

---

Effect of Ionic Liquid on the Viscosity Behavior and Size of Telechelic Ionomers in  
Nonpolar Solvent

By

LIZHUO SONG

A thesis submitted to the

Graduate School-New Brunswick

Rutgers, The State University of New Jersey

In partial fulfillment of the requirements

For the degree of

Master of Science

Graduate Program in Chemical and Biochemical Engineering

Written under the direction of

Dr. Masanori Hara

And approved by

---

---

---

New Brunswick, New Jersey

January 2018

---

## ABSTRACT OF THESIS

Effect of Ionic Liquid on the Viscosity Behavior and Size of Telechelic Ionomers in Nonpolar Solvent

By

Thesis Director: Dr. Masanori Hara

LIZHUO SONG

Ionomers (polymers containing a small amount of ionic groups) are used for various current technologies, such as hydrogen fuel cells, sensors, water purifications, and drug delivery. In addition, ionomers are widely used for solution studies due to their unique behavior and potential application to processing from solution (e.g., membrane fabrication). Recently, ionic liquid was found to be an effective additive (to a low-polarity solvent) to dissolve ionomers, which will be used for processing ionomer films and fibers. Despite the usefulness of the solution study, ionomers used so far are random ionomers in which ionic groups are randomly distributed along the polymer chain and thus data analysis and model calculation become complex.

In this study, a monofunctional telechelic ionomer that had an ionic group only at one chain end was used. This made analysis easier and simpler. In this work, viscosity and dynamic light scattering were used to study the effect of ionic liquid on the telechelic ionomers in nonpolar solvent, toluene. In nonpolar solvent, ionic groups formed ion pairs which were attracted each other to form ionic aggregates, resulting in molecular

---

aggregate formation. This was confirmed by an increase in reduced viscosity and effective (hydrodynamic) diameter of the telechelic ionomer solutions. Upon addition of ionic liquid, 1-ethyl-3-methylimidazolium trifluoromethane sulfonate (EMIM-TF), ionic aggregates were disrupted and the size of molecular aggregates was decreased, approaching to that of nonionic polymer of the same molecular weight.

---

## **Acknowledgement**

I would like to express the deepest appreciation to my advisor professor Hara for his continuous support during my thesis research at Rutgers. Dr. Hara has given his knowledge and put in the effort at all times for the benefit of this dissertation. Without his guidance and persistent help, this dissertation would not have been possible. I'd also like to thank my research group for providing me with an excellent atmosphere for doing research.

I would like to thank my research group member Elliot Taylor for being my mentor when I joined the group, his suggestion and help have been a important part of my research work.

Finally, to my parents, Zhouyao Song and Yihong Liu, who have supported me in continuing my study in college and their caring and encouragement have always made me feel warm. And to all my friends who have always been supportive all these years. Thank you for everything.

---

## Table of Contents

Abstract of Thesis .....	ii
Acknowledgement .....	iv
List of Tables.....	vi
List of Figures .....	vii
1. Introduction.....	1
1.1 Research Motivations.....	1
1.2 Viscosity Measurement .....	3
1.3 Dynamic Light Scattering (DLS) .....	4
2. Experimental Methods .....	6
2.1 Materials .....	6
2.2 Equipment.....	7
2.3 Experimental Procedure.....	8
2.3.1 Viscosity Measurement .....	8
2.3.2 DLS Measurement .....	9
3. Results and Discussion .....	11
3.1 Reliability of viscosity data for SPS-Li ionomer.....	11
3.2 Viscosity of Different Molecular Weight PS and SPS-Li .....	12
3.3 Viscosity of SPS-Li with Ionic Liquid.....	17
3.4 DLS for SPS-Li Containing Ionic Liquid .....	21
4. Conclusion and Future Work .....	24
5. References.....	26

---

## List of Tables

Table 1.1: Solution Viscosity Nomenclature.....	4
Table 2.1: Ionic liquid used in this study .....	6
Table 3.1: DLS Results for PS, SPS-Li and SPS-Li EMIM-TF Mixture in Toluene .....	22

---

## List of Figures

Figure 1.1: Schematic Structure of Random and Telechelic Ionomers.....	2
Figure 1.2: Ubbelohde Viscometer .....	3
Figure 1.3: Dynamic light scattering instrument.....	5
Figure 2.1 Chemical Structure of PS and SPS-Li used in This Study: .....	6
Figure 2.2: Chemical Structures of the Ionic Liquids Used in This Study .....	7
Figure 3.1: Reduced Viscosity vs. Concentration for the 50000 SPS-Li in Toluene .....	11
Figure 3.2: Reduced Viscosity vs. Concentration for the 50000 and the 38000 PS in Toluene .....	12
Figure 3.3: Reduced Viscosity vs. Concentration for the 50000, 38000 and 18000 SPS-Li in Toluene.....	13
Figure 3.4: Reduced Viscosity vs. Concentration for the 50000 PS and SPS-Li Sample in Toluene .....	13
Figure 3.5: Reduced Viscosity vs. Concentration for the 38000 PS and SPS-Li Sample in Toluene.....	14
Figure 3.6: Viscosity curves for mono- and difunctional telechelic ionomers as well as unquaternized polymer in toluene.....	15
Figure 3.7: Schematic Structure for intramolecular and intermolecular bonds in telechelic ionomer .....	16
Figure 3.8: Reduced Viscosity vs. Concentration for the 50000 SPS-Li and PS in Solvent Mixture of EMIM-TF .....	17

---

Figure 3.9: Reduced Viscosityratios vs. [IL]/[Ion] for the 50000 and the 38000 SPS-Li and PS in toluene .....	18
Figure 3.10: Reduced Viscosity ratios vs. [IL]/[Ion] at $c = 0.8\text{g/dl}$ for the 50000 SPS-Li and the 50000 PS .....	19
Figure 3.11: Reduced Viscosityratios vs. [IL]/[Ion] at $c = 0.8\text{g/dl}$ for the 38000 SPS-Li and the 38000 PS .....	20
Figure 3.12: Dynamic Light Scattering Results for 50000 the SPS-Li.....	22
Figure 3.13: The schematic of molecular structure of neutral polymers and telechellic polymers, telechellic polymer and telechellic ionomer plus ionic liquid.....	23

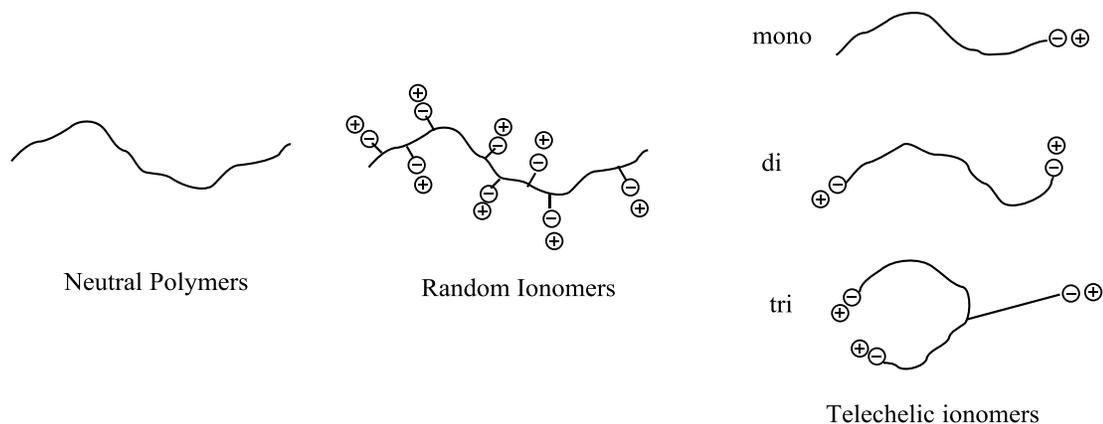
## **1. Introduction**

### **1.1 Research Motivations**

Ionomers are macromolecules which are predominantly of a nonpolar nature but contain ionic functionality as an integral part of the chain typically at less than ca. 15 mol %. Traditional ionomers have randomly placed ionic moieties and models have been used to describe their structure-property relationships [1-9]. Ionomers are used for numerous current technologies such as hydrogen fuel cells [10-12], sensors [13-14], water purifications [15], and drug delivery [16-17]. In addition, ionomers are widely used for solution studies due to their unique behavior and applications to processing from solution (e.g., membrane fabrication).

