr>
<th>Frequency (kHz)</th>
<th>Impedance (kΩ)</th>
<th>theta angle (degree)</th>
<th>Impedance</th>
<th>theta angle (degree)</th>
</tr>
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<td>-</td>
<td>0.727</td>
<td>17.2</td>
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<td>-</td>
<td>-</td>
<td>0.655</td>
<td>20.33</td>
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<td>0.4</td>
<td>-</td>
<td>-</td>
<td>0.598</td>
<td>15.55</td>
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<td>-</td>
<td>-</td>
<td>0.648</td>
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<td>-</td>
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<td>10.3</td>
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<td>-</td>
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<td>0.477</td>
<td>3.31</td>
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<td>20</td>
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<td>88.67</td>
<td>0.391</td>
<td>2.55</td>
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<td>200</td>
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<td>0.457</td>
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<tr>
<td>100</td>
<td>80.3</td>
<td>88.95</td>
<td>0.395</td>
<td>1.8</td>
</tr>
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</table>

Figure 5.111 The schematic representation of different regions of impedance plot
Similar impedance plot patterns were also observed by Kuo et al\textsuperscript{199} in TPU gel electrolytes swollen with 25 wt\% and 50 wt\% propylene carbonate (PC).

By comparing the ionic conductivity of TPU electrolytes containing lithium salt with different anions at a constant [O:Li], it can be concluded that TPU electrolytes with LiTFSI show the highest ionic conductivity among them. TPU electrolytes with LiClO\textsubscript{4} exhibit better ionic conductivity than TPU electrolytes with LiCl, as shown in Figure 5.112. The order of the size of anions is as following: Cl\textsuperscript{−} < ClO\textsubscript{4}\textsuperscript{−} < TFSI\textsuperscript{−}. This indicates that TPU with lithium salt composed of a larger sized anion shows a higher ionic conductivity. This can be explained by the good salt dissociation of lithium salt with a large anion. In a large anion, the negative charge is more widely distributed around different atoms (i.e. delocalization of the charge), so the charge density of the anion is low. While for small single atomic anions, the negative charge is highly concentrated. Therefore the ionic bond strength between a large sized anion and the highly concentrated positive charged lithium ion is weaker than one between a small sized anion with the lithium cation. The lithium salt with a large anion is easily dissociated by the polymer via the interaction of the lithium ion with the ether oxygen. This is already confirmed by the optical microscopy results discussed in previous chapter. In the other way, the size of Li\textsuperscript{+} is 0.68 Å and the size of Cl\textsuperscript{−} and ClO\textsubscript{4}\textsuperscript{−} are 1.67 Å and 2.36 Å respectively, so it is easy for Cl\textsuperscript{−} and Li\textsuperscript{+} to form densely packed crystal with high crystal lattice energy. The TFSI\textsuperscript{−} is an organic anion and the exact size data is not available, but according to its polyatomic structure, it is expected to have larger size than the other two anions.
Table 5.9 The ionic conductivity at room temperature $\sigma$ and the activation energies $E_a$ of TPU electrolytes with different types of salt prepared by the in-situ process

<table>
<thead>
<tr>
<th>Materials</th>
<th>$[O:Li]$</th>
<th>Conductivity at 300K (S/cm)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU/LiCl</td>
<td>32</td>
<td>--</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>--</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>$1.51 \times 10^{-9}$</td>
<td>0.032</td>
</tr>
<tr>
<td>TPU/LiClO$_4$</td>
<td>32</td>
<td>$2.12 \times 10^{-9}$</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>$7.51 \times 10^{-8}$</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>$2.24 \times 10^{-7}$</td>
<td>0.020</td>
</tr>
<tr>
<td>TPU/ LITFSI</td>
<td>32</td>
<td>$1.53 \times 10^{-6}$</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>$3.31 \times 10^{-6}$</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>$1.25 \times 10^{-5}$</td>
<td>0.028</td>
</tr>
</tbody>
</table>

Table 5.10 The ionic conductivity at room temperature $\sigma$ and activation energies $E_a$ of TPU/PEMPS electrolytes with different types of salt and various blend compositions prepared by the in-situ process

<table>
<thead>
<tr>
<th>Materials</th>
<th>TPU/PEMPS</th>
<th>Conductivity at 300K (S/cm)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU/PEMPS/LiCl</td>
<td>100/10</td>
<td>$9.51 \times 10^{-9}$</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>100/20</td>
<td>$2.34 \times 10^{-7}$</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>100/40</td>
<td>$2.25 \times 10^{-7}$</td>
<td>0.027</td>
</tr>
<tr>
<td>TPU/PEMPS/LiClO$_4$</td>
<td>100/10</td>
<td>$5.43 \times 10^{-7}$</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>100/20</td>
<td>$1.22 \times 10^{-7}$</td>
<td>0.024</td>
</tr>
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<td></td>
<td>100/40</td>
<td>$1.69 \times 10^{-6}$</td>
<td>0.026</td>
</tr>
<tr>
<td>TPU/PEMPS/LITFSI</td>
<td>100/10</td>
<td>$7.04 \times 10^{-6}$</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>100/20</td>
<td>$1.08 \times 10^{-5}$</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>100/40</td>
<td>$2.49 \times 10^{-5}$</td>
<td>0.020</td>
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</table>
Figure 5.112  The room temperature conductivity versus salt concentrations of TPU electrolytes with three different lithium salts

