SYNTHESIS AND CHARACTERIZATION OF ION CONTAINING POLYMERS

A Thesis in
Materials Science and Engineering

by

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ABSTRACT

Two types of ion-containing polymers are included in this dissertation. The first was focused on the rheology, solvation, and correlation length of polyelectrolyte solutions in terms of charge density, solvent dielectric constant, and solvent quality. The second was focused on the PEO-based polyester ionomers as single ion conductors.

A series of polyelectrolytes with varied charge density ($0.03 < \alpha < 0.6$) and counterions (Cl$^-$ and I$^-$) were investigated in good solvent (EG, NMF, and GC) and poor solvent (DW and F). The concentration dependence of the specific viscosity and relaxation time of polyelectrolytes in solution agrees with Dobrynin’s theoretical predictions at $c < c^{**}$. Effective charge density greatly impacts the viscosity of polyelectrolyte semidilute solutions, while residual salt significantly reduces the viscosity of polyelectrolyte solutions at concentrations $c < 2c_s / f$. For polyelectrolyte solutions with less condensed counterions, the correlation length obtained from SAXS and rheology perfectly matches and agrees with de Gennes prediction. Dobrynin scaling model successfully predicts the rheology of polyelectrolyte solutions in all cases: without salt, with low residual salt, and with high residual salt concentration.

PEO-based polyester ionomers were synthesized by melt polycondensation. $M_n$ was determined using the $^1$H NMR of ionomers. No ion-cluster was observed from the DSC, SAXS, and rheology measurements. Ionic conductivity greatly depends on the $T_g$, $T-T_g$ and ion content of the ionomers. PEG600-PTMO650 (z)-Li copolyester ionomers show microphase separation and much lower ionic conductivity, compared to that of PE600-Li. PTMO650-Li shows nonconductor behavior.
TABLE OF CONTENTS

LIST OF FIGURES .....................................................................................................vii
LIST OF TABLES.......................................................................................................xii
ACKNOWLEDGEMENTS.........................................................................................xiii

Chapter 1 Introduction to Ion-containing Polymers .................................................... 1
  1.1 Definition and applications ..............................................................................1
  1.2 Preparation of ion-containing polymers ...........................................................4
  1.3 Electrostatic interactions in ion-containing polymers ......................................5
  1.4 Properties of polyelectrolytes in solution ........................................................ 7
  1.5 Properties of ionomers......................................................................................9
  1.6 References.......................................................................................................11

Chapter 2 Charge Density Effects in Salt-Free Polyelectrolyte Solution Rheology ...12
  2.1 Introduction.....................................................................................................12
  2.2 Background theory..........................................................................................13
  2.3 Experimental...................................................................................................19
    2.3.1 Materials ...............................................................................................19
    2.3.2 Quaternization ......................................................................................19
    2.3.3 Degree of quaternization $\alpha$ ..............................................................21
    2.3.4 Effective charge $\gamma$ ........................................................................22
    2.3.5 Rheology...............................................................................................25
  2.4 Results and discussion ....................................................................................27
    2.4.1 Specific viscosity..................................................................................27
    2.4.2 Electrostatic blob size and the parameter $B$.............................................35
    2.4.3 Relaxation time $\tau$ and terminal modulus $G$ ........................................37
  2.5 Conclusions.....................................................................................................40
  2.6 References.......................................................................................................42

Chapter 3 Solvation of Polyelectrolyte Solutions Investigated by Dielectric
  Spectroscopy, SAXS, and Rheology ....................................................................45
  3.1 Introduction.....................................................................................................45
  3.2 Experimental...................................................................................................51
    3.2.1 Polymers ...............................................................................................51
    3.2.2 Autoprotolysis, stability, and residual salt .............................................52
    3.2.3 Solvents ...............................................................................................53
    3.2.4 Conductivity measurement...................................................................57
Chapter 6  Synthesis and Characterization of PEO-PTMO-Based Single Ion Conductors

6.1 Introduction .......................................................................................................................... 147
6.2 Experimental ...................................................................................................................... 150
  6.2.1 Materials .................................................................................................................... 150
  6.2.2 Synthesis ................................................................................................................. 150
  6.2.3 Polyester ionomer identification ................................................................................ 152
  6.2.4 Ion exchange ........................................................................................................... 152
  6.2.5 1H NMR ................................................................................................................ 152
  6.2.6 Thermal characterization ......................................................................................... 153
  6.2.7 SAXS ...................................................................................................................... 153
  6.2.8 Conductivity measurement ...................................................................................... 154
6.3 Results and discussion ..................................................................................................... 154
  6.3.1 Synthesis and chain characterization ........................................................................ 154
  6.3.2 X-ray scattering ....................................................................................................... 159
  6.3.3 DSC thermal analysis .............................................................................................. 160
  6.3.4 Ionic conductivity .................................................................................................... 163
6.4 Conclusions ....................................................................................................................... 169
6.5 References ........................................................................................................................ 171

Appendix 1  Synthesis of quaternized P2VP and P2VP(h) polyelectrolytes ................. 173
Appendix 2  Synthesis of PEO-based polyester ionomers as single ion conductors .... 179
Appendix 3  SAXS and normalization of polyelectrolyte solutions and ionomers ...... 183
Appendix 4  Rheology measurements of polyelectrolyte solutions and ionomers ...... 188
Appendix 5  Dielectric measurements of polyelectrolyte solutions and ionomers ...... 192
### List of Figures

<table>
<thead>
<tr>
<th>Fig.</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Samples of polymers containing acid functional groups</td>
<td>5</td>
</tr>
<tr>
<td>2.1</td>
<td>Concentration dependence of equivalent conductance for quaternized P2VP polyelectrolyte solutions in EG at 25 °C. Symbols are experimental data and lines are fits to determine the effective charge (see text)</td>
<td>24</td>
</tr>
<tr>
<td>2.2</td>
<td>The shear rate dependence of apparent viscosity (open squares) and the Carreau model fits (lines) for 17PMVP-Cl solutions with no added salt at 25 °C. Solution concentrations from top to bottom are 0.2198, 0.099, 0.0659, 0.0439, 0.0220, 0.0088, 0.0042, 0.0022 moles/liter.</td>
<td>25</td>
</tr>
<tr>
<td>2.3</td>
<td>Concentration dependence of (a) specific viscosity ($\eta_{sp} = (\eta - \eta_s) / \eta_s$) and (b) reduced viscosity ($\eta_{sp} / c$) for neutral polymer (P2VP), weakly charged polyelectrolytes (3PMVP-Cl and 4PMVP-Cl), and strongly charged polyelectrolytes (10PMVP-Cl and 17PMVP-Cl, 42PMVP-Cl and 55PMVP-Cl) in EG at 25 °C.</td>
<td>29</td>
</tr>
<tr>
<td>2.4</td>
<td>Scaling plots of (a) specific viscosity and (b) reduced viscosity data of Fig. 2.3, constructed by normalizing concentration with the overlap concentration $c^*$.</td>
<td>31</td>
</tr>
<tr>
<td>2.5</td>
<td>Determination of the chain overlap concentration $c^*$, the entanglement concentration $c_e$ and the electrostatic blob overlap concentration $c^{**}$ from the concentration dependence of specific viscosity and relaxation time of polyelectrolyte 17PMVP-Cl in EG. Symbols represent the experimental data and solid lines represent the predicted power laws from scaling theory, with the exception of the relaxation time for the highest concentrations.</td>
<td>32</td>
</tr>
<tr>
<td>2.6</td>
<td>Effective charge dependence of the chain overlap concentration $c^<em>$ (circles), entanglement concentration $c_e$ (stars) and overlap concentration of electrostatic blobs $c^{**}$ (triangles). The chain overlap concentration exhibits the scaling predicted by Eq. 2.5 up to the onset of counterion condensation, while the apparent trends for entanglement concentration and overlap concentration of electrostatic blobs are shown as power laws but are not understood. Note that the neutral parent polymer (P2VP) has significantly larger $c^</em> = 0.057$ M and $c_e = 0.95$ M because there is no charge repulsion to stretch the chain.</td>
<td>34</td>
</tr>
<tr>
<td>2.7</td>
<td>Concentration dependence of relaxation time determined from fitting the Carreau model (Eq. 2.17) to the shear rate dependence of apparent viscosity (filled symbols) and oscillatory shear measurements (open symbols).</td>
<td>37</td>
</tr>
</tbody>
</table>
Fig. 2.8 Concentration dependence of terminal modulus \( G = \eta/\tau \) calculated from steady shear relaxation time (filled symbols) and oscillatory shear relaxation time (open symbols) compared with the Dobrynin scaling predictions (solid lines) of \( G = c kT/N \) for \( c < c_c \) and \( G \sim c^{3/2} \) for \( c > c_c \).

Fig. 3.1 Quaternization and counterion exchange for poly (2-vinyl pyridine).

Fig. 3.2 Concentration dependence of (a) conductivity and (b) equivalent conductance for quaternized 60PMVP-I in EG, DW, GC, F and NMF, 4PMVP-I in EG, and 60PMVP-Cl in EG at 25 °C. Symbols are experimental data and the solid line shows equivalent conductance of 60PMVP-I in F.

Fig. 3.3 Concentration dependence of the product of equivalent conductance and solvent viscosity (cp) for quaternized 60PMVP-I in EG, DW, GC, F and NMF and 60PMVP-Cl in EG at 25 °C.

Fig. 3.5 Concentration dependence of the fitted effective charge density \( f \) determined from the equivalent conductance \( \Lambda \) and the correlation length \( \xi \) (obtained from rheology) at 25 °C by fitting to Eq. (3.10); \( \xi_c \) was determined from Eq. 3.11 for good solvents EG, NMF and GC, and from Eq. 3.12 for poor solvents DW and F.

Fig. 3.6 Conformation of polyelectrolyte solutions in the semidilute region.

Fig. 3.7 The SAXS profiles for 60PMVP-I in EG, DW, GC, F, and NMF at concentration 20mg/ml; \( I(q) \) was determined by subtracting the background scattering intensity and then normalized by the sample thickness, scattering time, and sample transmission (see Appendix 3).

Fig. 3.8 SAXS profiles and the concentration dependence of SAXS curves for 60PMVP-I in F at concentrations 5, 10, 20, 40, and 80 mg/ml; \( I(q) \) was determined by subtracting the background scattering intensity and then normalized by the sample thickness, scattering time, and sample transmission.

Fig. 3.9 Concentration dependence of (a) specific viscosity \( \eta_s = (\eta - \eta_s)/\eta_s \) (b) reduced viscosity \( \eta_s/c \), for neutral polymer P2VP(h) in EG and for the strongly charged polyelectrolyte 60PMVP-I in EG, DW, GC, F, and NMF at 25 °C.

Fig. 3.10 Concentration dependence of relaxation time for neutral polymer P2VP(h) in EG, strongly charged polyelectrolyte 60PMVP-I in GC, F, and NMF at 25 °C. The relaxation time was determined from the shear rate at which shear thinning starts.

Fig. 3.11 Concentration dependence of the specific viscosity of 60PMVP-I in NMF. The reduced viscosity is significantly impacted by residual salt concentration. For \( c > 2c_c/f \), polyelectrolyte scaling laws are observed, while \( c < 2c_c/f \) exhibits power laws consistent with the high salt limit.
Fig. 4.1 Quaternization and counterion exchange for poly (2-vinyl pyridine).

Fig. 4.2 (a) Concentration dependence of specific viscosity $\eta_{sp} = (\eta - \eta_s)/\eta_s$ for weakly charged polyelectrolytes (3PMVP-Cl and 4PMVP-Cl), and strongly charged polyelectrolytes (10PMVP-Cl and 17PMVP-Cl, 42PMVP-Cl and 55PMVP-Cl) (b) Concentration dependence of correlation length for all charged polymers in EG at 25 °C from specific viscosity in semidilute unentangled solution, based on Eq. 4.3.

Fig. 4.3 Concentration dependence of specific viscosity $\eta_{sp} = (\eta - \eta_s)/\eta_s$ in the dilute and semidilute regions for neutral polymer P2VP(h) in EG, strongly charged polyelectrolyte 60PMVP-Cl in EG, as well as 60PMVP-I in EG, DW and NMF at 25 °C.

Fig. 4.4 Concentration dependence of the correlation length $\xi$ of 60PMVP-I in EG, DW and NMF estimated from the specific viscosity of polyelectrolyte solutions in the semidilute unentangled region ($c_e \approx 0.2$ M) using Eq. 4.3; solid lines are the power law $\xi \sim c^{-1/2}$ fitting of semidilute unentangled polyelectrolyte solutions predicted by Dobrynin, et al.\(^5\) The values of $f$ are in Table 4.2 for different polyelectrolyte solutions.

Fig. 4.5 SAXS profiles and the concentration dependence of SAXS curves for 60PMVP-I in NMF in the semidilute region; $I(q)$ was subtracted from the background scattering intensity and then normalized using the sample thickness, experiment time, and transmission intensity (see Appendix 3).

Fig. 4.6 Correlation length $\xi$ of 60PMVP-I in EG, DW and NMF determined from SAXS based Eq. 4.6; correlation length of 45PMVP-Cl in DW and EG determined from SANS based on the results reported by Ermi and Amis;\(^6\) and solid lines are the power law $\xi \sim c^{-1/2}$ fitting based on the results of rheology (top: 60PMVP-I/EG, middle: 60PMVP-I/ DW, Bottom: 60PMVP-I/NMF, see Fig. 4.4).

Fig. 4.7 Correlation length $\xi$ of 60PMVP-I in EG and DW determined from SAXS based Eq. 4.6; Solid lines are the power law fitting of $\xi \sim c^{-1/2}$ at $c < c_s$ and $\xi \sim c^{-1/3}$ at $c > c_s$ based on the theoretical prediction of polyelectrolytes in poor solvent.\(^{36}\)

Fig. 4.8 Concentration dependence of chain contour length $L$ for weakly charged polyelectrolytes (3PMVP-Cl and 4PMVP-Cl), and strongly charged polyelectrolytes (10PMVP-Cl and 17PMVP-Cl, 42PMVP-Cl and 55PMVP-Cl) in EG at 25 °C, calculated from specific viscosity in the semidilute unentangled solution using Eq. 4.8.

Fig. 4.9 Concentration dependence of chain contour length $L$ (a) obtained from semidilute unentangled specific viscosity via Eq. 4.8 (b) obtained from SAXS via Eq. 4.7 for strongly charged polyelectrolyte 60PMVP-Cl in EG as well as 60PMVP-I in EG, DW and NMF at 25 °C, solid lines are the fitting of $L \sim c^0$ for the rheology data.
Fig. 4.10 Comparison on the concentration dependence of the correlation length $\xi$ of 60PMVP-I in NMF determined from SAXS (Eq. 4.6) and specific viscosity of semidilute unentangled solutions (Eq. 4.3).

Fig. 4.11 Comparison of the correlation length of 60PMVP-I and 60PMVP-Cl in EG determined using SAXS (Eq. 4.6) and specific viscosity of semidilute unentangled solutions (Eq. 4.3).

Fig. 5.1 Schematic representation of the PEG ionomer synthesis.

Fig. 5.2 Representative $^1$H NMR spectra of two PE400-Na ionomers: a) PE400-Na [$M_n = 4200$] and b) PE-400-Na-hmw [$M_n = 6700$].

Fig. 5.3 Combined SAXS and WAXD intensities (arbitrary units and offset for clarity) as a function of scattering vector for PE400-Na, PE600-Na, PE900-Na ionomers and the PE400-0 neutral polymer. Note that both intensity and wavevector are plotted on logarithmic scales.

Fig. 5.4 Master curves of storage modulus (triangles), loss modulus (squares) and complex viscosity (diamonds) at $T_{ref} = 30.0^\circ$C, for PE600-Na-hmw ($M_n = 8900$ g/mol).

Fig. 5.5 Comparison of measured $T_g$ of PE-Na ionomers with reported values for PEO complexes with NaClO$_4$ and NaCF$_3$SO$_3$ (from ref 23), as a function of Na content.

Fig. 5.6 Dielectric loss and conductivity of PE600-Li at 50 $^\circ$C. Filled symbols represent $\sigma'$ and open symbols $\varepsilon''$. The dc conductivity $\sigma_0$ is determined from the plateau in $\sigma'$.

Fig. 5.7 Temperature dependence of conductivity for ionomers made from different PEG spacer lengths. Longer spacer length raises the conductivity by lowering $T_g$.

Fig. 5.8 Conductivity as a function of $T - T_g$. Ionomers with the same cation have similar $\sigma_0$ at constant $T - T_g$.

Fig. 5.9 Correlation of ionomer $T_g$ with their room temperature conductivity. $\sigma_0$ increases significantly with decreasing ionomer $T_g$.

Fig. 5.10 Schematic representation of the PEO-based copolyester ionomer synthesis.

Fig. 6.2 $^1$H NMR spectra of PE600-xLi polyester ionomers.

Fig. 6.3 $^1$H NMR spectra of PEG600-PTMO650 (50/50)-Li (top) and PTMO-Li (bottom) polyester ionomers.

Fig. 6.4 The SAXS profile of PEG600-PTMO650 (z)-Li copolyester ionomers. The inset was plotted as $I(q) \cdot q^2 \sim q$. Note that the intensity is plotted on a logarithmic scale and the wavevector is plotted on linear scale. $I(q)$ is the normalized intensity with background scattering subtracted (see Appendix 3).

Fig. 6.5 DSC thermal analysis of PEO-based polyester ionomers; for clarity, the thermograms of PE600-xLi ionomers have been shifted vertically.

Fig. 6.6 DSC thermal analysis of PEG600-PTMO650 (z)-Li polyester ionomers.
Fig. 6.7 (a) Temperature dependence of conductivity for PE600-xLi ionomers with different ion content. (b) Ion content dependence of the ionic conductivity plotted against $T - T_g$.

Fig. 6.8 (a) Ion content dependence of ionomer $T_g$ and their conductivities at 25 °C. (b) Ion content dependence of ionomer dielectric constant and their conductivities at 25 °C.

Fig. 6.9 Temperature dependence of conductivity for PEG600-PTMO650 (z)-Li ionomers made from diols PEG600 and PTMO650; Increasing the PEG600 content raises the conductivity by better solvating of Li$^+$; (b) the influence of polymer hydrophilicity on the ionic conductivity at temperature $T - T_g$. 
List of Tables

Table 2.1  Experimental quantities for polyelectrolyte solutions in EG at 25 °C  30
Table 3.1  Summary of the solvent properties at 25 °C  53
Table 3.2  Parameters estimated from the measurements of dielectric spectroscopy and rheology for 60PMVP-I and 60PMVP-Cl in solution  66
Table 4.1  Summary of the quaternized polyelectrolytes and their parent polymers.  88
Table 4.2  Summary of the properties of solvents and polymer solutions at 25 °C.  89
Table 4.3  Correlation length of 60PMVP-I solutions from rheology and SAXS  97
Table 4.4  Parameter $B$ of polyelectrolytes in solution from rheology, SAXS and SANS.  110
Table 5.1  Characterization of PEG-based Ionomers  132
Table 6.1  Characterization of PEO-based polyester ionomers  158
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Chapter 1

Introduction to Ion-containing Polymers

1.1 Definition and applications

Ion-containing polymers are defined as a large category of natural and synthetic polymers carrying charged groups on the polymer chain. However natural charged polymers such as proteins (or other biomaterials) and synthetic hydrogels are not included in the work of this dissertation. All the discussion in the work will focus on two families of synthetic charged polymers: polyelectrolytes and ionomers. These special polymers are high performance raw materials that bestow their unique properties on the resulting products. Typically, charged polymers are used when the products must be resistant to some external stimuli (mechanical, thermal, electrostatic or chemical) or have special internal structures (interface interaction, crosslinking, molecular switch, surface adsorption). The market demands of these polymers have exploded in the last two decades due to the fast growth of automobile, aerospace, petroleum, personal care, and sporting goods industries.

Ionomers are defined as polymers in which dipolar interactions between the ion pairs consisting of ionic monomer and counterion dominate the properties of the materials. Ionomers are a family of synthetic ion-containing polymers which contain a small number, typically less than 15 mole %, of the monomers in polymer repeat units.
bearing an ionic functional group covalently bonded to the polymer chain backbone. However, the ionomer definition is principally connected to properties, forming ionic aggregates in the bulk materials, rather than the composition of ionic groups.\textsuperscript{1,4} A small amount of ionic groups introduced to the polymer backbone can enhance properties such as toughness and impact strength of the polymer materials greatly. An increase can be achieved in the modulus, tear resistance, and impact strength of the resulting product. Ionomers can be processed as thermoplastics using conventional injection molding equipment. Their excellent properties and “ease of processing” have led to many new applications in high performance materials including membranes, food packaging, fertilizers, golf ball covers, adhesives, and roofing materials.\textsuperscript{1}

Polyelectrolytes are defined as charged polymers in which the solution properties of the polymer are dominated by the electrostatic repulsion between ionic groups on the polymer backbone.\textsuperscript{1} Polyelectrolytes are a family of synthetic charged polymers which contain a significant number of the monomers bearing an ionic group. Weakly charged polymers can be either polyelectrolytes or ionomers, but strongly charged polymers are very useful as polyelectrolytes (as ionomers they are intractable). Solvent dielectric constant and solvent quality are crucial to the definition of polyelectrolytes with low charge density. It is the term of the physical properties of the charged polymer rather than their composition that dominates the definition of ion-containing polymers.\textsuperscript{1,5-7} Polyelectrolytes in water or other high dielectric solvents dissociate into a highly charged polyion and many counterions in solution. This unique physical property of polyelectrolytes in solution makes them demonstrate solution properties very different
from their counterpart neutral polymers in solution. Polyelectrolytes have found a number of important applications in the fields of science and engineering for instance chemistry, physics, biology, engineering of chemical and materials industry. Polyelectrolytes have been used in the food health and personal care industries as thickening agents, rheology modifiers and viscosity enhancers for shampoos, conditioners, deodorants and body lotions. In environmental engineering, they have been used in water treatment, waste treatment, and sludge dewatering because they can cause oppositely charged contaminants to flocculate. In the paper industry, they are used as retention aids, flocculating and coagulating agents for solid-liquid separations, they are used in aqueous products as water retention, adhesive strength, binding power, film formation and protective colloidal, suspending and emulsifying actions. Polyelectrolytes are used as antibacterial reagents both in solid plastic containers, solutions and protective coatings on surfaces.

Residual salts in polyelectrolyte solutions significantly impact the properties of polyelectrolyte solution. Residual salt is defined as all ionic species in the polyelectrolyte solutions other than the polyions and counterions which are dissociated from the polyelectrolytes. Residual salts come from the solvent used, air absorption, container, measurement process, or even from the polyelectrolyte itself due to the non-thorough purification. For instance, distilled water exposed to air has a residual salt level of $4 \times 10^{-6}$ M from carbonic acid,\textsuperscript{8,9} with pH = 5.4 and conductivity of 10 $\mu$S/cm. The concentration at the maximum value of the reduced viscosity for the sodium salt of sulfonated
polystyrene in water is independent of molar mass\textsuperscript{10} but proportional to the added salt concentration.\textsuperscript{8-10}

\subsection{1.2 Preparation of ion-containing polymers}

Synthetic ion-containing polymers can be subdivided into anionic, cationic, and ampholytic categories, according to the sign of the charges carried. The method of polymerization or copolymerization of charged monomers with charged or uncharged monomers by addition or step-reaction can be used to prepare ion-containing polymers directly. For instance, PEO-based ionomers can be synthesized using polyethylene glycol diols and dimethyl 5-sulfoisophthalate sodium salt through melt-polycondensation.\textsuperscript{11} However the charged monomers that can be used for direct polymerization are very limited. Most ion-containing polymers are prepared by suitable modification of neutral functionalized polymers or copolymers.

Polymers or copolymers that contain acid functional groups such as carbonyl (-COOH), sulfonic (-SO\textsubscript{3}H), phosphate (-OP(O)(OH)\textsubscript{2}), phosphonate (-PH(O)(OH) can be applied to prepare anionic charged polymers by neutralizing those functional groups with a base such as NaOH. The counterions of those anionic polymers depend on the base used for neutralization.\textsuperscript{3} The degree of neutralization (fraction of monomers in the salt form) can be used for the control of charge density of anionic polymers.\textsuperscript{11}
Cationic polymers are another important category of ion-containing polymers. They can be prepared from nitrogen containing polymers in which the nitrogen atom works as a functional group and can be ionized or quaternized by the reaction of protonation or methylation, forming protonated amines (-N⁺H₃X⁻, -N⁺R₂H₂X⁻, or -N⁺R₂HX⁻) or quaternary ammonium (-N⁺R₃X⁻). The charge density of cationic polymers can be controlled by the degree of ionization or quaternization.⁴,¹³

Polyampholytes, used as emulsifiers, are charged polymers that contain both negative and positive charges.⁴,¹⁴ They are prepared by copolymerization or suitable modification of two types of structures discussed above.

1.3 Electrostatic interactions in ion-containing polymers

A common characteristic of ionomers and polyelectrolytes is the oppositely charged counterions associated with these anionic or cationic polymers.¹,³ The counterions either simply form ion pairs in low dielectric constant environments to form ionomers or partly/fully dissociate into the solution of polyelectrolytes. The counterions
of ionomers can also dissociate into the median when the bulk dielectric constant is high enough. Those mobile ions dominate the conductivity of the materials.\textsuperscript{11,15-19} Manning counterion condensation theory predicts that counterions condense onto the polyion if the distance between two elementary charges is smaller than the Bjerrum length $l_B$.\textsuperscript{20} The bulk dielectric constant $\varepsilon$ significantly impacts the molar fraction of mobile ions based on the definition of Bjerrum length

$$l_B = \frac{e^2}{\varepsilon k_B T} \quad (1.1)$$

where $e$ is the elementary charge, $\varepsilon$ is the dielectric constant of the median and $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. In the chain potential energy, the Coulomb electrostatic interaction energy between elementary charges at a distance $l_B$ is equal to the thermal energy $k_B T$. The ability of small ions (counterions and salt ions) to rearrange themselves to screen a given charge is taken into account through the concentration dependence of the Debye screening length $r_D$.

$$r_D = \sqrt{\frac{1}{4\pi l_B \sum c_i z_i^2}} \quad (1.2)$$

where $c_i$ and $z_i$ are the concentration and valence of small ion of type $i$, where $i =$ salt anions, salt cations, and/or counterions. Debye screening length is the length scale over which an inserted probe charge can be detected by other ions in solution.\textsuperscript{6} This screening length is related to the solvent dielectric constant and the charge of small ions (Eq. 1.2). In salt-free polyelectrolyte dilute solution, the Debye screening length is larger than the
distance between polyions. Hence, polyions strongly interact as \( r_D \geq R_{cm} \). \( R_{cm} \) is the distance between centers of mass of neighboring chains \( R_{cm} \approx (N/c)^{1/3} \) (where \( N \) is the number of monomers in the chain and \( c \) is the polyelectrolyte concentrations). As \( r_D < R_{cm} \), counterions are localized within the polyions at the length scale of \( r_D \).

In the presence of added or residual salts, the coulomb interactions between charged monomers are screened by total small ions: counterions and salt ions as their contributions are summed in Eq. (1.2). If the salt ion concentration \( (c_s) \) is much larger than the counterion concentration \( (c_c) \): \( c_s >> c_c \), the Debye screening length is dominated by the concentration of salt ions, independent of polyelectrolyte concentration. Reversely, as \( c_c >> c_s \), the \( r_D \) is dominated by the concentration of counterions, independent of concentration of salt ions. The electrostatic interaction between two elementary charges is given by the Yukawa potential, the Coulomb energy with an exponential cutoff at the Debye length

\[
\varphi = k_BT \frac{l_p}{r} \exp(-r/r_D)
\]

### 1.4 Properties of polyelectrolytes in solution

Polyelectrolytes dissolve in high dielectric constant media and dissociate into polyions each with many small ions (counterions). Polyelectrolyte solution properties are quite different from the solution properties of neutral polymers and micro-electrolytes (small molecule salts). These different properties include higher solution viscosity, lower
surface tension at the air-water interface, formation of gels and Donnan equilibria, and compatibility with biomaterials, which enable polyelectrolyte useful in many applications.

Polyelectrolytes exhibit much higher solution viscosity in the dilute and semidilute unentangled regions due to the intermolecular and intramolecular interactions between charges. In the semidilute unentangled region, the viscosity of polyelectrolyte solutions is proportional to the square root of polymer concentration $\eta \sim c^{1/2}$, while for neutral polymers, the viscosity increases faster with increasing concentration.$^{6,21}$ There is an obvious scattering peak observed from both small angle neutron scattering (SANS) and small angle X-ray scattering (SAXS),$^{22,23}$ which determines the typical distance between chains (the correlation length $\xi$) as

$$\xi = 2\pi / q_{\text{max}} \sim c^{-1/2}$$  \hspace{1cm} (1.4)

where $q_{\text{max}}$ is the wavevector of the scattering peak. At higher concentrations, the wavevector corresponding to the peak decreases with increasing concentration.$^{24}$ However, in the same concentration region and wavevector range, neutral polymers in solution do not show any scattering peaks in SANS and SAXS. In addition, polyelectrolyte solutions show shear thinning at much lower polymer concentration, compared to that of neutral polymer solutions.$^{13,25}$ Those experimental results suggest that polyelectrolytes in solution have a conformation different from that of neutral polymers in solution. Charge density, solvent dielectric constant, solvent quality, counterion type & size, and added or residual salts show significant effects on the conformation of polyelectrolytes in solution based on the SANS and SAXS experiments.
Those effects can also be detected by measuring the rheological properties of polyelectrolyte solutions.

One important property of polyelectrolytes in solution is conductivity. Polyelectrolytes dissolve in high dielectric constant solvent and dissociate into polyions and many small counterions. Those mobile small ions and polyions are able to move and conduct electricity. The conductivity of polyelectrolyte solutions is related to counterion condensation, solvent properties, and polyelectrolyte concentration. Hence, the mobile ion concentration is crucial in the conductivity of the polyelectrolyte solution.13,19 On the other hand, the high osmotic pressure of polyelectrolytes in solution at low salt limit is also devoted to the small counterions dissociated from the polyelectrolyte backbone.26 The Manning counterion condensation model is only apparently valid in the semidilute region.19,27 In extremely dilute solutions, all the counterions of polyelectrolytes will eventually dissociate from the backbone or side groups into solution with dilution.

1.5 Properties of ionomers

In principle, the field of ionomers is even larger than that of neutral polymers because many ionomers are able to be prepared from one conceivable nonionic polymer structure. Counterions can be any type of stable ions and the valence of counterions can be monovalent or multivalent. The molar fraction of ionic groups can be controlled by both the degree of functionality and the degree of neutralization, protonation or quaternization on the basic structure of nonionic polymer. As indicated above, the bulk properties of ionomers are governed by ionic interactions.1 Hence, ionic aggregates or
ion-clusters can dominate the properties of ionomers. Both the ionic fraction and the counterion type significantly impact the formation, size, and distribution of ion-clusters in the bulk materials.

Morphology of ionomers is the most important internal material structure that is considered to impact all the properties of ionomers.\(^1\) The basic structure in bulk ionomers is the ion-pair of polyion and counterion due to the strong coulomb interactions between positive and negative charges in low dielectric constant media (in which Bjerrum length is very large). Those ion-pairs make strong dipoles which attract each other to form ion-aggregates or ion-clusters. The size and shape of ion-aggregates are governed by association energy of forming ion-clusters from ion-pairs. All those factors such as backbone flexibility, size of side group, ionic molar fraction, size and valence of counterion, dielectric constant, and surface energy of ion-aggregates will impact the size and shape of ion-aggregates. The size and shape of ion-clusters can be observed by using TEM and SEM technology, combining the measurement results of SAXS.\(^1\)

Ionomers have higher glass transition temperature due to the effect of crosslinking provided by ion-clusters. Some ionomers have two glass apparent transition temperatures, one is the \(T_g\) of polymer segment, another is the \(T_g\) of the ion-clusters. All ionomers exhibit much higher melt viscosity and storage modulus, compared to that of neutral polymers.\(^1\)

Aside from the properties above, the transport of gas, liquid, and ion is unique in ionomers so they are used in the separation, purification, and in fuel cells and battery applications. Ionomer membranes exhibit superselectivity due to the unique structure of
typical ion-cluster phase. Perfluorosulfonates (Nafion) have been successfully used in making fuel cell membranes.

1.6 References

Chapter 2
Charge Density Effects in Salt-Free Polyelectrolyte Solution Rheology

2.1 Introduction

The rheology of polyelectrolyte solutions has received considerable attention due to the practical application for aqueous industrial coatings.\textsuperscript{1-11} Polyelectrolyte molecular weight, effective charge, concentration and added salt concentration are recognized to impact polyelectrolyte solution rheology.\textsuperscript{6, 8-14} However, the combination of aqueous insolubility of many weakly charged polyelectrolytes and counterion condensation occurring at high charge density has severely limited studies of charge density effects. In this paper, we report how effective charge impacts the rheology of salt-free polyelectrolyte solutions over wide ranges of concentration and charge density. Ethylene glycol (EG) is a good solvent for the neutral parent poly(2-vinyl pyridine) (P2VP), allowing solubility of random copolymers of 2-vinyl pyridine and N-methyl-2-vinyl pyridinium chloride (PMVP-Cl) of any charge density.