Ionomers are divided into two types according to the location of ionic groups [18], random ionomers and telechelic ionomers as seen in Figure 1.1. In random ionomers, ionic groups are distributed randomly along backbone chains, so that interionic distance cannot be specified. In contrast, ionic groups are located only at chain ends in telechelic ionomers. The interest arises from the fact that telechelic polymers exhibit the possibility of gelation, micelle formation, and other interesting phases and structures which can have potentially significant consequences on the structural and dynamic properties. For that reason, studying the solution properties of telechelic ionomers is of great importance. The goal of this research is to investigate the relationship between the solution properties and chemical structure of telechelic ionomers. The viscosity of telechelic ionomers (SPS-Li) of various molecular weights was measured in a nonpolar

solvent. Then the effect of ionic liquid (EMIM-TF) on the solution properties was investigated.



**Figure 1.1** Schematic structure of random and telechelic ionomers

Ionic liquids are liquid electrolytes composed entirely of ions. Different from normal molten salts which are generally considered as the materials with high melting temperature, ionic liquids have a low melting temperature below 100 °C and often exist in the liquid state at room temperature [19-22]. They exhibit many desirable properties, such as negligible vapor pressure, high electric conductivity, non-volatility, non-flammability, low melting temperature, and a wide electrochemical window [23-32]. An increasing number of applications have attracted interests in the study of ionomer with ionic liquids [33-34]. However, only a few studies have been reported on the interactions between ionomers and ionic liquids, and little is known how ionic liquids changes the properties of ionomer solutions [35]. In this study viscosity and particle size of telechelic ionomers were investigated in a nonpolar solvent in the presence of different amounts of ionic liquid.

---

## 1.2 Viscosity

Viscosity is the mechanical friction between molecules in motion due to mutual attraction of the molecules. Viscosity measurement of the solution is of great importance for the study of the properties of the solution. Viscosity is measured with an Ubbelohde type viscometer (Figure 1.2) by using a capillary tube and measuring the time it takes for the fixed volume of liquid to pass through the capillary. A thermostated water bath was used to maintain the temperature of the viscometer tube. The viscosity of the pure solvent and solution was measured at first and then a series of diluted solution of varying concentrations were tested in sequence.



**Figure 1.2:** Ubbelohde Viscometer[35]

The solution viscosity can be calculated using the efflux time of the polymer solution  $t$ , the efflux time of the solvent  $t_0$ , and the polymer concentration  $c$  by using the following equations (see table 1.1). Ionomer solution is more viscous than the solvent and increasing the concentration of the ionomer in the solution will increase its viscosity, but this study is focused on the effect of ionic liquids on the solution viscosity rather than the effect of concentration. For that reason, reduced viscosity, or specific viscosity divided by the polymer concentration, is used to normalize the effect of concentration of the solution.

Table 1.1: Solution viscosity nomenclature [35]

Name	Equation
Relative Viscosity	$\eta_r = t/t_0$
Specific Viscosity	$\eta_{sp} = (t - t_0)/t_0$
Reduced Viscosity	$\eta_{red} = \eta_{sp}/c$
Intrinsic Viscosity	$[\eta] = \lim_{c \rightarrow 0}(\eta_{red})$

### 1.3 Dynamic light scattering (DLS)

Dynamic light scattering (DLS) is a technique that is widely used to determine the size and the size distribution of suspensions and polymers in solution. The basic principle is simple: solvent molecules collide with macromolecules in solution which leads to Brownian motion and the speed of Brownian motion is reduced when the particle becomes larger. The moving particles in the solution are illuminated with a laser light and the

scattered light fluctuation is detected by a fast photon detector. The intensity of the scattered light is measured during the given time interval. The timescale of the intensity fluctuations caused by Brownian motion is related to the time scale of the particle motion which depends on the diffusion coefficient  $D$ . Hydrodynamic particle sizes are calculated by applying Einstein-Stokes relationship,

$$D = \frac{kT}{6\eta\pi r} \quad (1)$$

where  $k$  is the Boltzmann constant,  $T$  is the temperature,  $D$  is diffusion coefficient,  $r$  is hydrodynamic radius and  $\eta$  is the viscosity. In DLS measurements,  $D$  is determined experimentally and hydrodynamic radius  $r$  of polymer molecules is calculated using Eq (1) with known  $\eta$ ,  $k$ ,  $T$  and  $D$  values.

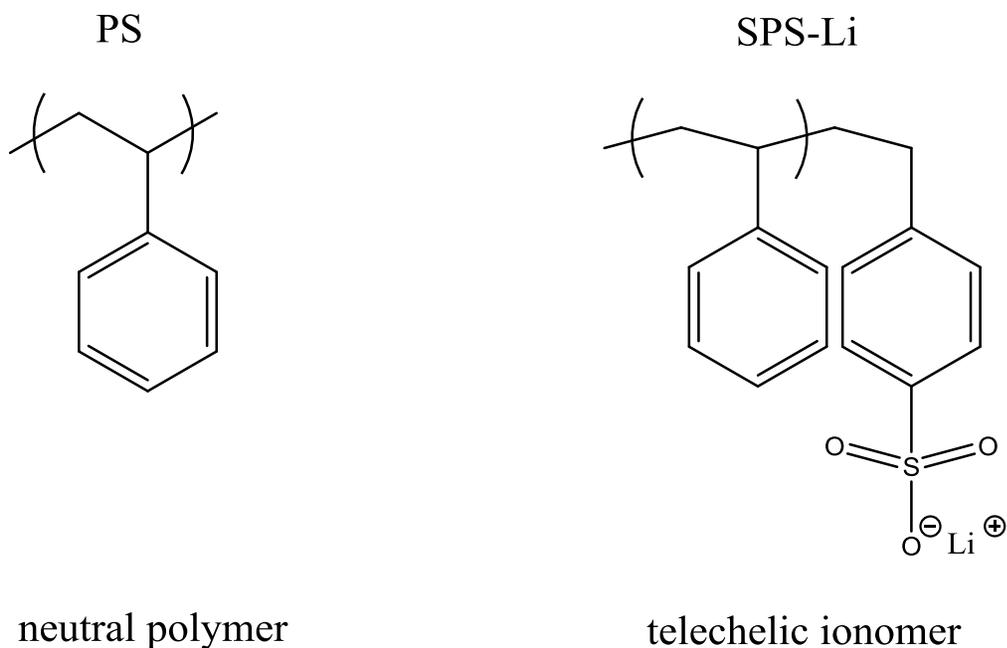


Figure 1.3: Dynamic light scattering instrument

## 2. Experimental Methods

### 2.1 Materials

In this study, polystyrenes (PS) of 50K and 38K molecular weight were obtained from Polysciences Inc as neutral polymers. Telechelic ionomers (SPS-Li) of 50K, 38K and 18K molecular weight were obtained from Dr. Jerome (Belgium). Chemical structures of both PS and SPS-Li are given in Figure 2.1. A nonpolar solvent toluene and an ionic liquid EMIM-TF were obtained from Aldrich and Iolitec, respectively.