Figure 5.113  The room temperature ionic conductivity versus PEMPS/TPU ratio for TPU/PEMPS electrolytes with different lithium salts
Unlike the covalent bond, the ionic bond between cations and anions is non-directional and non-saturated, i.e. a cation can form ionic bond with several anions around it or an anion can have several cations around them. As pointed out by Gray 1, the cation may exist in different ion forms in the polymer electrolytes: (a) the ion in crystal lattice, (b) the ion cluster, (c) the free ion. Due to the rigidity of the crystal lattice, the mobility of lithium ions in the crystal lattice is very low and the contribution of that portion of lithium ions to the ionic conductivity is negligible. The mobility of the ion clusters depends on the size of the cluster: the larger the size, the less the mobility given the polymer matrix same. Free ions have the highest mobility. In the case of TPU/LiCl, there is a large portion of Li ions remain in crystal lattice, corresponding to the DSC results. The poor solubility of LiCl in TPU limits the number of the charge carriers and results in low ionic conductivity. In the case of LiClO₄ and LiTFSI, they can be completely dissolved in TPU in the concentration range used in this study. As indicated in DSC, FTIR and morphological results, the majority of salt forms free ions or ionic clusters. If all LiTFSI and LiClO₄ are in the form of the ion cluster in TPU and the ionic cluster is composed of same number of cation and anions, LiTFSI ion cluster is larger than LiClO₄ ion cluster. As a result, the ionic conductivity of TPU/LiClO₄ electrolytes should be higher than that of TPU/LiTFSI. On the contrary, the ionic conductivity studies show that TPU/LiTFSI electrolytes show higher ionic conductivity than TPU/LiClO₄ electrolytes. This implies that in TPU/LiTFSI there is more free ions or small ion clusters.

The ionic conductivity of TPU electrolyte increases as the salt concentration increases. But the ionic conductivity increases varies with different lithium salts. The
logarithm of ionic conductivity (\(\log \sigma\)) of TPU/LiTFSI electrolytes increases linearly with the salt concentration. The \(\log \sigma\) of TPU/LiClO\(_4\) electrolytes increases greatly as salt concentrations change from \([\text{O:Li}]=32:1\) to \([\text{O:Li}]=16:1\) and it increases slowly as the salt concentration changes from \([\text{O:Li}]=16:1\) to \([\text{O:Li}]=8:1\). According to Duke et al\(^{200}\), generally the conductivity of conductive materials has a linear relationship with the number of the charge carrier under a constant mobility. In this research, the nonlinear relationship of conductivity (\(\sigma\)) to LiClO\(_4\) concentration in TPU electrolytes originates from the ion mobility difference at different phase transition. The variable, \([\text{O:Li}]\), is the average salt concentration in the bulk polymer matrix. According to the FTIR studies, salts not only interact with the soft segments of TPU but also with the hard segments of TPU. At the low salt concentrations, the distribution of salt in the hard segments of TPU is negligible. As more salt is added, some portion of salt goes to the hard segment phase. Therefore, the effective salt concentration in soft segment decreased and also the phase mixing between hard segment and soft segment occurs. This phase mixing and salt distribution in different segments explains steeper slope at the low salt concentrations in Figure 5.112. Due to the low ionic conductivity of TPU/LiCl electrolytes, their data at low salt concentrations is located out of measurement range of the LCR meter.

Ionic conductivity results of TPU/PEMPS electrolytes reveal that the addition of PEMPS into TPU electrolytes increases their ionic conductivity. Their ionic conductivity increases as the concentration of PEMPS increases in the concentration range used in this study. The ionic conductivity increases induced by the addition of PEMPS varies with the structure of the anions. For TPU/PEMPS/LiTFSI electrolytes, the \(\log \sigma\) almost changes
with the concentration of PEMPS linearly. However, for TPU/PEMPS/LiCl electrolytes the log $\sigma$ increases with the blend ratio first and then reaches to a plateau, i.e. the extra addition of PEMPS does not increase the ionic conductivity after TPU/PEMPS reaches up to 100/20. The morphological studies of the TPU/PEMPS/LiCl discussed in the previous section showed the large scale of phase separation and poor interfacial adhesion between PEMPS phase and TPU phase at TPU/PEMPS=100/20. The large scale phase separation and poor interface adhesion increase the effective path length for ion motion and leads to the high resistance at the interface. Therefore PEMPS has two opposite roles on the ionic conductivity of TPU/PEMPS electrolytes: firstly, it increase the portion of high ionic conductivity components in the blend because PEMPS electrolyte itself has high ionic conductivity; secondly if the salt has a poor compatiblization effect on PEMPS phase and TPU phase, their ionic conductivity will decrease due to the long effective ion transfer path length.

In order to study the effect of the preparation method on the ionic conductivity, the TPU/LiClO$_4$ electrolytes, TPU/PEMPS/LiClO$_4$ electrolytes, TPU/LiTFSI electrolytes and TPU/PEMPS/LiTFSI electrolytes with different salt concentrations and TPU/PEMPS compositions are studied using the LCR meter. The impedance plots of the TPU/LiClO$_4$ electrolytes and TPU/PEMPS/LiClO$_4$ electrolytes prepared by solution cast at different temperatures are plotted from Figure 5.114 to Figure 5.116 and from Figure 5.118 to Figure 5.120 respectively. The impedance plots of the TPU/LiTFSI electrolytes prepared by solution cast are shown from Figure 5.122 to Figure 5.124 and from Figure 5.126 to Figure 5.128 respectively. Their ionic conductivity temperature relationships of these
electrolytes are shown in Figure 5.117, Figure 5.121, Figure 5.125 and Figure 5.129. The electrolytes prepared by solution cast method shows similar trend as the corresponding ones prepared by the in-situ process with the respect to ionic conductivity/salt concentration relationship, ionic conductivity/ TPU/PEMPS blend composition relationship as well as ionic conductivity temperature dependence. The ionic conductivity of these electrolytes increases as the salt concentration increases as well as the increase of PEMPS concentration. Their ionic conductivity temperature dependence follows the Arrhenius equation with various activation energy values. However, it is found that the ionic conductivity of electrolytes prepared by solution casting shows slightly higher ionic conductivity than ones prepared by the in-situ process, with the comparison of the results listed in Table 5.9 with the results listed in Table 5.12. The significant difference of these two preparation methods is whether small molecular solvent is used to dissociate the salts and pull cation and anion apart. Although lithium salts can be dissociated by PTMPG in the in-situ process, the presence of the small molecular solvent can help to generate more free lithium ion, which leads to higher ionic conductivity.
Figure 5.114  Impedance plot of TPU/LiClO₄ electrolytes prepared by solution cast with [O:Li]=32:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C

