The Pennsylvania State University

The Graduate School

Department of Materials Science and Engineering

SYNTHESIS AND CHARACTERIZATION OF POLYSILOXANE-BASED SINGLE-ION CONDUCTORS

A Dissertation in

Materials Science and Engineering

by

Siwei Liang

© 2013 Siwei Liang

Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

May 2013

The dissertation of Siwei Liang was reviewed and approved* by the following:

Ralph H. Colby Professor of Materials Science and Engineering and Chemical Engineering Dissertation Advisor Chair of Committee

James Runt Professor of Polymer Science

Harry R. Allcock Evan PughProfessor of Chemistry

Michael Hickner Assistant Professor of Materials Science and Engineering

Joan M. Redwing Professor of Materials Science and Engineering, Chemical Engineering and Electrical Engineering Chair, Intercollege Graduate Degree Program in Materials Science and Engineering

*Signatures are on file in the Graduate School

ABSTRACT

Polysiloxane-based single-ion conductors containing different side groups and bulky ionic side chains have been discussed in this thesis.

Firstly, three borate monomers: lithium triphenylstyryl borate (B1), a variant with three ethylene oxides between the vinyl and the borate (B2) and a third with perfluorinated phenyl rings (B3) were synthesized and used to prepare polysiloxane ionomers based on cyclic carbonates via hydrosilylation. B1 ion content variations show maximum 25 °C conductivity at 8mol%, reflecting a tradeoff between carrier density and T_g increase. Ethylene oxide spacers (B2) lower T_g, and increase dielectric constant, both raising conductivity. Perfluorinating the four phenyl rings (B3) lowers the ion association energy, as anticipated by *ab initio* estimations. This increases conductivity, a direct result of 3X higher measured carrier density. The ~ 9 kJ/mol activation energy of simultaneously conducting ions is less than half that of ionomers with either sulfonate or bis(trifluoromethanesulfonyl) imide anions, suggesting that ionomers with weak-binding borate anions may provide a pathway to useful single-ion Li⁺ conductors, if their T_g can be lowered.

Then two groups of novel non-volatile plasticizers containing pendant cyclic carbonates and short ethylene oxide chains have been successfully synthesized, as confirmed by ¹H and ²⁹Si NMR spectra. After mixing with polysiloxane-based ionomer, the resulting polymer electrolyte blends show improved conductivity. At room temperature the d. c. conductivity has been improved to between 10⁻⁴ to 10⁻⁵ S/cm. Electrode polarization in dielectric relaxation spectroscopy reveals that part of the

increased conductivity comes from lowering T_g , which raises the mobility of the conducting ions. The number density of simultaneously conducting ions is also boosted by the plasticizers, particularly for those containing more of the strongly solvating oligo-(ethylene oxide).

Polysiloxane phosphonium single-ion conductors with ion contents ranging from 5 to 22 mol% were synthesized via hydrosilylation reaction. The parent Br- anion was exchanged to F- or bis(trifuoromethanesulfonyl)imide (TFSI-). Results of X-ray scattering experiments suggest the absence of ion aggregation in our phosphonium ionomers, which keeps glass transition temperatures (Tg) low. DSC Tg of the phosphonium ionomers are all below -70 °C, suggesting a weak dependence of Tg on both ion content and ion type; while conductivities weakly increase with ion content but exhibit a strong dependence on anion type. The highest conductivity at 30 °C, (2 x 10⁻⁵ S/cm) was obtained for the TFSI anion and is attributed to its relatively delocalized negative charge and its large size, both weakening the interaction between TFSI and phosphonium cation.

The linear viscoelastic (LVE) properties of polysiloxane-based phosphoniumcontaining ionomers with ion contents f = 0 to 0.22 have been studied. The master curves of those ionomers have been constructed with reduced frequency spanning 14 decades. The ionic association has been witnessed as a delayed polymer relaxation with increasing ion content, although there is no ion aggregate peak in X-ray scattering and LVE suggests only limited ionic associations with no ion clusters in our phosphonium ionomers. All observations are consistent with weak interchain ionic interactions determined by bulky weak-binding phosphonium salts. Ionomer LVE can be well fit by the KWW model on short time scales and the sticky Rouse model on long time scales, which proves that the ion association lifetime in our ionomers is shorter than that of polymer chain relaxation, despite the fact that the chains are short.

TABLE OF CONTENTS

List of Figures	viii
List of Tables	xii
Acknowledgements	xiii
Chapter 1 Introduction	1
1.1 Conducting salts in lithium-ion batteries	1
1.1.1 LiPF ₆ and its derivatives	2
1.1.2 Lithium perchlorate, lithium tetrafluoroborate and lithium	
hexafluoroarsenate	4
1.1.3 Lithium imide salts	5
1.1.3.1 Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI)	5
1.1.3.2 Other lithium imide salts	6
1.1.4 Boron-containing conducting lithium salts	7
1.1.4.1 Lithium chelatoborates	8
1.1.4.2 Lithium tetraalkyl or tetraaryl borate	10
1.1.5 Lithium aluminates	11
1.1.6 Imidazole-based lithium salts	12
1.2 Solid polymer electrolyte	12
1.2.1 Single-Ion Conductors	15
1.2.1.1 Carboxylate and sulfonate	16
1.2.1.2 Salts with bulky or steric alcohol groups	16
1.2.1.3 Perfluorinated sulfonates	17
1.2.1.4 Imide or amide salts	17
1.2.1.5 Borate and aluminate salts	18
1.2.1.6 Other salts	19
1.3 Gel Polymer Electrolytes	21
1.3.1 Polymer host and liquid electrolyte in gel polymer electrolytes	21
1.3.2 Conductivity and stability of gel polymer electrolytes	22
References	24
Chapter 2 Synthesis and Lithium Ion Conduction of Polysiloxane Single-Ion Conductors Containing Novel Weak-Binding Borates	29
2.1 Introduction	29
2.2 Results and Discussion.	34
2.2.1 Synthesis and NMR	34
2 2 2 Glass Transition Temperatures	40
2.2.3 Dielectric Constant and Ionic Conductivity	40
2.3 Conclusions and Outlook	
2.4 Experimental Section	46
References	51
Chapter 3 Synthesis and Lithium Ion Conduction of Ionomer blends Containing Polysiloxane-based Single-ion Conductor and Non-Volatile Plasticizers	56

3.1 Introduction	56
3.2 Result and discussion	58
3.2.1 Synthesis	58
3.2.2 Glass transition temperature	62
3.2.3 Ionic conductivities and dielectric properties	64
3.3 Conclusions:	74
3.4 Experimental	75
References	83
Chapter 4 Synthesis and Ion Conduction of Polysiloxane Phosphonium Ionomers	86
4.1 Introduction	86
4.2 Results and Discussion	88
4.2.1 Synthesis and ion exchange.	88
4.2.2 Glass transition temperature and thermal stability	91
4.2.3 Morphology	93
4.2.4 Conductivity	95
4.3 Conclusions	99
4.4 Experimental	100
References	104
5.1 Introduction	107 109
5.2.1 Material	109
5.2.2 LVE Measurements	110
5.3 Theoretical Analysis	111
5.3.1.1Relaxation spectrum	111
5.3.2 Sticky Rouse model	112
5.4 Results and Discussion	115
5.4.1 Linear viscoelastic behavior	115
5.4.1.1 Overview	115
5.4.1.2 T _g effect and glassy modulus	119
5.4.1.3 Rubbery modulus	119
5.4.1.4 Temperature dependence	120
5.4.2 Theoretical analysis	122
5.4.2.1 Fit experimental data with sticky Rouse model	122
5.4.2.2 Glassy dynamics affected by the ionic interaction	125
5.5 Concluding Remarks	128
References	129
Chapter 6 Future work	132
6.1 Single-ion conductors for lithium-ion batteries	132
6.2 The plasticizers composed of carbonate and ethylene oxide units	132
6.3 Phosphonium containing ionomers for fluoride battery and alkaline fuel cell	135
6.4 Block copolymer containing polystyrene and poly(ethylene oxide) blocks	135
References.	137

LIST OF FIGURES

Figure 1-1. Structure of lithium perfluoroalkyl phosphates	4
Figure 1-2 . Structure of lithium perfluoroalkyl phosphates. Structure of lithium perfluoroalkyl phosphates Two possible mechanisms for aluminum corrosion in LiTFSI/Propylene carbonate electrolytes. (a) aluminum oxidizes to form adsorbed Al[N(CF ₃ SO ₂) ₂] ₃ which ultimately desorbs from the suface. (b) the adsorbed Al [N(CF ₃ SO ₂) ₂] ₃ undergose a second oxidation before desorption.	6
Figure 1-3. Structures of novel lithium imide salts	7
Figure 1-4. Structures of lithium cheloatoborates	8
Figure 1-5. Structure of LiBOB crosslinked single-ion conductor.	9
Figure 1-6. Chemical structures of lithium tetraphenylborate and lithium	11
Figure 1-7. Chemical structures of lithium aluminates.	11
Figure 1-8. Chemical structures of imidazole-based lithium salts.	12
Figure 1-9. Comparison of energy densities of different battery systems.	13
Figure 1-10. Schematic illustration of lithium ion transport in polyether media	14
Figure 1-11. Structures of modified PEO copolymers	14
Figure 1-12. Representive Structures of polyphosphazene and polysiloxane electrolytes	15
Figure 1-13. Structures of salts containing bulky alcohol anions.	16
Figure 1-14. Structures of perfluorinated sulfonates	17
Figure 1-15. Structures of amide and imide salts	18
Figure 1-16. Reprenstative structures of borate and aluminate salts	18
Figure 1-17. Structure of sulfonyl dicyanomethide lithium salt.	19
Figure 1-18 . Conductivities of single-ion conductors as a function of T _g	20
Figure 1-19. Conductivity of LiPF ₆ -EC-PC-PAN electrolyte (molar ratio 4:60:20:16) at 25°C.	23
Figure 1-20. Conductivity of LiPF ₆ -EC-DMC-PAN gel polymer electrolytes with/without 6 wt% Al ₂ O ₃ at 75 °C.	23
Figure 2-1. Electronic charge distribution in (a) tetraphenyl borate anion and (b) perfluorinated tetraphenyl borate anion, calculated by Gaussian 03 using the	

B3LYP/6-31+G* basis set. Light green denotes a positive charge, red denotes a negative charge, with brighter red indicating stronger negative charge. The boron in the center of these borate anions is positively charged. The tetraphenyl borate anion has the negative charge distributed on the 24 carbons in the phenyl rings, particularly the ortho carbons (each with roughly -0.5e). The perfluorinated tetraphenyl borate anion has the negative charge distributed on the 20 fluorines (roughly -0.3e each), with strong positive charge on boron (roughly +0.5e), the alpha carbons (roughly +0.7e) and the para carbons (roughly +0.8e). The charge distributions impart strong dipoles to these anions (shown by arrows) of 16 Debye Figure 2-2 Representative ¹H NMR spectra of polysiloxane ionomers with (a) CECA and tetraphenyl borate (B1) as side chains (P-10, n/(n + m) = 0.1), (b) CECA and B2 as side chains (SP-2, n/(n+m) = 0.02), with inset showing the ¹¹B NMR spectrum and (c) CECA and B3 as side chains (FSP-5, n/(n + m) = 0.05), with insets showing ¹¹B Figure 2-3. Temperature dependence of ionic conductivity for siloxane borate ionomers vs. T/T_g (and vs. 1000/T in the inset). The short EO spacer between the borate ion Figure 2-4. Temperature dependence of simultaneously conducting ion concentrations Figure 2-5. Temperature dependence of ionic conductivity for P-10 and its blends with Figure 3-2. Tg of copolymer plasticizers and resulting blends (80 wt% of plasticizer and 20 wt% of 14 mol% ionomer) as a function of CECA molar content in the Figure 3-3. Temperature dependence of ionic conductivity for the 14 mol% borate ionomer and its blends with siloxane copolymer plasticizers that are 80 wt% Figure 3-4. Temperature dependence of conducting ion mobility for the 14 mol% borate ionomer and its blends with siloxane copolymer plasticizers that are 80 wt% Figure 3-5. Temperature dependence of conducting ion concentration for the 14 mol% borate ionomer and its blends with siloxane copolymer plasticizers that are 80 wt% Temperature dependence of ionic conductivity for the 49 mol% borate Figure 3-6. ionomer and its blends with oligomeric plasticizers and a mixture of propylene

carbonate and ethylene carbonate (1:1) that are 80 wt% plasticizer/20 wt% ionomer....69

Figure 3-7. Temperature dependence of ion mobility for the 49 mol% borate ionomer and its blends with oligomeric plasticizers and a 1:1 mixture of propylene carbonate and ethylene carbonate that are 80 wt% plasticizer/20 wt% ionomer70
Figure 3-8. Temperature dependence of conducting ion concentration for the 49 mol% borate ionomer and its blends with oligomeric plasticizers and mixture of propylene carbonate and ethylene carbonate (1:1) that are 80 wt% plasticizer/20 wt% ionomer71
Figure 3-9. Static dielectric constants of copolymer plasticizers, the 14 mol% borate ionomer and its blends with copolymer plasticizers that are 80 wt% plasticizer/20 wt% ionomer as a function of temperature. For the pure ionomer, (black symbols), the data are not reasonable due to the high T _g making it difficult to prepare a good sample.
Figure 3-10. Temperature dependence of static dielectric constants of oligomer plasticizers (filled symbols) and their blends with copolymer plasticizers (open symbols) that are 80 wt% plasticizer/20 wt% of the 49 mol% ionomer
Figure 3-11. Static dielectric constants at 298 K of copolymer plasticizers (open symbols) and their blends (filled symbols) that are 20 wt % of the14 mol% borate ionomer (filled black square) as a function of cyclic carbonate (CECA) content <i>f</i> in the random copolymer
Figure 3-12. ¹ H NMR of 4-((3-(chlorodimethylsilyl)propoxy)methyl)-1,3-dioxolan-2- one. Inset is ²⁹ Si NMR
Figure 3-13. ¹³ C NMR of 4-((3-(chlorodimethylsilyl)propoxy)methyl)-1,3-dioxolan-2- one
Figure 3-14. ¹ H NMR of OP-1. Inset is ²⁹ Si NMR
Figure 3-15. ¹ H NMR of 4-((3-(diethylsilyl)propoxy)methyl)-1,3-dioxolan-2-one. Inset is ²⁹ Si NMR
Figure 3-16. ¹ H NMR of OP-2. Inset is ²⁹ Si NMR
Figure 4-1 . Representative ¹ H NMR spectrum of the phosphonium ionomer with Branion (n / (n + m) = 0.05), with the inset showing the ³¹ P NMR spectrum (top left)89
Figure 4-2. TGA results of phosphonium monomer and ionomer with Br- anion
Figure 4-3. Small angle X-ray scattering of phosphonium ionomers with bromide anions and different ion content
Figure 4-4. Conductivity of phosphonium ionomers with different ion content as a function of temperature: (a) bromide counterion, (b) TFSI counterion, (c) fluoride counterion.

Figure 4-5. Conductivities of phosphonium ionomers with different counterions having $(n / (n + m) = 0.11)$ ion content	.96
Figure 4-6. Conductivities of phosphonium ionomers as a function of the product of $\omega_{\alpha 2}$ and $\Delta \epsilon$.98
Figure 5-1. Master curves of storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, as functions of angular frequency ω for phosphonium ionomers with different ionic contents at reference temperature $T_r = 198$ K. The solid curves represent theoretical fitting combining glassy modulus fitted by KWW model, and rubbery modulus fitted by sticky Rouse model.	.114
Figure 5-2. Shift factor a_T with DSC T_g as the reference temperature for phosphonium ionomers with different ionic contents as indicated, plotted against $T-T_g$. The fact that these curves merge at low temperature indicates fragility is independent of ion content.	.117
Figure 5-3. Master curves of storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, as functions of angular frequency ω for phosphonium ionomers with different ionic contents with DSC T_g as the reference temperature (listed in Table 5-1) with shift factor a_T summarized in Figure 5-2. The inset shows zero-shear viscosity and recoverable compliance, η_0 and J_e , at the DSC T_g , as functions of ionic content <i>f</i>	.118
Figure 5-4. Linear relaxation modulus, $G'(t)$, as functions of time t at reference temperature $T_r = -75^{\circ}$ C. The solid curves represent theoretical fitting combining glassy modulus fitted by KWW model, and rubbery modulus fitted by sticky Rouse model. The symbols represent the same samples as in Figure 1. For the non-ionic polymer (black diamond), the dashed and dotted curves attached to the symbols represent the KWW fit (eq 5) of the glassy modulus and the Rouse model fit (eq 6) of the rubbery modulus, respectively. The inset shows the apparent molecular weight distribution obtained in GPC measurements, which has been incorporated into the Rouse model fit.	.121
Figure 6-1. Conductivities of single-ion conductors as a function of their T _g s	.133
Figure 6-2. Structures of proposed new plasticizers.	.134
Figure 6-3. Structures of proposed new phosphonium salts.	.134
Figure 6-4. SEM image of pure polystyrene- <i>b</i> -poly(ethylene oxide) with molecular weights of polystyrene block 40000 and poly(ethylene oxide) block 54000	.136
Figure 6-5. Structures of proposed new block copolymers. $y/(x+y)$ should be < 0.1	.137

LIST OF TABLES

Table 1-1. Conventional lithium salts for lithium-ion batteries	2
Table 1-2. Polymer hosts in gel polymer electrolytes	21
Table 1-3 Physical properties of some organic solvents commonly used in lithium-ion batteries. Dielectric constant and density were measured at 25 °C.	22
Table 2-1 . Lithium Ion Pair and Positive Triple Ion Energies at 0 K in vacuum (left two columns) and in polar polymers at 300 K (PEO middle two columns; CECA right two columns).	31
Table 2-2. Synthesis and Physical Properties of Polysiloxane Single-ion Conductors	39
Table 3-1. Compositions and glass transition temperatures of copolymer plasticizers and the resulting polymer single-ion conductor/plasticizer blends	61
Table 3-2 . Compositions and glass transition temperatures of oligomer plasticizers and the resulting polymer single-ion conductor/plasticizer blends	63
Table 3-3. Ion activation energy of 14 mol% borate ionomer and its blends with siloxane copolymer plasticizers that are 80 wt% plasticizer/20 wt% ionomer.	66
Table 3-4. Viscosity of plasticizers measured at 21 °C.	67
Table 4-1. Physical properties of phosphonium ionomers	90
Table 4-2. Ion properties of different anions with 11 mol% ion content.	97
Table 5-1 . DSC T_g and parameters determined in WLF analysis	113
Table 5-2. Fitting parameters in sticky Rouse model	124

ACKNOWLEDGEMENTS

I have learned a lot from Professor Ralph Colby though. I still feel there are much more I should have learned. Dr. Colby's diligence on research and teaching sets a perfect target for me, which I would try my best through my whole life to reach. I sincerely appreciate that Dr. Colby has saved my dream to be a scientist when I was totally disappointed and maybe desperate in the beginning of my graduate study at Penn State. I feel so lucky having him always standing behind me during the past years. I wish that would be forever.

I would like to thank my committee members Dr. James Runt, Dr. Harry Allcock and Dr. Mike Hickner for their time. I want to specially thank Dr. Runt for his constructive suggestions and always being so kindly to me. Many thanks to Dr. U Hyeok Choi, Lalitha Ganapatibhotla and Mike O'Reilly from UPenn for their help in dielectric, DSC and morphology test. Especially I want to thank Dr. Quan Chen. He appeared in this lab magically, when I seriously needed help. I learned many things from him and it's a pleasant experience to collaborate with him.

I also want to acknowledge the useful discussion, interesting conversation and good time I had with Dr. Wenjuan Liu, Dr. Shih-Wa Wang, Dr. Jinguo Zhang, Dr. Jingling Yan, Dr. Min Zhang, Dr. Xuepei Yuan, Dr. Kevin Masser, Lizhu Wang, Yong He, Hanqing Zhao and my group members: Jinghan Wang, Huai Suen Shiau and Shushan Gong.

I still can remember the happy time I had with Greg Hogshead. I want to wish him the best and thank him for his strong belief in my research ability, which is one of the powers driving me forward along this research career path. Thanks to Jason Claude and Phillips Williams for their help in my career. It's so nice to have them as good buddies at PSU.

It's impossible to accomplish all I have right now without the strong, unselfish and endless support from my parents Zhenming, Xiuzhen and my sister Yiwei. I can always find the most important things I need from them.

To my wonderful wife Weihua and my lovely daughter Shirley

Chapter 1

Introduction

Polymer electrolytes including ionomers and polymer/salt mixtures have found many applications in membranes for water purification and fuel cells; packaging material; coatings; adhesive and catalysts for chemical reactions.^{1,2} Recently this class of material has received extensive attention in the lithium-ion battery field due to increasing safety standard for high energy storage devices.³⁻¹²

1.1 Conducting salts in lithium-ion batteries

Different lithium salts and different polymers have been explored as liquid and polymer electrolytes for lithium-ion batteries. The electrolytes used in lithium-ion batteries are expected to have the following properties: ^{13, 14}

- 1) High thermal and chemical stability (inert to solvent, Al current collector, cathode)
- 2) Exhibit high lithium mobility and thus high conductivity in the system
- 3) Be able to form stable solid electrolyte interface (SEI) layer on electrodes
- 4) Low toxicity towards the environment

So far none of the electrolytes have met all the requirements. The research on the conducting salts is challenging and this section is divided into subsections discussing various lithium salts.

1.1.1 LiPF₆ and its derivatives

 $LiPF_6$ is the most successful salt in the industry and has been widely applied in lithium-ion batteries because it is the best overall. The comparison of $LiPF_6$ with other common conducting lithium salts as shown below indicates that $LiPF_6$ is not the best in terms of any single comparison.^{15, 16}

Average ion mobility: $LiBF_4 > LiClO_4 > \underline{LiPF_6} > LiAsF_6 > LiTFSI$

Dissociation constant: $LiBF_4 < LiClO_4 < \underline{LiPF_6} < LiAsF_6 < LiTFSI$

salt	Tm/ °C	T _{decomposition} / °C in solution	Conductivity/ mS/cm ^a	problem
LiBF ₄	293 (d)	>100	4.9	Low conductivity
LiPF ₆	200 (d)	~80	10.7	Hydrolysis
LiAsF ₆	340	>100	11.1	Toxicity
LiClO ₄	236	>100	8.4	Explosive
LiTFSI	236	>360	9	Al corrosion and cost

Table 1-1. Conventional lithium salts for lithium-ion batteries¹³

a. 1M in EC/DMC at 25 °C

 $LiPF_6$ can passivate the Al current collector and form a low-resistance solid electrolyte interface (SEI) layer on the anode. The SEI layer was studied by Eshkenazi et al¹⁷ with XPS and the results suggested that a major component of the SEI is LiF.

Although $LiPF_6$ displays the best combination considering all the requirements, it still has obvious drawbacks. It is unstable and always exists in equilibrium as shown below:

$$\text{LiPF}_{6}(s) \Longrightarrow \text{LiF}(s) + \text{PF}_{5}(g)$$

This equilibrium is moved toward the right in the presence of moisture. Dangerous byproduct HF will be released, which is a big problem for this type of salt.

$$LiPF_6 + H_2O \longrightarrow POF_3 + LiF + 2 HF$$
$$PF_5 + H_2O \longrightarrow POF_3 + 2 HF$$

To improve the stability of LiPF₆, Xu et al.¹⁸ prepared a novel salt LiPF₄(C₂O₄) by the reaction of PF₅ gas with oxalic dilithium salt as shown in Scheme 1-1. The final salt LiPF₄(C₂O₄) they claimed exhibits much higher thermal stability without sacrifice of other properties.



Scheme 1-1. Synthesis route of LiPF₄(C₂O₄).

To overcome vulnerability of the P-F bond to moisture, lithium perfluoroalkyl phosphates (LiFAP) with F groups partially or totally replaced by perfluoroalkyl groups, have been synthesized with structure shown in Figure 1-1:¹⁹⁻²¹



Figure 1-1. Structure of lithium perfluoroalkyl phosphates.

Owing to the electron-withdrawing properties of fluoroalkyl groups, LiFAP inherits almost all the merits of LiPF_6 with improved thermal and moisture stability. If the cost of LiFAP can be lowered in the near future, it is very possible that LiFAP can replace LiPF_6 as the conducting lithium salt in the battery industry.

1.1.2 Lithium perchlorate, lithium tetrafluoroborate and lithium hexafluoroarsenate

These three salts are all common salts which have been studied as alternates to LiPF₆. They each have shortcomings limiting their practical application (Table 1-1).

LiClO₄ is a salt of a strong acid, with good ionic conductivity. It can form a stable SEI layer on graphite anodes without generating toxic HF gas. However the fact that perchlorate is a strong oxidant prevents it from application in lithium-ion battery due to possible explosion.^{22, 23}

LiBF₄ has very high mobility but its ionic conductivity is low compared to other salts (Table 1-1). Therefore although it has low toxicity,²⁴ it is not suitable for wide application in lithium-ion battery. We understand this because BF_4^- anion is small, allowing strong binding to Li⁺.

LiAsF₆ has been very popular in research labs as a promising candidate for lithiumion battery. Its conductivity is slightly higher than that of LiPF₆. It has very good solubility in low dielectric-constant solvents such as diethyl carbonate and dimethyl carbonate. It stays stable at both cathode and anode. The stability of anions has been given as follows: $CF_3SO_3 < ClO_4 < TFSI < BF_4 < PF_6 < AsF_6$.¹⁹ Nevertheless, the reduction products, AsF₃ and As are highly toxic and that's a big concern to the health of customers.²⁵⁻²⁷

1.1.3 Lithium imide salts

1.1.3.1 Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI)

Among lithium imide salts. the most studied one is lithium bis(trifluoromethanesulfonyl) imide (LiTFSI). It was invented by Foropoulos and DesMarteau²⁸ in 1984 and was later commercialized by 3 M. Due to the greatly delocalized negative charge over the imide anion by two trifluoromethanesulfonyl groups, it has the highest dissociation constant. It is found to have high thermal stability (> 360 °C)²⁹ and high oxidation potential 4.3 V vs. Li/Li⁺ in EC/DEC (1:1) solution,³⁰ better than most of common salts except for LiAsF₆. LiTFSI is compatible with many low dielectric constant solvents and polymer systems, and its conductivity is comparable to or better than other common salts.

