SYNTHESIS OF POLY(IONIC LIQUIDS) BOTH IN SOLUTION AND ON SURFACE OF SILICA NANOPARTICLES AS NOVEL QUASI-SOLID STATE ELECTROLYTES

By

Heyi Hu

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ABSTRACT

SYNTHESIS OF POLY(IONIC LIQUIDS) BOTH IN SOLUTION AND ON SURFACE OF SILICA NANOPARTICLES AS NOVEL QUASI-SOLID STATE ELECTROLYTES

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Ionic liquids (ILs) are compounds composed of cations and anions with low melting point, usually below room temperature. ILs have some unique properties, such as high intrinsic ionic conductivity, non-volatility, nonflammability, thermal and chemical stability. Based on these properties, ILs have been considered as promising electrolyte materials. However, the sealing and fabrication of IL electrolytes remained a challenge in industry applications due to their liquid property. One way to solve this problem was to polymerize the ILs. Compared to ILs, poly(ionic liquids) (PILs) have enhanced mechanical stability, improved processability and durability. However, PILs have their own drawback, which is that once polymerized, the ionic conductivity of PILs drops a lot, usually several orders of magnitude lower than that of their monomers. To successfully apply PILs as electrolyte materials, the ionic conductivity must be improved.

To have high conductivity, the PILs synthesized must have low T_{g} s. A series of low T_{g} polymer polyepichlorohydrin (polyEPCH) with molecular weight ranging from 22,000 to 76,000 were synthesized by anionic ring-opening polymerization. After quaternarization and ion exchange, a novel family of PIL electrolytes were synthesized and characterized. The PILs obtained showed not

only low T_g , high conductivity and good thermal stability, but also a high viscosity, which is beneficial in fabricating process.

To get even higher conductivity, another low T_{g} monomer, 2-((2-(2-(2-methoxy)ethoxy)ethoxy)methyl)oxirane (ME₃MO), was synthesized and randomly copolymerized with EPCH by cationic ring-opening polymerization. The resulting copolymer (polyEPCH-*co*-polyME₃MO) was quaternarized and ion exchanged to form a PIL copolymer (polyGBIMTFSI-*co*-polyME₃MO). By tuning the monomer composition, a series of PIL copolymers from polyGBIMTFSI-*co*-polyME₃MO-8/1 to polyGBIMTFSI-*co*-polyME₃MO-1/4 were synthesized. All PIL copolymer samples showed higher ionic conductivity than PIL homopolymer. Among them, polyGBIMTFSI-*co*-polyME₃MO-1/1 showed the highest ionic conductivity (around 1.2 x 10⁻⁴ S/cm at 25 °C), which was more than 1 order of magnitude higher than PIL homopolymer (9.3 x 10⁻⁶ S/cm at 25 °C).

We also synthesized PILs on the surface of silica nanoparticles via surface initiated atom transfer radical polymerization (ATRP). A gel electrolyte was formed by dispersing the PIL/silica nanocomposites in 1-methyl-3-propylimidazolium iodide and heating for 1 h. The gel electrolyte was used as a quasi-solid state electrolyte in DSSC and a 0.37 % conversion efficiency was achieved.

To My Beloved Family

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TABLE OF CONTENTS

LIST OF TABLES	.ix
LIST OF FIGURES	x
LIST OF SCHEMES	xiii
Chapter 1. Introduction	.1
Ionic liquids Histroy and formation of ILs Application of ILs ILs used as green alternatives to volatile organic solvents ILs used as absorbents of CO ₂ ILs as electrolyte ILs in lithium batteries ILs in fuel cells ILs in DSSCs Poly(ionic liquids) (PILs) Formation of PILs PILs composed of polycations and free anions PILs composed of polycations and free cations Zwitterionic PILs Synthesis of PILs Direct polymerization of IL monomers Chemical modification of existing polymers	1 3 4 9 12 14 16 16 16 17 18 20 20 21
Application of PILs Factors affecting ionic conductivity of PILs	23 23
Anion effect on ionic conductivity of PILs	23
PILs	26
Effect of alkyl chains on imidazolium ring on ionic conductivity of PILs	29
Effect of cation structures of ionic conductivity of PILs Effect of immobilizing anions on the backbone with free cations	30
on ionic conductivity of PILs Effect of degree of polymerization on ionic conductivity of PILs Effect of crosslinking on ionic conductivity of PILs Effect of copolymer on the conductivity of PILs.	32 35 36 43
REFERENCES	51
Chapter 2. Synthesis and characterization of novel low <i>T</i> _g PILs Introduction Results and discussion Synthesis of polyepichlorohydrin based PILs	.64 64 .69 .69

Thermal analysis of polyEPCH and polyGBIMTFSI samples	81
Ionic conductivity and viscosity measurement	84
	87
Experimental section	88
Materials.	88
Synthesis of polyEPCH with monomer to initiator molar ratio from 100 to	00
500	88
Synthesis of poly(1-glycidyl-3-butylimidazolium chloride) (polyGBINCI)	89
bis(trifluoromethanesulfonyl)imide) (polyGBIMTFSI)	90
Characterization	91
Ionic conductivity measurements	92
REFERENCES	94
Chapter 3. Synthesis and characterization of novel low T_q PILs random	
copolymers	98
Introduction	98
Results and discussion	100
Synthesis of polyGBIMTFSI- <i>co</i> -polyME ₃ MO	100
Thermal analysis of polyGBIMTFSI-co-polyME3MO samples	111
Conclusion	115
Experimental section	
Materials	117
Synthesis of ME-MO	117
Synthesis of polyEPCH by estionic ring opening polymorization	
Synthesis of polyEPCH by calionic ring-opening polymenzation	
Synthesis of polyME ₃ MO	119
Synthesis of polyEPCH- <i>co</i> -polyME ₃ MO random copolymer	120
Synthesis of poly GBIMTFSI-co-polyME ₃ MO	121
Characterization	121
Ionic conductivity measurements	122
REFERENCES	125
Chapter 4. Direct polymerization of IL monomers from surface of silica	
nanoparticles: kinetics, characterization, and application in	
DSSCs	126
Introduction	126
Results and discussion	128
Synthesis of VBBIT	128
Surface-initiated ATRP of VBBIT from silica nanoparticles	137
Application as novel quasi-solid state electrolyte in DSSCs	145
Conclusion	148
Experimental section	149
Materials	149
Synthesis of VBBIT	149

Synthesis of ATRP initiator modified silica nanoparticles	150
Synthesis of polyVBBIT/silica nanocomposites.	152
Characterization	152
Calculation of initiator content on the surface of silica nanoparticles	153
Kinetic study	154
DSSC fabrication	154
REFERENCES	157
APPENDIX	162

LIST OF TABLES

Table 1.1.	<i>T</i> g of macromonomers and PILs	25
Table 2.1.	Polymerization of epichlorohydrin initiated by NOct ₄ Br / i- Bu ₃ Al	71
Table 2.2.	Number average molecular weight (M_n), Weight average molecular weight (M_w) and PDI of polyEPCH 100 , 200 and 500 from GPC, PS as standard	78
Table 2.3.	Number average molecular weight (M_n), Weight average molecular weight (M_w) and PDI of polyEPCH 100 , 200 and 500 from GPC, PEO as standard	79
Table 2.4.	<i>T</i> g of polyEPCH and polyGBIMTFSI with different monomer to initiator ratio	83
Table 3.1.	Molecular weight of polyEPCH synthesized using different <i>i</i> - Bu ₃ Al/NOct ₄ Br ratio	106
Table 3.2.	Molecular weight of polyME ₃ MO synthesized using different <i>i</i> -Bu ₃ Al/NOct ₄ Br ratio	107
Table 3.3.	Molecular weight of polyEPCH, polyME ₃ MO and polyEPCH- <i>co</i> -polyME ₃ MO synthesized using BF ₃ OEt ₂ and 1,4- butanediol as initiator	109
Table 3.4.	$T_{\rm g}$ of the polyGBIMTFSI, polyME ₃ MO and their random copolymers with varying molar composition	113
Table 4.1.	Short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (<i>ff</i>) and conversion efficiency of DSSCs with PMII/polyVBBIT/silica nanocomposites gel electrolyte	147

LIST OF FIGURES

Figure 1.1.	Temperature dependence of the ionic conductivity of macromonomers (\bullet , X = TFSI; \blacktriangle , X = CI) and their corresponding polymers (\bigcirc , X = TFSI, \triangle , X = CI)	26
Figure 1.2.	Effect of spacer structure and length on the ionic conductivity for PILs	29
Figure 1.3.	Effect of alkyl chain on the ionic conductivity and T_g for macromonomer 1, 3, 4 and their corresponding PILs.	30
Figure 1.4.	Conductivities of PILs with different cation structures	32
Figure 1.5.	Temperature dependence of the ionic conductivity for EImVS, EImC3S, and their polymers. (\bigcirc) EImVS, (\bigcirc) P(EImVS), (\triangle) EImC3S, (\blacktriangle) P(EImC3S). P implies polymerized system.	35
Figure 1.6.	The photograph of film electrolyte composed of PIL and 3 mol% E_3V cross-linker.	38
Figure 1.7.	The effect of cross-linker (E_3V) concentration on the ionic conductivity and T_g of the PIL film	40
Figure 1.8.	Temperature dependence of the ionic conductivity for PIL films with different cross-linkers($x = 2 \text{ or } 3$).	41
Figure 1.9.	Temperature dependence of the ionic conductivity for PIL films with different cross-linkers($y = 4$ or 13-14)	42
Figure 1.10.	Temperature dependence of the ionic conductivity for PIL films with different cross-linkers($z = 2 \text{ or } 9$).	43
Figure 1.11.	Temperature dependence of ionic conductivity for poly(HMA- co-MEBIm-BF ₄)	46
Figure 1.12.	Composition and glass transition dependence of ionic conductivity for poly(HMA-co-MEBIm-BF ₄)	47

Figure 1.13.	Temperature dependence of ionic conductivity for poly(MEBIm-TFSI- <i>co</i> -MEBIm-BF ₄)48
Figure 1.13.	Composition and glass transition dependence of ionic conductivity for poly(MEBIm-TFSI- <i>co</i> -MEBIm-BF ₄)49
Figure 2.1.	¹ H NMR of polyEPCH with monomer to initiator ratio 500/1 (2.1a, top, CDCl ₃ as solvent) and the corresponding polyGBIMTFSI (2.1b, bottom, DMSO-d6 as solvent)
Figure 2.2.	gHSQC of polyEPCH with monomer to initiator ratio 500/175
Figure 2.3.	gHSQC of polyGBIMTFSI with monomer to initiator ratio 500/176
Figure 2.4.	GPC traces of polyEPCH with different monomer to initiator ratio. PolyEPCH 100, 200, 500 means polyEPCH with [M]/[I] = 100, 200 and 500 respectively. DMF was used as solvent at 50 °C and polystyrene was used as standard
Figure 2.5.	FT-IR of LiTFSI, butylimidazole, polyEPCH 500 and the corresponding polyGBIMTFSI50080
Figure 2.6.	Normalized TGA traces of polyEPCH with [M]/[I] 500 and the corresponding polyGBIMTFSI81
Figure 2.7.	DSC curves of polyEPCH100, 200 and 500 and the corresponding polyGBIMTFSI. From top to bottome, curves are for polyEPCH100, 200, 500 and polyGBIMTFSI100, 200, 500 respectively
Figure 2.8.	Temperature dependence of ionic conductivities for polyGBIMTFSI 100, 200 and 50085
Figure 2.9.	Temperature dependence of viscosities of polyGBIMTFSI 100, 200 and 500
Figure 3.1.	¹ H NMR of ME ₃ MO102
Figure 3.2.	gHSQC of ME ₃ MO103
Figure 3.3.	gHMBC of ME ₃ MO104

Figure 3.4.	¹ H NMR of polyGBIMTFSI- <i>co</i> -polyME ₃ MO-4/1110
Figure 3.5.	TGA traces of polyGBIMTFSI, polyME ₃ MO and their random copolymer with varying molar composition112
Figure 3.6.	Ionic conductivities of polyGBIMTFSI and its random copolymers with varying molar composition115
Figure 4.1.	¹ H NMR of VBBIT, DMSO-d6 as solvent130
Figure 4.2.	FT-IR spectra of (a) silica nanoparticles, (b) surface initiator, (c) polyVBBIT/silica nanocomposite, and (d) polyVBBIT homopolymer. Samples were made into pellets with KBr
Figure 4.3.	TGA data for (a) silica nanoparticles, (b) nanoparticles modified with surface anchored initiators, (c) polyVBBIT/silica nanocomposites (d) and polyVBBIT. All samples were run in air and at a heating rate of 10 °C/min134
Figure 4.4.	500 MHz ¹ H NMR spectra of a representative sample for kinetic study of surface initiated ATRP of VBBIT136
Figure 4.5.	Kinetic study of surface initiated ATRP of VBBIT, the concentration ratio of $[M]_0$: [Si-Ini]: [CuBr]: [PMDETA] is approximately 100: 1:2:6. [M]_0 and [M] represent the initial concentration of VBBIT monomer and the concentration of monomer at specific time
Figure 4.6.	TEM images of dried Snowtex-XS nanoparticles (a, top), and polyVBBIT/silica nanocomposites (b, bottom)139
Figure 4.7.	DSC curves of polyVBBIT homopolymer and polyVBBIT/silica nanocomposites141
Figure 4.8.	Conductivity of pure PMII and PMII with different amount of polyVBBIT/silica nanocomposites143
Figure 4.9.	J-V curve of the DSSC with PMII/polyVBBIT/silica nanocomposites gel electrolyte146
Figure A1.	Ideal Nyquist plot of Scheme A1164

Figure A2.	Example of a typical Nyquist plot obtained from AC
	impedance measurement. (Sample is polyGBIMTFSI-co-
	polyME ₃ MO-1/1 at 90 °C.)

LIST OF SCHEMES

Scheme 1.1.	Structures of most commonly used cations and anions in ILs	3
Scheme 1.2.	Diels-Alder cycloaddition of cyclopentadiene with methyl acrylate or methyl vinyl ketone in IL	4
Scheme 1.3.	Synthesis of polyimide by polycondensation reaction in IL	5
Scheme 1.4.	Carbamte mechanism for CO ₂ capature using aqueous amine solutions	6
Scheme 1.5.	Reaction between CO ₂ and 1-ethyl-3-methyl-imidazolium acetate via a carbene mechanism	8
Scheme 1.6.	Two examples of reaction schematics between CO ₂ and IL with amine group in its counter anion	9
Scheme 1.7.	Structures of the most common polycationic PILs	17
Scheme 1.8.	Structures of PILs with polyanions and free cations	18
Scheme 1.9.	Polyanionic PILs with trifluoromethanesulfonamide anion (left) and cations other than imidazolium like tetraalkylammonium cations (right)	19
Scheme 1.10	. Zwitterionic PILs reported in literature	20
Scheme 1.11	. General synthetic route to PILs from methacryloyl IL monomers bearing imidazolium species. (R: alkyl chain; X: halide)	21
Scheme 1.12	2. Synthesis of poly(1-butyl-3-vinylbenzylimidazolium chloride) by post-polymerization modification of poly(p-chloromethylstyrene).	22
Scheme 1.13	 Synthetic route to PS-b-PMVBI block copolymers via post- polymerization of a preformed diblock copolymer 	23
Scheme 1.14	. Structure of macromonomer (X = CI or TFSI)	25

Scheme 1.15	. Structures of macromonomers based on (meth)acryloyl groups	8
Scheme 1.16	. Monomers with different cation structures	1
Scheme 1.17	. Structures of IL monomers with immobilizing anions and free imidazolium cations	3
Scheme 1.18	. Synthesis of IL monomer with alkyl spacer between vinyl group and sulfonate	4
Scheme 1.19	. Monomer with vinyl imidazolium cation and vinyl sulfonate anion	6
Scheme 1.20	. Structure of acrylate based PIL with six repeating methylene units as the spacer	7
Scheme 1.21	. Structures of cross-linkers used	7
Scheme 1.22	. Structures of Nonionic-Ionic random copolymer and Ionic- Ionic random copolymer4	5
Scheme 2.1.	ACE and AM mechanism for cationic ring-opening polymerization of epichlorohydrin6	7
Scheme 2.2.	Mechanism for NOct ₄ Br, <i>i</i> -Bu ₃ Al initiated anionic polymerization of epichlorohydrin68	8
Scheme 2.3.	Synthesis of polyEPCH and polyGBIMTFSI7	1
Scheme 3.1.	Mechanism for trifluoroborate etherate and 1,4-butanediol initiated cationic polymerization of epichlorohydrin99	9
Scheme 3.2.	Synthesis of ME ₃ MO10	01
Scheme 3.3.	Copolymerization of EPCH and ME ₃ MO, followed by quaternatization10	08
Scheme 4.1.	Synthesis of IL monomer-VBBIT12	29
Scheme 4.2.	Synthetic route to polyVBBIT/silica nanocomposites13	32
Scheme 4.3.	Pictures of polyVBBIT/silica nanocomposites, PMII and their mixture	42

Scheme 4.4.	Gels formed after conductivity measurement from 25 °C to 90 °C. PMII with 20 wt% polyVBBIT/silica nanocomposites (a) and PMII with 15 wt% polyVBBIT/silica nanocomposites. (b)	144
Scheme A1.	Equivalent circuit of the electrochemical response of the cell used in conductivity measurement	163

Chapter 1 Introduction

Ionic liquids.

Ionic liquids (ILs), also called molten salts, are compounds composed of cations and anions with low melting point, usually below 100 °C. Room temperature ILs, more specifically, are ILs existing in liquid state at room temperature.

History and formation of ILs.