Furthermore, anhydrous EG has very low conductivity (0.2 µS/cm at 25 °C) meaning that concentrations of ionic contaminants are extremely small. This gives EG an enormous advantage over water because aqueous solutions exposed to air dissolve carbon dioxide, which forms carbonic acid\textsuperscript{8,10,15} with a concentration of roughly 4x10\textsuperscript{-6} M and considerably higher conductivity (10 µS/cm at 25 °C) from this residual salt. The low
residual ion content in EG allows us to study polyelectrolyte solution rheology far below the overlap concentration without any effects of salt contamination. Although the rheology of polyelectrolyte solutions in organic solvents with various polarity and solubility has been reported,\textsuperscript{5,16,17} no systematic study covering a wide range of charge density is available.

EG solutions of PMVP-Cl random copolymers provide an ideal system to test the predictions of scaling theory\textsuperscript{6,18} for polyelectrolyte solutions. For this reason, we first briefly review the scaling predictions before discussing our experimental data. This review necessarily focuses on the good solvent case, since this applies to our polymers in EG.

### 2.2 Background theory

The Bjerrum length $l_B$ is the scale at which the Coulomb energy of two charges equals the thermal energy $kT$

$$ l_B = \frac{e^2}{\epsilon kT} \tag{2.1} $$

where $e$ is the elementary charge and $\epsilon$ is the solvent dielectric constant. At 25 °C, water has $\epsilon = 78$ and $l_B = 7.1$ Å, whereas EG has $\epsilon = 37$ and $l_B = 15$ Å. According to the Manning counterion condensation theory,\textsuperscript{2} no condensation occurs (all counterions are free) if the charge spacing along the chain exceeds the Bjerrum length. However, if the distance between charges along the chain becomes smaller than the Bjerrum length,
counterions condense on the chain to lower the charge repulsion until the distance between effective charges equals the Bjerrum length. Such condensed counterions no longer contribute to the counterion activity or the conductivity of the solution, but do contribute to the polarizability.\textsuperscript{12,19} If correct, the Manning model could in principle be used to determine the fraction $f$ of monomers on the chain bearing an effective charge. However, the detailed local conformation of the polyelectrolyte is not known \textit{apriori}, so in practice $f$ must be measured, typically using a counterion selective electrode,\textsuperscript{13} osmotic pressure,\textsuperscript{20} or from dielectric/conductometric measurements.\textsuperscript{11,12,19,21} For strongly charged polyelectrolytes, the effective fraction of charged monomers $f$ is expected to be smaller than the chemical fraction of quaternized monomers $\alpha$, and independent of concentration in semidilute solutions. However, for sufficiently dilute solutions entropy dominates and $f$ eventually approaches $\alpha$ in the dilute limit.\textsuperscript{21,22}

The local conformation of a polyelectrolyte chain in solution is determined by charge repulsion and interaction of the monomers with solvent.\textsuperscript{4,6,18} For dilute solution in a good solvent, charge repulsion stretches the chain into a directed random walk of electrostatic blobs (of size $\xi_e$ containing $g_e$ monomers) within which the cumulative electrostatic repulsion equals the thermal energy.

$$\frac{(fg_e \varepsilon_e)^2}{b_\varepsilon} \approx kT$$

Inside the electrostatic blobs the chain conformation is not affected by electrostatics and hence is a self-avoiding walk in good solvent

$$\xi_e \approx b g_e^{3/5}$$

(2.2)
where $b$ is the monomer size. For vinyl monomers in good solvent, $b = 2.5$ Å. \(^{23}\)

The above two equations can be solved for $\xi_e$ and $g_e$.

$$\xi_e \approx b^{10/7} l_b^{-3/7} f^{-6/7} \quad \text{and} \quad g_e \approx \left(\frac{b}{l_b}\right)^{5/7} f^{-10/7}$$  \hspace{1cm} (2.3)

The contour length of the chain of electrostatic blobs is

$$L \approx \frac{\xi_e}{g_e} \approx \frac{bN}{l_b^{2/7}} f^{4/7} \approx \frac{bN}{B}$$ \hspace{1cm} (2.4)

where the last relation effectively defines the stretching parameter $B$ as the ratio of the contour length of the polyelectrolyte and the maximum possible contour length $bN$. In dilute solution $L$ is the end-to-end distance of the chain. The overlap concentration is \(^{6,18}\)

$$c^* \approx \frac{N}{L} \approx \frac{B^3}{b^3 N^2} \approx \frac{b^{-3} N^{-2}}{l_b^{6/7} f^{-12/7}}$$ \hspace{1cm} (2.5)

In dilute solution the specific viscosity $\eta_s p = (\eta - \eta_s)/\eta_s$, where $\eta$ is the (zero-shear-rate) viscosity and $\eta_s$ is the solvent viscosity, is predicted to be \(^{4,6}\)

$$\eta_s p \approx \frac{c}{c^*} \quad \text{for } c < c^*$$ \hspace{1cm} (2.6)

making the intrinsic viscosity simply the reciprocal of $c^*$. The overlap concentration in this work will be experimentally determined by averaging $c/\eta_s p$ for all dilute solution data.

Above the overlap concentration, charge repulsion is partially screened by other chains (and their free counterions). Such semidilute solutions are characterized by a correlation length \(^{4,6,18,24}\) $\xi$, which is the typical distance to the nearest chain.
\[ \xi \approx L \left( \frac{c}{c^*} \right)^{-1/2} \approx \left( \frac{B}{cb} \right)^{1/2} \quad \text{for } c > c^* \] (2.7)

Correlation length \( \xi \) of a strongly charged 45PMVP-Cl (the chloride salt of 45mole% quaternized P2VP) in EG has been reported by Ermi and Amis.\(^7\) Their study shows \( \xi \sim c^{-0.47} \), in agreement with the scaling prediction (Eq. 2.7).\(^6\) Charge repulsion extends the polyelectrolyte chains in EG, making the stretching parameter \( B \) small (\( B = 2.8 \) obtained from fitting the SANS data\(^7\) to Eq. 2.7 with \( b = 2.5 \) Å). On scales smaller than \( \xi \), the chain is still a directed random walk of electrostatic blobs (similar to dilute solution) but on scales larger than \( \xi \) the chain is a random walk of correlation volumes.\(^6,18\) The contour length is still \( L \) (given by Eq. 2.4) but the root-mean-square end-to-end distance \( R \) is smaller than in dilute solution, since the chain is a random walk on its largest scales.

\[ R \approx L \left( \frac{c}{c^*} \right)^{-1/4} \approx \left( \frac{b}{cb} \right)^{1/4} N^{1/2} \quad \text{for } c > c^* \] (2.8)

The Dobrynin scaling model\(^6\) predicts the chain in semidilute unentangled solutions relaxes by Rouse motion, with relaxation time

\[ \tau \approx \frac{\tau_0 N^2}{(cb^3B^3)^{1/2}} \quad \text{for } c^* < c < c_e \] (2.9)

where \( \tau_0 = \eta_b^3 / kT \) is the relaxation time of a monomer and \( c_e \) is the concentration at which polymer chains in solution start to show entanglement effects. The terminal modulus \( G \) is predicted to be \( kT \) per chain below \( c_e \).

\[ G = \frac{ckT}{N} \quad \text{for } c < c_e \] (2.10)

16
The specific viscosity is the product of relaxation time and terminal modulus divided by solvent viscosity. \(^{24}\)

\[
\eta_{sp} \approx \frac{\tau G}{\eta_s} \approx \left( \frac{cb^3}{B} \right)^{1/2} N \approx \left( \frac{c}{c^*} \right)^{1/2}
\]

for \(c^* < c < c_e\) \( (2.11) \)

This scaling prediction is the same as the empirical Fuoss law.\(^1,\text{25}\) Eqs. 2.9-11 quantitatively describe the rheology of semidilute unentangled aqueous polyelectrolyte solutions with more free counterions than residual salt ions.\(^8,\text{9,13}\) Eqs. 2.6 and 2.11 expect specific viscosity to only depend on \(c/c^*\) for \(c < c_e\). The entanglement concentration is expected to be proportional to the overlap concentration\(^6\)

\[
c_e \sim c^* \approx \frac{B^3}{b^3 N^2} \approx b^{-3} N^{-2} \left( \frac{b}{l_B} \right)^{6/7} f^{-12/7}
\]

with the constant of proportionality \(c_e/c^* \approx 1000\), making for a wide range of concentrations for which Eqs. 2.9-11 apply. Since polyelectrolytes in good solvent have highly swollen electrostatic blobs (see Eq. 2.2), a third important concentration is the overlap concentration of electrostatic blobs,\(^6\) \(c^{**}\).

\[
c^{**} \approx \frac{g_e}{\xi_e^3} \approx b^{-3} \left( \frac{l_B f^2}{b} \right)^{4/7} \approx \frac{1}{b^3 B^2}
\]

\( (2.12) \)

For \(c > c^{**}\), the electrostatic interactions no longer perturb the conformation of the chain and polyelectrolytes in good solvent are expected to be quite similar to an entangled solution of neutral polymers in good solvent,\(^{24,26}\) with \(\tau \sim c^{3/2}, G \sim c^{9/4}\) and \(\eta_{sp} \sim c^{15/4}\).

If \(c^{**} > c_e\) (the usual case), there is a semidilute entangled regime of polyelectrolyte solution rheology.\(^6\) The relaxation time is predicted to be
\[ \tau \approx \tau_0 \left( \frac{c^*}{c_e} \right)^{1/2} \left( \frac{N}{B} \right)^3 \quad \text{for } c_e < c < c^{**} \]  

(2.13)

which is \textit{independent of concentration}. The terminal modulus is

\[ G \approx \frac{kT}{b^3} \left( \frac{c^*}{c_e} \right)^{1/2} \left( \frac{cb^3}{B} \right)^{3/2} \quad \text{for } c_e < c < c^{**} \]  

(2.14)

and the specific viscosity is

\[ \eta_{sp} \approx \frac{\tau G}{\eta_s} \approx \frac{c^*}{c_e} \left( \frac{cb^3}{B^3} \right)^{3/2} N^3 \quad \text{for } c_e < c < c^{**} \]  

(2.15)

Comparing the concentration exponents in Eqs. 2.9-11 with those in Eqs. 2.13-15, it is evident that the entanglement concentration is easily identified by changes in slope in plots on logarithmic scales. The overlap concentration for electrostatic blobs \( c^{**} \) is similarly easily identified by such changes in slope for the concentration dependences of \( \tau, G \) and \( \eta_{sp} \).

### 2.3 Experimental

#### 2.3.1 Materials

Poly (2-vinyl pyridine) (P2VP, \( M_w = 364,000 \text{ g/mol, } M_w/M_n = 1.06, \ N = 3230 \), based on \( M_n \)) purchased from Polymer Source Inc. was used without further purification. Anhydrous reagents dimethyl sulfate (DMS, 99%, DuPont) and sodium chloride (J.T.
Baker, 99.9%) were used as received. N, N-dimethyl formamide (DMF: Aldrich, anhydrous, 99.8%) was redistilled under vacuum in the presence of sodium. Ethylene glycol (EG: J. T. Baker, 99.8%, anhydrous; water < 0.02 %) was used as the solvent for all samples in this study after being redistilled under low pressure and protection of argon. This freshly redistilled EG contains less than 0.007 wt % water, measured using a Coulometric KF Titrator, and shows very low conductivity at 25 °C (0.2 µS/cm, measured using a Broadband Dielectric Spectrometer, Novocontrol-GmbH-Germany).

\[
\begin{align*}
\text{N} & \xrightarrow{1. (\text{CH}_3)_2\text{SO}_4/\text{DMF}} \text{N} \\
\text{CH}_2\text{CH}_2 & \xrightarrow{2. \text{NaCl}/\text{H}_2\text{O}} \text{CH}_2\text{CH}_2 + \text{CH}_2\text{CH}_2 \\
\text{1.} & \text{2.} \quad 27,28
\end{align*}
\]

Scheme 2.1 Quaternization of P2VP

2.3.2 Quaternization

Random copolymers of 2-vinyl pyridine and N-methyl-2-vinyl pyridinium chloride were prepared by quaternization and ion-exchange (Scheme 2.1). Parent dry P2VP was added into a 100 mL reactor under argon, DMF was then added to make a 10 wt % solution of the P2VP in DMF. DMS was injected into the reactor when the P2VP had fully dissolved in DMF. The reaction was kept at room temperature 24 hrs under argon. Polyelectrolytes made by this method with more than 30 mole % charged monomers were precipitated into acetone, filtered and then redissolved in 2M NaCl solution in water with at least 50 fold excess of chloride to methyl pyridinium ion.\textsuperscript{7,27,28}
Polyelectrolytes with lower charge density were directly dissolved in 2 M NaCl water-methanol (50/50 volume). The quaternized polymer in 2 M NaCl solution was dialyzed against deionized water or a deionized water-methanol mixture until a constant conductivity ($< 2 \, \mu$S/cm) of the dialyzate was attained. Finally, the salt-free polyelectrolyte solution was lyophilized under vacuum, and the solid quaternized polymer was dried in a vacuum oven at 40 °C to a constant mass. The amount of water in dry strongly charged 55PMVP-Cl is lower than 0.6 wt % obtained from the measurement of this polymer solution in EG using Karl Fischer Titration. Quaternized random copolymers with various charge densities were obtained by varying the molar ratio of DMS and pyridine. Dry polymers were dissolved in fresh redistilled EG to prepare the highest concentration, and lower concentrations were prepared by serial dilution. In all cases, the water concentration in samples exposed to air for one hour is smaller than 0.3 wt % measured using Karl Fischer Titration. Polymer concentration is reported in moles of monomers (the sum of both vinyl pyridine and methyl vinyl pyridinium chloride) per liter of solution.

### 2.3.3 Degree of quaternization $\alpha$

The degree of quaternization of the partially quaternized polymers was determined using silver nitrate (Aldrich, 99.9%) conductometric counterion titration, calibrated with sodium chloride (Aldrich, 99.999%). The degree of quaternization is the ratio of moles of AgNO$_3$ and moles of total monomer.
\[ \alpha = \frac{\text{moles } AgNO_3}{\text{moles monomer}} = \frac{\text{moles } AgNO_3}{W / \left[ (1 - \alpha)M_{VP} + \alpha M_{MVP-Cl} \right]} \]

\( W \) is the mass of polymer, \( M_{VP} = 105.137 \text{ g/mol} \) is the molar mass of the vinyl pyridine monomeric repeat unit and \( M_{MVP-Cl} = 155.625 \text{ g/mol} \) is the molar mass of the N-methyl-2-vinyl pyridinium chloride monomeric repeat unit. The above equation is then solved for the degree of quaternization.

\[ \alpha = \frac{M_{VP}}{W / (\text{moles } AgNO_3) + M_{VP} - M_{MVP-Cl}} \quad (2.16) \]

To simplify our expression in this paper, we define the polymer samples with degree of quaternization \( \alpha = 0, 0.03, 0.04, 0.10, 0.17, 0.42, 0.55 \) as P2VP, 3PMVP-Cl, 4PMVP-Cl, 10PMVP-Cl, 17PMVP-Cl, 42PMVP-Cl, and 55PMVP-Cl, respectively. We were unable to obtain quaternized P2VP with more than 60 mole % charged monomers, presumably due to the steric hindrance of the pendant groups.

\(^1H\) NMR was used for the qualitative confirmation of the quaternization extent determined by titration. Owing to the tacticity of P2VP, there are two characteristic peaks of the quaternary methyl group, located in the chemical shift range \( \delta = 3.2-4.5 \) ppm. The \(^1H\) NMR result of 10PMVP-Cl shows that the fraction of quaternized monomers is 0.103, which is in agreement with the result obtained from titration (\( \alpha =0.10 \)). However, if the degree of quaternization is much higher, the signal of the methylated group is so strong that the peaks of the methylated group overlap with the peaks of other protons on the polymer chain backbone. For weakly charged P2VP, the \(^1H\) NMR signal (two peaks) of the methylated group is too weak to be correctly determined from the internal comparison of \(^1H\) NMR.
2.3.4 Effective charge $f$

Conductivity measurements were performed with a broadband dielectric spectrometer (Novocontrol GmbH, Germany). The conductivity of fresh polyelectrolyte solutions in the concentration range from 0.01 to 10 mg/mL in a liquid cell (spacer: 0.55 mm and diameter: 20 mm) was measured at 25 °C, frequency range from $10^1$ to $3 \times 10^6$ Hz, and 0.1V (AC). Conductivity was evaluated in the frequency range from $10^2$ to $10^4$ Hz. Higher frequencies show a relaxation from polarization of free counterions and lower frequencies show electrode polarization effects.\textsuperscript{19} Equivalent conductance $\Lambda = (\sigma - \sigma_e) / c$ was determined from the conductivity of polyelectrolyte solutions ($\sigma$), the conductivity of ethylene glycol ($\sigma_e = 2.0 \times 10^{-7}$ S/cm), and the molar concentration of monomer ($c$). The concentration dependence of equivalent conductance in EG is shown in Fig. 1.

Since the equivalent conductance of the chloride counterion in EG is not known, the usual methods to determine $f$ from equivalent conductance of the solution\textsuperscript{11,12,19,21} cannot be employed. However, we notice in Fig. 1 that the equivalent conductance of 4PMVP-Cl is independent of concentration, even far below $c^*$. This means that all counterions of 4PMVP-Cl in EG are free (no condensation) and $f = \alpha = 0.04$ for 4PMVP-Cl in EG. The effective charge $f$ of the other polyelectrolytes in EG was determined by plotting $\Lambda / f$ against $c / c^*$ for each polyelectrolyte, with $f$ adjusted to fit the curve $\Lambda / f$ against $c / c^*$ of 4PMVP-Cl in the semidilute unentangled regime.\textsuperscript{19} Such fits are shown as the horizontal lines in Fig. 2.1. The upturn in equivalent conductance below $c^*$,
noted for polyelectrolytes with higher extents of quaternization, indicates that condensed counterions gradually leave the chain as polyelectrolyte concentration is lowered.\(^{19,21,22}\) 10PMVP-Cl shows a small sign of counterion condensation (a small upturn in equivalent conductance below \(c^*\)). 42PMVP-Cl and 55PMVP-Cl show stronger upturns (indicating more condensed counterions) and the effective charge of these strongly charged polyelectrolytes in semidilute solution (\(f = 0.17\) for 42PMVP-Cl and \(f = 0.18\) for 55PMVP-Cl) approaches the maximum expectation of the Manning model\(^2\) \((f_{\text{max}} = b/l_B = 0.17)\) for vinyl polyelectrolytes (\(b = 2.5\ \text{Å}\))\(^{23}\) in EG (\(l_B = 15\ \text{Å}\)). Hence, the effective charge of polyelectrolytes in EG can be expressed as \(f \approx f_{\text{max}}\) for \(\alpha > f_{\text{max}}\) and \(f \leq \alpha\) for \(\alpha < f_{\text{max}}\). 17PMVP-Cl shows a strong upturn even above \(c^*\), which likely indicates some contamination of residual salt in the 17PMVP-Cl solutions in EG (unfortunately, our supply of this polymer was exhausted). The measured value of \(f = 0.10\) for 17PMVP-Cl (and \(f = 0.09\) for 10PMVP-Cl) suggests that there is some counterion condensation (not anticipated by the Manning model) even if \(\alpha \leq f_{\text{max}}\) probably because random quaternization makes 17PMVP-Cl a random copolymer that can be locally quaternized to have local charge density larger than 17%. This may mean that the charges on the 17PMVP-Cl are not evenly distributed along the polymer chains, as expected for random quaternization.

Our assumption of \(\Lambda \sim f\) is based on the leading term from the scaling predictions for polyelectrolyte solution conductivity\(^{11,12,19}\) \(\Lambda = Af + Bf^2 \log c\), where \(A\) and \(B\) are constants for a given polyelectrolyte/counterion/solvent system, related to the
specific conductance of the counterion and details regarding the local conformation of the chain that are simply not known for PMVP/Cl/EG. Since Fig. 2.1 shows the highest concentration decade of each solution has $\Lambda$ independent of $c$, we surmise that $B << A$, justifying the assumption that $\Lambda \sim f$.

![Graph showing concentration dependence of equivalent conductance for quaternized P2VP polyelectrolyte solutions in EG at 25 °C. Symbols are experimental data and lines are fits to determine the effective charge (see text).](image)

**Figure 2.1** Concentration dependence of equivalent conductance for quaternized P2VP polyelectrolyte solutions in EG at 25 °C. Symbols are experimental data and lines are fits to determine the effective charge (see text).
Figure 2.2 The shear rate dependence of apparent viscosity (open squares) and the Carreau model fits (lines) for 17PMVP-Cl solutions with no added salt at 25 °C. Solution concentrations from top to bottom are 0.2198, 0.099, 0.0659, 0.0439, 0.0220, 0.0088, 0.0042, 0.0022 moles/liter.

2.3.5 Rheology

The steady shear viscosity of polymer solutions in EG was measured at 25 °C using four rheometers: A Rheometric Scientific ARES (controlled strain) was used for highly concentrated solutions with viscosity above 20 Pas, a Rheometric Scientific SR-2000 (controlled stress) was used for concentrated solutions with viscosity in the range from 0.1 to 100 Pas, a computerized Contraves Low Shear 30 viscometer (controlled shear rate) was used for polymer solutions with viscosity from 0.03 to 0.3 Pas, and a capillary viscometer (Cannon Ubbelohde No. 2 with a diameter of 2.06 mm and a capillary length of 90 mm) was used for polymer solutions with viscosity lower than 0.03
Pas, each calibrated using standard Newtonian oils and EG at 25 °C. The flow time of EG in the capillary viscometer is 182 s ($\eta = 17$ mPa s at 25 °C) and the measured flow times of our quaternized copolymer solutions in EG are all above 225 s. The capillary viscometer has a wall shear rate of 19 s$^{-1}$ for EG (lower for all polymer solutions in EG, but significantly higher for water) and our other rheometers demonstrate that this shear rate is low enough to measure the zero-shear-rate viscosity. Polyelectrolyte solutions in EG at concentrations lower than $c^*$ did not show appreciable shear thinning up to 100 s$^{-1}$ in the Contraves Low Shear 30.

The apparent viscosity ($\eta$) of polymer solutions in EG was measured as a function of shear rate ($\dot{\gamma}$). Fig. 2.2 shows that the apparent viscosity of the 17PMVP-Cl solutions increases with increasing concentration and decreases with increasing shear rate at high shear rates due to shear thinning. The shear rate dependence of apparent viscosity for solutions with concentrations below 0.23 M were fit to the Carreau model$^{29}$

$$\eta(\dot{\gamma}) = \frac{\eta(0)}{[1 + (\tau \dot{\gamma})^p]^p}$$

(2.17)

to determine the relaxation time $\tau$ and the parameter $p$ by least squares regression. The parameter $p$ was found to systematically change with concentration, as seen in other studies of polyelectrolyte solution rheology, ranging from 0.05 at low concentration to 0.25 at high concentration. In Fig. 2.2, the curves obtained by fitting the Carreau model give a good description of the experimental results, suggesting that the relaxation time extracted from the fitting is meaningful.
For solutions with concentrations \( c > 0.037 \text{M} \), storage modulus \( G' \) and loss modulus \( G'' \) were measured as functions of frequency \( \omega \) at 25 °C using the ARES rheometer, with small strain amplitudes corresponding to linear response. For lower concentrations, the oscillatory shear method is not reliable because of inertial effects resulting from the viscosity being too small. Care was taken to ensure that the strain amplitudes were in the regime of linear viscoelastic response. The viscosity agreed nicely with the steady shear value in all cases and the low frequency data were fit to the standard liquid power laws\(^{24} \) \((G' \sim \omega^2 \text{ and } G'' \sim \omega)\) to determine the relaxation time as the reciprocal of the frequency at which those power laws intersect.

### 2.4 Results and discussion

#### 2.4.1 Specific viscosity

Specific viscosity \( \eta_p = (\eta - \eta_s)/\eta_s \) (where \( \eta_s \) is the viscosity of EG) of all polymer solutions was plotted against concentration spanning four decades and shown in Fig. 3a. Fig. 3b shows the concentration dependence of reduced viscosity \( \eta_p/c \). At low concentrations \((c < c^*)\) the data in Fig. 3 exhibit the simple scaling expected by Eq. 6 for dilute solution. Whereas aqueous polyelectrolyte solutions show a maximum in reduced viscosity;\(^{1,10,30-31}\) the polyelectrolyte solutions in EG show no maximum. The
concentration at the maximum value of the reduced viscosity for the sodium salt of
sulfonated polystyrene in water is independent of molar mass\textsuperscript{10} but proportional to the
added salt concentration.\textsuperscript{8,10,27} Distilled water exposed to air has a residual salt level of
4x10\textsuperscript{-6} M from carbonic acid,\textsuperscript{8,10} with pH = 5.4 and conductivity of 10 \(\mu\text{S/cm}\). The low
conductivity (0.2 \(\mu\text{S/cm}\)) of EG suggests that the residual salt is orders of magnitude
smaller in EG than in water. In Fig. 3b, it is observed that the intrinsic viscosity
\[
[\eta] = \lim_{c \to 0} \left( \frac{\eta_{sp}}{c} \right)
\]
of polyelectrolytes in EG depends on the extent of quaternization for the
weakly charged polyelectrolytes (\(\alpha = 0.03, 0.04\) and 0.10) but is essentially independent
of \(\alpha\) for \(\alpha > 0.10\).

Fig. 2.3 provides a clear picture of how specific viscosity depends on extent of
quaternization and concentration in salt-free polyelectrolyte solutions. The polymers in
Fig. 2.3 can be grouped into three categories: neutral (P2VP), weakly charged (3PMVP-
Cl and 4PMVP-Cl), and strongly charged (10PMVP-Cl, 17PMVP-Cl, 42PMVP-Cl and
55PMVP-Cl).

The specific viscosity of polymers in EG in both the dilute and semidilute
unentangled regimes greatly depends on quaternization extent until the degree of
quaternization \(\alpha = 0.1\) (10PMVP-Cl) where counterion condensation starts. The
concentration dependences of specific viscosity for the strongly charged polyelectrolytes
are nearly identical, consistent with their similar effective charge \(f\) dictated by counterion
condensation. While the effective charge of the four strongly charged polymers is not
identical (see Fig. 2.1 and Table 2.1) the repulsion from the higher effective charge is
partially compensated by a dipolar attraction from the condensed counterion / charged
Figure 2. Concentration dependence of (a) specific viscosity ($\eta_{sp} = (\eta - \eta_s) / \eta_s$) and (b) reduced viscosity ($\eta_{sp} / c$) for neutral polymer (P2VP), weakly charged polyelectrolytes (3PMVP-Cl and 4PMVP-Cl), and strongly charged polyelectrolytes (10PMVP-Cl and 17PMVP-Cl, 42PMVP-Cl and 55PMVP-Cl) in EG at 25 °C.
monomer pairs on the chain.\textsuperscript{14} Larger effective charge $f$ acts to stretch the chain, but the dipolar attraction from having more ion pairs acts to contract the chain and these opposing effects appear to nearly cancel for $\alpha \geq 0.1$, making all the strongly charged polyelectrolytes have nearly the same specific viscosity.

The specific viscosity of the weakly charged 3PMVP-Cl and 4PMVP-Cl differ slightly because these polymers have no counterion condensation ($f = \alpha$) and viscosity depends on effective charge (see Eqs. 2.6, 2.11 and 2.15). Even with $f = \alpha = 0.03$, the specific viscosity is an order of magnitude larger than the parent neutral polymer because 3PMVP-Cl has $fN \cong 100$ charges per chain.

The overlap concentration $c^*$ was determined by averaging $c/\eta_p$ for all dilute solution data for each polymer. Fig. 4a shows the specific viscosity data plotted as a function of $c/c^*$, which reduces all data to a common line for $c/c^* < 1$, as expected by Eq. 2.6, while the residual salt effects in aqueous solutions prevent such a data reduction. A similar data reduction is shown for reduced viscosity in Fig. 4b.
Figure 2.4 Scaling plots of (a) specific viscosity and (b) reduced viscosity data of Fig. 2.3, constructed by normalizing concentration with the overlap concentration $c^*$. 
For both the neutral and polyelectrolyte solutions, there are sharp changes in slope at $c^*$ and $c_e$ (Fig. 2.3a). These slope changes are even more evident in Fig. 2.4b. Fig. 2.5 shows how $c_e$ and $c^{**}$ were determined from specific viscosity ($c^* = 1/\eta$ was determined from dilute solution data and is also shown). The concentration at the crossover of $\eta_{sp} \sim c^{1/2}$ and $\eta_{sp} \sim c^{3/2}$ defines the entanglement concentration $c_e$ of polyelectrolyte solutions. Similarly, the crossover of $\eta_{sp} \sim c^{3/2}$ and $\eta_{sp} \sim c^{15/4}$ determines the overlap concentration of electrostatic blobs $c^{**}$. These important concentrations are listed in Table 2.1.

**Figure 2.5** Determination of the chain overlap concentration $c^*$, the entanglement concentration $c_e$, and the electrostatic blob overlap concentration $c^{**}$ from the concentration dependence of specific viscosity and relaxation time of polyelectrolyte 17PMVP-Cl in EG. Symbols represent the experimental data and solid lines represent the predicted power laws from scaling theory, with the exception of the relaxation time for the highest concentrations.
The specific viscosity of all charged polymers (PMVP-CIs) increases with concentration in a power law $\eta_{sp} \sim c^{0.5}$ (theory: $\eta_{sp} \sim c^{1/2}$) in the semidilute unentangled regime ($c^* < c < c_e$). In contrast, the specific viscosity of the neutral P2VP increases with concentration in a power law $\eta_{sp} \sim c^{1.2}$ (theory: $\eta_{sp} \sim c^{5/4}$). In the semidilute entangled regime (polyelectrolytes: $c_e < c < c^{**}$; neutral polymer: $c > c_e$), the specific viscosity of the strongly and weakly charged polymers increases with concentration in a power law $\eta_{sp} \sim c^{1.5}$ (theory: $\eta_{sp} \sim c^{3/2}$), while the specific viscosity of the neutral polymers increases with increasing concentration in a power law of $\eta_{sp} \sim c^{3.75}$ (theory: $\eta_{sp} \sim c^{15/4}$ for both neutral and charged polymers). The entanglement concentration of neutral P2VP is significantly higher than that of the polyelectrolytes, which all have slightly different $c_e$, that increases weakly with increasing effective charge. This result starkly contrasts the Dobrynin scaling prediction\(^6\), that $c_e$ be proportional to $c^*$. The Dobrynin model predicts correctly the strong decrease of $c^*$ with increasing $f$ (see Fig. 2.6) but instead of a similar strong decrease of $c_e$, the entanglement concentration actually weakly increases with increase in $f$. Similarly, the overlap concentration for electrostatic blobs $c^{**}$ of weakly charged polymers is less than that of strongly charged polyelectrolytes because the weakly charged polymers have larger electrostatic blobs (see Table 2.1 and explanation in the next section). Interestingly, $c^{**}$ of the strongly charged polyelectrolytes is essentially the same as the entanglement concentration of the neutral P2VP (0.95 M). At higher concentrations $c > c^{**}$, the specific viscosity of the weakly
charged polymers increases with increasing concentration in a power law of $\eta_{sp} \sim c^{3.75}$ (theory: $\eta_{sp} \sim c^{15/4}$), which is identical to the value of de Gennes’ prediction for neutral polymers in good solvent.\textsuperscript{4} It is interesting to find that the weakly charged 3PMVP-Cl in ethylene glycol has the highest specific viscosity among all the polymers studied when the polymer concentrations are larger than 0.75 M. Apparently, Dobrynin scaling model\textsuperscript{6} provides reasonable predictions for the experimental results on the concentration dependence of the specific viscosity of polyelectrolyte solutions.