LiTFSI had been a perfect candidate to replace LiPF_6 in lithium-ion battery industry until it was found that it can corrode the Al current collector.^{31, 32} The possible mechanism of this process has been proposed in Figure 1-2. ³³ Although there have been

some encouraging reports on passivating the Al surface with different methods, the cost of LiTFSI for the lithium-ion battery is still high. As a result, modifying the structure of the TFSI anion has been of great interest.



Figure 1-2. Structure of lithium perfluoroalkyl phosphates. Structure of lithium perfluoroalkyl phosphates Two possible mechanisms for aluminum corrosion in LiTFSI/Propylene carbonate electrolytes.³³ (a) aluminum oxidizes to form adsorbed $Al[N(CF_3SO_2)_2]_3$ which ultimately desorbs from the suface. (b) the adsorbed Al $[N(CF_3SO_2)_2]_3$ undergose a second oxidation before desorption.

1.1.3.2 Other lithium imide salts

Following the interesting structure of TFSI, new lithium imide salts with modified structures have been proposed. For example, phenyl groups and other cyclic structures have been introduced to further delocalize the negative charge.³⁴⁻³⁶ Some of the structures

of the new imide salts are shown in Figure 1-3. They exhibit slightly better thermal stability and electrochemical stability compared to LiTFSI. But no Al corrosion data has been reported for those salts.



Figure 1-3. Structures of novel lithium imide salts.

Han et al³⁷ synthesized a novel conducting salt lithium (fluorosulfonyl) (nonfluorobutanesulfonyl) imide (LiFNFSI). It has better cycle life than $LiPF_6$, particularly at elevated temperature, without indication of Al corrosion, which makes LIFNFSI an attractive candidate for lithium ion batteries.

1.1.4 Boron-containing conducting lithium salts

Boron-containing conducting salts have displayed delocalization of negative charge due to the weak electronegativity of boron. As a result, those lithium borates give high ionic conductivity with a wide electrochemical stability window and good thermal stability.

1.1.4.1 Lithium chelatoborates



Figure 1-4. Structures of lithium cheloatoborates.

Lithium chelatoborates were first synthesized by Barthel et al^{38-42} . They were found to have high thermal stability > 250 °C. A few years later, Lischka et al^{43} . discovered a novel chelatoborate called lithium bis(oxalato) borate (LiBOB), which had caught a great attention immediately due to the following merits:⁴⁴⁻⁴⁸

- 1. Stability toward anode (forming stable SEI layer) and Al current collector
- 2. Excellent thermal stability (>300 °C) and electrochemical stability (4.5 V)
- 3. Similar conductivity compared to LiPF_6 (7.5 mS/cm at 1M in EC/DMC)
- 4. Lower cost than LiPF₆ and more environmentally friendly

The preparation method of LiBOB is simple, as shown in scheme 1-2



Scheme 1-2. Synthesis route of LiBOB.

Sun et al⁴⁹ made single ion conductors using functionized LiBOB as a crosslinker. The free standing single-ion conducting films they made have conductivity as high as 10⁻⁶ S/cm. A synergistic effect has been observed when LiBOB was mixed with other salts. Jow and coworkers⁵⁰⁻⁵² found mixtures of LiBOB with LiPF₆ have much wider temperature range and better cell power performance than either individual salt.



Figure 1-5. Structure of LiBOB crosslinked single-ion conductor.⁴⁹

Nevertheless, the mild solubility of LiBOB in linear carbonate solvent and facile hydrolysis by moisture make scientists never stop pursuing better alternates. Lithium

oxalyl difluoroborate (LiODFB) made by Zhang et al^{53,54} demonstrates greatly improved solubility in linear carbonate and less sensitivity to moisture, due to replacement of two B-O bonds with B-F bonds. Andrew et al⁵⁵. used the phosphinate group to partially replace the oxalate group. The borate salts they made were claimed to have high air and moisture stability with an extra perk — fire retardant property owing to the phosphinate group.

1.1.4.2 Lithium tetraalkyl or tetraaryl borate

Due to the fact that the B-C bond is more hydrolysis resistant than the B-O bond, tetraalkyl and tetraaryl borates have been tested in lithium ion batteries. The DFT calculations conducted in our lab^{56} suggest that with four surrounding phenyl groups, the negative charge of borate anion is greatly delocalized (Figure 1-6). Actually B atoms of all borate anions carry positive charge. Therefore the interaction between tetraphenyl borate anions and lithium cations is much weaker than that of normal salts. As a result, they are expected to generate high conductivity. When perfluoro tetraphenyl groups are used, the negative charge is further delocalized. Kida et al.⁵⁷ tested LiB(C₆F₅)₄ in a secondary lithium battery and found the battery they prepared exhibits better charge-discharge cycle performance, especially at high temperature, compared to the batteries containing conventional lithium salts such as LiPF₆ and LiBF₄.



Figure 1-6. Chemical structures of lithium tetraphenylborate and lithium

perfluorotetraphenylborate.

1.1.5 Lithium aluminates

Lithium aluminate salts were developed by Fujinami and coworkers⁵⁸⁻⁶¹ with representative structure shown below



 R_1 = alkyl such as C(CF₃)₃or electron-withdrawing groups

Figure 1-7. Chemical structures of lithium aluminates.

Al has electronegativity 1.47, smaller than 2.01 of B. Hence the negative charge of aluminate will be more easily delocalized to the adjacent groups. The comparison of charge distribution between aluminates and borates with same structures proves that aluminate can further delocalize the negative charge.⁶⁰ In fact, the partial positive charge on Al is close to unity, much larger than 0.46 of borate. The lithum aluminates show high

conductivity (> 10^{-5} S/cm at room temperature) in solid polymer electrolyte film, while the extreme sensitivity to moisture limits their practical application.

1.1.6 Imidazole-based lithium salts



Figure 1-8. Chemical structures of imidazole-based lithium salts.⁶²⁻⁶⁴

In this type of salt, the negative charge has been delocalized by π electrons on the aromatic ring. Thus ion pairing should be very difficult. Those salts show good conductivity at 1M in EC/DMC solution (> 6 mS/cm, 20 °C).⁶⁴ They don't corrode the Al current collector in solution. But power capability of cells with imidazole-based lithium salts is worse than that of LiPF₆ cells. A higher capacity loss was found with lithium imidazole salts in lithium-ion batteries, which suggested that more energy was consumed in building up the SEI layer.¹³

1.2 Solid polymer electrolyte

Solid polymer electrolytes, which are free of small organic liquid molecules, have been claimed to be superior to the liquid electrolytes owing to the following advantages:³⁻

1. Good mechanical properties and excellent processability

- 2. Improved safety because they are non-volatile
- 3. Possibly able to prevent lithium dendrites from growing
- 4. Super energy density compared to other type of batteries (Figure 1-9), due to the reason that the separator can potentially be very thin.



Figure 1-9. Comparison of energy densities of different battery systems.⁹

The main component of most solid polymer electrolytes is ether-based polymer. Polyethylene oxide/salt mixtures are the first system studied as solid polymer electrolyte in lithium-ion battery.⁶⁶⁻⁶⁹ It is found that ether-based polymers can form crown ether like structures when coordinating with the lithium cation. In this case, PEO has the best structure to solvate and transport lithium ions compared to other ether-based polymers such as PPO and PTMO.⁷⁰ It is proved that lithium ion transportation in solid polymer electrolytes happens mostly in the amorphous region and it is coupled to polymer chain segmental motion (as in Figure 1-10). So the crystallization of high molecular weight

PEO at room temperature greatly impairs the conductivity of solid polymer electrolytes, by concentrating ions in the amorphous phase and thereby raising its T_g .



Figure 1-10. Schematic illustration of lithium ion transport in polyether media⁴.

To overcome the drawback caused by PEO crystallization, different approaches have been adopted to reduce the crystallinity of PEO, for example, incorporation of methylene oxide or propylene oxide into the PEO main chain (Figure 1-12), or using more flexible polymer such as PPO having melting point below -30 °C as the matrix.^{7, 65} These linear copolymers have shown no sign of crystallization as low as -100 °C.



PEO-methylene oxide-PEO

 ~ 0

PEO-b-PPO-b-PEO

Figure 1-11. Structures of modified PEO copolymers.

Another approach is preparing graft or comb-shape copolymers by attaching PEO oligomers to flexible polymer backbones like polyphosphazene⁷¹⁻⁷³ and polysiloxane⁷⁴⁻⁸².



Figure 1-12. Representive Structures of polyphosphazene and polysiloxane electrolytes.

1.2.1 Single-Ion Conductors

There is one specific type of solid polymer electrolytes called single-ion conductors that have all anions covalently bonded to polymers making an ionomer. They are generally accepted to have advantages over polymer/salt mixtures for application in lithium-ion batteries owing to unity transference number and complete elimination of detrimental anion polarization.^{83, 84}

The general structure of single-ion conductors is having soft backbone e.g. polysiloxane⁸⁰⁻⁸² and polyphosphazene⁷² or C-C backbone e.g. polymethacrylate⁸⁵, with PEO either as side chains or blocks along the backbone⁸⁶. Ionic side groups are covalently bonded to the polymer backbone. So far, the PEO structure is indispensable for the purpose of dissociating and transporting ions. Otherwise poor conductivity is always expected for solid single-ion conductors.

Significant effort has been put into finding proper salts which

- 1. can be feasibly attached to the polymer backbone
- 2. possesses high ion dissociation constant
- 3. have good thermal and electrochemical stability

The salts which have been tested can be categorized into the following groups:

1.2.1.1 Carboxylate and sulfonate

Singel-ion conductors carrying common carboxylates⁸⁵ and sulfonates⁸⁶ with various structures have been extensively studied owing to the fact that carboxylates and sulfonates are easy to make. But they can form tight ion pairs with Li+ due to strong ionic interactions, which may lead to insufficient ionic dissociation and thus poor conductivity. Another drawback is low solubility in low dielectric constant (nonpolar) solvents. The state-of-the-art lithium-ion battery requires low polarity solvents to keep the viscosity of the electrolyte low, precluding use of carboxylates and sulfonates in lithium-ion batteries thus far.

1.2.1.2 Salts with bulky or steric alcohol groups⁸

To minimize the interaction between anion and lithium cation, steric effect has been introduced. The structures of this type of salts have been displayed in Figure 1-13.



Figure 1-13. Structures of salts containing bulky alcohol anions.

In fact, for those anions, the steric effect is always more or less combined with electron-delocalized effect. The room temperature conductivities of ionomers containing those lithium salts are in the range of 10^{-7} to 10^{-6} S/cm.

1.2.1.3 Perfluorinated sulfonates⁸²

This type of salt with sulfonate ionic group connected to various perfluorinated groups such as $(CF_2)n$ or $(OCF_2CF_2)m$ are expected to further lower ion association energy between sulfonate anion and lithium cation. It is interesting to find that after replacing H of ethylene oxide group with F, the electrochemical stability has been significantly improved from less than 4 V to over 5 V (vs Li/Li⁺). The conductivities at room temperature have been improved to nearly 10^{-5} S/cm.⁸²

$\left\{ CF_{2} \right\}_{n} SO_{3}^{\Theta}$

Figure 1-14. Structures of perfluorinated sulfonates.

1.2.1.4 Imide or amide salts⁸⁷⁻⁹⁰

Inspired by the weak-binding character of TFSI salts, imide-like anions have also been incorporated into polymer backbones. The ionomers containing those imide salts display further improvement in terms of conductivity. It is worth pointing out that the temperature dependence of conductivity is more like Arrhenius instead of VFT behavior for those imide-containg ionomers.



Figure 1-15. Structures of amide and imide salts.

1.2.1.5 Borate^{56,91} and aluminate salts⁵⁹



Figure 1-16. Reprenstative structures of borate and aluminate salts.

Borate and aluminate have also been studied due to the fact that both borate and aluminate salts present srongly charge-delocalized structures and therefore weak anion-cation interactions. The resulting solid polymer electrolytes display room temperature conductivities in a range of 10^{-7} to 10^{-5} S/cm. The value is still lower than expected, which can be attributed to the limited polymer chain segmental motion.

1.2.1.6 Other salts

Salts with other function groups which can generate extensively negative-chargedistribution structures have been proposed, such as lithium sulfonyl dicyanomethide in Figure 1-17⁹².



Figure 1-17. Structure of sulfonyl dicyanomethide lithium salt.

The resulting perfluorinated ionomer with above salt exhibits reasonable conductivity (>10⁻⁴ S/cm with DMSO as plasticizer), excellent electrochemical stability (> 4.5 V) and long cycle and storage life, which suggests a new direction for next generation of polymer electrolyte in lithium-ion batteries.

The relationship between T_g and conductivities of some single-ion conductors is summarized in Figure 1-18. It is obvious that conductivity increases as T_g decreases, that is ion mobility greatly affect the conductivity. When T_g is lower than 220K, the conductivity levels off. This may suggest that the T_g effect on conductivities of ionomers has reached its limit at ~220 K.



Figure 1-18. Conductivities of single-ion conductors as a function of T_g.

The aforementioned solid polymer electrolytes are still suffering from overall lower room temperature conductivities (normally 10⁻⁶ to 10⁻⁵ S/cm) than those of liquid electrolytes. PEO has been found to be miscible with LiI, LiCl, LiSCN, LiClO₄, LiCF₃SO₃, LiBF₄, and LiTFSI.^{5, 65} A PEO-containing copolymer with polymer favorable salt LiTFSI can show conductivity close to 10⁻⁴ S/cm, which is still below the standard for practical application⁶⁵. The stability of the ether bond is another concern. It is reported that the oxidative decomposition potential of the ether group is well below 4 V.¹³ In addition, when assembled in a battery cell, the interfacial impedance arising from

imperfect interfacial contact between the electrodes and polymer electrolytes really has been a serious problem.

1.3 Gel Polymer Electrolytes

Poly(ethylene oxide)

Poly(acrylonitrile)

Poly(vinyl chloride)

^a Amorphous.

Poly(propylene oxide)

Poly(methyl methacrylate)

Poly(vinylidene fluoride)

Poly(vinylidene fluoride-hexafluoropropylene)

1.3.1 Polymer host and liquid electrolyte in gel polymer electrolytes

Gel polymer electrolytes (GPEs) were first proposed by Feuillade and Perche¹⁰² and have been reviewed¹⁰³⁻¹⁰⁷. GPEs carry both characters of solid and liquid. In GPE, liquid electrolytes are trapped in the polymer matrix to alleviate leakage. Some general polymer hosts are displayed in Table 1-2. Other polymer hosts such as poly(ethylene imine)¹⁰⁸ and poly (methoxy-co-ethoxy ethylmethacrylate) PMEEMA¹⁰⁹ have also been explored.

Polymer hosts generally studied					
Polymer host	Repeat unit	Glass transition			
		temperature, T_g (°C)			

-(CH2CH2O),-

-(CH2-CHCI),-

-(CH2-CF2),-

-(CH2-CH)

-(CH(-CH3)CH2O),-

-(CH2C(-CH3)(-COOCH3)),

-(CH2-CH(-CN))n-

				105
Table 1-2.	Polymer	hosts in	gel polyn	her electrolytes ¹⁰³

GPEs have been applied in lithium-ion batteries by many companies, such as Sony,
Sanyo and Bellcore ¹³ . As disclosed by Bellcore, the technology used in its GPE cell is
fluorinated polymer swollen by liquid electrolyte. Some physical properties of liquid
electrolytes used in GPEs are listed in Table 1-3. Besides those small-molecule

Melting point,

Tm (°C)

65

_a

317

-

171

135

-64

-60

125

105

85

-40

-90

carbonates, oligomer PEG¹¹⁰⁻¹¹⁶ and other oligomers containing both ethylene oxide group and carbonate group¹¹⁷ have been tested in GPE. This will be discussed in Chapter3.

Table 1-3. Physical properties of some organic solvents commonly used in lithium-ion batteries.¹⁰⁵ Dielectric constant and density were measured at 25 °C.

-	Melting point, MP(°C)	Boiling point, BP (°C)	Density, $g (cm^{-3})$	Dielectric constant, ɛ	Molecular weight	Solubility parameter (J cm ⁻³) ^{1/2}
Dimethyl carbonate (DMC)	2.4	90	1.06	3.12	90.08	20.3
Diethyl carbonate (DEC)	- 43.0	126	0.9752	2.82	118.13	18.0
y-Butyrolactone (BL)	-43.3	204	1.1284	39.0	86.09	25.8
Propylene carbonate (PC)	-48.8	242	1.2047	66.14	102.09	27.2
Ethylene carbonate (EC)	36.4	248	1.3214	89.78	88.06	30.1

1.3.2 Conductivity and stability of gel polymer electrolytes

The conductivities of GPEs are very close to these of liquid electrolytes, within a range of 10^{-3} to 10^{-2} S/cm. Appetecchi et al^{118, 119} prepared GPE with LiPF₆ and a PAN matrix. At room temperature, the conductivity was stable at around 6 x 10^{-3} S/cm over 40 days as demonstrated in Figure 1-19.

Inorganic particles are found to be valuable in terms of improving mechanical and thermal properties and the conductivity of GPEs. It is believed that inorganic particles can suppress the phase boundary and crystallinity of composite, and stabilize the electrode/liquid electrotype interface. Scrosati compared GPEs with and without $Al_2O_3^{120}$. The GPE composites with Al_2O_3 exhibited stable high conductivity at 75 °C, see Figure 1-20.


Figure 1-19. Conductivity of LiPF₆-EC-PC-PAN electrolyte (molar ratio 4:60:20:16) at 25°C¹¹⁸.



Figure 1-20. Conductivity of LiPF₆-EC-DMC-PAN gel polymer electrolytes with/without 6 wt% Al_2O_3 at 75 °C.¹²⁰

References:

- 1. Eisenberg, A.; Kim, J.-S., Introduction to Ionomers. Wiley: New York, 1998.
- 2. Elabd, Y. A. and Hickner, M. A. Macromolecules 2011, 44, 1.
- 3. Armand, M. B. Ch1 in *Polymer Electrolyte Reviews I* edited by MacCallum, J.R. and Vincent, C. A. Elsevier Applied Science, London and New York **1987**.
- 4. Ratner, M. A.; Shriver, D. F. Chem. Rev. 1988, 88, 109.
- 5. Gray, F. M. *Solid Polymer Electrolytes*, Fundamentals and Technological Applications, VCH, New York, **1991**.
- 6. Armand, M. B. Annu. Rev. Mater. Sci., 1986, 4, 245.
- 7. Bruce, P. G. and C. A. Vincent J. Chem. Soc. Faraday Trans., 1993, 89(17), 3187.
- 8. Scrosati, B.; Croce, F.; Panero, S. Journal of Power Sources 2001, 100, 93.
- 9. Agrawal, R.C. and Pandey, G. P. J. Phys. D: Appl. Phys. 2008, 41, 223001.
- 10. Chandrasekhar, U. Adv. Polym. Sci. 1998, 15, 140.
- 11. Armand, M.; Tarascon, J. P. Nature 2008. 451, 652.
- 12. Armand, M. B.; Bruce, P. G.; Forscyth, M.; Scrosati, B.; Wieczorek, W. Ch. 1 in *Energy Materials* edited by D. W. Bruce, D. O'Hare and R. I. Walton, Wiley **2011**.
- 13. Xu, K. Chem. Rev. 2004, 104, 4303.
- 14. Aravindan, V.; Gnanaraj, J; Madhavi, S.; and Liu, H.-K. Chem. Eur. J. 2011, 17, 14326.
- 15. Ue, M. J. Electrochem. Soc. 1995, 142, 2577.
- 16. Ue, M. J. Electrochem. Soc. 1994, 141, 3336.
- Eshkenazi, V.; Peled, E.; Burstein, L.; Golodnitsky, D. Solid State Ionics 2004, 170, 83.
- 18. Xu, M.; Xiao, A; Yang, L. and Lucht, B. L. ECS Transactions 2009, 16, 3.
- 19. Gnanaraj, J. S.; Levi, M. D.; Gofer, Y.; Aurbach, D.; Schmidt, M. J. Electrochem. Soc. 2003, 150, A445.
- Schmidt, M.; Heifer U.; Kuehner, A.; Oesten, R.; Jungnitz, M.; Ignat'ev, N.; Sartori, P. J. Power Sources 2001, 97/98, 557.
- Gnanaraj, J. S.; Zinigrad, E.; Levi, M. D.; Aurbach, D.; Schmidt, M. J. Power Sources 2003, 119/121, 799.
- 22. Newman, G. H.; Francis, R. W.; Gaines, L. H.; Rao, B. M. J. Electrochem. Soc. 1980, 127, 2025.
- 23. Jasinski, R.; Carroll, S. J. Electrochem. Soc. 1970, 117, 218.
- 24. Takata, K.; Morita, M.; Matsuda, Y. J. Electrochem. Soc. 1985, 132, 126.
- 25. Koch, V. R. J. Electrochem. Soc. 1979, 126, 181.
- 26. Webber, A. J. Electrochem, Soc. 1991, 138, 2586.
- 27. Ue, M.; Murakami, A.; Nakamura, S. J. Electrochem. Soc. 2002, 149, A1572.
- 28. Foropoulos, J.; DesMarteau, D. D. Inorg. Chem. 1984, 23, 3720.

- 29. Dominey, L. A.; Koch, v. R.; Blakley, T. Electrochim. Acta 1992, 37, 1551.
- Aurbach, D.; Markovsky, B.; Levi, M. D.; Levi, E.; Schechter, A.; Moshkovich, M.; Cohen, Y. J. power Sources 1999, 81-82, 95.
- 31. Peter, L. Arai, J. J. Appl. Electrochem. 1999, 29, 1053.
- 32. Krause, L.; Lamanna, W.; Summerfield, J. Engle, M.; Korba, G.; Loch, R.; Atanasoski, R. *J. Power Sources* **1997**, *68*, 320.
- 33. Yang, H.; Kwon, K.; Devine, T. M.; Evans, J. W. J. Electrochem. Soc. 2000, 147, 4399.
- 34. Chakrabari, A.; Filler, R.; Mandal, B. K. Solid State Ionics 2010, 180, 1640.
- 35. Baril, D.; Beranger, S.; Ravet, N. Michot, C. and Armand, M. *Mat. Res. Soc. Symp. Proc.* **2000**, *575*, 123.
- 36. Tamura, T.; Hachida, T.; Yoshida, K.; Tachikawa, N.; Dokko, K.; Watanabe, M. J. Power Sources 2010, 195, 6095.
- 37. Han, H.; Guo, J.; Zhang, D.; Feng, S. Feng, W. Nie, J. Zhou, Z. Electrochem. Commun. 2011, 13, 265.
- 38. Barthel, J.; Wuhr, M.; Buestrich, R.; Gores, H. J. J. Electrochem. Soc. 1995, 142, 2527.
- 39. Barthel, J.; Buestrich, R.; Carl, E.; Gores, H. J. J. Electrochem. Soc. 1996, 143, 3565.
- 40. Barthel, J.; Buestrich, R.; Carl, E.; Gores, H. J. J. Electrochem. Soc. 1996, 143, 3572.
- 41. Barthel, J.; Buestrich, R.; Gores, H. J. Schmidt, M. J. Electrochem. Soc. 1997, 144, 3866.
- 42. Barthel, J.; Schmidt, M.; Gores, H. J. J. Electrochem. Soc. 1995, 142, 2527.
- 43. Lischka, U.; Wietelmann, U.; Wegner, M. De 19829030 C1, 1999.
- 44. Xu, K.; Zhang, S.; Jow, T. R.; Xu, W.; Angell, C. A. *Electrochem. Solid-State Lett.* **2002**, *4*, A26.
- 45. Xu, K.; Angel, C. A. Science 2003, 302, 422.
- 46. Xu, K.; Zhang, S.; Poese, B. A.; Jow, T. R. Electrochem. Solid-State Lett. 2002, 5, A259.
- 47. Xu, K.; Zhang, S.; Jow, T. R. Electrochem. Solid-State Lett. 2002, 6, A117.
- 48. Xu, K.; Lee, S.; Zhang, S.; Wood, M.; Jow, T. R. *Electrochem. Solid-State Lett.* **2002**, *6*, A114.
- 49. Sun, X.-G. and Kerr, J. B. Macromolecules 2006, 39, 362.
- Xu, W.; Deng, Z.; Zhou, X.; Bolomey, P. 210th ECS Meet. Abstr. Electrochem. Soc. 2006, 602, 251.
- 51. Jow, T. R.; Ding, M. S.; Xu, K.; Zhang, S. S.; Allen, J. L.; Amine, K.; Henriksen, G. L. J. Power Sources 2003, 119/121, 343.
- 52. Xu, K.; Zhang, S. S.; Lee, J.; Allen, L.; Jow, T. R.; J. Power Sources 2005, 146, 79.
- 53. Zhang, S. S. Electrochem. Commun. 2006, 8, 1423.
- 54. Zhang, S. S. 210th ECS Meet. Abstr. Electrochem. Soc. 2006, 602, 267.