Figure 5.115  Impedance plot of TPU/LiClO₄ electrolytes prepared by the solution casting with [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 160°C
Figure 5.116  Impedance plot of TPU/LiClO$_4$ electrolytes prepared by the solution casting with [O:Li]=8:1 at different temperatures (a) from 27$^0$C to 80$^0$C (b) from 100$^0$C to 160$^0$C

Figure 5.117  The effect of temperature on the conductivity of TPU/LiClO$_4$ electrolytes with various salt concentration prepared by the solution casting
Figure 5.118  Impedance plot of TPU/PEMPS/LiClO₄ electrolytes prepared by the solution casting with TPU/PEMPS=100/10 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 160°C

Figure 5.119  Impedance plot of TPU/PEMPS/LiClO₄ electrolytes prepared by the solution casting with TPU/PEMPS=100/20 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 120°C (c) from 140°C to 160°C
Figure 5.120 Impedance plot of TPU/PEMPS/LiClO₄ electrolytes prepared by the solution casting with TPU/PEMPS=100/40 and [O:Li]=16:1 at different temperatures (a) from 27°C to 40°C (b) from 80°C to 100°C (c) from 120°C to 160°C
Figure 5.121 The effect of temperature on the conductivity of TPU/PEMPS/LiClO$_4$ electrolytes prepared by the solution casting with various blend compositions at [O:Li]=16:1

![Graph](a)

![Graph](b)

Figure 5.122 Impedance plot of TPU/LiTFSI electrolytes prepared by the solution casting with [O:Li]=32:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C

![Graph](a)

![Graph](b)

Figure 5.123 Impedance plot of TPU/LiTFSI electrolytes prepared by the solution casting with [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C
Figure 5.124 Impedance plot of TPU/LiTFSI electrolytes prepared by the solution casting with [O:Li]=8:1 at different temperature (a) from 27°C to 80°C (b) from 100°C to 180°C

Figure 5.125 The effect of temperature on the conductivity of TPU/LiTFSI electrolytes with various salt concentrations prepared by the solution casting
Figure 5.126  Impedance plot of TPU/PEMPS/LiTFSI electrolytes prepared by the solution casting with TPU/PEMPS=100/10 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C

Figure 5.127  Impedance plot of TPU/PEMPS/LiTFSI electrolytes prepared by the solution casting with TPU/PEMPS=100/20 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C
Figure 5.128  Impedance plot of TPU/PEMPS/LiTFSI electrolytes prepared by the solution casting with TPU/PEMPS=100/40 and [O:Li]=16:1 at different temperatures (a) from 27°C to 80°C (b) from 100°C to 180°C

Figure 5.129  The effect of temperature on the conductivity of TPU/PEMPS/LiTFSI electrolytes with various blend compositions at [O:Li]=16:1
Table 5.11  The ionic conductivity at room temperature $\sigma$ and activation energies $E_a$ of TPU electrolytes with different types of salt prepared by the solution casting

<table>
<thead>
<tr>
<th>Materials</th>
<th>[O : Li]</th>
<th>Conductivity at 300K (S/cm)</th>
<th>$E_a$ (eV)</th>
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<tr>
<td>TPU/LiClO$_4$</td>
<td></td>
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<tr>
<td>32</td>
<td>1.47x10$^{-9}$</td>
<td>0.019</td>
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<tr>
<td>16</td>
<td>1.60x10$^{-8}$</td>
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<td>8</td>
<td>1.60x10$^{-7}$</td>
<td>0.030</td>
<td></td>
</tr>
<tr>
<td>TPU/ LITFSI</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>3.35x10$^{-6}$</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>8.34x10$^{-6}$</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>3.49x10$^{-5}$</td>
<td>0.017</td>
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</table>

Table 5.12  The ionic conductivity at room temperature $\sigma$ and activation energies $E_a$ of TPU/PEMPS electrolytes with different types of salt and various blend compositions at [O:Li]=16:1 prepared by the solution casting

<table>
<thead>
<tr>
<th>Materials</th>
<th>TPU/PEMPS</th>
<th>Conductivity at 300K (S/cm)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU/PEMPS/LiClO$_4$</td>
<td></td>
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</tr>
<tr>
<td>100/10</td>
<td>5.57x10$^{-7}$</td>
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<tr>
<td>100/20</td>
<td>1.62x10$^{-6}$</td>
<td>0.026</td>
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<tr>
<td>100/40</td>
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<tr>
<td>TPU/ PEMPS/LITFSI</td>
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<tr>
<td>100/10</td>
<td>8.97x10$^{-6}$</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>100/20</td>
<td>1.33x10$^{-5}$</td>
<td>0.014</td>
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</tr>
<tr>
<td>100/40</td>
<td>1.03x10$^{-5}$</td>
<td>0.016</td>
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5.7 Ionic Conduction Mechanisms of TPU Electrolytes and TPU/PEMPS Electrolytes

In this research, the TPU electrolytes and TPU/PEMPS electrolytes were prepared by a solvent-free reactive process, where lithium salt was dissolved in low molecular weight monomer of TPU (PTMG melt) or liquid PEMPS first and then other components like isocyanate and chain extender were added for initiating polymerization. In the solution cast method, the salt was dissociated in a polar solvent such as methanol. The dissociation of lithium salt in the reactive process, i.e. separation of cation and anions from salt crystal lattice, is achieved by the interaction between the $\text{Li}^+$ and the ether oxygen or hydroxyl oxygen site on PTMG melt. Since the ions are the charge carriers in polymer electrolytes, the salt dissociation in polymer without using small molecular polar solvent plays an important role in the ionic conductivity of polymer electrolytes. Besides the solvent, the salt dissociation in PTMG or PEMPS is also dependent on the structure of the salt. Three different lithium salts were used in this study. It was found that the structure of the anion is also related to its ability to be dissociated from cations in the crystal lattice.