![Figure 2. 6](image)

**Figure 2. 6** Effective charge dependence of the chain overlap concentration $c^*$ (circles), entanglement concentration $c_e$ (stars) and overlap concentration of electrostatic blobs $c^{**}$ (triangles). The chain overlap concentration exhibits the scaling predicted by Eq. 2.5 up to the onset of counterion condensation, while the apparent trends for entanglement concentration and overlap concentration of electrostatic blobs are shown as power laws but are not understood. Note that the neutral parent polymer (P2VP) has significantly larger $c^* = 0.057$ M and $c_e = 0.95$ M because there is no charge repulsion to stretch the chain.
2.4.2 Electrostatic blob size and the parameter $B$

The parameter $B$ is of great importance for polyelectrolyte solutions. The actual contour length $L$ of the chain of electrostatic blobs in good solvent is much shorter than the fully extended length $N_b$ of a polyelectrolyte chain because of the self-avoiding walk conformation inside the electrostatic blobs (Eq. 2.2). The parameter $B$ is determined from the overlap concentration $c^*$ ($B \approx b N_b^{2/3} c^{*1/3}$, Eq. 2.5) and listed in Table 1. In this study, the number of monomers $g_e = B^{5/2}$ and size $\xi_e = bB^{3/2}$ of a polyelectrolyte solution were estimated from $B$, and listed in Table 2.1. The weakly charged polyelectrolyte 3PMVP-Cl in EG has the largest $B = 9$ resulting in large electrostatic blobs $\xi_e = 68 \text{ Å}$, while those of the strongly charged polyelectrolytes ($B = 5.5$ and $\xi_e = 32 \text{ Å}$) are much smaller due to their higher effective charge. Counterion condensation makes the four strongly charged polyelectrolytes have similar $B$, $g_e$ and $\xi_e$. However, $B = 5.5$ for the strongly charged polyelectrolytes is significantly larger than $B = 2.8$ determined from SANS data.\(^7\) Owing to unknown prefactors in any scaling model, the apparent $B$ deduced by assuming all prefactors are unity can be different from different experiments. A recent study comparing $B$ from rheology and scattering finds similar differences in $B$ for various polyelectrolytes in water.\(^32\) The product $f g_e$ (also listed in Table 2.1) tells the number of effective charges per electrostatic blob, which runs from 7 for the weakly charged polyelectrolytes to 13 for the strongly charged polyelectrolytes.
Note that all polymers in this study have the same degree of polymerization $N$. The concentrations $c^*$, $c_e$, and $c^{**}$ should depend only on the effective charge, since $N$, $b$, and $l_B$ are constants in EG at 25 °C. The $c^*$, $c_e$, and $c^{**}$ of our polyelectrolytes in EG listed in Table 1 are plotted against the effective charge $f$ in Fig. 2.6. The overlap concentration of polyelectrolytes depends strongly on effective charge $f$, and the Dobrynin scaling theory\(^6\) exactly predicts this dependence (Eq. 2.5) until counterion condensation occurs. Weakly charged 3PMVP-Cl and 4PMVP-Cl polyelectrolytes have relatively high overlap concentrations (0.0075 M and 0.0054 M, respectively), while counterion condensation forces the strongly charged polymers with degree of quaternization $\alpha$ from 0.10 to 0.55 to have similar $f$ and similar overlap concentrations (0.0016 ~ 0.0018 M). Neutral polymer P2VP ($f = \alpha = 0$) has the highest overlap concentration $c^*$ and entanglement concentration $c_e$ because there are no electrostatic interactions stretching the chain.

However, the scaling theory\(^6\) does not predict $c_e$ correctly. The scaling model expects the plot of $\eta_s c^*/c$ versus $c/c^*$ (Fig. 2.4b) to be universal for all neutral, weakly charged, and strongly charged polymers up to $c^{**}$ because $c_e$ is predicted to be proportional to $c^*(10^3 \leq c_e/c^* \leq 10^4)$. It has been reported that $c_e/c^*$ depends on chain length $N$ in aqueous polyelectrolyte solutions (NaPSS/water\(^8\), NaPAMS/water\(^9\), and NaIBMA/water\(^32\)). The entanglement concentration is predicted to be simply proportional to $c^*$ but since $c_e/c^*$ depends on $N$ and $f$ we conclude that the scaling theory fails to describe entanglement in polyelectrolyte solutions.
2.4.3 Relaxation time $\tau$ and terminal modulus $G$

The relaxation time $\tau$ of polyelectrolyte solutions at concentrations below $c_e \cong 0.23$ M was determined by fitting the Carreau model (Fig. 2.2 and Eq. 2.17) from the steady shear measurements. At concentrations above 0.037 M relaxation time was determined from the oscillatory shear viscosity measurement ($G'$ and $G''$). The relaxation times determined from steady and oscillatory shear experiments overlap in the concentration regime from 0.037 to 0.23 M, as shown in Fig. 2.7. The relaxation times of 17PMVP-Cl in EG were plotted against concentration in Fig. 5 to compare the concentration dependences of $\tau$ and $\eta_{sp}$ in the same concentration region.

![Figure 2.7](image)

**Figure 2.7** Concentration dependence of relaxation time determined from fitting the Carreau model (Eq. 2.17) to the shear rate dependence of apparent viscosity (filled symbols) and oscillatory shear measurements (open symbols).
Figure 2.8 Concentration dependence of terminal modulus ($G = \eta/\tau$) calculated from steady shear relaxation time (filled symbols) and oscillatory shear relaxation time (open symbols) compared with the Dobrynin scaling predictions (solid lines) of $G = c k T / N$ for \( c < c_c \) and $G \sim c^{3/2}$ for \( c > c_c \).

In the steady shear measurements, shear thinning of the polyelectrolyte solutions was observed at high shear rates. The shear thinning of neutral P2VP solutions was only observed in the semidilute entangled regime, owing to the low molecular weight of our P2VP sample. In semidilute unentangled solutions, the relaxation times of the polyelectrolyte solutions decrease with increasing concentration ($\tau \sim c^{-1/2}$) as predicted by the Dobrynin theory and increase with increasing effective charge (see Eq. 2.9). The weakly charged 3PMVP-Cl solutions have the shortest relaxation times. Increasing the effective charge of the quaternized polymers significantly increases the relaxation times of the polyelectrolyte solutions due to the electrostatic interactions making the chain contour length effectively longer. However, unlike the viscosity data plotted in Fig. 2.3,
the relaxation time data in Fig. 2.7 show $\tau$ increasing with $\alpha$ even for the strongly charged polymers, where counterion condensation makes them all have quite similar effective charge. In particular, the effective charges of the 42PMVP-Cl and 55PMVP-Cl polymers are quite similar due to counterion condensation, yet these polymers have quite different relaxation times. The number of condensed ion pairs on the polymer chains increases with the quaternization extent $\alpha$ and the resulting dipolar attraction\(^{14}\) could conceivably change the local conformation, effectively reducing the excluded volume pairwise interaction between monomers in EG. However, such changes should be reflected in the overlap concentration and $c^*$ seems insensitive to $\alpha$ in this range (see Fig. 2.6 and Table 2.1). Consequently, these differences in relaxation time observed for the strongly charged polymers are not understood.

In the highly concentrated regime for neutral P2VP, the relaxation times increase rapidly with increasing concentration in a power law $\tau \sim c^{3.6}$, while the relaxation times of the weakly charged polymer 3PMVP-Cl and 4PMVP-Cl solutions increase with increasing concentration as power laws with exponents 3.0 and 2.5, respectively. The strongly charged PMVP-Cl solutions show slightly weaker concentration dependence\(^{33}\) ($\tau \sim c^2$). Hence, the concentration dependence of the relaxation times of polymers in solution is a function of effective charge, while the Dobrynin model expects the polyelectrolytes to be indistinguishable from the neutral polymer for $c > c^{**}$ and show concentration dependence of $\tau \sim c^{3/2}$. The weakly charged 3PMVP-Cl has the highest relaxation time and the neutral P2VP has the lowest relaxation time at the same concentration above $c^{**}$ (or $c_e$ for the neutral P2VP). It can be concluded that the
relaxation time of the polymer solutions in EG is both charge density and concentration dependent.

Scaling theories\textsuperscript{6,34,35} predict that the relaxation time of a polyelectrolyte solution without added salt decreases with increasing concentration $\tau \sim c^{-1/2}$ in the semidilute unentangled regime. These predictions are based on the Rouse model and the assumption that the polyelectrolyte chain is a random walk of correlation blobs. Dobrynin, et al. predicted the relaxation time is independent of concentration in the semidilute entangled regime.\textsuperscript{6,35} These predictions below $c^\ast\ast$ were qualitatively observed for all polyelectrolyte solutions in EG.

The ratio of zero-shear-rate viscosity and relaxation time determines the terminal modulus of polymer solutions $G = \eta/\tau$.\textsuperscript{4,23} Fig. 2.8 shows the concentration dependence of the terminal modulus. The terminal modulus is $kT$ per chain for $c^* < c < c_e$, in quantitative agreement with Eq. 2.10. For $c > c_e$ the terminal modulus shows the scaling expected by Eq. 2.14 ($G \sim c^{3/2}$) for entangled polyelectrolyte solutions, but shows no sign of the stronger concentration dependence expected for $c > c^\ast\ast$ ($G \sim c^{9/4}$). Fig. 2.7 suggests $c^\ast\ast > 3$ M, although the independent results from viscosity and relaxation time (from which $G$ is calculated!) suggest $c^\ast\ast$ is considerably smaller.

2.5 Conclusions

We varied the charge density of a polymer chain at a fixed chain length to investigate the influence of charge density on the rheology of salt-free polyelectrolyte
solutions. Polyelectrolyte solutions in EG appear to be truly salt-free, with negligible ionic impurities. Consequently, there is no local maximum in the concentration dependence of their reduced viscosity and scaling works beautifully even far below $c^*$, where the specific viscosity is simply proportional to concentration. The overlap concentration decreases with increasing effective charge as the power law $c^* \sim f^{-12/7}$ predicted by scaling\textsuperscript{6,18,34} until $\alpha = 0.10$. At higher extents of quaternization, counterion condensation dominates, making $c^*$ independent of $\alpha$, although $f$ unexpectedly continues to change. Counterion condensation makes the viscosity of samples with $0.1 < \alpha < 0.55$ in EG equal at $c < c^*$ and slightly different above $c^*$, while the relaxation times of charged polymers in EG show a clear dependence on charge density. The weakly charged polyelectrolytes have large electrostatic blobs, resulting in a short contour length (large $B$), and strongly charged polyelectrolytes have smaller electrostatic blobs (small $B$). Dobrynin theory\textsuperscript{6} qualitatively describes viscosity and relaxation time for $c < c^{**}$ as well as modulus for the entire concentration regime. For $c > c^{**}(\approx 0.8$ M), the scaling model expects polyelectrolyte solutions to be rheologically indistinguishable from the neutral solutions, which is only qualitatively observed. At these high concentrations, the neutral polymer has the lowest viscosity and shortest relaxation time, the weakly charged polyelectrolyte (3PMVP-Cl) has the highest viscosity and longest relaxation time, and the strongly charged polyelectrolytes are between these limits. Such an observation suggests that much remains to be understood for high concentration polyelectrolyte solutions.

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2.6 References


33. The smaller exponent of 1.2 observed in Fig. 5 for the relaxation time of 17 PMVP-Cl at the highest concentrations in EG simply reflects the limited data range studied for that particular sample (see Fig. 2.7).


Chapter 3

Solvation of Polyelectrolyte Solutions Investigated by Dielectric Spectroscopy, SAXS, and Rheology

3.1 Introduction

Polyelectrolytes are polymer chains bearing positive or negative ionizable monomers. In polar solvents such as water, polyelectrolytes dissociate into polyions and counterions (small ions) and show some of the properties of polymers and simple electrolytes in a particular manner. Theoretical studies have suggested that the short-range interactions (between the chain backbone monomers) and the electrostatic repulsion (between charges) lead to a pearl-necklace conformation of polyelectrolytes in poor solvent.1-4 The interactions between backbone monomers with no effective charge lead to a locally collapsed conformation because of unfavorable monomer-solvent interactions, while the interactions between charges stretch the chain to an extended conformation. Polyelectrolytes in poor solvent show a cascade of abrupt transitions of configurations between globule and necklace with larger numbers of pearls as the charge on the chain is increased.1,2 For strongly charged polyelectrolytes, counterion condensation plays a vital role.5 Condensed counterions can cause phase separation of polyelectrolytes in poor solvent (dilute and concentrated phase) due to dipole-induced attraction.6,7 Charge density, solvent dielectric constant, and solvent quality significantly affect chain conformation, and chain contour length of polyelectrolytes in solution.5,8-22
Solvation of polyelectrolytes is crucial for understanding the properties of polyelectrolyte solutions because the chain conformation is dominated by both short-range interactions between chain segments, dipole-dipole and dipolar-charge attractions, and long-range electrostatic repulsion between charges. A cascade of variations in conformation (solvation transition) of polyelectrolytes has been clearly observed in the experiments of light scattering, proton NMR, and AFM.

Beer et al.\textsuperscript{23} reported that in light scattering measurements the counterion size, solvent dielectric constant, and the backbone hydrophobicity of quaternized poly(2-vinyl pyridine) (Q-P2VP) significantly influence the effective charge density $f$ and net excluded volume $w$ parameter ($\theta$ solvent: $w = 0$) of Q-P2VP in solution. They indicated that water imparts net positive excluded volume ($w > 0$) for sodium poly(styrenesulfonate) NaPSS ($\alpha = 0.9$, $f = 0.3$). Hence, solvation of hydrophobic polymers (polystyrene) in water is favored by the level of ionization. However, in theory, water is a poor solvent for polyelectrolytes made from parent polymers with hydrophobic backbone as seen in the development of theoretical models for polyelectrolytes in poor solvent.\textsuperscript{2,6,7,10} The resolution of this apparent contradiction is trivial because SANS clearly shows that strongly charged NaPSS is locally collapsed in water, with collapsed cylinder diameter $\sim 1.2$ nm.\textsuperscript{24} On larger scales charge repulsion stretches the chain to give it a positive net excluded volume in light scattering.

A $^1$H NMR study from Spevacek et al.\textsuperscript{25} shows that both linear and crosslinked poly(N,N,-diethylacrylamide) in D$_2$O collapse during a temperature-induced phase transition, owing to the variation of solvent quality. The NMR spectra of NaPSS,
NaPAA, NaPMA, and poly(acrylamide) (PAAm) solutions decrease when those polyelectrolytes precipitate in solution, as they lose their liquid character. Lee et al. indicated that for neutral polymers the coil-globule transition occurs in a single step and results in phase separation, whereas for polyelectrolytes, the polymer chains in solution first adopt a pearl-necklace conformation locally, with larger beads as solvent quality is lowered, finally collapsing to a globule and precipitating from solution.

Atomic force microscopy (AFM) has proved to be a very successful technique for imaging and characterizing polymers at surfaces. Minko and coworkers reported that the chain conformation and morphology of polyelectrolytes gradually changes from coil to pearl necklace conformation then into globules or big clusters when the concentration of added salt is increased, based on AFM images of poly (methacryloyloxyethyl dimethylbenzylammonium chloride) single chains (with large hydrophobic group) deposited from aqueous solutions. A similar cascade of transitions was observed for single flexible Q-P2VP (charge density $\alpha > 0.5$ at pH = 2 in HCl/water) when the concentration of added salt (NaCl) was increased gradually. The radius of gyration for highly quaternized Q-P2VP in water and organic solvents was found to gradually decrease with increasing concentration of added salt until a significant reduction in $R_g$ at high salt concentration $c_s \sim 1$M just before the polymer precipitates. This result clearly proves that water is a poor solvent for Q-P2VP, consistent with the fact that neutral P2VP does not dissolve in water. As salt is added to polyelectrolytes in poor solvent, the charge repulsion that imparts a positive net excluded volume is screened and the poor solvent interaction takes over causing the polymer to “salt out”.

47
The degree of ionization, solvent dielectric constant, hydrophobicity, counterion size, and salt concentration are significant factors that impact the solvation of polyelectrolytes. Polyelectrolytes in poor solvents can have positive net excluded volume. For instance, water (a solvent with high dielectric constant) imparts positive net excluded volume for polyelectrolytes with a high degree of ionization even if the parent polymer is hydrophobic, such as polystyrene (1H NMR result\textsuperscript{26}). Conversely, good solvents can impart negative net excluded volume. For instance, methanol (a solvent with low dielectric constant) is a good solvent for PAA, while NaPAA with a high degree of ionization precipitates from methanol solution due to counterion-induced attraction between condensed ion pairs.\textsuperscript{26} Those observations suggest that the solvent dielectric constant and the degree of ionization of polyelectrolytes are the primary factors that influence the solvation of polyelectrolytes in solution.

As reviewed above, solvent quality is affected by solvent dielectric constant, degree of ionization, and counterion condensation. Counterion condensation is dominated by the Bjerrum length $l_B$, the distance where the thermal energy exactly compensates the coulomb interaction energy between two elementary charges

$$ l_B = \frac{e^2}{\varepsilon k_B T} $$

where $e$ is the elementary charge, $\varepsilon$ is the dielectric constant of solvent, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. According to Manning counterion condensation theory,\textsuperscript{5} the maximum fraction of monomers bearing an effective charge (effective charge density) $f_{\text{max}}$ can be estimated from the Oosawa relation\textsuperscript{31}

$$ f_{\text{max}} = \frac{b}{l_B} $$

(3.2)
where $b$ is the average monomer length. The relevant monomer size depends on solvent quality\cite{32,33}. In a good solvent, the local conformation is swollen and $b$ is the monomer length along the chain contour ($b \approx 2.5$ Å for vinylic monomers\cite{33}). In a poor solvent the chain is locally collapsed and the relevant monomer size is presumably the cube root of the monomer volume by the scaling theory\cite{10} ($b \approx 5$ Å for vinylic monomers). However, let’s thinks about a polyelectrolyte with a degree of ionization 50%. If this polyelectrolyte dissolves into a poor solvent, ionic monomers and monomers with condensed ion pairs are favorable in the solvation, while the neutral monomers are unfavorable in the solvation. Solvent quality, side chain length, and degree of ionization (of polyelectrolytes) may impact the monomer length $b$ of polyelectrolytes in both good and poor solvents\cite{33}. NaPSS (the sodium salt of sulfonated polystyrene) with $\alpha > 0.9$ shows a positive net excluded volume, reflected in the second virial coefficient, in water.\cite{23}

In this study, $b$ is assumed to be 2.5 Å on average for good and poor solvent cases.

The interaction energy $U(r)$ between monomers or segments separated by a distance $r$ obeys Eq. 3.3.\cite{23}

$$\frac{U(r)}{k_BT} = w\delta(r) + \frac{z^2\mu b^4 e^{-r/r_D}}{r} \quad (3.3)$$

where $w$ is the net excluded volume strength (which greatly depends the solvation of polyelectrolytes in solution, for $\theta$ solutions, $w = 0$), $\delta(r)$ is the Dirac delta function, $z$ is the valence of the ionic group, $r_D$ is the Debye length. Throughout this chapter the term “solvent quality” indicates the solubility of a polyelectrolyte in solvent in terms of good solvent (in which polyelectrolyte chains show a local self-avoiding swollen conformation
inside their electrostatic blobs) and poor solvent (in which polyelectrolyte chains show a pearl-necklace or collapsed globular local conformation in solution).

In semidilute solutions, the solvation of polyelectrolytes is the same as in dilute solutions, however the interactions between polyelectrolyte chains dominate the conformation of polyelectrolytes and counterion condensation can become significant, owing to the interactions between charges. On length scales smaller than the electrostatic blob size $\xi_e$, polyelectrolytes in good solvent adopt a self-avoiding swollen conformation inside the electrostatic blob.\cite{10} However in poor solvent, polyelectrolytes collapse and have a pearl necklace conformation due to unfavorable non-electrostatic interactions between monomers and solvent molecules.\cite{34} On length scales larger than the electrostatic blob size and smaller than the correlation blob size (Debye screening length), polyelectrolytes with no added salt have an extended conformation of electrostatic blobs in both good and poor solvent in the semidilute region because of the electrostatic repulsion between the electrostatic blobs. The distance between chains is defined as the correlation length $\xi$ of a polyelectrolyte solution, which can be estimated by SAXS, SANS, AFM and rheology.\cite{10,11,18,35-38}

For linear flexible polyelectrolytes, the pearl-necklace model has been studied by many researchers,\cite{6,7,34,39} however those studies were restricted to counterion condensation effects on the conformation of hydrophobic polyelectrolytes or polyelectrolytes in poor solvent. Few investigators have paid attention to the counterion induced attraction of polyelectrolytes in good solvent, the ordered structure of the solvent itself, and the solvation of polyelectrolytes in semidilute solution on the solution properties.
In this chapter, we estimate the solvation of quaternized poly(2-vinyl pyridine) with iodide counterions in solution in five different solvents. The solvent dielectric constant is in the range $37 < \varepsilon < 182$. Solvation of polyelectrolytes will be discussed in terms of residual salt in the solvent, solvent dielectric constant, solvent quality, ordered structure of solvent (hydrogen-bonding), and solvent molecular weight. Considering those terms, polyelectrolyte behavior will be discussed according to the results from dielectric spectroscopy, SAXS, and rheology.

\[
\begin{align*}
\left[ \text{CH}_2\text{CH} \right]_n & \quad \xrightarrow{1. \text{(CH}_3\text{)}_2\text{SO}_4/ \text{DMF}} \quad \left[ \text{CH}_2\text{CH} \right]_x \left[ \text{CH}_2\text{CH} \right]_y \\
\text{P2VP(h): M}_w & = 1,222,000, \text{ PDI} = 1.10, N = 10500 & \text{60PMVP-X; } X = \text{I, Cl} \\
& & \text{4PMVP-X; } X = \text{I}
\end{align*}
\]

**Figure 3.1** Quaternization and counterion exchange for poly (2-vinyl pyridine).

### 3.2 Experimental

#### 3.2.1 Polymers

Poly(2-vinyl pyridine) (P2VP(h), $M_w = 1,220,000$ g/mol, $M_w/M_n = 1.1$, $N = 10500$, based on $M_n$) purchased from Polymer Source, Inc. was used without further purification. Random copolymers of 2-vinyl pyridine and N-methyl-2-vinyl pyridinium chloride or iodide (PMVP-Cl and PMVP-I) were prepared by quaternization and ion-exchange (Fig.3.1). The degree of quaternization $\alpha$ in this chapter is either 60% or 4%.
The details of the polyelectrolyte preparation and characterization were described previously (reference 22 and Chapter 2).

### 3.2.2 Autoprotolysis, stability, and residual salt

Autoprotolysis is the proton transfer reactions between two identical molecules, one acting as a proton donor and the other as a proton acceptor, the classical example is HS.\(^{40}\)

\[
\text{HS + HS} \rightleftharpoons \text{H}_2\text{S}^+ + \text{S}^- \tag{3.4}
\]

The ionization of water in organic solvent can be considered simultaneously.

\[
\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HO}^- \tag{3.5}
\]

\[
\text{HS} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{S}^+ + \text{HO}^- \tag{3.6}
\]

\[
\text{HS} + \text{H}_2\text{O} \rightleftharpoons \text{S}^- + \text{H}_3\text{O}^+ \tag{3.7}
\]

Quite generally,

\[
\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{HB}^+ + \text{HO}^- \tag{3.8}
\]

where B is any proton acceptor such as carbon dioxide (CO\(_2\)) or sulfur dioxide (SO\(_2\)), which are molecules that show acidity in water and some other organic solvents. If a solvent is exposed to atmosphere and carbon dioxide or other acidic gases dissolve, the proton transfer reaction Eq. 3.8 can be a source of residual salt in the solvent. The protolysis equilibria of the water (H\(_2\)O) and organic solvent (HS) binary mixture include all four ionization processes shown above.\(^{41}\) The negative logarithm of the general
equilibrium constant $K_a$ obtained from Eqs. 3.4-8 is defined as the $pK_a$, which is produced by the proton transfer between water and organic solvent based on their molar fraction in the mixture. Lower $pK_a$ value indicates stronger acidity.\textsuperscript{41}

![Chemical structures](image)

**Figure 3.2** Solvent chemical structures and acronyms.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$pK_a$</th>
<th>$\varepsilon$</th>
<th>$\sigma_s$ ($\mu S/cm$)</th>
<th>$\eta_s$ (cp)</th>
<th>$l_B$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG</td>
<td>17.4</td>
<td>37</td>
<td>0.2</td>
<td>17.1</td>
<td>15</td>
</tr>
<tr>
<td>DW</td>
<td>7</td>
<td>78.4</td>
<td>4.0</td>
<td>0.89</td>
<td>7.1</td>
</tr>
<tr>
<td>GC</td>
<td>N/A</td>
<td>109.6</td>
<td>8.3</td>
<td>95.5</td>
<td>5.1</td>
</tr>
<tr>
<td>F</td>
<td>17*</td>
<td>109.6</td>
<td>77</td>
<td>3.26</td>
<td>5.1</td>
</tr>
<tr>
<td>NMF</td>
<td>10.74</td>
<td>182</td>
<td>16</td>
<td>1.74</td>
<td>3.1</td>
</tr>
</tbody>
</table>

17* value at 20 °C

### Table 3.1 Summary of the solvent properties at 25 °C

#### 3.2.3 Solvents

Solvent properties after purification are summarized in Table 3.1. Ethylene glycol (EG: J. T. Baker, 99.8%; anhydrous; bp 198 °C; water < 0.02 %), Formamide (F: bp 210 °C, mp 2-3 °C, density 1.134 g/ml, grade ACS reagent ≥ 99.5%) and N-methylformamide (NMF: bp 198-199°C, mp -4°C, density 1.011 g/ml, grade ACS
reagent ≥ 99.0%) were purchased from Aldrich. Glycerine Carbonate (alternative name: 4-hydroxymethyl-1,3-dioxolan-2-one) (GC: glycerine carbonate ≥ 91%, water ≤ 0.06%, boiling range 125-130 °C at 0.1 mmHg) was kindly provided by Huntsman Corporation in Houston. Anhydrous EG, NMF, and F were each soaked in 4 Å active molecular sieves over 48 hrs, stirred, filtered, and then distilled under reduced pressure (< 100 mTorr) at temperature lower than 80 °C. The distillation procedure was repeated twice for the middle fraction. The entire process was protected under argon. GC was treated through the same procedure as that for EG, NMF and F except without distillation before use due to its high boiling point.

Formamide: Porras and Kenndler\textsuperscript{42} summarized the $pK_a$ values of neutral acids and cation acids between formamide (F) and water, and concluded that the influence from trace amounts of water (less than 1 wt %) is insignificant. The major impurities in commercial analytical grade formamide are water, ammonia, and formate. Formamide is a strongly hygroscopic solvent due to the formation of hydrogen-bonds with water (solvation). F can absorb large amounts of water (up to 4.0 wt %) at 21 °C and relative humidity 98% in 6 hrs (if pure F is exposed to air with high humidity)\textsuperscript{42}. Although F is chemically stable to water at room temperature, it can slowly hydrolyze into formic acid and ammonia, forming ammonium and formate\textsuperscript{42,43}. In the exposure of 8 hrs to atmospheric moisture, F reaches about the same concentration of the residual salt as in the “as received” formamide which shows strong ionic effects in capillary electrophoresis\textsuperscript{42}. It is possible that carbon dioxide dissolves in formamide and produces residual salt in F similar to Eq. 3.8
**N-methyl formamide**: NMF is a N-monoalkylated amide solvent with very high dielectric constant (182 at 25 °C) and shows both acidic and basic character by donating or accepting a proton. Oncescu et al.\(^44\) reported that the conductivity of NMF at 25 °C is 0.7 \(\mu S/cm\) after being carefully purified. However, Sehgal and Seery\(^45\) indicated that the concentration of residual salt in NMF “as received” is larger than 0.02 M and the conductivity of NMF “as received” is 509 \(\mu S/cm\),\(^45\) which is much larger than the conductivity of NMF purified by distillation (16 \(\mu S/cm\) in this study, 0.7 \(\mu S/cm\) reported by Oncescu et al.\(^44\)). NMF is a strongly hygroscopic solvent; it can absorb water and carbon dioxide and then slowly hydrolyze to form ammonia, formate, and carbonate due to its molecular structure and high dielectric constant. NMF demonstrates very low \(pK_a\) (10.74) compared to 17 for F and 18 for EG. Hence, NMF is a powerful dissociating solvent\(^44\) and acts as a protic solvent in the solvation of ions.\(^46\)

As P2VP dissolves in NMF, the relatively “active” proton possibly forms a protonated hydrogen bonding structure O−−H-N\(^+\), where N is the nitrogen on the pyridine ring of the P2VP polymer. This may be the reason that NMF is a good solvent for P2VP but F is a poor solvent for P2VP. There exists strong hydrogen bonding in F, and while the autoprotolysis constant of F is much lower than that of NMF, F is not a protic solvent and the hydrogen bonding structure in F is predominantly N−−H-N, where the two nitrogens are from the solvent F. The electronegativity of the pyridine nitrogen is too low to catch an inactive proton from the formamide molecules to form a hydrogen bonding structure between P2VP and F molecules. In the study of dielectric relaxation of organic solvents F and NMF, Barthel et al.\(^47\) indicated that the correlation factor (the average
The number of H-bonds per molecule) of NMF is significantly larger (4.57 at 25°C) and greatly decreases with increasing temperature, compared to that of F (2.09 at 25°C). NMF predominantly forms a chainwise association linked by H-bonds with the single amino hydrogen, so that the adjacent molecular dipoles are almost parallel to each other (causing high dielectric constant), while for formamide the moderate increase in its correlation factor with increasing temperature indicates various associated forms with only one or two amino hydrogens.\textsuperscript{48}

**Ethylene glycol** EG is a very weak proton donor due to its low autoprotolysis constant $pK_a = 18$. EG is very stable at room temperature even though it is hygroscopic. EG has a small dipole and shows low dielectric constant like other alcohols. The solubility of carbon dioxide in EG is low and EG has low reactivity to CO$_2$. The formation of residual salt in NMF and F is primarily due to both the instability of those solvents in the presence of traces of water and the absorption of carbon dioxide or other acidic gases, as discussed above. Anhydrous EG has very low conductivity (0.2 $\mu$S/cm at 25 °C), suggesting that the concentration of ionic contaminant is extremely small. This gives EG an enormous advantage over water or other organic solvents such as F and NMF in the study of salt-free polyelectrolyte solution rheology.\textsuperscript{22} The low residual ion content in EG allows us to study polyelectrolyte solution rheology below the overlap concentration without significant effects of salt contamination.\textsuperscript{22} EG is a good solvent for the neutral parent poly(2-vinyl pyridine).

**Water** DW is an extremely stable solvent with $pK_a = 7$. It is a poor solvent for most uncharged polymers. However polymers with sufficient fraction of charged groups
(30% for NaPPS and 10% for PMVP-Cl, depending on the backbone hydrophobicity) can dissolve in water due to the solvation of charged monomers in water. Freshly distilled water not exposed to air has conductivity $4 \mu S/cm$. It is well-known that water can absorb carbon dioxide when exposed to air. Carbon dioxide dissolves in aqueous solutions and reacts with $\text{H}_2\text{O}$ to form carbonic acid imparting a salt concentration of roughly $4 \times 10^{-6} \text{ M}$ which shows considerably higher conductivity ($10 \ \mu S/cm$ at 25 °C).\textsuperscript{49-51} The ionization of carbon dioxide in water is similar to the reaction in Eq. (3.8). Hence, the proton transfer reactions in water include Eqs. 3.5 and 3.8.

**Glycerol carbonate** GC (also called glycerine carbonate) is an alcohol solvent with high dielectric constant (109).\textsuperscript{52} It is difficult to purify GC due to its high boiling point and instability at high temperature. GC (provided by Huntsman Corp. Houston, TX) contains small amounts of polyglycerol or other polyols (confirmed by proton NMR). Autopolymerization occurs at room temperature to form polyols. Hence, solvent viscosity may increase slightly with time. GC absorbs water and then can hydrolyze to form carbonic acid, glycerol, and dihydroxy-glycerol carbonate. Furthermore, GC may be able to undergo autoprotolysis to produce ionic components as shown in Eq. 3.4.

### 3.2.4 Conductivity measurement.

Conductivity measurements were performed with a broadband dielectric spectrometer (Novocontrol GmbH, Germany). The conductivity of fresh solvent and polyelectrolyte solutions in the concentration range from 0.01 to 10 mg/ml in a liquid cell (spacer: 0.55mm and diameter: 20mm) was measured at 25 °C, frequency range from 0.1 to $3 \times 10^6$ Hz, using 0.1V (AC). Conductivity was evaluated from the plateau in the real
part of the conductivity in the frequency range from $10^2$ to $10^4$ Hz. Equivalent conductance $\Lambda = (\sigma - \sigma_s)/c$ was determined from the conductivity of polyelectrolyte solutions ($\sigma$), the conductivity of solvent ($\sigma_s$), and the molar concentration of polyelectrolytes ($c$). The effective charge density of 60PMVP-I in NMF, F, DW, GC and EG was estimated by fitting the equivalent conductance in semidilute solution to the theoretical prediction\textsuperscript{12}(as described in section 3.3.1), as the mobility and equivalent conductance of iodide and the correlation length of the polyelectrolyte in solution are known in these solvents.

### 3.2.5 Small angle X-ray scattering

The X-ray measurements were performed on a Molecular Metrology SAXS instrument with Cu K\textalpha radiation source (wavelength $\lambda = 1.54$ Å) and a 12.5 cm x 12.5 cm two dimensional detector. The distance between sample and detector is 224 cm. Liquid cells with 25 $\mu$m mica windows were used to hold the polymer solutions for SAXS measurements. The beam path length of these liquid cells is 1.2 mm (for polymer solutions with concentrations $c < 20$ mg/ml) and 0.4 mm (for polymer solutions with concentrations $c \geq 40$ mg/ml). All measurements were done at 25 °C, and the total scattering counts of all polymer solutions were larger than 100,000. Scattering time significantly depends on the polyelectrolyte concentration, and counterion electron density. For instance, for 0.05 M 60PMVP-I/EG solution, 3hrs were needed and for 0.05M60PMVP-Cl/EG solution, 10hrs were needed. The scattering intensity from the
sample solution was subtracted from the background and then normalized by using the thickness, scattering time and transmission of the sample (see Appendix 3).

3.2.6 Rheology

The measurement details of the steady shear viscosity of polymer solutions were described previously in reference 22 and Chapter 2. The steady shear viscosity data of P2VP(h), 60PMVP-I and 60PMVP-Cl solutions were obtained at 25 °C using three rheometers: A Rheometric Scientific ARES (controlled strain) was used for highly concentrated solutions with viscosity above 20 Pa s, a Rheometrics Fluids Spectrometer (RFS-II, controlled strain) was used for concentrated solutions with viscosity in the range from 0.04 to 20 Pa s, and a computerized Contraves Low Shear 30 viscometer (controlled shear rate) was used for polymer solutions with viscosity less than 0.04 Pa s.