- 55. Shaffer, A. R.; Deligonul, N.; Scherson, D. A. and Protasiewicz, J. D. *Inorg. Chem.* **2010**, *49*, 10756.
- 56. Liang, S.; Choi, U. H.; Liu, W.; Runt, J.; Colby, R. H. Chem. Mater. 2012, 24, 2316.
- 57. Kida, Y.; Yanagida, K.; Yonai, A.; Funahashi, A.; Nohma, T. Yonezu, I. U.S. Patent 6, 537, 697 B2, 2003.
- 58. Fujinami, T.; Buzoujima, Y. J. Power Sources 2003, 119-121, 438.
- 59. Fujinami, T.; Mehta, M. A.; Sugie, K. Mori, K. Electrochimica Acta 2000, 45, 1181.
- 60. Aoki, T.; Konno, A.; and Fujinami, T. J. Electrochem. Soc. 2004, 151, A887.
- 61. Fujinami, T.; Tokimune, A.; Mehta, M. A.; Shriver, D. F.; Rawsky, G. C. Chem. Mater. 1997, 9, 2236
- Niedzicki, L.; Zukowska, G. Z.; Bukowska, M.; Szczecinski, P.; Grugeon, S.; Laruelle, S.; Armond, M.; Panero, S. Scrosati, B.; Marcinek, M.; Wieczorek, W. *Electrochimica Acta* 2010, 55, 450.
- 63. Barbarich, T. J.; Driscoll, P. F. Electrochem. Solid-State Lett. 2003, 6, A113.
- 64. Niedzicki, L.; Kasprzyk, M.; Kuziak, K.; Zukowska, G. Z.; Bukowska, M.; Wieczorek, M.; Armond, M. J. Power Sources 2011, 196, 1386.
- 65. Kerr, J. B. Ch. 19 in *Lithium Batteries Science and Technology* edited by G.-A. Nazri and G. Pistoia, Kluwer Academic, Boston, **2004**.
- 66. Fenton, D. E.; Parker, J. M. Wright, P. V. Polymer 1973, 14, 589.
- 67. Wright, P. V. Br. Polym. J. 1975, 7, 319.
- 68. Wright, P. V. J. Polym. Sci., Polym. Phys. Ed. 1976, 14, 955.
- 69. Armand, M. B.; Chabagno, J. M.; Duclot, M. *The 2nd International Conference on Solid Electrolytes*, St. Anrews, Scotland, **1978**; Abstract No.65.
- 70. Armand, M. B.; Chabagno, J.-M. and Duclot, M. J. in *Fast Ion Transport in Solids* Elsevier **1979.**
- 71. Blonsky, P. M.; Shriver, D. F.; Austin, P. and Allcock, H. R. J. Am. Chem. Soc. 1984, 106, 6854.
- 72. Allock, H. R.; Ravikiran, R. and O'Connor, S. J. M. Macromolecules, 1997, 30, 3184.
- 73. Chen-Yang Y. W.; Hwang, J. J. and Chang, F. H. Macromolecules, 1997, 30, 3825.
- 74. Zhang, L.; Zhang, Z.; Harring, S.; Straughan, M.; Butorac, R.; Chen, Z.; Lyons, L.; Amine, K.; West, R. J. Mater. Chem. 2008, 18, 3713.
- 75. West, R. C.; Amine, K.; Zhang, Z.; Wang, Q.; Vissers, D. R. U.S. Patent 2006035154 A1.
- Rossi, N. A. A.; Zhang, Z.; Schneider, Y.; Morcom, K.; Lyons, L.; Wang, Q.; Amine, K.; West, R. *Chem. Mater.* 2006, 18, 1289.
- 77. Zhang, Z.; Lyons, L. J.; Jin, J. J.; Amine, K.; West, R. Chem. Mater. 2005, 17, 5646.
- 78. Zhang, Z.; Lyons, L. J.; West, R; Amine, K. and West, R. *Silicon Chemistry* **2005**, *3*, 259.
- 79. Oh, B.; West, R. and Amine, K. U.S. Patent 7588859 B1, 2009.

- 80. Okanmoto, Y.; Yeh, T. F.; Lee, H. S.; Skotheim, T. A. J. Polym. Sci.: Part A: Polym. Chem. 1993, 31, 2573.
- 81. Siska, D. P.; Shriver, D. F. Chem. Mater. 2001, 13, 4698.
- 82. (a) Snyder, J. F.; Hutchison, J. C.; Ratner, M. A. Chem. Mater. 2003, 15, 4223,; (b) Snyder, J. F.; Ratner, M. A.; Shriver, D. F. J. Electrochem. Soc., 2003, 150, A1090. Wright, P. V. MRS Bull. 2002, 27, 597.
- 83. Thomas, K. E.; Sloop, S. E.; Kerr, J. B.; Newman, J. J. Power Sources 2000, 89, 132.
- 84. Wright, P. V. MRS Bull. 2002, 27, 597.
- Ryu, S.-W.; Trapa, P. E.; Olugebefola, S. C.; Gonzalez-Leon, J. A. Sadoway, D. R.; Mayes, A. M. J. Electrochem. Soc. 2005, 152, A158.
- Bou, S.; Zhang, S.; Klein, R. J.; Runt, J. and Colby, R. H. Chem. Mater. 2006, 18, 4288.
- 87. Azimipor, B.; Reibel, L. C. Polymer Belletin 2002, 49, 225.
- Hofmann, M. A.; Ambler, C. M.; Maher, A. E.; Chalkova, E.; Zhou, X. Y.; Lvov, S. N. and Allcock, H. R. *Macromolecules* 2002, *35*, 6490.
- 89. Allcock, H. R.; Welner, D. T. and Maher, A. E Solid State Ionics 2006, 177, 741.
- 90. Meziane, R.; Bonnet, J.-P.; Courty, M.; Djellab, K. and Armand, M. *Electrochim* Acta 2011, 57,14.
- 91. Matsumi, N. and Ohno, H. Main Group Chemistry 2006, 5(4), 297.
- 92. Jin, Z.; Xie, K and Hong, X. J. Mater. Chem. A. 2013, 1, 342.
- 93. Siska, D. P.; Shriver, D. F Mat. Res. Soc. Symp. Proc. 2000, 575, 131,
- 94. (a) Trapa, P. E.; Acar, M. H.; Sadoway, D. R.; Mayes, A. M. J. Electrochem. Soc. 2005. 152, A2281; (b) Sadoway, D. R. J. Power Sources 2004, 129, 1.
- Wang, X.; Wang, L.; Li, H.; Tang, X. and Chang, F. J. Appl. Poly. Sci. 2000, 77, 184.
- 96. Zhou, G. B.; Khan, I. M.; Smid, J. Macromolecules, 1993. 26, 2202.
- 97. Xu, W.; Williams, M. D. and Angell, C. A. Chem. Mater. 2002, 14, 401.
- 98. Zhou, G. B.; Khan, I. M.; Smid, J. Poly. Commu. 1989, 30, 52.
- Okamoto, Y.; Yeh, T. F.; Lee, H. S. and Skotheim, T. A. J. Poly Sci. Poly. Chem. 1993, 31, 2573.
- 100. Fragiadakis, D.; Dou, S.; Colby, R. H. and Runt, J. J. Chem. Phys. 2009, 130, 064907.
- 101. Sun, J.; MacFarlane, D. R.; Forsyth, M. Solid State Ionics, 147, 333, 2002.
- 102. Feuillade, G.; Perche, P. J. Appl. Electrochem. 1975, 63, 5.
- 103. Dias, F. B.; Plomp, L.; Veldhuis, J. B. J. Power Sources 1999, 77, 813.
- 104. Song, J. Y.; Wang, Y. Y.; Wan, C. C. J. Power Sources 2000, 88, 169
- 105. Stephan, A. M. European Polymer Journal 2006, 42, 21.
- 106. Zhang, P.; Li, L.; He, D.; Wu, Y.; Shimizu, M. Acta Polymer Sinica 2011, 2, 125.

- 107. Li, G.; Li, Z.; Zhang, P.; Zhang, H. and Wu, Y. Pure Appl. Chem. 2008, 80, 2553.
- 108. Chiang, C. K.; Davis, G. T.; Harding, C. A.; Takahashi, T. Solid State Ionics 1986, 18-19, 300.
- 109. Immanuel, S.; Chaklanobis, S.; Chandrasekar, V. J. Electrochem. Soc. 1995, 142, 366.
- 110. Pradhan, D. K.; Choudhary, R. N. P.; Samantaray, B. K. *Materials Chemistry and Physics* 2009, *115*, 557.
- 111. Ito, Y.; Kanehori, K.; Miyauchi, K.; Kudo, T. J. Materials Science 1987, 22, 1845.
- 112. Kelly, I.; Owen, J. R. and Steele, B. C. H. J. Electroanal. Chem. 1984, 168, 467.
- 113. Lee, J. Y.; Lee, Y. M.; Bhattacharya, B.; Nho, Y.-C.; Park, J. K. J. Solid State Electrochem 2010, 14, 1445.
- 114. Kaneko, f.; Wada, S.; Nakayama, M.; Wakihara, M.; Koki, J.; and Kuroki, S. *Adv. Funct. Mater.* **2009**, *19*, 918.
- 115. Zhang, S.; Dou, S.; Colby, R. H. and Runt, J. J. Non-Crystalline Solids 2005, 351, 2825.
- 116. Li, Y.; Wang, J.; Tang, J.; Liu, Y. and He, Y. J. Power Sources 2009, 187, 305.
- 117. Liang, S.; Chen, Q.; Choi, U. H.; Runt, J.; Colby, R. H. to be submitted 2012.
- 118. Appetechi, G. B.; Croce, F.; Fomangnoli, P.; Scrosati, B.; Heider, U.; Oestern, T. *Electrochem Comm.* **1999**, *1*, 83.
- 119. Appetechi, G. B.; Croce, F.; Scrosati, B.; J. Power Sources 1997, 66, 77.
- 120. Scrosati, B. The Chemical Record, 2001, 1, 173.

Chapter 2

Synthesis and Lithium Ion Conduction of Polysiloxane Single-Ion Conductors Containing Novel Weak-Binding Borates

2.1 Introduction

Polymer electrolytes are of great interest as *energy materials* in energy storage and conversion devices, such as lithium ion batteries, fuel cells, solar cells, supercapacitors and actuators. Salt-in-polymer systems have been extensively studied using various polymeric matrices and salts.¹⁻³ Single-ion conductors that have anions covalently bonded to polymers are generally accepted to have advantages over polymer/salt mixtures for application in lithium-ion batteries; unity transference number and the absence of detrimental anion polarization.^{4,5} Unfortunately, low conductivity of current single-ion conductors hinders their practical application. Herein this problem is considered with a fresh approach – Can quantum chemistry calculations of ion interaction energies guide rational single-ion conductor design?

Polysiloxane-based ionomers are promising polymer electrolyte candidates, owing to their highly flexible backbone imparting low glass transition temperature (T_g). Nagaoka, et al.⁶ introduced dimethyl siloxane groups into a predominantly poly(ethylene oxide) (PEO) backbone via polycondensation. The highest conductivity observed was 1.5 x 10⁻⁴ S/cm for a polymer/salt system at 25 °C with T_g near -80 °C. Different complex systems of alkali metal salts and polysiloxane-based ionomers were explored afterwards. Inspired by Walden's rule that electrolyte conductivity is inversely proportional to viscosity,⁷ West and co-workers ⁸ developed a series of low viscosity polymers based on polysiloxane oligomers and PEO oligomers (typically 2 to 7 repeat units). After mixing with salt, the highest conductivities of the mixtures, of order 3 x 10^{-3} S/cm, are high enough for practical application.^{2, 5} To prepare polysiloxane-based single-ion conductors, novel anions such as di-t-butyl phenolate, naphtholate, hexafluoropropanolate, ⁹ CF₃SO₂N⁻CH₂CH₂¹⁰ and CH₂CH₂CF₂CF₂OCF₂CF₂SO₃⁻¹¹ anions have been fastened to polysiloxane backbones. The conductivities of those single-ion conductors are still of order 10^{-5} S/cm at 25 °C, 10X lower than the minimum practical requirement for single-ion conductors based on siloxyaluminate, having conductivity as high as 10^{-4} S/cm at 25 °C, with T_g = -53 °C. This is the highest ionic conductivity reported for a single-ion solvent-free conductor that is a free standing film and is considered the benchmark.

Like aluminum, boron has much lower electronegativity than sulfur or nitrogen. As a result, borate anions are more inclined to delocalize charge. Different borate salts have components of polymer electrolytes, e.g., been studied as key lithium bis(oxaloto)borate,14 tetraphenyl borate,15-17 tetrabutyl borate16 and other borates with novel structure.¹⁸ Of particular interest is tetraphenyl borate (LiBPh₄). LiBPh₄ had been extensively studied as an electrolyte in 1965 by Bhattacharyya and coworkers¹⁹. Later Klemann et al.²⁰ proposed its application in batteries with alkali metal anodes. According to the hard-soft acid-base principles suggested by Pearson,²¹ Li⁺ is one of the hardest cations and BPh₄⁻ is one of the softest anions.²² The ion dissociation energy of LiBPh₄ is similar to that of LiN(SO₂CF₃)₂ as shown by our *ab initio* calculations,²³ and much lower than that of LiClO₄,²⁴ which can be attributed to the four benzene rings around boron greatly delocalizing the negative charge. Besner et al.¹⁵ compared BPh₄⁻ and N(SO₂CF₃)₂⁻

, and their results demonstrated that BPh₄⁻ has greater polarizability, resulting in low iondipole stabilization energy. The lattice energies of tetraphenyl borate salts are relatively low and they have little tendency to form contact pairs. In addition, the extreme size difference between anion and lithium cation makes the simplest ion aggregate (the quadrupole; two ion pairs antiparallel to each other) difficult to form. Replacing the H atoms of BPh₄⁻ with F atoms is predicted to soften the interactions with Li⁺, lower the ion pair energy by 20% and positive triple ion energy by 40%, as summarized in Table 1. Kida et al.²⁵ explored LiB(C₆F₅)₄ as the electrolyte in a secondary lithium battery and found the battery they prepared exhibits superior charge-discharge cycle performance, especially at elevated temperature, compared to batteries containing conventional lithium salts such as LiPF₆ and LiBF₄. This was attributed to the absence of weak B-F or P-F bonds in LiB(C₆F₅)₄. Moreover, the primary decomposition products of LiB(C₆H₅)₄ are benzene and phenol²⁶. So most probably LiB(C₆F₅)₄ will generate C₆F₅H and C₆F₅OH which are far less corrosive than the HF produced on decomposition of either PF₆ or BF₄.

anion	E _{pair}	E_{triple^+}	E_{pair}/ϵ_{PEO}	$E_{triple^+}\!/\epsilon_{PEO}$	E_{pair}/ϵ_{CECA}	$E_{triple^+}\!/\epsilon_{CECA}$
	(kJ/mol) ²¹	(kJ/mol) ²¹	(kJ/mol) ^a	(kJ/mol) ^a	(kJ/mol) ^b	(kJ/mol) ^b
C ₂ H ₅ SO ₃	656	893	94	128	12.6	17.2
$C_2F_5SO_3^-$	584	778	83	111	11.2	15.0
$(C_6H_5)SO_3^-$	641	892	92	127	12.3	17.2
$(C_6F_5)SO_3$	604	819	86	117	11.6	15.8
$(C_6H_5)_4B^-$	539	860	77	123	10.4	16.5
$(C_6F_5)_4B^-$	448	611	64	87	8.6	11.8

Table 2-1. Lithium Ion Pair and Positive Triple Ion Energies at 0 K in vacuum ²³ (left two columns) and in polar polymers at 300 K (PEO middle two columns; CECA right two columns).

a. Calculated for PEO-ionomers ²⁸⁻³¹ using the 300 K dielectric constant of PEO $\varepsilon_{PEO} = 7$. b. Calculated for CECA-ionomers relevant to this paper using the 300 K dielectric constant of the siloxane-CECA homopolymer ^{33, 34} $\varepsilon_{CECA} = 52$.



Figure 2-1. Electronic charge distribution in (a) tetraphenyl borate anion and (b) perfluorinated tetraphenyl borate anion, calculated by Gaussian 03 using the B3LYP/6-31+G* basis set. Light green denotes a positive charge, red denotes a negative charge, with brighter red indicating stronger negative charge. The boron in the center of these borate anions is positively charged. The tetraphenyl borate anion has the negative charge distributed on the 24 carbons in the phenyl rings, particularly the ortho carbons (each with roughly -0.5e). The perfluorinated tetraphenyl borate anion has the negative charge distributed on the 20 fluorines (roughly -0.3e each), with strong positive charge on boron (roughly +0.5e), the alpha carbons (roughly +0.7e) and the para carbons (roughly +0.8e). The charge distributions impart strong dipoles to these anions (shown by arrows) of 16 Debye for tetraphenyl borate and 13 Debye for perfluorinated tetraphenyl borate.

Many single-ion conductors of Li^+ in the literature are based on a polymer that is primarily PEO^{9-11, 27-31} and since the dielectric constant of PEO $\varepsilon_{PEO} = 7$ at 300 K, two

columns of Table 2-1 estimate the ion pair energy and positive triple ion energy in such PEO-ionomers by dividing the 0 K/vacuum energies by $\varepsilon_{PEO} = 7$ (since ε is in the denominator of the Coulomb energy). While reasonably polar for a polymer, this dielectric constant is too small for construction of a good single-ion conductor. Cyclic carbonates have higher dielectric constant;³² ethylene carbonate $\varepsilon_{EC} = 90$ at 40 °C and propylene carbonate $\varepsilon_{PC} = 65$ at 25 °C. Both are fine examples of the classical 1/T Onsager temperature dependence of dielectric constant of polar liquids, with magnitudes well-anticipated by the dipoles calculated at 0 K in *ab initio* (see Supporting Information Figure S1). Siloxane polymers with highly polar cyclic [(allyloxy) methyl] ethylene ester carbonic acid (CECA) side chains have been reported to have 300 K dielectric constant^{33,} ³⁴ as high as $\varepsilon_{CECA} = 52$ and selecting this base-polymer dielectric constant allows us to divide the 0 K/vacuum energies by $\varepsilon_{CECA} = 52$ for the last two columns in Table2-1. This results in significantly reduced ion interactions, suggesting such ionomers might be superb single-ion conductors of Li^+ . BPh₄ and its perfluorinated counterpart have interesting charge distributions revealed by Gaussian 03, shown and discussed in Figure 2-1.

Motivated by the low ion interaction energies for CECA-borate copolymers denoted in red in Table 2-1, in this paper the synthesis of polysiloxane-based single-ion conductors with cyclic carbonates and three different lithium tetraphenyl borates as side chains are reported. The ionomers with ethylene oxide (EO) spacers display higher conductivities and dielectric constants compared to PEO-based sulfonate ionomers previously reported by our group.²⁸⁻³¹ Comparison of ionomers with different ionic groups but similar ion molar content indicates that ionomers containing

perfluorotetraphenyl borate salts have 3 times higher conducting ion concentration, consistent with the 40% lower triple ion energy in Table 1, since the 20 F atoms strongly delocalize the charge (Figure 2-1b).

2.2 Results and Discussion

2.2.1 Synthesis and NMR



Β1

Scheme 2-1. Synthesis of lithium triphenylstyrylborate (B1).

The synthesis schemes of weak-binding borate salts and resulting single-ion conductors are shown in Schemes 1-4. Lithium styryltriphenylborate (B1) was synthesized according to Scheme 2-1.³⁵ Due to the low water solubility of lithium carbonate, the final reaction yield is lower than 50%. To improve the yield, BuLi was used during the synthesis of lithium triphenyl(4-((2-(2-vinyloxy)ethoxy) ethoxy)methyl)phenyl)borate (B2, Scheme 2). B2 is extremely hygroscopic so that handling of B2 requires a glove box.



Scheme 2-2. Synthesis of lithium triphenyl(4-((2-(2-vinyloxy)ethoxy)methyl) phenyl) borate (B2).

Previously, efforts to incorporate ionic groups onto a polysiloxane backbone have focused on converting functional groups to ionic groups after the hydrosilylation reaction.^{9,11} Directly attaching ionic groups by hydrosilylation has rarely been reported. The reason may be ascribed to the concern of side reactions caused by salts and their trace water contaminants. In this paper, we successfully attached monomers containing weak-binding salts B1, B2 and B3 (see Figure 2-2 for structures) to the polysiloxane backbone via hydrosilylation reaction, which provided a straightforward and efficient way to produce polysiloxane-based ionomers.

The steric effect of the bulky styryltriphenyl group lead us to prepare triphenyl(4-((2-(2-vinyloxy) ethoxy))methyl)phenyl)borate (B2, Scheme 2-2) and tris(perfluorophenyl)(2,3,5,6-tetrafluoro-4-(2-(2-(vinyloxy)))) ethoxy)) phenyl)borate (B3, Scheme 2-3). The EO groups between the borate and the polysiloxane backbone are expected to reduce the steric effect of the tetraphenyl group and lower T_g.



Scheme 2-3. Synthesis of lithium tris(perfluorophenyl)(2,3,5,6-tetrafluoro-4-(2-(2-(vinyloxy) ethoxy) phenyl) borate (B3).

The single-ion conductors were synthesized from polymethylhydrosiloxane (PMHS), cyclic [(allyloxy) methyl] ethylene ester carbonic acid (CECA) and borates (B1, B2 and B3) by hydrosilylation (Scheme 4). Representative ¹H, ¹¹B and ¹⁹F NMR spectra and chemical structures of the ionomers discussed in this paper are shown in Figure 2-2 (Supporting Information contains such spectra for the borate monomers and seven ionomers in Figures S2-6 and for the CECA monomer and siloxane homopolymer in Figure S7). The disappearance of peaks belonging to the vinyl group in the region from 5 to 7 ppm, and appearance of new peaks at 0.6, 0.9, 1.6 and 2.5 ppm which can be assigned to ethylene groups bonded to silicon atoms, confirm the success of the reaction.



Figure 2-2 Representative ¹H NMR spectra of polysiloxane ionomers with (a) CECA and tetraphenyl borate (B1) as side chains (P-10, n /(n + m) = 0.1), (b) CECA and B2 as side chains (SP-2, n/(n+m) = 0.02), with inset showing the ¹¹B NMR spectrum and (c) CECA and B3 as side chains (FSP-5, n/(n + m) = 0.05), with insets showing ¹¹B and ¹⁹F NMR spectra (from left to right).

The chemical shift of borate (B2) in ¹¹B NMR spectrum is -6.42 ppm, close to the literature reports for $(C_6H_5)_4BK$ (-6.7 ppm) and $(C_6H_5)_4BNa$ (-6.4 ppm).³⁶ B3's boron NMR chemical shift moves downfield (to -3.68 ppm) due to the electron-withdrawing effect of the fluorine atoms. ¹⁹F NMR results of B3 are -136.2 ppm (*o*-C₆F₅), -142.8 ppm (*o*-C₆F₄), -159.3 ppm (*m*-C₆F₄), -163.8 ppm (*p*-C₆F₅), -167.6 ppm (m-C₆F₅), partially agreeing with the literature report of KB(C₆F₅)₄³⁷, (-133.2 (o-C₆F₅), -164.6 (*p*-C₆F₅), -168.6 (m-C₆F₅)). The nearly identical ¹¹B NMR chemical shift (-6.44 ppm, Figure 2-2b and -5.6 ppm, Figure 2-2c) and ¹⁹F NMR chemical shift (-134.2 ppm (*o*-C₆F₅), -142.4 ppm (*o*-C₆F₄), -158.5 ppm (*m*-C₆F₄), -165.4 ppm (*p*-C₆F₅), -168.7 ppm (m-C₆F₅), Figure

2-2c) of the borate groups after hydrosilylation prove that the borate groups are intact on our ionomers.



Scheme 2-4. Synthesis of comb polysiloxanes with CECA and B1, (B2, or B3 anions) as side chains.

The borate fractions of the single-ion conductors are calculated by the following equation: Borate Fraction = (P/19)/(P/19+C/2), here *P* is the integrated area of peaks belonging to phenyl groups and *C* is the integrated area of the methylene group between

the carbonate and polysiloxane backbone (peak *a* in Figure 2-2a and 2b). For FSP-5, the borate fraction was calculated by h/(h+a), here *h* and *a* are the integrated areas of peaks h at 0.9 ppm and a at 0.55 ppm (Figure 2-2c). The compositions of carbonate/borate polysiloxane ionomers synthesized are summarized in Table 2-2. Here we should point out that our borate fraction is only the ratio of borate content to the sum of the borate and CECA contents. During the reaction, a portion of Si-H groups reacted with trace water instead of the vinyl monomer, which complicated the analysis of the final product. Overall, the ratio of Si-H groups consumed by this side reaction is always less than 30%. The real borate content per Si-Me group is smaller.

	Anion	Borate Fraction [borate]•100% [borate]+[CECA] Feed NMR		T _g (°C)	Total ion concentration $p_0 (nm^{-3})$	ε _s (at 25 °C)	Conductivity at 25 °C (S/cm)
P-5	B1	5.5	5	-11	0.076	43	10 ^{-7.7}
P-8	B1	8.4	8	-6	0.12	39	10 ^{-7.1}
P-10	B1	9.7	10	10	0.15	40	10 ^{-8.2}
P-14	B1	18.5	14	30	0.21	38 ^a	10-11
SP-2	B2	2.7	2	-17	0.024	61	10 ^{-7.0}
SP-5	B2	6.7	5	-15	0.060	49	10 ^{-7.2}
FSP-5	В3	7.6	5	-16	0.042	53	10 ^{-6.9}
CECA Homopolymer	none	0		-30	0	52	N/A

Table 2-2. Synthesis and Physical Properties of Polysiloxane Single-ion Conductors

a. measured at 35 °C

2.2.2 Glass Transition Temperatures

Ionomer T_g generally increases with ion content.³⁸ As shown in Table 2-2, T_g increases roughly 4K/mol% lithium borate, roughly half the slope of Li-PEO-sulfonate ionomers,³¹ owing to the weaker binding borate anions. Comparing T_g of P-5, SP-5 and FSP-5, having similar ion content, demonstrates that EO spacers between the borate and polysiloxane backbone in SP-5 and FSP-5 lower T_g by 4-5 K. Ether oxygens solvate Li⁺ and discourage ion aggregates, reducing physical crosslinking and hence lowering T_g .