IL was first synthesized in 1914 by Paul Walden,¹ who reported that by neutralizing ethylamine with concentrated nitric acid, a salt, ethylammonium nitrate with melting point 13 - 14 °C was obtained. However, though his discovery was now widely accepted as the starting point of IL study, this paper did not attract much attention at that time. It was not until 1975 that a real breakthrough in IL research was made by Osteryoung group,² in which he studied detailed physical properties of 1-butylpyridium chloride and aluminium(III) chloride, the [C4py]Cl-AlCl₃ system and found that between 60 to 67 mol% of AlCl₃, this system was in liquid state at room temperature (melting point below 20 °C). However, one serious limitation of this system was its narrow liquid range. In 1982, Wilkes and Hussey³ developed a new system based on 1-ethyl-3-methylimidazolium chloride and aluminium(III) chloride, [C₂mim]Cl-AlCl₃, which showed a much wider liquid range from ~ 30 to 60 mol% of AlCl₃. The biggest problem related to this kind of AlCl₃ based ionic liquid system was that it was

moisture sensitive, which would be decomposed even when trace amount of water existed. Due to this problem, synthesis and use of AICI₃ based ionic liquid system was limited in glove box or other devices filled with inert gas. The first IL which could be synthesized and used on bench was discovered by Wilkes and Zaworotko in 1992.⁴ The new non-(moisture sensitive) IL still contained a 1-ethyl-3-methylimidazolium ([C₂mim]) cation, but with different anions, such as nitrate (NO₃), tetrafluoroborate (BF₄) and acetate (CH₃CO₂). However, Wilkes and Zaworotko's IL still needed to be used under inert atmosphere. Though they did not react with water, they would absorb quite a lot of moisture from the air. To solve this problem, Grätzel and coworkers prepared more hydrophobic anions,⁵ trifluoromethanesulfonate ($[CF_3SO_3]$), trifluoroacetate ($[CF_3CO_2]$), such as bis(trifluoromethanesulfonyl)imide ([N(CF₃SO₂)₂]) and heptafluorobutanoate $([C_3F_7CO_2])$. Since then, more and more papers studying ILs were published. ILs include imidazolium, Common cations in tetraalkylammonium, tetraalkylphosphonium, pyridinium, and pyrrolidinium. Common anions include chloride. bromide. tetrafluoroborate. hexafluoroborate. bis(trifluoromethanesulfonyl)imide and dicyanamide. Among them, imidazolium based ILs were the most popular. Scheme 1.1 shows the structures of most commonly used cations and anions in ILs.⁶



Scheme 1.1. Structures of most commonly used cations and anions in ILs.

Application of ILs

Currently, ILs have been used in a lot of areas, such as electrolytes in electrochemical devices,⁷ absorbents of CO₂,⁸ catalysts in organic synthesis and polymerization,⁹ green solvents,^{10,11} and separation reagents in analytical chemistry.¹²

ILs used as green alternatives to volatile organic solvents

One simple and qualitative definition for polar solvent is that a polar solvent can dissolve and stabilize polar or charged solutes. Under this definition, ILs are generally considered as highly polar solvents.¹³ Due to their good solubility to many organic and inorganic compounds, negligible volatility, chemical and thermal stability, ILs were used to replace traditional organic solvents in organic synthesis and polymerization in the past two decades. A lot of organic synthesis has been conducted in IL solvent, such as substitution, ^{14,15} elimination, ^{16,17} and addition reactions.^{18,19} Among all of these reactions, Diels-Alder cycloaddition was one of the first to be studied. Scheme 1.2 shows the Diels-Alder reaction of cyclopentadiene with methyl acrylate or methyl vinyl ketone.¹⁹ Compared to non-polar organic solvents, IL ethylammonium nitrate (mp ~ 12 °C) showed enhancement of endo stereoselectivity.



Polymerizations such as polycondensation,^{20,21} ionic polymerization (cationic and anionic)^{22,23} and radical polymerization (free radical, ATRP and RAFT)²⁴⁻²⁶ have also been conducted in ILs. Compared to traditional organic solvents, ILs have two main advantages. The first is that their thermal stability and non-volatility enable high temperature polymerization such as polycondensation reaction. The second is that their abilitites to dissolve inorganic or organometallic catalysts enable homogeneous polymerization, which sometimes is impossible with organic solvents.²⁷ Scheme 1.3 shows an example of polycondensation reaction between aromatic dianhydride and diamine to form polyimide.²¹ Quantitative yield was obtained.

n
$$\rightarrow$$
 + n H₂N-Ar-NH₂ $\xrightarrow{R_1^{-N} \rightarrow R_2^{-Y^{-}}}_{180 \ ^{\circ}C}$ + Ar-N + A

Scheme 1.3. Synthesis of polyimide by polycondensation reaction in IL

ILs used as absorbents of CO₂

The second important application of ILs is as CO₂ absorbents. Currently, more and more fossil fuels are burned on a global scale. As a result, CO₂ emission increases day by day, which is widely acknowledged as one of the causes of global warming. Physical absorption and chemical absorption are two main methods used nowadays in industry to remove CO₂ from large point sources such as power plants. For physical absorption, polyethylene glycol and methanol are the most commonly used gas absorbents.²⁸ For chemical absorption, aqueous monoethanol amine (MEA) is the gas absorbent used.²⁹ Currently, MEA process is used in more than 95 % of natural gas sweetening operations in U.S.³⁰ Scheme 1.4. shows the carbamate mechanism for CO₂ capture using aqueous amine solutions. However, both physical and chemical absorption methods currently used have serious drawbacks. Polyethylene glycol suffers problems such as thermal degradation. On the other hand, methanol suffers from its volatility. In the case of the MEA method, things get even worse. It suffers from volatility of water and amines. Furthermore, amines are prone to thermal degradation, and they are corrosive to steel.



Scheme 1.4. Carbamate mechanism for CO₂ capture using aqueous amine solutions

Due to their good solubility and selectivity to CO_2 , non-volatility and thermal stability, ILs have been studied as a promising candidate in CO_2

absorption.^{8,31,32} Using ILs as absorbents at least overcome two major problems encountered in the three methods mentioned above. ILs absorb CO_2 in two way, by physical absorption and chemical absorption respectively.

For physical absorption, the uptake mode is by intercalation of CO₂ into the natural cavities of ILs, which is confirmed by the fact that there would be a volume expansion after CO₂ absorption. The ability of ILs to physically absorb CO₂ was mainly affected by counter anions. A higher fluorination degree in counter anions results in a higher CO₂ absorption ratio, due to the interactions between Lewis basic fluorine atom and Lewis acidic CO2. 33-36 Compared to the widely used MEA process, the desorption of CO₂ in ILs is much easier and thermodynamically favored because absorption and desorption of CO₂ in ILs are based on weak physical interactions.³⁷ However, some drawbacks for physical absorption of CO₂ in ILs do exist. The first is that physical absorption in ILs must be conducted under high pressure to ensure a satisfactory absorption while in most cases this requirement cannot be met. The second is that physical absorption is a slow process in ILs due to their high viscosities. Another disadvantage is that the presence of water would decrease the ability of CO₂ absorption in ILs, especially for hydrophilic ones.⁸

Another way for CO_2 absorption in ILs is chemical absorption. ILs can trap CO_2 via a carbene mechanism when the 1,3-dialkylimidazolium cations are paired with a basic enough anion such as acetate.³⁸ Scheme 1.5 shows the reaction between CO_2 and 1-ethyl-3-methyl-imidazolium acetate. However, the CO_2 uptake stoichiometry is quite low in this case.



Scheme 1.5. Reaction between CO_2 and 1-ethyl-3-methyl-imidazolium acetate via a carbene mechanism

To improve CO₂ uptake stoichiometry, amine functional groups were introduced into ILs, either in imidazolium cation^{39,40} or its counter anion.^{29,41} A maximum stoichimetry of 0.5 was observed when amine group was introduced into imidazolium cation.³⁹ On the other hand, the maximum stoichiometry could be as high as 1 when the amine group was introduced into the counter anions.²⁹

Scheme 1.6 shows two examples of the reaction schematics between CO_2 and IL with amine group in its counter anion.



Scheme 1.6. Two examples of reaction schematics between CO_2 and IL with amine group in its counter anion

ILs as electrolyte

With no doubts, one of the most important applications of ILs is as electrolytes in electrochemical devices. Due to their non-volatility, non-flammability, wide electrochemical window, high inherent conductivity, good solubility to a wide range of materials including organic, inorganic and polymeric materials, and wide thermal operating range, ILs have been used in electrochemical devices such as lithium batteries, dye sensitized solar cells (DSSCs), fuel cells, supercapacitors and so on.⁷

ILs in lithium batteries

Due to their high energy density and energy efficiency, lithium battery has been used in various electronic devices such as cellular phones, digital cameras, laptops and even in vehicles and other large-scale power systems.⁴² However, the current lithium battery system has an inherent safety problem due to its use of volatile and flammable organic solvents as electrolyte solvents.⁴³ A typical example of electrolyte in commercialized lithium battery is composed of ethylene carbonate as the solvent and LiPF₆ as the solute, with the addition of a linear carbonate such as dimethyl carbonate as a co-solvent to increase the fluidity and reduce melting points of the electrolyte. Under certain circumstances, the electrolyte in lithium battery can ignite or even explode.⁴⁴ Therefore, it is highly demanding to develop new and safe electrolytes as replacement of organic solvent based electrolytes.

In recent years, ILs have received considerable interests as electrolyte materials for lithium battery.^{43,45-50} Compared to conventional organic solvent electrolytes, IL electrolytes have several unique properties making them promising candidates for lithium battery, such as non-volatility, non-flammability, wide electrochemical window, high inherent conductivity and wide thermal operating range.⁴² The non-volatility not only allows the IL electrolyte based lithium battery to be operated in sealed cells at elevated temperatures without venting, but also eliminates the possibility of vapor ignition, thereby increasing the overall safety of the cell. ILs have a wide electrochemical window of 4 ~ 5 eV, making them extremely resistant to electrochemical oxidation and reduction. In addition, ILs possess high ionic conductivities, usually around 10 mS/cm, which is equivalent to the best

current organic solvent based electrolytes. Besides, IL based electrolytes have a wide thermal operating range. Current organic solvent based lithium batteries suffer from a limited operating temperature range, since the electrolytes used in most commercial lithium batteries will deteriorate at temperatures higher than 60 °C. In addition, the irreversible reaction between dissolved lithium salts and organic solvents, negatively affect the cell performance. Performance also suffers when the temperature approaches - 20 °C, as most organic solvents used in lithium batteries have a freezing point around this temperature. The temperature limit problems can be easily addressed by IL electrolytes, as most ILs are thermally stable to temperatures greater than 200 °C, resulting in a much broader potential range of operating temperatures than current electrolytes.

Here shows a recent example of ILs as electrolytes in lithium battery.⁴⁵ In this work, a poly(vinylidene difluoride-*co*-hexafluoropropylene) (PVDF-HFP) membrane was prepared and served as the host matrix for the preparation of IL-based polymer electrolytes by activation with N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Py₁₄TFSI) complexed with 1 M LiTFSI. The IL-based polymer electrolyte showed high thermal and electrochemical stability, high ionic conductivity (1.1×10^{-4} S/cm at 0 °C), good compatibility with LiFePO4 electrode, good charge-discharge performance and delivering specific capacities of 143 mA·h/g at 0.1 C-rates. Also, the IL-based polymer electrolyte exhibited

stable cycle properties and therefore was demonstrated to be suitable for lithium battery applications.

ILs in fuel cells

Fuel cell is a device that converts chemical energy into electrical energy via a redox reaction. Fuel cells are different from batteries in that they require a constant input of fuels to run, but they can produce electricity continuously as long as fuels are supplied. In fuel cell, hydrogen is the most important fuel, but alcohols such as methanol and hydrocarbons such as natural gas are also used. Due to their high energy density, high conversion efficiency and low pollutant emission, ^{51,52} fuel cell has been recognized as one of the most promising energy sources which could provide clean and efficient energy for stationary and mobile applications.⁵³ There are three kinds of fuel cells under active development, including alkaline fuel cell (AFC), proton exchange membrane fuel cell (PEMFC) and phosphoric acid fuel cell (PAFC).⁵² Among them, PEMFC are considered one of the most promising technologies for stationary power generation and transportation applications.

In PEMFC, a major drawback of the most commonly used humidified perfluorosulfonic acid-based membranes, represented by NafionTM, is that they cannot be used at temperatures higher than 100 °C because of the evaporation of water and the resulting conductivity loss. However, operation at higher temperatures is critical for improving performance of PEMFCs because it could

enhance the reaction kinetic at both electrodes, improve the carbon monoxide tolerance of the platinum catalyst in the anode, and simplify heat and water managements.⁵³ For operation of PEMFC at higher temperatures, an anhydrous proton conductivity mechanism is required. To partially overcome this problem, one method is to use protic ILs instead of water.

Protic ILs, composed of Brønsted acids and bases, which can form hydrogen bonds and act as proton carriers, have been considered as effective protontransferring carriers for high temperature PEMFCs. Greenbaum and coworkers have prepared a homogeneous, freestanding, and thermal stable gel-type PEM based on protic IL, 1-methyl-3-propyl imidazolium dihydrogen phosphate, and phosphoric acid doped polybenzylimidazole. The PEM obtained had conductivity of up to 2.0 x 10⁻³ S/cm at 150 °C under anhydrous condition. While after absorbing some water vapor, the conductivity rises even higher.⁵⁴ In a recent paper, Watanabe and coworkers have also prepared a composite PEM based on sulfonated polyimide and а protic IL. diethylmethylammonium trifluoromethanesulfonate. The ionic conductivity of PEM obtained was higher than 10⁻² S/cm at 140 °C under anhydrous condition.⁵⁵ In addition, to prevent the leakage problem of protic ILs when doped in composite membrane, Yan and coworkers incorporated mesoporous silica nanoparticles.⁵⁴ The results revealed that incorporation of proper amounts mesoporous silica nanoparticles not only prevented the release of protic IL components from composite membrane, but also increased the proton conductivity, which was due to the capillary force of the mesoporous silica nanoparticles and the ion transport channel formed in the hybrid membranes.

ILs in DSSCs

Nowadays, one of the greatest challenges for global society is to find ways to replace the vanishing fossil fuel supplies with renewable resources such as wind energy, nuclear energy and solar energy.⁵⁶ Among them, solar energy is expected to play a key role, since the sun provides approximately 120,000 tetrawatts to the Earth, which is about 6,000 times more than the current world's energy consumption rate. It has been estimated that our current energy needs can be met by covering 0.1 % of the Earth's surface with photovoltaic installations with a light-to-power conversion efficiency of 10 %. So far, silicon-based solid-state junction devices have dominated in the area of photovoltaic solar energy converters and served a rapidly growing market, which was expected to rise to 300 GW by 2030.⁵⁷ However, compared to the fossil or nuclear energy, the cost of photovoltaic electricity production is still too high.

In recent years, DSSCs have been extensively studied as a low-cost alternative to commercial silicon-based cells.⁵⁸⁻⁶⁰ Photoexcitation of the sensitizer (S) is followed by electron injection into the conduction band of a semiconductor oxide film. The sensitizer is regenerated by the redox system, which itself is regenerated at the counter electrode by electrons passed through the load.⁵⁶

Here, ruthenium dye is the most commonly used sensitizer, with nanocrystalline TiO_2 as the semiconductor oxide film and $1^7/l_3^-$ as the redox couple. Till now, the highest light-to-power conversion efficiency of DSSCs achieved based on organic solvent electrolyte exceeds 12 %.⁶¹ However, hermetic sealing of volatile electrolytes is costly and counteracts the merit of DSSCs as low-cost alternatives to silicon-based photovoltaic devices. In addition, encapsulation of volatile solvents is a critical issue for long-term device stability. Hence, it is very important to investigate non-volatile electrolytes for the development of DSSCs.

ILs, due to their non-volatility, non-flammability, good thermal and chemical stability, have been extensively studied as electrolyte materials for DSSCs in recent years.^{62,63} However, due to the intrinsic high viscosity and the resulting low conductivity of ILs, DSSCs based on ILs electrolytes usually showed lower conversion efficiency compared to volatile solvent based ones.⁶⁴⁻⁶⁶ To reduce the viscosities of IL based electrolytes, Grätzel and coworkers have fabricated DSSCs based on mixtures of three different ILs (including1,3-dimethlymidazolium iodide, 1-ethyl-3-methylimidazolium iodide, and 1-ethyl-3-methylimidazolium tetracyanoborate) and achieved an efficiency of 8.2 %.⁶⁷ In addition, by further structure optimization of the ruthenium dye, higher efficiency 9.1 % was achieved.⁶⁸ Though ILs based DSSCs showed conversion efficiency lower than volatile solvents based ones, the long-term stability was greatly improved. Kato and coworkers compared the long-term performance of two different electrolytes,

one based on volatile solvents γ -butyrolactone and the other based on IL, 1,2dimethyl-3-propylimidazolium iodide.^{69,70} The results revealed that the DSSC using IL electrolyte reduced the deterioration factor to one sixth of the one using volatile solvents. The lifetime for outdoor use was estimated over 15 years for IL electrolyte based DSSC, while for volatile solvents based ones, the lifetime was only 2.5 years.

Poly(ionic liquids) (PILs)

Though ILs have been extensively studied and successfully applied in many areas, the intrinsic liquid properties of ILs presented a fabrication issue in industrial production. More recently, there has been growing interest in the polymeric forms of ILs (PILs), which combined the unique properties of ILs and polymer architecture. Compared to ILs, PILs have improved processability and durability, better mechanical stability, and improved control of their meso- to nano-structure.

Formation of PILs

There have been mainly three kinds of PILs reported in literature: PILs composed of polycations and free anions, PILs composed of polyanions and free cations, and zwitterionic PILs.