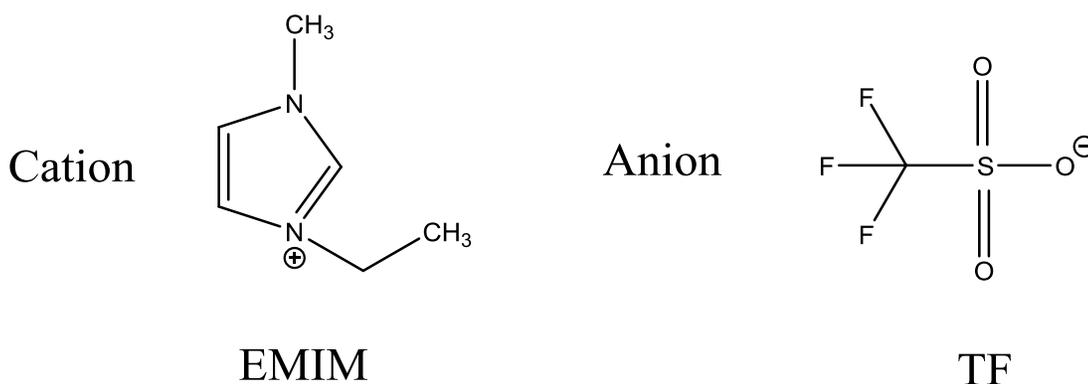


**Figure 2.1:** Chemical structures of PS and SPS-Li used in this study

**Table 2.1:** Ionic liquid used in this study

---

Abbreviation	Full Name	Formula	Molecular Weight (g/mol)
EMIM-TF	1-ethyl-3-methylimidazolium trifluoromethane sulfonate	$C_7H_{11}F_3N_2O_3S$	260.23



**Figure 2.2:** Chemical structures of the ionic liquid used in this study

## 2.2 Equipment

In this study, an Ubbelohde viscometer was used for the determination of reduced viscosity. An Ubbelohde viscometer is a type of capillary-based viscometer which is often used for polymer solution viscosity measurements. The advantage of the viscometer is that the measurement is independent of the amount of solution in the viscometer and measurement at a series of concentrations can easily be made by successive dilution. Viscosity measurements are conducted in a thermostated bath at a constant temperature and a cap is used to seal the viscometer to avoid evaporation and exposure to air to obtain accurate data.

Dynamic light scattering (DLS) is a technique that can be used to determine the size and the size distribution of particles in suspension or polymer solution. DLS can perform an accurate and reliable particle size analysis in several minutes, which is an efficient method for studying ionomer solutions.

## **2.3 Experimental Procedure**

### **2.3.1 Viscosity measurements**

Solutions of PS and the ionomer are prepared at least 3 days before the viscosity measurements. 100 mg of ionomer or PS in a flask was weighted by an electronic balance. Then 10 ml of pure solvent (toluene) was drawn into a pipette and mixed with ionomer in the flask. The ionomer solution was set on a magnetic stirrer for at least 3 days at room temperature to make sure that the sample would be fully dissolved for the measurements. Some ionomer samples could not be dissolved by solvent directly. In those cases, the sample would be recovered through freeze-drying so that it could be dissolved easily. The ionomer solution must maintain a homogenous mixture of ionomer and solvent to maintain the accuracy of the experiment. The sample showing solid precipitation in the flask could not be used for the experiment because the viscometer capillary could be blocked by these particles [35].

On the day of the experiment, the viscometer that was filled with sulfuric acid was taken out of the hood and cleaned. Sulfuric acid inside the viscometer was removed and the viscometer was rinsed with distilled water for several times. Acetone was used to remove residual water inside the viscometer and to speed up the drying when it was placed

in an oven. The viscometer was kept in an oven for at least 10 minutes, then removed from the oven. The sink aspirator was used to remove the hot air to avoid the condensation of water moisture inside the viscometer which would affect the concentration of the solution. Once the viscometer was prepared, 8ml of pure solvent was added into the viscometer by using a clean pipet. The viscometer was then placed in a water bath which is thermostated at  $25 \pm 0.1^{\circ}\text{C}$ . To make the data accurate, the viscometer must be placed vertically and a cap was placed on it. The relative error of 3 successive values of time must not exceed 0.5% and there should not be an increasing or decreasing trend.

After the solvent measurement, the viscometer was removed from the bath and cleaned. Acetone was used to remove the solvent in the viscometer and the viscometer was placed in an oven for at least 10 minutes to dry before the ionomer solution was measured. As before, an aspirator was used to remove the hot vapor inside the viscometer to ensure that no water was condensed in viscometer. This time, 8ml solution was added into viscometer by using a different clean pipet, and the measurement was conducted. In order to obtain the plot of reduced viscosity versus concentration, the solution was diluted and measured at a series of concentration. The 3ml, 5ml, 10ml and 20 ml of solvent was mixed with the solution in sequence and viscosity measurements were performed for each dilution.

### **2.3.2 Dynamic light scattering measurements**

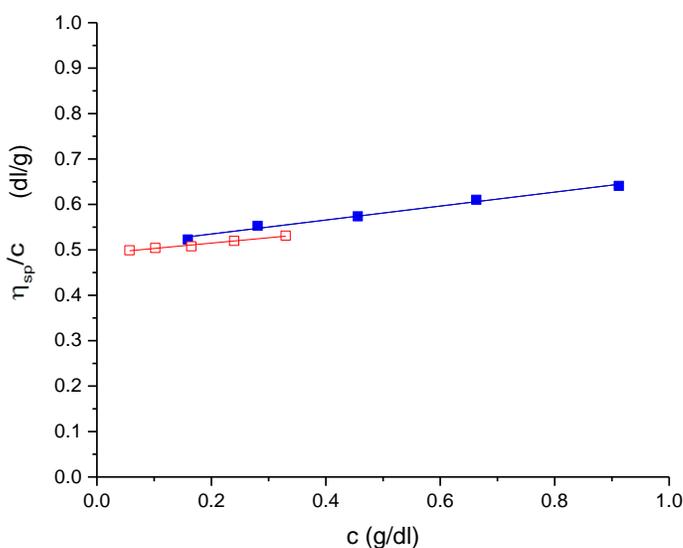
Dynamic light scattering (DLS) experiment is divided into a cleaning step and a measurement step.

In the cleaning step, a cell must be submerged in sulfuric acid for at least a day before the experiment. On the day of the experiment, the cell was washed thoroughly with water and rinsed with acetone. In order to make the cell clean enough for light scattering, a glass tower connected to a heater and a cooler was used for cleaning. After making sure that the bath of the glass tower contained adequate acetone, both heater and cooler were turned on to boil the acetone and the cell was placed on the glass tower for at least an hour. Meanwhile, a set of beakers and a syringe were prepared and cleaned for the experiment. Samples were prepared in the same way as the samples for viscosity measurement except that the concentrations of viscosity samples were higher. After the washing step is done, the cell must be transferred to a dust-free container and placed in a clean hood to avoid dust particles. Once the cell was prepared, 2.5ml of solvent was extracted into the syringe and 0.45 $\mu$ m and 0.20 $\mu$ m filters were used to make the final sample. The 0.45 $\mu$ m filter was placed on the syringe on one end and connected to the 0.20 $\mu$ m filter on the other end so any liquid will pass through two filters, first the 0.45 $\mu$ m filter then the 0.20 $\mu$ m filter. First, 2ml of solvent was pushed through the two filters into a waste container. Then 2.5ml of sample was passed through the filters into the waste container. Finally, as done previously, 2ml of the sample was pushed through two filters, but this time into the washed cell. This procedure was done to remove possible dust particles existing in the sample, which would affect the measurement of DLS. This way the sample was prepared and ready to be tested by DLS.