3.3 Results and discussion

3.3.1 Conductivity of polyelectrolyte solutions

The influence of solvent quality and solvent dielectric constant on the solvation of polyelectrolytes in solution in terms of good solvent and poor solvent for the neutral polymer has generated a number of experimental and theoretical studies over the past two decades. The electrical conductivity of polyelectrolyte solutions reveals the effective charge and extent of counterion condensation of polyelectrolytes in solution. The equivalent conductance $\Lambda$ of polyelectrolyte solutions is defined by Eq. 3.9
\[ \Lambda = \frac{(\sigma - \sigma_s)}{c} \]  

(3.9)

where \( \sigma \) is the conductivity of the polymer solution, \( \sigma_s \) is the conductivity of the solvent, and \( c \) is polymer concentration. Following the scaling model for polyelectrolyte semidilute solutions,\(^{10} \) Colby et al. developed a model for evaluating the effective charge density \( f \) from the equivalent conductance of polyelectrolyte solutions based on the effective charge density \( f \) of polymer chains in solution.\(^{12} \)

\[
\Lambda = f \left( \lambda_c + \frac{fc \xi^2 e^2 \ln(\xi / \xi_e)}{3\pi \eta_s} \right)
\]  

(3.10)

where \( f \) is the fraction of monomers bearing an effective charge, \( \lambda_c \) is the specific conductance of counterions, \( \eta_s \) is the solvent viscosity, \( \xi \) is the correlation length of polyelectrolytes in solution, \( \xi_e \) is the electrostatic blob size. It is noted that \( \xi_e \) depends on the solvent quality (swollen or collapsed local conformation).

\[
\xi_e = b \left( \frac{b}{f^2 l_B} \right)^{3/7} \]  

(good solvent)  

(3.11)

\[
\xi_e = b \left( \frac{b}{f^2 l_B} \right)^{1/3} \]  

(poor solvent)  

(3.12)

Solvents EG, GC and NMF are good solvents for the neutral polymer P2VP(h), whereas F and DW are poor solvents. Fig.3.3a shows that the conductivity of 60PMVP-I in EG, DW, GC, F, and NMF depends on concentration and solvent. 60PMVP-I in EG demonstrates the lowest conductivity due to the lowest dielectric constant of EG, suggesting that significant counterion condensation occurs in 60PMVP-I / EG solutions, as expected by the Manning counterion condensation model.\(^{5} \) While the conductivity of
60PMVP-Cl in EG is slightly higher than 60PMVP-I in EG, the smaller size of Cl\(^-\) presumably imparts a larger free energy of solvation, making the effective charge density of 60PMVP-Cl in EG higher than that of 60PMVP-I in EG\(^{54}\). Counterion size affects the effective charge density \(f\) and net excluded volume \(w\) when the counterion X of benzyl -quaternized poly (2-vinyl pyridine) PBzVP-X is changed from F\(^-\) (\(f = 0.25\)) to Cl\(^-\) (\(f = 0.21\)) to Br\(^-\) (\(f = 0.18\)) to I\(^-\) (\(f = 0.17\))\(^{23}\).

![Figure 3](image_url)

**Figure 3.** Concentration dependence of (a) conductivity and (b) equivalent conductance for quaternized 60PMVP-I in EG, DW, GC, F and NMF, 4PMVP-I in EG, and 60PMVP-Cl in EG at 25 °C. Symbols are experimental data and the solid line shows equivalent conductance of 60PMVP-I in F.

60PMVP-I in GC shows very low conductivity, compared to that of 60PMVP-I in F, even though F and GC have identical high dielectric constant (109) because GC is a much larger molecule than F, with 30x larger viscosity. 60PMVP-I in NMF shows the highest conductivity at high \(c\), followed by 60PMVP-I in DW and F. 4PMVP-I in EG
shows the lowest conductivity due to its lowest charge density ($\alpha = 0.04$). The conductivity of 60PMVP-I in GC or F does not vary much with dilution as the concentration of polyelectrolyte solutions approaches the concentration $c \approx 0.02\text{--}0.03\text{M}$ at which $\eta_r = 1$ because the residual salt dominates the conductivity of polyelectrolyte solutions in these solvents (as $c_s \gg fc$). This phenomenon was also clearly observed in the concentration dependence of the equivalent conductance of 60PMVP-I in F or GC (Fig. 3.3b).

In Fig. 3.3b, the equivalent conductance of 60PMVP-I in F is independent of concentration, and 60PMVP-I/GC shows a similar result. This concentration independence of equivalent conductivity of 60PMVP-I in F or GC does not suggest that there is no counterion condensation (which was assumed for 4PMVP-Cl in EG\textsuperscript{22}) in polyelectrolyte solutions but is evidence of a high residual salt concentration that is independent of polyion concentration. In the semidilute unentangled region, the equivalent conductance of 60PMVP-I in NMF increases slightly with dilution until the effects of residual salt become significant at concentration $c \approx 0.01\text{M}$. The weak increase in the equivalent conductance for $c \geq 0.01\text{M}$ in NMF is expected by Eq. 3.10 because $\ln(\xi/\xi_c)$ weakly grows on dilution in semidilute solution. The $\Lambda$ of 60PMVP-I in solvents F, GC and NMF is independent of $c$ at low concentrations because these solvents have considerable residual salt that is independent of $c$.

The two polymers in EG and the polymer in DW exhibit an increase in $\Lambda$ on dilution at low $c$ in Fig. 3.3b. There are two possible origins of this increase. Below the overlap concentration, condensed counterions are gradually released from the polyion,
increasing the effective charge $f$ until $f \to \alpha$ far below $c^*$ (with no condensation in the dilute limit).\textsuperscript{17,22,53,55} This explanation may be the sole reason at work in EG solutions, and was assumed to be the case in reference 22 and Chapter 2. However, in DW the increase is far too large to be explained by counterion release (also true for other polyelectrolytes such as NaPSS in DW\textsuperscript{12,53}). The large increase in $\Lambda$ of all polyelectrolytes in DW most likely indicates that the residual salt level is very sensitive to the presence of small amounts of polyion. Counterion release may also occur in DW below $c^*$ but this effect on $\Lambda$ is masked by an apparently much stronger effect of polyion on residual salt concentration, in which a small amount of polyion seems to boost the residual salt content over that of DW without any polyion.

Solvent viscosity drastically influences the conductivity of polyelectrolyte solutions. Counterions in solution move toward one electrode as a potential is applied, while polyions move toward the opposite electrode. Eq. 3.10 has two terms. The first term $f\lambda_c$ is the contribution from free counterions and the second term is the contribution from the polyions. Both terms are proportional to $1/\eta$ (directly evident in the second term). The effect of solvent viscosity on the specific conductance of a counterion is given by Eq. 3.13.

$$\lambda_c = \mu_e e = \frac{e^2}{6\pi\eta r_c}$$  \hspace{1cm} (3.13)

where $\mu_e$ is the mobility of counterions (ratio of velocity and field) and $r_c$ is the counterion radius. Putting the equivalent conductance of the counterion $\lambda_c$ into Eq. 3.10, one gets Eq. 3.14.
\[ \Lambda \eta_s = \frac{f e^2}{3\pi} \left( \frac{1}{2r_e} + f c \varepsilon^2 \ln \left( \frac{\varepsilon}{\varepsilon_0} \right) \right) \]  

(3.14)

It is important to point out that both \( f \) and \( r_e \) also depend on the particular solvent: \( f \) depends on the dielectric constant and solvent quality; \( r_e \) depends on the solvation sphere, strongly bound solvent molecules surrounding the counterion move with the counterion when it moves.

Figure 3.4 Concentration dependence of the product of equivalent conductance and solvent viscosity (cp) for quaternized 60PMVP-I in EG, DW, GC, F and NMF and 60PMVP-Cl in EG at 25 °C.

Fig. 3.4 compares the concentration dependence of the product of equivalent conductance and solvent viscosity of 60PMVP-I with different solvents and 60PMVP-Cl in EG. The values of \( \Lambda \eta_s \) at 0.01 M for 60PMVP-I increase systematically with solvent dielectric constant except for DW. A conclusion can be made from this observation: The
The effective charge density of 60PMVP-I in NMF, F, and GC is higher than that in DW and EG due to the high dielectric constants of NMF, F, and GC.

**Figure 3.5** Concentration dependence of the fitted effective charge density \( f \) determined from the equivalent conductance \( \Lambda \) and the correlation length \( \xi \) (obtained from rheology) at 25 °C by fitting to Eq. (3.10); \( \xi_c \) was determined from Eq. 3.11 for good solvents EG, NMF and GC, and from Eq. 3.12 for poor solvents DW and F.

Conductivity and osmotic pressure measurements are important methods to get the effective charge density of polyelectrolytes in solution. If the equivalent conductance of counterions \( \lambda_c \) and the correlation length \( \xi \) of polyions in solution are known, the effective charge density \( f \) can be estimated from Eq. 3.10. The specific conductance of I \(-\) in NMF\(^{56}\), F\(^{57}\), DW\(^{58}\), and EG\(^{59}\) is \( \lambda_c = 22.76, 16.6, 76.82, \) and 4.61 S/cm\(^2\)/mole, respectively. The \( \lambda_c \) of Cl\(-\) in EG\(^{59}\) is 5.07 S/cm\(^2\)/mole. The specific conductance of I \(-\) in GC (\( \lambda_c = 8.28 \) S/cm\(^2\)/mole) was roughly estimated from the
equivalent conductance of 60PMVP-I in GC at \( c = 0.105 \text{ M} \) by fitting to Eq. 3.10, 
assuming \( \Lambda = f \lambda_c \). While the fraction of the current carried by counterions does increase 
with polion concentration,\(^{12}\) this estimate of \( \lambda_c \) for \( I^- \) in GC may be too large by as 
much as a factor of two. The correlation length of 60PMVP-I in NMF, F, DW, EG, and 
GC was estimated from the results of specific viscosity in the semidilute unentangled 
region.\(^{10}\) NMF, EG, and GC are good solvents and Eq. 3.11 was used for estimating \( \xi_e \); 
while F and DW are poor solvents and Eq. 3.12 was used for estimating \( \xi_e \). The 
monomer length \( b = 2.5 \text{ Å} \) for all solvents.\(^{33}\)

| Polymer solution | \( \lambda_c \) \hspace{1cm} (Scm\(^2\)/mole) | \( B \) | \( f \) | \( \xi_e \) (Å) | \( g_e \) (M) | \( \eta \) (Scm\{2}/mole) | \( 2c_s/f \) | \( f^2/\varepsilon \) | \( \varepsilon \) (M) |
|------------------|---------------------------------|---|---|---|---|---|---|---|
| 60PMVP-Cl/EG     | 5.07                            | 6.4 | 0.066 | 12 | 13 | 1000 | 8.3E-05 | 2.5E-03 | 1.2E-4 |
| 60PMVP-I/EG      | 4.61                            | 11  | 0.027 | 26 | 49 | 900  | 1.4E-05 | 1.0E-03 | 2.0E-5 |
| 60PMVP-I/DW      | 76.82                           | 5.8 | 0.17  | 5.7| 800| 3.8E-04| 4.4E-03 | 3.7E-4 |
| 60PMVP-I/F       | 16.6                           | 14  | 0.078 | 11| 60 | 2.2E-03| 5.7E-02 | 5.5E-5 |
| 60PMVP-I/NMF     | 22.76                           | 2.3 | 0.23  | 8 | 7 | 1300 | 1.4E-03| 1.3E-02 | 2.9E-4 |
| 60PMVP-I/GC      | 8.28*                          | 4.7 | 0.051 | 27| 54| 140  | 3.1E-03| 1.2E-01 | 2.4E-5 |

1. \( \lambda_c \) from literature except for in GC where \( \lambda_c = \Lambda_{(20 \text{mg/ml})}/f \) was used.
2. \( B \) was determined from rheology as described in Chapter 2.
3. \( \xi_e \) was determined from Eq. 3.11 in good solvents (NMF, GC, and EG) and from Eq. 
   3.12 in poor solvents (F and DW).
4. \( g_e \) was determined by \( g_e = (\xi_e/b)^{5/3} \) in good solvent.\(^{65}\)
5. \( \eta \) was determined from the reduced viscosity of polyelectrolyte solutions (\( \eta \) of 
   60PMVP-I/GC was determined from \( 1/\varepsilon = 1/c_s \)) in the high salt limit).
6. \( c_s \) was determined from scaling\(^{10}\) by \( c_s = \left( \frac{f}{2} \right) \left( \frac{b}{B} \right)^2 N^{4/3} [\eta]^{5/3} \).
The effective charge density $f$ of 60PMVP-I was determined by fitting the measured equivalent conductance to Eq. 3.10. It was observed that the effective charge density of 60PMVP-I in DW slightly increases with dilution, while $f$ slightly decreases with dilution as 60PMVP-I in F and GC (Fig. 3.5). Table 3.2 shows that 60PMVP-I in NMF has the highest effective charge density, $f = 0.23$, followed by in DW, F, GC and EG. Those values are much lower than that expected by the Manning counterion condensation model ($f_{\text{max}} = b/l_b$, $f_{\text{max}} = 0.35$ in DW, $f_{\text{max}} = 0.49$ in F and GC, $f_{\text{max}} = 0.81$ in NMF, $f_{\text{max}} = 0.17$ in EG).\textsuperscript{5}

In Chapter 2, instead of using the specific conductance of Cl$^-$ in EG reported by Carmo Santos et al.,\textsuperscript{59} we assumed that 4PMVP-Cl has no condensed counterions, and that the concentration independent value of equivalent conductance $\Lambda = 1.7\times10^{-4}$ S/(cmM) corresponds to the polyelectrolyte with $f = \alpha = 0.04$. The similar equivalent conductance of 4PMVP-I in EG (Fig. 3.3b) of $\Lambda = 1.7\times10^{-4}$ S/(cmM), together with the similar specific conductance\textsuperscript{59} of Cl$^-$ (5.07 Scm$^2$/mole) and I$^-$ (4.61 Scm$^2$/mole) in EG make the assumptions used in Chapter 2 appear justified. However, the equivalent conductance of 60PMVP-I in EG is $\Lambda = 4.3\times10^{-4}$ S/(cmM) at high concentrations (see Fig. 3.3b), which is considerably smaller than that of 55PMVP-Cl ($\Lambda = 7.7\times10^{-4}$ S/(cmM) in Fig. 2.1). This suggests that if 4PMVP-I in EG is fully dissociated, then $f = 0.09$ for 60PMVP-I in EG, using the method of Chapter 2. However, using the literature value\textsuperscript{59} for the specific conductance of I$^-$ in EG is certainly preferable and suggests there is significantly more counterion condensation for 60PMVP-I in EG ($f = 0.027$, see Table 3.2).
Table 3.2 shows that the electrostatic blob size varies a lot with solvent dielectric constant and solvent quality. The size of electrostatic blobs of 60PMVP-I in NMF is about $\xi_e \approx 8 \, \text{Å}$ because of strong electrostatic stretching, while the electrostatic blob sizes of 60PMVP-I in EG and GC are much larger (26 and 27 Å, respectively). 60PMVP-I in DW shows the smallest electrostatic blobs ($\xi_e < 6 \, \text{Å}$) due to the strong solvation of ionic groups by water, requiring the ions to be at the surface. It is noticed that the effective charge density of 60PMVP-I in EG is much lower than that in other solvents and 60PMVP-I in EG has large electrostatic blobs due to significantly less electrostatic stretching owing to the lower dielectric constant of EG. The 60PMVP-I in GC demonstrates similar solvation and low $f$, although GC has a high dielectric constant (109). Aside from the unexpected low values of $f$, the solvating ability of EG, GC, and F is surprisingly similar, considering the big difference in dielectric constant of EG. Counterion effects were also found from the values of $f$, $\xi_e$ and $g_e$ of 60PMVP-I and 60PMVP-Cl in EG (Fig. 3.5 and Table 3.2).

The dielectric constant and viscosity of solvent significantly impact the equivalent conductance of 60PMVP-I solutions. The $f$ of polyelectrolytes can be estimated from the $\Lambda$ and the $\xi$ by fitting Colby’s scaling prediction.\textsuperscript{12} The fitted effective charge density $f$ of 60PMVP-I in NMF and DW in this study is roughly in agreement with the results obtained from the light scattering results of Q-P2VP solutions reported by Beer et al.\textsuperscript{23} However, the effective charge density is much smaller than $f_{\text{max}}$ predicted by the Manning model of counterion condensation and estimated by the method of Chapter 2 (e.g. 60PMVP-I in EG, $f = 0.09$). Therefore, it is possible that there are many
counterions condensed onto the polyions and the polyions locally collapse due to the counterion-induced attraction. The collapsed polyions become shorter and lead to a much lower effective charge density $f$, considering the number of effective charges depends on the repeat unit between charges $l$ (the direct distance between two effective charges). 60PMVP-I in EG and GC shows significant chain collapse and a very large electrostatic blob size.

### 3.3.2 Small angle X-ray scattering

Polyelectrolytes in both good and poor solvent have identical conformations on scales larger than the electrostatic blobs but different conformations on scales inside the electrostatic blobs (Fig. 3.6). On length scales larger than the electrostatic blobs and smaller than the correlation length, the polyelectrolytes in the low salt limit show a strongly extended conformation in both good and poor solvent because of the electrostatic repulsion between electrostatic blobs. The distance between chains is defined as the correlation length $\xi$ of a polyelectrolyte solution. Polyelectrolyte chains in semidilute solution show a random walk conformation of correlation blobs.

The difference in electron density of different part of a sample provides contrast in X-ray scattering. The electron density of counterions dominates the scattering unless the polyelectrolytes without counterions show higher electron density than its environment such as sulfonated poly(vinyl alcohol) in water. To get higher scattering intensity from the polyion backbone or electrostatic blobs, iodide and chloride were used as counterions for the quaternized polymers in the study. In the small angle X-ray
scattering experiment, $I(q)$ exhibits a maximum corresponding to the correlation length of polyelectrolyte solutions because interchain charge repulsion forces the intermolecular separation to be quite close to a single length $\xi$. The wavevector $q_{\text{max}}$ at the maximum of $I(q)$ determines the correlation length of polyelectrolytes in solution.\textsuperscript{10,61}

$$\xi = \frac{2\pi}{q_{\text{max}}} \quad (3.15)$$

The correlation length $\xi$ is the typical distance between two adjacent extended chains of electrostatic blobs (see Fig. 3.6).
Figure 3.7 The SAXS profiles for 60PMVP-I in EG, DW, GC, F, and NMF at concentration 20mg/ml; $I(q)$ was determined by subtracting the background scattering intensity and then normalized by the sample thickness, scattering time, and sample transmission (see Appendix 3).

Fig. 3.7 shows the scattering profiles of 60PMVP-I in solvents EG, DW, GC, F, NMF at a typical concentration 20mg/ml (0.105 M). Fluctuations in interchain distance from the mean value $\xi$ are controlled by coulomb repulsion between neighboring chains. At 20 mg/ml, Fig. 3.7 shows that the $q_{\text{max}}$ (wavevector of the peak, see Eq. 3.15) is in the range from 0.04 to 0.06 Å$^{-1}$, controlled by the dielectric constants of the solvents. However, Coulomb’s law suggests that the peak integral intensity will be controlled by the dimensionless parameter $f^2/\varepsilon$. The $f^2/\varepsilon$ values of 60PMVP-I in solution (Table 3.2) suggest that the strongest peak is for 60PMVP-I in DW ($f^2/\varepsilon = 3.7\times10^{-4}$), followed by in NMF ($f^2/\varepsilon = 2.9\times10^{-4}$), having nearly as strong a SAXS peak. 60PMVP-I in the
other solvents EG, F and GC show weaker SAXS peaks because the \( f^2/\epsilon \) values of those polyelectrolyte solutions are considerable smaller (Table 3.2). Weaker charge repulsion (smaller \( f^2/\epsilon \)) allows more fluctuations that broaden the SAXS peak in the low salt limit. 60PMVP-I in GC does not show a polyelectrolyte behavior at 20 mg/ml = 0.105 M because 60PMVP-I in GC has the highest residual salt \( c_s = 0.003 \) M and \( 2c_s/\epsilon = 0.12 \) M among all polyelectrolyte solutions (see Table 3.2). Hence, 20mg/ml is the high salt limit where the SAXS peak disappears.\(^{10,61}\) No SAXS peak was observed for polyelectrolyte solutions in GC in the concentration range 5 mg/ml < \( c < 40 \) mg/ml.

Fig. 3.8 shows the SAXS scattering profile (broad peaks) of 60PMVP-I in F with increasing concentration from 5 to 80 mg/ml. There is no scattering peak at concentrations lower than 5 mg/ml (= 0.026 M) because \( 2c_s/\epsilon = 0.057 \) M (Table 3.2). It is noted that the scattering of 60PMVP-I in F is weak at concentration less than 10 mg/ml (Fig. 3.7) due to its high residual salt concentration. The 60PMVP-I in F shows high effective charge density and lower residual salt concentration (\( \epsilon = 0.078 \), boundary concentration \( 2c_s/\epsilon = 0.057 \) M), compared to that of 60PMVP-I in GC. This explains why 60PMVP-I in F shows a scattering peak, while 60PMVP-I/GC does not (Fig. 3.7). However, at concentration 10 mg/ml = 0.053 M, slightly lower than the boundary concentration 0.057 M, 60PMVP-I/F only shows a very weak scattering peak due to the residual salt effects (Fig. 3.8).
Figure 3. 8 SAXS profiles and the concentration dependence of SAXS curves for 60PMVP-I in F at concentrations 5, 10, 20, 40, and 80 mg/ml; $I(q)$ was determined by subtracting the background scattering intensity and then normalized by the sample thickness, scattering time, and sample transmission.

3.3.3 Solvation and rheology

Solvation of polyelectrolytes in water and non-aqueous solvents has received considerable efforts due to the practical application of polyelectrolytes in oil reclamation, industrial coatings, drug delivery and personal health-care products. de Gennes et al.$^{61}$ developed a scaling model for the polyelectrolyte conformation in salt-free solutions and later Pfeuty$^{62}$ extended the model to include salt effects. Khokhlov$^{63}$ introduced the notion of a globular conformation inside an electrostatic blob for weakly charged polyelectrolytes in poor solvent, the formation of the uncharged globule is due to the favorable interactions between monomers relative to the unfavorable interactions between solvent molecules and monomers. This globular conformation is unperturbed by
the coulomb interactions that stretch a polyelectrolyte chain to a rod-like conformation in
dilute region. Dobrynin et al.\textsuperscript{2,10} extended the de Gennes scaling model to treat dynamics
of semidilute polyelectrolyte solutions in good solvent and poor solvent.

Klooster et al.\textsuperscript{64} reported that poly(acrylic acid) shows a coil-globule
conformation transition in the range of the degree of neutralization $\alpha$ from 0.1 to 0.25 as
it is titrated in methanol (good solvent) using CH$_3$ONa. If CH$_3$ONa is replaced with
CH$_3$OLi, the same transition is not observed because the smaller counterion Li$^+$ of
LiPAA is more favorably solvated in methanol. Later in the potentiometric and
viscosimetric titration experiment of PMA and PAA in methanol with lithium methoxide
(CH$_3$O$_3$Li) reported by Morawetz and Wang,\textsuperscript{65} poly (methacrylic acid) was found to be a
much weaker acid (higher $\rho K$ and hydrophobicity). The lower reduced viscosity of
LiPMA in methanol (good solvent) is due to the attraction between ion pairs formed by
the counterion condensation, while there is no counterion-induced attraction the
LiPAA/methanol solution. Hence, the counterion size and backbone hydrophobicity of
polyelectrolytes greatly impact the solvation of polyelectrolytes in solution.

Dobrynin scaling predicts that the rheology of polyelectrolyte solutions is
significantly influenced by both the effective charge density\textsuperscript{10} and the residual salt
concentration.\textsuperscript{10,49} The specific viscosity of polyelectrolyte solutions in dilute solution is
given by Eq. 3.16.

$$\eta_s = N^{4/5} (cb^3)^{2/5} B^{-6/5} (1 + 2c_s / fc)^{-3/5} \quad c_f < c < c^* \quad (3.16)$$

where $c_f$ is the monomer concentration above which polymer chains are flexible. The
concentration $2c_s / f$ is the boundary concentration between the high salt limit $c < 2c_s / f$
and the low salt limit \( c > 2c_s / f \). In the high salt limit, the intrinsic viscosity \([\eta]\) of polyelectrolyte solutions can be estimated by Eq. 3.17. The residual salt concentration in polyelectrolyte solutions can be estimated from Eq. 3.18 based on the intrinsic viscosity and the effective charge density \( f \) obtained from the dielectric and rheology measurements.

\[
[\eta] = (b / B)^{6/5} N^{4/5} (2c_s / f)^{-3/5} \tag{3.17}
\]

\[
c_s = \left( \frac{f}{2} \right)^2 \left( \frac{b}{B} \right)^2 N^{2/3} [\eta]^{-5/3} \tag{3.18}
\]

where \( B \) is the ratio of the maximum chain length \( N_b \) and the actual contour length of the chain of electrostatic blobs \( L \). In the semidilute unentangled region, in the low salt limit \( c > 2c_s / f \), \( \eta_{sp} \sim c^{1/2} \) and \( \tau \sim c^{-1/2} \); in the high salt limit \( c < 2c_s / f \), \( \eta_{sp} \sim c^{5/4} \) and \( \tau \sim c^{1/4} \).

Here we present the effects of the solvation of polyelectrolytes in solution on rheology, by considering the influence of solvent dielectric constant, solvent quality, solvent molecular size and residual salt concentration (Table 3.1 and Table 3.2). Fig.3.9 indicates that 60PMVP-I in EG, DW, and NMF each shows strong polyelectrolyte behavior over the entire concentration region in comparison with the specific viscosity of the neutral parent polymer P2VP(h) in EG. By this we mean the specific viscosity is considerably larger and has some characteristic slopes that are quite distinct from that of the parent neutral polymer. However, the specific viscosity of 60PMVP-I in GC and F shows the same concentration dependence as the neutral P2VP(h) in EG \( \eta_{sp} \sim c \) for \( c < c^* \), and \( \eta \sim c^{1.2} \) for \( c > c^* \) in the semidilute unentangled region rather than \( \eta_{sp} \sim c^{1/2} \).
at $c^* < c < c_\varepsilon$ for polyelectrolyte solutions. Higher specific viscosity was observed in the semidilute unentangled region, compared to that of neutral polymer solutions in EG (see Fig. 3.9a).

Figure 3.9 Concentration dependence of (a) specific viscosity $\eta_{sp} = (\eta - \eta_s)/\eta_s$ (b) reduced viscosity $\eta_{sp}/c$, for neutral polymer P2VP(h) in EG and for the strongly charged polyelectrolyte 60PMVP-I in EG, DW, GC, F, and NMF at 25 °C.

Strong polyelectrolyte behavior was observed for 60PMVP-I in NMF and this result agrees with the SAXS measurements. 60PMVP-I in F shows the same $\eta_{sp}$ as neutral polymer solutions at low concentrations ($c < 0.05 \text{ M, } 2c_s/f = 0.066 \text{ M}$) and the same concentration dependence of $\eta_{sp}$ as in GC (with high residual salt $2c_s/f = 0.123 \text{ M}$), while the higher concentrations $c \geq 0.05 \text{ M}$ of 60PMVP-I/F have lower $\eta_{sp}$ than that of P2VP(h) and shows polyelectrolyte behavior as in DW. The polyelectrolyte behavior
of 60PMVP-I in F at higher concentrations was observed in the SAXS results shown in Fig. 3.8. 60PMVP-I in EG shows the lowest specific viscosity, compared to that in NMF and DW, owing to the lowest dielectric constant of EG and the lowest effective charge density. Inside the electrostatic blobs, the chain segment may collapse due to the solvation of polyelectrolyte so that a shorter contour chain length leads to a lower solution viscosity as reported. 60PMVP-I in DW (poor solvent) shows higher specific viscosity than that in EG because the higher effective charge density of 60PMVP-I leads to a longer chain contour length in DW.

The effects of residual salt greatly impact the polyelectrolyte behavior in SAXS or rheology experiments. Other polyelectrolytes in NMF, do not report polyelectrolyte behavior in rheology and SAXS measurements due to the high salt concentration of the “as received” solvent. Aldebert et al. also reported that Nafion 117 in NMF and F does not exhibit polyelectrolyte behavior possibly due to the effect of residual salt. In the study reported by Garg et al., the reduced viscosity of heparin in F did not show polyelectrolyte behavior as the residual salt concentration is 0.02 M.

Fig. 3.9b shows the concentration dependence of the reduced viscosity for 60PMVP-I and neutral P2VP(h). 60PMVP-I in F shows the same concentration independence of \( \eta_s/c \) as the neutral P2VP(h) in the concentration region \( c \leq 0.05 \) M, \( \eta_s \sim c^0 \) due to the residual salt in F. 60PMVP-I in GC demonstrates very weird reduced viscosity over the entire concentration region (because of the residual salt effect). A peak was observed in reduced viscosity for 60PMVP-I in DW and NMF due to their
slightly lower residual salt concentration, while this phenomenon was not observed for 60PMVP-I in EG because of its very low residual salt concentration.\textsuperscript{22}

Peiffer et al.\textsuperscript{68} reported that terpolymer SAA composed of sodium vinyl sulfonate, acrylamide, and 2-acrylamide-2-methylpropane sulfonic acid (AMPS) does not show polyelectrolyte behavior until the fraction of water reaches 75\% in the mixture of water-formamide. The added water is favorable for the solvation of the polyelectrolyte. However, Fig. 3.9b exactly shows the transition (decrease with dilution) of the reduced viscosity of 60PMVP-I in F and GC at concentration for F at about 0.05 M and for GC at about 0.1 M, which are close to the boundary concentration $\frac{2c_s}{f}$ of those two polyelectrolyte solutions. The polyelectrolyte behavior of 60PMVP-I in F and GC is impacted by only the effects of residual salt in those two solvents.

Aside from the upturn of the reduced viscosity $\eta_{\text{red}}$ of polyelectrolyte solutions, the relaxation time $\tau$ of polyelectrolytes in solution was also studied to judge the polyelectrolyte behavior. Fig.3.10 shows the concentration dependence of the relaxation time of 60PMVP-I in GC, F and NMF. The relaxation time of 60PMVP-I in GC is much higher than that in NMF and F due to the high solvent viscosity, although 60PMVP-I in GC does not behave like a polyelectrolyte until $c > 2c_s/f \approx 0.12$ M. 60PMVP-I in F shows polyelectrolyte behavior at concentrations $c \geq 0.06$ M, consistent with SAXS results (Fig. 3.8). The relaxation time of 60PMVP-I in NMF and GC shows a transition in the concentration dependence at the boundary concentration $2c_s/f$ (Fig. 3.10). The $\tau$ of NaPSS in water without added salt has a high concentration dependence\textsuperscript{49} $\tau \sim c^{-0.9}$ for
\( c > 2c_s/f \) in the semidilute region, however, the \( \tau \) of 60PMVP-I in all solvents NMF, GC and F shows a much weaker concentration dependence in the same region (Fig. 3.10).

**Figure 3.10** Concentration dependence of relaxation time for neutral polymer P2VP(h) in EG, strongly charged polyelectrolyte 60PMVP-I in GC, F, and NMF at 25 \(^\circ\)C. The relaxation time was determined from the shear rate at which shear thinning starts.22

Fig.3.11 summarizes the concentration dependence of the specific viscosity of 60PMVP-I in NMF. Dobrynin scaling theory\(^5\) exactly predicts the polyelectrolyte behavior in solutions with residual salt in the entire concentration region \( c < c_e \). In the semidilute unentangled region, in the high salt limit \( c < 2c_s/f \), the specific viscosity of 60PMVP-I/NMF demonstrates a power law of the concentration dependence of the neutral polymer P2VP (\( \eta_{sp} \sim c^{5/4} \)); while in the low salt limit \( c > 2c_s/f \), the specific viscosity of semidilute unentangled polyelectrolyte solutions shows concentration dependence of \( \eta_{sp} \sim c^{1/2} \). In addition, the reduced viscosity shows a maximum at roughly \( 2c_s/f \), as expected by the Dobrynin scaling theory.
Figure 3.11 Concentration dependence of the specific viscosity of 60PMVP-I in NMF. The reduced viscosity is significantly impacted by residual salt concentration. For $c > 2c_s/f$ , polyelectrolyte scaling laws are observed, while $c < 2c_s/f$ exhibits power laws consistent with the high salt limit.