PILs composed of polycations and free anions

Most PILs synthesized so far are PILs composed of cations in their polymer backbone and free anions. Among them, imidazolium cations⁷¹⁻⁷⁹ were the most common ones used. Other cations such as tetraalkyl ammonium,⁸⁰⁻⁸⁵ pyridinium,^{80,86,87} pyrrolidonium,⁸⁸⁻⁹¹ and guanidinium^{92,93} have also been synthesized. On the other hand, the most popular anions in PILs include chloride, bromide, iodide, thiocyanate, tetrafluoroborate, hexafluorophosphate and bis(trifluoromethanesulfonyl)imide.⁶ For polymerizable functional groups, vinyl,^{71,72,80,86,87,94-97} styrenic, ^{74,75,81,98} and (meth)acrylic^{80,82,83,85,88,93,99} are the most popular ones. Scheme 1.7 shows the most commonly seen polycationic PILs in literature.



R = H, or alkyl, R' = H, or methyl X = Cl, Br, BF₄, PF₆, TFSI, SCN, etc...

Scheme 1.7. Structures of the most common polycationic PILs

PILs composed of polyanions and free cations

So far, the number of PILs composed of polyanions and free cations has been much smaller compared to those polycationic ones. In 2004, Ohno and coworkers published a paper describing the synthesis of a new class of PILs with polyanion backbones. In this paper, a series of PILs based on vinyl carbonate, vinyl sulphonate, vinyl phosphonate, styrenyl sulphonate, methacryloyl sulphonate anions and free imidazolium cations were synthesized.¹⁰⁰ The structure of PILs synthesized are shown in Scheme 1.8.



Scheme 1.8. Structures of PILs with polyanions and free cations.

On the other hand, PILs with more sophisticated anions such as trifluoromethanesulfonamide and cations other than imidazolium like tetraalkylammonium cations have also been synthesized.^{101,102} The structures are shown in Scheme 1.9.



Scheme 1.9. Polyanionic PILs with trifluoromethanesulfonamide anion (left) and cations other than imidazolium like tetraalkylammonium cations (right)

Zwitterionic PILs

Another type of PILs called zwitterionic PILs has also been synthesized, in which both cations and anions are covalently linked in the polymer backbone. The conductivities of zwitterionic PILs are quite low, which are around 10⁻⁹ S/cm. This is because the cations and anions in PILs cannot move under external voltage. However, when salts like LiTFSI were added, the dissociated ions from added salts could behave as charge carriers and the conductivity of the PILs electrolytes could be elevated, usually several orders of magnitude higher. Several examples of reported zwitterionic PILs were listed in Scheme 1.10.¹⁰³⁻¹⁰⁵



Scheme 1.10. Zwitterionic PILs reported in literature

Synthesis of PILs

PILs can be synthesized in two methods: (1) direct polymerization of IL monomers, (2) chemical modification of existing polymers. In each method, several polymerization techniques have been employed, including conventional^{94,105-108} and controlled radical polymerization,¹⁰⁹⁻¹¹² step-growth polymerization,¹¹³ ring-opening polymerization¹¹⁴ and others.^{115,116}

Direct polymerization of IL monomers

An IL monomer is an IL containing one or more polymerizable units, such as vinyl, (meth)acryloyl and stryrenic groups. The polymerization of IL monomers is a straightforward and widely adopted strategy to form PILs, which results in a homogeneous polyelectrolyte possessing the same type of IL moiety in each repeating unit. Scheme 1.11 shows a general approach for the preparation and polymerization of methacryloyl based IL monomers⁶. Methacryloyl chloride first reacted with an hydroxyl-containing haloalkane to form an ester. Then, the
haloalkane bearing ester obtained was further quarternized by an N-alkyl imidazole to form an IL monomer. In the third step, the IL monomer was polymerized in the presence of a initiator, such as 2,2'-azo-bis-isobutyronitrile (AIBN).



Scheme 1.11. General synthetic route to PILs from methacryloyl IL monomers bearing imidazolium species. (R: alkyl chain; X: halide)

Chemical modification of existing polymers

PILs can also be prepared by chemical modification of existing polymers. This strategy ensures the PILs formed have the same architecture, monomer composition and degree of polymerization present in the original polymers. Besides, by chemical modification of the carefully chosen precursor polymers, this strategy enables preparation of some PILs with unique structures and compositions, which are inaccessible by direct polymerization of IL monomers. In 2005, Shen and coworkers reported the preparation of a PIL by chemical modification.¹⁰⁹ As shown in Scheme 1.12, 4-chloromethylstryrene was first polymerized via RAFT polymerization and then guarternized with N-

butylimidazole to form a PIL, poly(1-butyl-3-vinylbenzylimidazolium chloride). The quarternization reaction was quantitative, as confirmed by vanishing signals of chloromethyl group in ¹H NMR spectrum. Block copolymers containing PIL segment could also be prepared by post-polymerization modification.¹¹⁷ As shown in Scheme 1.13. diblock copolymer polystryrene-b-poly(4а chloromethylstyrene) first synthesized nitroxide-mediated was via а polymerization. Since the polystyrene segment would not react with Nmethylimidazole, only the poly(4-chloromethylstyrene) segment was converted to poly(1-methyl-3-vinylbenzylimidazolium chloride). Again, a nearly quantitative conversion (> 99%) was observed for poly(4-chloromethylstyrene) segment, as confirmed by ¹H NMR and microanalysis.



Scheme 1.12. Synthesis of poly(1-butyl-3-vinylbenzylimidazolium chloride) by post-polymerization modification of poly(*p*-chloromethylstyrene).



Scheme 1.13. Synthetic route to PS-*b*-PMVBI block copolymers *via* post-polymerization modification of a preformed diblock copolymer

Application of PILs

With no doubts, one of the major driving forces for preparing and studying PILs is to harness their potential as novel polymer electrolyte in electrochemical devices such as lithium battery, ^{91,118} DSSC^{119,120} and fuel cell.⁹² Compared to IL electrolyte, solid state polymer electrolyte has important advantages such as mechanical stability, safety and easy processing. In addition, polymeric electrolyte may potentially permit production of flexible and transparent ion

conductive materials with defined size and shape, such as thin films, fibers and coatings. However, compared to ILs, PILs generally have lower conductivity, usually several orders of magnitude, which is due to both reduced number of mobile ions after covalent bonding of the polymerizable ions and the increased glass transition temperature.^{94,106}

Factors affecting ionic conductivity of PILs

There are a lot of factors affecting the ionic conductivity of PILs, such as the counter anion, the structure and length of spacer between backbone and imidazolium cation, the alkyl chain on the imidazolium ring, the structures of the cations, the immobilization of anions on the backbone, degree of polymerization, crosslinking and presence of copolymers.

Anion effect on ionic conductivity of PILs

Ohno and coworkers have systematically studied the structure-related ionic conductivity of (meth)acryloyl- and N-vinylimidazolium-based PILs. In 1999, Yoshizawa and Ohno first reported an methacryloyl-based PIL prepared for this purpose.¹⁰⁶ In this article, a poly(ethylene oxide) (PEO) derivative with both methacryloyl group and imidazolium salt structure on its ends were prepared and polymerized. The structure of the macromonomer was shown in Scheme 1.14. The macromonomer was polymerized in bulk via free radical polymerization using AIBN as the initiator to form PIL. The obtained PIL was a rubber-like material with high ionic conductivity and low T_q , though the degree of

polymerization was not clear. The effect of different anions on PIL conductivity was examined. As shown in Table 1.1 and Figure 1.1, PIL (X = CI or TFSI) showed quite close T_g , while the conductivity differed a lot, around 3 orders of magnitude. This was attributed to the molten salts formation and much weaker interaction force of ether oxygens towards TFSI or CI. Since TFSI has a much larger ion radius (325 pm) compared to CI (181 pm) and the surface charge density should be much smaller in TFSI. PIL with TFSI as counter anion showed an excellent conductivity of 1.20 x 10⁻⁴ S/cm at 30 °C.



Scheme1.14. Structure of macromonomer (X = CI or TFSI).

Table 1.1. T_g of macromonomers and PILs

	τ _g / °C
Macromonomer X = Cl	-74
Macromonomer X = TFSI	-72
PIL X = CI	-62
PIL X = TFSI	-64



Figure 1.1. Temperature dependence of the ionic conductivity of macromonomers (igodot, X = TFSI; igodot, X = CI) and their corresponding polymers (\bigcirc , X = TFSI, \triangle , X = CI). (Reprinted with permission from *Chem Lett* **1999**, 889-890. Copyright 1999 The Chemical Society of Japan)

Effect of spacer structure and length on ionic conductivity of PILs

The effect of different spacer structure and spacer length on conductivity of PIL was also systematically studied.^{100,121} For this purpose, two sets of macromonomers based on (meth)acryloyl polymerizable groups were synthesized. The structures of macromonomers are shown in Scheme 1.15. The

PILs were prepared by free radical polymerization of these macromomomers and no degree of polymerization was reported. As shown in Figure 1.2, the ionic conductivity increased with increasing spacer length, which was attributed to the fact that imidazolim cation turned more mobile with longer flexible spacer. In addition, the ionic conductivity of PILs with alkyl chain spacer was higher than that of PEO spacer in all chain length. This improvement was mainly due to much weaker interaction force of alkyl chains toward TFSI anions compared to PEO ones. The highest conductivity achieved was 3.62×10^{-4} S/cm from PIL7 with six ethylene repeating units as spacer.

$$\int_{-1}^{0} \int_{-1}^{1} \int_{-1}^{R_{2}} \int_{-1}^{x} \int_{-1}^{x} \int_{-1}^{x} \int_{-1}^{x} \int_{-1}^{-1} \int_{-1}^{R_{2}} \int_{-1}^{x} \int_{-1}^{-1} \int_{-1}^{R_{2}} \int_{-1}^{x} \int_{-1}^{-1} \int_{-1}^{R_{2}} \int_{-1}^{x} \int_{-1}^{-1} \int_{-1}^{R_{2}} \int_{-1}^{x} \int_{-1}^{-1} \int_{-1}^{-1}$$

X = Br or TFSI (b)

Scheme 1.15. Structures of macromonomers based on (meth)acryloyl groups



Figure 1.2. Effect of spacer structure and length on the ionic conductivity for PILs. (Reprinted with permission from *Electrochim Acta* **2001**, *46*, 1723-1728. Copyright 2001 Elsevier Science Ltd)

Effect of alkyl chains on imidazoium ring on ionic conductivity of PILs

The effect of alkyl chain on imidazolium ring was also studied. Three methacrylate based macromonomers 1, 3, and 4 with different alkyl chains were prepared and polymerized. (Structures shown in Scheme 1.15) As shown in Figure 1.3, PILs with ethyl group on imidazolium ring had the highest conductivities. However, the effect of alkyl chains on imidazolium ring was not as significant as spacer length and counter anions on the conductivity of PILs.



Figure 1.3. Effect of alkyl chain on the ionic conductivity and T_g for macromonomer 1, 3, 4 and their corresponding PILs. (Reprinted with permission from *Electrochim Acta* **2001**, *46*, 1723-1728. Copyright 2001 Elsevier Science Ltd)

Effect of cation structures on ionic conductivity of PILs

Cation structures other than imidazolium were prepared and their effects on ionic conductivity were also studied.⁸⁸ A series of acryloyl-bearing monomers with different cation structures including imidazolium, pyrrolinium, pyrrolidinium and piperidinium were polymerized via free radical polymerization. The structures were shown in Scheme 1.16. The conductivities of the corresponding PILs were shown in Figure 1.4. As shown in Figure 1.4, PILs with imidazolium cations showed higher conductivities compared to PILs with other cation structures,

except in the case of 1-ethyl-2-methylimidazolium. And again, as mentioned above, PILs with ethylimidazolium cation showed the highest conductivity. These studies revealed that modification of the cation structures was not as significant as spacer length (i.e., chain flexibility) and anion size in determining the conductivities of the PILs.



Scheme 1.16. Monomers with different cation structures



Figure 1.4. Conductivities of PILs with different cation structures (Reprinted with permission from *Electrochim Acta* **2006**, *51*, 2614-2619. Copyright 2006 Elsevier Science Ltd)

Effect of immobilizing anions on the backbone with free cations on ionic conductivity of PILs

Another attempt to improve the polymer ionic conductivity was to prepare polyanion type of PILs.¹⁰⁰ Polymerization through the anion was considered to be effective in maintaining the flexibility of imidazolium cation, potentially resulting in higher ionic conductivity of the PILs. To investigate the effect of anion structure on the ionic conductivity, four different monomers were prepared by neutralizing N-ethylimidazole with acrylic acid, vinylsulfonic acid, vinylphosphonic

acid and *p*- styrenesulfonic acid, as shown in Scheme 1.17. All four monomers were polymerized via free radical polymerization and PILs based on vinylsulfonic acid exhibited the lowest T_g and thus the highest ionic conductivity (1.1 x 10⁻⁴ S/cm) at room temperature, which was in the same range compared to polycation type PILs with long flexible spacers.¹⁰⁶



ElmX

Scheme 1.17. Structures of IL monomers with immobilizing anions and free imidazolium cations

The effect of alkyl spacer on the ionic conductivity of polyanion type PILs was also studied. Scheme 1.18 shows the synthesis of IL monomer with alkyl spacer between methacrylate and sulfonate group. After polymerization, the conductivity

was measured and compared to that of PIL based on vinylsulfonic acid, as shown in Figure 1.5. Both PILs showed ionic conductivity around 10⁻⁴ S/cm at room temperature, which was explained by the fact that the flexibility of imidazolium cation in polyanion type PILs was inherently high and the conductivity would not be improved by the introduction of alkyl spacers.



Scheme 1.18. Synthesis of IL monomer with alkyl spacer between vinyl group and sulfonate



Figure 1.5. Temperature dependence of the ionic conductivity for EImVS, EImC3S, and their polymers. (\bigcirc) EImVS, (\bigcirc) P(EImVS), (\triangle) EImC3S, (\blacktriangle) P(EImC3S). P implies polymerized system. (Reprinted with permission from *Electrochim Acta* **2004**, *50*, 255-261. Copyright 2004 Elsevier Science Ltd)

Effect of degree of polymerization on ionic conductivity of PILs

The effect of degree of polymerization on ionic conductivity of PIL was also examined.^{100,108} PIL based on a vinyl imidazolium cation with a vinyl sulfonate anion was prepared by free radical polymerization, Scheme 1.19. After 3 h, the resultant copolymer showed a poor conductivity of 8.5 x 10^{-5} S/cm at 30 °C.

However, increased polymerization time decreased the ionic conductivity. After 6 h, the resultant copolymer showed a much poorer conductivity of lower than 10^{-9} S/cm, suggesting that increased molecular weight lowered ionic conductivity.



Scheme 1.19. Monomer with vinyl imidazolium cation and vinyl sulfonate anion

Effect of crosslinking on ionic conductivity of PILs

As mentioned above, PIL with a long alkyl spacer would have high ionic conductivity. PIL based on acrylate with six repeating methylene units as spacer showed an ionic conductivity of 1.37×10^{-4} S/cm at 30 °C, Scheme 1.20.¹²² However, it was difficult to handle due to its sticky characteristics. One way to solve this problem was to make flexible films by the addition of cross-linkers. The structures of cross-linkers used were shown in Scheme 1.21. After addition of a small amount of cross-linkers, PIL formed flexible films and it was confirmed that adding only 1 mol% cross-linker was enough to obtain flexible films. With increasing amount of the cross-linker, the film formation changed gradually into a self standing film.



Scheme 1.20. Structure of acrylate based PIL with six repeating methylene units as the spacer



Scheme 1.21. Structures of cross-linkers used



Figure 1.6. The photograph of film electrolyte composed of PIL and 3 mol% E_3V cross-linker (Reprinted with permission from *Polymer* **2004**, *45*, 1577-1582. Copyright 2004 Elsevier Science Ltd)

Figure 1.6 shows the picture of a flexible self-standing film prepared with 3 mol% of cross-linker E₃V. The effect of cross-linker on ionic conductivity of PIL films was examined. As shown in Figure 1.7, with the addition of 0.5 mol% E₃V, the T_g of PIL film increased about 5 °C compared to that of the linear polymer, and thus ionic conductivity dropped to nearly half of that of the linear polymer. In addition, with more E₃V added, the T_g and ionic conductivity did not change much. The T_g increase could be explained as cross-linking restricted the motion of polymer backbone thus resulting in a decrease of ionic conductivity. The effect of spacer length and polymerizable group of the cross-linkers on the ionic conductivity of PIL films were also examined. Different cross-linkers, as shown in Scheme 1.22,

were added to PILs, while keeping the concentration constant as 1.3 mol%. The conductivity data was shown in Figure 1.8. For cross-linker E_xV , PIL film with E_3V showed higher conductivity. For cross-linker E_yA , E_4A performed the best and the film showed almost same conductivity compared to linear PIL. While in the case of E_zM , E_9M exhibited slightly higher conductivity than the other two. It was concluded that introducing cross-linker had a negative effect on the ionic conductivity of PILs. However, with selection of an appropriate spacer, this negative effect could be alleviated.