TPU is a block polymer composed of soft segments and hard segments. The polyether-based soft segments can complex with salts and subsequently exhibit ionic conductivity. The hydrogen bonding of the hard segments forms a hard domain dispersed among the soft domains. The hard domains form a network structure, which provides good dimensional stability for TPU/PEMPS electrolytes. The phase morphology such as phase mixing induced by the interaction of the salt with both soft and hard segments, has an effect on the ionic conductivity.
In TPU/PEMPS electrolytes, the PEMPS was blended with TPU to improve ionic conductivity. The role of PEMPS for ionic conductivity involves the following aspects: (1) the PEMPS electrolyte has high ionic conductivity, but itself cannot form a solid film; and (2) it can decrease the crystallinity and enhance the flexibility of the soft segments of polyurethane electrolyte. As a result, the ionic conductivity of these blends can be improved. The good dimensional stability of TPU/PEMPS electrolytes originates from their network formation generated by cross-linked hard segments of polyurethane and their physically interlocked co-continuous phase morphology. The phase morphology of TPU/PEMPS electrolytes also has a significant effect on the ionic conductivity.

PTMG/salt mixture, PEMPS/salt mixture and PTMG/PEMPS/salt mixture were characterized by the DSC, FTIR, and optical microscopy to determine the salt dissolution in PTMG and PEMPS as well as salt/polymer interactions. TPU electrolytes and TPU/PEMPS electrolytes with various compositions were characterized by TGA, DSC, FTIR, optical microscopy, SEM, AFM and impedance measurements to determine the salt/polymer interaction, the chain flexibility and crystallinity of electrolytes, the phase morphology and their relationship with the ionic conductivity of polymer electrolytes. Based on these results, the ionic conductivity mechanism of these electrolytes is proposed.

Optical microscopy studies of PTMG/salt mixture and PEMPS/salt mixture showed that LiClO₄ and LiTFSI can be completely dissolved in PTMG or PEMPS by the direct melt mixing process in the salt concentration range used in this study. The salt was added to the PTMG and PEMPS at a temperature above the melting point of PTMG.
However, a large portion of undissolved LiCl crystal was observed in both PTMG/LiCl mixture and PEMPS/LiCl mixture prepared by melt mixing. A similar result was also obtained in the samples prepared by the solution casting. The undissolved LiCl crystal in PTMG or PEMPS mixtures was also identified in the DSC study. It was noticed that an endothermic peak of LiCl crystal around 102°C remains in the DSC thermograms of LiCl/PTMG mixtures. The difference in the solubility of lithium salts in PTMG or PEMPS is related to the structure of the anion. The small Cl⁻ interacts strongly with Li⁺, which results in the high lattice energy of LiCl. In the melt mixing process, the interaction of the ether oxygen with Li⁺ is not sufficient enough to overcome such high lattice energy, which leads to the poor dissolution of LiCl. In the solution casting process, although LiCl is dissociated from crystal lattice to form free ions via the methanol, the dissociated free ions tend to form salt crystals again after the removal of methanol.

The FTIR results revealed that the intensity of the ether group absorption peak at 1110cm⁻¹ decreased as the salt concentration increased, and the –OH peak around 3300cm⁻¹ became much broader and shifted to lower frequency. This indicates that Li⁺ can interact with both the ether oxygen and hydroxyl oxygen sites on PTMG. The schematic representation of the interaction of Li⁺ with oxygen atom on these two active sites is illustrated in Figure 5.130.

Both PTMG and PEMPS have very flexible chains with T_g's at -66°C and -78°C respectively. Their T_g's decreased with the addition of LiCl and increased with the addition of LiClO₄ and LiTFSI. The T_g increase is a further evidence of the interaction of Li⁺ and PTMG or PEMPS. The Li⁺ acts as a binder to connect the ether groups from the
different polymer chains as shown in Figure 5.131(a) or form an intra-chain structure as shown in Figure 5.131(b). The network structure formed via the bonding between Li$^+$ and ether oxygen limits the flexibility of the ether chain and raises the glass transition temperature. The depression of $T_g$ in PTMG/LiCl is caused by the plasticizer effect of the undissolved LiCl crystal. This indicates the poor LiCl dissociation in PTMG and the weak interaction between LiCl with ether oxygen. The degree of the crystallinity of PTMG was found to be depressed by the addition of lithium salts. This is believed to be related to the formation of the structures shown in Figure 5.131. The cross-linking restricts the folding of the polymer chain to form a well ordered crystal structure and generates more amorphous or less ordered polymer structures. The PTMG becomes the soft segment of TPU after polymerization, which contributes most of the ionic conductivity. Thus, the salt solvation in PTMG can significantly influence the ionic conductivity of the TPU electrolytes. The ionic conductivity data of TPU electrolytes showed that among electrolytes with three different lithium salts the one with LiTFSI had the highest ionic conductivity, the one with LiClO$_4$ was next, and the one with LiCl showed the lowest value. This order agrees well with the decreasing order of the salt dissolution ability in PTMG and the order of the interaction of lithium salts with PTMG as well as the order of the anion size. This means lithium salts with larger sized anions can be easily dissociated in PTMG and have strong interactions with PTMG, resulting in the high ionic conductivity. It was found that the ionic conductivity increased with the
Figure 5.130 Schematic representation of the interaction between Li\(^+\) and oxygen at different site of PTMG: (a) ether group (b) hydroxyl group

Figure 5.131 Schematic representation of the network structure formed via (a) the interaction of Li\(^+\) with ether oxygen atoms from same polymer chain and (b) the interaction of Li\(^+\) with the different ether oxygen atoms from different polymer chains
salt concentration in all TPU electrolytes. This is because more salt leads to more charge carriers in the polymer electrolytes, which results in higher ionic conductivity. In the case of TPU electrolytes with LiCl, it has already been noticed that there was undissolved LiCl existing in the PTMG/LiCl mixture at [O:Li]=16:1, which indicates that LiCl is saturated in PTMG and the number of charge carrier reaches its maximum in this case. However, the ionic conductivity of TPU/LiCl electrolytes at [O:Li]=8:1 is greater than the corresponding one at [O:Li]=16:1. This seems to imply that the addition of the undissociated salt can also increase the ionic conductivity. One possible explanation is that the hard segments can interact with LiCl and help dissociate more LiCl.