3.4 Conclusions

We have studied the solvation of 60PMVP-I in EG, DW, GC, F, and NMF using dielectric spectroscopy, SAXS, and rheology. The equivalent conductance of polyelectrolytes significantly depends on the solvent dielectric constant and solvent viscosity. The fitted effective charge density of 60PMVP-I in NMF and DW obtained from fitting the Colby’s model is in agreement with the results obtained the light scattering measurements$^{23}$ in the range of $0.1 < f < 0.3$, much smaller than $f_{\text{max}}$ predicted by the Manning counterion condensation theory. The SAXS scattering is
dominated by the electron density \((\alpha - f)\) of the polyions, the residual salt concentration, and the fluctuation of polyelectrolyte chains in solution. The residual salt concentration of polyelectrolyte solutions dominates the results of the equivalent conductance, SAXS and rheology of polyelectrolyte solutions. The Dobrynin scaling model can be used to rationalize the viscosity of all polyelectrolyte solutions in NMF, F, GC, DW and EG both in the low salt limit \(c > 2c_s/f\) and in the high salt limit \(c < 2c_s/f\) in the entire concentration region \(c < c_c\). SAXS shows a peak for \(c > 2c_s/f\), as expected by scaling, with no peak in the high salt limit \((c < 2c_s/f)\). Hence, residual salt greatly impacts the conformation of polyelectrolytes in solution. 60PMVP-I in F only shows polyelectrolyte behavior at high concentrations \(c > 2c_s/f\). 60PMVP-I in GC does not show polyelectrolyte behavior at all because \(2c_s/f = 0.12 \text{ M}\) is so large in GC. Dobrynin scaling theory successfully predicts the polyelectrolyte solution behavior based on \(2c_s/f\) being the boundary between the high salt and low salt limits. In the high salt limit, the specific viscosity, reduced viscosity and relaxation time are significantly impacted by the residual salt concentration.

3.5 References

8. Oosawa, F., Polyelectrolytes. **1971**.
Chapter 4
Correlation Length of Polyelectrolyte Solutions
Investigated by Rheology and SAXS

4.1 Introduction

Polyelectrolytes are polymer chains carrying positive or negative ionizable monomers. In polar solvent such as water they show the properties of polymers and small molecule electrolytes in a particular manner. Polyelectrolyte solutions have received considerable attention due to their practical application for oil reclamation, industrial coatings, drug delivery, and personal health-care products. Although polyelectrolyte solutions have been studied for more than 5 decades, the unique properties of polyelectrolytes are still poorly understood in comparison with their neutral counterparts. The molecular weight and concentration of polyelectrolyte and added salt concentration greatly impact polyelectrolyte solution rheology. Many studies show that polyelectrolyte charge density, solvent dielectric constant, and solvent quality control counterion condensation, chain conformation and chain contour length of polyelectrolytes in solution. The influence of charge and solvent on polyelectrolyte rheology is not yet well understood.

The charge density along polyion chains shows the most important effect on the interactions between polyions and counterions. Manning counterion condensation theory predicts that counterions condense on the chain when the distance $\ell$ between
two effective charges is smaller than the Bjerrum length $l_b$ of solvent. Recent experimental results$^{10,11,13,21-23}$ demonstrate clearly counterion condensation in polyelectrolyte solutions by simply measuring their electrical conductivity, from which the molar fraction of free mobile counterions can be estimated.$^{24}$ The conformation, chain contour length and rheology of polyelectrolytes in solution change with the effective charge density of polyelectrolytes.$^5$ Effective charge density is usually altered by changing pH$^{13}$ or by changing the fraction of ionic monomers.$^{22}$ However, effective charge density may also be changed by dissolving a strongly charged polyelectrolyte in solvents of differing high dielectric constant and this approach is considered here and chapter 3.

Although Hara,$^{12}$ Konop,$^{13}$ Kawaguchi$^{17}$ and their coworkers published results on how the charge density of polyelectrolytes in solution impacts the rheological properties of polyelectrolyte solutions, their studies are limited in scope. Theoretical predictions$^{5,25,26}$ have not yet been fully tested. In addition, combining with SAXS measurement of solution structure allows rheological properties to be correlated with chain structure/conformation of polyelectrolytes in solution.

Solvent dielectric constant and solvent quality are also important factors. Solvent quality influences the conformation of polyelectrolytes in solution, while solvent dielectric constant changes the effective charge density of polyelectrolytes in solution through the Bjerrum length. The Bjerrum length is the distance where the thermal energy exactly compensates the Coulomb interaction energy between two elementary charges

$$l_b = \frac{e^2}{(e k_B T)}$$ (4.1)
where $e$ is the electron charge, $\varepsilon$ is the dielectric constant of solvent, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. According to the Manning counterion condensation theory, the maximum fraction of monomers bearing an effective charge (effective charge density) $f_{\text{max}}$ can be estimated from the Oosawa relation

$$f_{\text{max}} = \frac{b}{l_B}$$

where $b$ is the monomer length along the direction of the chain contour length. The relevant monomer length greatly depends on both the solvent quality and the size of side group because real monomers have three length scales (length, width and height). In good solvent the local conformation is swollen (self-avoiding walk) inside the electrostatic blob and $b$ is the repeat length unit along the chain. For a polyvinylic backbone in good solvent, $b = 2.5$ Å. In poor solvent the chain is locally collapsed, possibly adopting a pearl necklace conformation, and the relevant monomer size is presumably the cube-root of the occupied volume of a special monomer. On length scales larger than the electrostatic blob and smaller than the correlation blob, polyelectrolytes have an extended conformation in both good and poor solvent in semidilute solutions because of electrostatic repulsion. The typical distance between chains is defined as the correlation length $\xi$ of a polyelectrolyte solution, which can be estimated by SAXS, SANS, AFM and rheology.

The term “solvent quality” (i.e., good or poor) indicates the solubility of the equivalent neutral polymer in a given solvent. Several groups have reported solvent effects on the reduced viscosity of polyelectrolytes in polar solvents with different dielectric constant and quality, however, their studies were performed only in a
very narrow concentration range (one decade) and the correlation length $\xi$ was not reported. Study of a much broader range of polyelectrolyte concentration is necessary to understand solvent effects on the correlation length and rheology of salt-free polyelectrolyte solutions.

In this work, we estimated the correlation length of quaternized poly(2-vinyl pyridine) with chloride or iodide counterions in solution using rheology and SAXS. The correlation length of polyelectrolytes will be discussed in terms of charge density, solvent dielectric constant, solvent quality, and counterion size.

4.2 Experimental

4.2.1 Materials

Two poly(2-vinyl pyridine) (P2VP: $M_w = 364,000$ g/mol, $M_w/M_n = 1.06$, $N = 3230$, based on $M_n$; P2VP(h), $M_w = 1,220,000$ g/mol, $M_w/M_n = 1.1$, $N = 10500$, based on $M_n$) samples were purchased from Polymer Source Inc. and used without further purification. Random copolymers of 2-vinyl pyridine and N-methyl-2-vinyl pyridinium chloride or iodide (PMVP-Cl and PMVP-I) were prepared by quaternization and ion-exchange (Fig. 4.1). The preparation and characterization of polyelectrolytes were described in detail previously. All polymers in this study are shown in Table 4.1.

Solvent properties are summarized in Table 4.2. Ethylene glycol (EG: J. T. Baker, 99.8%; anhydrous; bp 198 °C; water < 0.02 %) and N-methylformamide (NMF:
ACS reagent, 99.5%, bp 210°C, density 1.134 g/ml) were purchased from Aldrich. They are good solvents for the neutral polymers P2VP and P2VP(h), and were used after being

\[
\begin{align*}
\text{a) } & \quad \text{P2VP} \\
& \quad 1. \text{(CH}_3\text{)}_2\text{SO}_4/\text{DMF} \\
& \quad 2. \text{NaCl} / \text{H}_2\text{O} \\
\text{PMVP-Cl: } & \quad \alpha = \frac{y}{(x+y)} \\
& \quad \alpha = 0.03, 0.04, 0.1, 0.17, 0.42 \text{ and } 0.55 \\
\text{Mw} = 364,000 \text{ g/mol, PDI = 1.06} \\
\end{align*}
\]

\[
\begin{align*}
\text{b) } & \quad \text{Pyridine} \\
& \quad 1. \text{(CH}_3\text{)}_2\text{SO}_4/\text{DMF} \\
& \quad 2. \text{NaI} / \text{H}_2\text{O} \\
\text{60PMVP-I: } & \quad \alpha = \frac{y}{(x+y)} = 0.6 \\
\text{Mw} = 1,220,000 \text{ g/mol, PDI = 1.1} \\
\end{align*}
\]

\[
\begin{align*}
\text{c) } & \quad \text{Pyridine} \\
& \quad 1. \text{(CH}_3\text{)}_2\text{SO}_4/\text{DMF} \\
& \quad 2. \text{NaCl} / \text{H}_2\text{O} \\
\text{60PMVP-Cl: } & \quad \alpha = \frac{y}{(x+y)} = 0.6 \\
\text{Mw} = 1,220,000 \text{ g/mol, PDI = 1.1} \\
\end{align*}
\]

Figure 4.1 Quaternization and counterion exchange for poly (2-vinyl pyridine).

Table 4.1 Summary of the quaternized polyelectrolytes and their parent polymers.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Mw (g/mol)</th>
<th>PDI</th>
<th>N</th>
<th>(\alpha)</th>
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<tr>
<td>P2VP</td>
<td>364000</td>
<td>1.06</td>
<td>3230</td>
<td>0</td>
</tr>
<tr>
<td>3PMVP-Cl</td>
<td>3230</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4PMVP-Cl</td>
<td>3230</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10PMVP-Cl</td>
<td>3230</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17PMVP-Cl</td>
<td>3230</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>42PMVP-Cl</td>
<td>3230</td>
<td>0.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>55PMVP-Cl</td>
<td>3230</td>
<td>0.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P2VP(h)</td>
<td>1220000</td>
<td>1.1</td>
<td>10500</td>
<td>0</td>
</tr>
<tr>
<td>60PMVP-Cl</td>
<td>10500</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60PMVP-I</td>
<td>10500</td>
<td>0.6</td>
<td></td>
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Table 4.2 Summary of the properties of solvents and polymer solutions at 25 °C.

<table>
<thead>
<tr>
<th>Polymer/solvent</th>
<th>$\varepsilon_s$</th>
<th>$l_0$</th>
<th>$\sigma_s$</th>
<th>$\eta_s$</th>
<th>$f$</th>
<th>$f_{\text{max}}$</th>
<th>$\xi$</th>
<th>$c_s$</th>
<th>$2c_s / f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60PMVP-Cl/EG</td>
<td>37</td>
<td>15</td>
<td>0.2</td>
<td>17.1</td>
<td>0.66</td>
<td>0.17</td>
<td>12</td>
<td>0.0825</td>
<td>2.5</td>
</tr>
<tr>
<td>60PMVP-I/EG</td>
<td>37</td>
<td>15</td>
<td>0.2</td>
<td>17.1</td>
<td>0.027</td>
<td>0.17</td>
<td>49</td>
<td>0.014</td>
<td>1.01</td>
</tr>
<tr>
<td>60PMVP-I/DW</td>
<td>78.4</td>
<td>7.1</td>
<td>4</td>
<td>0.89</td>
<td>0.17</td>
<td>0.35</td>
<td>38</td>
<td>0.38</td>
<td>4.4</td>
</tr>
<tr>
<td>60PMVP-I/NMF</td>
<td>182</td>
<td>3.1</td>
<td>16</td>
<td>1.74</td>
<td>0.23</td>
<td>0.81</td>
<td>7</td>
<td>1.44</td>
<td>12.5</td>
</tr>
</tbody>
</table>

redistilled under low pressure and protection of argon. The properties of EG were described previously in Chapters 2 and 3. Sehgal and Seery\textsuperscript{34} indicated that the concentration of residual salt in NMF “as received” is larger than 0.02 M and the conductivity of NMF “as received” is 509 $\mu S/cm$,\textsuperscript{34} which is much larger than the conductivity of EG (0.2 $\mu S/cm$ at 25 °C). Polyelectrolyte poly[2-(methacryloyloxy)ethyltrimethylammonium 1, 2, 3, 3-pentacyanopropenide] (P(M-PCP)) in “as received” NMF does not show polyelectrolyte effects (upturn reduced viscosity) due to the salt contaminants in NMF.\textsuperscript{19,35} Waigh, et al. found that P(M-PCP) in “as received” NMF does not show a scattering peak in SAXS which is a characteristic of strongly charged polyelectrolyte solutions, again due to the high salt concentration of the “as received” solvent.\textsuperscript{18} Table 4.2 shows that 60PMVP-I in fresh NMF has a very high content of residual salt, although the conductivity of NMF at 25 °C is low (16 $\mu S/cm$). Hence, for polyelectrolytes in NMF the salt contamination in the process of sample preparation and measurement is significant.

Deionized water (DW) is a poor solvent for the strongly charged polymers in this study. Neutral uncharged P2VPs in water collapse into a dense globule (or bead) which can be viewed as a liquid droplet.\textsuperscript{4} For a polyelectrolyte in poor solvent, the backbone
monomers at short length scales show strong non-electrostatic attractive interactions due to the interactions of van der Waals forces, hydrogen bonding or hydrophobic effects. Therefore, polyelectrolytes in poor solvent locally collapse and can adopt a pearl-necklace conformation due to the monomer attraction of neutral segments on a polyelectrolyte chain.\textsuperscript{36-40} The concentration of the maximum reduced viscosity for the sodium salt of sulfonated polystyrene in water is independent of molar mass but proportional to the added salt concentration.\textsuperscript{7,8,41} Distilled water exposed to air has a residual salt level of $4 \times 10^{-6}$ M from carbonic acid,\textsuperscript{7,8} with pH = 5.4 and conductivity of 10 $\mu S/cm$.

### 4.2.2 Rheology

The measurement details of the steady shear viscosity of polymer solutions were described previously in Chapter 2. The steady shear viscosity data of P2VP(h), 60PMVP-I and 60PMVP-Cl solutions were obtained at 25 °C using three rheometers: A Rheometric Scientific ARES (controlled strain) was used for highly concentrated solutions with viscosity above 20 Pa s, a Rheometrics Fluids Spectroscrometer (RFS-II, controlled strain) was used for concentrated solutions with viscosity in the range from 0.04 to 20 Pa s, a computerized Contraves Low Shear 30 viscometer (controlled shear rate) was used for polymer solutions with viscosity less 0.04 Pa s.
4.2.3 Small angle X-ray scattering

The X-ray measurements were performed on a Molecular Metrology SAXS instrument with Cu Kα radiation source (wavelength $\lambda = 1.54$ Å) and a 12.5 cm x 12.5 cm two-dimensional detector. The distance between sample and detector is 224 cm. Liquid cells with 25 μm mica windows were used to hold the polymer solutions for SAXS measurements. The thickness of these liquid cells is 1.2 mm (for polymer solutions with concentrations $c < 20$ mg/ml) and 0.4 mm (for polymer solutions with concentrations $c \geq 40$ mg/ml). All measurements were done at 25 °C, and the total scattering counts of all polymer solutions were larger than 100,000. Scattering time significantly depends on the polyelectrolyte concentration, and counterion electron density. For instance, for 0.05 M 60PMVP-I/EG solution, 3hrs were needed and for 0.05M60PMVP-Cl/EG solution, 10hrs were needed. The scattering intensity from the sample solution was subtracted from the scattering intensity of the background (as solvent and mica windows) and then was normalized by sample thickness, experiment time, and the beam transmission intensity (see Appendix 3). 4.3 Results and Discussion

4.3 Results and discussion

4.3.1 Specific viscosity and correlation length

Fig. 4.2a shows the concentration dependence of the specific viscosity of the polymers with a wide range of charge density from weakly charged polyelectrolytes ($\alpha = 0.03, 0.04$) to more strongly charged polyelectrolytes ($\alpha = 0.1, 0.17, 0.42, 0.55$) in the
good solvent EG. This Figure shows how specific viscosity depends on the quaternization extent and polyelectrolyte concentration (as discussed in Chapter 2). The specific viscosity of polymers in EG in the semidilute unentangled regime greatly increases with increasing quaternization extent except for 55PMVP-Cl, for which the repulsion from the higher effective charge is partially compensated by a dipolar attraction from the condensed counterion / charged monomer pairs on the chain.\textsuperscript{14}

![Figure 4.2](image)

**Figure 4.2** (a) Concentration dependence of specific viscosity $\eta_s = (\eta - \eta_0)/\eta_0$ for weakly charged polyelectrolytes (3PMVP-Cl and 4PMVP-Cl), and strongly charged polyelectrolytes (10PMVP-Cl and 17PMVP-Cl, 42PMVP-Cl and 55PMVP-Cl) (b) Concentration dependence of correlation length for all charged polymers in EG at 25 °C from specific viscosity in semidilute unentangled solution, based on Eq. 4.3.

Scaling theory\textsuperscript{5} predicts that the correlation length of polyelectrolytes in solution can be estimated from the specific viscosity in the semidilute unentangled region.
\[
\xi = \left( \frac{N}{c\eta_{sp}} \right)^{1/3}, \quad c^* < c < c_e
\] (4.3)

Taking into account the concentration dependence of the specific viscosity \( \eta_{sp} \sim c^{1/2} \), the correlation length in Eq. (4.3) exhibits the concentration dependence expected by the de Gennes model\textsuperscript{42}: \( \xi \sim c^{-1/2} \). According to Eq. 4.3, the correlation length of quaternized PMVP-Cl in EG was estimated from the specific viscosity of polyelectrolyte solutions in the semidilute unentangled region (Fig. 4.2a). Fig. 4.2b indicates that the correlation length of polyelectrolytes in good solvent is a function of the effective charge density until counterion condensation dominates to give all chains with \( \alpha > 0.2 \) similar effective charge density. The concentration dependence of \( \xi \) determined from Eq. 4.3 for polyelectrolytes with charge density from \( \alpha = 0.03 \) to 0.55 is in agreement with the prediction of the de Gennes scaling theory.\textsuperscript{42} The correlation length of the low charge density polyelectrolytes 3PMVP-Cl and 4PMVP-Cl in EG is much larger than that of highly charged polyelectrolytes (Fig. 4.2b). This is corroborated by the SAXS measurements of polyelectrolytes in good solvent reported by Nishida et al.\textsuperscript{15}

In low dielectric constant solvents (\( \varepsilon < 10 \)), the dissociation of condensed counterions from polyions is not significant.\textsuperscript{19} The solubility of polyelectrolytes in poor solvents with \( \varepsilon < 10 \) is relatively low in comparison with the solubility of polyelectrolytes in poor solvents with high dielectric constant. The intermolecular and intramolecular interactions induced by strong dipole-dipole interactions result in ion-clusters or aggregates in those non-solvating media.\textsuperscript{12,19} Hence, we only study low dielectric constant solvents that are good solvents for the neutral polymer, such as EG.
with moderate dielectric constant ($\varepsilon = 37$). In high dielectric constant solvents ($\varepsilon > 50$), the number of free counterions increases with increasing dielectric constant (or decreasing Bjerrum length) of solvent according to the Manning theory. In other words, the effective charge density of 60PMVP-I in solution increases with increasing dielectric constant of solvent.

Figure 4.3 Concentration dependence of specific viscosity $\eta_{sp} = (\eta - \eta_s) / \eta_s$ in the dilute and semidilute regions for neutral polymer P2VP(h) in EG, strongly charged polyelectrolyte 60PMVP-Cl in EG, as well as 60PMVP-I in EG, DW and NMF at 25 °C.

Fig. 4.3 shows that 60PMVP-I in all of the solvents studied exhibits strong polyelectrolyte behavior over the entire concentration region, in comparison with the specific viscosity of the neutral parent polymer P2VP(h) in EG. A specific viscosity concentration dependence $\eta \sim c^{1/2}$ unique to polyelectrolytes is observed for polyelectrolyte solutions in the semidilute unentangled region. The specific viscosity in
the semidilute region increases with increasing dielectric constant of solvent because the chain contour length increases, owing to additional charge repulsion. The increase in the chain contour length of 60PMVP-I can be ascribed to the increase of the effective charge density $f$ of polyelectrolytes in solution, as solvent dielectric constant increases (see Table 4.2).

In dilute solution, all condensed counterions eventually release from the polyions into solution and the effective charge density $f$ gradually approaches the degree of quaternization $\alpha$ ($f = \alpha$),\textsuperscript{21,22,43} perhaps causing the specific viscosity of 60PMVP-I in the dilute region to not exhibit much difference as the dielectric constant and quality of solvent are changed. It is noted that the effective charge density $f$ of polyelectrolytes in solution listed in Table 4.2 was obtained from the rheology and dielectric measurements in the semidilute unentangled region. However, the values of $2c_s/f$ are in the range from about 0.001 to 0.01 M, far above the overlap concentration. The influence of residual salt greatly reduces the specific viscosity of polyelectrolyte solutions at concentrations below $2c_s/f$. Above this cut-off concentration, polyelectrolyte rheology is not impacted very much by the residual salt ($c > 2c_s/f$ is the low salt limit). Although 60PMVP-I in NMF shows a much higher effective charge density, its specific viscosity decreases starting at $c = 2c_s/f \approx 0.01$ M from its enhanced value (compared to that in EG in the semidilute region) to a value similar to that in EG at $c^*$ due to its high residual salt concentration. Hence, the increase in $f$ does not enhance the specific viscosity of polyelectrolyte solutions in NMF near $c^*$, presumably because the effect of residual salt (free ions) on the electrostatic interactions is significant (the Debye
screening length is very large $r_D = 9 \text{ nm}$ for $c_s = 1.4 \text{ mM}$ as seen in Chapter 1 Eq. 1.2).  

60PMVP-I in water (Table 4.2: $f = 0.17$ much higher that in EG $f = 0.027$) has even lower specific viscosity, presumably in poor solvent the short-range interactions between the uncharged monomers result in a locally collapsed chain conformation.$^{44,45}$

It should be pointed out that our results on the properties of polyelectrolytes in NMF (purified before use) are very different from the results reported in the literature.$^{18,19,35}$ There are residual salt effects (the peak in the semidilute region$^7,8$) observed in the reduced viscosity of 60PMVP-I in DW or NMF (see Chapter 3). The residual salt effect in 60PMVP-I/EG solutions is not significant, as seen in the low conductivity of EG (Table 4.2). The major ionic materials in DW and NMF are small ions possibly from the glass container used for holding polyelectrolyte solutions and the environment (air) in which polyelectrolyte solutions are exposed to during measurement. Both DW and NMF are stable at 25 °C and show very low conductivity when freshly distilled. While they have very strong dipoles which show strong interactions to small polar molecules in the environment, those small molecules dissociate into ions in DW or NMF. Polyelectrolyte solutions in the high salt limit ($c < 2c_s/f$) show the properties of neutral polymers due to the screening effects of added salts. Our measurements on the specific viscosity of polyelectrolyte solutions have clarified the behavior of polyelectrolytes in NMF. There is an obvious residual salt effect controlling specific viscosity of polyelectrolyte solutions in NMF at concentration below $2c_s/f \approx 0.01 \text{ M}$ (see Fig. 3.9, Table 4.2 and Fig. 4.3).
Figure 4.4 Concentration dependence of the correlation length $\xi$ of 60PMVP-I in EG, DW and NMF estimated from the specific viscosity of polyelectrolyte solutions in the semidilute unentangled region ($c_c \approx 0.2$ M) using Eq. 4.3; solid lines are the power law $\xi \sim c^{-1/2}$ fitting of semidilute unentangled polyelectrolyte solutions predicted by Dobrynin, et al.\(^5\) The values of $f$ are in Table 4.2 for different polyelectrolyte solutions.

Table 4.3 Correlation length of 60PMVP-I solutions from rheology and SAXS

<table>
<thead>
<tr>
<th>c (M)</th>
<th>60PMVP-I/EG</th>
<th>60PMVP-I/DW</th>
<th>60PMVP-I/NMF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\xi$ (Å)</td>
<td>$\xi$ (Å)</td>
<td>$\xi$ (Å)</td>
</tr>
<tr>
<td></td>
<td>rheology</td>
<td>SAXS</td>
<td>rheology</td>
</tr>
<tr>
<td>0.0131</td>
<td>700</td>
<td>340</td>
<td>540</td>
</tr>
<tr>
<td>0.0263</td>
<td>530</td>
<td>280</td>
<td>390</td>
</tr>
<tr>
<td>0.0526</td>
<td>370</td>
<td>220</td>
<td>290</td>
</tr>
<tr>
<td>0.1051</td>
<td>280</td>
<td>160</td>
<td>170</td>
</tr>
<tr>
<td>0.2102</td>
<td>180</td>
<td>130</td>
<td>120</td>
</tr>
</tbody>
</table>

Fig. 4.4 indicates that the correlation length of 60PMVP-I in good solvent (EG and NMF) obeys de Gennes’ prediction.\(^42\) The correlation length of 60PMVP-I in the poor solvent water was also determined from Eq. 4.3. Fig. 4.4 shows that the $\xi$ of
60PMVP-I increases with decreasing solvent dielectric constant through its effects on the effective charge density $f$ of polyelectrolyte solutions. The correlation length of 60PMVP-I in EG is larger because the low dielectric constant of EG imparts a low very low effective charge density to 60PMVP-I in EG ($f = 0.027$). The Bjerrum length increases with decreasing solvent dielectric constant (as seen in Table 4.2). For highly charged polyelectrolytes in good solvent, if the effective charge density $f$ of polyelectrolytes in the semidilute region is known, the correlation length $\xi$ ($\xi = (B/cb)^{1/2}$ and $B = (b/f^2l_B)^{2/7}$ in good solvent case) can be estimated by Eq. 4.4:

$$\xi = b^{-5/14} f^{-2/7} l_B^{-1/7} c^{-1/2}$$ (4.4)

The average length of monomers (charged and uncharged) $b$ in poor solvent and good solvent can be estimated by using Eq. 4.4 because $l_B$ and $c$ are known and the $\xi$ is measurable by using rheology or SAXS ($f$ can be determined from the osmotic pressure or equivalent conductance of polyelectrolyte solutions). The $\xi$ of 60PMVP-I in EG, DW and NMF is summarized in Table 4.3 in the concentration region from 0.013 to 0.21 M (corresponding to the low salt limit $c > 2c_\text{e} / f$ and semidilute unentangled solutions $c < c_\text{e}$ for 60PMVP-I in all three solvents).

### 4.3.2 Small angle X-ray scattering and correlation length

Polyelectrolytes in both good and poor solvent have identical conformations on scales larger than the electrostatic blobs but different conformations on scales less than the electrostatic blob size (Fig. 3.6). In good solvent, polyelectrolytes have a self-
avoiding swollen conformation inside the electrostatic blob. However in poor solvent, polyelectrolytes collapse and can adopt a pearl necklace conformation due to the poor solubility.\textsuperscript{36,40} In both good and poor solvent, the Bjerrum length dominates the distance between two effective charges on the chain. Counterions condense onto the polyelectrolyte chains if the distance between two effective charges is smaller than the Bjerrum length. On length scales larger than the electrostatic blob, the polyelectrolytes show a rod-like conformation in both good and poor solvent because of the interactions between the electrostatic blobs of other chains. The distance between rod-like chains is defined as the correlation length \( \xi \) of a polyelectrolyte solution. Polyelectrolyte chains in the semidilute region show a random walk conformation of correlation blobs.

The X-ray scattering of polyelectrolyte chains in the semidilute regime is significantly related to the electron density of the polymer chains or in the vicinity of the polymer chains\textsuperscript{46} in comparison with their surroundings. The average electron density of quaternized P2VP (including methyl group) without condensed counterions is lower than its environments (ethylene glycol and counterions). The atomic number of iodine is 53 and it has a very high mass attenuation coefficient \( Mac \) for Cu \( K_\alpha \) (294 cm\(^2\)/g), compared to that of chlorine (atomic number 17, \( Mac = 106 \) cm\(^2\)/g), oxygen (atomic number 8, \( Mac = 11.5 \) cm\(^2\)/g), nitrogen (atomic number 7, \( Mac = 7.52 \) cm\(^2\)/g), carbon (atomic number 6, \( Mac = 4.8 \) cm\(^2\)/g), and hydrogen (atomic number 1, \( Mac = 0.435 \) cm\(^2\)/g). For the sake of getting higher scattering intensity from the polyion with condensed counterions in the SAXS experiments, poly (methyl vinyl pyridinium iodide) (60PMVP-
I, \( \alpha = 0.60 \) was prepared to obtain a polyelectrolyte with high electron density counterions.

In good solvent EG, a fraction \( \alpha - f = 0.43 \) of monomers on the polyion 60PMVP-I in the semidilute region have condensed counterions, according to the Manning theory.\(^2,3\) Iodide has much higher electron density than chloride due to its higher atomic number. This high electron density of I\(^-\) around the polyions allows us to readily probe the correlation length of 60PMVP-I in solution using SAXS, which is a well-established and straightforward measurement tool that has been applied to probe the structures of semidilute polyelectrolyte solutions.\(^32\) The structure factor of a salt-free polyelectrolyte solution at small wavevectors is related to the osmotic compressibility and is dominated by the free counterion concentration.\(^5\)

![SAXS profiles and the concentration dependence of SAXS curves for 60PMVP-I in NMF in the semidilute region; \( I(q) \) was subtracted from the background scattering intensity and then normalized using the sample thickness, experiment time, and transmission intensity (see Appendix 3).](image-url)

**Figure 4.** SAXS profiles and the concentration dependence of SAXS curves for 60PMVP-I in NMF in the semidilute region; \( I(q) \) was subtracted from the background scattering intensity and then normalized using the sample thickness, experiment time, and transmission intensity (see Appendix 3).
At finite wavevectors, there is a maximum in $S(q)$ that determines the correlation length.

$$S(q = 0) \approx 1/ f$$

(4.5)

where $q_{\text{max}}$ is the wavevector of the scattering peak. The correlation length $\xi$ is the typical distance between the local extended chains of electrostatic blobs (Fig. 3.6). According to X-ray scattering theory, the ordered structure of higher electron density along the local extended chains of electrostatic blobs (see Fig. 3.6) results in a characteristic maximum in the scattering profile of $I(q)$ as a function of the scattering vector $q (q = (4\pi / \lambda) \sin \theta)$ in the small angle X-ray scattering experiment, $2\theta$ is the scattering angle and $\lambda$ is the X-ray wavelength. Semidilute solutions of neutral polymers and polyelectrolytes in the high salt limit do not have a peak in $S(q)$. Electrostatic repulsion between chains is strong for polyelectrolytes in the low salt limit because the Debye screening length is also of order $\xi$ (Fig. 3.6). Neutral polymer solutions have weak interactions between chains and the distance between chains fluctuates greatly, whereas polyelectrolytes exhibit a single characteristic distance that gives a peak in $S(q)$.

As seen in Fig. 4.5, the normalized intensity $I(q)$ plotted against the scattering wavevector $q$ shows a strong maximum for 60PMVP-I in NMF. This suggests that the 60PMVP-I in NMF shows strong polyelectrolyte behavior, in agreement with the results from rheology (Fig. 4.2b). Our results disagree with the previous results reported in literature.\textsuperscript{18, 19} Waigh, et al.\textsuperscript{18} reported no SAXS peak for flexible polyelectrolytes in NMF, presumably because of the residual salts in NMF when used “as received”. The
conductivity \((509 \, \mu S/cm)\) of NMF “as received” corresponds to a residual salt concentration larger than 0.02 M.\(^{34}\) In this study, NMF was redistilled twice under low pressure after soaking in 4Å active molecular sieves for 24 hrs under the protection of argon. The conductivity of this carefully purified NMF is 16.2 \(\mu S/cm\). 60PMVP-I in NMF shows a residual salt concentration about \(c_s = 1.44 \text{ mM}\) and the low salt limit concentration \(2c_s/f = 0.0125 \text{ M}\) (Table 4.2). All concentrations of 60PMVP-I in NMF show any scattering peak (Fig. 4.5) because all concentrations are in the low salt limit with \(c > 2c_s/f \approx 2 \text{ mg/ml}\). Therefore, we ascribe the previous results in the literature to the influence of a high concentration of residual salt on the properties of polyelectrolyte solutions. SAXS of 60PMVP-I in DW and EG also shows strong polyelectrolyte behavior in the semidilute region. A single scattering peak was observed in the SAXS measurement of 60PMVP-I solutions in water, EG and NMF. At concentration 150 mg/ml, the polyelectrolyte solution so concentrated that the transmission is low when a liquid cell with 0.4 mm thickness was used, preventing measurement of high concentrations.

The correlation length of polyelectrolytes in solution was determined from Eq. 4.6 and is reported in Table 4.3. To show the concentration dependence of the correlation length, \(\xi\) obtained from SAXS and SANS\(^6\) experiments as a function of concentration are plotted in Fig. 4.6. The correlation length \(\xi\) of 60PMVP-I (\(\xi\) from SAXS measured in EG, DW, and NMF) and 45PMVP-Cl (\(\xi\) from SANS\(^6\) measured in DW and EG) shows the same concentration dependence \(\xi \sim c^{-0.4}\) from 0.02 to 0.2 M in the semidilute unentangled region. The correlation length \(\xi\) obtained from both SAXS and SANS
experiments shows a slightly weaker concentration dependence $\xi \sim c^{-0.4}$ than that obtained from rheology $\xi \sim c^{-0.5}$ which obeys the theoretical prediction of the de Gennes model.\textsuperscript{42} The correlation length of 45PMVP-Cl in EG and DW from SANX is slightly larger than that of 60PMVP-I in NMF from SAXS but smaller than that of 60PMVP-I in DW and EG from SAXS in the range shown in Fig. 4.6.