2.2.3 Dielectric Constant and Ionic Conductivity

The purpose of attaching the polar carbonate group (CECA) to the polysiloxane backbone is to increase the dielectric constant, which weakens ionic interactions and may allow more counterions to participate in conduction. At the same time, carbonate functional groups are expected to solvate Li⁺ ions, as PEO does. In Table 2-2, the CECA homopolymer exhibits much higher dielectric constant compared to that of pure polysiloxane.³⁴ Ionomers with some of the carbonate groups replaced by lithium borates (P-5, 8, 10 and 14) exhibit slightly *lower* dielectric constant. This is an unexpected result, as ion pairs have large dipoles that dramatically increase the dielectric constant of properly solvated ionomers.^{28-30, 39} This might be explained by microphase separation, induced by incompatibility of the aromatic borate and CECA. If correct, that suggests a need to design some favorable interaction between the polar neutral monomer and the anionic monomer. When short EO spacers are placed between the polymer backbone and functional groups, the conductivity is boosted. Moreover, the dielectric constant increases

to become comparable to, or slightly higher than, the CECA homopolymer. Indeed, comparing siloxane homopolymers with vinyl carbonate versus CECA side chains,³⁴ the 25 °C dielectric constant is found to be more than twice as large with CECA, due to the flexible EO spacer imparting less hindrance to motion of the large dipole.

Figure 2-3 displays the dc ionic conductivity as a function of T/T_g and the inset shows conductivity vs. 1000/T. The conductivity of 10^{-11} S/cm at T_g is typical of Li single-ion conductors. The highest 25 °C conductivity obtained is 10^{-6.9} S/cm in Table 2-2 for the ionomer with perfluorophenyl borate anions. This disappointing result is comparable to the results reported previously by our group²⁸⁻³¹ for PEO-based sulfonate ionomers. For ionomers without ethylene oxide (EO) spacers, the conductivities show a maximum value when ion content is around 8%, easily explained by the conduction mechanism proposed in the literature.^{1,27-30, 39-40} The conducting species are most likely triple ions of Li⁺BPh₄-Li⁺. Ion 'hopping' is required for ion transport, whereby a triple ion moves by segmental motion and exchanges its extra Li⁺ with a nearby ion pair. The ion mobility not only depends on polymer chain segmental motion, but also on the potential barriers, E_{hop}, that cations must overcome to move.³ At low ion concentration, as ion content increases, Ehop decreases due to overlapping segmental exploration volumes of neighboring ion pairs, and conductivity increases. Increasing ion content further leads to more ion aggregation, higher T_g, and lower conductivity.

EO spacers between the borate anion and the polymer backbone provide more freedom for ionic side chains to respond to the external electric field, resulting in higher dielectric constant and conductivity (see Table 2-2). The ionomer SP-2, with the lowest total ion content, has the highest static dielectric constant (61) at 25 °C. Additionally, EO

spacers can assist in dissociating ion aggregates, lowering T_g, and boosting the mobility of the conducting ions. When H atoms on the phenyl groups of the B2 borate are replaced by F atoms to give B3, the borate's charge is even more delocalized and ionic interactions are further softened, boosting carrier concentration. Figure 2-4 compares electrode polarization analysis results^{28, 29} of three of our single-ion conductors, containing the three different borates at similar ion content (~5%). The ionomer with the perfluoroborate anion exhibits > 3X higher simultaneously conducting ion concentration compared to the other two ionomers. For each ionomer, the conducting ion content shows Arrhenius temperature dependence: $p = p_{\infty} \exp(-E/RT)$



Figure 2-3. Temperature dependence of ionic conductivity for siloxane borate ionomers vs. T/T_g (and vs. 1000/T in the inset). The short EO spacer between the borate ion and the siloxane backbone raises the conductivity by lowering T_g .



Figure 2-4. Temperature dependence of simultaneously conducting ion concentrations for three siloxane borate ionomers with borate fraction 5%.

The value of p_{∞}/p_o (p_o is the calculated total ion concentration of the ionomer in Table 2-2) of ionomer FSP-5 is 0.12, compared to 0.012 and 0.05 for P-5 and SP-5, respectively. This indicates that the ionomer with the perfluoroborate has the largest portion of ions participating in conduction, as anticipated by the *ab initio* calculations presented in Table 1. The Arrhenius temperature dependence of the conducting ion concentration in Figure 2-4 shows activation energy in the range of 7 to 10 kJ/mol, much lower than single-ion conductors containing either sulfonate groups $(18 - 22 \text{ kJ/mol})^{28,29}$ or bis(trifluoromethanesulfonyl) imide groups $(17 - 20 \text{ kJ/mol})^{41}$ that have recently been

used to construct lithium single-ion conductors.⁴²⁻⁴⁴ This substantially lower activation energy suggests that our borate anions have enormous potential for ion conduction, if T_g can be kept low.



Figure 2-5. Temperature dependence of ionic conductivity for P-10 and its blends with PEG600.

When normalized by T_g , the conductivity far above T_g actually increases strongly with ion content (Figure 2-3), suggesting that high ion contents would be beneficial for single-ion conductors, if T_g can be kept low. At high ion content, 10^{-4} S/cm requires T = $1.5T_g$, meaning that $T_g = -70$ °C is needed to achieve 10^{-4} S/cm at room temperature. Such has been realized in polymer/salt mixtures^{3e, 6} but remains a challenge for single-ion conductors, without addition of polar solvent to solvate ions and lower T_g . Figure 2-5 displays the conductivities of blends of the styryl triphenyl borate ionomer P-10 with different weight percents (13, 25, 34, 54, and 70 wt%) of polyethylene glycol (PEG600) oligomer with $M_n = 600$. The ambient conductivities were greatly improved, from 10⁻⁸ to 10⁻⁵ S/cm, by plasticizing with PEG600. This is partly a direct result of lowering the T_g but also the ether oxygens of PEG600 seem to help solvate Li⁺. The full report of how PEG600 affects the number density, activation energy and mobility of the simultaneously conducting ions and the dielectric constant, will be detailed in a forthcoming publication.

2.3 Conclusions and Outlook

Polysiloxane-based single-ion conductors containing novel borates and cyclic carbonate side chains were directly synthesized via one-pot hydrosilylation reaction. ¹H, ¹⁹F and ¹¹B NMR spectra before and after hydrosilylation reactions prove that the borate anions are attached intact to the polysiloxane. This approach allows us to directly synthesize polar ionomers with bulky weak-binding anions.

The ionomers exhibit relatively high conducting ion content and low activation energy. At similar ion content (~5%), the ionomer with perfluorinated borate has the lowest T_g and the highest conductivity. In Figure 2-4, this ionomer displays the highest intercept, suggesting more ions participate in conduction. Therefore, if T_g is kept low by some clever means, dielectric constant should increase, potentially allowing orders of magnitude increase in conductivity because more ions will participate in conduction. All of our experimental results are consistent with expectations from our *ab initio* calculations, strongly suggesting that such can be utilized to design single-ion conductors to transport ions.

The conductivities of the borate-containing ionomers are still relatively low, which is likely due to the relatively high T_g of these ionomers. Further improvement in the conductivity is expected when either incorporating PEO side chains on the polymer backbone or short poly(ethylene glycol) (PEG) oligomer as plasticizer. Our preliminary results ⁴⁵ show that after mixing borate-containing polymers (P-10) with PEG-600, the conductivity was boosted by over 1000X.

2.4 Experimental Section

Materials. Diethyl carbonate, potassium carbonate, 4-bromostyrene, 2-(2-(vinyloxy)ethoxy)ethanol, diethyl carbonate, potassium carbonate, 3-(allyloxy)-1,2propane diol. 1-bromo-4-(bromomethyl) benzene, 1-bromo-pentafluorobenzene, tris(pentafluorophenyl)boron, magnesium, triphenylboron, toluene and anhydrous acetonitrile were purchased from VWR and used without further purification. Platinum divinyltetramethyldisiloxane complex (Pt[dvs]) (3% in xylene) catalyst, sodium hydride (60% in mineral oil) and polymethylhydrosiloxane (PMHS, $M_n = 1700 - 3200$) were purchased from Aldrich and used as received. Tetrahydrofuran (THF) from EMD Chemicals was refluxed over sodium metal before use.

Characterization. ¹H, ¹³C and ¹¹B NMR spectra were recorded on a Bruker AM 300M spectrometer. Glass transition temperatures (T_g) were determined using a TA Q100 differential scanning calorimeter (DSC) with 10 K/min heating and cooling rates. For

dielectric and conductometric measurements, samples were sandwiched between two polished brass electrodes with 50 μ m silica spacers placed on top of the sample under < 1 mTorr vacuum at 80 °C for at least 24 h. The sandwiched samples were positioned in a Novocontrol GmbH Concept 40 broadband dielectric spectrometer and the dielectric permittivity and conductivity were measured using an AC voltage amplitude of 0.1 V and $10^{-2} - 10^7$ Hz frequency range. Each sample was annealed in the Novocontrol at 120 °C in a heated stream of dry nitrogen for 1 hour prior to measurements to drive off any moisture picked up during loading of these hygroscopic materials. Data were collected in isothermal frequency sweeps from 120 °C to near T_g.

Cyclic [(allyloxy) methyl] ethylene ester carbonic acid (CECA). CECA was prepared according to the method by Zhu et al.³³ Potassium carbonate (3 g, 21.7 mmol) was added to a mixture of 3-(allyloxy)-propane-1, 2-diol (92.475 g, 0.1875 mol) and diethyl carbonate (24.75 g, 0.1875 mol). After stirring at 120 °C for 24h, the mixture was filtered to isolate the solid. The residue was purified by Kügelrohr distillation to isolate the pure product as a colorless liquid (23.7 g, 80%). ¹H NMR (in CDCl₃), δ (ppm) 5.87 (m, 1H, C=CH), 5.25 (d, 1H, cis H of CH₂=C), 5.14 (d, 1H, trans H of CH₂=C), 4.86 (m, 1H, CCH(C)O), 4.38-4.55(m, 2H, CH₂C), 4.06 (m, 2H, OCH₂C=C), 3.60-3.74 (m, 2H, OCCH₂O).

Lithium triphenylstyryl borate (B1). B1 was synthesized via a modified literature method³⁵ (Scheme 2-1). To a pre-degassed three-neck flask equipped with addition funnel and septa, were added magnesium (0.4774 g) and 20 mL THF. BrCH₂CH₂Br (0.1 mL) was added to the mixture to initiate the reaction. 5 minutes later, under protection of argon, 4-bromostyrene (3.71 g) in 20 mL dry THF was added through

an addition funnel. The temperature of the reaction mixture was maintained under 20 °C. 2 hours later, this Grignard reagent solution was transferred into a solution of triphenyl boron (2.4664 g) in 40 mL THF. The entire mixture was allowed to stir at room temperature for 2 hours. Then the reaction solution was poured into 100 mL of saturated lithium carbonate aqueous solution. Ethyl acetate was used to extract the aqueous phase (40 mL x 3). The organic phases were combined and condensed. Recrystallization from diethyl ether yields B1 as a white powder (1.8g, 52%). ¹H NMR (in d6-acetone), δ (ppm) 5.09 (d, 1H, trans H of = CH₂), 5.65 (d, 1H, cis H of = CH₂), 6.78 (m, 1H, CH=), 6.95 (t, 3H, *p*- C₆H₅), 7.1 (m, 6H, *m*-C₆H₅), 7.2 (d, 2H, *m*-C₄H₄), 7.38 (m, 8H, *o*-C₄H₄ and *o*-C₆H₅); ¹¹B NMR (in d6-acetone) shows a single peak at δ = -6.44 ppm.

Lithium triphenyl(4-((2-(2-vinyloxy)ethoxy)ethoxy)methyl)phenyl)borate (B2). To a mixture of NaH (1.44g, 60% in mineral oil) dispersed in 20 mL dry THF was added 2-(2-(vinyloxy)ethoxy)ethanol (4.047 g) at 0 °C via addition funnel. The mixture was stirred for 3 hours before being transferred into a solution of 1-bromo-4-(bromomethyl)benzene (7.42 g) in 20 mL dry THF. The mixture was allowed to react overnight to complete the reaction. The solvent was evaporated and the residue was purified by column chromatography on SiO₂ with hexane/ethyl acetate (10:1 to 7:1) to obtain M1 as a colorless liquid (8g, 89%). ¹H NMR (in d6-acetone), δ (ppm) 7.52 (d, 2H, o-C₆H₄), 7.36 (d, 2H, m-C₆H₄), 6.51(m, 1H, CH=), 4.549 (s, 2H, CH₂C₆H₄), 4.19(d, cis H of = CH₂), 3.96 (d, trans H of = CH₂), 3.8-3.6 (m, 8H, OCH₂CH₂O); ¹³C NMR (in d6-acetone), δ (ppm) 152.4 (CH=), 138, 131, 129,7, 120.1 (c-Br), 86 (=CH₂), 72.1, 70.8, 70, 69.8, 67.9.

A solution of M1 (5.7g, 0.019 mol) in 20 mL THF was cooled to -78 °C by dry ice/acetone. 8.1 mL BuLi (2.5 M) in hexane solution was added dropwise into the mixture over 30 minutes. The mixture was stirred at -78 °C for another hour before the solution of triphenyl boron (4.47g, 0.019mol) in 20 mL THF was added. The reaction mixture was allowed to warm up to room temperature while stirring overnight to complete the reaction. The mixture was dried by vacuum distillation and anhydrous pentane (20mL x 3) was used to wash the yellow residue. The upper pentane solution was removed by syringe and the yellow residue was further dried in a vacuum oven at 50 °C for 24 hours to yield B2 as an ivory-white powder (9.49g). (¹H NMR (in d6-acetone), $\delta(\text{ppm})$ 7.35 (m, 8H, o-C₄H₄ and o-C₆H₅), 7.05 (d, 2H, m-C₄H₄), 6.93 (m, 6H, m-C₆H₅), 6.82 (t, 3H, p-C₆H₅), 6.51(m, 1H, CH=), 4.43 (s, 2H, CH₂C₆H₄), 4.22(d, cis H of = CH₂), 3.96 (d, trans H of = CH₂), 3.8-3.6 (m,8H, OCH₂CH₂O); ¹³C NMR (in d6-acetone), δ(ppm) 165 (m, C-B), 152.4 (CH=), 136, 132, 126, 120.1, 86.4 (CH₂=), 74.3, 70.8, 70, 69.7, 67.8; ¹¹B NMR (in d6-acetone), shows a single peak at $\delta = -6.42$ ppm; see Figures S3, S5 and S6.

Lithium tris(perfluorophenyl)(2,3,5,6-tetrafluoro-4-(2-(2-(vinyloxy)ethoxy) ethoxy) phenyl) borate (B3). To a mixture of NaH (1.5470g, 60 % in mineral oil) dispersed in 20 mL dry THF was added 2-(2-(vinyloxy)ethoxy)ethanol (4.2098 g) at 0 °C via addition funnel. The mixture was stirred for 3 hours before being transferred into a solution of 1-bromo-pentafluorobenzene (5.7376 g) in 20 mL dry THF. The mixture was allowed to react overnight to complete the reaction. The solution was condensed and the residue was purified by column chromatography on SiO₂ with ethyl acetate in hexane

(0% to 8%) as eluent to obtain M2 as a colorless liquid (5g, 72%). ¹H NMR (in d6-acetone), δ (ppm) 6.46 (m, 1H, CH=), 4.465 (s, 2H, CH₂OC₆F₄) 4.16 (d, cis H of = CH₂), 3.94 (d, trans H of = CH₂), 3.85-3.671 (t, 3H, OCH₂CH₂OCH₂); ¹³C NMR (in d6-acetone), δ (ppm) 152.4 (CH=), 140-143 (C-F), 92.5 (C-Br), 86 (=CH₂), 74.72 – 67.73 (CH₂CH₂O); ¹⁹F NMR (in d6-acetone), δ (ppm) -137.51 (d, 2F, *o*-C₆F₄), -156.75 (d, *m*-C₆F₄).

A solution of M2 (3.74g, 0.01 mol) in 20 mL diethyl ether was cooled to -78 °C by dry ice/acetone. 7.2 mL BuLi (1.6 M) in hexane solution was added dropwise to the mixture over 30 minutes. The mixture was stirred at -78 °C for another hour before the solution of tris(pentafluorophenyl)borane (4.87g, 0.0095mol) in 20 mL diethyl ether was added. The reaction mixture was allowed to warm up to room temperature while stirring overnight to complete the reaction. The mixture was dried by vacuum distillation and anhydrous pentane (20mL x 3) was used to wash the yellow residue. The upper pentane solution was removed by syringe and the lower yellow phase was further dried in a vacuum oven at 50 °C for 24 hours to give B3 as a yellow powder (2.2g, 25%). ¹H NMR (in d6-acetone), $\delta(\text{ppm})$ 6.46 (m, 1H, CH=), 4.40 (s, 2H, CH₂OC₆F₄) 4.15 (d, cis H of = CH₂), 3.93 (d, trans H of = CH₂), 3.83-3.61 (t, 3H, OCH₂CH₂OCH₂); ¹¹B NMR (in d6-acetone), shows a single peak at $\delta = -3.68$ ppm; see Figures S4 and S5; ¹⁹F NMR (in d6-acetone), δ (ppm) -136.2 (d, 6F, $o-C_6F_5$), -142.8 (d, 2F, $o-C_6F_4$), -159.3 (d, 2F, $m-C_6F_4$), -163.8 (m, 3F, p- C_6F_5), -167.6 (m, 6F, m- C_6F_5). Fluorine NMR indicated that there were ~ 20% unreacted starting materials left. Due to the difficulty of purification, the salt B3 was used without further purification.

General procedure for synthesis of single-ion conductors. PMHS was added into a pre-dried flask equipped with a condenser. The desired amount of CECA and borate salt monomers were charged into the flask followed by 10 mL anhydrous CH₃CN and 0.2 mL Pt catalyst. The reaction mixture was stirred at 90 °C. The completion of the reaction was judged by ¹H NMR. The mixture was condensed and the residue was dissolved in THF and precipitated in water 3 times. Then the polymer was dissolved in acetone and precipitated in toluene 3 times as well. Afterwards, the product was dried in a vacuum oven at 80 °C for 24 hours. The final product is in dark color due to ppm level residual Pt catalyst. It is difficult to completely remove the catalyst possibly as a result of the strong interaction between Pt and ionomer. The exact feeding ratios of the reactants for each ionomer can be found in Table 2-2. Representative ¹H and ¹¹B NMR spectra are shown in Figure 2-2; all others are in support information Figures S2-S5. Thermogravimetric Analysis at 10K.min in nitrogen suggests these ionomers are stable to at least 180 °C.

References:

- 1. Ratner, M. A.; Shriver, D. F. Chem. Rev. 1988, 88,109.
- 2. Meyer, W. H. Adv. Mater. 1998, 10, 439.
- 3. (a) Chandrasekhar, U. Adv. Polym. Sci. 1998, 15, 140; (b) Tarascon, J. P.; Armand, M. Nature 2001 414, 359; (c) Sadoway, D. R. J. Power Sources 2004, 129, 1; (d) Armand, M.; Tarascon, J. P. Nature 2008, 451, 652; (e) Armand, M. B.; Bruce, P. G.; Forscyth, M.; Scrosati, B.; Wieczorek, W. Ch. 1 in Energy Materials edited by D. W. Bruce, D. O'Hare and R. I. Walton, Wiley 2011.

- 4. Thomas, K. E.; Sloop, S. E.; Kerr, J. B.; Newman, J. J. Power Sources 2000, 89, 132.
- 5. Wright, P. V. MRS Bull. 2002, 27, 597.
- Nagaoka, K.; Naruse, H.; Shinohara, I.; Watanabe, M. J. Polym. Sci.: Polym. Lett. Ed. 1984, 22, 659.
- 7. Walden, P. Z. Phys. Chem. 1906, 55, 207.
- (a) Zhang, L.; Zhang, Z.; Harring, S.; Straughan, M.; Butorac, R.; Chen, Z.; Lyons, L.; Amine, K.; West, R. J. Mater. Chem. 2008, 18, 3713; (b) West, R. C.; Amine, K.; Zhang, Z.; Wang, Q.; Vissers, D. R. U.S. Patent 2006035154 A1; (c) Rossi, N. A. A.; Zhang, Z.; Schneider, Y.; Morcom, K.; Lyons, L.; Wang, Q.; Amine, K.; West, R. Chem. Mater. 2006, 18, 1289; (d) Zhang, Z.; Lyons, L. J.; Jin, J. J.; Amine, K.; West, R. Chem. Mater. 2005, 17, 5646; (e) Zhang, Z.; Lyons, L. J.; West, R; Amine, K. and West, R. Silicon Chemistry 2005, 3, 259; (f) Oh, B.; West, R. and Amine, K. U.S. Patent 7588859 B1, 2009.
- Okanmoto, Y.; Yeh, T. F.; Lee, H. S.; Skotheim, T. A. J. Polym. Sci.: Part A: Polym. Chem. 1993, 31, 2573.
- 10. Siska, D. P.; Shriver, D. F. Chem. Mater. 2001, 13, 4698.
- Snyder, J. F.; Hutchison, J. C.; Ratner, M. A.; Shriver, D. F. Chem. Mater. 2003, 15, 4223.
- Kerr, J. B. Ch. 19 in *Lithium Batteries Science and Technology* edited by G.-A. Nazri and G. Pistoia, Kluwer Academic, Boston, 2004.
- 13. (a) Fujinami, T.; Tokimune, A.; Mehta, M. A.; Shriver, D. F.; Rawsky, G. C. Chem. Mater. 1997, 9, 2236; (b) Fujinami, T.; Buzoujima, Y. J. Power Sources 2003, 119-121, 438.

- 14. (a) Xu, W.; Williams, M. D. and Angell, A. *Chem. Mater.* 2002, *14*, 401; (b) Xu, W.; Angell, A. *Electrochim. Acta* 2003, *48*, 2029; (c) Sun, X; Kerr, J. B. *Macromolecules* 2006, *39*, 362; (d) Aravindan, V.; Vickraman, P. *Solid State Sciences* 2007, *9*, 1069; (4) Matsumi, N.; Ohno, H. *Main Group Chemistry* 2006, *5*, 297; (f) Matsumi, N.; Sugai, K.; Saramoto, K.; Mizumo, T.; Ohno, H. *Macromolecules* 2005, *38*, 4951; (g) Aoki, T.; Konna, A.; Fujinami, T. *Electrochim. Acta* 2004, *43*, 7764.
- Besner, S.; Vallee, A.; Bouchard, G.; Prud'homme, J. Macromolecules 1992, 25, 6480.
- 16. Shacklette, L. W. EP 122381 A1 19841024, 1984.
- 17. Nagai, T.; Matsumoto, K.; Kajita, K. JP 61214364 A 19860924, 1986.
- 18. Barthel, J.; Schmid, A. and Gores, H. J. J. Electrochem. Soc. 2000, 147, 21.
- Bhattacharyya, D. N.; Lee, C. L.; Smid, J. and Szwarc, M. J. Phys. Chem. 1965, 69, 608.
- 20. (a) Klemann, L.P. and Newman, G.H. U.S. Patent 4, 060, 674, 1977; (b) Klemann,
 L.P. and Newman, G.H. U.S. Patent 4, 104, 451, 1978; Klemann, L.P.; Newman,
 G.H. Stogryn, E. L. U.S. Patent 4, 139, 681, 1979.
- 21. Pearson, R. G. J. Amer. Chem. Soc. 1963, 85, 3553,
- 22. Gray, F. M. Solid Polymer Electrolytes: Fundamentals and Technological Applications VCH Publishers, Inc. **1991**.
- 23. Liu, W.; Janik, M. J. and Colby, R. H. ACS Symposium Series, submitted (2011).
- 24. Salomon, M. Electrochim. Acta 1985, 30, 1021.
- Kida, Y.; Yanagida, K.; Yonai, A.; Funahashi, A.; Nohma, T. Yonezu, I. U.S. Patent 6, 537, 697 B2, 2003

- 26. Crawford, C.L.; Barnes, M.J.; Peterson, R.A.; Wilmarth, W.R.; Hyder, M.L. Journal of Organometallic Chemistry **1999**, 581, 194.
- Duclot, M.; Alloin, F.; Brylev, O.; Sanchez, J. Y.; Souquet, J. L. Solid State Ionics
 2000, 136-137, 1153.
- Klein, R. J.; Zhang, S.; Dou, S.; Jones, B. H.; Colby, R. H.; Runt, J. J. Chem. Phys.
 2006, 124, 144903.
- 29. Fragiadakis, D.; Dou, S.; Colby, R. H.; Runt, J. Macromolecules 2008, 41, 5725.
- 30. Fragiadakis, D.; Dou, S.; Colby, R. H.; Runt, J. J. Chem. Phys. 2009, 130, 064907.
- Dou, S.; Zhang, S.; Klein, R. J.; Runt, J. and Colby, R. H. *Chem. Mater.* 2006, *18*, 4288.
- Chernyak, Y. J. Chem. Eng. Data 2006, 51, 416; Payne, R. and Theodorou, I. E. J. Phys. Chem. 1972, 20, 2892.
- Zhu, Z.; Einset, A. G.; Yang, C-Y, Chen, W-Y; Wnek, G. E. *Macromolecules* 1994, 27, 4076.
- Wang, Y-J.; Liang, S.; Liu, W.; Choi, U H. and Colby, R. H. Polymer Preprints 2009, 50 (2), 866.
- Sablong, R.; Vlugt, J. I. V. D.; Thomann, R.; Mecking, S.; Vogt, D. Adv. Synth. Catal. 2005, 347, 633.
- Noth, H. and Wrackmeyer, B. Nuclear Magnetic Resonance Spectroscopy of Boron Compounds Springer-Verlag, New York 1978.
- Romanato, P.; Dutwyler, S.; Linden, A.; Baldridge, K. K.; and Siegle, J. S. J. Amer. Chem. Soc. 2010, 132, 7828–7829
- 38. Eisenberg, A. and Kim, J.-S. *Introduction to Ionomers*, Wiley, New York **1998**.