Figure 1.7. The effect of cross-linker (E_3V) concentration on the ionic conductivity and T_g of the PIL film (Reprinted with permission from *Polymer* **2004**, *45*, 1577-1582. Copyright 2004 Elsevier Science Ltd)



Figure 1.8. Temperature dependence of the ionic conductivity for PIL films with different cross-linkers (X = 2 or 3) (Reprinted with permission from *Polymer* **2004**, *45*, 1577-1582. Copyright 2004 Elsevier Science Ltd)



Figure 1.9. Temperature dependence of the ionic conductivity for PIL films with different cross-linkers (y = 4 or 13-14) (Reprinted with permission from *Polymer* **2004**, *45*, 1577-1582. Copyright 2004 Elsevier Science Ltd)



Figure 1.10. Temperature dependence of the ionic conductivity for PIL films with different cross-linkers (z = 2 or 9) (Reprinted with permission from *Polymer* **2004**, *45*, 1577-1582. Copyright 2004 Elsevier Science Ltd)

Effect of copolymer on the conductivity of PILs

Introducing an additional component to PIL backbone was another way to increase ionic conductivity. Elabd and coworkers studied the effect of random copolymer composition on ionic conductivity of PILs.¹²³ Two different sets of random copolymer were synthesized which they named as nonionic-ionic copolymer and ionic-ionic copolymer respectively. Nonionic-ionic copolymer was prepared by free radical polymerization of a nonionic monomer *n*-hexyl

methacrylate (HMA) and an ionic monomer 1-(2-methacryloyl)ethyl)-3butylimidazolium tetrafluoroborate (MEBIm-BF₄). Ionic-ionic copolymer was prepared by replacing a proportion of the BF4 anions in the homopolymer of poly(1-(2-methacryloyl)ethyl)-3-butylimidazolium tetrafluoroborate) with TFSI. Scheme 1.22 shows the structures of two kinds of random copolymers. A series of nonionic-ionic copolymers with different composition of HMA were obtained by tuning the HMA concentration in the free radical polymerization. The effect of introducing HMA on T_g and ionic conductivity was studied, as shown in Figure 1.9. The conductivity increased with increasing amount of HMA. This was explained as that the reduction in T_g with increasing HMA composition had a more significant effect on ionic conductivity compared to the reduction in charge carriers concentration, which one would expect a decrease in ionic conductivity. On the other hand, ionic conductivity of copolymer started to decrease at 67.5 mol% HMA composition. This was probably due to that the effect of low concentration of charge carriers overwhelmed that of T_g decrease.



Nonionic-Ionic random copolymer Ionic-Ionic random copolymer

Scheme 1.22. Structures of Nonionic-Ionic random copolymer and Ionic-Ionic random copolymer



Figure 1.11. Temperature dependence of ionic conductivity for poly(HMA-*co*-MEBIm-BF₄) (Reprinted with permission from *Macromolecules* **2009**, *42*, 4809-4816. Copyright 2009 American Chemical Society)



Figure 1.12. Composition and glass transition dependence of ionic conductivity for poly(HMA-*co*-MEBIm-BF₄) (Reprinted with permission from *Macromolecules* **2009**, *42*, 4809-4816. Copyright 2009 American Chemical Society)

The effect of anion exchange on ionic conductivity of copolymers was also studied with the results shown in Figure 1.10. As expected, with the increase of TFSI composition in the copolymer, the ionic conductivity increased. This was mainly attributed to the reduction in T_g after introducing TFSI, because the negative charge on TFSI was more delocalized than BF₄ resulting in much weaker interactions between the counter anions and imidazolium cations.

Besides, unlike the HMA copolymers, the increase in ionic conductivity was continuous over the composition range investigated.



Figure 1.13. Temperature dependence of ionic conductivity for poly(MEBIm-TFSI-*co*-MEBIm-BF₄) (Reprinted with permission from *Macromolecules* **2009**, *42*, 4809-4816. Copyright 2009 American Chemical Society)



Figure 1.14. Composition and glass transition dependence of ionic conductivity for poly(MEBIm-TFSI-*co*-MEBIm-BF₄) (Reprinted with permission from *Macromolecules* **2009**, *42*, 4809-4816. Copyright 2009 American Chemical Society)

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Chapter 2 Synthesis and characterization of novel low T_g poly(ionic liquids)

Introduction

In the past few years, poly(ionic liquids) (PILs), which combined the unique properties of ionic liquids and polymer architecture, have attracted a lot of attention.¹⁻⁸ Compared to ILs, PILs have enhanced mechanical stability, improved processability and durability. In addition to utilities as polymer electrolytes in electrochemical devices,^{1-5,9-11} PILs also found applications in gas absorption and separation,¹²⁻¹⁵ porous polymers^{16,17} and components in block copolymers.^{18,19} However, one critical drawback for PILs is that once polymerized, the conductivity usually suffers a huge decrease compared to their monomers.¹

To obtain high ionic conductivity PILs, people have tried many different methods, such replacing halide anion with anions like as larger bis(trifluoromethanesulfonyl)imide (N(SO₂CF₃)₂), ¹⁻⁴ introducing long alkyl chain or oligo-ethylene oxide chain between the vinyl group and the imidazolium ion,²⁻⁴ and polymerizing the IL anion to retain the mobility of imidazolium cation.²⁰⁻²² Among these methods, introducing long alkyl or oligo-ethylene oxide chain turned out to be very effective due to their flexible nature, which could greatly enhance the mobility of imidazolium cations. For example, an ionic monomer 1-

64

ethyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide had an ionic conductivity around 2 x 10^{-2} S/cm at 30 °C. Once polymerized, the conductivity dropped to around 10⁻⁷ S/cm at 30 °C, a decrease of more than 5 orders of magnitude.¹ However, the huge ionic conductivity decrease could be greatly alleviated by introducing a poly(ethylene oxide) (PEO) oligomer spacer. For example, а macromonomer 1-ethyl-3-(poly(ethylene oxide) monomethacrylate)imidazolium bis(trifluoromethanesulfonyl)imide (molecular weight of PEO part is about 350 g/mol) had an ionic conductivity of around 2 x 10^{-3} S/cm at 30 °C. After polymerization, the polymer showed a conductivity of 1.2 x 10^{-4} S/cm at 30 °C, only 1 order of magnitude decrease.² In a recent study, Döbbelin and co-workers synthesized a pyrrolidinium-based PIL with poly(ethylene glycol) (PEG) side chains on the pyrrolidinium ring to improve its ionic conductivity.²³ The results confirmed that ILs or IL/PIL mixture with a pendant PEG chain exhibited a higher conductivity compared to those with a butyl group. However, due to the solid nature of PILs synthesized, there was no conductivity data about those pure PILs.

In this chapter, a series of novel PILs based on flexible polyepichlorohydrin backbone were synthesized and the effect of increasing chain length was studied. The first step was to synthesize high molecular weight polyEPCH using a literature method.²⁴ The ring-opening polymerization of epichlorohydrin has been

studied for many years. Generally speaking, there are two main methods for ringopening polymerization, that is, anionic^{25,26} and cationic.²⁷⁻²⁹ For epichlorohydrin, anionic ring-opening polymerization is generally prohibited due to the predominant reaction between the chloromethyl group of epichlorohydrin and strong nucleophilic bases used as initiator in conventional anionic polymerization. Therefore, the strategies developed up to now are mainly based on cationic or coordinated ring-opening polymerizations.²⁴

For cationic ring-opening polymerization of epichlorohydrin, there are two different mechanisms: one is called activated chain end mechanisms (ACE) and the other called monomer activated mechanism (AM),²⁸ shown in Scheme 2.1. In the ACE mechanism, the active propagating center is an oxonium cation located in the chain end while the monomer is neutral. The initiating system for ACE mechanism usually contained a Lewis acid in combination with a small portion of protogenic species (often water). Due to the side reactions including chain transfer, backbiting and termination between propagating species and the oxygen atoms in the polymer chain, the product in ACE mechanism was usually a mixture of ill-defined linear or cyclic polyEPCH oligomers. On the other side, in AM mechanism, the chain end was a neutral hydroxyl, while the monomer formed an ionic complex with a protonic species (a Brönsted acid). The ring-opening polymerization took place at low instantaneous EPCH concentration. In the presence of initiator system containing a Lewis acid (usually BF₃) and a low mass diol (PEG oligomer or 1,4-butanediol), the formation of cyclic oligomer was

strongly suppressed (lower than 0.7 wt%), and the main product was dihydroxytelechelic polyEPCH. However, even in AM mechanism, the molecular weight of polyEPCH obtained was lower than 2,500 g/mol.²⁷



ACE mechanism



AM mechanism

Scheme 2.1. ACE and AM mechanism for cationic ring-opening polymerization of epichlorohydrin

One of the ways to improve on the anionic polymerization is to use a novel weakly nucleophilic initiating system, including triisobutylaluminum (*i*-Bu₃AI) and tetraoctylammonium bromide (NOct₄Br). *i*-Bu₃AI formed not only a low nucleophilicity 1 : 1 complex with NOct₄Br, but also a strongly activating complex with EPCH monomer (Scheme 2.2). For this reason, the amount of *i*-Bu₃AI added should be slightly more than NOct₄Br. Under this condition, the reactivity

of EPCH toward nucleophiles was greatly enhanced and the polymerization could proceed well without using strong nucleophiles as in conventional anionic ring-opening polymerizations. More importantly, the chloromethyl group in EPCH was preserved and could be used for further chemical modification.





In this chapter, a series of polyEPCH with molecular weight from 21.6 x 10^3 to 76.2 x 10^3 g/mol were synthesized. The polyEPCH obtained was treated with 1-

butylimidazole to form a PIL with Cl⁻, which was followed by an ion exchange reaction in water to replace Cl⁻ with TFSI⁻. All PILs obtained revealed good thermal stabilities, high ionic conductivities and high viscosities, making them promising electrolyte candidates for a wide range of electrochemical device applications.

Results and discussion

Synthesis of polyepichlorohydrin based poly(ionic liquids)

The synthesis of polyEPCH was carried out by anionic polymerization using a literature method.²⁴ As shown in Scheme 2.3, tetraoctylammonium bromide (NOct₄Br) was used as initiator and triisobutylaluminum (*i*-Bu₃Al, 1M in toluene) as catalyst. The polymerization was carried out in a toluene solution from -30 °C to room temperature. PolyEPCH with different molecular weight was obtained by tuning the monomer to initiator molar ratio from 100 to 500. The key point to ensure successful polymerization was the amount of *i*-Bu₃Al added. As shown in Table 2.1, no polymerization took place at a ratio [M]/[Al]/[NOct₄Br] equal to 100/1/1, whereas 100 % conversion was achieved at the ratio 100/1.5/1. With the increase of [M]/[NOct₄Br] ratio, more *i*-Bu₃Al should be added, because more *i*-

Bu₃Al was needed to activate the EPCH monomer. With the addition of appropriate amount of *i*-Bu₃Al, the conversion for all three polymerization of EPCH was 100 %, and a yield around 88 % was achieved. PolyGBIMCI was synthesized by quaternarization of polyEPCH with 1-butylimidazole. In this case, 1-butylimidazole was used both as the reactant and the solvent. The solution was degassed with the freeze-pump-thaw procedure three times, inserted into oil bath at 115 °C and refluxed under N₂ overnight. In this step, degassing and refluxing under N₂ proctection was very important because if not, side reactions such as oxidation would happen and the product would turn black. In the end, the product was dissolved in chloroform and precipitated from ethyl ether. Unreacted polyEPCH and 1-butylimidazole dissolved in ethyl ether while polyGBIMCI did not. The product was dried by heating at 100 °C in vacuo. PolyGBIMCI was a highly hygroscopic solid at room temperature. PolyGBIMTFSI was then obtained by an ion exchange reaction. After dissolving PolyGBIMCI in aqueous solution, LiTFSI was added and the solution turned milky immediately. The product was precipitated out after 30 min centrifugation and purified by washing with Milli-Q water three times. The product was dried by heating at 100 °C in vacuo overnight. PolyGBIMTFSI was a highly viscous liquid.

70



Scheme 2.3. Synthesis of polyEPCH and polyGBIMTFSI

Table 2.1. Polymerization of epichlorohydrin initiated by NOct₄Br/ *i*-Bu₃Al

Sample	[M]/[AI]/[NOct ₄ Br] ^a	Time (h)	Conversion %	Yield %
polyEPCH 100	100/1/1	12	0	0
polyEPCH 100	100/1.5/1	12	100	88
polyEPCH 200	100/2.0/1	12	100	87
polyEPCH 500	100/2.7/1	12	100	90

a: [M], [AI] and [NOct₄Br] represented molar concentration of EPCH, *i*-Bu₃AI and NOct4Br respectively.

NMR spectroscopy was used to examine the chemical structures of polyEPCH and polyGBIMTFSI. Figure 2.1 showed the ¹H NMR spectra of polyEPCH with monomer to initiator ratio of 500 to 1 and the corresponding polyGBIMTFSI. There were two broad peaks shown in Figure 2.1a, one larger peak with chemical shift from 3.80 to 3.66 ppm and a smaller peak at 3.66-3.59 ppm. The

integration ratio of the two peaks was 4 to 1. The peaks were assigned according to gHSQC spectrum, shown in Figure 2.2. The peak at 44 ppm in ¹³C spectrum correlated to two separate protons in ¹H NMR, and was assigned to the C in CH_2 Cl group. The peak at around 70 ppm in ¹³C spectrum was assigned to the C in CH_2O group. The peak at 79 ppm in ¹³C spectrum was assigned to the C in CHO group. Based on the gHSQC spectrum, the larger peak in ¹H NMR was assigned to four protons including CH_2O , CHO, and 1H from CH_2CI , and the smaller peak was assigned to the other proton left in CH₂Cl. Figure 2.1b showed the ¹H NMR spectra of polyGBIMTFSI. The three peaks with chemical shift higher than 7.2 ppm were assigned to the three protons in imidazolium ring, while the sharper peak ~4.2 ppm and the three peaks below 2.0 ppm were assigned to the butyl group attached to imidazolium ring. The sharp peak ~3.3 ppm was assigned to the residual water dissolving in DMSO-d6. The rest of the peaks were from the polyEPCH backbone. For accurate assignment of each peak, gHSQC spectrum was also done for polyGBIMTFSI. Figure 2.3 shows part of the gHSQC spectrum, which is related to the peaks from polymer backbone. The peak at 50 ppm in 13 C spectrum was assigned to the C in CH₂ connected to the imidazolium group. Compared to the corresponding peak in polyEPCH. It was shifted higher about 5 ppm, which was because of the replacement of CI with a more electron attracting cationic imidazolium group. In ¹H NMR spectrum, the chemical shift of peaks for the two protons attached to the C at 50 ppm was also shifted higher, from between 3.5 and 3.7 ppm to 4.0 and 4.4 ppm. The peaks at 67 and 77 ppm in 13 C spectrum were assigned to the C in *CH*₂O and *CH*O respectively. Based on the gHSQC spectrum, the peaks in 1 H NMR spectrum were labelled, shown in Figure 2.1 b. Peak 10 represented a CH₂ in butyl group on the imidazolium ring and had a integral of 2.00. While peak 3 and 4 represented one proton from *CH*O and one proton from *CH*₂O of the polyEPCH backbone. Peak 3 and 4 had a combined integral of 1.96. By comparing the integrals of peak 10 and peak 3, 4, and taking consideration of integration error, we can conclude that the quaternarization was quantitative.



Figure 2.1. ¹H NMR of polyEPCH with monomer to initiator ratio 500/1 (2.1a, top, CDCl₃ as solvent) and the corresponding polyGBIMTFSI (2.1b, bottom, DMSO-d6 as solvent).



Figure 2.2. gHSQC of polyEPCH with monomer to initiator ratio 500/1. For interpretation to the references to color in this and all other figures, the reader is referred to the electronic version of this dissertation.



Figure 2.3. gHSQC of polyGBIMTFSI with monomer to initiator ratio 500/1

GPC was used to investigate the molecular weight of polyEPCH synthesized. In Figure 2.4, GPC traces of polyEPCH with monomer to initiator ratio of 100/1, 200/1 and 500/1 were displayed. From left to right, curves were for polyEPCH 500, polyEPCH 200 and polyEPCH 100 respectively. As shown in Table 2.1, polyEPCH with different molecular weight was synthesized and all three samples showed a low PDI, which was around 1.16. The highest M_n was 7.62 x 10⁴ g/mol obtained in the case of polyEPCH 500.The M_n obtained by GPC was around two times of the theoretical values, which was due to the use of polystyrene (PS) as standard in GPC, since PS and polyEPCH have very different chemical structure and at the same molecular weight, PS has a much larger hydrodynamic volume compared to polyEPCH in DMF solution. To get more reasonable molecular weight data, PEO which has a similar chemical structure as polyEPCH was also used as GPC standard, with the data shown in Table 2.2. In this case, the GPC data was smaller than theoretical value. This was attributed to the difference in hydrodynamic volumes as well. GPC characterization for polyGBIMTFSI did not provide satisfactory data because the elution would be delayed, which was most likely due to the strong interaction between ions of polyGBIMTFSI and the stationary phases. However, thanks to the quantitative quaternarization, the molecular weight of polyGBIMTFSI can be roughly calculated based on that of polyEPCH.



Figure 2.4. GPC traces of polyEPCH with different monomer to initiator ratio. PolyEPCH 100, 200, 500 means polyEPCH with [M]/[I] = 100, 200 and 500 respectively. DMF was used as solvent at 50 °C and polystyrene was used as standard.

Table 2.2. Number average molecular weight (M_n), Weight average molecular weight (M_w) and PDI of polyEPCH 100 , 200 and 500 from GPC, PS as standard

Sample	M _n × 10 ^{−3} g/mol ^a	M _n × 10 ^{−3} g/mol ^b	M _w × 10 ^{−3} g/mol ^b	PDI ^b
polyEPCH100	9.3	21.6	25.1	1.16
polyEPCH200	18.5	37.8	42.7	1.13
polyEPCH500	46.3	76.2	89.9	1.18

a: Theoretical value, calculated by [Monomer]/[Initiator] x 92.5 g/mol.

b: data from GPC, PS standard.

Table 2.3. Number average molecular weight (M_n), Weight average molecular weight (M_W) and PDI of polyEPCH 100 , 200 and 500 from GPC, PEO as standard

Sample	M _n × 10 ^{−3} g/mol ^a	M _n × 10 ^{−3} g/mol ^b	M _w × 10 ^{−3} g/mol ^b	PDI ^b
polyEPCH100	9.3	6.3	8.1	1.29
polyEPCH200	18.5	11.8	15.0	1.27
polyEPCH500	46.3	28.2	36.4	1.29

a: Theoretical value, calculated by [Monomer]/[Initiator] x 92.5 g/mol.b: data from GPC, PEO standard.