**Figure 4.6** Correlation length $\xi$ of 60PMVP-I in EG, DW and NMF determined from SAXS based Eq. 4.6; correlation length of 45PMVP-Cl in DW and EG determined from SANS based on the results reported by Ermi and Amis;\textsuperscript{6} and solid lines are the power law $\xi \sim c^{-1/2}$ fitting based on the results of rheology (top:60PMVP-I/EG, middle: 60PMVP-I/DW, Bottom: 60PMVP-I/NMF, see Fig. 4.4).
Figure 4.7 Correlation length $\xi$ of 60PMVP-I in EG and DW determined from SAXS based Eq. 4.6; Solid lines are the power law fitting of $\xi \sim c^{-1/2}$ at $c < c_x$ and $\xi \sim c^{-1/3}$ at $c > c_x$ based on the theoretical prediction of polyelectrolytes in poor solvent. At $c < c_x$ ($c_x \approx 0.05$ M), Fig. 4.7 shows the correlation length $\xi$ of 60PMVP-I in EG and DW shows a concentration dependence $\xi \sim c^{-1/2}$, as expected for polyelectrolytes in good solvent. At $c > c_x$, the $\xi$ (SAXS) of 60PMVP-I in DW and EG has a weaker concentration dependence $\xi \sim c^{-1/3}$, as expected by Dobrynin-Rubinstein model for polyelectrolytes in poor solvent. Counterion condensation dramatically modifies the conformation of polyelectrolyte chains in DW and EG, even if EG is a good solvent based on the assumption of scaling theories. Our result is in agreement with the prediction of the Dobrynin-Rubinstein model $\xi \sim c^{-1/2}$ for $c < c_x$ and $\xi \sim c^{-1/3}$ for $c > c_x$ (see Fig. 4 of reference 36). 60PMVP-I in EG possibly collapses inside the electrostatic blobs in the same manner as in DW due to the counterion-induced attraction. This
observation suggests that the SAXS measurements are more sensitive to the change in the conformation of polyelectrolytes in poor solvent, considering there is no transition in the concentration dependence of $\xi$ calculated from specific viscosity in the same concentration region (see Fig. 4.4, where the data go up to 0.2 M, which is far above $c^*$). The value of the correlation length at $c_x$, roughly 200 Å in both DW and EG, determines the length of strings between beads in the pearl necklace model.\textsuperscript{36}

A comparison of the solvent effects on the correlation length was reported by Waigh, et al.\textsuperscript{18} They found that the concentration dependence of $\xi$ changes from $\xi \sim c^{-1/2}$ to $\xi \sim c^{-1/7}$ in poor solvent and stays unchanged $\xi \sim c^{-1/2}$ in good solvent. This transition of concentration dependence in poor solvent corresponds to the expected conformation change.\textsuperscript{36} Similar results can also be seen in the SAXS results of hydrophobic sodium maleate copolymers in water.\textsuperscript{30} Essafi and coworkers showed the correlation length $\xi$ of highly charged polyelectrolytes significantly depends on the solvent quality to the polymer backbone when polyelectrolyte chain was changed from hydrophilic to hydrophobic backbone.\textsuperscript{15} In a study of charge density effects, Baigl et al.\textsuperscript{31} reported that there exists a continuous transition from $\xi \sim c^{-1/2}$ to $\xi \sim c^{-1/3}$ in hydrophobic polyelectrolyte solutions studied using AFM and SAXS when $\alpha$ decreased from 100% to 35%. In our study, the correlation length of polyelectrolytes in solution increases with increasing dielectric constant of solvent. Hence, $\xi$ reasonably decreases with increasing dielectric constant of the solvent, possibly due to the increasing effective charge density of polyelectrolytes in solution as seen in Eq. 4.4 ($l_b$ effects) and Fig. 4.7. In addition, as seen in Table 4.3, the correlation length obtained from rheology is larger
than that from SAXS measurements except for the 60PMVP-I/NMF solutions (see section 4.3.4 for a complete discussion of this).

### 4.3.3 Chain contour length \( L \)

Dobrynin scaling theory\(^5\) predicts that the correlation length \( \xi \) of flexible polyelectrolytes in solution is a function of concentration and related to parameter \( B \) (\( B = Nb / L \): the ratio of the fully stretched chain length and the actual chain contour length \( L \), \( B \) increases as the chain is less stretched and equals to unity when the chain is fully stretched.) Eq. 4.7 presents the relation between the chain contour length and the correlation length of the semidilute solution.\(^5\)

\[
\xi = 2/(Lc) > c^*> \quad (4.7)
\]

The chain contour length \( L \) should be independent of concentration \( L \sim c^0 \) due to the internal relation of \( \xi \sim c^{-1/2} \) as predicted in the theoretical models.\(^4,5\) Combining Eqs. 4.3 and 4.7, the chain contour length \( L \) of polyelectrolytes in good solvent can be estimated from the specific viscosity in the semidilute unentangled region.

\[
L = \frac{N}{c}^{1/3} \eta_s^{2/3} \quad c^* < c < c_e \quad (4.8)
\]
Figure 4.8 Concentration dependence of chain contour length $L$ for weakly charged polyelectrolytes (3PMVP-Cl and 4PMVP-Cl), and strongly charged polyelectrolytes (10PMVP-Cl and 17PMVP-Cl, 42PMVP-Cl and 55PMVP-Cl) in EG at 25 °C, calculated from specific viscosity in the semidilute unentangled solution using Eq. 4.8.

The concentration dependence of chain contour length $L$ of all charged polymers PMVP-Cl in EG is plotted against concentration in Fig. 4.8. $L$ is independent of concentration, and increases with increasing effective charge of polyelectrolytes in solution except for 55PMVP-Cl, which shows a shorter contour length than that of 42PMVP-Cl, possibly due to the effects of counterion-induced interactions (discussed in section 4.3.4). For weakly charged polyelectrolytes, $L$ slightly increases with increasing concentration because the concentration dependence of the correlation length of weakly charged polyelectrolytes is slightly stronger than that of strongly charged polyelectrolytes ($\xi \sim c^{-0.61}$ for 3PMVP-Cl/EG and $\xi \sim c^{-0.56}$ for 4PMVP-Cl). It is noted that $L$ increases with the effective charge of the polyelectrolytes. The interactions between charges
stretch the chain until the counterion-induced interactions become significant in the
strongly charged polyelectrolyte solution.

Fig. 4.9 compares the chain contour length $L$ from rheology with $L$ from SAXS for 60PMVP-I in EG, DW and NMF (as well as 60PMVP-Cl in EG). The entanglement concentration $c_e$ of those polyelectrolyte solutions is about 0.2 M. From the rheology measurements (Fig. 4.9a), the chain contour length $L$ at concentrations below $c_e$ is independent of concentration; this result obeys Dobrynin’s prediction. Solvent dielectric constant and solvent quality greatly impact the chain contour length of polyelectrolytes in solution. 60PMVP-I shows the largest $L$ in NMF and the smallest $L$ in EG. 60PMVP-I in DW and 60PMVP-Cl in EG show similar chain contour length, only slightly higher than that of 60PMVP-I in EG, owing to the effects of solvent quality and counterion size. However in the SAXS measurements, the chain contour length $L$ (estimated from the correlation length $\xi$ via Eq. 4.7) slightly decreases with increasing concentration, $L \sim c^{-0.25}$. This concentration dependence was observed for 60PMVP-I in all solvents. In addition, the effects of counterion size and solvent quality are not as strong as observed in the rheology experiments. On average, $L$ obtained from SAXS is larger than that from rheology. Data at concentrations above $c_e$ are not available because Eq. 4.8 for determining chain contour length $L$ from $\eta_{sp}$ is only valid for $c^* < c < c_e$.

Recently, the parameter $B$ for a series of hydrophobic negatively charged polyelectrolytes in aqueous solution has been investigated using rheology, SANS and SAXS. The $B$ estimated from the three different techniques matches very well ($B = 2.1 \sim 3.2$) excepting the data set of NaPSS ($B = 1.0$ from rheology in poor solvent, which
is clearly too small). Information from Di Cola, et al.\textsuperscript{30} indicates that the strongly charged weakly hydrophobic polyelectrolytes with Na\textsuperscript{+} counterions in water are highly stretched. However, in the study of quaternized positively charged PMVP-I solutions with I\textsuperscript{−} counterions (Table 4.4), we only found that the parameter $B$ of 60PMVP-I/NMF (Table 4.4 and Fig. 4.10) obtained from different techniques matches well, possibly

**Figure 4.9** Concentration dependence of chain contour length $L$ (a) obtained from semidilute unentangled specific viscosity via Eq. 4.8 (b) obtained from SAXS via Eq. 4.7 for strongly charged polyelectrolyte 60PMVP-Cl in EG as well as 60PMVP-I in EG, DW and NMF at 25 $^\circ$C, solid lines are the fitting of $L \sim c^0$ for the rheology data.

because of the low extent of counterion condensation in NMF. In other cases, the chain contour length $L$ of polyelectrolytes in solution obtained from rheology and SAXS does not match well, due to the low solvent dielectric constant (EG) and the poor solvent
quality (DW). The chain contour length $L$ increases with solvent dielectric constant and is also impacted by the solvent quality. This poor matching of the chain contour length obtained from rheology and SAXS may be due to the presence of condensed counterions leading to short range dipole-dipole interactions which are ignored in the Dobrynin scaling models of polyelectrolyte solutions. However, the $B$ (SAXS) of 60PMVP-I in EG and DW matched well with the $B$ (SANS) of 45PMVP-Cl in EG and DW, suggesting that Dobrynin scaling model may predict the chain contour length better if the counterion-induced attraction is considered.

<table>
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<th>Polymer/solvent</th>
<th>$\alpha$</th>
<th>$/, /$</th>
<th>$\beta (\eta_{\text{sp}})$</th>
<th>$B$ (SAXS)</th>
<th>$B$(SANS)*</th>
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<td>45PMVP-Cl/H2O</td>
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<td>0.230</td>
<td>2.3</td>
<td>2.0</td>
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</tr>
</tbody>
</table>

* the $B$ was determined from SANS data reported in reference 6.

**4.3.4 Counterion-induced interactions**

Investigations on the intra and intermolecular interactions induced by the dipole-monopole and dipole-dipole attraction have received extensive attention in the last decade. The dipole-dipole attraction is an important factor that leads to local collapse inside the electrostatic blobs. Hribar and coworkers found evidence of attraction induced by divalent and trivalent counterions (multivalent counterions) using Monte
Carlo simulation.\textsuperscript{51,52} Grønbech-Jensen et al. developed a minimal model for rigid polyelectrolytes,\textsuperscript{48} they argued that large attractive forces are responsible for the chain collapse of stiff biopolymers in the presence of multivalent counterions. On the experimental side, the formation of actin rings and loops was observed after the addition of divalent cations.\textsuperscript{49}

For linear flexible polyelectrolytes, the pearl-necklace model has been studied by many researchers,\textsuperscript{29,36,50,53} however those studies were restricted to counterion condensation effects on the conformation of hydrophobic polyelectrolytes or polyelectrolytes in poor solvent. Few investigators have paid attention to the counterion-induced attraction of polyelectrolytes in good solvent. Are there counterion-induced interactions for polyelectrolytes in good solvent? The answer is clear from our experiments, from which we show for the first time that counterion-induced attraction alters the conformation of flexible polyelectrolytes in good solvent.

Fig. 4.2a shows that the specific viscosity of 42PMVP-Cl/EG solutions in the semidilute region is higher than that of 55PMVP-Cl/EG solutions. Provided that the effective charge densities of those two polymers are similar because they are highly charged (measured results are \( f = 0.17 \) and \( f = 0.18 \), respectively), there are more counterions condensed on the 55PMVP-Cl chains (fraction of monomers with a condensed-ion pair \( \alpha - f = 0.37 \) for 55PMVP-Cl and \( \alpha - f = 0.25 \) for 42PMVP-Cl). The condensed counterions on the 55PMVP-Cl chain segments induce intermolecular interactions, which shrink the polyelectrolyte chain in good solvent (effectively bringing it closer to the \( \theta \) point).
Fig. 4.6 shows that the correlation length $\xi$ of 60PMVP-I in the good solvent EG exhibits a weaker concentration dependence at $c > c_x$, compared to the concentration dependence of $\xi$ for 60PMVP-I in the good solvent NMF. Our interpretation of this result is that 60PMVP-I has many condensed counterions in EG. EG is a good solvent for the backbone of the neutral polymer P2VP(h) and locally a good solvent for the uncharged monomers, while EG is not a good solvent for the monomers with condensed counterions, owing to dipolar attraction. In addition, at higher polyelectrolyte concentrations, the fraction of the condensed counterions increases and the polymer chains shrink, decreasing the contour length of the chain of electrostatic blobs. Is the transition of the concentration dependence of $\xi$ for 60PMVP-I in EG (observed at about $c_x \approx 0.05$ M in Fig. 4.7) indicating formation of globules analogous to poor solvent? This transition is similar to that of 60PMVP-I in the poor solvent DW at a lower concentration: $c_x \approx 0.05$ M. This scenario suggests that the apparent chain contour length $L$ and the specific viscosity of 60PMVP-I in water might decrease due to enhanced condensation at high $c$. This suggestion is supported by the correlation length obtained from SAXS measurements at higher concentrations. In addition, it is noted that the electrostatic blob size of 60PMVP-I in EG is much larger than that of the polymer in other solvents. The lowest effective charge density ($f = 0.027$) of 60PMVP-I in EG, much smaller than that in other solvents, leads to forming large electrostatic blobs filled with many counterion-condensed monomers ($g_e = 49$, $(\alpha - f) g_e = 28$).

There may be a prefactor in the scaling models\textsuperscript{5} used for calculating $\xi$ from specific viscosity in semidilute unentangled solutions. This prefactor is changed by
counterion-induced attraction: the dipole-monopole and dipole-dipole interactions of condensed ion pairs (and the counterions in solution).\textsuperscript{14} The counterion-induced attraction tends to shrink the chain, counter-balanced by electrostatic repulsion. The attraction greatly depends on the extent of counterion condensation and becomes significant at concentrations $c > c_x$ (0.05 M) as seen in Figs. 4.6, 4.7, and 4.8. This is supported by the specific viscosity of 60PMVP-I/EG in the semidilute region, which is lower, compared to that of 60PMVP-Cl in EG (Fig. 4.4). Counterion condensation of 60PMVP-I in EG ($f_0=0.027$) or DW ($f_0=0.17$, poor solvent) is more significant than that in NMF ($f_0 = 0.23$, good solvent). That is the major reason why the correlation length of 60PMVP-I/NMF solutions shows the usual concentration dependence of $\xi$ expected by the Dobrynin scaling model, with less variation at higher concentrations (see Chapter 3) than EG and DW solution show. This effect is also observed in comparing $\xi$ from rheology and SAXS for 60PMVP-I/NMF solutions (Fig. 4.10), where the independent measures of $\xi$ agree perfectly.

In the concentrated region, Fig. 2.1a (chapter 2) shows that the 3PMVP-Cl has the highest specific viscosity due to the electrostatic interactions of the charges between chains or chain segments (ionomer effects), compared to the specific viscosity of the neutral polymer P2VP. However, it is important to note that the 55PMVP-Cl demonstrates the lowest specific viscosity at high concentration of all polymers shown in Fig. 2.1a. The specific viscosity of other polymers (4PMVP-Cl, 10PMVP-Cl, 17PMVP-Cl and 42PMVP-Cl) at high concentration has essentially the same concentration dependence as the neutral polymer P2VP because the electrostatic interactions of those
polyelectrolytes in EG were screened in the concentrated region, where the correlation length becomes smaller than the electrostatic blob. However, the counterion-induced attraction of 55PMVP-Cl in EG is more significant. This attraction between dipoles causes the polymer chain to collapse somewhat locally and reduces the specific viscosity of 55PMVP-Cl.14

![Graph showing concentration dependence of correlation length ξ of 60PMVP-I in NMF determined from SAXS (Eq. 4.6) and specific viscosity of semidilute unentangled solutions (Eq. 4.3).](image)

**Figure 4.10** Comparison on the concentration dependence of the correlation length $\xi$ of 60PMVP-I in NMF determined from SAXS (Eq. 4.6) and specific viscosity of semidilute unentangled solutions (Eq. 4.3)

Fig. 4.3 shows that the specific viscosity of strongly charged polyelectrolytes in the semidilute region is much higher than that of the neutral polymer P2VP(h) due to the electrostatic repulsion between charges. The concentration dependence of the neutral polymer P2VP(h) and charged polymers overlap in the concentrated region, according to Dobrynin’s prediction$^{5, 22} \eta_{sp} \sim c^{15/4}$. (In this study, we do not have data extending far enough into this region to test this power law). In the semidilute region, the difference in
the concentration dependences of specific viscosity (neutral polymers: $\eta_{sp} \sim c^{5/4}$ at $c < c_c$ and $\eta_{sp} \sim c^{15/4}$ at $c > c_c$; polyelectrolytes: $\eta_{sp} \sim c^{1/2}$ at $c < c_c$ and $\eta_{sp} \sim c^{3/2}$ at $c > c_c$) mathematically results in the fact that the specific viscosity of the neutral polymer is larger than that of polyelectrolytes at high concentrations.$^{5,22}$

The specific viscosity of 60PMVP-I in NMF is the highest among the charged polymers due to its lowest extent of the counterion-induced attraction and the highest effective charge density ($f = 0.23$). The 60PMVP-I in EG demonstrates the lowest specific viscosity among all polymers due to its lowest effective charge density and highest extent of counterion-induced attraction ($\alpha = 0.6$, $f = 0.027$). Although DW is a poor solvent, 60PMVP-I/DW only shows a moderate extent of counterion-induced attraction because $\varepsilon_{DW} > \varepsilon_{EG}$ and water strongly solvates the ionic groups ($f = 0.17$). Strongly charged polyelectrolytes in good solvent may collapse due to counterion-induced attraction. This chain collapse is dominated by the fraction of monomers with condensed counterions and the counterion size,$^{54}$ as evidenced by a strong effect for 60PMVP-I/EG compared to 60PMVP-Cl/EG.

### 4.3.5 Counterion size effects

Theoretical modeling of polyelectrolyte solutions deals with both solvent effects and long range coulomb forces. For simplicity, the modeling ignores the effects of short-range interactions and the effects of counterion size. Solvent in the modeling is treated merely as a dielectric continuum due to the complexity of the system. However, ionic
hydration or solvation of polyelectrolytes in solution is considered to be an important factor that impacts the local structure of solvent molecules in solution. Realizing the restrictions of the modeling with polymer-solvent interactions strictly dictated by the interactions with a similar neutral polymer, special attention has been paid to the local structures related to individual ions in electrolyte solutions. Hribar et al. reported that the charge density of ions greatly affects the solvation of ions and that small ions impart a higher degree of electrostatic ordering to neighboring solvent molecules.

Figure 4.11 Comparison of the correlation length of 60PMVP-I and 60PMVP-Cl in EG determined using SAXS (Eq. 4.6) and specific viscosity of semidilute unentangled solutions (Eq. 4.3).

Fig. 4.11 compares the correlation length of 60PMVP-I and 60PMVP-Cl in EG based on the results from rheology and SAXS. Those two polymers were prepared from the same parent polymer P2VP (h). The principal difference is that iodide I has a 20% larger radius (0.216 Å) than chloride Cl (0.181 Å). It is interesting to note that the correlation length $\xi$ of 60PMVP-I is almost the same as that of 60PMVP-Cl in the SAXS
measurements (effective charge density effects), while in the rheology measurements (counterion-induced attraction effects), the correlation length of 60PMVP-Cl is smaller due to weaker counterion-induced interactions, compared to the $\xi$ of 60PMVP-I. This suggests that the intramolecular interaction of 60PMVP-I in EG is more significant because the iodide ion has lower charge density because of its larger volume. The PMVP-I ion pair has a stronger dipole than that of PMVP-Cl ion pair. Hence, the chain shrinkage of 60PMVP-I in EG is stronger than 60PMVP-Cl in EG. This is the reason that the 60PMVP-Cl in EG shows higher specific viscosity over the entire concentration region (Fig. 4.3).

In the SAXS experiment, the correlation length $\xi$ of polyelectrolytes in solution is obtained directly from the wavevector of the scattering peak (Eq. 4.6). However in the rheology experiments (with external shear force), the interactions (or attraction forces, including counterion-induced attraction force) between molecules are effectively measured (in the measured shear stress) and the correlation length $\xi$ is determined using a scaling model that ignores the counterion-induced attraction resulting in overestimation of the shear stress in the measurement. That is possibly the reason why the result from rheology shows the effects of counterion-induced attraction, more strongly than SAXS.

It should be pointed out that although the parameter $B$ of polyelectrolytes with Na$^+$ counterion (shown in Table 3 in reference$^{30}$) matches very well between the results obtained from rheology and SAXS/SANS, this good matching must be ascribed to the low extent of counterion-induced attraction due to the small size of Na$^+$ (radius: 0.095 Å, which is much smaller even than the size of chloride) and its higher charge density,$^{54}$ compared to the extent of counterion-induced attraction of $\Gamma$ and Cl$^-$ in this study.
4.4 Conclusions

We have explored the effects of polyelectrolyte charge density, counterion size, solvent quality and solvent dielectric constant on the correlation length of salt-free polyelectrolyte solutions. The correlation length $\xi$ of polyelectrolytes with a wide range of charge density (prepared from P2VP) in EG was determined using specific viscosity of semidilute unentangled solutions. $\xi$ was found to depend on the effective charge density $f$ of polyelectrolytes in solution. The influence of solvent (EG, DW, and NMF) on the correlation length of strongly charged polyelectrolytes, 60PMVP-I and 60PMVP-Cl, was investigated using rheology and SAXS at 25 °C. We found that the correlation length of polyelectrolytes in solution greatly depends on both solvent dielectric constant and solvent quality. The concentration dependence of the correlation length obtained from rheology agrees with the de Gennes prediction $\xi \sim c^{-1/2}$, while the SAXS results show a slightly weaker concentration dependence $\xi \sim c^{-0.4}$ in agreement with the result from SANS reported by Ermi and Amis for the same type of polymer in EG and DW. NMF is a good solvent for P2VP and quaternized P2VP with either Cl$^-$ and I$^-$ counterions. Water is a poor solvent for P2VP and for quaternized P2VP with either Cl$^-$ or I$^-$ counterions. EG is good solvent for P2VP and for quaternized P2VP with Cl$^-$ counterions but is a poor solvent for quaternized P2VP with I$^-$ counterions due to dipolar attraction.

The factors that can impact the counterion-induced attraction of polyelectrolytes in solution include counterion size, solvent dielectric constant, solvent quality, and effective charge density. The chain contour length $L$ obtained from rheology is independent of concentration in the semidilute unentangled region, while $L$ obtained
from SAXS decreases weakly with increasing concentration $L \sim c^{-0.25}$, owing to the weaker apparent concentration dependence of correlation length $\xi \sim c^{-0.4}$. $L$ increases with increasing effective charge density or solvent dielectric constant. For those polyelectrolytes with strong counterion-induced interactions, the chain contour length $L$ obtained from rheology is larger than that from SAXS measurements, possibly because the theoretical prediction in modeling did not take into account the counterion-induced interactions. Rheology experiments appear to be more sensitive to counterion-induced attraction, which is a weak intramolecular force that can locally shrink a polyelectrolyte chain. This shrinkage in the contour length results in a reduction in the apparent viscosity of polyelectrolyte solutions. According to the SAXS measurements, counterion-induced interactions become more significant for $c > c_c$. A transition in the concentration dependence of the correlation length from $\xi \sim c^{-1/2}$ to a weaker dependence $\xi \sim c^{-1/3}$ near $c_c \approx 0.05$ M was observed for 60PMVP-I in both DW and EG in the SAXS measurements. This result agrees with the prediction of Dobrynin-Rubinstein model for polyelectrolytes in the poor solvent DW. However, the observation that the same crossover occurs in EG suggests that EG behaves like a poor solvent to 60PMVP-I, although EG is a good solvent for neutral polymer P2VP.
4.5 References

43. Liao, Q.; Dobrynin, A. V.; Rubinstein, M., Macromolecules 2003, 36, 3399.
Chapter 5

Synthesis and Characterization of PEO-Based Single Ion Conductors

5.1 Introduction

Poly(ethylene oxide) (PEO) has been extensively investigated as a candidate electrolyte for lithium rechargeable batteries due to its high solvating power for a variety of alkali and alkaline earth cations. The cations diffuse through PEO (and other polymers) cooperatively with the matrix segmental relaxation, and this results in macroscopic ionic conductivity. Compared with traditional ceramic electrolytes, polymer electrolytes are relatively flexible and can be readily fabricated to different shapes for a variety of electrochemical applications. Flexible polymer electrolytes can also readily accommodate the volume change of the cell during charge-recharge cycling, avoiding physically disassembling the electrolyte-electrode interfacial contact. In addition, polymers can be easily crosslinked to make a solid with any desired modulus in the range 1 – 30 MPa, which effectively resolves the leakage problem encountered with solvent containing electrolytes but is likely too small to prevent dendritic growth from the lithium electrode.

While most prior studies have been performed on solvent-free PEO/salt complexes, anions of the salt have very high mobility and aggregate over time at the
cathode surface. This internal polarization arising from the ion concentration gradient significantly deteriorates cell performance. Hence electrolytes in which the anions are covalently bound to the polymer chains (i.e., ionomers or single-ion conductors) are highly desirable.\(^1\) Due to the size and relatively immobile nature of the polymer chains, only cations are able to migrate over long distances in the solid state on reasonable time scales, and a transference number of unity can be achieved.\(^{1-4}\)

Single ion polymer electrolytes have been prepared for the purpose of improving the conductivity and lifetime of lithium ion batteries.\(^5-11\) For example, aluminosilicate/poly(ethylene glycol) (PEG) copolymers were synthesized by Rawsky et al. with sodium as the cations;\(^5\) siloxyaluminate-Li\(^+\) polymers were reported by Fujinami et al.;\(^6\) and polyanionic electrolytes with mono-oxalato-capped and mono-malonato-capped orthoborate structures were synthesized by Angell and coworkers.\(^7\) More recently, Sun, et al. synthesized single ion polymer conductors by grafting lithium bis(allylmalonato)borate onto alkyl group-containing comb-branched polyacrylate or polymethacrylate ethers.\(^8\) Although these solvent-free electrolytes provide promising ionic conductivities \((\sigma_0)\) ranging from \(10^{-7}\) to \(10^{-5}\) S/cm at ambient temperature, their synthesis usually involves multi-step reactions and purifications. Moreover, the polymer chain structures and molecular weights have often not been clearly defined.

In the present study, we synthesize a series of novel single-ion conducting ionomers by a two-step melt condensation between PEG and dimethyl 5-sulfoisophthalate sodium salt. The sodium was easily converted to lithium or cesium by dialysis after exposure to an excess of LiCl or CsCl. Initial experiments demonstrate that
these ionomers provide reasonable ionic conductivities at room temperature. A second publication describes the quantification of the free ion mobility and concentration in these ionomers, using the phenomenon of electrode polarization.\textsuperscript{12}

5.2 Experimental

5.2.1 Materials

The reagents used for ionomer synthesis in this study are commercially available. Polyethylene glycol 400 (PEG400, Mn = 400 g/mol), polyethylene glycol 600 (PEG600, Mn = 600 g/mol), triphenyl phosphate (TPP, 97%), titanium (IV) isopropoxide (99.999%), lithium chloride (99+ %) and dimethyl isophthalate (DMI, 99%) were supplied by Aldrich. Polyethylene glycol 900 (PEG900, Mn = 900 g/mol) was purchased from Fluka Chemie GmbH. Dimethyl 5-sulfoisophthalate sodium salt (DM5SIS, 98%) and cesium chloride (optical grade, 99.99%) were supplied by Alfa Aesar and ICN Biomedicals, Inc., respectively. All reagents were used without further purification.

5.2.2 Synthesis

The preparation of the polyester ionomers was carried out by a two-step catalyzed melt transesterification (see Fig. 5.5.1). A glass reactor was charged with the appropriate amounts (PEG:DM5SIS = 1:0.9 molar ratio) of the oligomeric diol, DM5SIS and catalyst
titanium (IV) isopropoxide (0.05 wt %) and were maintained under an argon atmosphere. The mixture was stirred mechanically and the temperature of the reaction maintained at 210 °C for 4 hrs, and then 230 °C for 2 hrs. The by-product methanol was removed using a cold trap. Secondly, DM5SIS (10 mole % of PEG400) and triphenyl phosphate (0.05

Figure 5.1 Schematic representation of the PEG ionomer synthesis
wt % of total reagents) were added, and then the reaction temperature was raised to 250 °C and maintained at this temperature for 2-3 hrs. The total molar ratio of diol / DM5SIS was controlled at 1:1. Vacuum (100 mTorr) was applied for the final 0.5-1 hr at 250 °C to remove low molecular weight species. The completion of the reaction was signaled by a rapid increase in the viscosity, at which point the reactor was refilled with argon gas and cooled to room temperature. Neutral polymers were prepared in the same manner, replacing DM5SIS with DMI.

5.2.3 Diafiltration and ion exchange

The sodium polyester ionomer was dissolved in water and then diafiltered with deionized water using a 1000/3000 molecular weight cut-off membrane. This ionomer was then dissolved in 0.5 M LiCl/H₂O (or 0.5M CsCl/H₂O) and diafiltered to prepare lithium or cesium ionomers. Diafiltration was considered complete when the dialyzate exhibited constant conductivity. The concentrated ionomer solution was then freeze dried and then vacuum dried at 120 °C to constant mass. The ionomers in this paper are identified as PEy-M, where y is the molecular weight of the PEG oligomer used in the synthesis and M represents the type of cation (Li, Na or Cs). The neutral polymers are denoted PEy-0.

5.2.4 ¹H NMR

¹H NMR spectra were acquired on a DPX-300 Spectrometer with perdeuterated dimethyl sulfoxide as the solvent. The spectra were used to verify the polyester ionomer
structure and to determine the number-average molar mass ($M_n$) as all samples have $M_n < 10000$, most likely due to hydrolysis during the diafiltration stage of sample preparation.

5.2.5 Rheology

Dynamic modulus and viscosity were measured using a Rheometric Scientific ARES rheometer with 7.9 mm diameter parallel plates, with 4.0 mm diameter plates used near $T_g$. The ionomers were loaded directly into the instrument and then pressed between two parallel plates to the required geometry, at a temperature $T - T_g = K$. Temperature stability was better than ± 0.1 °C. Strain sweeps were used to ensure that the reported data represent linear response.

5.2.6 X-ray scattering

Small angle X-ray scattering (SAXS) measurements were performed using a Molecular Metrology instrument equipped with a Cu target (λ = 1.542 Å) and a two-dimensional area proportional counter. Typical specimen count times were on the order of 3 hrs. Wide-angle X-ray diffraction data were collected using a Scintag diffractometer with wavelength 1.542 Å.
5.2.7 Thermal characterization

Glass transition temperatures \( (T_g) \) were determined using a TA Q100 differential scanning calorimeter (DSC). Sample sizes were ~15 mg. All samples were held at 120 °C for 3 minutes, then cooled to -90 °C at 20 °C/min. After soaking at the lowest temperature for 5 min, samples were heated to 200 °C at 10 °C/min. \( T_g \) was defined as the midpoint of the heat capacity transition. A TA Q600 thermogravimetric analyzer (TGA) was used to examine the thermal stability.

5.2.8 Conductivity measurement

Void-free ionomers were sandwiched between two round gold-sputtered stainless steel electrodes and the thickness was controlled by 0.2 mm Teflon spacers. A Novocontrol GmbH Concept 40 broadband dielectric (impedance) spectrometer was used to measure the ionic conductivity \( (\sigma_0, \text{ in S/cm}) \). An AC voltage amplitude of 0.5 V was used for all experiments. Frequency sweeps were performed isothermally from 10 MHz to 0.01 Hz in the temperature range from 120 °C to the corresponding \( T_g \). Temperature stability during data acquisition was better than ± 0.1 °C.

5.3 Results and discussion

5.3.1 Ionomer chain characterization

Fig. 5.5.2 shows the \(^1\)H NMR peak assignments for two PE400-M ionomers with different molecular weights. The two peaks at ~8.2 ppm are assigned to the adsorption of
aromatic protons $\lambda$ and $\epsilon$. The peaks of the $\alpha$ protons at 4.2 ppm and $\beta$ protons at 3.5 ppm are separated from those of other protons, reflecting the interactions between the carbonyl group and the OCH$_2$CH$_2$ repeat unit at the ends of the PEG400 segments. The chemical shifts at 4.5 ppm and 3.7 ppm correspond to OH ($\delta'$) and OCH$_3$ ($\delta$) groups at the chain ends, respectively. The peak at 4.35 ppm corresponds to the CH$_2$ ($\alpha'$) connected to the hydroxyl group at the chain ends. The more complicated chemical shifts around 3.3 ppm are assigned to the adsorption of the other protons ($\gamma$) in the PEG400 segments.

There are three aromatic protons ($\lambda$ and $\epsilon$) in the phenyl ring and four protons in two OCH$_2$ ($\alpha$) connected to two carbonyl groups in one repeat unit. Provided that the end groups are CH$_2$OH ($\alpha'$) and OCH$_3$ ($\delta$), degrees of polymerization ($n$) can be calculated from the ratio of monomers and end groups. The results of TGA experiments demonstrate that there is essentially no weight loss below 160 °C in air for any of the ionomers under investigation here. When N$_2$ was used as the purge gas, PE600-Li did not exhibit any detectable weight loss until 270 °C, suggesting that thermal oxidation is the most important degradation mechanism. The weight fraction of residual mass after heating to 800 °C is provided in Table 5.1. It is evident that more mass remains for ionomers with shorter PEG spacers and with heavier cations, suggesting that the final residue is likely the SO$_4^{2-}$ or SO$_3^{2-}$ salt of the corresponding cation. The estimated cation concentrations, assuming that the final product is M$_2$SO$_4$, are provided in Table 5.1. These values are very close to those calculated based on the theoretical stoichiometry.
\[ n = \frac{(I_{(\lambda+\varepsilon)/3}) + (I_{\alpha}/4)}{(I_{\alpha}/2) + (I_{\delta}/3)} \]

where \( I_i \) is the integrated intensity of the \( i \) protons, with \( i = \lambda + \varepsilon \) denoting the sum of the \( \lambda \) and \( \varepsilon \) peaks. The degree of polymerization of the PE400-Na-hmw in Fig. 2b \((n = 10; \quad M_n = 6700)\) is significantly higher than that of PE400-Na in Fig. 2a \((n = 6; \quad M_n = 4200)\).