In the in-situ reactive process investigated in this study, MDI and BDO added into PTMG/salt mixture or PTMG/PEMPS/salt mixture formed the hard segments of TPU after the polymerization. The FTIR study showed that Li+ not only interacted with ether oxygen; but also interacted with the carbonyl oxygen in the hard segments of TPU. The intensity of the ether group absorption peak at 1110cm\(^{-1}\) decreased with the addition of the salts, which agreed well with the FTIR results of PTMG/salt mixture. Also this peak became much boarder and flater due to the overlapping of peaks of the Li+ bonded ether, free-bonded ether and hydrogen-bonded ether. The peak around 3320cm\(^{-1}\) shifted to high frequency, which indicates more free N-H group. The peak at 1700cm\(^{-1}\) of the bonded carbonyl became broader with a multi-splitting due to its association with LiFTSI.

The DSC thermograms of TPU electrolytes showed that the \(T_g\) of the soft segment increased and the melting temperature as well as the degree of the crystallinity decreased as the salt concentration increased. The endothermic transition shift of the hard
segment was less obvious as more salt was added. At high salt concentrations, the endothermic transition of the dissociation of hydrogen bonding between hard/hard segment was barely detected. This indicates the phase mixing of soft segments and hard segments of TPU induced by salts. The phase mixing was also observed in the studies of optical microscopy and AFM. After the addition of salt, the phase separation of the hard segment and soft segment decreased and resulted in less roughness in the optical micrographs. In the AFM topographic images of TPU/LiTFSI electrolytes, the bright phase of the hard segments almost disappeared into the dark background of the soft segment matrix at [O:Li] =16:1. Based on these results, the schematic representation of the interaction of salt with both the soft segment and the hard segment of TPU as shown in Figure 5.132 is proposed.

Figure 5.132  Schematic representation of the interaction of lithium ions with the soft segments and the hard segments in TPU
PEMPS was added into TPU to increase its ionic conductivity. Morphological studies revealed that PEMPS/TPU blend formed multi-phase structure and the addition of lithium salts enhanced the compatibility of TPU with PEMPS. Due to the high content of soft segments in TPU, the two-phase morphology generated from the phase separation of soft segments and hard segments in TPU was not clearly identified by SEM. Neat TPU showed a homogenous morphology in SEM micrographs. However, SEM micrographs of PEMPS/TPU blends without salts exhibited phase separation structures with clear boundaries due to their poor adhesion and incompatibility. The extracted PEMPS/TPU blend with PEMPS/TPU=100/40 showed porous structures. This indicates that PEMPS phase and TPU phase formed the co-continuous structure. However, after the addition of lithium salt, the morphology of TPU/PEMPS electrolytes became less rough and the compatibility of TPU and PEMPS was improved. The compatibilizer effect of the lithium salts on PEMPS and TPU phase are dependent on the structure of the salts. LiTFSI showed the best compatibilizer effect, LiClO₄ second and LiCl last. This order follows the order of the interaction strength between lithium salt and polymer. The stronger the interaction of lithium salt with polymer, the better compatibilizer effect.

Although the surface of TPU/PEMPS electrolyte films was smooth and uniform in SEM micrographs, the separated PEMPS phases could clearly be identified by AFM with the tapping mode and PEMPS was found to form a droplet domain around 1-5 µm in TPU matrix. The two-phase separation morphology of TPU/PEMPS electrolytes with PEMPS phase forming droplets in the TPU matrix or with PEMPS and TPU forming co-continuous structure are illustrated in Figure 5.136 (a) and Figure 5.136 (b), respectively.
Figure 5.133  Schematic representation of (a) the morphology of TPU/PEMPS electrolyte with PEMPS Phase dispersed in TPU matrix and (b) the morphology of TPU/PEMPS electrolyte with PEMPS and TPU forming a co-continuous structure.
DSC results of TPU/PEMPS electrolytes showed that both the degree of crystallinity and melting temperature of soft segments of TPU decreased with adding PEMPS in TPU/PEMPS electrolytes. Interestingly, the endothermic peak associated with the dissociation of hydrogen bonding between the hard/hard segments was more obvious as the PEMPS concentration increased. This indicates that the addition of PEMPS induces the formation of hard/hard segment interaction. The intensity change and shifting of the carbonyl group in the FTIR of TPU/PEMPS electrolytes showed that more hard segment bonded carbonyl groups and less Li$^+$ bonded carbonyl groups were present after the addition of PEMPS. It indicates that there is interaction competing between Li$^+$ /PEMPS and Li$^+$/hard segment. The PEMPS interacts more strongly with Li$^+$ than the hard segments of TPU. Thus, instead of soft /hard phase mixing, more soft phase/PEMPS phase mixing is produced. The compatibilization of PEMPS and TPU can be explained by the interaction of soft segment of TPU with PEMPS via Li$^+$ as shown in Figure 5.132 (a). The interaction of hard segments of TPU with PEMPS via Li$^+$ as shown in Figure 5.132 (b) is relatively rare due to the less interaction between Li$^+$ and the hard segments of TPU.

Based on the experimental studies, it can be concluded that the TPU/PEMPS electrolytes can form semi-interpenetrating network structure (semi-IPN). The structure consists of the network formed by physically cross-linking of the hard segments of TPU with PEMPS trapped inside it. The formation of IPNs originates from the superposition of two processes: the chemical process of polymerization or cross-linking and a physical process of the phase separation. The morphology of the IPN structure depends on the
Figure 5.134  Schematic representation of (a) the interaction of lithium ions with soft segments of TPU and PEMPS (b) the interaction of lithium ions with hard segments of TPU and PEMPS
competitive phenomenon between the phase separation process of polyurethane and PEMPs controlled by diffusion phenomena and the solidification process of polymerization which impedes the diffusion. If the polymerization occurs very fast, the high viscosity of TPU matrix is induced, thereby retarding the phase separation due to the diffusion impedance.