- Wang, W.; Tudryn, G. T.; Colby, R. H.; Winey, K. I. J. Amer. Chem. Soc. 2011, 133, 10826.
- 40. Bruce, P. G.; Gray, F. M. Solid State Electrochemistry Cambridge, 1995.
- 41. Klein, R. J.; Welna, D. T.; Weikel, A. C.; Allcock, H. R. and Runt, J. Macromolecules 2007, 40, 3990.
- Meziane, R.; Bonnet, J.-P.; Courty, M.; Djellab, K.; Armand, M. *Electrochim. Acta* 2011, 57, 14.
- Shaplov, A. S.; Vlasov, P. S.; Armand, M.; Lozinskaya, E. I.; Ponkratov, D. O.; Malyshkina, I. A.; Vidal, F.; Okatova, O. V.; Pavlov, G. M.; Wandrey, C.; Godovikova, I. A.; Vygodskii, Y. S. *Polym. Chem.* 2011, *2*, 2609.
- Shaplov, A. S.; Lozinskaya, E. I.; Ponkratov, D. O.; Malyshkina, I. A.; Vidal, F.; Aubert, P.-H.; Okatova, O. V.; Pavlov, G. M.; Komarova, L. I.; Wandrey, C.; Vygodskii, Y. S. *Electrochim. Acta* 2011, *57*, 74.

Chapter 3

Synthesis and Lithium Ion Conduction of Ionomer blends Containing Polysiloxane-based Single-ion Conductor and Non-Volatile Plasticizers

3.1 Introduction

Polymer electrolytes as energy materials are of great interest for lithium-ion battery, fuel cell, solar cell and actuator applications, due to the inherent polymeric merits, e. g. mechanical strength and ease of processing to make thin film membranes. Among different types of polymer electrolytes, single-ion conductors with one type of ion covalently bonded to the polymer backbone have recently attracted much attention, owing to the advantages of unity lithium ion transference number and elimination of detrimental anion polarization.^{1, 2}

Our group recently reported novel borate-containing single-ion conductors.³ The ionomers containing tetraphenyl borate salts or derivatives are proved to have so far the lowest conducting ion activation energy; while the low conductivity due to high T_g and low ion mobility hinders their practical application. The ionic groups attached to the polymer backbone apparently slow down the segmental motion of the polymer.⁴ In polymer electrolytes, ion motion is usually coupled to polymer chain segmental motion.⁵⁻

Different approaches have been tested to improve the conductivity of polymer electrolytes such as addition of nanoparticles⁸⁻¹⁰ and utilization of plasticizers.¹¹⁻¹³ When mixing with single-ion conductors, plasticizers can solvate Li⁺ and transport with this small cation, significantly weakening ionic interactions and lowering T_g. Poly(ethylene glycol) has proved to be an efficient ion conduction promoter due to the electron donor ability of ether oxygen atoms, forming specific interaction with lithium ion and breaking ion aggregates.¹⁴ In industry, mixtures of different carbonates have been used as plasticizers partly due to a combination of strong solvation and high dielectric constant, therefore promoting ion dissociation. However safety issues caused by evaporation and leakage of those small-molecule carbonates prompt scientists to pursue non-volatile alternates. In our group¹⁵, a non-volatile plasticizer, polyethylene glycol (PEG) with number-average molecular weight of 600, has been shown to greatly enhance conductivity of cyclic carbonate-based single-ion conductors; while crystallization of the PEG oligomers around room temperature led to an abrupt drop in conductivity at lower temperatures, if more than ~40 wt% PEG is added. Poly(ethylene glycol) oligomers have also proven to be efficient plasticizers by many other groups.¹⁶⁻²⁰

This paper explores non-volatile oligomers with ether-oxygens (lower T_g , lower polarity and stronger solvation) and cyclic carbonates (higher T_g , higher polarity and some solvation) as plasticizers. The resulting polymer single-ion conductors blended with these plasticizers exhibit improved conductivity. Furthermore, no conduction loss due to crystallization was observed, allowing a wider temperature range for application. Analysis of electrode polarization of these plasticized single-ion conductors allows

quantification of the enhanced mobility (arising from lower Tg) and enhanced population of conducting ions and dielectric constant (from ion solvation and increased polarity).

3.2 Result and discussion

3.2.1 Synthesis

The siloxane homopolymers with PEO₃ side chains (CP-0) and cyclic carbonate side chains (CP-100) and copolymer plasticizers(CP-19, 33, 45, 80) were synthesized by hydrosilylation using a method described in ref. 3 (Scheme 3-1). The compositions of the copolymer plasticizers shown in Table 3-1 were determined by the integrated areas of ¹H f

NMR peaks in Figure 3-1:

$$r = \frac{a/2 - d/3}{a/2}.$$



Scheme 3-1. Synthesis of siloxane copolymer plasticizers CP-(19, 33, 60, 80).
As seen in Table 1, the molecular weight of these siloxane oligomers are slightly larger than 10000. To achieve lower viscosity and maintain low vapor pressure, five plasticizers with $300 < M_n < 700$ were also synthesized.

The oligomer plasticizer 1 (OP-1) was synthesized by condensation reaction with triethyl amine as acid scavenger (**Scheme 3-2**). The resulting product (OP-1) has Si-OR bonds which make OP-1 moisture sensitive.

During the first attempt to synthesize of OP-2 and OP-3 (**Scheme 3-3**), platinum catalyst which works for most of hydrosilylation reactions gave nearly no reaction. Rh catalyst suggested by Hartwig et al.²¹ exhibited better catalyzing capability. The hydrosilylation for the second SiH didn't start until all the first SiH groups were consumed, which has been confirmed by ¹H NMR.



Figure 3-1. Representative ¹H NMR of copolymer plasticizer.



Scheme 3-2. Synthesis of oligomer plasticizer OP-1.



Scheme 3-3. Synthesis of oligomer plasticizer OP-2 and OP-3.

	CP-0	CP-19	CP-31	CP-57	CP-80	CP-100
f^{a}	0	18.4	29.8	56.5	79.6	100
f ^b	0	19.5	32.4	58.8	79.9	100
Molecular weight ^c	12400	12000	11700	11200	10700	10200
T _g of pure polar copolymer (K)	193	205	210	226	234	243
T _g of pure ionomer (K) (14mol% of borate)				301		
T _g of blends with 20 wt% ionomer (K)	N/A	210	217	227	238	251

Table 3-1. Compositions and glass transition temperatures of copolymer plasticizers and the resulting polymer single-ion conductor/plasticizer blends.

a. Calculated by the method using the integrated area of peaks a and d: $f = \frac{a/2 - d/3}{a/2}.$

b. Calculated by the method using the integrated area of peaks n and d: $f = \frac{o}{o + d/3}.$

c. Number-average Mw, calculated by the composition f, assuming

number-average DP=36.

The synthesis of OP-4 (**Scheme 3-4**) is straightforward. The reaction was not possible to stop at the monosubstitution state, even with excess dihydrosilane. Plasticizer OP-5 provides a material with ester linkages and no silicon (**Scheme 3-5**).



Scheme 3-4. Synthesis of oligomer plasticizer OP-4.



Scheme 3-5. Synthesis of oligomer plasticizer OP-5.

3.2.2 Glass transition temperature

The T_gs of copolymer plasticizers and their blends were calculated by the Fox

equation
$$\frac{1}{T_g} = \frac{\varphi_{ionomer}}{T_{g\,ionomer}} + (1 - \varphi_{ionomer})(\frac{1-f}{T_{g\,CP-0}} + \frac{f}{T_{g\,CP-100}})$$
, and

compared with DSC data in Figure 2. Glass transition temperatures (T_g) of copolymer plasticizers (with Φ *ionomer* = 0) increase with increasing polar carbonate group content *f*. The copolymer T_g data are above the Fox prediction which might indicate favorable interaction between PEO and cyclic carbonate (CECA) units. The 20 wt% ionomer/80 wt% plasticizer blends prepared by mixing with single-ion conductors synthesized in our group display higher T_g than plain plasticizers, because the ionomer has significantly higher T_g =301 K. The blend T_g data are below Fox equation prediction, providing the first indication that the copolymer plasticizers are breaking the ion aggregates present in the pure ionomer.

The five oligomeric plasticizers show Tg similar to the copolymer plasticizer with $f \approx$ 0.5, all with $213 \le T_g \le 219$ K. These oligomers were blended with 20 wt% of 49 mol% borate ionomer resulting in mixtures with $225 \le T_g \le 230$ K.



Figure 3-2. T_g of copolymer plasticizers and resulting blends (80 wt% of plasticizer and 20 wt% of 14 mol% ionomer) as a function of CECA molar content in the plasticizers.

Table 3-2 .	Compositions	and glass	transition	temperatures	of oligomer	r plasticizers	and
the resulting	g polymer sing	le-ion con	ductor/plas	sticizer blends			

	OP-1	OP-2	OP-3	OP-4	OP-5
Molecular Weight	626	695	651	450	334
T _g of pure oligomer (K)	213	213	214	219	216
T _g of pure ionomer (K) (49 mol%, borate)	No T _g de	tected in a	range of 2	240 to 473	K
T _g of blends with 20 wt% ionomer (K)	230	225	228	230	226

3.2.3 Ionic conductivities and dielectric properties

Electrode Polarization happens when mobile conducting species respond to external electric field and migrate to electrodes, resulting in build-up internal electric field, increased dielectric constant and decreased conductivity. Utilization of a physical model to analyze electrode polarization (EP) has been developed and practiced in our group for single-ion conductors above T_{g} .²² In this mode, the loss tangent curves associated with electrode polarization are fit to the following Debye equation

$$\tan \delta = \frac{\omega \tau_{EP}}{1 + \omega^2 \tau_{\sigma} \tau_{EP}}.$$

Then the number density of simultaneously conducting ions p and their mobility μ can be determined from the time scale for electrode polarization τ_{EP} and the time scale for diffusive ion motion τ_{σ}

$$p = \frac{1}{\pi l_B L^2} \left(\frac{\tau_{EP}}{\tau_{\sigma}}\right)^2$$
$$\mu = \frac{eL^2 \tau_{\sigma}}{4\tau_{EP}^2 kT},$$

wherein $l_B \equiv e^2 / (4\pi\varepsilon_s \varepsilon_0 kT)$ is the Bjerrum length, *L* is the spacing between electrodes, *k* is the Boltzmann constant, and *T* is absolute temperature.



Figure 3-3. Temperature dependence of ionic conductivity for the 14 mol% borate ionomer and its blends with siloxane copolymer plasticizers that are 80 wt% plasticizer/20 wt% ionomer, (a) as a function of 1/T; (b) as a function of T_g/T .

Blends of single-ion conductors with copolymer plasticizers demonstrate much higher conductivity than the neat ionomer (10^{-6} S/cm vs 10^{-11} S/cm at room temperature) (**Figure 3-3**). This enhanced conductivity is partly from lowering T_g (reflected in mobility **Figure 3-4**) and partly from solvation (reflected in the number density of simultaneous charge carriers **Figure 3-5**).

Electrode polarization (EP) analysis indicates that (**Figure 3-4**) at high temperature, the higher the polar carbonate group contents, the faster the ion mobility. When temperature is lower than 10 $^{\circ}$ C, the order is reversed because ion mobility of polymer electrolytes is coupled to polymer chain segmental motion (T_g). Therefore more polar groups with stronger dipole-dipole interaction lead to slower ion mobility at low temperatures due to higher T_g.



Figure 3-4. Temperature dependence of conducting ion mobility for the 14 mol% borate ionomer and its blends with siloxane copolymer plasticizers that are 80 wt% plasticizer/20 wt% ionomer.

Table 3-3. Ion activation energy of 14 mol% borate ionomer and its blends with siloxanecopolymer plasticizers that are 80 wt% plasticizer/20 wt% ionomer.

	Neat	CP-0	CP-19	CP-31	CP-57	CP-80	CP-100
	ionomer	blend	blend	blend	blend	blend	blend
Ea (kJ/mol)	21.7	20.2	20.2	10.1	9.8	11.8	9.5

Figure 3-5 shows the temperature dependence of the number density of simultaneously conducting Li^+ from the EP analysis. The pure ionomer (black squares) and its blend with CP-100 (grey hexagons) have very low conducting ion content, with

intercepts (at infinite temperature) that suggest most ions are trapped and not contributing to conduction because the borate anions microphase separate from the cyclic carbonate side chains. Incorporating just 20 wt% PEO₃ (CP-80, blue diamonds) raises the population of simultaneous conductors by roughly a factor of 10, compared with CP-100, suggesting that ether oxygens are better at breaking up the ion aggregates than cyclic carbonates. The activation energies obtained from the slopes in Figure 5 are summarized in Table 3-3. The neat ionomer and its blends with copolymers having f < 0.2 (CP-0 and CP-19) have roughly twice the activation energy that the blends with higher carbonate content copolymers (f > 0.3) display. This suggests that while ether oxygens are needed to break up the ion aggregates, cyclic carbonates are lowering the activation energy of the conducting ions, presumably because they are significantly more polar.

Table 3-4. Viscosity of plasticizers measured at 21 °C.

	CP-0	CP-19	CP-31	CP-57	CP- 80	CP 100	OP-1	OP-2	OP-3	OP-4	OP-5	PEG 600
Viscosit												
у												
(Pa.s)	.70	.83	.39	.21	4.8	8.6	.18	.51	.87	.30	.22	.19
21°C												
CECA		16	29	55	76	100	51	46	49	67	52 ^a	0
content												
wt %												

a. Carbonate content



Figure 3-5. Temperature dependence of conducting ion concentration for the 14 mol% borate ionomer and its blends with siloxane copolymer plasticizers that are 80 wt% plasticizer/ 20 wt% ionomer.

The highest conductivity at room temperature for 20 wt% ionomer blends with copolymer plasticizers is around 10^{-6} S/cm. It is lower than those of the blends with PEG 600 having similar ion content, which can be explained by Walden's rule ²⁴ that electrolyte conductivity is inversely proportional to electrolyte viscosity. This has been validated by the viscosity value of those plasticizers in Table 4. The viscosities of copolymers with $M_n > 10K$ are significantly higher than those of oligomeric plasticizers. The conductivities of polymer single-ion conductor blends with low viscosity oligomer plasticizers have been boosted to as high as 10^{-5} S/cm (**Figure 3-6**) around room temperature. The highest conductivity was achieved by the OP-1 blend, which has the most flexible structure, and thus lowest viscosity. The correlation of conductivity with

plasticizer viscosity instead of T_g suggests that the smaller plasticizers travel with the Li⁺ counterions (at least partly) as they conduct, diminishing the connection between ion conductivity and segmental motion and weakening the temperature dependence of conducting ion mobility.



Figure 3-6. Temperature dependence of ionic conductivity for the 49 mol% borate ionomer and its blends with oligomeric plasticizers and a mixture of propylene carbonate and ethylene carbonate (1:1) that are 80 wt% plasticizer/20 wt% ionomer.

Compared with blends of copolymer plasticizers, the blends of oligomeric plasticizers show similar conducting ion content and ion mobility across the whole temperature range. For comparison, this same 49 mol% borate ionomer was blended with a 1: 1 mixture of propylene carbonate : ethylene carbonate, displaying a large increase in conductivity (at room temperature from 5 x10⁻⁵ to 4x10⁻⁴ S/cm, **Figure 3-6**) with a weak

temperature dependence. The conducting ion content of this blend with small molecule carbonates is similar to those of blends with oligomeric plasticizers, which may suggest that ion solvation has reached its limit with all of these plasticizers (**Figure 3-88**). Therefore the very high ion mobility imparted by the small molecule carbonates, ~ 5×10^{-3} cm²/Vs (**Figure 3-7**) that is surprisingly insensitive to temperature, accounts for the high conductivity with these small molecule plasticizers and has a markedly weaker temperature dependence because the solvating small carbonates can fully move with the Li cation, decoupling its dependence on polymer segmental motion.



Figure 3-7. Temperature dependence of ion mobility for the 49 mol% borate ionomer and its blends with oligomeric plasticizers and a 1:1 mixture of propylene carbonate and ethylene carbonate that are 80 wt% plasticizer/20 wt% ionomer.



Figure 3-8. Temperature dependence of conducting ion concentration for the 49 mol% borate ionomer and its blends with oligomeric plasticizers and mixture of propylene carbonate and ethylene carbonate (1:1) that are 80 wt% plasticizer/20 wt% ionomer.



Figure 3-9. Static dielectric constants of copolymer plasticizers, the 14 mol% borate ionomer and its blends with copolymer plasticizers that are 80 wt% plasticizer/20 wt% ionomer as a function of temperature. For the pure ionomer, (black symbols), the data are not reasonable due to the high T_g making it difficult to prepare a good sample.



Figure 3-10. Temperature dependence of static dielectric constants of oligomer plasticizers (filled symbols) and their blends with copolymer plasticizers (open symbols) that are 80 wt% plasticizer/20 wt% of the 49 mol% ionomer.

The static dielectric constant data obtained through EP analysis indicate that (**Figure 3-9**) the copolymers with higher polar group content have higher dielectric constant (CP-100 > CP-80 > CP-57 > CP-31 > CP-19 > CP-0). When blended with single-ion

conductors, the ionic groups enhance the dielectric constant. The five oligomeric plasticizers (**Figure 3-10**) show an even stronger enhancement of dielectric constant on blending with the ionomer, suggesting that these smaller molecules are better at breaking up the ion aggregates.



Figure 3-11. Static dielectric constants at 298 K of copolymer plasticizers (open symbols) and their blends (filled symbols) that are 20 wt % of the14 mol% borate ionomer (filled black square) as a function of cyclic carbonate (CECA) content f in the random copolymer.

The 300 K static dielectric constants of copolymer plasticizers and blends have been plotted in **Figure 3-11** as a function of carbonate content in the copolymer *f*. The data can be fit very well with an empirical blending rule, shown as the solid curve in Figure 3-3-11.

$$\varepsilon_s = \frac{(1-f)\varepsilon_{CP-0} + 0.55f\varepsilon_{CP-100}}{1-0.45f}$$

 $\mathcal{E}_{CP-0} = 5$ is the static dielectric constant of the PEO₃ siloxane homopolymer. $\mathcal{E}_{CP-100} =$ 43 is the static dielectric constant of the cyclic carbonate siloxane homopolymer. The blends show \mathcal{E}_s above the pure copolymers, indicating contributions from the ionomers.

3.3 Conclusions:

We synthesized two groups of non-volatile plasticizers composed of highly polar cyclic carbonate and short ethylene oxide chains. Polymer single-ion conductor blends containing those plasticizers and borate ionomers have room temperature conductivity varying from 10^{-7} to 10^{-5} S/cm, always a great enhancement compared to the neat ionomer. The plasticizers lower T_g allowing enhanced mobility and boost simultaneously conducting ion content by Li⁺ solvation. Those blends are potential candidates as precursors to make gel polymer electrolytes for lithium-ion rechargeable battery separators, however they are not nearly as good as the benchmark plasticizer: EC:PC (1:1) because those small molecules can travel with the lithium ion and decouple its motion from the segmental motion of the polymer.

The analysis supports that conductivities of polymer electrolytes are determined by both viscosity and structures of the plasticizers. So the future research should be focused on reducing the viscosity of oligomer plasticizer and at the same time keeping its nonvolatile character.

3.4 Experimental

Materials. Dichloromethane, diethyl carbonate, chlorodimethylsilane, NEt₃, tetraethylene glycol, potassium carbonate, 2-(2-vinyloxy) ethoxy) ethanol, diethyl carbonate, toluene and anhydrous acetonitrile were purchased from VWR and used without further purification. Platinum divinyltetramethyldisiloxane complex (Pt[dvs]) (3% in xylene) catalyst, diethyldihydrosilane, tri(ethylene glycol) divinyl ether, di(ethylene glycol) divinyl ether, RhCl(PPh₃)₃ and polymethylhydrosiloxane (PMHS, M_n = 1700 - 3200) were purchased from Aldrich and used as received. Tetrahydrofuran (THF) from EMD Chemicals was refluxed over sodium metal before use. The polysiloxane-based ionomer was prepared by the method reported in ref. 3 with ion content s of either 14 mol% or 49 mol%.

Characterization. ¹H, ¹³C and ²⁹Si NMR spectra were recorded on a Bruker AM 300M spectrometer. Glass transition temperatures (T_g) were determined using a TA Q100 differential scanning calorimeter (DSC) with 10 K/min heating and cooling rates. For dielectric and conductometric measurements, samples were sandwiched between two polished brass electrodes with 50 µm silica spacers placed on top of the sample under < 1 mTorr vacuum at 80 °C for at least 24 h. The sandwiched samples were positioned in a Novocontrol GmbH Concept 40 broadband dielectric spectrometer and the dielectric permittivity and conductivity were measured using an AC voltage amplitude of 0.1 V and $10^{-2} - 10^7$ Hz frequency range. Each sample was annealed in the Novocontrol at 120 °C in a heated stream of dry nitrogen for 1 hour prior to measurements to drive off any

moisture picked up during loading of these hygroscopic materials. Data were collected in isothermal frequency sweeps from 120 °C to near T_g.

Cyclic [(allyloxy) methyl] ethylene ester carbonic acid (CECA). CECA was prepared according to the method reported in ref. 3. Potassium carbonate (3 g, 21.7 mmol) was added to a mixture of 3-(allyloxy)-propane-1, 2-diol (92.475 g, 0.1875 mol) and diethyl carbonate (24.75 g, 0.1875 mol). After stirring at 120 °C for 24h, the mixture was filtered to isolate the solid. The residue was purified by Kügelrohr distillation to isolate the pure product as a colorless liquid (23.7 g, 80%). ¹H NMR (in CDCl₃), δ (ppm) 5.87 (m, 1H, C=CH), 5.25 (d, 1H, cis H of CH₂=C), 5.14 (d, 1H, trans H of CH₂=C), 4.86 (m, 1H, CCH(C)O), 4.38-4.55(m, 2H, CH₂C), 4.06 (m, 2H, OCH₂C=C), 3.60-3.74 (m, 2H, OCCH₂O).

Tri(ethylene glycol) allyl methyl ether (Vinyl PEO₃). Vinyl PEO₃ was prepared according to literature method. To a mixture of NaH (1.44g, 60% in mineral oil) dispersed in 20 mL dry THF was added solution of tri(ethylene glycol) methyl ether (4.7 mL, 0.03 mol) in 150mL of THF dropwise at ice-bath temperature. The mixture was stirred for 3 hours before being transferred into a solution of allyl bromide (3.58g, 0.03mol) in 20 mL dry THF. The mixture was allowed to react overnight to complete the reaction. The reaction was quenched by ice water and extracted by ethyl acetate (20 mL x3). The organic phases were combined and condensed by rotavap. The yellowish liquid was then purified by vacuum distillation to yield 5.5 g (90%). ¹H NMR (d, 2H), 3.65–3.45 (m, 12H), 3.30 (s, 3H)¹H NMR (in d6-acetone), δ (pap) 5.85(m, 1H, CH=), 5.2 (s, (d, cist H of = CH₂), 5.1 (d, trans H of = CH₂), 3.95 (d, 2H, C=CCH₂), 3.8-3.6 (m, 8H, OCH₂CH₂O), 3.35 (s, CH₃).