FT-IR spectra of polyEPCH500 and the corresponding polyGBIMTFSI500 were shown in Figure 2.5. To confirm the successful synthesis of polyGBIMTFSI, FT-IR spectra of LiTFSI and 1-butylimidazole were also measured. In polyEPCH spectrum, peaks between 3000 and 2800, peak at 1120 and peak at 748 cm⁻¹ were assigned to sp³ C-H stretching, C-O-C and CH₂-Cl stretching respectively, which was consistent with the structure of polyEPCH. In polyGBIMTFSI spectrum, peaks between 3200 and 3100 cm⁻¹ were assigned to the C-H···F hydrogen bonding bands between hydrogen atoms in imidazolium ring and fluorine atoms in TFSI⁻ anion.³⁰ In addition, peaks between 3100 and 3000 cm⁻¹ were assigned to sp² C-H stretching, which were absent in polyEPCH, but present in 1-butylimidazole. This observation provided direct evidence for the successful synthesis of polyGBIMTFSI. There were other evidence too. Peak at

1566 cm⁻¹ was assigned to C=N stretching, also absent in polyEPCH. This peak (1508 cm⁻¹) existed in FT-IR spectrum of 1-butylimidazole, though it was shifted higher due to the quaternarization reaction. Other peaks at 1350, 1188, 1136 cm⁻¹ were assigned to SO₂ asymmetric, C-F and SO₂ symmetric stretching respectively, which supports the existence of TFSI⁻ counterion.



Figure 2.5. FT-IR of LiTFSI, butylimidazole, polyEPCH 500 and the corresponding polyGBIMTFSI500

Thermal analysis of polyEPCH and polyGBIMTFSI samples

The thermal stability of polyEPCH and polyGBIMTFSI was studied by TGA. Figure 2.4 showed the TGA traces of polyEPCH with monomer to initiator ratio of 500 to 1 and the corresponding polyGBIMTFSI. Both samples were heated to 120 °C and held for 30 minutes before proceeding heating to ensure all physically adsorbed water was removed. As shown in Figure 2.6, polyGBIMTFSI showed excellent thermal stability with thermal degradation temperatures above 375 °C. On the other hand, polyEPCH showed relatively poor thermal stability which started to lose weight at ~ 200 °C. PolyEPCH100, 200 and polyGBIMTFSI100, 200 also showed similar degradation patterns.



Figure 2.6. Normalized TGA traces of polyEPCH with [M]/[I] 500 and the corresponding polyGBIMTFSI.

DSC was used to study the glass transition temperature (T_g) change of polyEPCH with increasing molecular weight and the corresponding polyGBIMTFSI. Figure 2.7 and Table 2.4 showed the results from DSC measurements. PolyEPCH was a colorless liquid. With the increase of molecular weight, the T_g increased too. PolyEPCH100 had a T_g of - 36 °C, while polyEPCH200 and 500 had a T_g of - 30 and - 28 °C respectively. Compared to the T_g difference between polyEPCH100 and 200, the difference between polyEPCH200 and 500 was much smaller. It seemed that the T_g of polyEPCH had reached a plateau as the molecular weight increased, which was also confirmed in the case of polyGBIMTFSI. As shown in Table 2.4, after quaternarization, polyGBIMTFSI showed a higher T_g compared to polyEPCH. However, the T_g of polyGBIMTFSI with different molecular weight was almost the same. PolyGBIMTFSI100, 200 and 500 had $T_{\rm g}$ of -14, -13 and -12 $^{\circ}{\rm C}$ respectively, which confirmed the plateau formation as the molecular weight increased. One point worth to mention was that there was no crystallization region in all polyGBIMTFSI samples, which was preferred as a potential electrolyte material. Due to the same structure and very close T_{g} , similar conductivity would be expected for polyGBIMTFSI100, 200 and 500, which was confirmed in the conductivity measurement.

82



Figure 2.7. DSC curves of polyEPCH100, 200 and 500 and the corresponding polyGBIMTFSI. From top to bottome, curves are for polyEPCH100, 200, 500 and polyGBIMTFSI100, 200, 500 respectively.

Table 2.4. Tg of polyEPCH and polyGBI	MTFSI with different monomer to initiator
ratio	

Sample	τ _g / °C
polyEPCH100	-36
polyEPCH200	-30
polyEPCH500	-28
polyGBIMTFSI100	-14
polyGBIMTFSI200	-13
polyGBIMTFSI500	-12

Ionic conductivity and viscosity measurement

lonic conductivity of polyGBIMTFSI over a temperature range from 30 to 90 °C was measured, as shown in Figure 2.8. The logarithm of conductivity of polyGBIMTFSI decreased linearly against increase of 1000/T, which can be well explained by the Arrhenius equation. However, slight convex curvatures in Figure 2.8 suggested that the ion conduction mechanism in polyGBIMTFSI should be the same as that of general solid polymer electrolytes. This suggests migration of ions in highly viscous matrix,³¹ and the empirical Vogel-Fulcher-Tammann (VFT) equation would provide a better fitting, as shown in Equation 1,

$$\sigma = \sigma_{\infty} \times \exp\left(\frac{-B}{T - T_0}\right) \tag{1}$$

where σ_{∞} is the infinite temperature conductivity, *B* is a fitting parameter related to the activation energy of ion conduction, and T_0 is the Vogel temperature where ion motion first occurs ($T_0 = T_g - 50$ K). For polyGBIMTFSI 100, the obtained values for these fitting parameters are $\sigma_{\infty} = 3.25$ S/cm, B = 1500 K, $T_0 = 191$ K, and the corresponding T_g is 241K, which is in good accordance with the T_g (259 K) obtained by DSC measurement. PolyGBIMTFSI with different molecular weight showed similar conductivity, especially at high temperatures. This can be explained by the fact that all three polyGBIMTFSI samples had the same repeating units and very close T_g s. At 30 °C, polyGBIMTFSI 100 showed a conductivity of 1.2 x 10^{-5} S/cm, while polyGBIMTFSI 200 and 500 showed conductivity of around 8.1 x 10^{-6} and 5.3 x 10^{-6} S/cm. However, as the temperature increases, the difference of conductivity between different samples gets smaller. At 90 °C, all samples showed almost identical conductivity, which was around 8.5 x 10^{-4} S/cm.



Figure 2.8. Temperature dependence of ionic conductivities for polyGBIMTFSI 100, 200 and 500.

The viscosities of polyGBIMTFSI were also measured. As shown in Figure 2.9, the viscosities of polyGBIMTFSI almost followed the opposite trend observed for conductivity, which indicated that the conducting species in PIL was restricted as

the viscosity increased. All three polyGBIMTFSI samples showed high viscosities. For example, at 32 °C, polyGBIMTFSI showed a viscosity of around 4000 Pa·s, making it almost cannot flow at all. As electrolyte materials, such a high viscosity is very beneficial in fabrication process. The viscosity increased with higher molecular weight and dropped at higher temperature. However, at 90 °C, polyGBIMTFSI 500 still showed a high viscosity around 80 Pa·s, which was 80,000 times higher compared to that of water at 20 °C



Figure 2.9. Temperature dependence of viscosities of polyGBIMTFSI 100, 200 and 500.

Conclusion

A novel family of polyEPCH based PIL electrolytes have been synthesized and characterized. The PILs obtained showed not only low T_g , high conductivity and good thermal stability, but also a high viscosity, which is beneficial in fabricating process. All these properties make this kind of PIL promising electrolyte materials in electrochemical devices such as lithium battery and dye sensitized solar cell. It has also been revealed that with the increase of molecular weight, the viscosity of PILs increased. But the conductivity did not drop much. At high temperatures, PILs with different molecular weight showed almost identical conductivity. Currently, a copolymer of PIL and PEO derivative is being studied, which shows a conductivity of over 10 times higher compared to PIL homopolymer.

Experimental section

Materials

Unless otherwise specified, all chemicals and solvents were ACS reagent grade and used as received from commercial suppliers without further purification. Epichlorohydrin (EPCH, 99%, Aldrich) was purified over CaH₂, distilled under vacuum and stored in a glove box until use. 1-Butylimidazole was distilled under vacuum and stored in refrigerator. Toluene was dried by refluxing with sodium pbenzylphenol, distilled under N₂ protection and stored in glove box until use. Triisobutylaluminium (*i*-Bu₃Al) (1 mol/L in toluene, Aldrich), tetraoctylammonium bromide (NOct₄Br, 98%, Aldrich) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, >98%, TCI) were kept in a glove box and used without further purification.

Synthesis of polyepichlorohydrin (polyEPCH) with monomer to initiator molar ratio from 100 to 500

PolyEPCH was synthesized according to a literature procedure²⁴. All polymerizations were performed between -30 °C and room temperature under N₂ protection in Schlenk flasks. For instance, polyEPCH with monomer to initiator molar ratio 100 (polyEPCH 100) was synthesized as follows. In a glove box, epichlorohydrin (EPCH, 10.2 g, 0.11 mol) was dissolved in dry toluene (40 mL) in a 200 mL Schlenk flask, followed by addition of initiator NOct₄Br (0.61 g,

1.1x10⁻³ mol). The solution was then taken out of the glove box and stirred in a liquid nitrogen/xylene mixture bath under N₂ protection for 15 minutes to cool to - 30 °C. Catalyst *i*-Bu₃Al (1.7 mL, 1 mol/L in toluene) was added via a syringe. Reaction started immediately. Polymerization was stopped after 12 h by adding a few drops of ethanol. PolyEPCH was purified as follows. Toluene was removed first with a rotavap. The resulting residue was washed with acidic ethanol solution (3 vol% of HCl in EtOH). The ethanol solution was decanted and the residue was washed with Milli-Q water until pH was neutral. The product was dissolved in acetone, filtered to remove undissolved salts, and dried at 50 °C *in vacuo* overnight. PolyEPCH with different molecular weight was synthesized by tuning the monomer to initiator molar ratio, and the amount of catalyst *i*-Bu₃Al. PolyEPCH obtained was a transparent, colorless liquid. Yield: 9.0 g, 88 %. ¹H NMR (CDCl₃, 500 MHz) δ 3.78 - 3.66 (4H), 3.66 - 3.59 (1H).

Synthesis of poly(1-glycidyI-3-butylimidazolium chloride) (polyGBIMCI) PolyGBIMCI was synthesized by quarternization of polyEPCH with 1butylimidazole. PolyEPCH (9.3 g, 0.1 mol for its repeating unit) was first added into a 100 mL Schlenk flask, followed by addition of 1-butylimidazole (37.2 g, 0.3 mol) and a magnetic stir bar. The mixture was stirred until homogeneous. 1-Butylimidazole was used both as reactant and solvent in this case. The solution was degassed with the freeze-pump-thaw procedure three times, then inserted into an oil bath at 115 °C, and refluxed under N₂ overnight. In the end, product precipitated out from 1-butylimidazole solution and stayed in the bottom. PolyGBIMCI was purified as follows. The top 1-butylimidazole layer was decanted first. The residue was then dissolved in chloroform and precipitated from ethyl ether. Unreacted polyEPCH and 1-butylimidazole dissolved in ethyl ether while polyGBIMCI did not. The product was dried by heating at 100 °C *in vacuo*. PolyGBIMCI was a highly hygroscopic solid at room temperature. Yield: 20.6 g, 95 %. ¹H NMR (CDCl₃, 500 MHz) δ 10.46 - 10.32 (1H), 8.36 - 8.22 (1H), 7.82 - 7.56 (1H), 4.94 - 3.58 (7H), 1.96 - 1.82 (2H), 1.42 - 1.30 (2H), 0.98 - 0.86 (3H).

Synthesis of poly(1-glycidyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide) (polyGBIMTFSI)

PolyGBIMTFSI was obtained by an ion exchange reaction. PolyGBIMCI (10.8 g, 0.050 mol for its repeating unit)was dissolved in 100 mL water, which was followed by addition of excess amount of LiTFSI (21.5 g, 0.075 mol). The reaction mixture immediately turned milky. The product was precipitated out by a 30 min centrifugation. PolyGBIMTFSI was purified by washing with Milli-Q water three times and then dried at 100 °C *in vacuo* overnight. polyGBIMTFSI was a highly viscous, transparent liquid with a pale yellow color. Yield: 22.6 g, 98 %. ¹H NMR (a^6 -DMSO, 500 MHz) δ 9.08 - 8.96 (1H), 7.87 - 7.78 (1H), 7.63 - 7.49 (1H), 4.44 - 4.00 (4H), 3.82 - 3.54 (2H), 3.34 - 3.04 (1H), 1.82 - 1.68 (2H), 1.30 - 1.17 (2H), 0.92 - 0.80 (3H).

Characterization

The ¹H and ¹³C NMR spectra were recorded with an Varian UnityPlus-500 spectrometer in CDCl₃ or DMSO-d6 at room temperature using the residual solvent proton signals as chemical shift standards. FT-IR spectra were recorded from a Mattson Galaxy 300 spectrometer purged with dry nitrogen, with signal averaging 128 scans at a resolution of 4 cm⁻¹. All IR samples were dried before measurement. Polymer molecular weight was measured by gel permeation chromatography (GPC) at 35 °C using two PL-gel 10µm mixed-B columns in series. DMF was used as eluting solvent at a flow rate of 1 mL/min and Waters 2410 differential refractometer as detector. Mono-dispersed polystyrene or poly(ethylene oxide) was used as standard to calibrate molecular weight. Thermogravimetric analyses (TGA) was performed using a Perkin-Elmer TGA 7 instrument at a heating rate of 10 °C/min in the temperature range of 30 °C to 850 °C under air atmosphere. TGA samples were dried in vacuo overnight prior to use. After increasing the temperature to 120 °C, samples were held in the TGA apparatus for 30 min before proceeding the heating. Differential scanning calorimetry (DSC) measurements were performed on a TA DSC Q100 instrument at a heating/cooling rate of 10 °C/min under nitrogen. Temperature dependent shear viscosity measurement was carried out in a TA orchestrator rotational rheometer, version v7.2.0.2, over a temperature range of 30 °C to 90 °C, with a temperature increasing rate of 2 °C/min and rotation frequency of 10 rad/s.

Ionic conductivity measurements

lonic conductivity measurement were carried out in a home-made cell by impedance spectroscopy measurements on a AC impedance analyzer HP 4192A over the frequency range of 5Hz to 13 MHz with an applied voltage of 10 mV. The sample cell contains two steel disks which serve as symmetric electrodes and separated by a Teflon collar. All samples were equilibrated at a pre-determined temperature for 15 minutes before measurement. The resistance of the sample was estimated from Nyquist plot, and then the conductivity of the sample was calculated using the electrodes distance and cell cross-sectional area, as shown in equation 2:

$$\sigma = \frac{L}{R \cdot A} \tag{2}$$

where σ is the ionic conductivity of the sample, *L* represents the distance between two electrodes, *A* stands for the cell cross-sectional area, and *R* is the bulk resistance of the sample estimated from Nyquist plot.
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Chapter 3 Synthesis and characterization of novel low T_g poly(ionic liquids) random copolymers

Introduction

In Chapter 2, a series of poly(ionic liquids) based on polyepichlorohydrin (polyEPCH) have been synthesized. Among them, polyGBIMTFSI 100 had the highest ionic conductivity, which was 1.2 x 10⁻⁵ S/cm at 30 °C. However, compared to that of 1-methyl-3-propylimidazolium iodide (PMII), a commonly used ionic liquid, the conductivity was still two orders of magnitude lower. It was well known that lower glass transition temperature (T_q) leads to higher conductivity.¹⁻³ One way to reduce the T_g of polymers was to introduce another low T_g component to the polymer backbone, *i.e.*, forming copolymers.^{4,5} Elabd and coworkers studied the effect of introducing a low T_{g} component on the ionic conductivity of PILs.⁵ The copolymer was made by free radical polymerization of a nonionic monomer n-hexyl methacrylate (HMA) and an ionic monomer 1-(2methacryloyl)ethyl)-3-butylimidazolium tetrafluoroborate (MEBIMBF₄). A series of copolymers with different composition of HMA were obtained by tuning the HMA concentration in the free radical polymerization. The results indicated that the T_{g} of the copolymer decreased with the increase of the HMA composition, and the conductivity increased correspondingly. In this report, the second component chosen for copolymer synthesis was a PEO analogue. PEO is synthesized by polymerization of ethylene oxide and has a T_q ranging from -50 to -57 °C.

However, ethylene oxide is a gas at room temperature, making it hard to handle at regular polymerization conditions. For this reason, an liquid analogue of ethylene oxide, 2-((2-(2-(2-methoxyethoxy)ethoxy)methyl)oxirane (ME₃MO), was synthesized. Unlike the synthesis of polyEPCH, the random copolymer polyEPCH-co-polyME₃MO was synthesized by cationic ring-opening polymerization via activated monomer mechanism using trifluoroborate etherate and 1,4-butandediol as initiator, Scheme 3.1.⁶ After quaternarization and ion exchange reaction, the PIL copolymer showed a conductivity of more than one order of magnitude higher compared to that of PIL homopolymer.



Scheme 3.1. Mechanism for trifluoroborate etherate and 1,4-butanediol initiated cationic polymerization of epichlorohydrin.