The morphology studies of PTMG/PEMPS blend with and without lithium salt suggest that the mixture of PEMPS and polyurethane monomers, PTMG, form a multi-phase with very fine dispersion in the presence of salts. The morphology studies of TPU/PEMPS blend, TPU/PEMPS electrolytes with different lithium salts also showed phase separation and the compatibilization effects of the salts via the interaction of Li$^+$ with both phases. Actually, the morphology of PU/PEMPS electrolytes is complex due to the multi-phase morphology of the neat TPU itself and the ions/polymer interaction generated by the addition of salts. The TPU/PEMPS electrolytes form a multi-phase morphology with various separated phases including a pure PEMPS/salt phase, PEMPS/salt/soft segment mixture phase, soft segment/salt crystal phase, PEMPS/salt/hard segment phase, et al., depending on their blend composition. Based on the morphological studies, FTIR, DSC results of a series TPU and TPU/PEMPS electrolytes, the schematic representation of the multi-phase morphology of TPU/PEMPS blend and electrolytes is illustrated in Figure 5.135. In Figure 5.135 (a), there are no lithium salts and most of PEMPS phase are separated from the TPU phase. After the addition of salts, the compatibilization effect of salts on different phases appears and
Figure 5.135  Schematic presentation of multi-phase morphology of TPU/PEMPS electrolytes (a) without salt and (b) with salt

(a)  PU/PEMPS blend without salt

(b)  PU/PEMPS electrolyte with salt

331
results in inducing more phase mixing between PEMPS and the soft segments of TPU due to the interaction as shown in Figure 5.135 (b).

Finally, the relationship between the multiphase morphology of TPU/PEMPS electrolytes and their ionic conductivity is discussed as follows. The ionic conductivity data of TPU/PEMPS electrolytes with LiClO₄ and LiTFSI showed that the ionic conductivity increased as the concentration of PEMPS increased in the range of the studied blend composition. From the FTIR and DSC results, it can be concluded that the improvement of the ionic conductivity with the addition of PEMPS originates from the following contributions: (1) PEMPS depresses the crystallinity of soft segments and generates more amorphous soft segment phase; (2) stronger Li⁺ interaction with the PEMPS than with the hard segments of TPU reduces the soft segment/hard segment phase mixing and increases the conductivity of soft segments; (3) the interaction of soft segment of TPU with PEMPS via the compatibilizer effect of Li⁺ improves compabilization of TPU and PEMPS and results in good interfacial adhesion. Therefore the Li⁺ can transfer from one phase to the other phase easily instead of going around the interface boundary; (4) PEMPS phase itself provides high ionic conductivity, but PEMPS cannot form a solid film without the support from the TPU matrix.

As for the relationship of the interface between PEMPS and TPU with ionic conductivity, the possible pathways for different morphology are proposed in this research as shown in Figure 5.136. In the morphology with PEMPS forming droplet dispersed in the TPU matrix as illustrated in Figure 5.133(a), there are two possible pathways. When the interaction of PEMPS of soft segment of TPU is poor, gaps along
the sharp boundary will be generated between two phases. This gap prevents Li\(^+\) moving from one phase to the other phase and makes Li\(^+\) tend to move around the boundary instead of going into the other phase, which leads to the tortuous pathway (path B) as illustrated in Figure 5.136 (a). The tortuous movement of Li\(^+\) increases the effective length of the pathway. However, good interfacial adhesion enables Li\(^+\) to move easily from one phase to the other phase, which is illustrated as the path A in Figure 5.136(a). The length of path A is much shorter than that of path B. Thus, the addition of PEMPS into TPU could not increase the ionic conductive of TPU electrolytes and, on the contrary, their conductivity decreases due to the much longer effective pathway. However, in the TPU/PEMPS electrolytes studied in this research, it was found that the ionic conductivity of TPU electrolytes increased with adding PEMPS. This implies that path A is dominating in these electrolytes due to their good interfacial adhesion.

In the morphology with PEMPS phase and TPU phase forming a co-continuous structure as illustrated in Figure 5.133(b), three different pathways as illustrated in Figure 5.136 (b) can exist. The Li\(^+\) can transfer only in continuous TPU phase (Path B), only in the continuous PEMPS phase (Path C) or transfer from one phase to the other phase (Path A). If the path B is dominating, the poor interface between PEMPS and TPU can make it hard for Li\(^+\) to go through the dispersed high ionic conductive PEMPS phase.

In TPU/PEMPS/LiCl electrolytes, it was noticed that their ionic conductivity first increased with PEMPS concentration then reached to a plateau at TPU/PEMPS= 100/40. Also the SEM micrographs showed at this blend composition there was a phase
Figure 5.136 Schematic representation of (a) the two possible Li$^+$ transport pathways in the morphology of TPU/PEMPS electrolyte with PEMPS Phase dispersed in TPU matrix and (b) the three possible Li$^+$ transport pathways in the morphology of TPU/PEMPS electrolyte with PEMPS and TPU forming a co-continuous structure.

Legend:
- Green: PEMPS
- White: PU
- Black: Ion or ion cluster
separation with poor interface. The plateau of the ionic conductivity indicates that an overdose of PEMPS and poor LiCl interaction with polymer leads to poor interface, so that more Li\(^+\) takes the longer pathway. Therefore the ionic conductivity is not improved. This phenomenon was not found in either the TPU/PEMPS electrolytes with LiClO\(_4\), or the ones with LiTFSI with respect to their salt solubility and strong Li\(^+\) /polymer interaction.