100). PMHS was added into a pre-dried flask equipped with a condenser. The desired amount of CECA and vinyl PEO₃ were charged into the flask followed by 20 mL anhydrous CH₃CN and 0.2 mL Pt catalyst. The reaction mixture was stirred at 70 °C. The completion of the reaction was judged by ¹H NMR. The reaction time is in the range of 2 days to 1 week. The mixture was condensed and the residue was dissolved in toluene and precipitated in hexane 3 times. Afterwards, the product was dried in a vacuum oven at 80 °C for 24 hours.²⁵

4,4'-(6,6,21,21-tetramethyl-2,7,10,13,16,19,25-heptaoxa-6,21-disilahexacosane -1,26-divl)bis (1,3-dioxolan-2-one) (OP-1) CECA (10.86g, 0.068mol), anhydrous CH₃CN (20mL) and chlorodimethylsilane (7.67g, 0.081mol) were added into a pre-dried flask. The mixture was cooled by icebath before 0.3 ml Pt catalyst was charged. The mixture was allowed to react overnight to complete the reaction. The solvent was evaporated residue distilled and the was vacuum to obtain 4-((3-(chlorodimethylsilyl)propoxy)methyl)-1,3-dioxolan-2-one as a colorless liquid (15.2g, 89%). ¹H NMR (in d6-acetone), δ(ppm) 4.95 (m, 1H, CCH(C)O), 4.4-4.6(m, 2H, CH₂C), 3.75 (m, 2H, CCH₂OCH2CH₂H₂), 3.55 (m, 2H, OCH₂CH₂CH₂), 1.7 (m, 2H, OCH₂CH₂CH₂), 0.9 (m, 2H, OCH₂CH₂CH₂), 0.35 (m. CH₃); ²⁹Si NMR (in d6-acetone) 33 (s); (Figure 3-12) 13 C NMR (in d6-acetone), δ (ppm) 160, 75.1, 74.8, 74, 73.2, 23, 15, 0.2. (Figure 3-13)

4-((3-(chlorodimethylsilyl)propoxy)methyl)-1,3-dioxolan-2-one (8.7g, 0.034 mol) was added dropwise into the mixture of NEt₃ (7.5g), tetraethylene glycol (6.67g, 0.034mol) and 20 mL dry THF over 30 minutes. The reaction mixture was allowed to stir overnight to complete the reaction. The mixture was filtered to remove solid. The liquid was condensed by rotavap and further dried by vacuum oven to yield OP-1 as brown liquid (13g). ¹H NMR (in d6-acetone), 4.95 (m, 1H, CCH(C)O), 4.4-4.6(m, 2H, CH₂C), 3.75 (m, 2H, CC<u>H₂OCH₂CH₂H₂), 3.63 (s, 16 H, OCH₂CH₂O) 3.55 (m, 2H, OC<u>H₂CH₂CH₂CH₂), 1.7 (m, 2H, OCH₂C<u>H₂CH₂), 0.9 (m, 2H, OCH₂CH₂C<u>H₂), 0.35 (m. CH₃); ²⁹Si NMR (in d6-acetone) 17.57 (s). (**Figure 3-14**)</u></u></u></u>

4,4'-(6,6,22,22-tetraethyl-2,9,12,15,19,26-hexaoxa-6,22-disilaheptacosane-

1,27-diyl)bis(1,3-dioxolan-2-one) (**OP-2**) Diethyldihydrosilane (7.2g, 0.082 mol), CECA (8.4g, 0.053 mol) and 10 mL benzene were added into flask followed by 0.1g Rh catalyst. The mixture was stirred at room temperature overnight to complete the reaction. The solvent was evaporated and the residue was vacuum distilled to afford 4-((3-(diethylsilyl)propoxy)methyl)-1,3-dioxolan-2-one as colorless liquid (20g, 100%). ¹H NMR (in d6-acetone), 4.95 (m, 1H, CCH(C)O), 4.4-4.6(m, 2H, CH₂C), 3.45 to 3.8 (m, 5H, CC<u>H₂OCH₂CH₂CH₂, OC<u>H₂CH₂CH₂CH₂ and SiH), 1.64 (m, 4H, OCH₂C<u>H</u>2CH₂Si), 1 (m, 6H, OCH₂CH₂C<u>H₂ and SiCH₂), 0.67 (m, 6H, CH₃); ²⁹Si NMR (in d6-acetone) -1.38 (s). (**Figure 3-15**)</u></u></u>

4-((3-(diethylsilyl)propoxy)methyl)-1,3-dioxolan-2-one (5g, 0.02 mol) and tri(ethylene glycol) divinyl ether (2g, 0.01mol) were mixed followed by 0.1g Rh catalyst. The mixture was stirred at room temperature overnight to complete the reaction. The solvent was evaporated and the residue was washed by heptanes to afford product as brown liquid (7g). ¹H NMR (in d6-acetone), 4.95 (m, 1H, CCH(C)O), 4.4-4.6(m, 2H, CH₂C), 3.45 to 3.8 (m, 12H, CCH₂OCH₂CH₂CH₂CH₂, OCH₂CH₂CH₂CH₂ and OCH₂CH₂O), 1.64

(m, 4H, OCH₂C<u>H</u>₂CH₂Si), 1 (m, 6H, OCH₂CH₂C<u>H</u>₂ and SiCH₂), 0.67 (m, 6H, CH₃); ²⁹Si NMR (in d6-acetone) 5.25 (s). (**Figure 3-16**)

4,4'-(6,6,20,20-tetraethyl-2,9,13,17,24-pentaoxa-6,20-disilapentacosane-1,25diyl)bis(1,3-dioxolan-2-one) (OP-3). The same procedure as synthesis of OP-2 was used with di(ethylene glycol) divinyl ether as linker. ¹H NMR (in d6-acetone), 4.95 (m, 1H, CCH(C)O), 4.4-4.6(m, 2H, CH₂C), 3.45 to 3.8 (m, 10H, CC<u>H₂OCH₂CH₂CH₂CH₂CH₂, OC<u>H₂CH₂CH₂ and OCH₂CH₂O), 1.64 (m, 4H, OCH₂C<u>H₂CH₂Si), 1 (m, 6H, OCH₂CH₂CH₂ and SiCH₂), 0.67 (m, 6H, CH₃) (Figure 3-17)</u></u></u>

Sample Preparation. Polysiloxane-based ionomer and plasticizers were weighted into 10 mL vials to make final product contain 20 wt% ionomer. The mixtures were dissolved by acetone to give a homogenous solution. The solvent was evaporated by rotavap and the residue was further dried in a vacuum oven overnight at 80 °C before testing.

Viscosity Measurement. Linear viscoelastic measurements were conducted with Advanced Rheometric Expansion System (ARES, Rheometric Scientific). Parallel plates with diameters of 25mm, were utilized to conduct dynamic frequency sweeps at room temperature (21 °C). Strain lower than 10% were applied and confirmed to be in the linear response region.



Figure 3-12. ¹H NMR of 4-((3-(chlorodimethylsilyl)propoxy)methyl)-1,3-dioxolan-2one. Inset is ²⁹Si NMR.



Figure 3-13. ¹³C NMR of 4-((3-(chlorodimethylsilyl)propoxy)methyl)-1,3-dioxolan-2one.



Figure 3-14. ¹H NMR of OP-1. Inset is ²⁹Si NMR



Figure 3-15. ¹H NMR of 4-((3-(diethylsilyl)propoxy)methyl)-1,3-dioxolan-2-one. Inset is ²⁹Si NMR.



Figure 3-16. ¹H NMR of OP-2. Inset is ²⁹Si NMR.



Figure 3-17. ¹H NMR of OP-3.

References:

- 1. Thomas, K. E.; Sloop, S. E.; Kerr, J. B.; Newman, J. J. Power Sources 2000, 89, 132.
- 2. Wright, P. V. MRS Bull. 2002, 27, 597.
- 3. Liang, S.; Choi, U H.; Liu, W.; Runt J. and Colby, R. H. *Chemistry of Materials*, **2012**, *24*, 2316.
- 4. Eisenberg, A.; Kim, J.-S., Introduction to Ionomers. Wiley: New York, 1998
- 5. Ratner, M. A.; Shriver, D. F. Chem. Rev. 1988, 88,109.

- 6. Fragiadakis, D.; Dou, S.; Colby, R. H.; Runt, J. Macromolecules 2008, 41, 5725.
- 7. Bruce, P. G.; Gray, F. M. Solid State Electrochemistry Cambridge, 1995.
- 8. Kurian, M.; Galvin, M. E.; Trapa, P. E.; Sadoway, D. R. and Mayes, A. M. *Electrochimica Acta* **2005**, *50*, 2125.
- 9. Stephan, M. A.; Nahm, K.S. Polymer 2006, 47, 5952.
- 10. Croce, F.; Appetecchi, G. B.; Persi, L.; and Scrosati, B. Nature 1998, 394, 456.
- 11. Song, J. Y.; Wang, Y.Y.; Wan, C.C.; J. Power Sources 1999, 77, 183.
- 12. Stephan, M. A European Polymer Journal 2006, 42, 21.
- Zhang, P.; Li, Y.; He, D.; Wu, Y. and Makoto, S. Acta Polymerica Sinica 2011, 2, 125.
- 14. MacCallum, J.R. and Vincent, C.A. *Polymer Electrolyte review 1* Elsevier Applied Science, **1987.**

15. Choi, UH.; Liang, S. O'Reilly, M.; Winey, K. I.; Runt J. and Colby, R. H to be submitted.

16. Pradhan, D. K.; Choudhary, R.N.P.; Samantaray, B.K. *Materials Chemistry and Physics* **2009**, *115*, 557.

 Ito, Y.; Kanehori, K.; Miyauchi, K.; Kudo, T. Journal of Materials Science 1987, 22, 1845.

18. Lee, J. Y.; Lee, Y. M.; Bhattacharya, B.; Nho, Y.-C.; Park, J.-K. *Journal of Solid State Electrochemistry* **2009**, *14*, 1445.

19. Kaneko, F.; Wada, S.; Nakayama, M.; Wakihara, M.; Koki, J.; Kuroki, S. Advanced Functional Materials 2009, 19, 918

20. Li, Y.; Wang, J.; Tang, J.; Liu, Y.; He, Y. Journal of Power Sources 2009, 187, 305.

- 21. Tsukada, N. and Hartwig, J. F. J. Am. Chem. Soc. 2005, 127, 5022.
- 22. (a) Klein, R. J.; Zhang, S.; Dou, S.; Jones, B. H.; Colby, R. H.; Runt, J. J. Chem. Phys. 2006, 124, 144903; (b) Fragiadakis, D.; Dou, S.; Colby, R. H.; Runt, J. Macromolecules 2008, 41, 5725; (c) Fragiadakis, D.; Dou, S.; Colby, R. H.; Runt, J. J. Chem. Phys. 2009, 130, 064907.
- 23. (a) Choi, U. H.; Lee, M.; Wang, S. R.; Liu, W. J.; Winey, K. I.; Gibson, H. W.; Colby, R. H. *Macromolecules* 2012, 45, (9), 3974-3985; (b) Wang, S.; Liu, W. and Colby, R. H. *Chem. Mater.* 2011, 23, 1862.
- 24. Walden, P. Z. Phys. Chem. 1906, 55, 207.
- 25. Wang, Y-J.; Liang, S.; Liu, W.; Choi, U H. and Colby, R. H. *Polymer Preprints* 2009, *50 (2)*, 866.

Chapter 4

Synthesis and Ion Conduction of Polysiloxane Phosphonium Ionomers

4.1 Introduction

Anion exchange ionomers (AEI) have been widely used in many areas, such as water purification, antimicrobial agents, desalination and alkaline fuel cell membranes.¹⁻⁴ Recently, potential applications of AEI in the energy storage and conversion areas have prompted the study of ion conduction in AEI.^{1, 5-7} Ammonium salts were the first cations investigated in hydroxide exchange fuel cell membranes.^{1, 8} However due to the issues of poor chemical and thermal stabilities of ammonium salts, alternate salts such as phosphonium and imidazolium have attracted increasing attention.^{3, 5, 6, 9}

Phosphorus has empty 3d orbital and is more inclined to delocalize charge than nitrogen.¹⁰ The lower electronegativity of P (2.06) than N (3.07) relative to C (2.5) makes positive P of phosphonium be shielded by negative carbons, leading to less interaction between phosphonium cation and anion. Phosphonium salts naturally have weaker ionic interaction and possible higher stability and conductivity. Moreover, phosphorus-containing materials have proven to be fire-retardant.¹¹ It was found that phosphonium salts synthesized from tributylphosphine, or phosphines with longer alkyl groups, are ionic liquids.¹² Gu, et al.⁵ prepared hydroxide exchange membranes for fuel cells with a phosphonium-based ionomer. The membrane possesses superior conductivity and chemical stability. Zhou and Blumstein¹³ compared phosphonium and ammonium salts

having nearly identical structures and concluded that the phosphonium salts had better thermal and chemical stability. Long and coworkers ¹⁴ have synthesized a series of copolymers and polyurethane ionomers based on phosphonium salts. The resulting ionomers were reported stable above 300 °C.

Polysiloxane-based ionomers are one of the promising ion conducting candidates owing to their highly flexible backbone that lowers Tg, as well as the versatility of ions and polar side groups which can be attached to the polysiloxane backbone via hydrosilylation reactions. Polyanionic polysiloxane-based ionomers have been studied extensively as lithium conductors.¹⁵⁻¹⁸ Our group¹⁹ recently attached bulky tetraphenylborate anions to a polysiloxane backbone to synthesize a series of novel ionomers with very low activation energy for the conducting ions. Polysiloxane ionomers with side chains incorporating ammonium salts have been reported²⁰⁻²³ and a conductivity as high as 10⁻⁵ S/cm has been reported for the I⁻ anion.

Herein, we report the synthesis of allyltributylphosphonium bromide monomer and resulting phosphonium-containing ionomers with ion contents varying from 5 to 22mol% and different counter anions (F, Br, and bis(trifluoromethanesulfonyl)imide (TFSI)). The ionomers with TFSI show the highest conductivity and X-ray scattering results of those ionomers indicate no ion aggregation in these weak-binding phosphonium ionomers. The phosphonium ionomers with F⁻ anion display conductivity as high as 10⁻⁶ S/cm, which makes our phosphonium ionomers potential electrolyte separators the novel fluoride-ion battery²⁴.

4.2 Results and Discussion

4.2.1 Synthesis and ion exchange



Scheme 4-1. Synthesis of tri(ethylene glycol) allyl methyl ether (PEO₃), allyltributylphosphonium bromide (ATPB) and ionomers P-Br-5(8, 11, 22).

Scheme 4-1 shows the synthesis of the monomers and ionomers. No solvent was involved in the synthesis of allyltributylphosphonium bromide (ATPB). The allyltributylphosphonium bromide was prepared under "dry" conditions with very good yield (90%), which provides an economical and facile avenue for the preparation of phosphonium-based ionic liquids. The polymer synthesis reaction was monitored by proton NMR spectroscopy and completion of the reaction was confirmed when there was no further change of the integrated area of the peak at \sim 4.7 ppm, which is assigned to the

Si-H group. The compositions of these phosphonium ionomers were determined by the ratio of the integrated areas of the peaks at 0.6 ppm and 2.6 ppm assigned to SiCH₂CH₂CH₂O and PCH₂CH₂CH₂CH₃ respectively (Figure 4-1). The ³¹P NMR spectrum of the monomer ATPB shifts downfield from -32ppm for tributylphosphine ²⁵ to around 35 ppm, consistent with the literature.^{13c} After the hydrosilylation reaction, the ³¹P NMR spectra of the ionomers (see Figure S3, in supporting information) display a single peak at 35.4 ppm, nearly identical to that of the ATPB monomer, suggesting intact phosphonium salts after the chemical reaction.



Figure 4-1. Representative ¹H NMR spectrum of the phosphonium ionomer with Branion (n / (n + m) = 0.05), with the inset showing the ³¹P NMR spectrum (top left).

Aqueous solutions of PSPE-Br-5(8, 11, 22) are cloudy and colloid-like. When the Br anions were replaced by TFSI, the solutions turned more turbid. This is partially consistent with Ye and Elabd's observation²⁶ that imidazolium ionomers with bromide anions are water soluble, while the same ionomers with TFSI anions are insoluble in water. This phenomenon results from the combined effects of large hydrophobic butyl groups, weaker ionic interaction between phosphonium and TFSI, and the water miscibility imparted by PEO side groups.

When Br- is replaced by F-, it was found that the ionomers with high ionic content (>11 mol%) were unstable in aqueous solution for a long time. Some ionic groups were lost as confirmed by proton NMR spectra (see table 1), which might be explained by the strong nucleophilicity of the fluoride anion. The phosphonium ionomers can be completely decomposed by OH- in aqueous solution due to the fact that polysiloxane is unstable in strong base condition.

	Anion	Anion Composition		Ion Conten $(10^{20} \text{ cm}^{-3})$	t	$DSC T (^{0}C)$	Conductivity
		n	m	Theoretical prediction ^a	NMR ^b	$DSC I_g(C)$	(µ S/chi, @ 30 °C)
PSPE_Br_5		5	95	1.15	1.15	-75	0.56
PSPE_Br_8		8	92	1.83	1.83	-75	0.75
PSPE_Br_11	Br	11	89	2.28	2.28	-74	0.68
PSPE_Br_22		22	78	4.41	4.41	-74	1.44
PSPE_TFSI_5		5	95	1.16	1.16	-74	10.9

Table 4-1. Physical properties of phosphonium ionomers

PSPE_TFSI_8	TFSI	8	92	1.83	1.83	-73	31.2
DODE TEQL	-	1	20	2.20	2.29	70	21.2
PSPE_IFSI		1	89	2.28	2.28	-/0	21.2
-11 DSDE E 5		5	05	1 16	1 16	80	0.10
		5)5	1.10	1.10	-00	0.17
PSPE_F_8		8	92	1.83	1.83	-79	0.2
	F						
PSPE_F_11		11	89	2.28	2.1	-79	0.17
PSPE F 22	-	22	78	4 4 1	12	-73	0.74
		22	70	1.71	1.2	,5	0.74

a. Values are based on the analysis of NMR results of ionomers with Br- as the counter ion. For ionomers with different counter ions, the ion contents are assumed to be the same.

b. Values calculated from NMR were determined by the ratio of integrated area of the peaks at 0.6 ppm and 2.6 ppm.

4.2.2 Glass transition temperature and thermal stability

Table 4 - 1 shows DSC Tgs of the phosphonium ionomers with different anions and varying ion content. For each anionic counterion, as ion content increases, Tg stays almost the same within experiment uncertainty. Chen, et al^{14c} observed the same behavior for their phosphonium ionomers with ion contents up to 21%. As will be shown in the next section, this is very likely a consequence of negligible ion aggregation in our ionomers, thus no limitation of chain segmental motion by physical ionic crosslinkings.

It was reported²⁶ that when counter anions were exchanged from bromide to TFSI, Tg of imidazolium ionomers decreased substantially, owing to a plasticizing effect of TFSI and much weaker ionic interactions between TFSI and imidazolium. It is worth to point out that, when ion content is lower than 11%, at the same ion content, our phosphonium ionomers with TFSI counterions exhibit similar Tg but superior

91

conductivity to the ionomers containing Br or F anions. The backbone of our phosphonium ionomers is polysiloxane, the most flexible polymer chain, which endows our ionomers with lower Tgs than typical ionomers having C-C backbones. The low-Tg character of polysiloxane may weaken the plasticizer effect of larger anions. On the other hand, the PEO side chains attached to the polysiloxane backbone can efficiently break up ion aggregation of not only TFSI salts but also Br or F salts. Consequently, Tgs of those abovementioned phosphonium ionomers are quite close. We have recently shown that the molar volume of the side group (including the counterion) controls the Tg of this class of ionomer,²⁷ although here the PEO side chains attached to the polysiloxane backbone also play some role in making these phosphonium ionomers have Tg insensitive to counterion and ion content.

Thermal stability of phosphonium ionomers (Figure 4-2) studied by TGA exhibits similar behavior to the phosphonium ionomers reported by Long¹⁴ et al. There is no significant weight loss at temperature up to 300 °C in TGA at 10 K/min, regardless of counterion. After dielectric spectroscopy measurement, with over one hour at 120 °C, these ionomers maintain thermal stability.



Figure 4-2. TGA results of phosphonium monomer and ionomer with Br- anion.

4.2.3 Morphology

Typical ionomer small angle X-ray scattering (SAXS) patterns show evidence of ionic aggregation in the *q* range of $0.5 - 5 \text{ nm}^{-1}$.²⁸ Long, et al¹⁴ studied the morphology of several types of phosphonium ionomers. For random copolymer ionomers, wide-angle X-ray diffraction (WAXD) and SAXS experimental data didn't give clear proof of ion aggregation existing in their ionomers. For block copolymer and polyurethane phosphonium ionomers, the characteristic peaks of block and polyurethane structure obscure the peaks due to ion aggregation. As to our phosphonium ionomers, three characteristic X-ray scattering features were observed. The peaks at ~14 and 8 nm⁻¹ are amorphous halos from PEO-side chain and siloxane backbone spacing repectively.²⁹ The

peaks at $\sim 3.7 \text{ nm}^{-1}$ (Figure 4-3), corresponding to a d-spacing of 1.8 nm, are due to microphase separation of PEO oligomer side chains from polysiloxane backbones. There are no peaks assigned to ion aggregation observed but those peaks would only occur at lower q where there are effects of residual catalyst. This may be attributed to the bulky phosphonium cations and ion solvation by the PEO side chains, explaining why Tg remains low in our phosphonium ionomers through the whole ion content range.



Figure 4-3. Small angle X-ray scattering of phosphonium ionomers with bromide anions and different ion content.


Figure 4-4. Conductivity of phosphonium ionomers with different ion content as a function of temperature: (a) bromide counterion, (b) TFSI counterion, (c) fluoride counterion.

Ionic conductivity of the phosphonium single-ion conductors with different ion contents are shown in Figure 4-4. The ionomers show a weak dependence on ion content. It is well known that ion conduction in polymers is usually coupled to chain segmental motion.³⁰ As discussed in previous section, when phosphonium salts concentration increases from 5 to 22%, Tg barely changes (see Table 1-1). Therefore the conductivities

of ionomer with Br and F as counterions show abnormal behavior when normalized by Tg (not shown). Instead of falling on one curve, the ionomer with highest ion content exhibits highest conductivity, which means ion content dominates conductivity for our phosphonium-containing ionomers.

The conductivities of phosphonium ionomers with F⁻ mobile anions increase with ion content up to the highest ion content studied with target of 22 mole% phosphonium and actual $p_0 = 1.2 \times 10^{20} \text{ cm}^{-3}$ from NMR. The conductivity is as high as 10^{-6} S/cm at room temperature. It is a promising material towards the potential application as a separator for the fluoride-ion battery.



Figure 4-5. Conductivities of phosphonium ionomers with different counterions having (n / (n + m) = 0.11) ion content.

Conductivities of phosphonium ionomers with the same ion content but different anion species are shown in Figure 4-5. The conductivities of those ionomers increase with increasing counterion size: F < Br < TFSI. Ye, et al.²⁶ studied imidazolium-based polymerized ionic liquid and found conductivity of ionomers with TFSI anion was greater than those of ionomers with PF₆ or BF₄ anions. They attributed the difference to not only the size effect but also greater negative charge distribution and flexibility of TFSI anion.^{31, 32} Our electrode polarization (EP) analysis gives conducting ion activation energies (E_a) for these counterions summarized in Table 2-2. The lowest E_a of TFSI containing phosphonium ionomer is consistent with its highest conductivity, which might suggest that E_a is the key factor deciding conductivity in our low-Tg phosphonium ionomers.

Ionomer	PSPE_11_TFSI	PSPE_11_Br	PSPE_11_F
Ea [kJ/mol]	9.4	14.2	18.3
Ion Size $(Å^3)$	347	32	10
Ion Pair Energy[kJ/mol]	284	369	481

Table 4-2. Ion properties of different anions with 11 mol% ion content.

In a single dielectric relaxation spectrum experimental sweep for our phosphonium ionomers, the EP process and α relaxation cannot be fully covered in the same window. EP analysis indicates that the derivative spectra of ϵ " only exhibit one peak which is assigned to α_2 . Figure 4-6 shows that our phosphonium ionomers follow the Barton-

Nakajima-Namikawa (BNN) relation's prediction, that ionic conductivity is proportional to the product of ion motion peak relaxation frequency and the strength of that relaxation $\omega_{\alpha 2} \cdot \Delta \epsilon$. As Choi, et al.³³ and Fragiadakis, et al.³⁴ suggested, this means the ionic segmental relaxation controls ionic conductivity, as expected.



Figure 4-6. Conductivities of phosphonium ionomers as a function of the product of $\omega_{\alpha 2}$ and $\Delta \epsilon$.

4.3 Conclusions

Allyltributylphosphonium bromide has been successfully synthesized under solvent-free condition and those phosphonium salts with vinyl PEO₃ have been attached to polysiloxane backbone as side chains to produce single-ion conductors. Ion exchange has been applied to replace Br⁻ with different anions (F⁻ or TFSI⁻). The ionomers with F⁻ counterion seem stable in water (when ion content < 11 mol%) or at 120 °C with all water removed. OH⁻ anion has been tested and it was found that the ionomer with OH⁻ counterions is not stable in water (under basic condition). It is not clear at this time whether the stability in base is from the phosphonium being unstable or just the siloxane backbone.

The phosphonium ionomers we synthesized exhibit weak ion content dependence of Tg and conductivity with each counterion (F⁻, Br⁻, TFSI⁻). The reason has been attributed to the inherent flexibility of the polysiloxane backbone, the cation solvation ability of PEO side chains and the electronic structure of the phosphonium cation. The weak electronegativity of P makes the α -carbon bear –e/5 charge that partially shields the strongly positive P from anionic counterions.^{10a}

X-ray scattering indicates no ion aggregation in any of the phosphonium ionomers and this helps to keep Tg low. The conductivities of phosphonium ionomers are enhanced by increasing anion size. The ionomers with TFSI show the highest conductivity across the whole temperature range owing to the largest size of TFSI and weakest ionic interactions between TFSI and phosphonium.

4.4 Experimental

Materials. Allylbromide, diethyl ether, toluene, dichloromethane, ethyl acetate and anhydrous acetonitrile were purchased from VWR and used without further purification. Sodium hydride (60% in mineral oil), tri(ethylene glycol) methyl ether, Platinum divinyltetramethyldisiloxane complex (Pt[dvs]) (3% in xylene) catalyst, tributylphosphine and polymethylhydrosiloxane (PMHS, Mn = 1700 - 3200) were purchased from Aldrich and used as received. Tetrahydrofuran (THF) from EMD Chemicals was refluxed over sodium metal before use.

Characterization. ¹H and ³¹P NMR spectra were recorded on a Bruker AM 300M spectrometer. Glass transition temperatures (Tg) were determined using a TA Q100 differential scanning calorimeter (DSC) with 10 K/min heating and cooling rates. For dielectric and conductometric measurements, samples were sandwiched between two polished brass electrodes with 50 μ m silica spacers placed on top of the sample under < 1 mTorr vacuum at 80 °C for at least 24 h. The sandwiched samples were positioned in a Novocontrol GmbH Concept 40 broadband dielectric spectrometer and the dielectric permittivity and conductivity were measured using an AC voltage amplitude of 0.1 V and $10^{-2} - 10^7$ Hz frequency range. Each sample was annealed in the Novocontrol at 120 °C in a heated stream of dry nitrogen for 1 hour prior to measurements to drive off any moisture picked up during loading of these hygroscopic materials. Data were collected in isothermal frequency sweeps from 120 °C to near Tg.

A physical model of electrode polarization (EP) makes it possible to separate ionic conductivity into the number density of simultaneously conducting ions and their mobility, as has recently been done for other single-ion conductors above T_g . Electrode polarization occurs at low frequencies, where the transporting ions have sufficient time to polarize at the blocking electrodes during the cycle. That polarization manifests itself in (1) an increase in the effective capacitance of the cell (increasing the dielectric constant) and (2) a decrease in the in-phase part of the conductivity, as the polarizing ions reduce the field experienced by the transporting ions.