### 3.Results and Discussion

#### 3.1 Reliability of viscosity data for SPS-Li ionomer

In order to study the relationship between reduced viscosity and concentration of SPS-Li, the viscosity of the 50K of SPS-Li dissolved in toluene at a sequence of concentration was measured. SPS-Li of 30mg and 100mg were successfully dissolved in 10ml toluene. These samples and dilutions were measured and reduced viscosity was obtained from 0.05 g/dl to 0.9 g/dl concentration range. For SPS-Li of both 30mg and 100mg, the reduced viscosity increased proportionally when the concentration of ionomer increased. In addition, plots for SPS-Li of 30mg and 100mg almost overlapped at the concentration range from 0.15g/dL to 0.33g/dL and the same trend was observed. This proves that the viscosity data for ionomer at different concentrations is reproducible and thus reliable.

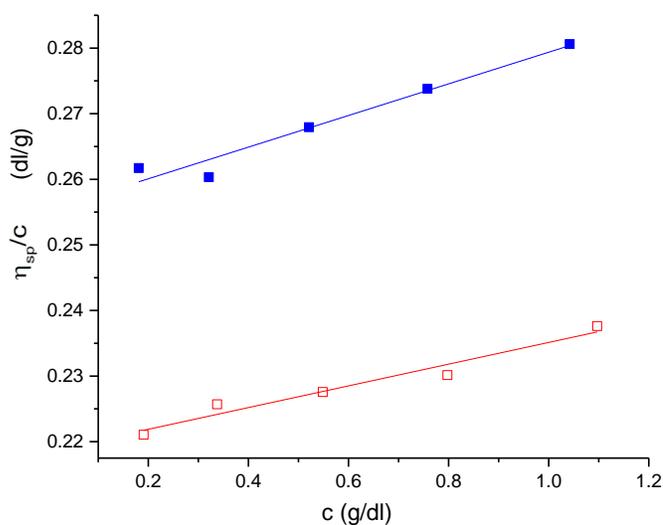


**Figure 3.1** Reduced viscosity vs. concentration for the 50000 SPS-Li in toluene

-■- 100mg SPS-Li sample      -□- 30mg SPS-Li sample

### 3.2 Viscosity of PS and SPS-Li without ionic liquid

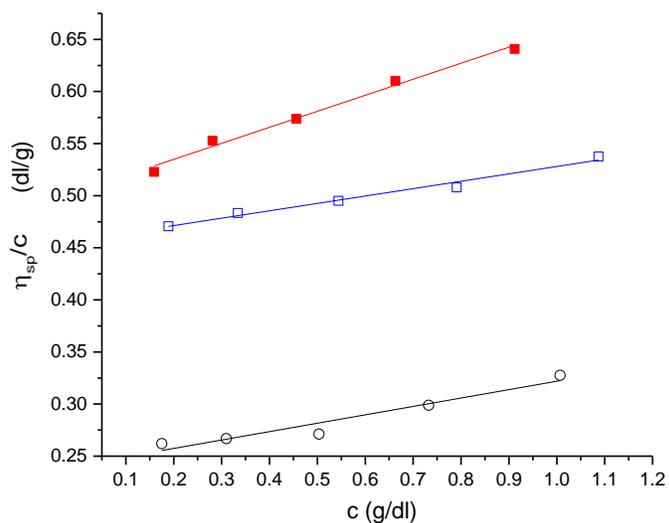
Five types of samples: the 50000 PS, the 38000 PS, the 50000 SPS-Li, the 38000 SPS-Li and the 18000 SPS-Li, were selected to study the effect of molecular weight on the reduced viscosity. The 100mg of polymer was dissolved in 10ml of toluene and the sample was diluted with 3ml, 5ml, 10ml and 20ml of toluene and viscosity was measured in a row.