Results and discussion

Synthesis of polyGBIMTFSI-co-polyME₃MO

The 2-((2-(2-(2-methoxy)ethoxy)ethoxy)methyl)oxirane synthesis of (ME₃MO) was shown in Scheme 3.2. Triethylene glycol monomethyl ether was deprotonated by sodium hydride first and then reacted with epichlorohydrin (EPCH). The product ME₃MO was obtained in a 71 % yield and characterized by ¹H NMR, shown in Figure 3.1. The easiest peak to assign in ¹H NMR was peak 7. It was assigned to the CH_3 group in the end of PEO oligomer chain, due to its distinct chemical shift and integral of 3.03. The rest peaks in ¹H NMR were assigned according to gHSQC and gHMBC (Figure 3.2 and 3.3). From gHSQC, most of the peaks could be assigned except peak 6. The peak at 44 ppm in 13 C spectrum was assigned to the C in CH₂O group of the oxirane ring. The peak at 51 ppm in 13 C spectrum was assigned to the C in CHO group of the oxirane ring. The peak at 72 ppm in 13 C spectrum was assigned to the C in CH₂O group next to the oxirane ring. Based on the correlation between the carbons and protons, the peaks from 1 to 5 in ¹H NMR were assigned. The peak 6 was assigned according to gHMBC. Because the protons of peak 6 interacted with the carbon of peak 7, peak 6 was assigned to the protons attached to the C closest to the

peak 7 in 13 C spectrum. In the end, the broad peak with an integral of 10.66 in 1 H NMR was assigned to the rest five CH₂ protons in the PEO oligomer chain.



Scheme 3.2. Synthesis of ME₃MO



Figure 3.1. ¹H NMR of ME_3MO



Figure 3.2. gHSQC of ME₃MO



Figure 3.3. gHMBC of ME₃MO

The polyEPCH-*co*-polyME₃MO was synthesized by cationic ring-opening polymerization using BF₃OEt₂ and 1,4-butanediol as initiator, instead of the initiators in anionic one used in Chapter 2 using *i*-Bu₃Al and NOct₄Br. This is because in anionic ring-opening polymerization, the amount of *i*-Bu₃Al added must be precisely controlled to achieve high molecular weight product. For example, the molecular weight of polyEPCH synthesized using different *i*-

Bu₃Al/NOct₄Br ratio was shown in Table 3.1. When [M]/[Al]/[NOct₄Br] equals to 100/1/1, no polymerization happened. When [M]/[Al]/[NOct₄Br] equals to 100/1.5/1, the highest M_n and lowest PDI was obtained. And further increase of [M]/[Al]/[NOct₄Br] ratio resulted in lower M_n and higher PDI. It was concluded that increasing *i*-Bu₃Al/NOct₄Br ratio had a negative effect on the synthesis of polyEPCH. On the other hand, the molecular weight of polyME₃MO synthesized using different *i*-Bu₃Al/NOct₄Br ratio was shown in Table 3.2. Increasing *i*-Bu₃Al/NOct₄Br ratio generally increased the M_n of polyME₃MO. However, in all 5 samples, the M_n of polyME₃MO was very low compared to the theoretical value calculated by the monomer to initiator ratio. Based on the data in Table 3.1 and 3.2, the anionic ring-opening polymerization using *i*-Bu₃Al and NOct₄Br as initiator was not suitable for the synthesis of polyEPCH-*co*-polyME₃MO.

Table 3.1. Molecular weight of polyEPCH synthesized using different *i*-Bu₃Al/NOct₄Br ratio

[M]/[Al]/[NOct ₄ Br] ^a	M _n x 10 ⁻³ g/mol ^b	M _w x 10 ⁻³ g/mol ^b	M _p x 10 ⁻³ g/mol ^b	PDI ^b
100/1/1	No polymerization			
100/1.5/1	5.7	8.0	8.2	1.40
100/3/1	5.1	11.0	8.7	2.17
100/5/1	2.1	5.0	6.1	2.38
100/10/1	1.6	4.1	5.2	2.56

a: [M], [AI] and [NOct₄Br] represented molar concentration of EPCH, *i*-Bu₃AI and NOct₄Br respectively.

b: M_n is the number average molecular weight, M_w is the weight average molecular weight, M_p is the peak molecular weight and PDI is the polydispersity index. Data was from GPC, using PEO as standard.

 $M_{\rm n}$ x 10^{-3} $M_{\rm W} \times 10^{-3}$ $M_{\rm p} \, \times \, 10^{-3}$ PDI^b [M]/[AI]/[NOct₄Br]^a g/mol^b g/mol^b g/mol^b 100/2/1 1.8 2.3 2.4 1.28 1.25 100/3/1 2.4 3.0 3.1 100/4/1 2.6 3.3 3.4 1.27 100/5/1 1.32 2.5 3.3 3.5 2.7 100/10/1 3.5 3.6 1.30

 Table 3.2.
 Molecular weight of polyME₃MO synthesized using different *i*-Bu₃Al/NOct₄Br ratio

a: [M], [AI] and [NOct₄Br] represented molar concentration of ME₃MO, *i*-Bu₃AI and NOct₄Br respectively.

b: M_n is the number average molecular weight, M_w is the weight average molecular weight, M_p is the peak molecular weight and PDI is the polydispersity index. Data was from GPC, using PEO as standard.

Cationic ring-opening polymerization was used to synthesize polyEPCH, polyME₃MO and polyEPCH-*co*-polyME₃MO, as shown in Scheme 3.3. Six copolymer samples with different monomer composition and polyEPCH, polyME₃MO homopolymer were synthesized. The molecular weight data was shown in Table 3.3. PolyEPCH homopolymer had a M_n of 2.2 x 10³g/mol, and polyME₃MO homopolymer had a M_n of 3.4 x 10³g/mol. The M_n of copolymer increased with the increase of polyME₃MO composition.



Scheme 3.3. Copolymerization of EPCH and ME₃MO, followed by quaternatization

Table 3.3. Molecular weight of polyEPCH, polyME₃MO and polyEPCH-*co*-polyME₃MO synthesized using BF₃OEt₂ and 1,4-butanediol as initiator.

[M] ₁ /[M] ₂ /[diol]/[BF ₃ OEt ₂] ^a	M _n x 10 ⁻³ g/mol ^b	$M_{\rm W} \times 10^{-3}$ g/mol ^b	M _p x 10 ⁻³ g/mol ^b	PDI ^b
100/0/6/1	2.2	3.3	2.8	1.50
0/100/6/1	3.4	4.8	3.6	1.41
100/12.5/6/1	3.9	5.8	4.0	1.49
100/25/6/1	4.4	6.4	5.0	1.45
100/50/6/1	4.9	7.4	6.0	1.51
100/100/6/1	5.4	8.7	7.1	1.61
100/200/6/1	7.3	11.7	9.4	1.60
100/400/6/1	12.0	19.8	15.4	1.65

a: [M]₁, [M]₂, [diol] and [BF₃OEt₂] represented molar concentration of EPCH, ME₃MO, 1,4-butanediol and BF₃OEt₂ respectively.

b: M_n is the number average molecular weight, M_w is the weight average molecular weight, M_p is the peak molecular weight and PDI is the polydispersity index. Data was from GPC, using PEO as standard.

PolyGBIMTFSI-co-polyME₃MO was synthesized by quaternarizing the polyEPCH-*co*-polyME₃MO with 1-butylimidazole, and followed by an ion exchange reaction. Only the polyEPCH component in the copolymer was quaternarized, while the polyME₃MO was left intact. High yield was achieved for all samples. The structure of the polyGBIMTFSI-co-polyME₃MO was characterized by ¹H NMR, as shown in Figure 3.4. The peaks between 3.0 and

4.5 ppm represented protons from the polyGBIMTFSI backbone, all protons from polyME₃MO and one CH₂ from butyl group. The three peaks above 7.4 ppm were assigned to the three protons from imidazolium ring. And the three peaks below 1.8 ppm were the protons from CH₂CH₂CH₃ of the butyl group on the imidazolium ring. The integral of CH₃ group was set to be 3, and the integral of broad peaks between 3.0 and 4.5 ppm was 12.23. The integrals corresponded to the composition of copolymer polyGBIMTFSI-co-polyME₃MO-4/1 very well.



Figure 3.4. ¹H NMR of polyGBIMTFSI-*co*-polyME₃MO-4/1

Thermal analysis of polyGBIMTFSI-co-polyME₃MO samples

The thermal stability of polyGBIMTFSI and its random copolymers was studied by TGA, as shown in Figure 3.5. PolyGBIMTFSI and polyGBIMTFSI-*co*polyME₃MO with higher molar ratio of polyGBIMTFSI (from 8/1 to 2/1) showed showed excellent and similar thermal stability with thermal degradation temperatures above 375 °C. One the other hand, polyGBIMTFSI-*co*-polyME₃MO with higher molar ratio of polyME₃MO (from 1/1 to 1/4) showed relatively poor thermal stability, which started to lose weight at ~ 200 °C. Besides, as shown in Figure 2.4 in the previous chapter, polyEPCH also started to lose weight at ~ 200 °C. The thermal stability enhancement of polyGBIMTFSI was from the quaternarization which replaced the weak bonding between the pending CH₂-CI or CH₂-O(CH₂CH₂O)₃CH₃.



Figure 3.5. TGA traces of polyGBIMTFSI, polyME3MO and their random copolymer with varying molar compositionThe glass transition temperatures (T_{gs}) of polyGBIMTFSI, polyME₃MO and their random copolymers were studied by DSC. As shown in Table 3.4, polyGBIMTFSI showed the highest T_{g} (-25 °C), and polyME₃MO showed the lowest T_{g} (-52 °C). All the random copolymers showed T_{gs} between them. With higher molar composition of polyME₃MO, the copolymer showed lower T_{g} .

Table 3.4. T _g of the second	he polyGBIMTFSI,	polyME ₃ MO	and their	random	copolymers
with varying molar	composition.				

Sample	<i>T</i> g / [°] C
polyGBIMTFSI	-25
polyGBIMTFSI-co-polyME ₃ MO (8/1)	-29
polyGBIMTFSI-co-polyME ₃ MO (41)	-33
polyGBIMTFSI-co-polyME ₃ MO (2/1)	-36
polyGBIMTFSI-co-polyME ₃ MO (1/1)	-41
polyGBIMTFSI-co-polyME ₃ MO (1/2)	-43
polyGBIMTFSI-co-polyME ₃ MO (1/4)	-45
polyME ₃ MO	-52

Ionic conductivity measurement

lonic conductivities of polyGBIMTFSI and polyGBIMTFSI-co-polyME₃MO over a temperature range from 25 to 90 °C was measured, as shown in Figure 3.6. The ionic conductivity data agrees well with the T_g data. PolyGBIMTFSI with highest T_g showed the lowest ionic conductivity. With the increase of the composition of polyME₃MO, the conductivity increased up to polyGBIMTFSI-*co*-polyME₃MO-1/1. However, at higher compositions of polyME₃MO, the conductivity started to decrease. PolyGBIMTFSI-*co*-polyME₃MO-1/1 and polyGBIMTFSI-*co*-polyME₃MO-1/4 showed lower conductivity compared to their 1/1 analogue. This

phenomenon is easy to understand and similar results have been reported in literature.⁵ Introduction of polyME₃MO lowered the T_g , which had a positive effect on the ionic conductivity of the copolymer. On the other hand, increasing polyME₃MO composition meant decreasing polyGBIMTFSI composition, resulting in lower concentration of charge carriers, which had a negative effect on the ionic conductivity of the copolymer. In the beginning, the conductivities of copolymers increased with the increase of polyME₃MO composition, because the reduction in T_g had a more significant effect on ionic conductivity compared to the reduction in charge carriers concentration. However, in the case of polyGBIMTFSI-co-polyME₃MO-1/2 and polyGBIMTFSI-co-polyME₃MO-1/4, as the concentration of charge carriers got very low, the negative effect overwhelmed the positive effect.

PolyGBIMTFSI-*co*-polyME₃MO-1/1 showed the highest conductivity (around 1.2 x 10^{-4} S/cm at 25 °C), which was more than 1 order of magnitude higher compared to that of polyGBIMTFSI homopolymer (9.3 x 10^{-6} S/cm at 25 °C). On the other hand, the conductivity of a commonly used ionic liquid, 1- methyl-3-propylimidazolium iodide (MPII), was 1.1×10^{-3} S/cm at 25 °C (Figure 4.8. in next chapter). The conductivity of polyGBIMTFSI-*co*-polyME₃MO-1/1 was only less than 1 order of magnitude lower than that of MPII. Introducing low *T*_g component

to form PIL copolymer proved to be very effective in improving the ionic conductivity of poly(ionic liquids).



Figure 3.6. Ionic conductivities of polyGBIMTFSI and its random copolymers with varying molar composition.

Conclusion

2-((2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl)oxirane (ME₃MO**)**, a liquid analogue of ethylene oxide, was synthesized and copolymerized with EPCH. The resulting copolymer (polyEPCH-*co*-polyME₃MO) was quaternarized with 1-butylimdazole and followed by an ion exchange reaction to form a PIL copolymer

(polyGBIMTFSI-*co*-polyME₃MO). By tuning the monomer composition, a series of PIL copolymers from polyGBIMTFSI-*co*-polyME₃MO-8/1 to polyGBIMTFSI-*co*-polyME₃MO-1/4 were synthesized. All PIL copolymer samples showed higher ionic conductivity than PIL homopolymer. Among them, polyGBIMTFSI-*co*-polyME₃MO-1/1 showed the highest ionic conductivity (around 1.2 x 10⁻⁴ S/cm at 25 °C), which was more than 1 order of magnitude higher than PIL homopolymer (9.3 x 10⁻⁶ S/cm at 25 °C). On the other hand, the ionic conductivity of a commonly used ionic liquid, 1- methyl-3-propylimidazolium iodide (MPII), was 1.1 x 10⁻³ S/cm at 25 °C. The conductivity of polyGBIMTFSI-*co*-polyME₃MO-1/1 was only less than 1 order of magnitude lower than that of PMII. Introducing low *T*_g component to form PIL copolymer proved to be very effective in improving the ionic conductivity of PIL.

Experimental section

Materials

Unless otherwise specified, all chemicals and solvents were ACS reagent grade and used as received from commercial suppliers without further purification. Epichlorohydrin (EPCH, 99%, Aldrich) was purified over CaH₂, distilled under vacuum and stored in a glove box until use. 1-Butylimidazole was distilled under vacuum and stored in refrigerator. Toluene was dried by refluxing with sodium *p*benzylphenol, distilled under N₂ protection and stored in glove box until use. Boron trifluoride diethyl etherate (BF₃OEt₂) (\geq 46% BF₃ basis, Aldrich) and 1,4butanediol (99%, Aldrich) were distilled under N₂ protection and stored in golve box until use. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, >98%, TCI) were kept in a glove box and used without further purification.

Synthesis of 2-((2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl)oxirane (ME₃MO)

 ME_3MO was synthesized according to a literature method.⁷ NaH (60 wt% in mineral oil, 9 g, 0.23 mol) was rinsed with toluene and added to 200 mL THF. The triethylene glycol monomethyl ether (32.8 g, 0.2 mol) was then added and stirred for 2 h. The solution was then cooled to 0 °C in ice bath, and followed by addition of epichlorohydrin (18.4 g, 0.2 mol) gradually. The solution was stirred at 0 °C to room temperature overnight. After the reaction, the solution was

neutralized with 30 % methanolic H₂SO₄. The solution was then filtered, concentrated with a rotavap and distilled under vacuum. The yield was 31.2 g, 71 %. ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 3.66 (dd, *J* = 11.7, 3.0 Hz, 1H), 3.61 - 3.49 (br, 10H), 3.44 - 3.40 (m, 2H), 3.29 (dd, *J* = 11.7, 5.9 Hz, 2H), 3.25 (s, 3H), 3.05 - 3.00 (m, 1H), 2.66 (dd, *J* = 5.0, 4.2 Hz, 1H), 2.48 (dd, *J* = 5.0, 2.7 Hz, 1H). ¹³C NMR (CDCl₃, 500 MHz) δ (ppm) 71.55, 71.50, 70.28, 70.16 (overlapping signals), 70.06, 58.50, 50.32, 43.66. MS (TOF MS ES+) calculated for C₁₀H₂₀O₅Na⁺ (m/z), 243.1208; found, 243.1213.

Synthesis of polyEPCH by cationic ring-opening polymerization.

PolyEPCH was synthesized by cationic ring-opening polymerization according to a literature method.⁶ In a dry Schlenk flask, 1,4-butanediol (0.44 g, 4.8 mmol) was added to 22.5 mL dry toluene. This solution was degassed by freeze-pumpthaw procedure three times and then protected by N₂ gas flow. To this solution, BF₃OEt₂ (0.12 g, 0.81 mmol) was slowly added under N₂ atmosphere and stirred for 60 mins at room temperature. The solution was cooled to 0 °C in an ice bath, followed by addition of EPCH (7.5 g, 81 mmol) drop by drop. The polymerization was stopped after 8 h by adding small amount of distilled water. The polymer solution was washed with sodium bicarbonate solution (5 % wt/v), followed by several washings with distilled water until pH neutral. The solvent was removed by vacuum distillation. The product was then dried under vacuum at 60 °C overnight. The yield was 6 g, 80 %.¹H NMR (CDCl₃, 500 MHz) δ 3.78 - 3.66 (4H), 3.66 - 3.59 (1H).

Synthesis of polyME₃MO

PolyME₃MO was synthesized in the same way as polyEPCH. In a dry Schlenk flask, 1,4-butanediol (0.44 g, 4.8 mmol) was added to 22.5 mL dry toluene. This solution was degassed by freeze-pump-thaw procedure three times and then protected by N₂ gas flow. To this solution, BF₃OEt₂ (0.12 g, 0.81 mmol) was slowly added under N₂ atmosphere and stirred for 60 mins at room temperature. The solution was cooled to 0 °C in an ice bath, and followed by addition of ME₃MO (17.8 g, 81 mmol) drop by drop. The polymerization was stopped after 18 h by adding small amount of distilled water. The purification method was a little bit different, since polyME₃MO dissolved in water. The polymer solution was washed with sodium bicarbonate solution (5 % wt/v) first. After that, the polymer was extracted by CHCl₃ and precipitated from hexane. The yield was 13.4 g, 75 %. ¹H NMR (CDCl₃, 500 MHz) δ 3.74 - 3.22 (20H).

Synthesis of polyEPCH-co-polyME₃MO random copolymer.