The time scale for conduction is the time where counterion motion becomes diffusive

$$\tau_{\sigma} \equiv \frac{\varepsilon_s \varepsilon_0}{\sigma_{DC}}.$$
 (1)

At low frequencies the conducting ions start to polarize at the electrodes and fully polarize at the electrode polarization time scale

$$\tau_{EP} = \frac{\varepsilon_{EP}\varepsilon_0}{\sigma_{DC}},\tag{2}$$

wherein ε_{EP} is the (considerably larger) effective permittivity after electrode polarization is complete. The Macdonald and Coelho model treats electrode polarization as a simple Debye relaxation with loss tangent

$$\tan \delta = \frac{\omega \tau_{EP}}{1 + \omega^2 \tau_\sigma \tau_{EP}}.$$
(3)

In practice, the loss tangent associated with electrode polarization is fit to Eq. 3 to determine the electrode polarization time τ_{EP} and the conductivity time τ_{σ} . The Macdonald and Coelho model then determines the number density of simultaneously conducting ions p and their mobility μ from τ_{EP} and τ_{σ}

$$p = \frac{1}{\pi l_B L^2} \left(\frac{\tau_{EP}}{\tau_{\sigma}}\right)^2 \tag{4}$$

$$\mu = \frac{eL^2 \tau_{\sigma}}{4\tau_{FP}^2 kT},\tag{5}$$

wherein $l_B \equiv e^2 / (4\pi \varepsilon_s \varepsilon_0 kT)$ is the Bjerrum length, *L* is the spacing between electrodes, *k* is the Boltzmann constant, and *T* is absolute temperature.

SAXS data was collected using a Molecular Metrology pin hole camera instrument with a copper k-alpha radiation source (λ =1.5418 angstrom) and a two dimension multiwire detector. The sample-to-detector distances are 1.5 meter and 0.5 meter. Samples are dried and loaded into boron-rich glass capillaries, and furthered dried under vacuum at 80oC overnight before flame sealed. Specimen count time is 2.5 hours for each sample. Background scattering from an empty capillary is subtracted from the scattering data of the samples.

Synthesis of tri(ethylene glycol) allyl methyl ether (PEO₃): PEO₃ was synthesized followed the report of Zhang et al. ³⁵ To a mixture of NaH (1.44g, 60% in mineral oil) dispersed in 20 mL dry THF was added solution of tri(ethylene glycol) methyl ether (4.7 mL, 0.03 mol) in 150mL of THF dropwise at ice-bath temperature. The mixture was stirred for 3 hours before being transferred into a solution of allyl bromide (3.58g, 0.03mol) in 20 mL dry THF. The mixture was allowed to react overnight to complete the reaction. The produced NaBr was vacuum filtrated and the volatiles were removed by rotovap. The yellowish liquid was then purified by vacuum distillation to yield 5.5 g (90%). ¹H NMR (d, 2H), 3.65–3.45 (m, 12H), 3.30 (s, 3H)¹H NMR (in d6-

acetone), δ(pap) 5.85(m, 1H, CH=), 5.2 (s, (d, cist H of = CH₂), 5.1 (d, trans H of = CH₂), 3.95 (d, 2H, C=C-CH₂), 3.8-3.6 (m, 8H, OCH₂CH₂O), 3.35 (s, CH₃).

Synthesis of allyltributylphosphonium bromide (ATPB): To a pre-degassed threeneck flask were added allylbromide (3.58g, 30 mmol) and tributylphosphine(3.6 g, 16mmol). The entire mixture was allowed to stir at room temperature for 10 hours before being diluted with diethyl ether (50 mL). The mixture was filtered and the solid was washed by diethyl ether to afford product as white powder (5g, 87%). ¹H NMR (in d6acetone), δ (ppm) 0.96 (t, 9H, -CH₃), 1.51 (m, 6H, -CH₂-), 1.73 (m, 6H, -CH₂-), 2.57 (m, 6H, CH₂P), 3.64 (q, 2 H, CH₂-CH=CH₂, 5.41 (dd, 1H, trans H of = CH₂), 5.65 (dd, 1H, cis H of = CH₂), 5.95 (m, 1H, CH=); ³¹P NMR (d6-acetone) δ (ppm) 35.5 (s).

General procedure of synthesis of ionomers: PMHS was added into a pre-dried flask equipped with a condenser. The desired amount of ATPB and vinyl PEO₃ were charged into the flask followed by 20 mL anhydrous CH₃CN and several drops of Pt catalyst solution. The reaction mixture was stirred at 90 °C. The completion of the reaction was judged by ¹H NMR. The mixture was condensed and the residue was redissolved in DI water and dialyzed against ultrapure water. Afterwards, the ionomers with Br- were dried in a vacuum oven at 80 °C for 24 hours. The ionomers with TFSI-were prepared by dialysis with much excess LiTFSI salts against DI water. The ionomers with F⁻ and OH⁻ were prepared by passing an aqueous solution through a column packed with anion exchange resin.

References

- Couture, G.; Alaaeddine A.; Boschet, and Ameduri, B. *Progress in Polymer Science* 2011, *36*, 1521.
- (2) Brenner, D.; Oswald, A. A. Adv Chem Ser 1980, 187, 53-66.
- (3) Ghassemi, H.; Riley, D. J.; Curtis, M.; Bonaplata E. and McGrath J. E. Appl. Organometal. Chem. 1998, 12, 781.
- (4) Worley, S.D.; Sun, G. *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.;
 CRC: Boca Raton, FL, **1996**; Vol. 1, 550.
- (5) Gu, S.; Cai, R.; Cui, T.; Sun, M.; Liu, Y.; He, G. and Yan, Y. Angew. Chem. Int. Ed.
 2009, 48, 6499.
- (6) (a) Lu, S.; Pan, J.; Huang, A.; Zhuang, L. and Lu, J. *PNAS*, **2008**, *105*, 20611; (b)
 Tang, D.; Pan, J.; Lu, S.; Zhuang, L.; and Lu. J. *Science China* **2010**,*53*, 357
- (7) Ye, Y. and Elabd, Y. A. in Polymer for Energy Storage and Delivery: Polyelectrolytes for Batteries and Fuel Cells, ACS Symp. Ser. 2012, 233, 1096.
- (8) Yamamoto, M.; Toi, K. JP Patent 61192311(assigned to Tokuyama Soda KK),1986.
- (9) Ye, Y. and Elabd, Y.A. *Macromolecules* **2011**, *44*, 8494.
- (10) (a)Wang, S.; Liu, W. and Colby, R. H. *Chem. Mater.* **2011**, *23*, 1862; (b) Haav, K.; same, J.; Kutt, A. and Leito, I. Euro. *J. Org. Chem.* **2012**, 2167
- (11) Riley, D. J.; McGrath, J. E. and Kashiwagi, T. K. Polym. Eng. Sci. 1997, 37, 1501
- (12) Fraser, K.J.; Macfarlane, D. R. Aus. J. Chem. 2009, 62, 309
- (13) Zhou, P. and Blumstein, A. *Polymer* **1997**, *38*, 595.

- (14) (a) Cheng, S.; Zhang, M.; Wu, T.; Hemp, S.T.; Mather, B.D.; Moore, R.B. Long, T.E. J. Polym. Sci.: Part A: Polym. Chem. 2012, 50, 166; (b) Williams, S. R.; Wang, W.; Winey, K. I.; Long, T. E. Macromolecules 2008, 41 (23), 9072; (C) Cheng, S.; Beyer, F. L.; Mather, B. D.; Moore, R. B. and Long T. E. Macromolecules 2011, 44, 6509–6517.
- (15) Okanmoto, Y.; Yeh, T. F.; Lee, H. S.; Skotheim, T. A. J. Polym. Sci.: Part A: Polym. Chem. 1993, 31, 2573.
- (16) Siska, D. P.; Shriver, D. F. Chem. Mater. 2001, 13, 4698.
- (17) Snyder, J. F.; Hutchison, J. C.; Ratner, M. A.; Shriver, D. F. Chem. Mater. 2003, 15, 4223.
- (18) Fujinami, T.; Buzoujima, Y. J. Power Sources 2003, 119-121, 438.
- (19) Liang, S.; Choi, U H.; Liu, W.; Runt, J. and Colby, R. H. Chem. Mater. 2012, 24, 2316-2323.
- (20) Kang, J.; Li, W.; Lin, Y.; Li, X.; Xiao, S. Fang, S. Polym. Adv. Technol. 2004, 15, 61.
- (21) Kang, J.; Fang, S. Polymer Bulletin 2002, 49, 127.
- (22) Sauvet, G.; Dupond, S.; Kazmierski, K.; Chojnowski, J. Journal of Polymer Science: Part A: Polymer Chemistry, 2000, 75, 1005.
- (23) Huang, Z.; Yu, Y.; Huang, Y. Journal of Polymer Science: Part A: Polymer Chemistry, 2001, 83, 3099.
- (24) (a) Rachid Y. WO 2008105916A2 20080904; (b) US 20090029237 A1 20090129
- (25) Xu, S.; Chen, R. and He, Z. J. Org. Chem. 2011, 76, 7528.
- (26) Ye, Y.; Elabd, Y. A. *Polymer* **2011**, *52*, 1309.

- (27) Choi, U H.; Mittal, A.; Price, T. L. Jr.; Gibson, H. W.; Runt J. and Colby, R. H. *Macromolecules* 2013, 46, 1175.
- (28) Cooper, S. L.; Visser, S. A. Macromolecules 1991, 24, 2584.
- (29) (a) Albouy, P. A. *Polymer* 2000, *41*, 3083; (b) Inomata, K.; Yamamoto, K.; Nose,
 T. *Polymer Journal* 2000, *32*, 1044.
- (30) Ratner, M. A.; Shriver, D. F. Chem. Rev. 1988, 88,109.
- (31) Benrabah D.; Arnaud R.; Sanchez J.Y. *Electrochim Acta* **1995**, *40*, 2437.
- (32) Arnaud R.; Benrabah, D.; Sanchez J. Y. J. Phys. Chem. 1996, 100, 10882.
- (33) Choi, U H.; Lee, M.; Wang, S.; Liu, W.; Winey, K. I.; Gibson, H. W. and Colby,
 R. H. *Macromolecules* 2012, 45, 3974.
- (34) Fragiadakis, D.; Dou, S, Colby, R.H. and Runt, J. J. Chem. Phys. 2009, 130, 064907.
- (35) Zhang, Z.; Lyons, L. J.; West, R; Amine, K. and West, R. Silicon Chemistry 2005, 3, 259.

Chapter 5

Linear Viscoelastic Properties of Ionomers with Bulky Phosphonium Cations

5.1 Introduction

Ionomers generally contain relatively small percentage of ionic groups (less than 15 mol %) distributed along their backbones. Ionomers have been known to have some characteristics of "thermoplastic elastomers" materials for decades due to the thermally reversible networks formed by ion associations. The structure and dynamics of ionomers are more complicated than those of their non-ionic counterparts because of the electrostatic interaction between the ionic groups.¹⁻⁶ Ionomers with anionic groups covalently bonded to the polymer backbone (polyanions), such as sulfonate and carboxylate, have been extensively studied in the last four decades. ^{1, 7} For these ionomers, increase of ion content leads to structural changes, e.g., microscopic ion aggregation as suggested from X-ray scattering measurements. As a result, ionomers exhibit different dynamic behavior compared to their non-ionic counterparts, e.g. delayed terminal relaxation, two distinct T_{gs} , appearance of a second rubbery plateau, and thermoplasticity attributed to the long lifetime ionic associations serving as the thermally reversible crosslinks. Ionomers with cationic groups (e.g., ammonium', quaternized pyridine⁸, imidazolium⁹ and phosphonium¹⁰) attached to the backbone (polycations) exhibit similar structural and dynamic features as polyanions. Nevertheless, polycation

ionomers are of particular interest recently owing to their potential applications such as water purification, antimicrobial agents, and alkaline fuel cell membranes.

To understand the structural and dynamic behavior of ionomers, different morphology models have been proposed, such as hard-sphere model¹¹, core-shell model¹² and the EHM model¹³ by Eisenberg, Hird and Moore, which might be the most successful at explaining experimental observations. Many models have been proposed to explain and predict dynamic behavior of ionomers as well. A simple sticky reptation model by Leibler, Rubinstein and Colby¹⁴ appears to describe well the viscoelastic behavior affected by specific reversible interchain interactions such as hydrogen bonding^{15, 16} and ionic interactions^{17, 18}. In this model, the groups subjected to interactions are regarded as stickers, which limit polymer chain motion on length scales larger than the sticker-sticker distance. The dynamics could become more complicated if the chains are entangled as well, due to the varied conditions depending on relative characteristic lengths and life times for the two types of constraints, i.e., stickers and entanglements. In this paper we report LVE for polymer chains and ionomers that are short and non-entangled, which are much simpler.

In our previous study, ¹⁹ a group of novel phosphonium-containing polysiloxanebased ionomers have been synthesized. The physical properties, morphology and dielectric properties of those phosphonium ionomers support an argument that interaction between phosphonium cation and counterion is very weak. Consequently the weak interchain interaction keeps T_g low, even when ion content is high. This study focuses on linear viscoelastic (LVE) properties of these phosphonium ionomers. The results demonstrate the delayed relaxation seen in other ionomers, but also a significant broadening of the glassy mode distribution as ion content increases, which is believed to be the outcome of enhanced of cooperative motion of polymer segments due to increased ionic interaction. A sticky Rouse model has been developed that describes our LVE data very well.

5.2 Experimental

5.2.1 Material



Polysiloxane-based phosphonium ionomers were synthesized by hydrosilylation reaction in our lab. The synthesis details could be found in our previous paper.¹⁹ The phosphonium ionomers are extensively dialyzed by deionized water thoroughly before drying in a vacuum oven at 80 °C overnight. The ion content *f*, defined as the molar fraction of Si with an attached ionic group, has been determined by proton nuclear magnetic resonance (¹H-NMR). Molecular weight distribution (MWD) of the non-ionic sample having f = 0 is determined by gel permeation chromatography (GPC) with tetrahydrofuran (THF) as eluent solvent and columns calibrated using standard

monodispersed polystyrene. Differential scanning calorimetry (DSC) T_g of the ionomer samples were reported previously¹⁹ and are listed in Table 1.

5.2.2 LVE Measurements

Linear viscoelastic measurements were conducted with an Advanced Rheometric Expansion System (ARES, Rheometric Scientific). Parallel plates with diameters of 25mm, 8mm, and 3mm were utilized. The 3mm plate is chosen for measuring glassy modulus to avoid instrument compliance (which manifests for the 8mm plate in measuring $|G^*| \ge 10^7$ Pa). Nevertheless, the 3mm plates are vulnerable to boundary effect and thermal expansion incompatibility. In relation to this point, the measurement with 3mm plates was started at *T* identical to the lowest *T* at which the 8mm plate is still valid, to confirm the reproducibility of measurements with different plates and precisely determine the geometry constant of the 3mm plates. *T* was decreased slowly (less than 5K change each time) and the gap was adjusted by following a change of normal force. A small compressional force was applied at *T* close to T_g to ensure a good adhesion to the plates. The oscillatory strain amplitude was kept small (≤ 0.1) to ensure linear response to storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, measured as functions of angular frequency in a frequency range of 10^{-2} rad/s $\le \omega \le 10^2$ rad/s.

5.3 Theoretical Analysis

5.3.1.1Relaxation spectrum

The shear stress relaxation modulus of any viscoelastic liquid in the time domain can be expressed as a generalized Maxwell model: ²⁰

$$G(t) = \sum_{q \ge 1} g_q \exp(-t / \tau_q)$$
⁽¹⁾

where g_q and τ_q are the amplitude and characteristic time of the q-th mode. The corresponding storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, in the frequency domain can be expressed using the same set of g_q and τ_q as:

$$G'(\omega) = \omega^{2} \sum_{q \ge 1} g_{q} \frac{\tau_{q}^{2}}{1 + \omega^{2} \tau_{q}^{2}}; \ G''(\omega) = \omega \sum_{q \ge 1} g_{q} \frac{\tau_{q}}{1 + \omega^{2} \tau_{q}^{2}}$$
(2)

At low frequency $\omega \ll \tau_1$, where τ_1 is the characteristic time of the slowest relaxation mode, we have $\omega^2 \tau_q^2 \ll 1$ in the denominator of eq 2 and accordingly the terminal tails, $G'(\omega) \propto \omega^2$ and $G'(\omega) \propto \omega$. The zero-shear viscosity can be obtained as:

$$\eta_0 = \sum_{q \ge 1} g_q \tau_q = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega}$$
(3)

Similarly, the steady-state recoverable compliance $J_e \equiv \gamma_r / \sigma$, with γ_r and σ being the recoverable strain after removing a stress of σ , can also be determined from the terminal tails as:

$$J_{e} = \frac{\sum_{q \ge 1} g_{q} \tau_{q}^{2}}{\left\{\sum_{q \ge 1} g_{q} \tau_{q}\right\}^{2}} = \lim_{\omega \to 0} \frac{G'(\omega)}{\left[G''(\omega)\right]^{2}}$$
(4)

It is well known that the glassy relaxation modulus, $G_G(t)$, can usually be well fit phenomenologically by a stretched exponential model known as Kohlrausch-Williams-Watts (KWW) model, although the molecular origin of this model is still debated.^{21, 22}

$$G_{g}(t) = G_{g,0} \exp\left(-\left[t / \tau_{KWW}\right]^{\beta}\right)$$
(5)

5.3.2 Sticky Rouse model

In a longer time scale, the localized monomeric motion has been accumulated and the polymer chain can be regarded as composed of internally equilibrated flexible Rouse segments.^{20, 23} For varied polymer species, the elementary Rouse segments determined in rheo-optical measurements have a size comparable to Kuhn segments.^{20, 21} The Rouse relaxation modulus can be written in terms of Rouse modes as: ^{20, 26, 27}

$$G_{\rm R}(t) = \sum_{i} \frac{\rho w_i RT}{M_i} \sum_{p=1}^{N_i} \exp(-tp^2 / \tau_0 N_i^2)$$
(6)

Here, we consider a distribution of molecular weight: w_i is the weight fraction of *i*-th component and M_i is the molecular weight of the *i*-th component. $N_i = M_i/m_0$ is the number of elementary Rouse segments and $\tau_0 N_i^2$ is the Rouse relaxation time of *i*-th chain, where m_0 and τ_0 are the molecular weight and characteristic time of the elementary Rouse segment, respectively. For ionomers, the lower Rouse modes should be delayed if the association lifetime $\tau_s \propto \exp(E_s/k_BT)$ is considerably longer than the Rouse time of the chain between ionic groups, where E_s is the association energy and k_B the Boltzmann constant.¹⁴ We define the Rouse segment between two-nearby ionic groups (or one ionic group and its nearby chain end) as a *sticky Rouse segment* having molecular weight m_s .

Then, the *i*-th chain has a number of sticky Rouse segments $N_{s,i} = M_i/m_s$. We further define the delay ratio between a sticky Rouse segment and its corresponding "unstuck" Rouse segment as $r_{\tau} = \tau_s/n_s^2 \tau_0$, where τ_s is association lifetime and $n_s = N_i / N_{s,i}$ is the number of elementary segments per sticky Rouse segment, making $n_s^2 \tau_0$ the Rouse time of the segment without stickers. The relaxation modulus incorporating a delay due to ionic dissociation can be written as, ¹⁴

$$G_{\rm s}(t) = \sum_{i} \frac{\rho w_i RT}{M_i} \left\{ \sum_{p=N_{\rm s,i}}^{N_i} \exp(-tp^2 / \tau_0 N_i^2) + \sum_{p=1}^{N_{\rm s,i}} \exp(-tp^2 / \tau_{\rm s} N_{\rm s,i}^2) \right\}$$
(7)

Obviously, eq 7 can be regarded as equivalent to eq 6 in the limit of $r_{\tau} = 1$. The fast Rouse modes ($N_{s,i}) are not affected by the associations while the slower Rouse$ $modes (<math>1 < P < N_{s,i}$) are each delayed by the same delay ratio r_{τ} , which increases with ion content.

Table 5-1. DSC T_g and parameters determined in WLF analysis.

f	C_1	$C_2(\mathbf{K})$	$T_0(\mathbf{K})$	$T_{g}(\mathbf{K})$	т
0	10.4	36.0	157	193	56
0.05	11.0	45.0	153	198	48
0.08	11.0	45.0	153	198	48
0.11	12.2	44.0	155	199	55
0.22	13.1	46.0	156	202	58



Figure 5-1. Master curves of storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, as functions of angular frequency ω for phosphonium ionomers with different ionic contents at reference temperature $T_r = 198$ K. The solid curves represent theoretical fitting combining glassy modulus fitted by KWW model, and rubbery modulus fitted by sticky Rouse model.

5.4 Results and Discussion

5.4.1 Linear viscoelastic behavior

5.4.1.1 Overview

Figure 5-1 shows the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, measured as functions of ω for all ionomer samples having ionic content f = 0.0.22 multiplied by T_r/T and reduced at reference temperature $T_r = -75^{\circ}$ C, which is close to (within $\pm 5^{\circ}$ C) the thermally determined T_g of all the ionomer samples (cf. Table 1-1). The solid curves are theoretical fits as explained later in more detail.

Generally ions tend to aggregate in low-dielectric-constant media and it is ion aggregation that influences dynamic properties. When each ion association is formed by only a few ion pairs, often termed multiplet¹, there is no detectable microphase separation in X-ray Scattering measurements. As the number of ion pairs forming ion associations increases, clusters form and microphase separate. So there is a critical ion concentration beyond which ion clusters form. As a result, a second rubbery plateau, extra loss *tanð* peak and *G*" peak may be observed. Eisenberg and Navratil²⁸ studied poly (styrene-co-sodium methacrylate) and found the critical ion concentration was 6 mol%. Wu and Weiss²⁹ decided that 2.4 mol% was the critical ion concentration for copolymers of styrene and vinylphosphonate. As to the phosphonium ionomers studied in this paper, with ion content up to 22 mol%, no rubbery plateau is observed. The morphology data reported in our previous paper¹⁹ for the phosphonium ionomers suggests only modest ion

association (multiplets) with no clustering of ions and this is consistent with the LVE results presented here.

It is surprising to find that time-temperature superposition (tTs) works well for our phosphonium ionomers through the whole ion concentration range from f = 0 to 0.22, with the shift factors summarized in Figure 5-2 (The difference between the temperature dependence of glassy and rubbery modulus, ^{30, 31} is insufficient to lead to clear thermorheological complexity in the glassy-rubbery transition region.). One characteristic feature of microphase-separated ionomers is the failure of tTs.^{1, 2} Therefore successful application of tTs to our ionomers confirms that there is no microphase separation of ionic clusters, in our phosphonium ionomers. Eisenberg et al.²⁸ found that time-temperature superposition was reestablished at high temperature for microphase-separated polystyrene-based ionomers. Once the ion association lifetime $\tau < 0.01$ s, all LVE at frequency $\omega < 100$ rad/s have tTs work at higher temperature as all observed dynamics are controlled by the association lifetime.

In Figure 5-1, it is noted that all the ionomer samples and the nonionic polymer exhibit glassy modulus with very similar amplitude at high ω . This feature is different from the results of Weiss et al ³², in which glassy modulus for lightly sulfonated polystyrene is independent of ion concentration and counterion type but about 40% higher than that of nonionic polystyrene. The glassy relaxation is followed by a Rouse like relaxation until the terminal relaxation at low ω , characterized by terminal tails $G'(\omega) \propto \omega^2$ and $G''(\omega) \propto \omega$. With an increase of ionic content, the mode distributions of the glassy relaxation become broader and the terminal relaxations are further delayed. For the

highest ionic content in this study (f = 0.22), the transition from glassy to rubbery modulus is not clearly observed; $G'(\omega)$ and $G''(\omega)$ exhibit a single very broad relaxation process! The delay of the terminal relaxation with increasing ionic content has been reported in various experiments, ³²⁻³⁶ owing to electronic interaction of the ionic groups constraining/retarding the thermal motion of the ionomer chain. The degree of delay increases with ion content.



Figure 5-2. Shift factor a_T with DSC T_g as the reference temperature for phosphonium ionomers with different ionic contents as indicated, plotted against $T-T_g$. The fact that these curves merge at low temperature indicates fragility is independent of ion content.



Figure 5-3. Master curves of storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, as functions of angular frequency ω for phosphonium ionomers with different ionic contents with DSC T_g as the reference temperature (listed in Table 5-1) with shift factor a_T summarized in Figure 5-2. The inset shows zero-shear viscosity and recoverable compliance, η_0 and J_e , at the DSC T_g , as functions of ionic content f

5.4.1.2 Tg effect and glassy modulus

In principle, the delay of glassy relaxation caused by increasing T_g can be normalized through comparing different samples at their DSC T_g (cf. Table 5-1). This point is tested in Figure 5-3, where $G'(\omega)$ and $G''(\omega)$ of all the samples in Figure 5-1 are compared at their DSC T_g . It is noted that at T_g , the glassy $G''(\omega)$ peaks for all these samples locate at almost the same frequency of 100 rad/s, in accordance with the natural expectation²⁰ that the glassy relaxation can be normalized by T_g . Nevertheless, it is noted that the mode distribution of glassy moduli are very similar for samples having $f \le 0.08$, but broadens significantly as f is further increased, reflected in smaller KWW β in Table 5-2. A molecular interpretation of this crossover is proposed later in section 5.4.2.2.

5.4.1.3 Rubbery modulus

In Figure 5-3, the rubbery moduli of the ionomer samples are more delayed with increasing ionic content even if compared at $T_{\rm g}$. To quantify this delay, as well as a change of relaxation mode distribution for terminal relaxation, we evaluate zero-shear viscosity η_0 and recoverable compliance $J_{\rm e}$ from viscoelastic terminal tails as shown in solid lines attached to G^* at low ω by utilizing eqs 3 and 4. η_0 (circle symbols) and $J_{\rm e}$ (square symbols) are plotted against f in the inset of Figure 5-2. It is noted that η_0 is very similar for f = 0 and 0.05 at their $T_{\rm g}$, which increases if f is further increased. In contrast, $J_{\rm e}$ is quite insensitive to ionic content for low f (=0, 0.05, and 0.08) samples, and is reduced slightly for samples having f = 0.11 and 0.22. The similar $J_{\rm e}$ reflects a similar

viscoelastic mode distribution for these samples, which is not surprising since all the ionomer samples are synthesized by incorporating ionic (phosphonium) and nonionic (ethylene glycol) groups onto *the same polysiloxane backbone*.