**Figure 3.2** Reduced viscosity vs. concentration for the 50000 PS and the 38000

PS

-■- 50000 MW PS      -□- 38000 MW PS

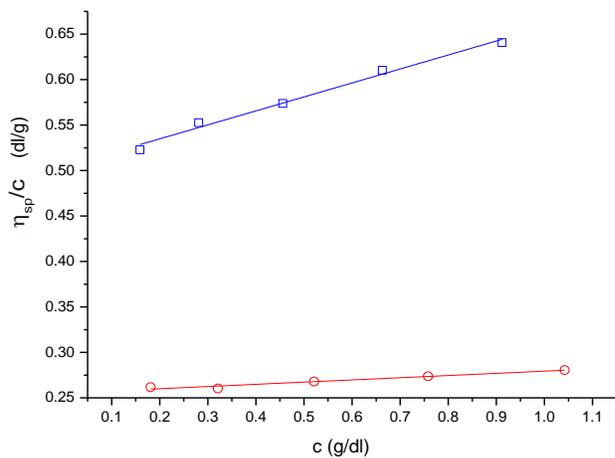


**Figure 3.3** Reduced viscosity vs. concentration for the 50000, 38000 and 18000

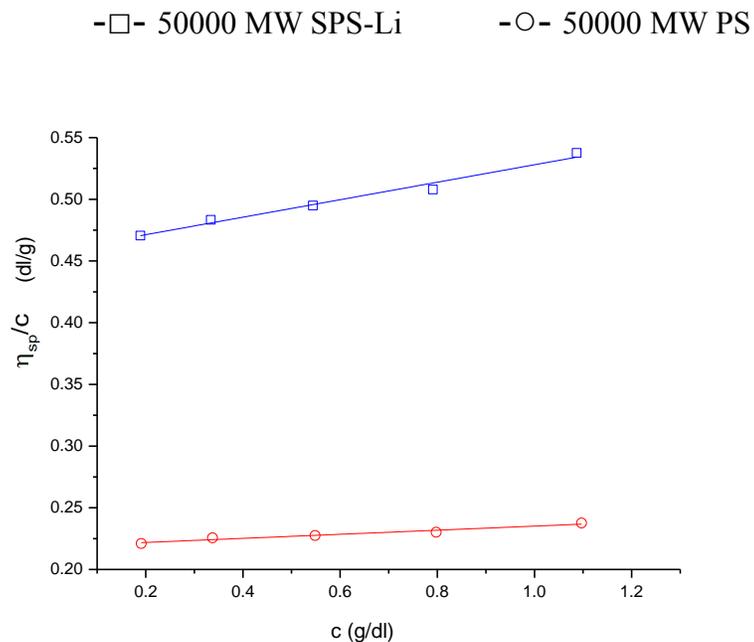
SPS-Li

-■- 50000 MW SPS-Li      -□- 38000 MW SPS-Li

-○- 18000 MW SPS-Li



**Figure 3.4** Reduced viscosity vs. concentration for 50000 the PS and SPS-Li



**Figure 3.5** Reduced viscosity vs. concentration for the 38000 molecular weight PS and SPS-Li

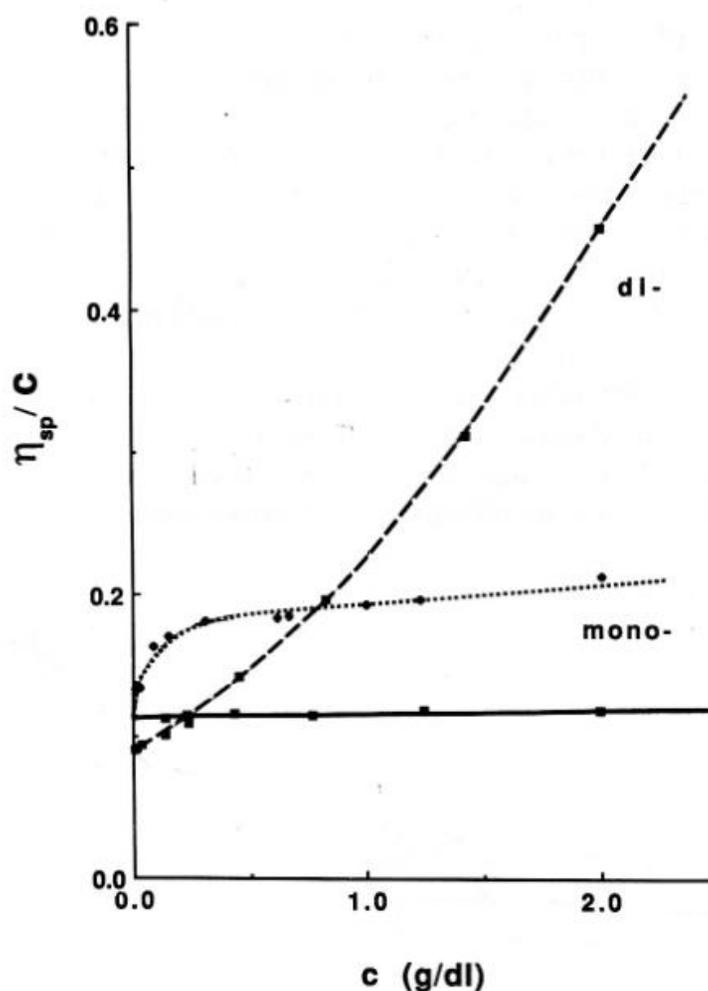
-□- 38000 MW SPS-Li      -○- 38000 MW PS

Figure 3.2 and 3.3 show the reduced viscosity vs. concentration for these samples. All of the samples show the same trend in that the reduced viscosity is decreased when diluted. The 38000 PS has the lowest reduced viscosity of almost 0.22-0.24. The highest viscosity of 0.5-0.7 is observed for the 50000 SPS-Li. For both PS and SPS-Li, a larger molecular weight sample shows higher reduced viscosity compared to a lower molecular weight sample. The result can be explained by using Mark-Houwink-Sakurada equation,

$$[\eta] = KM^a \quad (2)$$

where  $[\eta]$  is the intrinsic viscosity in units of mL/g,  $M$  is the polymer molecular weight,  $K$

and  $a$  are the Mark–Houwink constants which depend on the particular-polymer solvent system. Samples used in this study (neutral polymer: PS and ionomer: SPS-Li) have different  $K$  and  $a$  values due to the difference in their structures. Equation (2) indicates that for the same type of polymer the reduced viscosity becomes higher when the molecular weight is larger. Furthermore, Figure 3.4 and 3.5 indicate that the reduced viscosity of SPS-Li is much higher than that of PS at the same concentration for both the 50000 and 38000 samples. This significant increase in viscosity for SPS-Li is due to the aggregation of telechelic ionomers compared to the neutral polymer, which shows no aggregation.



---

**Figure 3.6** Viscosity curves for mono- and difunctional PS telechelic ionomers as well as neutral polymer (PS) in toluene [37]

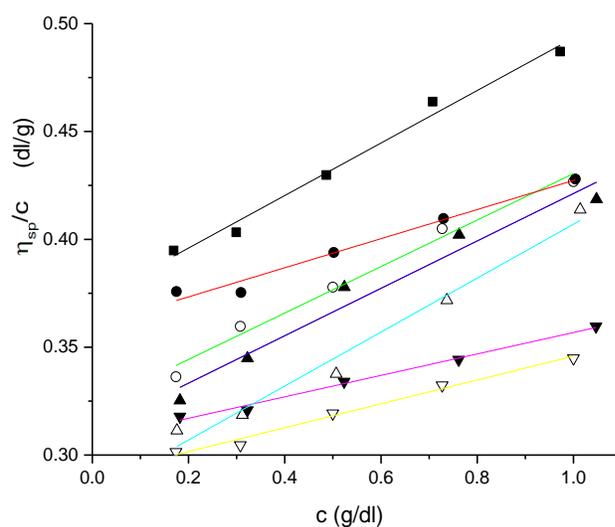
Telechelic ionomers are divided into monofunctional, difunctional and trifunctional ionomers according to their structures (see Figure 1.1). Figure 3.6 shows the viscosity behavior of mono- and difunctional (PS-based) telechelic ionomers in toluene. For difunctional telechelic ionomers, both inter- and intramolecular interactions are possible (see Figure 3.7) as seen for random ionomers. The lower viscosity of difunctional ionomers compared with parent polymer is closely related to intramolecular association. In contrast, monofunctional ionomers in toluene show that the reduced viscosity values are always higher than those of the ionomer precursor at all concentrations. This is due to the fact that intramolecular interactions are not available for this type of ionomer. Also, at high concentrations, the reduced viscosity increased slightly and the curve is concave-down, suggesting the much smaller degree of aggregation compared with difunctional ionomers[36]. The viscosity behavior of monofunctional telechelic ionomers in Figure 3.4 and 3.5 is consistent with that of monofunctional telechelic ionomer in Figure 3.6.



**Figure 3.7** Schematic structure for intramolecular and intermolecular bonds formed in ditelechelic ionomer

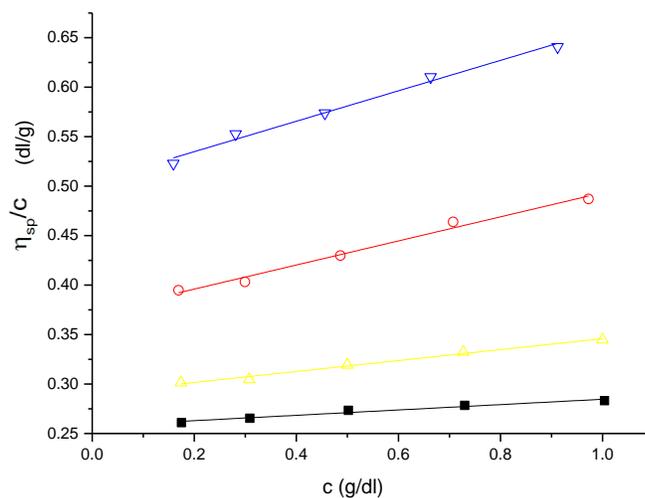
### 3.3 Viscosity of SPS-Li containing ionic liquid

After the viscosity behavior of SPS-Li and PS has been established, viscosity measurement was performed on SPS-Li containing an ionic liquid. Two sets of experiments were carried out for SPS-Li with 38000 molecular weight and SPS-Li with 50000 molecular weight. To investigate the effect of the ionic liquid on the solution behavior of telechelic ionomers, the ionomer concentration of each sample was fixed at 0.1g/dl and toluene was chosen to be a solvent. Different amounts of ionic liquid were added into the sample to disrupt the aggregation of ionic groups that was formed between the ionomer chains. The ionic liquid used in the experiment was EMIM-TF which as an additive successfully dissolved several ionomers, such as PMMA-Na, SPS-Na and SPS-Ca in THF[35].