### 5.3.2 X-ray scattering

Fig. 5.5.3 presents the combined small- and wide-angle scattering of the PE400-Na, PE600-Na, PE900-Na ionomers and the neutral polymer PE400-0. All four polymers exhibit a single peak in the WAXD region, associated with the amorphous halo of PEO. There are no peaks originating from the small-angle scattering from ion-clusters, in contrast with many previous studies of conventional ionomers.\textsuperscript{13-16} Based on our charge densities, we would expect to see a strong peak\textsuperscript{16} near wavevector \( q = 0.1 \ \text{Å}^{-1} \), but no peak is seen. There is considerable extra scattering at low wavevectors in the ionomers, compared with PE400-0, which may indicate some interesting new structure for the ions in our ionomers.
Figure 5.2 Representative $^1$H NMR spectra of two PE400-Na ionomers: a) PE400-Na [$M_n = 4200$] and b) PE-400-Na-hmw [$M_n = 6700$].
Table 5.1 Characterization of PEG-based Ionomers

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<th>Polymer</th>
<th>$M_n$</th>
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</table>

a. The number-average molecular weight ($M_n$) was determined by $^1$H-NMR
b. $T_g$ measured by DSC
c. Residual mass after heating to 800 °C
d. The derived cation concentration, assuming the final residual is $M_2SO_4$
e. This polymer is highly crystalline and a $T_g$ could not be detected by DSC, even after quenching into liquid N$_2$. 
Figure 5. 3 Combined SAXS and WAXD intensities (arbitrary units and offset for clarity) as a function of scattering vector for PE400-Na, PE600-Na, PE900-Na ionomers and the PE400-0 neutral polymer. Note that both intensity and wavevector are plotted on logarithmic scales.

Figure 5. 4 Master curves of storage modulus (triangles), loss modulus (squares) and complex viscosity (diamonds) at $T_{\text{ref}} = 30.0$ °C, for PE600-Na-hmw ($M_n = 8900$ g/mol).
5.3.3 Rheological properties

Fig. 5.4 shows a master curve of the storage and loss moduli of a particularly high molar mass PE600-Na-hmw ($M_n = 8900$). The ionomer chains are weakly entangled (the entanglement molar mass of poly(ethylene oxide)\textsuperscript{17} is $M_e = 2000$ but the ionomers with their bulky isophthalate group may have considerably larger $M_e$). A clear relaxation of ionic aggregates is observed in conventional ionomers,\textsuperscript{18,19} but this relaxation is not evident in Fig. 3 PE600-Na shows interesting viscoelastic response between the glassy modulus (at the highest frequencies in Fig. 3) and the terminal response at the lowest frequencies, but no strong relaxation at intermediate frequencies is observed. Recently, Han, \textit{et al.}\textsuperscript{20} reported a clear ion-aggregate relaxation in their oscillatory shear data for a sulfonated polyester ionomer made from DM5SIS. Consequently, we expect the very different aggregate structure of our ionomers, seen in both SAXS and rheology, are caused by the ether oxygens of the PEO segments stabilizing the ions. The dielectric constant of the polymers is still low (roughly 12) so the ions are expected to be mostly paired (our dielectric analysis\textsuperscript{12} suggests the ions are more than 99.99% paired) but those pairs are stabilized by the ether oxygens and consequently do not form the large ionic aggregates that characterize most ionomers.

All of our ionomers exhibit a single $T_g$ in DSC. For those with the same cation, $T_g$ decreases rapidly with increasing PEG spacer length (Table 5.1). $T_g$ of the PE400 ionomers generally reside around 285-295 K and are high viscosity liquids ($\eta \sim 10^7$ Pa s) at room temperature. Those with PE600 spacers exhibit $T_g \leq 270$ K and have lower viscosities at room temperature ($\eta \sim 10^5$ Pa s). The PE900 ionomers have $236 \leq T_g \leq$
238 K and are pourable high-viscosity liquids at ambient temperature ($\eta \sim 10^2$ Pa s). No clear dependence on cation type can be discerned.

![Figure 5.5](image)

**Figure 5.5** Comparison of measured $T_g$ of PE-Na ionomers with reported values for PEO complexes with NaClO$_4$ and NaCF$_3$SO$_3$ (from ref 23), as a function of Na content.

### 5.3.4 Thermal properties

It is worth pointing out that although similar single $T_g$ behavior has also been observed for other single-ion ionomers, two glass transitions have been reported for the complex of LiClO$_4$ with poly(propylene oxide), arising from the coexistence of ion-rich and ion-poor domains.$^{21-23}$ Clearly, similar ion clusters do not exist in the present ionomers, based on the results of the rheological, thermal and X-ray scattering measurements.
Fig. 5.5 displays a comparison of the Na$^+$ single ion conductors $T_g$ prepared in the present study with values reported previously for PEO complexes with NaClO$_4$ and NaCF$_3$SO$_3$.\(^{23}\) Although similar at low Na$^+$ content, the concentration dependences of $T_g$ are markedly different, with a much greater influence on our PEG ionomers at a given Na$^+$ content. The stronger concentration dependence of $T_g$ for the ionomers is a telltale mark of what Eisenberg calls the ‘ionomer effect’ and is usually associated with the presence of ionic domains in the ionomers.\(^{16}\) Indeed, the slope in Fig. 5 of 8 K/mole% is considerably larger than the 1 K/mole% reported for other polyester ionomers made from sulfonated isophthalate.\(^{24}\) There is no evidence of ion-cluster formation in either our PEG-based ionomers or the PEO complexes in ref 23. However, the nature of the salts in the three systems is quite different and we do not have enough information at this juncture to explain the relative changes in segmental motion in these systems.

While most of the ionomers under investigation here are amorphous at room temperature, PE900-Li is in fact semi-crystalline. DSC reveals a weak melting process at 27 °C with an enthalpy ($\Delta H_m$) of 2.4 J/g. Based on a perfect crystal heat of fusion of PEO of 203 J/g,\(^{25}\) this represents a degree of crystallinity of only ~1%. After holding at 10 °C for 30 min, a significant amount of the PE900-Li crystallizes and the crystal phase melts at 28 °C with $\Delta H_m = 35$ J/g (~17% PEO crystallinity). At the same time, $T_g$ increases from -37 °C to -27 °C after crystallization. No crystallization is observed for PE900-Na and PE900–Cs under the same annealing conditions.
Figure 5.6 Dielectric loss and conductivity of PE600-Li at 50 °C. Filled symbols represent $\sigma'$ and open symbols $\varepsilon''$. The dc conductivity $\sigma_0$ is determined from the plateau in $\sigma'$.  

5.3.5 Ionic conductivity

In the dielectric loss spectrum in the frequency domain, a rapid increase in $\varepsilon''$ is observed at low frequencies as a consequence of dc conduction (Fig. 5.6). The ionic conductivity $\sigma_0$ (S/cm) can be obtained by fitting $\varepsilon'' = \sigma_0 / (\varepsilon_{\text{Vac}} \omega)$, in which $\varepsilon_{\text{Vac}}$ is the vacuum permittivity and $\omega$ the angular frequency. A slope of -1 should be observed in the logarithmic plot of $\varepsilon''$ vs. $\omega$ if the conduction is dominated by contributions from ion drift. However, dipolar polarization from the ionomer dominates at higher frequencies and electrode polarization (i.e., the accumulation of cations at the electrode/electrolyte interface) inhibits ion migration at lower frequencies. Reliable conductivities can be obtained by limiting the fitting to the frequency range where a slope of -1 is observed.
The complex conductivity $\sigma^* = \sigma' + \sigma''$ is related to the complex permittivity $\varepsilon^*$ by $\varepsilon'' = \sigma' / \omega$, $\varepsilon' = \sigma'' / \omega$. Therefore, the conductivity $\sigma_0$ can also be assessed from the plateau value of the real part of conduction spectra (Fig. 5.6). The two procedures produce the same $\sigma_0$. We focus on $\varepsilon''$ in the present study, since the dynamics of the ionomer chain can be simultaneously obtained to explore the fundamental correlation between ion migration and segmental relaxation.\cite{26,27} Conductivities at 25.0 °C are reported in Table 5.1.

PE900-Li is semi-crystalline having a melting temperature slightly above ambient. Continued crystallization with time leads to a dramatic reduction in $\sigma_0$. Immediately after cooling from the melt, PE900-Li has a conductivity of $6.3 \times 10^{-7}$ S/cm at 25 °C. However, after aging under ambient conditions overnight inside the dielectric sample holder, $\sigma_0$ decreases to $1.2 \times 10^{-8}$ S/cm at 23 °C, a reduction by a factor of 50X.

Although the isothermal conductivity only weakly depends on cation type for ionomers synthesized from the same PEG, it increases significantly with increasing PEG spacer length. For the lithium ionomers, $\sigma_0$ at room temperature is raised from $1.7 \times 10^{-10}$, to $7.7 \times 10^{-8}$, and then to $6.3 \times 10^{-7}$ S/cm when the PEG400 spacer is changed to PEG600 and PEG900, respectively. The dramatic increase in $\sigma_0$ is also observed at other temperatures (Fig. 5.7), although the difference diminishes as temperature is raised. Similar behavior is also observed for the sodium and cesium ionomers. A room temperature conductivity of $\sim 10^{-6}$ S/cm can be achieved for the ionomers with PEG900
Figure 5.7 Temperature dependence of conductivity for ionomers made from different PEG spacer lengths. Longer spacer length raises the conductivity by lowering $T_g$. spacers, close to the performance reported for other solvent-free single-ion conductors. The conductivity increases to $10^{-6}$ - $10^{-4}$ S/cm at 80 °C.
The strong dependence of isothermal conductivity on PEG spacer length suggests that the matrix $T_g$ plays a critical role in ion migration. To examine this, Fig. 5.8 compares the conductivities as a function of $T-T_g$. It is immediately evident that all three lithium ionomers have essentially the same $\sigma_0$ at the same $T-T_g$. As discussed above, the low $\sigma_0$ of PE900-Li at low temperatures is simply a result of partial crystallization during the experiment. The Na and Cs ionomers with PEG600 and PEG900 segments have nearly the same ionic conductivity at a given $T-T_g$, although those prepared with PEG400 have slightly (~3X) higher conductivity, which likely results from their higher ion concentrations. The independence of $\sigma_0$ on the molar mass of the precursor PEG oligomer suggests that not all cations are dissociated from the sulfonate anions and that there is significant ion pairing, which reduces the effective mobile ion concentration. In fact, we demonstrate in a recent publication on these same ionomers that the fraction of mobile ions in these materials is remarkably low (e.g., < 0.004% of the total Li content in PE600-Li at 20 °C).\textsuperscript{12}

To further examine the $T_g$ effect, PE600-Na(½) was synthesized from PEG600 with a 50/50 mixture of dimethyl 5-sulfoisophthalate sodium salt and dimethyl alkali ions and oxygens. Consequently, its $T_g$ is 25 K lower than that of isophthalate. This polymer is similar to the PE600-Na ionomer, but with significantly lower Na content, and thus less dense coordination between the PE600-Na. Despite its much lower Na concentration, PE600-Na(½) has substantially higher conductivity than PE600-Na, and the difference becomes more significant as temperature decreases. $\sigma_0$ of PE600-Na(½) at 25 °C is ~30 times higher than PE600-Na.
Figure 5.8 Conductivity as a function of $T - T_G$. Ionomers with the same cation have similar $\sigma_0$ at constant $T - T_G$. 
Fig. 5.9 displays the strong correlation between conductivity at 25 °C and the $T_g$ of corresponding ionomers. $\sigma_0$ exhibits a clear increase with decreasing $T_g$. The $T_g$ of ionomers bearing the same cation decreases ~45 K when the spacer is changed from PEG400 to PEG900, leading to a $10^4$ increase in $\sigma_0$ at 25 °C.

The strong correlation between ionic conductivity and the matrix $T_g$ supports the mechanism that ion migration is realized through cooperative polymer segmental relaxation,\textsuperscript{26,27} and suggests that the ionic conductivity can be improved by decreasing the $T_g$ of the ionomers. Although this can be achieved by increasing the PEG spacer molecular weight, unfortunately, ionomers with longer PEG oligomers are semi-crystalline materials. Plasticization of these ionomers with low volatility high dielectric constant liquids can more significantly decrease $T_g$, while also avoiding crystallization. In
initial experiments we observed a 1000X increase in $\sigma_0$ by adding 20% amorphous PEG400 oligomer to the PE400-Li ionomer.\textsuperscript{27}

It is a common practice to use the molar ratio of ethylene oxide (EO) to lithium to express the cation concentration. For the ionomers synthesized here, EO/Li $\approx$ 8.7, 13.2, and 20.0 for PE400-Li, PE600-Li, and PE900-Li, respectively. Their conductivities are comparable to other polymer single-ion conductors with similar PEG spacer lengths, but are significantly lower than that of the P(EO)$_{10}$-LiTFSI complex reported by Armand et al.\textsuperscript{28} However, anions contribute to most of the measured conduction in the latter and the lithium transference number is very low.

5.4 Conclusions

Inexpensive ionomers incorporating Na, Li, and Cs cations were synthesized by a two-step melt condensation of PEG oligomers and dimethyl 5-sulfoisophthalate sodium salt. Their chemical structures and molecular weights were characterized by $^1$H-NMR. Cation concentrations were estimated using a TGA procedure and the results were consistent with the polymerization feed ratio. No scattering peaks associated with ion-clusters were observed in SAXS and WAXD experiments. Time-temperature superposition can be successfully applied to the storage and loss moduli for all of our ionomers but there is no obvious ion domain relaxation present. The glass transition
temperature is strongly dependent on ion content, despite the fact that the conventional ion domains are neither observed in SAXS nor rheology.

The ionic conductivity exhibits a strong dependence on ionomer $T_g$. At constant temperature, cations are more mobile in low-$T_g$ systems and therefore higher conductivity results, even though the cation content is lower. Consistent with the change in $T_g$, PE900 ionomers have conductivities significantly higher than the PE600 and PE400 ionomers. By normalizing temperature with the corresponding $T_g$, different ionomers have similar conductivity at the same $T - T_g$ without significant dependence on cation content. This supports the correlation between polymer segmental motion and ion mobility\textsuperscript{27} in these ionomeric single-ion conductors.

Acknowledgments

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5.5 References


Chapter 6

Synthesis and Characterization of PEO-PTMO-Based Single Ion Conductors

6.1 Introduction

Solid state polymer electrolytes have been extensively investigated in the last three decades as candidate materials for lithium ion batteries, due to the leakage of conventional liquid electrolytes in the application of electronic devices.\textsuperscript{1-4} To conduct electric current at high efficiency, the basic requirements for electrolytes include (1) high dielectric constant, (2) low glass transition temperature $T_g$, (3) long lifetime in the work condition and inert to other components in the battery. Since Wright reported the ionic conductivity of PEO/Na\textsuperscript{+} complex in 1975,\textsuperscript{4} poly(ethylene oxide) (PEO) has been well-known for its ability to solvate Li\textsuperscript{+}, leading to macroscopic ionic conductivity.\textsuperscript{5} PEO electrolytes can be prepared by mixing PEO containing polymers with Li ion salts\textsuperscript{6-9} or synthesizing PEO-based single-ion conductors.\textsuperscript{10-20} In the PEO/salt complex system, cations, anions and ion-clusters (multiple ions) all migrate towards opposite electrodes. The anions build up in the vicinity of one electrode impeding the transport of Li cations. In the system of single ion conductors, migration of anions is negligible because anions are fixed on the backbone of polymer electrolytes, and a transference number of unity can be achieved.\textsuperscript{3} Hence, PEO-based single ion conductors have the potential to effectively
resolve the leakage problem encountered with liquid electrolytes and provide high conductance of only \( \text{Li}^+ \) for electronic devices such as advanced batteries.

In our previous study (Chapter 5 and reference 19), the ionic conductivity of PEO-based single ion conductors demonstrates a strong dependence on the ionomer’s \( T_g \). At the same temperature, \( \text{Li}^+ \) ion readily moves in a medium with lower \( T_g \) and therefore shows higher conductivity, even though the \( \text{Li}^+ \) concentration is lower. For instance, PE900-Li ionomer exhibits greatly higher conductivity than the PE600-Li and PE400-Li ionomers, owing to its lower \( T_g \). Interestingly, all three ionomers show similar conductivity at the same \( T - T_g \) without significant dependence on cation content. \(^{19,21}\) Allcock et al. \(^7\) found that the conductivity of gel electrolytes changes very little as the glass transition temperature effects are considered by plotting \( \sigma(T) \) vs \( T - T_g \). On the other hand, Sun et al. \(^{22}\) reported that the conductivity of polyMOB and polyBOP single ion conductors at ambient temperature decreases with increasing ion content due to the enhancement of their \( T_g \)s with increasing ion concentration. However, this group \(^{22,23}\) only covers a narrow ion concentration region, whereas data at very low ion concentrations are useful to understand how ion content impacts the conductivity of PEO-based ionomers. How does the ion content of single-ion conductors impact its conductivity, glass transition temperature, and dielectric constant? To understand the conduction mechanism in depth, we design a series of single-ion conductors with a generic structure that can be changed to obtain a series of single ion conductors with a varied ionic composition and EO content.
Aside from poly(ethylene oxide), both poly(propylene oxide) (PPO)\textsuperscript{24} and poly(tetramethylene oxide) (PTMO)\textsuperscript{25,26} have also attracted researcher’s attention. Shilov et al.\textsuperscript{25} reported that the polyurethane (PU) prepared via carboxyl-containing oligoether (made from PTMO and pyromellitic anhydride) shows very low protic conductivity owing to the poor solvation of ionic groups in the PTMO-rich domain (soft segment). Polizos et al.\textsuperscript{26} indicated that the ionic conductivity of PEO-PTMO based PU ionomers increases with increasing molar fraction of PEO segments. The ether oxygens in PEO show better solvation of Li\textsuperscript{+} ions than in PTMO. Can ionic groups really solvate in a PTMO matrix? How does the molar fraction of non-solvating components in the matrix of polymer electrolytes impact the ionic conductivity? We will focus on those queries by comparing the ionic conductivity of PEG600-PTMO650 copolyesters with that of PEO-based ionomers and PTMO-based ionomers.

In this study, we synthesized a series of novel copolyester ionomers as single-ion conductors by melt polycondensation between diols (PEG600 and PTMO650) and diesters (dimethyl 5-sulfoisophthalate sodium salt and dimethyl isophthalate). The sodium cation was converted to lithium by dialysis after exposure to an excess of LiCl in deionized water. The preparation details are described in a previous study.\textsuperscript{19} Those novel ionomers were characterized with proton NMR, SAXS, DSC and dielectric spectroscopy.
6.2 Experimental

6.2.1 Materials

All reagents used for ionomer synthesis in this study are commercially available. Poly(ethylene glycol) 600 (PE600, $M_n = 600$ g/mol, 99%), poly(tetramethylene oxide) 650 (PTMO650, $M_n = 650$ g/mol, 99%), triphenyl phosphate (TPP, 97%), titanium (IV) isopropoxide (99.999%), lithium chloride (99+ %), and dimethyl isophthalate (DMI, 99%) were supplied by Aldrich. Dimethyl 5-sulfoisophthalate sodium salt (DM5SIS, 98%) was supplied by Alfa Aesar. All reagents were used without further purification.

6.2.2 Synthesis

The synthesis of polyester ionomers was performed by a two-step melt polycondensation. All monomers (diols and diesters) were degassed in the vacuum oven 12 hrs at 80 °C before use. A dry glass reactor (purged three times using argon) with a mechanical stirrer and three openings was charged with the appropriate amounts (diols:diesters = 1:0.88 molar ratio) of the oligomeric diol, diesters and catalyst titanium (IV) isopropoxide (0.05 wt %) and were maintained under an argon atmosphere. The mixture of about 60 grams was stirred mechanically and the temperature of the reaction maintained at 210 °C for 4 hrs, and then 230 °C for 2 hrs. The polycondensation by-product methanol was removed using a liquid N$_2$ cold trap. Secondly, diesters (12 mole % of diols) and triphenyl phosphate (0.05 wt % of total reagents) were added after the mixture in the reactor was cooled to 180 °C, and then the reaction temperature was raised
to 250 °C and maintained at this temperature for 2-3 hrs. The total molar ratio of diols / diesters was controlled at 1:1. Vacuum (100 mTorr or less) was applied for the final 0.5-1 hr at 250 °C to remove low molecular weight species. The completion of the reaction was signaled by a rapid increase in the viscosity, at which point the reactor was refilled with argon gas and cooled to room temperature. Neutral polymers were prepared in the same manner, replacing DM5SIS with DMI. Copolymers were prepared by using diols (PEG600 and PTMO650) and diesters (DM5SIS and DMI) (Fig. 1).

Figure 6. 1 Schematic representation of the PEO-based copolyester ionomer synthesis
6.2.3 Polyester ionomer identification

Polyester ionomers are identified as PE600-xLi (x is the molar fraction of the DM5SIS in the mixture of DM5SIS and DMI; x = 0, 0.025, 0.05, 0.1, 0.25, 0.5, 1) and PEG600-PTMO650 (z)-Li (z is the molar ratio of PEG600 and PTMO650 in a copolymer (z = 1/0, 75/25, 50/50, 0/1). It is noted that as x = 0, the polymer is neutral polymer PE600-0; as x = 1 or z = 1/0, the polymer is PE600-Li (it was studied in the previous work\textsuperscript{19}); as z = 0/1, the polymer is PTMO650-Li.

6.2.4 Ion exchange

The sodium polyester ionomers synthesized above were dissolved in water and then diafiltered with deionized water using an Amicon 1000 molecular weight cut-off membrane. Those ionomers were then dissolved in 0.5 M LiCl/H\textsubscript{2}O and diafiltered to prepare the lithium salt. Diafiltration was considered complete when the dialyzate exhibited constant conductivity (about 10 \(\mu\)S/cm). The concentrated ionomer solution was then freeze dried and then vacuum dried at 120 °C to constant mass.

6.2.5 \textsuperscript{1}H NMR

\textsuperscript{1}H NMR spectra were acquired on a DPX-300 Spectrometer with perdeuterated dimethyl sulfoxide (DMSO-d\textsubscript{6}) as the solvent. The spectra were used to verify the polyester ionomer structure and to estimate the number-average molar mass (\(M_n\)) as all
samples have $M_n < 20,000$, most likely due to hydrolysis during the diafiltration stage of sample preparation.\textsuperscript{19}

\textbf{6.2.6 Thermal characterization}

Glass transition temperatures ($T_g$) were determined using a TA Q100 differential scanning calorimeter (DSC). All experiments were performed under a dry nitrogen purge. Sample sizes were \textasciitilde8 mg. All samples were quickly heated (20 °C/min) to 90 °C and held at the temperature for 5 minutes, then cooled to -90 °C at 5 °C/min. After soaking at the lowest temperature for 5 min, samples were heated to 90 °C at 10 °C/min. $T_g$ was defined as the midpoint of the heat capacity transition.

\textbf{6.2.7 SAXS}

SAXS measurements were performed using a Molecular Metrology instrument equipped with a Cu target ($\lambda$ =1.542 Å) and a two-dimensional detector. Scattering time was about 3 hrs for polyester ionomers (Li\textsuperscript{+} salt). All samples for SAXS were prepared using a liquid cell with thickness 1.3 mm (kapton windows). The scattering intensity of samples was subtracted from background and then normalized using the scattering time (seconds), thickness (cm), and transmission of each measurement (see Appendix 3).
6.2.8 Conductivity measurement

The ionomers in this study are low $T_g$ viscous polymers. A dry melt ionomer was transferred onto one gold-sputtered electrode (3 cm diameter, three pieces of Teflon spacers on it) in a vacuum oven at about 100 °C and then dried in the vacuum oven until all bubbles disappear. Another electrode was put on the melt polymer slowly and extra sample was squeezed away. The sandwiched void-free ionomers between two round gold-sputtered electrodes was inserted between two electrodes of Novocontrol GmbH Concept 40 broadband dielectric (impedance) spectrometer. The ionic conductivity ($\sigma_0$, S/cm) was measured using an AC voltage amplitude of 1.5 V for all experiments. Frequency sweeps were performed isothermally from 0.01Hz to 5x10^6 Hz in the temperature range from a temperature near $T_g$ to 120 °C. Temperature stability during data acquisition was better than ± 0.1 °C.

6.3 Results and discussion

6.3.1 Synthesis and chain characterization

Polyester chemistry is a broad research field that has attracted many researchers’ attention due to its advantage in the design of new polymers endowed with specific properties. There is an infinite choice in formulation and targeted polymers can be prepared from many commercial reagents by block copolymerization leading to linear or chemically crosslinked polyester structures. In this work, we have synthesized a series of polyester ionomers by chemically incorporating an ionic monomer DM5SIS into the
backbone of polyesters. The design of the structure of polyester ionomers was focused on the ionic content and solvating power by varying the molar fraction of DM5SIS and PTMO650 in the polyesters (Fig. 6.1).

In route (A), monomers DMI, DM5SIS, and PEG600 were used in the preparation of polyester ionomers (PE600-xLi) by changing the molar ratio of diesters DM5SIS and DMI from 0 to 0.025, 0.05, 0.1, 0.25, 0.5 and 1, leading to the change of the ion content in the ionomers from 0 to 0.85 wt % (Table 1). In the $^1$H NMR spectra of PE600-xLi copolymers (Fig. 6.2), the intensity of $^1$H NMR from the three protons of DM5SIS

![Figure 6.2  $^1$H NMR spectra of PE600-xLi polyester ionomers.](image)
monomer corresponds to the increase of the DM5SIS molar fraction and the decrease of
the DMI molar fraction. The two peaks at about 8.4 ppm are assigned to the NMR
absorbance of DM5SIS aromatic protons. The three peaks at about 7.8, 8.3, and 8.6 ppm
are assigned to the NMR absorbance of DMI aromatic protons. The $\alpha$ protons $\text{CH}_2$
connected to a carbonyl group show a $^1\text{H}$ NMR peak at about 4.5 ppm and the $\text{CH}_2$
protons connected to OH groups at the chain ends show a peak at about 4.6 ppm. The
chemical shifts at about 3.95 ppm correspond to the OCH$_3$ groups at the chain ends. The
$^1\text{H}$ NMR peaks of the protons in the repeat unit or chain ends do not overlap with other
peaks, the degrees of polymerization ($n$) can be evaluated from the ratio of monomers in
the repeat unit and end groups (the end groups are -CH$_2$OH and -OCH$_3$ in this study).$^{19,27-29}$
However, the determination of polymer molecular weight by $^1\text{H}$ NMR is limited to
$M_n<20,000$ due to overlapping and resolution of proton NMR spectroscopy.$^{28}$ The $M_n$ of
PE600-xLi obtained from proton NMR spectra is listed in Table 6.1.

In route (B), Diols PEG600 and PTMO650 together with DM5SIS were applied
to synthesize PEG600-PTMO650 (z)-Li (Fig. 6.1). The real copolyester ionomers are
PEG600-PTMO650(75/25)-Li and PEG600-PTMO650(50/50)-Li, PE600-Li and
PTMO650 were produced by using the extreme molar ratio of PEG600 and PTMO650.
However, we can investigate the continuous properties of copolyesters better, in
comparing with the properties of the products made from only monomer PEG600 or
PTMO650. Fig. 3 shows the $^1\text{H}$ NMR of the ionomers PTMO650-Li and PEG600-
PTMO650 (50/50)-Li. The absorbance at chemical shifts about 8.4 ppm indicates three
aromatic protons from the phenyl ring of DM5SIS monomer, and the chemical shifts at
about 4.35 ppm correspond to the $\text{CH}_2$ group connected to the carbonyl group. The other
chemical shifts at $\delta < 2$ppm are related to the protons of two CH$_2$ in the middle of PTMO650 repeat unit (Fig. 6.3). The $M_n$ of PEG600-PTMO650 (z)-Li obtained from proton NMR spectra are shown in Table 6.1.

**Figure 6.3** $^1$H NMR spectra of PEG600-PTMO650 (50/50)-Li (top) and PTMO-Li (bottom) polyester ionomers.
Table 6.1 Characterization of PEO-based polyester ionomers

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<td>PE600-Li</td>
<td>4700</td>
<td>258</td>
<td>0.85</td>
<td>1.40E-08</td>
</tr>
<tr>
<td>PEG600-PTMO650(75/25)-Li</td>
<td>6400</td>
<td>255</td>
<td>0.83</td>
<td>8.76E-09</td>
</tr>
<tr>
<td>PEG600-PTMO650(50/50)-Li</td>
<td>7300</td>
<td>255</td>
<td>0.82</td>
<td>1.60E-09</td>
</tr>
<tr>
<td>PTMO650-Li</td>
<td>6700</td>
<td>211</td>
<td>0.80</td>
<td>1.07E-11</td>
</tr>
</tbody>
</table>

Figure 6.4 The SAXS profile of PEG600-PTMO650 (z)-Li copolyester ionomers. The inset was plotted as \(I(q) \times q^2 \sim q\). Note that the intensity is plotted on a logarithmic scale and the wavevector is plotted on linear scale. \(I(q)\) is the normalized intensity with background scattering subtracted (see Appendix 3).
6.3.2 X-ray scattering

Fig. 6.4 exhibits the SAXS profiles of polyester ionomers PE600-Li, PEG600-PTMO650 (75/25)-Li, PEG600-PTMO650 (50/50)-Li and PTMO650-Li. It indicates that the PE600-Li does not form ionic clusters or microphase separate in the wavevector range under investigation, which is in agreement with the result reported for PE600-Na previously.19 There is no peak observed in the SAXS from ion-clusters for PTMO650-Li either, while an ionic peak may exist in the higher q range, owing to the upturn in the SAXS profile $I(q) \sim q^2$ at high q. It is noted that the $I(q) \sim q^2$ profile of the ionomer PTMO650-Li is very different that of PE600-Li. On the contrary, many conventional ionomers show ionic peaks in SAXS measurements,30, 31 with the wavevector of the peak giving the average spacing between ionic domains.

Polizos et al26 reported that the PEO-based PU ionomers in their study show a weak microphase separation of hard segments (HS) and soft segments (SS), however there is no ionic peak observed in their SAXS experiments. For PTMO-based PU ionomers, they found a stronger microphase separation of HS and SS, while the neutral sample studied also shows a strong microphase separation. Therefore, their study indicates that both the ionization level and the hydrophilic level of chain segments impact the microphase separation of HS and SS (PEO segments are more hydrophilic than PTMO segments). In our study, two copolyester ionomers demonstrate a weak microphase separation of PEO segments and PTMO segments based on the transition of $I(q)$ curves, while the microphase separation is perhaps caused by two soft segments. The distance between the scattering microphases (PTMO650-rich domain) in PEG600-PTMO650
(75/25)-Li is larger (157 Å; \( q \approx 0.04 \text{ Å}^{-1} \)) than that in PEG600-PTMO650 (50/50)-Li (79 Å; \( q \approx 0.08 \text{ Å}^{-1} \)), owing to the different molar fraction of PEG600 in two copolymers. This suggests that the continuous phase may be PEO with ions and PTMO-rich droplets dispersed. Considering that the small ionic aggregates (multiplets) may exist in PTMO650-Li, it is possible that there are many multiplets dispersed in the PTMO650-rich domain of the copolyester ionomers.

At very low \( q \), strong scattering was observed for all polyester ionomers (see the comparison with that of neutral polymer PE400-0 with the same backbone structure\(^1\)). Ding et al.\(^3\) suggested that the considerable extra scattering at low wavevectors in the ionomers is related to an inhomogeneous distribution of ionic domains in the polymer matrix.

### 6.3.3 DSC thermal analysis

Polyester ionomers were dried at 120 °C for 48 hrs before they were used for thermal analysis. All of them exhibit a single \( T_g \) in DSC measurements. Table 6.1 shows that the \( T_g \) of PE600-xLi with the same PEG600 spacer does not greatly increase with increasing molar fraction of the ionic group or ion content in ionomers until \( x = 0.25 \) or the ion content reaches 0.23 wt%, below which the \( T_g \) of copolyester ionomers is about 228 K on average that is the \( T_g \) of the neutral polyester PE600-0. At the ion content above 0.23 wt%, the \( T_g \) of those ionomers increases rapidly from 230 K (PE600-0.25Li, ion content 0.23 wt%) to 258 K (PE600-Li, ion content 0.85 wt%) with increasing ion content. Most of the PE600-xLi ionomers are semi-crystalline polymers and show a
strong melting process at about 285 K (same as that of the neutral polymer) (Fig. 6.5), therefore they are liquid-like amorphous polymers at room temperature. However PE600-0.5Li and PE600-Li are amorphous at all temperatures, possibly owing to the coordination interaction between Li$^+$ and oxygens in PEO segments.