5.4.1.4 Temperature dependence

The shift factors a_T for LVE with DSC T_g as the reference temperature are plotted against $T - T_g$ in Figure 5-2. In Figure 5-2, we note that the temperature dependence is very similar for f = 0.05 and 0.08, and becomes stronger for f = 0.11 and 0.22. These plots are well fit by Williams-Landel-Ferry (WLF) equations shown in the solid curves,¹⁶, ²³

$$\log a_{\rm T} = \frac{-C_1(T - T_{\rm g})}{C_2 + T - T_{\rm g}} \tag{8}$$

The fitting parameters C_1 and C_2 allow us to calculate the Vogel temperature $T_0 = T_g - C_2$ and fragility $m = C_1 T_g/C_2$. The values of C_1 , C_2 , T_0 , and m are listed in Table 5-1, along with DSC T_g is also added for comparison. C_1 is inversely proportional to f_g , the fractional free volume at T_g , and $C_2 \propto f_g/\alpha_f$, where α_f is thermal expansion coefficient above T_g . C_1 increases as ion content increases, meaning f_g decreases, which is a consequence of stronger interchain interaction; while C_2 stays almost the same, which contradicts the reports by Eisenberg²⁸ and Weiss³². It is also noted that either T_g or T_0 is similar for all the ionic samples (differences within 5°C), and $T_g - T_0 \cong 45^{\circ}$ C can be consistently determined, in consistence with nearly constant fragility m = 53 ± 5. One possible reason is the bulky phosphonium-containing cationic groups, which sterically hinder dense packing of multiple ion pairs, leading to a small increase of T_g and nondetectable ionic aggregation in SAXS measurements.



Figure 5-4. Linear relaxation modulus, G'(t), as functions of time *t* at reference temperature $T_r = -75^{\circ}$ C. The solid curves represent theoretical fitting combining glassy modulus fitted by KWW model, and rubbery modulus fitted by sticky Rouse model. The symbols represent the same samples as in Figure 1. For the non-ionic polymer (black diamond), the dashed and dotted curves attached to the symbols represent the KWW fit (eq 5) of the glassy modulus and the Rouse model fit (eq 6) of the rubbery modulus, respectively. The inset shows the apparent molecular weight distribution obtained in GPC measurements, which has been incorporated into the Rouse model fit.

5.4.2 Theoretical analysis

5.4.2.1 Fit experimental data with sticky Rouse model

To analyze the experimental data in more detail, we attempt to fit linear viscoelastic modulus with the theory explained in eqs 5-7 *in the time domain*. For this purpose, we first express $G'(\omega)$ and $G''(\omega)$ in Figure 2 in terms of relaxation spectrum $[g_q, \tau_q]$, where a set of τ_q are chosen having small logarithmic span of $\Delta = \log [\tau_q/\tau_{q-1}] = 0.2$. A set of g_q are determined through ~20s iterations until the deviation between calculated (cf. eq 2) and experimental $G^*(\omega)$ are within $\pm 10\%$, roughly the size of symbols in Figure 5-2.

From $[g_q, \tau_q]$ thus-determined, the linear stress relaxation modulus G(t) of the ionomer samples are calculated from eq 1, shown as symbols in Figure 5-4. As an example, the fitting results for glassy and rubbery modulus of the non-ionic counterpart are shown in dashed and dotted curves in Figure 5-4, respectively. The glassy modulus was fit to eq 5, where $G_{G,0}$ is found to be slightly larger than the modulus measured at the highest frequency, τ_{KWW} and β are two fitting parameters giving the best fit for $G^*(\omega)$ at high ω . The fitting of rubbery modulus with eq 7, on the other hand, includes two fitting parameters in short time/length scale, i.e., τ_0 and m_0 corresponding to characteristic time and molecular weight of the elementary Rouse segment. In fact, m_0 and τ_0 can be estimated from the specific modulus and frequency where the glassy-rubbery transition is observed. In the long time/length scale, the calculation of rubbery modulus (cf. eq 7) requires knowledge of MWD. For this purpose, the MWD function for apparent

molecular weight, M_i^{app} , determined in GPC for non-ionic counterpart is shown in the inset of Figure 5-4, which shows a broad peak. From the MWD function, the number and weight average molecular weights are evaluated as: $M_w = \sum_i w_i / \sum_i w_i / M_i^{app} = 19200$ and $M_n = \sum_i w_i M_i^{app} / \sum_i w_i = 7600$, which gives polydispersity index of $M_w/M_n = 2.5$. We

should note that M_i^{app} determined by utilizing PS as standards is a relative molecular weight instead of a real molecular weight. For the rubbery part of G' and G'' of non-ionic counterpart, we found that a choice of $M_i^{\text{non-ionic}} = M_i^{\text{app}}/2$ gives the most satisfactory fitting (dotted curve).

For ionomer samples, the fit of glassy modulus is similar to that of the non-ionic counterpart, which includes three parameters $G_{G,0}$, τ_{KWW} , and β , with $G_{G,0}$ being very close to that of the non-ionic polymer(cf. Table 5-2 where all these fitting parameters are summarized). The rubbery modulus, on the other hand, includes two parameters in short length/time scale, m_0 and τ_0 , where m_0 (= 300) is chosen as being identical to that of the non-ionic counterpart (cf. Table 5-2). For long length/time scales, the molecular weight of the *i*-th component is slightly larger than $M_i^{\text{non-ionic}}$ because the monomer with incorporated ionic phosphonium group has larger M than that with incorporated non-ionic PEO group. Then, we can use $M_i^{\text{ionie}} / M_i^{\text{non-ionic}} = 1 + f \times (r_M - 1)$ to represent the molecular weight of the ionic samples, where r_M is the ratio of molecular weights between ionic and non-ionic monomers.

Table 5-2. Fitting parameters in sticky Rouse model

f	$G_{\rm g}$ (Pa)	$ au_{\rm KWW}({ m s})$	$\tau_{\max}(s)$	β	m_0	τ_0 (s)	$\tau_0/\tau_{\rm max}$	
0	8.13×10 ⁸	4.17×10 ⁻⁵	5.91×10 ⁻⁵	0.35	300	3.31×10 ⁻³	5.6×10 ¹	
0.05	7.24×10 ⁸	7.94×10 ⁻⁴	1.13×10 ⁻³	0.35	300	6.31×10 ⁻²	5.6×10 ¹	
0.08	7.94×10 ⁸	7.94×10 ⁻⁴	1.13×10 ⁻³	0.35	300	1.58×10 ⁻¹	1.4×10 ²	
0.11	1.02×10 ⁹	1.78×10 ⁻³	2.52×10 ⁻³	0.25	300	2.24	8.9×10 ²	
0.22	1.15×10 ⁹	5.89×10 ⁻⁴	1.05×10 ⁻³	0.12	300	-	-	

In the data fit, it is noted that the factor $r_{\tau} = 1$ gives satisfactory prediction of the experimental result. This feature suggests that ionic aggregation (or quadropole) delay due to ionic association does not initiate from the sticky Rouse segment between ionic groups as defined earlier, but from some smaller motional unit not considered in the molecular picture of the sticky Rouse model. One possible explanation is the motion of Rouse segments in between the ionic groups, in particular those segments nearby the ionic groups, is also restricted somehow due to the ionic groups quenched in the ionic cluster. Those restricted Rouse segments need to wait for the dissociation of the ionic groups to relax. The number $m_0 = 300$ possibly allows an estimation of number density of those restricted Rouse segments. A more detailed molecular picture corresponding to this restricted region is considered as an interesting future work.

In summary, the linear viscoelastic modulus of the phosphonium ionomer samples can be well reproduced through combination of glassy and rubbery modulus, the latter introducing no extra delay from intrinsic Rouse to sticky Rouse, i.e., $r_{\tau} = 1$ for f = 0, 0.05, 0.08, and 0.11. One possible reason is the bulky phosphonium-containing cationic group, which prevents formation of long life time/stable association having $\tau_{s} \propto \exp(E_{s}/k_{\rm B}T)$ considerably longer than the Rouse time between ionic groups. ³⁷

One special case is the ionomer sample with f = 0.22: The linear viscoelastic modulus shows a broad relaxation process and a glassy-rubbery transition is not clearly observed. For this relaxation process, we could even successfully reproduced the whole relaxation process with a single KWW equation having very low $\beta = 0.12$. In related to this point, it is noted that a same $\beta = 0.35$ was chosen for samples having f = 0, 0.05, and 0.08, which reduces to $\beta = 0.25$ for f = 0.11 and further to $\beta = 0.12$ for f = 0.22. This result suggests that the glassy dynamics may experience a percolation threshold between f= 0.08 and 0.11. This result is in accordance with an abrupt change of temperature dependence from f = 0.08 to 0.11 (cf. Figure 5-3). Physics behind these observations is discussed in below. The fitting curves in Figure 5-4 are numerically converted into frequency domain and shown as curves in Figure 5-1, which agree well with G' and G''data directly obtained in viscoelastic measurements.

5.4.2.2 Glassy dynamics affected by the ionic interaction

It is well accepted that the β value in the KWW model reflects the degree of cooperative motion,^{21, 22} which strongly correlated to fragility for varied glassy liquids.²¹ Following this reported correlation:²¹ $\beta = (m_{inf}-m)/s$ with two parameters $m_{inf} = 250$ and s = 320, we expected $\beta \sim 0.6$ for ionomer samples with $m \sim 50$ in this study. Obviously, our samples with high ionic content exhibit considerably lower β than this expectation.

For the non-ionic counterpart, on one hand, the backbone and associated side chains have different chemical structures. We may regard the backbone as comparable to polydimethylsiloxane having $T_g \approx -120^{\circ}$ C, which is considerably anti-plasticized by the side chains (polyethylene oxide have $T_g \approx -60^{\circ}$ C) to give $T_g \approx -80^{\circ}$ C. Then, the broad viscoelastic mode distribution, as indicated by $\beta = 0.35$, may reflect a local concentration fluctuation due to chemical/frictional contrast between the backbone and the side chains. The same $\beta = 0.35$ is also applicable for ionomers having f = 0.05 and 0.08, but is smaller for samples having f = 0.11 ($\beta = 0.25$) and 0.22 ($\beta = 0.12$). With these higher ion content ionomers, there is a significant third slower source of ffiction involving ions that broadens the glassy relaxation greatly.

If we take a cooperative motion picture in a glassy liquid, we may express the glassy modulus in terms of a distribution of cooperative clusters of n motional units with relaxation time τ_n .³⁵

$$G_{\rm G}(t) = \int_0^\infty P(n) \exp(-t/\tau_n) dn \tag{9}$$

where P(n) is the distribution function of number *n* motional units in a cooperative cluster. It is obvious that a change of distribution function would lead to a change of viscoelastic mode distribution.

A mode distribution of $G_G(t)$ can be more straightforwardly obtained as distribution of relaxation time if a relationship between τ_n and n is available. For example, if we allow a scaling law $\tau_n \sim n^3$ and the cluster size distribution in a power-law manner, $P(n) \sim n^{-\tau} \exp(-n/S)$, where τ is the Fisher exponent and *S* the number of particles in the largest cluster, we would finally be able to obtain $P(\tau_n) d\tau_n \sim \tau_n^{-1/3} \exp[-(\tau_n/\tau)^{1/3}] d\tau_n$ by taking Fisher exponent $\tau = 2$ applicable for glassy liquids. This distribution function gives a mode distribution of $G_G(t)$ that can be fit to the KWW equation (eq 5) with $\beta = 0.33$.³⁸ Thus, $\beta = 0.35$ for f = 0.05 and 0.08 samples and $\beta = 0.25$ for f = 0.11 sample are still explainable under the molecular picture established for common glass formers without consideration of ionic interaction. However, $\beta = 0.12$ for f = 0.22 is definitely not expected for the common glass formers,²¹ suggesting that f = 0.22 requires more cooperative motion of glassy segments and leads to an extremely broad relaxation mode distribution. This point is next discussed in terms of overlapping of polarizability volume.

In general, the polarizability volume V_p can be defined as polarizability α divided by a constant $4\pi\varepsilon_0$ so that the V_p has the unit of volume. V_p can be regarded as the volume over which ionic groups influence their suroundings.

The polarizability of the sample is governed by orientation of ion pairs, which appears to be the case for various ionomers. The average of the dipole moment of ion pairs can be written as $\langle \mu \rangle = \mu^2 E/3kT$ and the polarizability volume can be written as:³⁹

$$V_p = \frac{\mu^2}{12\pi\varepsilon_0 k_{\rm B}T} \tag{10}$$

DFT calculation at 0K in vacuum shows that dipole moment of tri-*tert*-butyl phosphine bromide is $\mu = 12.32$ Debye. Inserting this value into eq 10 we estimated $V_p = 1.89$ nm³ for phosphonium ionomers in this study at T = -75°C, a temperature close to T_g of those samples. In addition, we calculate multiply of V_P and number density of ionic

groups, $V_pP_0 = 0.21$, 0.22, 0.45, and 0.91 for samples having f = 0.05, 0.08, 0.11, and 0.22, respectively. Obviously, V_pP_0 characterizes a degree of overlapping of polarizability volume in space. The value of $V_pP_0 = 1$ at $f_c = 0.25$ specifies a threshold above which the electrostatic interaction becomes significant, which probably boosts a cooperative motion of glassy segments thereby leading to the extraordinarily low β value of 0.12 observed at f = 0.22.

5.5 Concluding Remarks

This study examines the linear viscoelastic behavior of polysiloxane ionomers with bulky cationic phosphonium-containing groups attached to the main backbone. The ionomers exhibit typical Rouse-like terminal relaxation profile with no hint of entanglement effects. The relaxation of the ionomers is retarded by the interchain ionic interaction. The extent of delay increases with increasing ion content.

Due to the strong steric hindrance and resulting weak ion-dipole interaction, the phosphonium groups appears to stay in a slightly associated manner with life time of ion association shorter than that of polymer chain relaxation, leading to an absence of plateau associated to the dissociation of ionic groups. Time-temperature superposition works very well with ion concentrations f = 0 to 0.22 molar ratio, consistent with no microphase separation of ion clusters.

The linear viscoelastic moduli in a wide frequency range have been well fitted by a simple model combining KWW-type glassy relaxation and Rouse-type rubbery relaxation. No extra delay due to ionic association is necessary to reproduce the experimental results, which is consistent with the non-detectable associated structure revealed in our previous study.

The glassy dynamics exhibit a clear crossover behavior, as suggested from a change of glassy mode distribution as well as the temperature dependence. This crossover is attributed to the overlapping of cooperative region surrounding ionic groups, which boosts the cooperative motion of glassy segments. Following this molecular assignment, the estimated cooperative length is similar to Kuhn length of the main backbone and side chains.

References:

- 1. Eisenberg, A.; Kim, J.-S. Introduction to ionomers. Wiley: New York, 1998.
- 2. Capek, I. Advances in Colloid and Interface Sciences 2004, 112, 1.
- 3. Clark, A. H.; Ross-Murphy, S. B. Adv. Polym. Sci. 1987, 83, 57.
- 4. Tant, M. R.; Wikes, G. L. J. *Macromol. Sci. Rev. Macromol. Chem. Phys.* **1988**, *C28*, 1.
- Kim, J.-S. and Eisenberg, A. Ion Aggregation and Its Effect on Ionomer Properties.
 In *Ionomers Characterization, Theory and Applications*; Schlick, S. Ed. CRC Press, Boca Raton, 1996.
- 6. Green, M. S. and Tobolsky, A.V. J. Chemical Physics 1946, 14, 80.
- 7. Charlier, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1990**, 23, (6), 1831-1837.
- Bazuin, C. G.; Eisenberg, A. Journal of Polymer Science Part B-Polymer Physics
 1986, 24, (5), 1121-1135.

9. Ye, Y. S.; Elabd, Y. A. *Macromolecules* **2011**, 44, (21), 8494-8503.

10. Ghassemi, H.; Riley, D. J.; Curtis, M.; Bonaplata, E.; McGrath, J. E. *Applied Organometallic Chemistry* **1998**, 12, (10-11), 781-785.

11. Yarusso, D. J.; Cooper, S. L. Macromolecules 1983, 16, (12), 1871-1880.

12. Macknight.W. J.; Taggart, W. P.; Stein, R. S. *Journal of Polymer Science Part C-Polymer Symposium* **1974**, (45), 113-128.

13. Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, 23, (18), 4098-4107.

Leibler, L.; Rubinstein, M.; Colby, R. H. *Macromolecules* 1991, 24, (16), 4701 4707.

15. Stadler, R. Prog. Coll. Polym. Sci. 1987, 75, 140.

16. Müller, M.; Seidel, U. and Stadler, R. Polymer 1995, 36, 3143.

17. Register, R. A. and Prud'homme, R. K. in *Ionomers*, edited by Tant, M. R.; Mauritz, K. A. and Wilkes, G. I. Blackie Academic, London, **1997**.

Colby, R. H.; Zheng, X.; Rafilovich, M. H.; Sokolov, J.; Peiffer, D. G.; Schwarz, S. A.; Strzhemechny, Y.; Nguyen, D. *Phys. Rev. Lett.* **1998**, *81*, 3876.

Liang, S.; Choi, U. H.; O'Reilly, M. V.; Zhao, H.; Chen, Q.; Winey, K. I.; Runt,
 J.; Colby, R. H. **2012**.

20. Ferry, J. D., Viscoelastic properties of Polymers, 3rd ed. Wiley: New York, 1980.

Bohmer, R.; Ngai, K. L.; Angell, C. A.; Plazek, D. J. *Journal of Chemical Physics* **1993**, 99, (5), 4201-4209.

22. Kremer, F.; Schönhals, A., *Broadband dielectric spectroscopy*. Springer: Berlin ; New York, **2003**.

23. Watanabe, H. Progress in Polymer Science 1999, 24, (9), 1253-1403.
- 24. Inoue, T.; Ryu, D. S.; Osaki, K. *Macromolecules* **1998**, 31, (20), 6977-6983.
- 25. Inoue, T.; Uematsu, T.; Osaki, K. *Macromolecules* **2002**, 35, (3), 820-826.
- 26. Graessley, W. W., *Polymeric liquids and networks : dynamics and rheology*. Garland Science: London ; New York, **2008**.
- 27. Rubinstein, M.; Colby, R. H., *Polymer Physics*. Oxford University Press: New York, **2003**.
- 28. Eisenberg, A. and Navratil, M. *Macromolecules* 1973, 6, 604.
- 29. Wu, Q. and Weiss, R.A. *Polymer* **2007**, *48*, 7558.
- 30. Santangelo, P. G.; Roland, C. M. *Macromolecules* **1998**, 31, (11), 3715-3719.
- Roland, C. M.; Ngai, K. L.; Plazek, D. J. *Macromolecules* 2004, 37, (18), 7051-7055.
- 32. Weiss, R. A.; Fitzgerald, J. J.; Kim, D. *Macromolecules* **1991**, 24, (5), 1071-1076.
- 33. Weiss, R. A.; Fitzgerald, J. J.; Kim, D. *Macromolecules* **1991**, 24, (5), 1064-1071.
- 34. Weiss, R. A.; Yu, W. C. *Macromolecules* **2007**, 40, (10), 3640-3643.
- 35. Weiss, R. A.; Zhao, H. Y. Journal of Rheology 2009, 53, (1), 191-213.
- 36. (a)Tierney, N. K.; Trzaska, S. T.; and Register, R. A. *Macromolecules* **2004**, *37*, 10205; (b) Vanhoorne, P. and Register, R. A. *Macromolecules* **1996**, *29*, 598; (c) Tierney, N. K. and Register, R. A. *Macromolecules* **2002**, *35*, 6284; (d) Tierney, N. K. and Register, R. A. *Macromolecules* **2003**, *36*, 1179.
- 37. Tudryn, G. J.; Liu, W. J.; Wang, S. W.; Colby, R. H. *Macromolecules* 2011, 44,
 (9), 3572-3582.
- 38. Colby, R. H. *Physical Review E* **2000**, 61, (2), 1783-1792.
- 39. Atkins, P. W., *Physical Chemistry*. Freeman: New York, **2010**.

Chapter 6

Future work

6.1 Single-ion conductors for lithium-ion batteries

Figure 6-1 shows the summary of conductivities of single-ion conductors as a function of respective T_g with our borate ionomers by larger size of symbols. The blends of borate ionomers with non-volatile plasticizers give the results near the best. But overall, the conductivities of the single-ion conductors discussed here are still lower than expected, although the value has been continuously pushed forward by different approaches. Our current results indicate that plasticizer is indispensable component in polymer electrolyte to generate gel polymer electrolyte. As we have found that the conductivity of gel polymer electrolyte greatly depends on the structure, composition and viscosity of the plasticizer. Therefore the future work should focus on exploring new plasticizers

6.2 The plasticizers composed of carbonate and ethylene oxide units

This is an extension of chapter 3. In chapter 3, the oligomer plasticizers have two carbonate groups on both ends of the molecules. It seems that, due to the interaction between carbonates, two carbonate groups per molecule may limit the mobility of the plasticizer, and thus low conductivity. Therefore the content of polar group in future

plasticizers should perhaps be reduced. The chemical structures shown in Figure 6-2 are for the target new plasticizers. These new plasticizers contain ion solvation groups: carbonate and ethylene oxide. Short instead of long PEG chain should be used to avoid crystallization and high viscosity. In the meantime, we want to keep its non-volatile property. Therefore carbonate group is attached to one end. Different length of EO units should be tested and compared to find the optimum composition



Figure 6-1. Conductivities of single-ion conductors as a function of their T_gs . The large green diamonds are the borate ionomers discussed in Ch. 2 and the largergree open diamonds are the plasticized borate ionomers discussed in Chp. 3, indicating that

the weak-binding borate ionomers are superior to other Li single-ion conductors in the literatures for 25 °C conductivity at the same Tg.



n=3 to 6

Figure 6-2. Structures of proposed new plasticizers.

.



Figure 6-3 Structures of proposed new phosphonium salts.

6.3 Phosphonium containing ionomers for fluoride battery and alkaline fuel cell

The structures shown in Figure 6-3 are the interesting phosphonium salts for the future work. We have finished the synthesis of new phosphonium salts a and b. The stability of new phosphonium salts compared to the phosphonium salt discussed in chapter 4 has been greatly improved. Especially for the new salt b, it stays intact in 1 M NaOH aqueous solution for over 1 month as proved by ³¹P NMR spectra. The reason can be attributed to the steric effect as suggested by Gu, et al¹. As to new phosphonium salt c, with P completely surrounded by phenyl groups, the stability and conductivity shall be further improved.

6.4 Block copolymer containing polystyrene and poly(ethylene oxide) blocks

Block copolymers composed of polystyrene and poly(ethylene oxide) (PEO) blocks have been extensively studied^{2, 3}. PEO can be either on the main chain² or grafted as side chain.³ One of the advantages of the block copolymer is forming a very regular structure. The morphology of the complex of block copolymers and lithium salt has been reported as shown below. Lamellar structure was observed, as expected for nearly symmetric diblock copolymers.

The polystyrene blocks provided reasonable modulus ~ 10^8 Pa; while the PEO phase formed an ion conduction channel when LiTFSI salt is added. The room temperature conductivity is low (< 10^{-6} S/cm) due to the crystallinity of the high molecular weight PEO block but the conductivity at 80 C is > 10^{-4} S/cm with amorphous PEO.



Figure 6-4. SEM image of pure polystyrene-*b*-poly(ethylene oxide) with molecular weights of polystyrene block 40000 and poly(ethylene oxide) block 54000.²

We can utilize the monomers reported in previous chapter to synthesize a block copolymer with structure shown in Figure 6-5. Less than 10 mol% vinyl borate will be randomly polymerized with styrene to form hard ionic block. Then the hard block will be connected to PEO conducting blocks. Anions in hard blocks may lead to physically separate lithium cation and anion, and thus decrease the possibility forming ion pairs, triple ions and quadrupoles, giving that right process method will be applied. We may consider decreasing the length of PEO blocks to improve the conductivity at low temperature. In the meantime, oligomer PEG plasticizers⁴ and anion receptor BF₃⁵ can be used to further improve conductivity while keeping good mechanical properties of the films.



Figure 6-5. Structures of proposed new block copolymers. y/(x+y) should be < 0.1.

References:

- Gu, S.; Cai, R.; Cui, T.; Sun, M.; Liu, Y.; He, G. and Yan, Y. Angew. Chem. Int. Ed. 2009, 48, 6499.
- (2) (a) Singh, M.; Odusanya, O.; Wilmes, G. M. Eitouni, H. B.; Gomez, E. D.; Patel, A. J.; Chen, V. L.; Park, M. J.; Fragouli, P.; Iatrou, H.; Hadjichristidis, N.; Cookson, D. and Balsara, N. P. *Macromolecules* 2007, *40*, 4578; (b)
- (3) Wang, C. X.; Sakai, T.; Watanabe, O.; Hirahara, K.; Nakanishi, T. J. Electrochem. Soc. 2003, 150, A1166.
- (4) Schaefer, J.; Moganty, S. S.; Yonaga, D. A. and Archer, L. A. J. Mater. Chem. 2011, 21, 10094.
- (5) Chinnam, P. R. and Wunder, S. L. J. Mater. Chem. 2013, 1, 1731.

VITA

Siwei Liang

Siwei Liang was born in Panzhihua, Sichuan, southwest of China Mainland in 1976. He went to Fudan University, Shanghai in 1995 and received his bachelor degree from Department of Macromolecular Science in 1999. Then he went to Beijing and finished his first master degree in Polymer Chemistry and Physics at Institute of Chemistry, Chinese Academy of Sciences in 2003. He came to Penn State in 2005 and accomplished his second master degree in 2008 and PhD degree in 2013 with Dr. Ralph H. Colby from Department of Materials Science and Engineering.