The ionic conductivity of all the TPU electrolytes or TPU/PEMPS electrolytes increased as the temperature increased. Their temperature dependence of ionic conductivity follows Arrhenius law equation. In Jeung's\(^{55}\) studies of the ionic conductivity of PEO electrolytes, it was found PEO electrolytes followed the Arrhenius law equation with different activation energy in different temperature ranges, which indicated the change of the activation energy is related to the phase transition. Below its melting temperature (60\(^{0}\)C), the high crystallinity of PEO reduces the mobility of charge carrier. Above its melting temperature, the melted PEO electrolyte greatly increases the mobility of charge carrier.

Typically, TPU has several endothermic transitions in the studied range of temperatures, such as the glass transition of the hard segment. Therefore the slope of the plot \(\log \sigma \text{ vs. } 1/T\) of TPU electrolytes is expected to change at the corresponding phase transition temperature. However, there was no slope change of the line in \(\log \sigma \text{ vs. } 1/T\) of TPU or TPU/PEMPS electrolytes observed within the whole temperature range. There are several possible explanations. First, the DSC results of TPU or TPU/PEMPS electrolytes in this research show that these endothermic transitions are not obvious,
Unlike the crystalline melting of PEO. Therefore the flexibility of TPU is not greatly dependent on the transition temperature. The slope change of the plot associated with the glass transition of hard segments is expected to be observed in TPU electrolytes with TPU formulated with high concentration of hard segments. Second, the soft/hard phase mixing caused by the addition of lithium salts will make the transition distributed broader and less visible. Third, the ionic conductivity of TPU is mainly contributed by the soft segments. The phase transition in the hard segments does not influence the mobility of ions associated with the soft segments. Fourthly, the transition temperature of the dissociation of the hydrogen bonding of the hard segments is beyond the range of the ionic conductivity temperature studied in this research.

The electrolytes prepared by the solution casting method showed slightly higher ionic conductivity than the one prepared by the in-situ process for the electrolytes with LiClO$_4$. Because the small molecular polar solvent can dissociate lithium salt better than PTMG. However, for electrolytes with LiTFSI, the difference caused by different preparation methods is nearly negligible. This can be explained by the fact that LiTFSI is easily dissociated in both methanol and PTMG.
CHAPTER VI
CONCLUSIONS

6.1 Conclusion of Studies on TPU/PEMPS Electrolytes

The goal of this research was to develop novel solid polymer electrolytes with high ionic conductivity and good dimensional stability based on TPU/PEMPS blends with three different lithium salts via a solvent-free reactive process. The dissolution of salts in monomer, the miscibility of monomer with TPU, the effect of lithium salts on the kinetics of TPU polymerization, the interaction of salt with polymers, the morphology of TPU and TPU/PEMPS electrolytes, and the ionic conductivity of electrolytes and their temperature dependence were investigated using characterization techniques including DSC, FTIR, optical microscopy, SEM, AFM, and impedance measurement. An ionic conductivity mechanism of TPU/PEMPS electrolytes was proposed based on the anion structure, the salt-polymer interaction, and the multi-phase morphology.

TPU/PEMPS electrolytes were successfully developed by a solvent-free reactive process. This method showed several advantages over the conventional solution cast method. The monomer, PTMG, functions as a common solvent to dissolve lithium salts instead of the highly volatile solvent, methanol. The process included two steps: (a) dissolve lithium salts in PTMG and PEMPS; (b) add MDI and BDO to start polymerization of polyurethane in the presence of PEMPS and lithium salts. The kinetics of polyurethane polymerization was studied by tracing the heat generated during the
reaction with the isothermal DSC measurement. The lithium salts slightly reduced the reaction rate of polyurethane polymerization due to the interaction of Li⁺ with the reactive functional groups, i.e. the hydroxyl groups at both ends of PTMG. The PEMPS also decreased the polymerization reaction rate, which was attributed to the dilution effect caused by PEMPS by reducing the reactive functional group concentration.

The TGA results showed that TPU/PEMPS electrolytes had good thermal stability and that they could withstand temperatures above 200°C. The dissociation temperature of the hydrogen bonded TPU is well above 150°C. Unlike the conventional PEO-based electrolytes, TPU/PEMPS electrolytes have good dimensional stability and form films within the range of operation temperature, -25°C to 120°C, for common applications.

The FTIR studies indicated that the lithium salt solvation in PTMG was related to the interaction of lithium salt with PTMG at two reactive sites: ether oxygen and hydroxyl oxygen. Lithium salt with various anion structures exhibited different solubility in both PTMG and PEMPS. The order of their solubility is LiCl< LiClO₄< LiTFSI. Some undissolved aggregate of LiCl in PTMG was detected by optical microscopy and DSC. The interaction of lithium salts with PTMG and PEMPS was determined by quantifying the intensity decrease and frequency shift of the characteristic absorption peaks of the –C-O-C- group and –OH groups. The DSC results of PTMG/salt mixtures and PEMPS/salt mixtures including T_g elevation, T_m decrease and the depression of crystallinity further confirmed the strong interaction between lithium salt with PTMG and PEMPS. From the difference in intensity change in the FTIR and DSC results corresponding to the different lithium salts, the interaction strength between lithium salts and polymers is in the
following order: LiCl < LiClO₄ < LiTFSI, which agrees well with the order of the size of the anion: Cl⁻ < ClO₄⁻ < TFSI⁻. The explanation is based on the fact that the large polyatomic anion with delocalized charge has weak interaction with small Li⁺, which makes lithium salts with these anions easily dissociated and less competitive with the ether oxygen.

TPU/PEMPS electrolytes were found to have a multi-phase morphology with the PEMPS droplets dispersed in the TPU matrix using optical microscopy, SEM and AFM. Compared with the two-phase morphology of the TPU/PEMPS blend without salt, it seems that TPU/PEMPS electrolytes with salts exhibited a two-phase morphology with the small phase uniformly dispersed in the TPU matrix, and the salts promoted better compatibilization between the different phases. The lithium salt has a compatibilization effect on their morphology, and this effect also varies with the anion structure. Based on morphological studies together with the information obtained from FTIR and DSC results, a schematic morphology of TPU/PEMPS electrolytes with PEMPS trapped in the polyurethane network formed by the physical cross-linking via the hydrogen bonding of the hard segment of TPU was proposed in this research, and their multi-phase domains were illustrated.