**Figure 3.8** Reduced viscosity vs. concentration for the 50000 SPS-Li in solvent mixtures of toluene and EMIM-TF. [IL]/[Ion] ratios are indicated below:

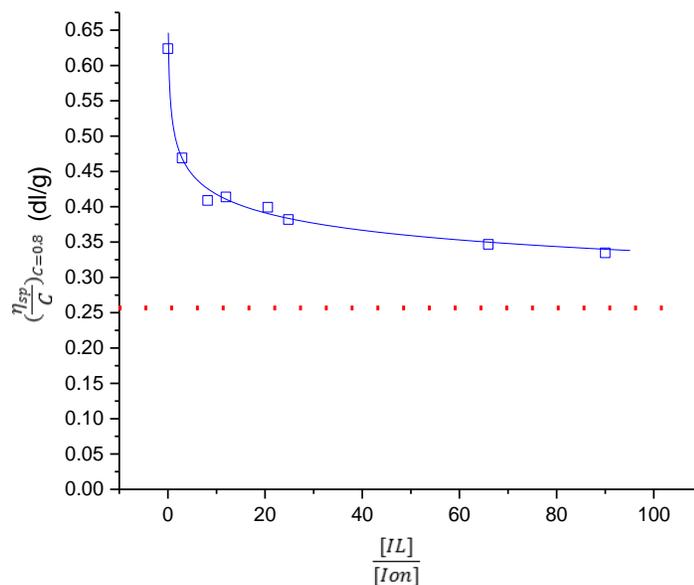
$-\nabla-$  : 90     $-\blacktriangledown-$  : 65.77     $-\triangle-$  : 24.81     $-\blacktriangle-$  : 20.57     $-\circ-$  : 11.94  
 $-\bullet-$  : 8.17     $-\blacksquare-$  : 2.92



**Figure 3.9** Reduced viscosity vs. concentration for the 50000 and 3800 SPS-Li and PS in a toluene

-○- SPS-Li with minimum [IL]/[Ion]    -△- SPS-Li with maximum [IL]/[Ion]  
 -■- PS    -▽- SPS-Li

First, the viscosity of the 50000 SPS-Li was measured by adding 0.0059g, 0.0085g, 0.0106g, 0.0131g, 0.0187g, 0.0359g and 0.0468g of ionic liquid. The amount of ionic liquid added into the sample was depicted as the ratio of the mole of ionic liquid to the mole of ionomer's ionic groups: the ratio for each ionic liquid becomes 2.92, 8.17, 11.94, 20.57, 24.81, 65.77 and 90. Figure 3.8 shows a plot of reduced viscosity versus concentration for seven ratios. In Figure 3.9, curves for the 50000 PS and SPS-Li without ionic liquid curves were also plotted for comparison. It can be seen that the reduced viscosity of ionomer decreased with increasing the [IL]/[Ion] ratio.

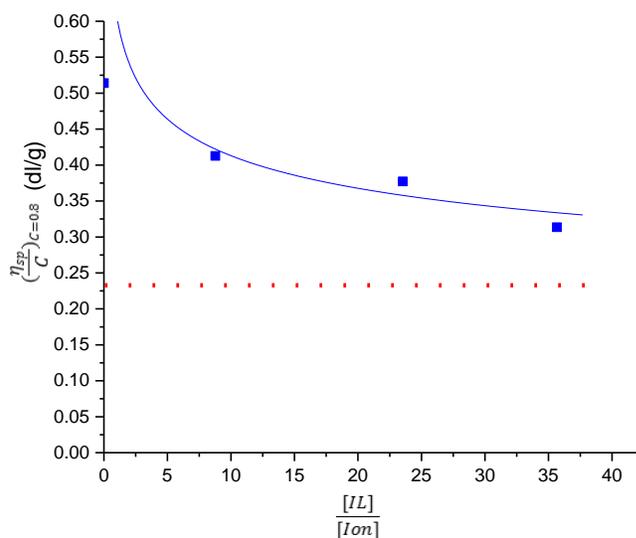


**Figure 3.10** Reduced viscosity vs. [IL]/[Ion] ratios at  $c = 0.8\text{g/dl}$  for the 50000 SPS-Li

..... 50000 MW PS      - □ - 50000 MW SPS-Li

To demonstrate the effect of the ionic liquid on the viscosity of SPS-Li more explicitly, the reduced viscosity at a fixed ionomer concentration ( $c = 0.8\text{g/dl}$ ) was plotted against the [IL]/[Ion] ratios shown in Figure 3.10. [IL]/[Ion] ratios for these samples are from 2.92 to 65.77 and the [IL]/[Ion] ratio of SPS-Li without the ionic liquid was set to be 0. As the [IL]/[Ion] ratios increased to 8.17, the reduced viscosity was decreased to 0.409. When the value of [IL]/[Ion] ratio was increased further, it was observed that the viscosity plateaued. The reduced viscosity changed slightly (from 0.409 to 0.335) when the value of [IL]/[Ion] ratios was increased further from 8.17 to 65.77. In addition, it is

also observed that even when the  $[IL]/[Ion]$  ratio reaches to 65.77, there still is a noticeable gap between the viscosity of the ionomer and that of the neutral polymer.



**Figure 3.11** Reduced viscosity vs.  $[IL]/[Ion]$  ratios at  $c = 0.8\text{g/dl}$  for the 38000 SPS-Li

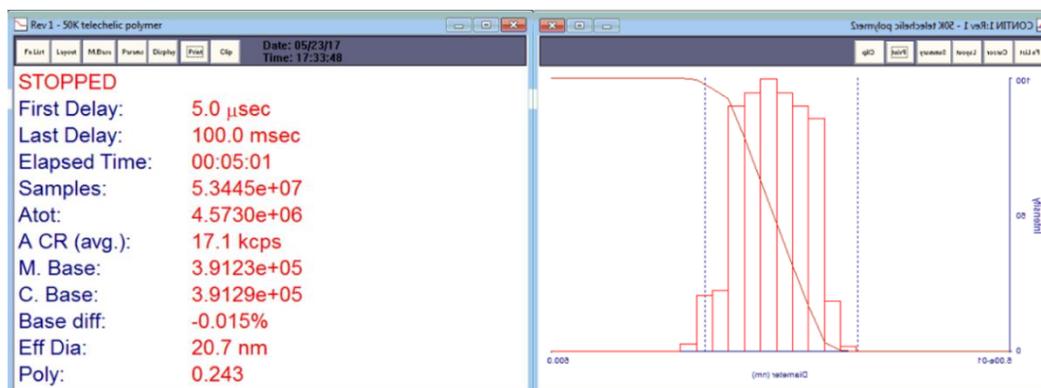
- ■ - 38000 MW SPS-Li      ..... 38000 MW PS

For the 38000 SPS-Li, the samples were tested at 3 different  $[IL]/[Ion]$  ratios, 8.77, 23.53 and 35.66. Figure 3.11 shows the plot of reduced viscosity versus the ionic liquid ratio for these three cases as done previously. The system shows the same trend in that the reduced viscosity was decreased when  $[IL]/[Ion]$  ratios increased. The reduced viscosity decreased dramatically with increasing  $[IL]/[Ion]$  ratio at the beginning and plateaued thereafter. Also, there was a gap.