Fig. 6.6 shows that the copolyester ionomers with PTMO650-rich domains and PTMO650-Li are amorphous, and have one only $T_g$, although the SAXS results of those ionomers suggest microphase separation. PEG600-PTMO650 (75/25)-Li and PEG600-PTMO650(50/50)-Li show a significant difference in the microphase size due to the

![Figure 6.5 DSC thermal analysis of PEO-based polyester ionomers; for clarity, the thermograms of PE600-xLi ionomers have been shifted vertically.](image_url)
Figure 6.6 DSC thermal analysis of PEG600-PTMO650 (z)-Li polyester ionomers.

difference of the molar ratio of PEG600 and PTMO650 in the ionomers, while they have similar glass transition temperature at about 255 K. This $T_g$ is only slightly lower than the $T_g$ of PE600-Li ($T_g = 258$ K, ion content 0.85 wt%). It is possible that some of the ionic groups connected to the PTMO650 segments accumulate at the interphase of the PEG600-rich domains and the PTMO650-rich domains so that the ionic groups can embed within the microphase of PEG600 segments and have a better solvating effect. In the case of this conjuncture, the coordination between Li$^+$ and PEO ether oxygens can still occur and contribute to the increase in $T_g$. This explains the miniscule variation of $T_g$ for the three PEO-PTMO copolymer ionomers. The PEO microphase and the PTMO microphase contain segments of the other (the same as that seen in PUs$^{33}$). A much lower $T_g$ (211 K) of PTMO650-Li (ion content 0.82 wt%) further supports this conjuncture that most of the ionic groups in the PTMO segments tend to disperse into the
interphase of two microphases. The possibility for Li$^+$ to form stable coordination structures with PTMO segments is very low, PTMO650-Li has a low $T_g$, although which is still much higher than that of PTMO650 oligomeric monomer. The microphase separation may be not complete, however, the nature of the ionic groups in the PTMO650 system is not quite understood and we do not have enough information to explain the conjuncture at the interphase and PTMO-650-rich domain of those ionomers.

6.3.4 Ionic conductivity

In our previous studies, we found that the ionic conductivity of PEO-based ionomers with different PEG spacer lengths (400, 600, and 900) is greatly impacted by the glass transition temperature of those ionomers due to the conducting mechanism depending on the segmental motion of the polymer host. However, the ionic conductivity of PEO-based Li$^+$ ionomers does not change with increasing PEO spacer length at constant $T-T_g$. As the PEG spacer used for making an ionomer is changed, the ion content of the ionomer also changes. In this study, PEG (600) and PTMO (650) spacers remain unchanged, while (A) the ion content of polyester ionomers was changed from 0 to 0.85 wt% by incorporating neutral DMI monomer and (B) the spacer was changed from PEG600 to PTMO650 (Fig. 6.1 and Table 6.1)
Figure 6.7 (a) Temperature dependence of conductivity for PE600-xLi ionomers with different ion content. (b) Ion content dependence of the ionic conductivity plotted against $T - T_g$.

Ion content in PEO-based polymer electrolytes is crucial to the $T_g$ of the electrolytes. Fig. 6.7 shows the temperature dependence of the ionic conductivity of PE600-xLi ionomers. At temperatures $T < 300$ K, the ionic conductivity of PE600-Li is lower than that of all other ionomers due to its much higher $T_g$. As the temperature increases, the ionic conductivity of PE600-Li increases quickly until it merges with the conductivity of PE600-0.5Li ($2 \times 10^{-5}$ S/cm) at about 390 K. All ionomers with low ion content except PE600-0.025Li show a similar ionic conductivity at $T < 300$ K. The influence of the ion content on the ionic conductivity increases with increasing temperature due to the constriction of the
chain segmental motion which is related to the proximity of $T_g$. However, the
increase in ionic conductivity with increasing temperature slows down at high
temperature.\textsuperscript{34} In Fig. 6.7b, PE600-Li and PE600-0.5Li show the highest ionic
conductivity at a given $T-T_g$, followed by two ionomers with moderate ion content
PE600-0.25Li and PE600-0.1Li (they show the same ionic conductivity at $T-T_g$),
PE600-0.05Li, PE600-0.025Li. Remember, PE400-Li, PE600-Li, and PE900-Li
also show the same ionic conductivity at constant $T-T_g$.\textsuperscript{19} Clearly, the ion content
significantly impacts the ionic conductivity. Neutral polymer PE600-0 shows the
lowest conductivity in all polymers studied at $T > 270$ K.

Fig. 6.8a indicates that the ionic conductivity of PE600-xLi ionomers at 25
°C is greatly influenced by the $T_g$ and ion content of the ionomers and there are
three regions observed: At very low ion contents, the $T_g$ does not change very
much, while the ionic conductivity increases rapidly with increasing ion content;
At moderate ion contents, the $T_g$ increases slightly, while the ionic conductivity
does not change at all with increasing $T_g$ and ion content; At high contents, the $T_g$
increases rapidly, causing the ionic conductivity to decrease quickly. Many
studies on the ionic conductivity of polymer electrolytes is limited to the high ion
content region.\textsuperscript{22,35-38} Sun et al compared the ambient ionic conductivity of the
single ion conductors “polyBOP” with that of “polyMOP” and indicated that the
increases in $T_g$ is higher and the decrease in $\sigma_0$ is lower with increasing ion
content.\textsuperscript{22}
Figure 6. 8 (a) Ion content dependence of ionomer $T_g$ and their conductivities at 25 °C. (b) Ion content dependence of ionomer dielectric constant and their conductivities at 25 °C.
However, attention has also been paid to the ionic conductivity of electrolytes with low ion content. Siska et al.\textsuperscript{37} found that at ion content Li\textsuperscript{+}/EO larger than 0.04 the ionic conductivity of polysiloxane-trifluoromethylsulfonamide Li\textsuperscript{+} salt (single ion conductors) at 25 °C decreases significantly with increasing ion content, because the $T_g$ of the ionomer increases. At lower ion contents, both the $T_g$ and the ionic conductivity increase slightly with Li\textsuperscript{+}/EO. MacFarlane et al.\textsuperscript{39} show a research result similar to our study that there are regions in the ion content dependence of the ionic conductivity of PEO-based polymer electrolytes: rapid increase, retain, and quick decrease. Xu et al.\textsuperscript{35} concluded in their study that the increment in ionic conductivity is due to the decrease in $T_g$ and the increase in decoupling index (dielectric constant) as ionic plasticizer is used. In the single ion conductors, the dielectric constant of PEO-based ionomers increases with increasing ion content (Fig. 6.8b), however, the quick increase in dielectric constant is limited to the low ion content region. At the high ion content region ($c_{Li} > 0.23$ wt%), the dielectric constant only increases slightly with increasing ion content. Therefore, the high ionic conductivity of PEO-based ionomers with moderate ion content is ascribed to their relatively low $T_g$ and high dielectric constant (Fig. 6.8).
Figure 6.9 Temperature dependence of conductivity for PEG600-PTMO650 (z)-Li ionomers made from diols PEG600 and PTMO650; Increasing the PEG600 content raises the conductivity by better solvating of Li$^+$. (b) the influence of polymer hydrophilicity on the ionic conductivity at temperature $T - T_g$. 
It is noted that the ionic conductivity of copolyester ionomers PEG600-PTMO650 (z)-Li decreases with increasing molar fraction of PTMO650 segment (Fig. 6.9). This result correlates well with the SAXS result of microphase separation and the conjuncture of poor solvation of Li\(^+\) by the PTMO650 ether oxygen. PEG600-PTMO650 (75/25)-Li shows much higher ionic conductivity than that of PEG600-PTMO650 (50/50)-Li, although they have almost the same \(T_g\) (-18 °C) and ion content (0.82 and 0.83 wt%, respectively). PTMO650-Li with the lowest \(T_g\) (-62 °C) shows insulator behavior in the entire experiment temperature region, and its ionic conductivity is much lower than that of the neutral polymer PE600-0. We conclude that PTMO650-Li cannot conduct electric current because it is completely dry. The ionic conductivity of those ionomers at constant \(T-T_g\) also increases with increasing molar fraction of PEG600 segments. Hence, the volume fraction of PEG600 segments greatly impacts the ionic conductivity. Our results are in agreement with Polizos et al.’s study.\(^{26}\) They indicated that PEO-based PU ionomers shows higher ionic conductivity than that of PTMO-based PU ionomers. However, the ionic conductivity of PTMO-based ionomers under study is much lower than that reported in literature.\(^{26}\)

### 6.4 Conclusions

PEO-based polyester ionomers with Li\(^+\) counterion PE600-xLi were synthesized by a two-step melt polycondensation. PEG600-PMTO650 (z)-Li copolyester ionomers were prepared by changing the molar fraction of diols PEG600 and PTMO650. \(^1\)H-NMR was used to characterize the chain structure and to evaluate the number-average
molecular weights of those ionomers. Cation content was controlled by varying the molar fraction of diesters DM5SIS and DMI. In the SAXS measurements, no scattering peak was observed for PE600-xLi, while microphase separation was found for the copolymers PEG600-PTMO650 (75/25)-Li and PEG600-PTMO650 (50/50)-Li. Multiplets of ion-clusters may exist in the microphase of PTMO650 rich domain according the upturn scattering intensity of PTMO650-Li at high $q$. The $T_g$ of ionomers increases rapidly with increasing ion content in the high ion content region. However, the $T_g$ of PE600-xLi ionomers with low ion content approaches to the $T_g$ of neutral polymer PE600-0. This suggests that there is a limitation in reducing $T_g$ of ionomers if the ionomer backbone is PEO segments. The PTMO650-Li shows the lowest $T_g$ in polymers under investigation possibly due to the low $T_g$ of PTMO650 oligomeric monomer and the poor solvation of Li$^+$ in PTMO650. The ionic conductivity of PE600-xLi exhibits a strong dependence on the ion content at constant $T-T_g$, while the dependence is weaker at lower $T-T_g$. At higher $T-T_g$, the higher mobile ion concentration of ionomers with high ion content dominates the ionic conductivity. The ionic conductivity of PEG600-PTMO650 (z)-Li ionomers increases greatly with increasing molar fraction of PEG600 segment. PTMO650-Li shows a strong insulator behavior as it is dry possibly because Li$^+$ is immobile in the PTMO650-Li.

Future work should focus on increasing mobile ion content in such materials, considering the limitation of a minimum $T_g$ for PEO-based ionomers and the effects of ion content on the ionic conductivity. Fig. 5.8 shows that crystallization lowers conductivity, so avoiding crystallinity is very important. Microphase separation is not favorable to the ionic conductivity, although the $T_g$ of ionomers is low because the
conductance is measured based on specific volume of materials that conducts electric current. Raising ion content without increasing $T_g$ much through additives with high dielectric constant and low viscosity and possibly crosslinking the polymer electrolyte matrix are favorable for increasing mobile ion concentration and still keeping polymer electrolyte in the solid state. Also, quantitative analysis of water content in single-ion conductors, using Karl-Fisher titration, is vital for future work, as small amounts of water may play an important role in conductivity.

Acknowledgments

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6.5 References

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172
Appendix 1 Synthesis of quaternized P2VP and P2VP(h) polyelectrolytes

**Quaternization** Poly (2-vinyl pyridine) (P2VP: \( M_w = 364,000 \) g/mol, \( M_w/M_n = 1.06, N = 3230 \), based on \( M_n \); P2VP(h), \( M_w = 1,220,000 \) g/mol, \( M_w/M_n = 1.1, N = 10500 \), based on \( M_n \)) purchased from Polymer Source Inc. was used without further purification. Random copolymers of 2-vinyl pyridine and N-methyl-2-vinyl pyridinium chloride or iodide (PMVP-Cl and PMVP-I) were prepared by quaternization and ion-exchange. Powder parent P2VP (or P2VP(h)) was molded to small pellets at room temperature and then dried in the vacuum oven 48 hrs at about 50 °C. The dry P2VP pellets were added into a 100 mL reactor (with magnetic stirrer and three openings) under argon and then the reactor was sealed and argon was used to purge the reactor several times. Anhydrous DMF (N, N-dimethyl formamide (DMF was redistilled under vacuum in the presence of sodium) and was then injected to make a 10 wt % solution of P2VP in DMF. DMS was injected into the reactor after the P2VP had fully dissolved in DMF. The reaction was kept at room temperature 24 hrs under argon atmosphere (water and oxygen free environment). Polyelectrolytes made by this method with more than 30 mole % charged monomers were precipitated into acetone, filtered and then redissolved in 2M NaCl (or NaI) solution in water with at least 50 fold excess of halide to methyl pyridinium ion. Polyelectrolytes with lower charge density were directly dissolved in 2 M NaCl (or NaI) mixed solvent water-methanol (50/50 volume). The quaternized polymer in 2 M NaCl (or NaI) solution was dialyzed against deionized water or a deionized water-methanol
mixture until a constant conductivity (< 2 μS/cm) of the dialyzate was attained. Finally, the salt-free polyelectrolyte solution was lyophilized under vacuum, and the solid quaternized polymer was dried in a vacuum oven (about 2 weeks) at about 40 °C to a constant mass. The amount of water in “dry” strongly charged 55PMVP-Cl is lower than 0.6 wt % obtained from the measurement of this polymer solution in EG using Karl Fischer Titration. Quaternized random copolymers with various charge densities were obtained by varying the molar ratio of DMS and pyridine. Dry polymers were dissolved in fresh redistilled EG to prepare the highest concentration, and lower concentrations were prepared by serial dilution. In all cases, the water concentration in samples exposed to air for one hour is smaller than 0.3 wt % measured using Karl Fischer Titration. Polymer concentration is reported in moles of monomers (the sum of both vinyl pyridine and methyl vinyl pyridinium chloride) per liter of solution.

**DQ α measurement:** The degree of quaternization of the partially quaternized polymers was determined using silver nitrate (AgNO₃, Aldrich, 99.9%) conductometric counterion titration, calibrated with sodium chloride (NaCl, Aldrich, 99.999%). The degree of quaternization is the ratio of moles of AgNO₃ and moles of total monomer.

\[
\alpha = \frac{\text{moles } AgNO_{3}}{\text{moles monomer}} = \frac{\text{moles } AgNO_{3}}{W / \left[\left(1 - \alpha \right)M_{VP} + \alpha M_{MVP-Cl}\right]}
\]

\(W\) is the mass of polymer, \(M_{VP} = 105.137 \text{ g/mol}\) is the molar mass of the vinyl pyridine monomeric repeat unit and \(M_{MVP-Cl} = 155.625 \text{ g/mol}\) is the molar mass of the N-methyl-2-vinyl pyridinium chloride monomeric repeat unit. The above equation is then solved for the degree of quaternization.
\[ \alpha = \frac{M_{VP}}{W / (\text{moles AgNO}_3) + M_{VP} - M_{MVP-Cl}} \]

$^1$H NMR was used for the qualitative confirmation of the quaternization extent determined by titration. Owing to the tacticity of P2VP (Figure 1), there are two characteristic peaks of the quaternary methyl group (Figure 2), located in the chemical shift range $\delta = 3.2-4.5$ ppm. The $^1$H NMR result (two peaks at 2.6 ppm and 3.0 ppm indicate the protons of the methyl group) of 10PMVP-Cl shows that the fraction of quaternized monomers is 0.103, which is in agreement with the result obtained from titration ($\alpha = 0.10$). However, if the degree of quaternization is much higher, the signal of the methylated group is so strong that the peaks of the methylated group overlap with the peaks of other protons on the polymer chain backbone. For weakly charged P2VP, the $^1$H NMR signal (two peaks) of the methylated group is too weak to be correctly determined from the internal comparison of $^1$H NMR.

The UV-vis absorbance of quaternized P2VP in EG (Figure 3) indicates that the DQ cannot be determined from the UV results correctly. The peak at 263 nm is the critical absorbance of the uncharged monomers, while the peak at 268 nm is the critical absorbance of the charged monomers (Figure 3). They are so close in absorption wavelength that it is very hard to separate the absorbance intensity into that caused by charged monomers or uncharged monomers.

**Molecular Weight:** The molar mass of quaternized polymers was determined from the DQ of quaternized P2VP and the chain length of the parent neutral P2VP(or P2VP(h)). The SEC measurements show that the quaternized P2VPs still have low PDI
and polyelectrolyte chains did not break in the process of reaction and dialysis (Figure 4). Although the chain length of quaternized polymers does not change, the molar mass of polyelectrolytes varies with $\alpha$ and counterions (chloride or iodide).

Figure 1 The proton NMR of P2VP in CDCl$_3$ at room temperature
Figure 2. The proton NMR of 10PMVP-Cl in D$_2$O at room temperature.

\[ \frac{n_{H-CH_3}}{n_{H-C_6NH_4}} = x \]

Figure 3. UV-vis absorbance of quaternized P2VP in EG at room temperature. c = 0.00025M
Figure 4 The SEC result of 60PMVP-I in an aqueous solvent of 0.7M sodium nitrate, 0.1M Tris buffer, 200ppm sodium azide, pH = 6.0 (adjusted with glacial acetic acid). This measurement was kindly performed by John Layman at VT.
Appendix 2 Synthesis of PEO-based polyester ionomers as single ion conductors

Synthesis: The preparation of the polyester ionomers was performed by a two-step catalyzed melt transesterification. All monomers (diols and diesters) were dried in the vacuum oven 12 hrs at 80 °C before they were used. A dry glass reactor (purged three times using argon) with mechanical stirrer and three openings was charged with the appropriate amounts (diols:diesters = 1:0.9 molar ratio) of the oligomeric diol, diesters and catalyst titanium (IV) isopropoxide (0.05 wt %) and were maintained under an argon atmosphere. The mixture of about 60 grams was stirred mechanically and the temperature of the reaction maintained at 210 °C for 4 hrs, and then 230 °C for 2 hrs. The by-product methanol was removed using a liquid N₂ cold trap. Secondly, diesters (10 mole % of diols) and triphenyl phosphate (0.05 wt % of total reagents) were added after the mixture in the reactor was cooled to 180 °C, and then the reaction temperature raised to 250 °C and maintained at this temperature for 2-3 hrs. The total molar ratio of diols / diesters was controlled at 1:1. Vacuum (100 mTorr or less) was applied for the final 0.5-1 hr at 250 °C to remove low molecular weight species. The completion of the reaction was signaled by a rapid increase in the viscosity, at which point the reactor was refilled with argon gas and cooled to room temperature. Neutral polymers were prepared in the same manner, replacing DM5SIS with DMI. Copolymers were prepared by using diols (PEG and PTMO) and diesters (DM5SIS and DMI). All temperatures mentioned in the reaction steps are the temperatures of the heat bath that the reactor is immersed in.

Ion exchange: The sodium polyester ionomer was dissolved in water and then diafiltered with deionized water using a 1000/3000 molecular weight cut-off membrane.
This ionomer was then dissolved in 0.5 M LiCl/H\textsubscript{2}O (or 0.5M CsCl/H\textsubscript{2}O) and diafiltered to prepare lithium or cesium ionomers. Diafiltration was considered complete when the dialyzate exhibited constant conductivity. The concentrated ionomer solution was then freeze dried and then vacuum dried at 120 °C to constant mass. The ionomers are identified as PE\textsubscript{y}-M, where \textit{y} is the molecular weight of the PEG oligomer used in the synthesis and M represents the type of cation (Li, Na or Cs). The neutral polymers are denoted PEx-0. Copolyesters are identified as PE600-xLi (x is the molar fraction of the DM5SIS in the mixture of DM5SIS and DMI; x = 0, 0.025, 0.05, 0.1, 0.25, 0.5, 1) and PEG600-PTMO650 (z)-Li (z is the molar fraction of PEG600 and PTMO650 in a copolymer; z = 1, 0.75, 0.5, 0). It is noted that as x = 0, the polymer is PE600-0; as z = 1, the polymer PE600-Li; as z = 0, the polymer is PTMO650-Li.

\textit{\textsuperscript{1}H NMR} : \textsuperscript{1}H NMR spectra were acquired on a DPX-300 Spectrometer with deuterated dimethyl sulfoxide (DMSO) as the solvent. The spectra were used to verify the polyester ionomer structure and to determine the number-average molar mass (\(M_n\)) as all samples have \(M_n < 20000\), most likely due to hydrolysis during the diafiltration stage of sample preparation. There are three aromatic protons (\(\lambda\) and \(\varepsilon\)) on the phenyl ring and four protons in two OCH\textsubscript{2} (\(\alpha\)) connected to two carbonyl groups in one repeat unit. Provided that the end groups are CH\textsubscript{2}OH (\(\alpha'\)) and OCH\textsubscript{3} (\(\delta\)), degrees of polymerization (\(n\)) can be calculated from the ratio of monomers and end groups

\[
n = 2 \frac{I_{\text{backbone}} \text{ per proton}}{I_{\text{end1}} \text{ per proton} + I_{\text{end2}} \text{ per proton}}
\]
Figure 1. The proton NMR of PTMO650-Li in DMSO (Mn = 6.7K)

Figure 2. The proton NMR of PEG600-PTMO650 (50/50)-Li in the mixture of CD$_3$OD and DMSO (Mn = 5.7k)
Figure 3  The proton NMR of PEG600-polyurethane in DMSO (Mn = 17k)
Appendix 3 SAXS and normalization of polyelectrolyte solutions and ionomers

Experimental: The X-ray measurements were performed on a Molecular Metrology SAXS instrument with Cu K\textalpha radiation source (wavelength $\lambda = 1.54$ Å) and a 12.5 cm x 12.5 cm two dimensional positional sensitive detector. The distance between sample and detector is 224 cm. Liquid cells with 25 μm mica windows (or Kapton film windows for copolyester ionomers) were used to hold the polymer solutions or melt polymer for SAXS measurements. The beam path length of these liquid cells is 1.2 mm (for polymer solutions with concentrations $c < 20$ mg/ml, lithium and sodium salt ionomers) and 0.4 mm (for polymer solutions with concentrations $c \geq 40$ mg/ml, or cesium salt ionomers). All measurements were done at 25 °C, and the total scattering time depends on the samples. Scattering time significantly depends on the polyelectrolyte concentration, and counterion electron density. For instance, for 0.05 M 60PMVP-I/EG solution, 3hrs were needed and for 0.05M60PMVP-Cl/EG solution, 10hrs were needed; for ionomers, 3hrs are enough to get The scattering intensity from the sample solution was subtracted from the scattering intensity of the background (as solvent and mica (or kapton film) windows) and then was normalized by sample thickness (centimeter), experiment time (seconds), and the beam transmission intensity.

Sample loading: To prevent from the leakage of liquid samples, vacuum grease is recommended to use for sealing flat O-ring (two sides). The liquid cell should be filled to about two thirds of its volume, then tighten the screws (two sides) completely and make sure that no bubbles are seen through the liquid cell windows. For melt polymers
(PEO-based ionomers), the sample was dried at a temperature $T_g + 100 \, ^\circ C$ in the vacuum oven, and then transferred into the liquid cell. The sample in the liquid cell was dried under vacuum again until all bubbles disappear. Finally, the sample was cooled down in the vacuum oven slowly and sealed in the liquid cell between two mica (or kapton) windows.

**Scattering intensity correction:** To obtain accurate normalized scattering intensity, the samples must use the same scattering time as the background empty cell. First, the intensity correction of samples was performed based on the transmission intensity of sample ($I_s$), the transmission intensity of the background ($I_b$), the dark counts ($I_{DC}$, the transmission intensity with the shuttle closed and nothing in the beam path, it can be negative. In this study, unfortunately, $I_{DC}$ was not recorded, so $T_s = I_s / I_b$, but $I_s$ and $I_b$ were measured in the same day). The transmission of the sample can be determined by equation (1)

$$T_s = \frac{I_s - I_{DC}}{I_b - I_{DC}}$$

(1)

If $T_b$ is the transmission of the background, $t_s$ is the live time of the sample, $t_b$ is the live time of the background. The background correction factor $f$ can be determined by equation (2)

$$f = \frac{T_s t_s}{T_b t_b}, \quad T_b = 1$$

(2)
If $I_{scounts}(q)$ is the total intensity (counts) recorded for the sample and $I_{bcounts}(q)$ is the total intensity (counts) recorded for the background, the correction intensity subtracted from background $I_{corr b}(q)$ can be determined from equation (3)

$$I_{corr b}(q) = I_{scounts}(q) - fI_{bcounts}(q) \quad (3)$$

**Normalization:** If $d_s$ is the thickness of the sample and $d_b$ is the thickness of the background (it should be the same thickness as that of the sample), the normalized scattering intensity of the sample is given by equation (4)

$$I(q) = I_{corr b}(q)/(t_sT_b d_s) \quad (4)$$

Figure 1 shows that the original scattering intensity (counts) of solvent NMF is very low, compared to that of 60PMVP-I in NMF at $c = 10$ mg/ml. The normalized intensity profile of 60PMVP-I/NMF indicates that 60PMVP-I in NMF is highly ordered and has strong polyelectrolyte behavior.
Figure 1. The SAXS profiles (raw data with background mica windows) of 60PMVP-I in NMF (c = 10 mg/ml) and solvent NMF; The scattering peaks at extremely low q were caused by the scattering from the beam stop in the front of the SAXS detector; for the insert plot, I(q) is the normalized intensity and subtracted from the background.

Figure 2. The SAXS profiles of 60PMVP-I in EG, I(q) is the normalized intensity and q is the wavevector.
Figure 3. The SAXS profiles of 60PMVP-I in H₂O, I(q) is the normalized intensity and q is the wavevector.

Figure 4. The SAXS profiles of 60PMVP-Cl in EG, I(q) is the normalized intensity and q is the wavevector (living time 10hrs). The thickness of mica window sample cell is 0.13cm used for 60PMVP-Cl/EG at concentrations 2.5, 5.0, 10, and 40 mg/ml; the thickness of kapton window sample cell is 0.045 cm used for 60PMVP-Cl/EG at concentration 20mg/ml.
Appendix 4 Rheology measurements of polyelectrolyte solutions and ionomers.

**Before measurement:** 1) Purify solvents carefully before they are used and dry polymers in the vacuum oven 24 hrs at 50 °C. 2) Prepare polymer solutions with fresh purified solvents (which is very important) and dried polymers in the same way for all polymer solutions and seal them for at least 12 hrs (slowly stirring is helpful for dissolving). 3) Apply a balance to prepare polymer solutions or dilute polymer solutions (do not use volumetric pipettes). 4) Calibrate the rheometers every day with Newtonian liquid with viscosity close to the sample viscosity. 5) Clean and dry the sample holder (cups, bars, plates) every time carefully. 6) Wait 3 minutes for the stable temperature in the sample after the sample is loaded. 7) Stop the measurement if the data are noisy if correct transducer and strain are applied (possibly there are bubbles in the sample).

**Steady shear measurement:** The steady shear viscosity of polymer solutions in EG was measured at 25 °C using four rheometers: A Rheometric Scientific ARES (controlled strain) was used for highly concentrated solutions with viscosity above 20 Pa.s, a Rheometric Scientific SR-2000 (controlled stress) was used for concentrated solutions with viscosity in the range from 0.1 to 100 Pa.s, a computerized Contraves Low Shear 30 viscometer (controlled shear rate) was used for polymer solutions with viscosity from 0.03 to 0.3 Pa.s, and a capillary viscometer (Cannon Ubbelohde No. 2 with a diameter of 2.06 mm and a capillary length of 90 mm) was used for polymer (P2VP, α PMVP-Cls made from P2VP) solutions with viscosity lower than 0.03 Pa.s, each calibrated using standard Newtonian oils and EG at 25 °C. The viscosity of
polyelectrolyte 60PMVP-I solutions was measured at RFS II and ARES except for the viscosity of 60PMVP-I in DW and NMF at low concentrations.

**Dynamic shear measurement:** Dynamic measurements were applied to get moduli \( G' \) and \( G'' \) and complex viscosity \( \eta^* \) for polymer solutions and ionomers. Strain sweep measurement in the frequency range from 0.01 to 100 Hz was used to determine the strain that was applied in the dynamic measurement at a typical frequency range. For polyelectrolyte solutions, the dynamic measurements were performed at 25 °C in the frequency range from 0.01 to 100 Hz. For PEO-based ionomers, the dynamic measurements were carried out at varied temperatures in the frequency range from 0.01 to 100 Hz.

**Relaxation time from shear thinning:** The shear rate dependence of apparent viscosity for solutions with concentrations below 0.23 M were fit to the Carreau model

\[
\eta(\dot{\gamma}) = \frac{\eta(0)}{[1 + (\dot{\gamma} \tau)^2]^{p}}
\]

to determine the relaxation time \( \tau \) and the parameter \( p \) by least squares regression. The parameter \( p \) was found to systematically change with concentration, as seen in other studies of polyelectrolyte solution rheology, ranging from 0.05 at low concentration to 0.25 at high concentration.

**Relaxation time from \( G' \) and \( G'' \):** For solutions with concentrations \( c > 0.037 \) M, storage modulus \( G' \) and loss modulus \( G'' \) were measured as functions of frequency \( \omega \) at 25 °C using rheometers ARES and RFS II, with small strain amplitudes corresponding to linear response. For lower concentrations, the oscillatory shear method
is not reliable because of inertial effects resulting from the viscosity being too small (50 cp). Care was taken to ensure that the strain amplitudes were in the regime of linear viscoelastic response. The relaxation time was determined as the reciprocal of the frequency at which those power laws intersect (Figure 1).

![Figure 1 Evaluation of the relaxation time of polymer solutions from $G'$ and $G''$ at 25 °C.](image)
Figure 2. Evaluation of the overlap concentration of polyelectrolyte solutions with residual salt.

Figure 3. The evaluation of the entanglement concentration of polyelectrolyte solutions (clear description shown in chapter 2).
Appendix 5 Dielectric measurements of polyelectrolyte solutions and ionomers

**Polyelectrolyte solutions:** Conductivity measurements were performed with a broadband dielectric spectrometer (Novocontrol GmbH, Germany). The preparation of polyelectrolyte solutions is the same as that in the rheology measurements. The copper electrodes were sputtered using gold carefully to prevent from any contamination and chemical reaction in the measurement (brass electrodes turns black indicating electrochemistry). Liquid cells must be cleaned and dried carefully before a liquid sample was loaded. After the sample was loaded, the liquid cell was assembled and then vibrated tenderly as it was set on a table to remove any bubbles between electrodes in the sample. The conductivity of fresh polyelectrolyte solutions in the concentration range from 0.01 to 10 mg/mL in a liquid cell (spacer: 0.55mm and diameter: 20mm) was measured at 25 °C, frequency range from $10^1$ to $3 \times 10^6$ Hz, and 0.1V (AC). Conductivity was evaluated from the plateau in the real part of conductivity in the frequency range from $10^2$ to $10^4$ Hz (the precise frequency range depends on samples measured). Equivalent conductance $\Lambda=\frac{(\sigma-\sigma_s)}{c}$ was determined from the conductivity of polyelectrolyte solutions ($\sigma$), the conductivity of solvent $\sigma_s$, and the molar concentration of monomer ($c$).

**Effective charge density:** If the equivalent conductance of the counterion in solvent is not known, the usual methods to determine $f$ from equivalent conductance of the solution cannot be employed (Chapter 2). However, if we have an internal known
reference, the effective charge \( f \) of the other polyelectrolytes in solvent can be determined by plotting \( \Lambda / f \) against \( c / c^* \) for each polyelectrolyte, with \( f \) adjusted to fit the curve \( \Lambda / f \) against \( c / c^* \) of the known reference in the semidilute unentangled regime.

If the equivalent conductance of counterions \( \lambda_c \) and the correlation length \( \xi \) of polyions in solution are known, the effective charges can be estimated from the following equation (see chapter 3).

\[
\Lambda = f \left( \lambda_c + \frac{fc\xi^2e^2 \ln(\xi / \xi_c)}{3\pi \eta_s} \right)
\]

The specific conductance \( \lambda_c \) of I\(^-\) (22.76 S cm\(^{-2}\)/mole in NMF, 16.6 S cm\(^{-2}\)/mole in F, and 76.82 S cm\(^{-2}\)/mole in DW) was applied to fit the equivalent conductance data obtained from dielectric measurements for 60PMVP-I in NMF, F, and DW. The correlation length of 60PMVP-I in NMF, F, and DW was estimated from the results of the SAXS measurements and the rheology measurements in the semidilute unentangled region.

**Ionomers:** Our ionomer samples are low \( T_g \) viscous polymers. Dry melt ionomers were transferred onto one gold-sputtered electrode (three pieces of Teflon spacers on it) in a vacuum oven at about 100 °C and then dried in the vacuum oven until all bubbles disappear. Another electrode was put on the melt polymer slowly and extra sample was squeezed away. The void-free ionomers sandwiched between two round gold-sputtered electrodes was inserted between two electrodes of Novocontrol GmbH Concept 40 broadband dielectric (impedance) spectrometer. The ionic conductivity (\( \sigma_0 \), in S/cm) was
measured by using an AC voltage amplitude of 1.5 V for all experiments. Frequency
sweeps were performed isothermally from 10 MHz to 0.01 Hz in the temperature range
from 120 °C to a temperature close to the $T_g$ of ionomers. Temperature stability during
data acquisition was better than ±0.1 °C.

Figure 1. Solvent effects on the specific viscosity of 17PMVP-Cl and 55PMVP-Cl at 25 °C.

Figure 2. Conductivity of polyelectrolytes in EG at 25 °C.
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