The three absorption regions corresponding to the -C-O-C-, -C=O, and -N-H bond in TPU and TPU/PEMPS with various compositions were studied. Similar to the reports from other researchers including Wen et al.⁷ and Jeung,⁵⁵ the salt not only existed in the soft segment, but also presented in the hard segment. The soft/hard domain phase mixing caused by the interaction of Li⁺ with both the soft segment and the hard segment was
found. However, it was noticed after the addition of PEMPS, more hard segment bonded carbonyl groups appear, which indicated that PEMPS helped the formation of hard-hard domain or soft-soft domain instead of the soft-hard domain. This is opposite to the effect of lithium salts on the formation of the soft-hard domain. The possible mechanism of this phenomenon is that compared with the hard segment of TPU, the PEMPS can interact with Li⁺ better, which results in less Li⁺ interactions with the hard segment; therefore, the soft/hard phase mixing is reduced. The reduction of the soft-hard phase mixing was confirmed by the DSC results where the endothermic transition of the associated hard segments appeared more clearly in TPU/PEMPS/LiClO₄ electrolytes as the PEMPS concentration increased, and the Tm and degree of crystallinity of TPU electrolytes decreased with adding PEMPS.

The tensile properties study of TPU/PEMPS electrolytes showed that TPU/PEMPS blends without lithium salts had poor elongation due to the immiscibility of TPU/PEMPS blends. However, the addition of lithium salts into TPU/PEMPS blends improved the elongation significantly due to the effect of the lithium ion on their compatibilization.

The ionic conductivity of TPU electrolytes increased as the salt concentration increased. However, the structure of anions exhibited a significant effect on the ionic conductivity. The ionic conductivity at room temperature of TPU electrolytes at [O:Li]=16:1 are $8.34 \times 10^{-6}$ S/cm, $7.51 \times 10^{-8}$ and below $10^{-9}$ S/cm for LiTFSI, LiClO₄, LiCl respectively. The order of the ionic conductivity in TPU electrolytes is: LiCl<LiClO₄<LiTFSI. The solubility of lithium salts in PTMG and the degree of
interaction of lithium salts with the polymer follow the same order, i.e. they increase with the size of the anion. It was believed that TPU electrolytes with the lithium salt having a large polyatomic counter anion have high ionic conductivity due to the weak cation and anion interaction. The ionic conductivity temperature dependence of TPU electrolytes followed the Arrhenius equation. Although a different phase transition had been observed in the DSC of these electrolytes, no transition region was found in the $\log \sigma$ vs. $1/T$ plot due to the low concentration of hard segments in the formulation of TPU used in this study and the phase mixing.

The addition of PEMPS into TPU increased the ionic conductivity of TPU/PEMPS electrolytes. The ionic conductivity of TPU/LiCl electrolytes increased from below $10^{-9}$ S/cm to $2.25 \times 10^{-7}$ S/cm when TPU/PEMPS = 100/20, which is nearly two orders of magnitude. Based on the experimental data, the contribution of PEMPS to the improvement of TPU electrolytes can be explained by the following: (1) PEMPS depresses the crystallinity of soft segments and leads to a more amorphous soft segment; (2) the interaction between PEMPS and Li$^+$ makes less Li$^+$ ions interact with hard segments of TPU, resulting in less phase mixing of soft segment/hard segment caused by the Li$^+$; (3) the interaction of soft segments of TPU with PEMPS via the binder effect of Li$^+$ increases the phase compabilization of TPU and PEMPS and enhances the good interfacial adhesion, which makes the Li$^+$ transfer from one phase to the other phase more easily instead of circumventing the interface boundary as suggested in the conduction mechanism for polymer blend electrolytes; (4) PEMPS phase itself provides high ionic conductivity.
Two different ion transfer pathways at the interfaces were proposed for TPU/PEMPS electrolytes: (a) the ion directly transfers from TPU phase to the PEMPS phase; (b) the ion goes through a tortuous way around the boundary of TPU and PEMPS. The selection of the pathway depends on the interfacial adhesion between TPU matrix and PEMPS. Due to the interaction of soft segments of TPU with PEMPS via the binder effect of Li\(^+\), the TPU/PEMPS electrolytes exhibit good adhesive interfaces, which favor pathway (a) over pathway (b). Therefore the ionic conductivity is enhanced by the incorporation of PEMPS into TPU matrix.

The ionic conductivity of polymer electrolytes prepared by the conventional solution casting was also studied. By comparing the ionic conductivity of polymer electrolytes prepared by the solution casting method with ones prepared by the in-situ process, it was found that the preparation method had little effect on the ionic conductivity. The difference of the ionic conductivity of the electrolytes with LiClO\(_4\) prepared by these two methods was larger than the one of the electrolytes with LiTFSI. The difference originated from the role methanol played in the salt dissociation. For salts which are difficult to dissociate in polymers, such as LiClO\(_4\), more free ions or small ion clusters can be generated using methanol. However, this difference is negligible for salts which are easily dissociated, such as LiTFSI.

6.2 Recommendations

Studies for improving the ionic conductivity of TPU/PEMPS electrolytes by controlling the morphology, the structure of polyether-modified polysiloxane and the
structure of the salt are recommended. Based on the studies conducted in this dissertation, the co-continuous morphology of TPU/PEMPS electrolytes with lithium salts can provide good ionic conductivity, therefore, the controlled reactive preparation method should be explored. The reactive process of TPU/PEMPS electrolytes to form a multi-layered structure will also be useful. Instead of using crystalline salts, the amorphous salt can be used in TPU/PEMPS electrolytes to increase the salt dissociation in polymers and result in more highly mobile free ions. In this case, the ionic conductivity can be enhanced.
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