The results indicate that ionic liquid was able to disrupt ionic aggregates and ionic bonds in toluene. The structure of SPS-Li changed, thus the viscosity also changed. However, the reduced viscosity decreased disproportionately when the [IL]/[Ion] ratios increased, which suggests that this ionic liquid has a limited effect in disrupting the ionic bonds of the ionomer solution and changing the properties of ionomer. The gap in the plateau region indicates that not all of the ionic aggregates existing in the ionomer are broken by the ionic liquid.

### **3.4 Dynamic Light Scattering for SPS-Li containing ionic liquid**

To study the size and the size distribution of the telechelic ionomer, dynamic light scattering experiments were performed on the system in which both ionomer and ionic liquid were present. In addition, neutral polymer and ionomer without the addition of ionic liquid were also tested as control samples. All the samples used for the experiment have the same molecular weight, therefore, it can eliminate the change in polymer size caused by the change in molecular weight. First, the 50000 of PS and the 50000 of SPS-Li were dissolved in toluene and the concentration of both samples used was set to be 0.2g/dl for dynamic light scattering experiments. Figure 3.12 shows the diameter and size distribution of the sample. The effective diameter of the 50000 PS is 8.1nm and the effective diameter of the 50000 SPS-Li is 20.7nm.



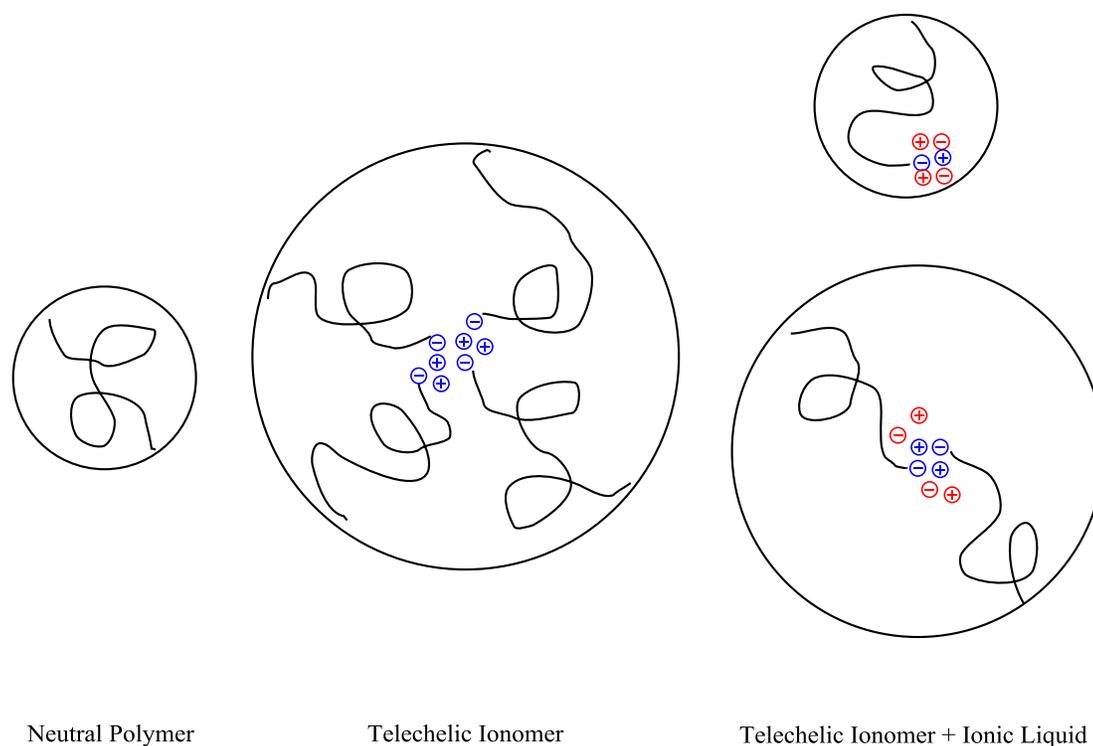
**Figure 3.12** Dynamic light scattering results for the 50000 SPS-Li in toluene

Unlike random ionomers, monofunctional telechelic ionomer SPS-Li has only one ionic group per chain, so that intramolecular electrostatic interactions are no longer available at all concentration[35]. Therefore, the effective diameter of the ionomer is expected to be higher at all concentrations compared to the neutral polymer. Similarly, reduced viscosity of SPS-Li is larger than that of neutral polymer because the reduced viscosity is proportional to the size of molecules. For SPS-Li in toluene, ionic bonds formed between the chain end of each polymer chain are disrupted by EMIM-TF. Thus the value of effective diameter as well as the reduced viscosity were decreased and approached to that of the neutral polymer.

**Table 3.1:** Dynamic Light Scattering results for PS, SPS-Li, SPS-Li with EMIM-TF in toluene

Sample	Effective Diameter	Poly	$A_{tot}$
PS	8.1 nm	0.245	$2.151 \times 10^6$
SPS-Li	20.7 nm	0.247	$4.828 \times 10^6$

SPS- Li+IL([IL]/[Ion]=16.69)	15.7 nm	0.215	$1.971 \times 10^6$
---------------------------------	---------	-------	---------------------



**Figure 3.13:** The schematic molecular structure of neutral polymer, telechelic polymer and telechelic ionomer plus ionic liquid. Blue color represents ions from ionomer and red color represents ions from ionic liquid

Like viscosity experiments, the same amount of SPS-Li was dissolved in a mixture of toluene and EMIM-TF. Table 3.1 shows that the effective diameter of SPS-Li in the presence of EMIM-TF is 15.7 nm which is between those of PS and SPS-Li without EMIM-TF. The effective diameter decreased upon addition of EMIM-TF. It

---

indicates that the aggregates formed between ionomer chains dissociate upon the addition of the ionic liquid and that the structure of ionomers returns to that of the neutral polymer and the aggregate size is reduced accordingly. The schematic structures are shown in Figure 3.13. Although we don't know the aggregation number for our system, Chassenieux et al[36] determined the aggregation number to be 4 for monofunctional SPS-Li (MW:120000) by using static light scattering. We used that number for drawing Figure 3.13

#### **4.Conclusion and Future Work**

Viscosity behaviors of neutral polymers and (monofunctional) telechelic ionomers were investigated and compared. The effect of the ionic liquid on telechelic ionomers in nonpolar solvent was examined in this study using viscosity experiments. In addition, the average size of telechelic ionomers and neutral polymers were determined using dynamic light scattering.

The viscosity of the 50000 SPS-Li was measured at different polymer concentrations. The data was reproducible and the reduced viscosity of SPS-Li was proportional to the concentration of SPS-Li in the concentration range studied (0.1-1.0g/dl). Then, the viscosity of PS and SPS-Li dissolved in toluene was measured. The reduced viscosity increased when the molecular weight was increased for both PS and SPS-Li. For PS and SPS-Li that have the same molecular weight, the viscosity is much

higher for SPS-Li than for PS at the same concentration. This is because molecular aggregates are formed due to ionic aggregate formation between ion pairs of telechelic ionomers.