PolyEPCH-co-polyME₃MO random copolymer was also synthesized in the same way as polyEPCH. A series of copolymers were obtained by changing the molar concentration of ME₃MO monomer, while keeping that of EPCH monomer constant. For example, polyEPCH-co-polyME₃MO random copolymer with 1 to 1 monomer molar ratio (polyEPCH-co-polyME₃MO-1/1) was prepared as follows. In a dry Schlenk flask, 1,4-butanediol (0.44 g, 4.8 mmol) was added to 22.5 mL dry toluene. This solution was degassed by freeze-pump-thaw procedure three times and then protected by N₂ gas flow. To this solution, BF₃OEt₂ (0.12 g, 0.81 mmol) was slowly added under N₂ atmosphere and stirred for 60 mins at room temperature. The solution was cooled to 0 °C in an ice bath, and followed by addition of pre-mixed EPCH (7.5 g, 81 mmol) and ME₃MO (17.8 g, 81 mmol) drop by drop. The copolymer was purified the same way as polyME₃MO. The yield was 18.5 g, 73 %. For copolymers with different monomer molar ratio, the yield varied from 60 % to 80 %.¹H NMR (CDCl₃, 500 MHz) δ 3.66 - 3.44 (22H), 3.39 - 3.36 (3H).

Synthesis of polyGBIMTFSI-co-polyME₃MO

A series of polyGBIMTFSI-co-polyME₃MO were synthesized based on different polyEPCH-co-polyME₃MO samples obtained. PolyGBIMTFSI-co-polyME₃MO-1/1 was synthesized as follows. PolyEPCH-co-polyME₃MO-1/1 (12.5 g, 40 mmol for its repeating unit) was first added into a 100 mL Schlenk flask, followed by addition of 1-butylimidazole (14.9 g, 120 mmol) and a magnetic stir bar. The mixture was stirred until homogeneous. 1-Butylimidazole was used both as reactant and solvent again. The solution was degassed with the freeze-pumpthaw procedure three times, then inserted into an oil bath at 115 °C, and refluxed under N₂ overnight. After reaction, the polyGBIMCI-co-polyME₃MO polymer was precipitated from ethyl ether, collected and dried under vacuum for 8 h. The polymer was dissolved in 100 mL Milli-Q water and followed by addition of excess amount of LiTFSI (17.2 g, 60 mmol). The polyGBIMTFSI-co-polyME₃MO-1/1 product was collected by a 30 mins centrifugation, purified by washing with Milli-Q water three times, and dried at 100 °C in vacuo overnight. The yield was 23.7 g, 87 %. ¹H NMR (*d*⁶-DMSO, 500 MHz) δ 9.20 - 8.98 (1H), 7.88 - 7.50 (2H), 4.50 - 3.00 (27H), 1.82 - 1.72 (2H), 1.28 - 1.14 (2H), 0.92 - 0.80 (3H).

Characterization

The ¹H and ¹³C NMR spectra were recorded with an Varian UnityPlus-500 spectrometer in CDCl₃ or DMSO-*d6* at room temperature using the residual

solvent proton signals as chemical shift standards. gHSQC and gHMBC 2D NMR spectra were recorded with an Agilent DDR2 500 MHz NMR spectrometer equipped with 7600AS 96 sample autosamplers. Polymer molecular weight was measured by gel permeation chromatography (GPC) at 35 °C using two PL-gel 10 μ mixed-B columns in series. DMF was used as eluting solvent at a flow rate of 1 mL/min and Waters 2410 differential refractometer as detector. Mono-dispersed poly(ethylene oxide) was used as standard to calibrate molecular weight. Thermogravimetric analyses (TGA) was performed using a Perkin-Elmer TGA 7 instrument at a heating rate of 10 °C/min in the temperature range of 30 °C to 850 °C under air atmosphere. TGA samples were dried *in vacuo* overnight prior to use. After increasing the temperature to 120 °C , samples were held in the TGA apparatus for 30 min before proceeding the heating. Differential scanning calorimetry (DSC) measurements were performed on a TA DSC Q100 instrument at a heating/cooling rate of 10 °C/min under nitrogen.

Ionic conductivity measurements

lonic conductivity measurements were carried out in a home-made cell by impedance spectroscopy measurements on a AC impedance analyzer HP 4192A over the frequency range of 5 Hz to 13 MHz with an applied voltage of 10 mV. The sample cell contains two steel disks which serve as symmetric electrodes and separated by a Teflon collar. All samples were equilibrated at a pre-determined temperature for 15 minutes before measurement. The resistance of the sample was estimated from Nyquist plot, and then the conductivity of the

sample was calculated using the electrodes distance and cell cross-sectional area, as shown in equation 1:

$$\sigma = \frac{L}{R \cdot A} \tag{1}$$

where σ is the ionic conductivity of the sample, *L* represents the distance between two electrodes, *A* stands for the cell cross-sectional area, and *R* is the bulk resistance of the sample estimated from Nyquist plot. REFERENCES

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Chapter 4 Direct polymerization of IL monomers from surface of silica nanopaticles: kinetics, characterization, and application in DSSCs

Introduction:

Because of the possible low production cost and expected high conversion efficiency, DSSCs have been extensively studied in recent years.^{1,2} DSSCs were usually assembled with liquid electrolytes. The highest conversion efficiency of DSSCs employing liquid electrolytes has exceeded 12 %.³ However, for long-term stability consideration, liquid electrolytes must be avoided since the evaporation of organic solvents would decrease the cell performance. Due to their negligible volatility, high intrinsic conductivity, good chemical and thermal stability, ILs have been considered as a promising replacement to liquid electrolytes.^{4,5}

However, for material application, the liquid property of ILs presents a great challenge for sealing and fabrication. To overcome this problem, while keeping the specific properties of ILs, a new class of hybrid materials called ionogels was made.^{6,7} lonogels were prepared by hybridizing ILs with another component such as organic gelator,^{8,9} polymer,^{10,11} carbon nanotubes^{12,13} and inorganic metal oxide nanoparticles.^{14,15} Among these methods, due to their chemical stability, inorganic nanoparticles are preferred over organic gelators, which can exhibit secondary reactions in long-term operations.⁶ Gelation of ILs with

inorganic silica nanoparticles was first studied by Grätzel's group. 5 wt% fumed silica nanoparticles was hybridized with 1-methyl-3-propylimidazolium iodide (MPII) and used as the electrolyte in quasi-solid DSSC. Compared to liquid MPII electrolyte, gel electrolyte not only showed essentially same performance in power conversion efficiency, but also enabled fabrication of flexible, compact, free-of-leakage DSSCs.¹⁴ More recently, Watanabe *et al.* studied the colloidal stability of PMMA-grafted silica nanoparticles in ILs.^{16,17} They found that PMMA-grafted silica nanoparticles in ILs at low concentrations. However, when the particle concentration increased to 15 wt% or higher, gelling material was formed. Archer's group reported a novel class of silica ionogel formed by dispersing IL-grafted silica nanoparticle in an IL host.¹⁸ They found that with the addition of appropriate amount of IL-grafted silica nanoparticles, the host IL's crystallization could be completely suppressed, which opened the way for facile synthesis of ILs with extended operation temperature range.

Herein, we report a novel ionogel composed by PIL-tethered silica nanoparticle and MPII. Poly(1-(4-vinylbenzyl)-3-butylimidazolium tetrafluoroborate) (polyVBBIT) was grown from the surface of silica nanoparticle via atom transfer radical polymerization (ATRP). ATRP was chosen because it was a controlled/living polymerization technique, which enabled fine tuning of the polymer chain length on silica particles.¹⁹ MPII was used in our study because among the 1,3-dialkylimidazolium iodide compounds, MPII has the lowest viscosity, and its liquid domain extends down to -55 °C. An ionogel was formed

127

by dispersing polyVBBIT-tethered silica nanoparticle into MPII, heated at 60 °C for 3h and then cooled to room temperature. The ionogel formed retained high conductivity, which was only slightly below that of pure MPII. The ionogel electrolyte was employed in DSSC and a conversion efficiency of 0.37 % was obtained.

Results and Discussion

Synthesis of 1-(4-vinylbenzyl)-3-butylimidazolium tetrafluoroborate (VBBIT)

Synthesis of VBBIT was shown in Scheme 4.1. 4-Vinylbenzyl chloride was first quaternarized with 1-butylimidazole to form 1-(4-vinylbenzyl)-3-butyl imidazolium chloride (VBBICI), a water-soluble hygroscopic wax-like solid. Since the chloride anion (Cl⁻) in VBBICI had a negative effect on ATRP polymerization, tetrafluoroborate (BF4⁻) was introduced by an ion exchange reaction to replace the Cl⁻. VBBICI was dissolved in dry acetone and followed by adding an excess amount of sodium tetrafluoroborate (NaBF4), and stirring for 3 days at room temperature. After removing NaCl salt by filtration, followed by rotavap to remove acetone, a viscous ionic liquid monomer 1-(4-Vinylbenzyl)-3-butyl imidazolium tetrafluoroborate (VBBIT) was obtained. In both steps, small amount of 2,6-di*tert*-butyl-4-methylphenol (DBMP) was added to prevent autopolymerization. After reaction, the crude VBBIT product was washed with water 3 times to remove all the un-reacted VBBICI and NaBF4 salt. In addition, the residual DBMP
was washed away with diethyl ether 3 times. The completion of the ion exchange reaction was confirmed by silver nitrate test. A small amount of VBBIT was dissolved in acetone and followed by addition of some silver nitrate salt. After stirring, no white precipitate was observed. After dring under vacuum at 80 °C overnight, a viscous IL monomer, VBBIT was obtained. The chemical structure was characterized by ¹H NMR, shown in Figure 4.1.



Scheme 4.1. Synthesis of IL monomer-VBBIT



Figure 4.1. ¹H NMR of VBBIT, DMSO-d6 as solvent.

Surface-Initiated ATRP of VBBIT from silica nanoparticles.

The synthetic route of polyVBBIT/silica nanocomposite is shown in Scheme 4.2. Colloidal silica (Snowtex-XS, Nissan Chemical Corporation) was received in the form of an aqueous dispersion in pH 9 ~ 10 water. Cetyltrimethylammonium bromide (CTAB) was added to precipitate silica nanoparticles from aqueous dispersion. Figure 4.2 shows FT-IR spectra of precipitated silica particles and their derivatives. In spectrum a, peaks at 1100 and 800 cm⁻¹ are assigned to Si-O-S and Si-OH stretching respectively. In addition, peaks between 3000 and 2800 cm⁻¹ are assigned to sp³ C-H stretching, which are from the CTAB salt physically adsorbed on the surface of silica nanoparticles. An ATRP initiator, (11-(2-bromo-2-methyl)propionyloxy)undecyltrichlorosilane, was then anchored onto the silica nanoparticle surface by reacting with silanol groups. In spectrum b, the peak at 1730 cm⁻¹, which is assigned to C=O stretching, is a direct evidence for successfully anchoring initiators onto the silica nanoparticle surface. Finally, VBBIT was grown from the nanoparticle surface via ATRP in butyronitrile at 90 °C, using N,N,N',N',N'-pentamethyldiethylene triamine (PMDETA) as ligand. The polyVBBIT/silica nanocomposites were collected by centrifugation and washed with acetone several times. No polyVBBIT homopolymer was found in the reaction solution indicated that the polymerization was restricted to the particle surfaces. In spectrum c, a new peak at 3010 cm⁻¹ for sp² C-H stretching, and a broad peak at 1640 cm⁻¹ for C=C and C=N stretching, are consistent with successfully growing polyVBBIT on silica nanoparticle surface. For better comparison, a homopolymer of polyVBBIT was also synthesized via ATRP in solution. In Figure 4.2, spectrum d for polyVBBIT homopolymer and sprctrum c for polyVBBIT/silica nanocomposite are very similar, which is another evidence for successful growth of a thick layer of polyVBBIT on silica nanoparticles.



Scheme 4.2. Synthetic route to polyVBBIT/silica nanocomposites.



Figure 4.2. FT-IR spectra of (a) silica nanoparticles, (b) surface initiator, (c) polyVBBIT/silica nanocomposite, and (d) polyVBBIT homopolymer. Samples were made into pellets with KBr.

The thermal gravimetric analysis (TGA) data was consistent with the FT-IR data. As shown in Figure 4.3, silica nanoparticle lost 14 % of the weight at 850 °C, which was mainly due to the decomposition of cetyltrimethylammonium bromide (CTAB) salt adsorbed on the nanoparticle surface and structural water release due to bonded hydroxyl groups. For surface initiator, the weight loss was 18 % at 850 °C. Since part of the CTAB salt would be replaced by the initiator, it was concluded that more than 4 % of the total weight initiator was anchored to the silica nanoparticle. For polyVBBIT/silica nanocomposites, the weight loss was 78%, which corresponded to a thick layer of polyVBBIT growing on the surface of nanoparticles. The polyVBBIT homopolymer lost more than 98 % of its weight in the end. The 2 % residual weight was probably from some remaining copper salts since it was synthesized via ATRP.



Figure 4.3. TGA data for (a) silica nanoparticles, (b) nanoparticles modified with surface anchored initiators, (c) polyVBBIT/silica nanocomposites (d) and polyVBBIT. All samples were run in air and at a heating rate of 10 °C/min.

To confirm the surface initiated ATRP of VBBIT was a controlled, living polymerization, the kinetics of the reaction was studied. Due to the poor solubility of polyVBBIT/silica nanocomposites in polymerization solution (butyronitrile), tracking the course of polymerization was difficult. Instead, following monomer consumption by ¹H NMR was chosen and an internal standard 4,4-dichlorodiphenyl sulfone was used. 4,4-dichlorodiphenyl sulfone was chosen because of its similar solubility with VBBIT monomer, non-volatility, and its distinct proton chemical shifts. Monomer consumption was calculated from the comparison of the integration of C-H groups (a, 7.98 ppm) in the phenyl ring of 4,4-dichlorodiphenyl sulfone and that of C-H group (b, 6.75 ppm) in VBBIT monomer (Figure 4.4).



Figure 4.4. 500 MHz ¹H NMR spectra of a representative sample for kinetic study of surface initiated ATRP of VBBIT.

The polymerization was well-behaved, and when plotted as ln([M]₀/[M]) vs time. The data approximated a line, which was consistent with a first order reaction up to 400 mins (Figure 4.5).



Figure 4.5. Kinetic study of surface initiated ATRP of VBBIT, the concentration ratio of $[M]_0$: [Si-Ini] : [CuBr] : [PMDETA] is approximately 100 : 1 : 2 : 6. $[M]_0$ and [M] represent the initial concentration of VBBIT monomer and the concentration of monomer at specific time.

The sizes of dried Snowtex-XS silica nanoparticles and polyVBBIT/silica nanocomposites were studied by Transmission Electron Microscopy (TEM)

(Figure 4.6.). The colloidal silica nanopaticles in aqueous solution have a diameter of 7 nm. However, after precipitating from solution by adding CTAB salts, the particles aggregated. The diameters of aggregates varied from 20 nm to 80 nm. After growing a thick layer of polyVBBIT on silica surface, the particles were better dispersed. In Figure 4.6 b, the dark spots were cores of silica nanoparticles, while the gray part was the polymer on the surface of nanoparticles.



Figure 4.6. TEM images of dried Snowtex-XS nanoparticles (a, top), and polyVBBIT/silica nanocomposites (b, bottom).

The working temperature for an outdoor installed DSSCs can be as high as 60 °C. For this reason, the desired polyVBBIT/silica nanocomposites used as electrolytes in solid state DSSC should have glass transition temperature (T_{q}) lower than 60 °C. The T_g of polyVBBIT homopolymer and polyVBBIT/silica nanocomposites was studied by Differential Scanning Calorimetry (DSC), shown in Figure 4.7. PolyVBBIT homopolymer had a Tg of 84 °C, while polyVBBIT/silica nanocomposites had a T_g of 95 °C. The reason for T_g increase from the free homopolymer to the surface tethered polymer is easy to understand. In surface tethered polymers, the mobility of polymer chains was more constrained compared to that of free polymer, and more energy would be needed to pass through the glassy state to the rubbery state, resulting to higher T_{g} .^{20,21} To obtain lower T_g , the BF₄ anion in polyVBBIT could be replaced by a larger anion, such as TFSI. Besides, other monomers with more flexible structure could be synthesized and polymerized to replace VBBIT monomer. These work will be done in future.

140



Figure 4.7. DSC curves of polyVBBIT homopolymer and polyVBBIT/silica nanocomposites.

Application as novel quasi-solid state electrolyte in DSSCs

Since polyVBBIT/silica nanocomposite is a white powder at room temperature, it is difficult to use directly as electrolyte in DSSC. As shown in Scheme 4.3, we mixed it with PMII, a commonly used IL in DSSCs.^{22,23} The ionic conductivity of polyVBBIT/silica nanocomposites and PMII mixture was measured, as shown in Figure 4.8. Pure PMII showed the highest conductivity in all five samples, which was 1.1 mS/cm at room temperature and 34.6 mS/cm at 90 °C respectively. After

adding polyVBBIT/silica nanocomposites, the conductivity decreased. The more polyVBBIT/silica nanocomposites was added, the lower was the conductivity, which was mainly attributed to the viscosity increase and free volume decrease of PMII. However, the conductivity decrease was relatively small. As in the case of PMII/polyVBBIT/silica nanocomposites (20 wt%), the conductivity was 0.8 mS/cm at room temperature and 14.7 mS/cm at 90 °C, still quite high. The conductivities of PMII mixed with more than 20 wt% polyVBBIT/silica nanocomposites was also studied. The results showed incontinuous conductivity data, which may be caused by uneven dispersion of polyVBBIT/silica nanocomposites at high concentration.



polyVBBIT/silica nanocomposites



PMII

Mixing and Stirring



Mixture of PMII and polyVBBIT/silica nanocomposites

Scheme 4.3. Pictures of polyVBBIT/silica nanocomposites, PMII and their mixture.