Subsequently, the 50000 and 38000 SPS-Li were dissolved in a mixture of toluene and an ionic liquid EMIM-TF, to study the effect of the ionic liquid on the viscosity behavior of SPS-Li in toluene. The result showed that the reduced viscosity was decreased when the  $[IL]/[Ion]$  ratio increased. The reduced viscosity decreased dramatically with increasing  $[IL]/[Ion]$  ratios in the beginning and plateaued thereafter. The result shows that the ionic liquid destroys the ionic aggregates in ionomers and decreases the viscosity. There still was a small gap between PS and SPS-Li/ ionic liquid mixture, because this ionic liquid cannot completely destroy ionic aggregates.

The sizes of SPS-Li and PS in the presence of EMIM-TF were also examined by dynamic light scattering and compared with that of PS. DLS showed that PS had the lowest effective diameter whereas SPS-Li had the highest effective diameter and the effective diameter decreased upon addition of EMIM-TF. These results are consistent with those obtained by viscosity measurements.

In future studies, the interaction between different types of ionic liquids and ionomers and their effect on the size and structure of ionomer can be investigated. Polymers based on PMMA may also be used for viscosity and dynamic light scattering experiments. Furthermore, the mechanism of the conformational change due to the ionic interaction can be explored through further study. In addition to viscosity behavior and

---

dynamic scattering behavior of the telechelic ionomer solutions, rheological behavior and conductance behavior would be interesting areas to explore.

## References

- [1] A. Eisenberg, *Macromolecules*, 3, 147 (1970).
- [2] W. J. MacKnight, T. P. Taggart, and R. S. Stein, *J. Polym. Sci., Polym. Symp.*, 45, 113 (1974).
- [3] M. Fujimura, T. Hashimoto, and H. Kawai, *Macromolecules*, 15, 136 (1982).
- [4] W. C. Forsman, *Macromolecules*, 15, 1032 (1982).
- [5] D. J. Yarusso and S. L. Cooper, *Macromolecules*, 16, 1871 (1983).
- [6] D. J. Yarusso and S. L. Cooper, *Polymer*, 26, 371 (1985).
- [7] D. Lee, R. A. Register, C. Yang, and S. L. Cooper, *Macromolecules*, 21, 998 (1988).
- [8] K. A. Mauritz, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, C28, 65 (1988).
- [9] A. Eisenberg, B. Hird, and R. B. Moore, *Macromolecules*, 23, 4098 (1990).
- [10] M. A. Hickner, *J. Polym. Sci., Part B: Polym. Phys.* 50, 9 (2012).
- [11] A. Donnadio, M. Pica, A. Carbone, I. Gatto, T. Posati, G. Mariangeloni, and M. Casciola, *J. Mater. Chem. A* 3, 23530 (2015).
- [12] A. Strong, B. Britton, D. Edwards, T. J. Peckham, H. F. Lee, W. Y. Huang, and S. Holdcroft, *J. Electrochem. Soc.* 162, F513 (2015).
- [13] G. Hatipoglu, Y. Liu, R. Zhao, M. Yoonessi, D. M. Tigelaar, S. Tadigadapa, and Q. M. Zhang, *Smart Mater. Struct.* 21, 055015 (2012).
- [14] A. Giuliani, M. Placidi, F. Di Francesco, and A. Pucci, *React. Funct. Polym.* 76, 57 (2014).
- [15] J. Li, J. K. Park, R. B. Moore, and L. A. Madsen, *Nat. Mater.* 10, 507 (2011).

- 
- [16] K. T. Oh, T. K. Bronich, L. Bromberg, T. A. Hatton, and A. V. Kabanov, *J. Controlled Release* 115, 9 (2006).
- [17] S. H. Wu, L. C. Zheng, C. C. Li, S. D. Huo, Y. N. Xiao, G. H. Guan, and W. X. Zhu, *Polym. Chem.* 6, 1495 (2015).
- [18] Hara, M. (1993). *Polyelectrolytes : science and technology*. New York: Marcel Dekker.
- [19] *Electrochemical aspects of ionic liquids*. John Wiley & Sons, 2011.
- [20] Dupont J, de Souza R F, Suarez P A Z. Ionic liquid (molten salt) phase organometallic catalysis. *Chemical reviews*, 2002, 102(10): 3667-3692.
- [21] Wasserscheid P, Keim W. Ionic liquids—new “solutions” for transition metal catalysis. *Angewandte Chemie International Edition*, 2000, 39(21): 3772-3789.
- [22] Rogers R D, Seddon K R. Ionic liquids--solvents of the future? *Science*, 2003, 302(5646): 792-793.
- [23] E. J. Maginn, “Molecular simulation of ionic liquids: Current status and future opportunities,” *J. Phys.: Condens. Matter* 21, 373101 (2009).
- [24] J. F. Wishart, “Energy applications of ionic liquids,” *Energy Environ. Sci.* 2, 956–961 (2009).
- [25] J. Dupont, “From molten salts to ionic liquids: A “nano” journey,” *Acc. Chem. Res.* 44, 1223–1231 (2011).
- [26] H. Niedermeyer, J. P. Hallett, I. J. Villar-Garcia, P. A. Hunt, and T. Welton, “Mixtures of ionic liquids,” *Chem. Soc. Rev.* 41, 7780 (2012).
- [27] H. Liu, E. Maginn, A. E. Visser, N. J. Bridges, and E. B. Fox, “Thermal and transport properties of six ionic liquids: An experimental and molecular dynamics study,” *Ind. Eng. Chem. Res.* 51, 7242–7254 (2012).
- [28] Y. Wang, W. Jiang, T. Yan, and G. A. Voth, “Understanding ionic liquids through atomistic and coarse-grained molecular dynamics simulations,” *Acc. Chem. Res.* 40, 1193–1199 (2007).
- [29] B. Gurkan, B. F. Goodrich, E. M. Mindrup, L. E. Ficke, M. Massel, S. Seo, T. P. Senftle, H. Wu, M. F. Glaser, J. K. Shah et al., “Molecular design of high capacity, low viscosity, chemically tunable ionic liquids for CO<sub>2</sub> capture,” *J. Phys. Chem. Lett.* 1, 3494–3499 (2010).
- [30] Z. Ma, J. H. Yu, and S. Dai, “Preparation of inorganic materials using ionic liquids,” *Adv. Mater.* 22, 261–285
- [31] C. Schröder, “Comparing reduced partial charge models with polarizable simulations of ionic liquids,” *Phys. Chem. Chem. Phys.* 14, 3089 (2012).
- [32] J. P. Hallett and T. Welton, “Room-temperature ionic liquids: Solvents for synthesis and catalysis. 2,” *Chem. Rev.* 111, 3508–3576 (2011).
- [33] R. H. Brown, A. J. Duncan, J.-H. Choi, J. K. Park, T. Wu, D. J. Leo, K. I. Winey, R.

---

B. Moore and T. E. Long, *Macromolecules* 43:790-796 (2009).

[34] M. D. Bennett, D. J. Leo, G. L. Wilkes, F. L. Beyer and T. W. Pechar, *Polymer* 47:6782-679 (2006)

[35] *Solution properties of ionomers in low-polarity solvents containing ionic liquids*  
Taylor, Elliot. Rutgers The State University of New Jersey - New Brunswick, ProQuest  
Dissertations Publishing, 2016. 10292042.

[36] Hara, M. (1993). *Polyelectrolytes : science and technology*. New York: Marcel  
Dekker.

[37] M. Hara, J. Wu, Y Wang, Jerome, and M. Granville, *Solution properties of  
polystyrene-based halato-telechelic ionomers*, *Polym. Prepr. (Am. Chem. Soc. Div.  
Polym. Chem.)* 30(2):219 (1989)