Figure 4.8. Conductivity of pure PMII and PMII with different amount of polyVBBIT/silica nanocomposites.

The PMII/polyVBBIT/silica nanocomposites mixture was gelated just after conductivity measurement from 25 °C to 90 °C. In Scheme 4.4a, the gel formed was opaque. While in Scheme 4.4b, the gel formed was not as good as in Scheme 4.4a, which was transparent. The concentration of polyVBBIT/silica nanocomposites was critical in gel formation. PMII with lower concentration of polyVBBIT/silica nanocomposites cannot form a gel after heating. To study the

mechanism for gel formation, six different samples were made, including PMII with bare silica nanoparticle, PMII with polyVBBIT homopolymer, PMII with polyVBBIT/silica nanocomposites and another less viscous IL, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIHP), with bare silica, BMIHP with polyVBBIT homopolymer, and BMIHP with the concentration polyVBBIT/silica nanocomposites. All additives to IL were set to be 20 wt%. The results showed that only ILs (PMII and BMIHP) with polyVBBIT/silica nanocomposites were gelated after heating at 60 °C for 3 h, which indicated that both the silica nanopaticle core and the polyVBBIT on its surface played a role in the gel formation. The silica nanoparticle core worked as immobilized node while the surface-anchored polymer chains entangled with each other after heating to form a 3-D network in the system, resulting to gel formation.



Scheme 4.4. Gels formed after conductivity measurement from 25 °C to 90 °C. PMII with 20 wt% polyVBBIT/silica nanocomposites (a) and PMII with 15 wt% polyVBBIT/silica nanocomposites. (b)

Application in DSSC

The PMII/polyVBBIT/silica namocomposites gel electrolyte has been used in DSSC. Three cells were fabricated and the cell performances were tested, as shown in Figure 4.9 and Table 4.1. The photoelectric conversion efficiency was calculated, as shown in Equation 1:

$$Efficiency = \frac{J_{sc} \times V_{oc} \times ff}{P} \times 100\%$$
(1)

where J_{sc} is the short circuit current density, V_{oc} is the open circuit voltage, *ff* is the fill factor, and *P* is the power density of the light source (0.1 A/cm²). Cell 2 showed the best performance, which had a photoelectric conversion efficiency of 0.37 %. However, this conversion efficiency was quite low compared to the 7 % conversion efficiency obtained in some similar studies.¹⁴ There were a couple of reasons for this poor performance. The first was the fabrication skills. As a newcomer in this area, we could only achieve a 1/5 conversion efficiency in repeating the literature method. The second was that we did not tune the iodine concentration in electrolyte. The iodine concentration played an important role in the performance of DSSCs. Gerald Meyer and co-workers' study revealed that by finely tuning the iodine concentration, the cell performance could be improved by more than 100 %.²⁴ The third was that we did not add any additives to the gel electrolyte. Additives such as 4-*tert*-butylpyridine and N-methylbenzimdazole could greatly elevate the open circuit voltage by shifting the conduction band edge of TiO_2 and preventing recombination reactions with triiodides.²⁵



Figure 4.9. J-V curve of the DSSC with PMII/polyVBBIT/silica nanocomposites gel electrolyte

Table 4.1. Short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (*ff*) and conversion efficiency of DSSCs with PMII/polyVBBIT/silica nanocomposites gel electrolyte.

Cell number	J _{sc} / 10 ⁻³ A/cm ²	V _{oc} / V	ff	Conversion efficiency / %
1	1.87	-0.45	0.38	0.32
2	1.90	-0.38	0.52	0.37
3	1.86	-0.46	0.41	0.35

Conclusion

A novel PIL modified silica nanoparticle composite (polyVBBIT/silica nanocomposite1-(4-vinylbenzyl)-3-butylimidazolium tetrafluoroborate) was successfully synthesized by surface initiated ATRP. The polymerization was confirmed to be a first order reaction by kinetic study. FT-IR and TGA confirmed a high density of polyVBBIT was grown on the surface of silica nanoparticle. When finely dispersed in PMII and heated, a gel was formed. The gel electrolyte was used as a quasi-solid state electrolyte in DSSC and a 0.37 % conversion efficiency was achieved. The conversion efficiency was quite low compared to the results reported by other researchers. However, by improving the cell fabrication skills, finely tuning the iodine concentration in the electrolyte and adding additives, a higher conversion efficiency can be expected and will be done in future.

Experimental Section

Materials

4-Vinylbenzyl chloride, 1-butylimidazole, sodium tetrafluoroborate, 2,6-di-tertbutyl-4-methylphenol (DBMP), CuBr (99.999 %), cetyltrimethylammonium bromide, 2,2'-dipyridyl (bpy, 99+%), 2-propanol (anhydrous 99.5%), N,N,N',N',N''pentamethyl diethylenetriamine (PMDETA) and 1,1,4,7,10,10hexamethyltriethylenetetramine (HMTETA) were used as received from Sigma-Aldrich except for bpy, which was sublimed before use. Silver nitrate was purchased from Spectrum. Butyronitrile was purchased from Matheson Coleman & Bell. Snowtex-XS colloidal silica, as an aqueous dispersion in pH 9-10 water, was a gift from Nissan Chemical Industries. TEC-15 FTO glass was purchased from Hartford Glass Co. TiO₂ paste (DSL 18NR-T) was purchased from Dyesol. N3 dye was given to us by the Nate Lewis group. Iodine 99.5% and hydrogen hexachloroplatinate (IV) hydrate 40 % Pt were purchased from Acros. All other chemicals and solvents were ACS reagent grade and used as received from commercial suppliers without any further purification unless otherwise mentioned.

Synthesis of 1-(4-vinylbenzyl)-3-butylimidazolium tetrafluoroborate (VBBIT)

1-Butylimidazole (6.2 g, 50 mmol) was dissolved in 40 mL of CHCl₃ in a dry flask, followed by addition of 4-vinylbenzyl chloride (8.4 g, 55 mmol) and an polymerization inhibitor, 2,6-di-*tert*-butyl-4-methylphenol (0.055 g, 0.25 mmol). The solution was stirred under N₂ at 50 °C for 8 h. After that the solvent was

removed by rotary evaporation. The resulting viscous liquid was washed with 25 mL diethyl ether three times and then dried under vacuum overnight at room temperature. Yield: 12.4 g, 85 %. VBBICI (11 g, 40 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (0.044 g, 0.2 mmol) were dissolved in dry acetone (60 mL) in a dry flask, followed by slow addition of sodium tetrafluoroborate (5.2 g, 48 mmol). The reaction mixture was stirred for 3 days at room temperature and then filtered. After the acetone was evaporated under reduced pressure, the unreacted VBBICI and the inhibitor were removed from the waxy residue by washing with distilled water and then diethyl ether until no AgCl precipitate was observed when tested by silver nitrate. Yield: 11.8 g, 90 %. ¹H NMR (d^6 -DMSO, 300 MHz) δ 9.24 (s, 1H), 7.80 (d, *J* = 1.6 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 6.73 (dd, *J* = 17.7, 11 Hz, 1H), 5.89 (dd, *J* = 11, 0.9 Hz, 1H), 5.40 (s, 2H), 5.30 (dd, *J* = 17.7, 0.9 Hz, 1H), 4.16 (t, *J* = 7.2 Hz, 2H), 1.82 - 1.71 (m, 2H), 1.31 - 1.17 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

Synthesis of ATRP initiator modified silica nanoparticles.

The initiator precursor was synthesized according to a literature procedure. ω -Undecylenyl alcohol (1.703 g, 10 mmol) and pyridine (0.84 mL, 11 mmol) were dissolved in 10 mL of dry THF, followed by dropwise addition of 2bromoisobutyryl bromide (1.24 mL, 10 mmol). The reaction mixture was stirred at room temperature overnight and then diluted by 20 mL hexane, washed with 3N HCl (3 times, 10 mL each) and distilled water (3 times, 10 mL each). The organic phase obtained was dried over sodium sulfate and filtered. Afterwards, hexane was removed by a rotavap and the oil-like product 10-undecen-1-yl 2-bromo-2methylpropionate was purified with a column (hexane/ethyl acetate 25:1 v/v). The yield was 2.81 g, 88 %. R_f (hexane/ethyl acetate 10:1 v/v): 0.70. ¹H NMR (CDCl₃, 300 MHz) δ 5.85 - 5.72 (m, 1H), 5.02 - 4.86 (m, 2H), 4.15 (t, *J* = 6.6 Hz, 2H), 2.06 - 1.97 (m, 2H), 1.92 (s, 6H), 1.70 - 1.60 (m, 2H), 1.41-1.22 (br, 12H).

10-Undecen-1-yl 2-bromo-2-methylpropionate (1.35 g, 4.23 mmol) and trichlorosilane (5 mL, 50.7 mmol) was charged to a dry flask, followed by addition of Karstedt's catalyst (10 μ L). The reaction mixture was stirred at room temperature overnight and then passed through a pipet column. Excess trichlorosilane was removed under reduced pressure at 30 °C to provide (11-(2-bromo-2-methyl)propionyloxy)undecyltrichlorosilane as an oil. Yield: 1.44 g, 75 %. ¹H NMR (CDCl₃, 300 MHz) δ 4.16 (t, *J* = 6.6 Hz, 2H), 1.92 (s, 6H), 1.75-1.46 (m, 4H), 1.40-1.20 (br, 16H).

(11-(2-Bromo-2-methyl)propionyloxy)undecyltrichlorosilane (1.00 g, 2.20 mmol) was dissolved in 100 mL dry toluene, and then added to a well-dispersed mixture of silica nanoparticles in toluene (1.00 g silica, 100 mL dry toluene). The reaction mixture was heated to 65 °C and stirred under nitrogen overnight. The product was collected by centrifugation and washed three imes with acetone to remove adsorbed (11-(2-bromo-2-methyl)propionylxoy)undecyltrichlorosilane. Yield: 1.7 g, 85 %.

Synthesis of polyVBBIT/silica nanocomposites.

In a dry Schlenk flask, VBBIT (656 mg, 2.0 mmol), the surface initiator (148 mg, $\sim 2 \times 10^{-5}$ mol) and PMDETA (20.8 mg, 1.2 x 10^{-4} mol) were dissolved in molecular sieve dried butyronitrile (2 mL). After 3 freeze pump thaw cycles, CuBr (5.7 mg, 4 x 10^{-5} mol) was charged into the Schlenk flask under nitrogen. The reaction was run in nitrogen atmosphere at 90 °C with magnetic stirring. After 16 h, the reaction was stopped. The product was collected by centrifugation and washed 3 times with acetone and DMF to remove residual reactants and adsorbed homopolymer. The product was dried under vacuum (8 mTorr) at 60 °C. Yield: 0.71 g, 88 %.

Characterization

¹H NMR analyses were performed on a Varian 500 MHz spectrometer with the residual solvent proton signals as chemical shift standards. FT-IR spectra were acquired from a Nicolet IR/42 spectrometer purged with dry nitrogen, signal averaging 128 scans at 4 cm⁻¹ resolution. All IR samples were dried under vacuum, grounded and mixed with dry KBr, and then pressed into pellets. TGA was carried out in air on Perkin-Elmer TGA 7 instruments at a heating rate of 10 °C/min. TGA samples were first dried under vacuum overnight at 80 °C prior to test. Samples were held at 120 °C in the TGA apparatus for 30 min to remove all the physically adsorbed water before the heating process proceeded. DSC was carried out on TA instruments DSC Q100 at a heating rate of 10 °C/min. The

ionic conductivities of the Si-PVBBIT, PMII electrolytes were measured with an AC impedance analyzer HP 4192A over the frequency range from 5 Hz to 13 MHz. Electrolytes were placed between a home-made cell. Conductivities of different temperatures from 298 K to 363 K were measured. From the Nyquist plot, the resistance of the electrolyte was estimated, and then the conductivity of the electrolyte was calculated using the distance between two electrodes and cross-section area of the cell. The cell performance was measured by potentiostat 650D CH Instrument, and a Xe arc lamp (Horiba Jobin Yvon) equipped with an AM 1.5 global filter set (Solar Light Co.) was used for solar simulation.

Calculation of initiator content on the surface of silica nanoparticle

The content of initiator on the surface of silica nanoparticle can be roughly calculated according to TGA data. As shown in Figure 4.3, the surface initiator have a 4 % more weight loss compared to the bare silica nanoparticle. By ignoring the displacement reaction of initiator to CTAB salts on the surface of nanoparticle, and assuming the initiator has a complete decomposition and 0 % weight retention at 850 °C, the initiator content can be calculated as follows: assuming the content of initiator on the surface is X %, then the content of silica nanoparticle is (100-X) %. The total weight of initiator anchored silica nanoparticle is 1 g. Silica nanoparticles loses 14 % of weight at 850 °C. Free initiator loses 100 % of weight at 850 °C, and surface initiator loses 18 % of weight at 850 °C.

153

 $(1g) \times (100 - 14) \% \times (100 - X) \% + (1g) \times (0\%) \times (X) \% = 1g \times (100 - 18) \%$

X = 4.7

The initiator content on the surface of silica nanoparticle is 4.7 % of the total weight of surface initiator.

Kinetic Study.

The polymerization condition was kept the same as mentioned above, except that 4,4-dichlorobiphenyl sulfone (0.100 g) was added as an internal standard. At certain time intervals, a syringe was used to sample reaction mixture (0.1 mL) and diluted with acetone (3 mL) association with quick shaking to stop the reaction. These samples were kept undisturbed overnight to allow the particles to settle. The clear upper layer was drawn with a pipet and the solvent was removed by rotary evaporation. The residue was dissolved in d^6 -DMSO, analyzed by ¹H NMR. The consumption of monomer was calculated by comparing the integrals of specific peaks from the standard and monomer.

DSSC fabrication.

The DSSC was fabricated and tested by Lisa Harlow in Prof. McCusker's group. The photoanode was prepared as follows: TiO_2 paste was doctor-bladed onto the FTO glass using a scotch tape mask with an area of 1 cm x 1 cm. It was then baked at 375 °C for 10 mins, 450 °C for 5 mins, 500 °C for 10 mins, 550 °C for 5 mins. Once cooled to 90 °C they were immersed into a 0.3 mM N3 dye ethanol solution for 24 hours. For the cathode: thermalized platinum was used. 5 mM hydrogen hexachloroplatinate (IV) hydrate in anhydrous isopropanol was drop casted onto the FTO glass with two pre-drilled holes for electrolyte insertion. They were let dry for 5 minutes on a flat surface then baked at 350 °C for 15 mins. The DSSC was fabricated as follows: PolyVBBIT/silica nanocomposties were suspended in 0.6 g PMII (2.38 mmol), with the addition of 0.0604g l₂ (2.38x10⁻⁴ mol). The mixture was stirred for a half hour and then one drop was placed onto the dyed photoanode. The electrolyte was spread over the film using a glass pipet, and no pressure was applied. The electrolyte was pulled around. The films were then baked at 90 °C for 1 hour. Surlyn was used as a spacer and the electrodes were clamped together using binder clips and copper wires were attached with silver conductive epoxy. The cells were tested after the epoxy set 4 hours later.

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APPENDIX

Ionic conductivity measurement - AC impedance spectroscopy

Ohms law (Equation 1) describes the current, I as a function of the applied voltage, V and the resistance, R of an electrolyte.

$$R = V/I \tag{1}$$

Conductivity, σ , is defined as the reciprocal of resistivity, ρ . (Equation 2)

$$\sigma = 1/\rho \tag{2}$$

and

$$\rho = \mathsf{R}(\mathsf{A}/\mathsf{I}) \tag{3}$$

where A is the area and I is the length of the electrolyte sample. It follows then that

$$\sigma = I/RA \tag{4}$$

Resistivity and therefore conductivity is measured best by AC impedance spectroscopy. An alternating voltage signal is applied to an electrolyte containing cell, and the resulting current measured. This current is inversely proportional to the impedance, *Z*, of the cell, and is frequency dependent. The electrochemical response of the cell under measurement is rationalized in terms of an equivalent circuit (Scheme A1), where C_1 is the capacitance between the two electrodes, R_1

is the resistance of the electrolyte, C₂ and R₂ is the capacitance and resistance between electrode and electrolyte respectively. The capacatance is calculated by Equation (5), where ε_r is dielectric constant, ε_0 is the permittivity of free space, A is the area of the two electrodes and d is the distance.

$$C = \varepsilon_r \varepsilon_0 A/d \tag{5}$$

Since d₁ (the distance between the two electrodes) >> d₂ (the distance between the electrode and the double layer), C₁ << C₂. The impedance of a capacitor, X_C, is calulated by Equation 6, where ω is the angular frequency and C is the capacitance. Since C₁ << C₂, X_{C1} >> X_{C2}.

$$X_{\rm C} = -1/\omega C \tag{6}$$



Scheme A1: Equivalent circuit of the electrochemical response of the cell used in conductivity measurement.

At $\omega = 0$, both X_{C1} and X_{C2} approach ∞ , the total impedance, Z_{tot} = R₁ + 2R₂.

As ω increases, X_{C2} gets smaller and smaller, and approaches 0. While X_{C1} is

still very large, $Z_{tot} = R_1$. When ω approaches ∞ , both X_{C1} and X_{C2} approach 0, $Z_{tot} = 0$.

So ideally, the Nyquist plot of the above mentioned circuit should show like Figure A1.



Figure A1. Ideal Nyquist plot of Scheme A1.

However, we cannot measure the impedance at frequency approaching 0 and ∞ , so we do not have the full right semicircle and the left semicircle does not end at 0. Figure A2 shows the Nyquist plot of a real sample. R₁ is determined by the point who has Z'' closest to 0.


Figure A2: Example of a typical Nyquist plot obtained from AC impedance measurement. (Sample is polyGBIMTFSI-co-polyME₃MO-1/1 at 90 °C.)